



# Sulfates in Valles Marineris as Indicators of the Aqueous Evolution of Mars

Leah Hutchison Roach

B.S. Massachusetts Institute of Technology, 2004

M.S. Brown University, 2006

Submitted in partial fulfillment of the requirements for the  
degree of Doctor of Philosophy in Geological Science at Brown  
University.

Providence, Rhode Island

May 2009

© Copyright 2009 by Leah Hutchison Roach

This dissertation by Leah Hutchison Roach is accepted in its present form by  
the Department of Geological Sciences as satisfying the dissertation requirement  
for the degree of Doctor of Philosophy.

Date \_\_\_\_\_

Professor John F. Mustard, Brown University

Recommended to the Graduate Council

Date \_\_\_\_\_

Professor James W. Head, III, Brown University

Date \_\_\_\_\_

Professor Youngsong Huang, Brown University

Date \_\_\_\_\_

Professor Michael Wyatt, Brown University

Date \_\_\_\_\_

Outside Reader, Outside Institution

Approved by the Graduate Council

Date \_\_\_\_\_

Dr. Sheila Bonde, Dean of the Graduate School

# Leah Hutchison Roach

---

[Leah\\_Roach@Brown.edu](mailto:Leah_Roach@Brown.edu)

[www.planetary.brown.edu/grad\\_pages/Roach/](http://www.planetary.brown.edu/grad_pages/Roach/)  
(401) 863-3485

Dept. of Geological Sciences  
Box 1846  
Brown University  
Providence, RI 02906

## Education

**Brown University**; Providence, RI

Ph. D., Geological Sciences (May 2009)

Thesis title: Sulfates in Valles Marineris as Indicators of the Aqueous  
Evolution of Mars

Advisor: Dr. John F. Mustard

**Brown University**; Providence, RI

M. Sc., Geological Sciences (June 2006)

Thesis title: Finding Mineralogically Interesting Targets for Exploration  
from Spatially Coarse Visible and Near IR Spectra

Advisor: Dr. John F. Mustard

**Massachusetts Institute of Technology**; Cambridge, MA

S.B., Geosciences, minor in Literature (June 2004)

## Research Experience

Research Assistant     June 2007-Aug 2008, with Prof. Mustard, remote sensing  
and spectroscopy of Mars, using data from CRISM and  
OMEGA, hyperspectral visible-near infrared  
spectrometers orbiting Mars

June 2005-Dec 2006, with Prof. Mustard, remote sensing  
and spectroscopy of Earth (Rio Tinto, Spain) and Mars

**Research Topics:** planetary geology, remote sensing, spectroscopy, spatial  
scaling of datasets, Mars, sulfate and iron oxide  
mineralogy

## Teaching

### Collegiate Teaching Experience

Teaching Assistant     *Intro to Geographic Information Systems* (Fall 2008)

*Environmental Remote Sensing* (Spring 2007)



|                |                                                                                                                                                                                                                      |
|----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| GRE Instructor | For Brown Leadership Alliance and REU summer programs (~20 students), Summer 2008                                                                                                                                    |
| Instructor     | With The Princeton Review, May 2004-May 2006. Tutored SAT and GRE test material in one-on-one and classroom settings (up to 12 students). Taught content from prepared curriculum, graded practice tests and essays. |
| Undergrad TA   | <i>Intro to Earth System Engineering &amp; Science, Mission 2006: Solving Complex Problems, and Mission 2005: Solving Complex Problems</i>                                                                           |

## Other Teaching Experience

|                    |                                                                                                                                                                                                                     |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Science outreach   | Occasional volunteer science instructor at Vartan-Gregorian Elem., Providence, RI. Develop and teach earth science modules, 2005-2008<br><br>Space Grant science outreach in Providence classrooms grades 1-6, 2008 |
| Space Grant Docent | "A New Perspective on Mars: Mars in 3D" exhibit at Roger William Museum of Natural History, Providence, RI. Fall 2007                                                                                               |
| Organizer          | Remote Sensing event, Rhode Island Science Olympiad. 2007, 2008                                                                                                                                                     |

## Pedagogical Professional Development

Sheridan Center Teaching and Learning in Higher Education Certificate Programs. More details at [http://brown.edu/Administration/Sheridan\\_Center/certificateprograms/](http://brown.edu/Administration/Sheridan_Center/certificateprograms/)

Certificate I: The Sheridan Teaching Seminar (Jan 2006)

Certificate II: Classroom Tools Seminar (April 2007)

Certificate III: Professional Development Seminar (April 2008)

Sheridan Center Teaching Consultant (2006-2009): observe, videotape, and provide constructive feedback to grad students, post-docs, and faculty on teaching effectiveness and techniques

Sheridan Center Geology Dept. Graduate Student Liaison (2006-2009)

## Publications (peer reviewed)

- Roach, L.H.**, J.F. Mustard, M. Lane, S.L. Murchie, B.L. Ehlmann, and co-authors (in prep). Diagenetic hematite and sulfate assemblages in Valles Marineris.
- Roach, L.H.**, J.F. Mustard, G.A. Swayze, R.E. Milliken, J.L. Bishop, B.L. Ehlmann, S.L. Murchie, and K. Lichtenberg (in prep). Stratigraphy of Ius Chasma, Valles Marineris. *Icarus*.
- Murchie, S.L., **L.H. Roach**, F. Seelos, R. Milliken, J.F. Mustard, R.E. Arvidson, S. Wiseman, K. Lichtenberg, J. Andrews-Hanna, J.-P. Bibring, J. Bishop, M. Parente, and R. Morris (submitted). Compositional Evidence for the Origin of Layered Deposits in Valles Marineris, Mars. *J. Geophys. Res.*
- Calvin, W.M., **L.H. Roach**, F.P. Seelos, K.D. Seelos, R.O. Green, S.L. Murchie, and J. F. Mustard (submitted). CRISM observations of northern latitudes in the first MRO summer. *J. Geophys. Res.*
- Lichtenberg, K., R. Arvidson, R. Morris, S. Murchie, J. Bishop, D. Fernandez Remolar, T. Glotch, E. Noe Dobrea, J. Mustard, J. Andrews-Hanna, and **L.H. Roach** (submitted). Stratigraphy of Hydrated Sulfates in the Depositional Unit in Aram Chaos, Mars. *J. Geophys. Res.*
- Bishop, J.L., M. Parente, C. Weitz, E. Dobrea, **L.H. Roach**, S.L. Murchie, P. McGuire, N. McKeown, Rossi, A.J. Brown, W.M. Calvin, R. Milliken, and J.F. Mustard (submitted). Mineralogy of Juventae Chasma: sulfates in the light-toned mounds, mafic minerals in the bedrock, and hydrated silica and hydroxylated ferric sulfate on the plateau. *J. Geophys. Res.*
- Ehlmann, B.L., J.F. Mustard, G.A. Swayze, R.N. Clark, J.L. Bishop, F. Poulet, D.J. Des Marais, **L.H. Roach**, R.E. Milliken, J.J. Wray, O. Barnouin-Jha, and S.L. Murchie (submitted). Identification of hydrated silicate minerals on Mars using MRO-CRISM: geologic context near Nili Fossae and implications for aqueous alteration. *J. Geophys. Res.*
- Poulet, F., D. Beaty, J.-P. Bibring, D. Bish, J. Bishop, E. Dobrea, J. Mustard, S. Petit, and **L.H. Roach** (accepted). Key science questions and key investigations from the first international conference on Martian phyllosilicates. *Astrobiology*.
- Roach, L.H.**, J.F. Mustard, S.L. Murchie, J.-P. Bibring, F. Forget, K.W. Lewis, O. Aharonson, M. Vincendon, and J.L. Bishop (in press). Testing evidence of recent hydration state change in sulfates on Mars. *J. Geophys. Res.* doi:10.1029/2008JE003245.
- Horgan, B.H., J.F. Bell III, E. Noe Dobrea, E. Cloutis, D. Bailey, M. Craig, **L.H. Roach**, and J.F. Mustard (2009). The distribution of hydrated minerals in the North Polar region of Mars. *J. Geophys. Res.*, 114, E01005, doi:10.1029/2008JE003187.

- Ehlmann, B.L., J.F. Mustard, S.L. Murchie, F. Poulet, J.L. Bishop, A.J. Brown, W.M. Calvin, R.N. Clark, D.J. DesMarais, R.E. Milliken, **L.H. Roach**, T.L. Roush, G.A. Swayze, J.J. Wray (2008). Orbital Identification of Carbonate-Bearing Rocks on Mars. *Science*, 322(5909), 1828-1832.
- Mustard, J.F., S.L. Murchie, S.M. Pelkey, B.L. Ehlmann, R.E. Milliken, J.A. Grant, J.-P. Bibring, F. Poulet, J. Bishop, E. Noe Dobrea, **L.H. Roach**, and 25 others (2008). Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter CRISM Instrument. *Nature*. doi:10.1038/nature07097.
- Roach, L.H.**, Mustard, J.F., A. Gendrin, D. Fernandez-Remolar, R. Amils, and L. Amaral-Zettler (2006). Finding Mineralogically Interesting Targets for Exploration from Spatially Coarse Visible and Near IR Spectra. *Earth and Planetary Science Letters*, 252:201-214.

## Conference Abstracts for Poster Presentations

- Roach, L.H.**, J.F. Mustard, S.L. Murchie, J.L. Bishop, B.L. Ehlmann, K. Lichtenberg, M. Parente, and the CRISM Science Team (2009). Sulfate and iron oxide stratigraphy in Capri Chasma, Valles Marineris. *Lunar and Planetary Science Conference XL*. Houston, TX. March 23-27, 2009.
- Roach, L.H.**, J.F. Mustard, S.L. Murchie, R.E. Milliken, J. Crowley, J.L. Bishop, R.E. Arvidson (2008). Sulfates and Other Hydrated Minerals in Ius Chasma, Valles Marineris and Implications for Water Geochemistry. *Eos Trans. AGU*, Fall Meet. Suppl. San Francisco, CA. December 15-19, 2008.
- Roach, L.H.**, J.F. Mustard, S.L. Murchie, O. Aharonson, T. Lowenstein, C.M. Weitz, R.E. Arvidson, J.L. Bishop, K. Lewis, K. Lichtenberg, F. Seelos, and the CRISM Science Team (2008). Sulfate mineral stratigraphy in Valles Marineris Interior Layered Deposits. *Lunar and Planetary Science Conference XXXIX*. Houston, TX. March 9-14, 2008.
- Roach, L.H.**, J.F. Mustard, S.L. Murchie, J.L. Bishop, R.E. Arvidson, R.V. Morris, R.E. Milliken, and K.A. Lichtenberg (2007). Multi-sulfate and Iron Oxide Assemblages Within the Valles Marineris Interior Layered Deposits. *Eos Trans. AGU*, Fall Meet. Suppl. San Francisco, CA. December 10-14, 2007.
- Roach, L.H.**, J.F. Mustard, S.L. Murchie, J.L. Bishop, C.M. Weitz, A.T. Knudson, J.-P. Bibring, S.M. Pelkey, B.L. Ehlmann, and the CRISM team (2007). Magnesium and Iron Sulfate Variety and Distribution in East Candor and Capri Chasma, Valles Marineris. *7<sup>th</sup> International Mars Conference*. Pasadena, CA. July 9-13, 2006.
- Roach, L.H.**, J.F. Mustard, S. Murchie, Y. Langevin, J.-P. Bibring, J. Bishop, N. Bridges, A. Brown, S. Byrne, B.L. Ehlmann, K. Herkenhoff, P.C. McGuire,

R.E. Milliken, S. Pelkey, F. Poulet, F.P. Seelos, K. Seelos, and the CRISM team (2007). CRISM spectral signatures on the North Polar gypsum dunes. *Lunar and Planetary Science Conference XXXVIII*. Houston, TX. March 12-16, 2006.

**Roach, L.H.**, J.F. Mustard, S. Murchie, C.M. Weitz, B.L. Ehlmann, S. Pelkey, F.P. Seelos, K. Seelos, J.-P. Bibring, and the CRISM team (2007). Sulfate identifications in East Candor, Valles Marineris with CRISM visible-infrared spectra. *Lunar and Planetary Science Conference XXXVIII*. Houston, TX. March 12-16, 2006.

**Hutchison, L.**, J.F. Mustard, D. Fernandez-Remolar, R. Amils (2006). Quantifying mineralogic diversity from remotely sensed VNIR spectra to identify mineralogic hotspots. *Eos Trans. AGU*, 87(52), Fall Meet. Suppl. San Francisco, CA. December 11-15, 2006.

**Hutchison, L.**, Mustard, J.F., Gendrin, A., Amaral-Zettler, L.A., Amils, R. & Fernández-Remolar, D. (2006). Using a Visible and Near IR Spectral Variance Index in Rio Tinto, Spain to Combine Datasets of Different Spatial Resolution [Abstract]. *Astrobiology*, 6(1):225. Washington, DC. March 26-30, 2006.

**Hutchison, L.**, J.F. Mustard, A. Gendrin, L.A. Amaral-Zettler, and D. Fernández-Remolar (2005). Implications of scaling visible and near IR spectroscopic data on detection of mineralogy: A case study in Rio Tinto, Spain, *GSA Abstracts with Programs*, 37(7). Salt Lake City, UT. October 16-19, 2005.

**Hutchison, L.**, Mustard, J.F., Gendrin, A., Amaral-Zettler, L.A., Amils, R. and Fernández-Remolar, D. (2005). In-Situ Spectroscopic Characterization of Acidic Sulfate Deposits of Rio Tinto, a Mars Analog [Abstract]. *Astrobiology*, 5(2):311. Boulder, CO. April 11-14, 2005.

**Hutchison, L.**, J.F. Mustard, A. Gendrin, J.-P. Bibring, Y. Langevin, B. Gondet, N. Mangold, and the OMEGA Science Team (2005). Mafic Polyhydrated Sulfates and Kieserite in Capri Chasma. *Lunar and Planetary Science Conference XXXVI*. Houston, TX. March 14-18, 2005.

**Hutchison, L.** and S. Desch (2002). Mineralogy of Silicate Dust Grains in the Disk around TW Hydra. *Division of Planetary Sciences of the AAS Annual Meeting*. Birmingham, AL. October 6-11, 2002.

## Oral Presentations

**Roach, L.H.**, J.F. Mustard, S.L. Murchie, J.L. Bishop, B.L. Ehlmann, R.E. Milliken, K. Lichtenberg, M. Parente, and the CRISM Science Team (2009). Hydrated mineral stratigraphy in Ius Chasma, Valles Marineris. *Lunar and*

*Planetary Science Conference XL*. Houston, TX. March 23-27, 2009.

**Roach, L.H.**, J.F. Mustard, S. Murchie, R.E. Milliken, K. Lichtenberg, B.L. Ehlmann, J. Bishop, R.E. Arvidson, and the CRISM team (2008). New hydrated spectral phase and stratigraphy of smectite clays, sulfates and other hydrated minerals in Ius Chasma, Valles Marineris. *Workshop on Martian phyllosilicates: Records of Aqueous Processes*. Paris, France. Oct 21-23, 2008.

**Roach, L.H.**, J.F. Mustard, S. Murchie, J.-P. Bibring, R.E. Arvidson, J.L. Bishop, R.E. Milliken, F. Seelos, and the CRISM Science Team (2008). Constraints on the rate of sulfate phase changes in Valles Marineris Interior Layered Deposits. *Lunar and Planetary Science Conference XXXIX*. Houston, TX. March 9-14, 2008.

**Roach, L.H.** J.F. Mustard, S. Murchie, J. Bishop, R. Arvidson, K. Lichtenberg, F. Seelos, and the CRISM Team (2008). Sulfates in Valles Marineris: Assemblages and Formation Processes. *Brown University Planetary Science Lunch Bunch*. Providence, RI. January 24, 2008.

**Roach, L.H.**, J.F. Mustard, S.L. Murchie, J.L. Bishop, C.M. Weitz, A.T. Knudson, J.-P. Bibring, S.M. Pelkey, B.L. Ehlmann, and the CRISM team (2007). Magnesium and Iron Sulfate Variety and Distribution in East Candor and Capri Chasma, Valles Marineris. *7<sup>th</sup> International Mars Conference*. Pasadena, CA. July 9-13, 2007.

**Roach, L.H.**, J.F. Mustard, S. Murchie, Y. Langevin, J.-P. Bibring, J. Bishop, N. Bridges, A. Brown, S. Byrne, B.L. Ehlmann, K. Herkenhoff, P.C. McGuire, R.E. Milliken, S. Pelkey, F. Poulet, F.P. Seelos, K. Seelos, and the CRISM team (2007). CRISM spectral signatures on the North Polar gypsum dunes. *Lunar and Planetary Science Conference XXXVIII*. Houston, TX. March 12-16, 2007.

**Hutchison, L.**, J.F. Mustard, A. Gendrin, L.A. Amaral Zettler, R. Amils, and D. Fernández-Remolar (2006). Using a Visible and Near IR Spectral Variance Index in Rio Tinto, Spain to Combine Datasets of Different Spatial Resolution. *Astrobiology Science Conference Annual Meeting*. Washington, DC. March 26-30, 2006.

**Hutchison, L.**, J.F. Mustard, A. Gendrin, L.A. Amaral Zettler, and D. Fernandez-Remolar (2005). Implications of Scaling Visible and Near IR Spectroscopic Data on Detection of Mineralogy: A Case Study in Rio Tinto, Spain. *Geological Society of America Annual Meeting*. Salt Lake City, UT. October 16-19, 2005.

**Hutchison, L.**, J.F. Mustard, A. Gendrin, L.A. Amaral Zettler, and D. Fernandez-Remolar (2005). Exploring Rio Tinto, an Iron Oxide/Sulfate mars Analog. *Brown University Planetary Science Lunch Bunch*. Providence, RI. November 10, 2005.

## **Invited Talks**

Brown University, Providence, RI. "The raster data model and the Spatial  
GIS Winter Analyst extension for GIS," January 7, 2009  
Institute  
Ecole des Mines St. Etienne, France. "Recent results from CRISM, Mars  
Reconnaissance Orbiter, and Phoenix Lander," June 17,  
2008

## **Professional Society Membership**

American Geophysical Union 2006, 2007, 2008  
Geological Society of America 2005

## **Honors and Awards**

2009 Brown University Dissertation Fellowship  
2008 Dwornik Planetary Geoscience Student Paper Award for  
oral presentation, Lunar and Planetary Sciences  
Conference  
2006 AGU Outstanding Student Paper award, American  
Geophysical Union fall meeting, Planetary Sciences  
section  
2006-2007 Zonta International Amelia Earhart Fellowship  
2006 TSETSE Art Gallery "Art of Science" photography winner  
Aug 2004-June 2005 Brown University Graduate Fellowship  
2004, 2005 National Science Foundation Graduate Research  
Fellowship Program, Honorable Mention  
2004 Christopher Goetze Prize for Undergraduate Research,  
for senior thesis "Determining Land Use Change and  
Desertification in China using Remote Sensing Data"  
2003 Howard T. Fisher Prize in GIS, given by Harvard to an  
undergraduate enrolled at Harvard for original work in  
GIS

## **Other Training and Skills**

Mathematica, Matlab, ENVI, IDL and Fortran programming languages  
ESRI GIS software experience (ArcView 3 and ArcGIS 9.1, 9.2, and 9.3).

Extensions: Spatial Analyst, Georeferencing, Model Builder

## **Service**

Organizer, Geology Grad Student Professional Development Seminar, Nov 2006

Organizer, Planetary Geology Lunch Bunch Lecture Series, Fall 2008

# Acknowledgements

There are so many people to thank and acknowledge for their help, friendship, and support over the past 5 years. It has been an enjoyable, challenging, and rewarding journey, and one where I have learned as much about myself as I have about Mars or sulfates.

The tightly-knit graduate student community in the Geology department was one of the reasons I decided to come to Brown, and I would like to thank everyone for being such a relaxed, cool, smart and funny bunch of people. Here is the obligatory shout out section: Rachel Klima, for sharing an office and showing me the ropes my first year, for Craft Night, and for hilarious lunch conversations; Joe Levy, for being the funniest and punniest guy I've ever met and who is an unstoppable life force; Noah Petro, for sharing his love of teaching and of Queen (We Will Rock You!); Wes Patterson, for introducing me to the sandal bottle opener; Ralph Milliken, for perfectly playing the jaded older grad student while dispensing lots of advice; Jeremy Fischer, for the pep talks and Bethany Bradley, for making it all look so easy; Sam Schon, for being niceness personified and a ray of sunshine whenever we talked; Tina Calvin, for being my gym buddy and squash partner and early morning motivator; Linda Chernak, for her sense of enthusiasm and for commiserating about med school (why is it we feel we are in med school too?); Shannon Pelkey, for showing me how a postdoc is supposed to be lived; Aline Gendrin, who is an inspiration for her scientific dedication and drive; Sarah Milkovich, Sarah Noble, and Jenn Anderson, for advice when I was a wee grad student; and the newest crop of grad students, including Mark Salvatore, Leah Cheek, Kerri Donaldson-Hanna, and LeAnne Edwards for reminding me of being a wee grad student.



I'd like to especially thank my two closest friends at Brown: Lisa Kanner and Bethany Ehlmann. Lisa and I got each other through two years of grad school with lunch time swims, commiseration dinners, and lots of laughs. She introduced me to the world of competitive ultimate (of which I am a fan, not a participant!) and the joys of the Moosewood cookbook's black bean soup. When she left with a masters, I didn't know how I would cope with grad school without her. I briefly wondered if I should leave too. Luckily we kept in touch, and I also met Bethany Ehlmann. Bethany is a great soundingboard, the most critical paper reviewer I have ever met, and has such a lively and kind personality. She has a work ethic I could only aspire to match. I'd like to thank her for not getting impatient with my more-than-occasional forgetfulness and for gently pushing me to be a better (and better-read) scientist. Also, thanks for not minding too much when I accidentally turned on the power strip to our computers for the THIRD time. I consider it a privilege to be able to have worked with Bethany for three years, and I know she will go to the top of whatever field she ultimately choses.

The faculty in the Geology department are no less spectacular. I've enjoyed taking classes and learning from and with all of them. Carle Pieters's seminars are exactly how I would want to teach a seminar in the future, and I know I will be returning to my compiled notes from her classes in the future. Jim Head's Planetary Volcanology class gave me a great opportunity to read the seminal papers in the field and to debate the controversies in them. I also appreciated Jim's probing intellect, as he pushed me to stretch myself in class or in committee meetings. Pete Schultz's Impact Cratering class was a hoot; I also enjoyed serving as a Space Grant Docent at the 3D Mars exhibit he helped to organize. Mike Wyatt's Martian Geochemistry class was exactly what I needed – a really detailed look at the chemistry and interpretations behind all of these Martian observations as well as a collegial forum to explore new ideas and

see things through fresh eyes. I'd also like to thank him for his advice throughout my career at Brown, be it thesis, research, or how to navigate the grad student-post PhD transition. Also, thanks to Cathy Weitz, for agreeing to be an outside reader for the thesis.

My biggest thanks are for Jack Mustard, a wonderful advisor, mentor, and colleague. I'll never forget the way he introduced me to grad school - by sending me to Santander, Spain for a weeklong International Summer School in Astrobiology. I had been in Providence for a month and barely settled into my apartment, let alone the department, when off I went to Spain! He has given me many, many opportunities to travel for conferences, fieldwork, and collaboration, including two trips to Rio Tinto, Spain and three to Paris and innumerable national conferences. I've valued the chances to meet others in the field and present my research and ideas in a variety of venues. Jack has also been a laid-back mentor, always interested when I have a cool, new CRISM observation to show him and always with an insightful comment that prompts further research. I'd like to applaud him for his service to the Mars community as MEPAG chair; it has been illuminating to see a little bit behind the scenes of how Mars scientific agenda is shaped. Go Phyllosian!

There are many in the Mars community that have had a hand in shaping my science and me as a scientist. I would be remiss if I did not thank Scott Murchie, Janice Bishop, Shannon Pelkey, Aline Gendrin, Jean-Pierre Bibring, Nicolas Mangold, Tim Lowenstein, Dave Bish, Dave Beaty, Jim Crowley, Ray Arvidson, Frank Seelos, Nick Tosca, Alice Baldridge, Geoff Collins, and Wendy Calvin.

In addition to the wonderful people in Providence, my family and friends across the country have been an important support network. My parents have always been big inspirations to me. I'm amazed how easily Mom could run a house as well as her optometry practice and still find time to drive me and my brother to endless

after-school activities. My dad has been an academic role model by deciding to get a PhD after retiring from a career in the Army. Both of my parents made it clear I could be whatever I want and go to whatever school I want, and most importantly, that they would love me regardless of how successful I was. Thanks to my brother, Brad, for rooting for me from Iraq, and to all my friends and family who have been cheerleaders all along the way – Jennie Luter; Lindsay Potter; the Hutchison aunts; the Roach family; Kate Brandley; and fellow grad students and friends.

Finally, I want to thank my husband Ken, for helping me through this thesis and grad school in general in a million ways. I love you.

# Contents

|                                                                                              |           |
|----------------------------------------------------------------------------------------------|-----------|
| Title Page . . . . .                                                                         | i         |
| Copyright Page . . . . .                                                                     | i         |
| Signature Page . . . . .                                                                     | iii       |
| Curriculum Vitae . . . . .                                                                   | iv        |
| Acknowledgements . . . . .                                                                   | xii       |
| Table of Contents . . . . .                                                                  | xvi       |
| List of Figures . . . . .                                                                    | xx        |
| List of Tables . . . . .                                                                     | xxiii     |
| <b>1 Introduction . . . . .</b>                                                              | <b>1</b>  |
| 1.1 Motivation . . . . .                                                                     | 2         |
| 1.2 Background on Sulfates . . . . .                                                         | 6         |
| 1.2.1 Sulfate locations on Mars . . . . .                                                    | 6         |
| 1.2.2 Sulfate formation mechanisms on Mars . . . . .                                         | 8         |
| 1.3 Formation of Valles Marineris . . . . .                                                  | 10        |
| 1.3.1 Formation of ILDs . . . . .                                                            | 13        |
| Sub-ice volcanism or volcanism . . . . .                                                     | 15        |
| Aeolian deposition of ash and dust . . . . .                                                 | 16        |
| Lacustrine deposition . . . . .                                                              | 17        |
| Mass wasting . . . . .                                                                       | 18        |
| 1.4 Visible-Near Infrared Spectroscopy . . . . .                                             | 18        |
| 1.4.1 Crystal field transitions . . . . .                                                    | 18        |
| 1.4.2 Charge transfers . . . . .                                                             | 19        |
| 1.4.3 Vibrational features . . . . .                                                         | 19        |
| 1.4.4 Spectrally Bland Minerals . . . . .                                                    | 20        |
| 1.5 CRISM instrument . . . . .                                                               | 21        |
| 1.6 New sulfate types identified with CRISM . . . . .                                        | 24        |
| 1.6.1 New sulfate phases identified . . . . .                                                | 26        |
| 1.6.2 Phases associated with sulfates . . . . .                                              | 27        |
| 1.7 Thesis Structure . . . . .                                                               | 30        |
| <b>2 Stability of Hydrated Mg Sulfates to Changes in Martian Environ-<br/>ment . . . . .</b> | <b>36</b> |
| 2.1 Introduction . . . . .                                                                   | 37        |

|          |                                                                        |            |
|----------|------------------------------------------------------------------------|------------|
| 2.2      | Thermodynamic and kinetic models of hydrated sulfate stability . . .   | 40         |
| 2.2.1    | T, P, and RH at Valles Marineris . . . . .                             | 43         |
|          | Other factors affecting hydration . . . . .                            | 44         |
| 2.2.2    | Visible-Near Infrared (VNIR) Spectra . . . . .                         | 45         |
| 2.2.3    | Geologic setting of East Candor ILD . . . . .                          | 48         |
| 2.3      | Temporal observations of sulfates . . . . .                            | 53         |
| 2.4      | Implications and Conclusions . . . . .                                 | 59         |
| 2.4.1    | Active hydration of kieserite hypothesis . . . . .                     | 59         |
| 2.4.2    | High obliquity hydration of kieserite hypothesis . . . . .             | 60         |
| 2.4.3    | Multi-sulfate evaporite deposit hypothesis . . . . .                   | 61         |
| 2.4.4    | Discussion . . . . .                                                   | 62         |
| <b>3</b> | <b>Sulfate Stratigraphy in Ius Chasma, Valles Marineris</b>            | <b>67</b>  |
| 3.1      | Introduction . . . . .                                                 | 68         |
| 3.2      | Background . . . . .                                                   | 70         |
| 3.2.1    | Geologic history . . . . .                                             | 70         |
| 3.2.2    | Mars Reconnaissance Orbiter (MRO) datasets . . . . .                   | 74         |
| 3.2.3    | MOLA topography . . . . .                                              | 75         |
| 3.3      | Methods . . . . .                                                      | 75         |
| 3.3.1    | CRISM data reduction . . . . .                                         | 75         |
| 3.3.2    | Spectral interpretation of minerals . . . . .                          | 76         |
| 3.4      | Results . . . . .                                                      | 80         |
| 3.4.1    | Spectral results . . . . .                                             | 80         |
| 3.4.2    | Stratigraphic results . . . . .                                        | 88         |
| 3.5      | Discussion . . . . .                                                   | 97         |
| 3.5.1    | Formation and transportation of Fe/Mg smectite . . . . .               | 101        |
| 3.5.2    | Evidence for sulfate evaporites in a paleobasin . . . . .              | 102        |
| 3.5.3    | Relationships between smectites, sulfates, and hydrated silicate       | 105        |
| 3.6      | Conclusion . . . . .                                                   | 107        |
| <b>4</b> | <b>Diagenetic hematite and sulfate assemblages in Valles Marineris</b> | <b>110</b> |
| 4.1      | Introduction . . . . .                                                 | 111        |
| 4.2      | Background . . . . .                                                   | 115        |
| 4.2.1    | Datasets . . . . .                                                     | 115        |
| 4.2.2    | Study locale . . . . .                                                 | 117        |
| 4.3      | Methods . . . . .                                                      | 118        |
| 4.3.1    | CRISM data reduction . . . . .                                         | 118        |
| 4.3.2    | VNIR spectroscopy of sulfates and ferric oxides . . . . .              | 120        |
| 4.4      | Spectral Results . . . . .                                             | 125        |
| 4.4.1    | Minerals identified in Capri Chasma . . . . .                          | 125        |
| 4.4.2    | Ferric oxide variability throughout Valles Marineris . . . . .         | 129        |
| 4.5      | Stratigraphic Results . . . . .                                        | 131        |
| 4.5.1    | Stratigraphic section and regional unit map of Capri Chasma .          | 131        |

|          |                                                                                               |            |
|----------|-----------------------------------------------------------------------------------------------|------------|
| 4.5.2    | Hematite and sulfate association in Capri Chasma . . . . .                                    | 136        |
| 4.5.3    | Interpreted stratigraphic section across Valles Marineris basins                              | 139        |
| 4.6      | Discussion . . . . .                                                                          | 141        |
| 4.6.1    | Implications for formation . . . . .                                                          | 141        |
| 4.6.2    | Evaporite diagenesis . . . . .                                                                | 146        |
| 4.6.3    | Connections to Meridiani Planum . . . . .                                                     | 151        |
| 4.7      | Conclusions . . . . .                                                                         | 152        |
| <b>5</b> | <b>Synthesis of sulfate distribution and formation mechanisms throughout Valles Marineris</b> | <b>156</b> |
| 5.1      | Introduction . . . . .                                                                        | 156        |
| 5.2      | Timing of ILD formation . . . . .                                                             | 157        |
| 5.3      | Plausible ILD formation mechanisms . . . . .                                                  | 159        |
| 5.3.1    | Aeolian or lacustrine deposition of dust and ash . . . . .                                    | 160        |
| 5.3.2    | Evaporite . . . . .                                                                           | 166        |
| 5.3.3    | Volcanic . . . . .                                                                            | 167        |
|          | Types of Volcanic Features . . . . .                                                          | 167        |
|          | ILDs interpreted to be Volcanic . . . . .                                                     | 168        |
|          | Questions about HRSC structural analyses . . . . .                                            | 170        |
| 5.3.4    | Spring mounds . . . . .                                                                       | 171        |
| 5.4      | General sulfate stratigraphy and diagenesis . . . . .                                         | 173        |
| 5.4.1    | Non-sulfate bearing ILDs . . . . .                                                            | 175        |
| 5.5      | Summary of ILD formation and sulfate enrichment . . . . .                                     | 178        |
| 5.6      | Sulfate Distribution by Chasma . . . . .                                                      | 180        |
| 5.6.1    | Tithonium . . . . .                                                                           | 182        |
| 5.6.2    | Melas/Coprates . . . . .                                                                      | 186        |
| 5.6.3    | Ganges . . . . .                                                                              | 187        |
| 5.6.4    | Ophir . . . . .                                                                               | 191        |
| 5.6.5    | East Candor . . . . .                                                                         | 195        |
| 5.6.6    | West Candor . . . . .                                                                         | 198        |
| 5.6.7    | Hebes . . . . .                                                                               | 201        |
| 5.6.8    | Juventae . . . . .                                                                            | 202        |
| 5.6.9    | Aram Chaos . . . . .                                                                          | 206        |
| 5.7      | Post-depositional weathering of sulfate . . . . .                                             | 208        |
| <b>6</b> | <b>Implications for Valles Marineris's aqueous geologic history</b>                           | <b>213</b> |
| 6.1      | Introduction . . . . .                                                                        | 213        |
| 6.2      | Comparing salt giants on Earth to Martian sulfate-rich deposits . . .                         | 214        |
| 6.3      | Relative timing of crustal alteration . . . . .                                               | 218        |
| 6.4      | Implications for mineralogic timeline . . . . .                                               | 221        |
| 6.5      | Outstanding questions . . . . .                                                               | 223        |
| 6.5.1    | Spectral uncertainties . . . . .                                                              | 224        |
| 6.5.2    | Unknown mineral assemblages and abundance of sulfates . . .                                   | 226        |

|          |                                                                                              |            |
|----------|----------------------------------------------------------------------------------------------|------------|
| 6.5.3    | Thermodynamic and kinetic concerns . . . . .                                                 | 228        |
| 6.6      | Future Directions . . . . .                                                                  | 230        |
| <b>A</b> | <b>Sulfate mineral names and formulas</b>                                                    | <b>234</b> |
| <b>B</b> | <b>CRISM targeted observations in Valles Marineris with sulfate and/or<br/>ferric phases</b> | <b>236</b> |
|          | <b>Bibliography</b>                                                                          | <b>240</b> |

# List of Figures

|      |                                                                                                                   |    |
|------|-------------------------------------------------------------------------------------------------------------------|----|
| 1.1  | Composite view of Mars, centered on Valles Marineris, from Viking 1 Orbiter . . . . .                             | 1  |
| 1.2  | Mineralogic timeline – Phyllosian, Theikian, Siderikian . . . . .                                                 | 2  |
| 1.3  | Martian chemical divides in evaporating brines . . . . .                                                          | 11 |
| 1.4  | Common minerals with no VNIR absorption features . . . . .                                                        | 22 |
| 1.5  | RELAB library spectra of polyhydrated sulfates that potentially match Martian spectra . . . . .                   | 31 |
| 1.6  | CRISM ratioed reflectance type spectra of sulfates that potentially match library spectra . . . . .               | 32 |
| 2.1  | Context map of East Candor Chasma . . . . .                                                                       | 39 |
| 2.2  | General stability diagram for Mg-sulfates under terrestrial and Martian conditions . . . . .                      | 42 |
| 2.3  | Representative CRISM spectra of kieserite and polyhydrated sulfate . . . . .                                      | 49 |
| 2.4  | CRISM wavelength-resampled . . . . .                                                                              | 50 |
| 2.5  | CRISM and OMEGA observations of East Candor Chasma and paired ratio reflectance spectra . . . . .                 | 53 |
| 2.6  | Paired OMEGA and CRISM ratio reflectance spectra of East Candor Chasma . . . . .                                  | 55 |
| 2.7  | False color and sulfate parameter images for HRS00002FAF, East Candor Chasma . . . . .                            | 56 |
| 2.8  | Sulfate parameter image for FRT0000C470, East Candor Chasma . . . . .                                             | 57 |
| 2.9  | Location and ratioed reflectance spectra of paired OMEGA and CRISM data in Ius Chasma . . . . .                   | 58 |
| 2.10 | Relief of layering visible in HiRISE PSP_2076_1735 draped on HiRISE-derived digital elevation model . . . . .     | 65 |
| 2.11 | Structural measurements of East Candor Chasma layered sulfate deposit with an interpreted cross section . . . . . | 66 |
| 3.1  | MDIM of linear Ius Chasma . . . . .                                                                               | 67 |
| 3.2  | RELAB library spectra and CRISM ratioed spectra of hydrated minerals identified with Ius Chasma. . . . .          | 81 |
| 3.3  | Opal deposit in Louros Valles, Ius Chasma . . . . .                                                               | 82 |



|      |                                                                                                                                      |     |
|------|--------------------------------------------------------------------------------------------------------------------------------------|-----|
| 3.4  | CRISM spectra with 2.21 and 2.27 $\mu\text{m}$ doublet and potential library and terrestrial matches . . . . .                       | 84  |
| 3.5  | Regional geologic map of Ius Chasma . . . . .                                                                                        | 89  |
| 3.6  | Cross-section A-A' in Ius Chasma . . . . .                                                                                           | 90  |
| 3.7  | Cross-section B-B' and C-C' in Ius Chasma . . . . .                                                                                  | 91  |
| 3.8  | Relative timeline of hydrated mineral formation in Ius Chasma. . . .                                                                 | 94  |
| 3.9  | Contact between layered sedimentary Fe/Mg smectite with massive hydrated silicate showing erosional unconformity . . . . .           | 94  |
| 3.10 | Evaporite basin with kieserite and polyhydrated sulfate . . . . .                                                                    | 96  |
| 3.11 | Opal and sulfate contact in Ius Chasma . . . . .                                                                                     | 97  |
| 3.12 | Hydrated mineralogy in breccia blocks . . . . .                                                                                      | 98  |
| 3.13 | Fe/Mg smectite-rich layers in Geryon Montes wallrock. . . . .                                                                        | 99  |
| 4.1  | Central mound and surrounding knobs in Capri Chasma, in eastern Valles Marineris . . . . .                                           | 116 |
| 4.2  | RELAB library spectra 0.38–2.5 $\mu\text{m}$ . . . . .                                                                               | 121 |
| 4.3  | Continuum-removed RELAB library spectra 0.41–0.97 $\mu\text{m}$ . . . . .                                                            | 123 |
| 4.4  | CRISM spectra of typical kieserite/hematite location and of hematite-poor PHS location in Capri Chasma . . . . .                     | 126 |
| 4.5  | CRISM spectra of typical “red hematite,” “probable hematite,” and “ferric phases” over 0.4–1.1 $\mu\text{m}$ . . . . .               | 126 |
| 4.6  | Regional unit map of sulfate distribution in Capri Chasma . . . . .                                                                  | 130 |
| 4.7  | Example textures of units with kieserite and PHS . . . . .                                                                           | 132 |
| 4.8  | Contact between kieserite/hematite and PHS in Capri Chasma . . . .                                                                   | 133 |
| 4.9  | Mineral stratigraphy on northern edge of Capri Chasma ILD . . . . .                                                                  | 135 |
| 4.10 | Stratigraphic cross-section of sulfates within the central mound of Capri Chasma . . . . .                                           | 135 |
| 4.11 | Gray hematite distribution in Capri Chasma from TES data . . . . .                                                                   | 139 |
| 4.12 | Sulfate occurrences in Western Valles Marineris in CRISM data . . . .                                                                | 142 |
| 4.13 | Sulfate occurrences in Eastern Valles Marineris in CRISM data . . . .                                                                | 143 |
| 4.14 | Schematic of ILD formation and sulfate enrichment in basinal chasmata                                                                | 144 |
| 4.15 | Equilibrium mineralogy in a system containing $\text{K}_2\text{-Na}_2\text{-Mg-Cl}_2\text{-SO}_4$ solutes at 25° and 40° C . . . . . | 149 |
| 5.1  | MDIM mosaic of basinal chasma with central ILDs - Ganges, W Candor, Melas, Juventae, and Capri . . . . .                             | 161 |
| 5.2  | Detail of CTX image of Juventae Chasma, showing fluted texture of ILDs. . . . .                                                      | 162 |
| 5.3  | Tithonium Chasma ILD: location of sulfates and ferric oxides. . . . .                                                                | 184 |
| 5.4  | Tithonium Chasma ILD: location of sulfates and ferric oxides. . . . .                                                                | 185 |
| 5.5  | Melas Chasma ILD: location of sulfates and ferric oxides, and sulfate contact in FRT000063BD . . . . .                               | 188 |
| 5.6  | HiRISE imagery over contact between sulfates in Melas Chasma. . . .                                                                  | 189 |

|      |                                                                                                                                  |     |
|------|----------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.7  | Ganges Chasma ILD: location of sulfates and ferric oxides. . . . .                                                               | 192 |
| 5.8  | Spectrally neutral ILDs in Ganges Chasma right next to sulfate-rich central ILD. . . . .                                         | 193 |
| 5.9  | CRISM targeted observations in Ganges Chasma of ILDs lacking spectral signatures or having strong kieserite signatures . . . . . | 194 |
| 5.10 | Ophir Chasma ILD: location of sulfates and ferric oxides. . . . .                                                                | 196 |
| 5.11 | CRISM FRT0000BB63 in Ophir Chasma showing kieserite at base, but not in bulk, of ILD . . . . .                                   | 197 |
| 5.12 | East Candor Chasma ILD: location of sulfates and ferric oxides. . . .                                                            | 198 |
| 5.13 | CRISM exceptionally long HRL00004F38 in East Candor Chasma. . .                                                                  | 199 |
| 5.14 | Location of sulfates and ferric oxides within West Candor Chasma ILD.                                                            | 202 |
| 5.15 | Hebes Chasma ILD: location of sulfates and ferric oxides. . . . .                                                                | 203 |
| 5.16 | Juventae Chasma ILDs: location of sulfates and ferric oxides. . . . .                                                            | 207 |
| 5.17 | Aram Chaos ILDs: location of hydrated mineralogy, from [Lichtenberg et al. 2009], Fig. 2. . . . .                                | 209 |
| 5.18 | Tithonium Chasma ILD with kieserite and polyhydrated sulfate indicating hydration state transition. . . . .                      | 211 |
| 5.19 | Coprates Chasma ILD with kieserite and polyhydrated sulfate indicating hydration state transition. . . . .                       | 212 |
| 6.1  | Hydrated mineralogy in Valles Marineris covers a range in pH conditions                                                          | 221 |

# List of Tables

|     |                                                                              |     |
|-----|------------------------------------------------------------------------------|-----|
| 1.1 | Calculated evaporite sequences from brines with Martian starting chemistries | 9   |
| 2.1 | Targeted observations of East Candor Chasma ILD . . . . .                    | 55  |
| 3.1 | Geologic units in Ius Chasma, Valles Marineris . . . . .                     | 83  |
| 4.1 | Location of CRISM type spectra . . . . .                                     | 155 |

# Chapter 1

## Introduction

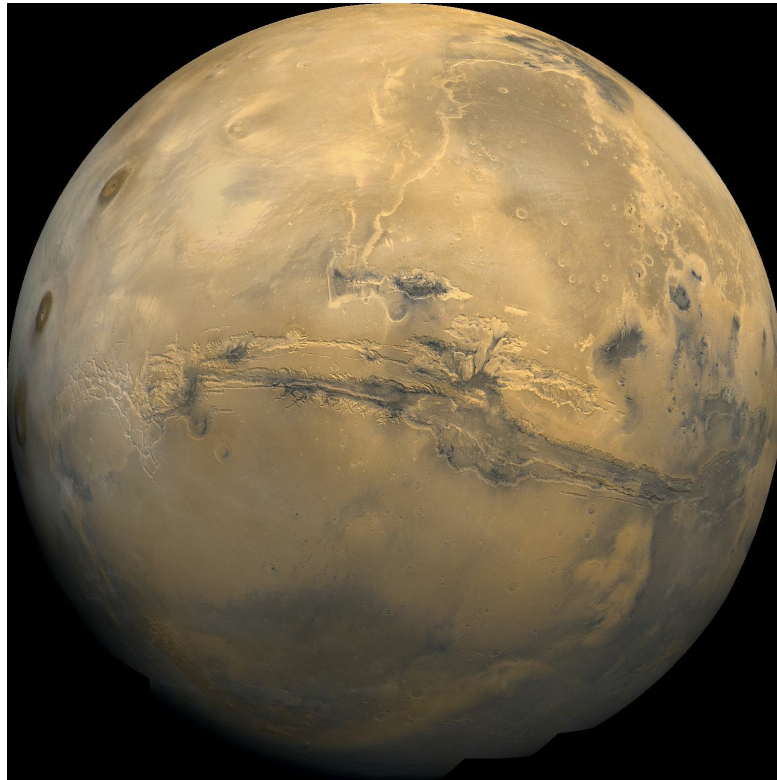


Figure 1.1: Composite view of Mars, centered on Valles Marineris, from Viking 1 Orbiter. Image MG07S078-334SP.

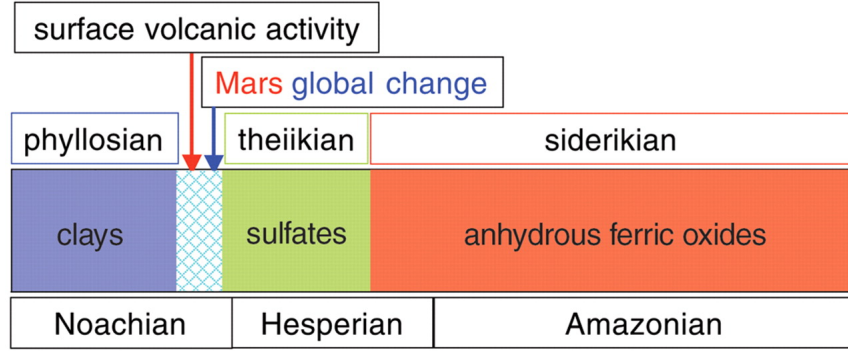


Figure 1.2: Mineralogic timeline of Mars, divided into the Phyllosian, Theikian, and Siderikian, caused by decreasing water activity with time. Figure from [Bibring et al. 2006].

## 1.1 Motivation

Recent orbital and landed investigation of Mars have revealed a diversity of hydrated mineralogy exposed on the surface [Christensen et al. 2000; Bibring et al. 2004; Squyres et al. 2004; Murchie et al. 2009a]. The mineral identified include: sulfates, hydrated silica, smectite clays, zeolites, chlorites, and other phyllosilicates. These findings have provoked a revolution in our understanding of the geologic history of Mars. Prior to the TES (Thermal Emission Spectrometry) and OMEGA (Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activite) orbital spectrometers, Mars was seen as generally a dry, basaltic planet. The abundance of geomorphic features indicating aqueous erosion were not backed up by outcrops of aqueous mineralogy. In the light of recent results from TES, OMEGA, and CRISM (Compact Reconnaissance Imaging Spectrometer for Mars), the surface of Mars can now be studied from a geochemical as well as a geomorphic perspective.

Understanding the role of water in the evolution of the Martian surface has always been a central focus to the Mars exploration program in its search for past and present habitable environments. While the Martian surface is currently cold and dry, channels

and deltas indicate fluvial erosion was a common planetary-wide process in the past (Fig 1.1 shows the most dramatic evidence of fluvial erosion). River and channel morphologies tell us water once flowed over the surface, but more information is needed to estimate the amount of time or volume of water involved – that is, what type of climate formed these fluvial features. Mapping the type and distribution of hydrated mineralogy is one way to track the aqueous history of Mars. Sulfates are a potentially good tracer of past climate because they form by aqueous processes, so their presence, volume, and process of formation can characterize how much water was available. Additionally, some sulfates indicate acidic conditions (e.g. jarosites and romerite), and when compared with the type and distribution of more alkaline minerals (e.g. carbonates or phyllosilicates), provide insight into regional groundwater chemistry.

Sulfates are important secondary minerals produced from the evaporation of fluids involved in the aqueous alteration of Mars' primary lithology [Tosca et al. 2005]. They indicate an interaction of volcanic  $\text{SO}_2$ , in the form of gas or sulfide, with crustal materials in the presence of water and may be the mineral remnants of an early wetter climate on Mars. Sulfates are a product of dissolution and precipitation reactions that may occur over a range in pH. Sulfates can form as evaporites in standing bodies of water, by precipitation from saturated groundwater, or by acid fog alteration of primary minerals [Schreiber and El Tabakh 2000; Spencer 2000; Settle 1979].

The layered sediments at Meridiani Planum, investigated in detail by the Mars Exploration Rover (MER) Opportunity, is one significant sulfate deposit. While an evaporite model best fits the MER results, different models have also been proposed, including an impact surge deposit [Knauth et al. 2005], a basaltic pyroclastic deposit subsequently altered by acidic water [McCollom and Hynek 2005], and a sublimation

residue from a former ice deposit [Niles and Michalski 2009]. The Burns formation at Meridiani Planum consists of a sedimentary sequence of sand-sized evaporitic and basaltic grains, transported by wind and cemented by multiple fluctuations in groundwater level [McLennan et al. 2005]. Syndepositional evaporite minerals and hematite concretions indicate several episodes of chemically distinct groundwater flow [McLennan et al. 2005]. This interaction of acidic groundwater with basaltic material produced considerable Mg, Fe, and Ca sulfates [Clark et al. 2005; Tosca et al. 2005]. The bright subsurface sulfate soils exposed in Gusev crater at Paso Robles and other sites indicate the presence of acidic aqueous processes here as well [Johnson et al. 2007; Lane et al. 2008]. Acid sulfate alteration processes may have been widespread across Mars.

A recent model of Mars mineralogic history suggests three distinct alteration periods — eras of phyllosilicate, sulfate, and anhydrous ferric oxide formation as Mars cooled and water was increasingly unavailable [Bibring et al. 2006]. The water may have been sequestered in the frozen subsurface or removed by  $H_2$  escape from the upper atmosphere [Rossbacher and Judson 1981; Kass and Yung 1995]. These periods are named the Phyllosian, Theiikian, and Siderikian, after the Greek roots for “clay minerals,” “sulfates,” and “iron oxides.” In this model, sulfate formation predominantly occurred after a global climate change from an alkaline, wet environment to a drying environment. This climate change could have been triggered by extensive Tharsis volcanism and  $SO_2$  outgassing and/or by loss of the atmosphere from sputtering after the internal dynamo weakened [Bibring et al. 2006]. After volcanism subsided and the water in the atmosphere was sufficiently depleted, sulfate formation ceased. The only mineral forming was anhydrous ferric oxides in the dust, which coat the now cold and dry surface of Mars. Currently on Mars, the dominant active phases of water are frost and atmospheric water vapor. However, the lack of liquid

water might not prevent ongoing alteration. Understanding the potential for sulfates to change hydration states under current conditions could help constrain how active groundwater, frost, and atmospheric vapor have been in the most recent period on Mars.

This model is controversial for making sweeping statements about the global geologic history based on isolated mineral outcrops. The model makes predictions about the dominant secondary mineralogy expected in geologic units of different ages, but these predictions have not yet been fully tested. Key questions that need to be addressed include:

1. Relative timing of formation of clay minerals and sulfates
2. Types of sulfates present and implications for surface geochemical interactions
3. Stability of sulfates (and clay minerals) in the dry Siderikian period

This thesis will test the OMEGA model of decreasing water activity with time through high-resolution observations from the Mars Reconnaissance Orbiter (MRO) mission together with imagery and topographic data. The Valles Marineris canyon system is an excellent location to test the OMEGA mineralogic model because it has extensive sulfate layering and deposits of phyllosilicates [Murchie et al. 2009a], hydrated silica [Milliken et al. 2008a; Roach et al. 2008c], and iron oxide [Bibring et al. 2007; Roach et al. 2009a]. The thesis addresses the types of sulfates present, their stratigraphic relationship with other mineralogic units, and the evidence for alteration in the hydration state since deposition. The sulfate deposits are found in association with primary mafic mineralogy as well as alteration minerals including phyllosilicates, hematite, hydrated silica, and other hydrated silicates, so understanding the relative timing of the multiple alteration events necessary to produce this diverse suite of secondary minerals is key to testing the OMEGA model.



## 1.2 Background on Sulfates

### 1.2.1 Sulfate locations on Mars

Orbital data has shown that significant sulfate deposits on Mars occur in two main regions in the equatorial region and in dunes around the north polar ice cap. The equatorial sulfates are found throughout Valles Marineris, in related outflow channels such as Aram Chaos, and in areas east of Valles Marineris such as Meridiani Planum [Bibring et al. 2005; Gendrin et al. 2005; Mangold et al. 2008b]. The OMEGA spectrometer aboard the Mars Express (MEx) spacecraft has revealed the monohydrate, kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ), and a polyhydrated sulfate of unknown cation in many massive or finely-layered interior layered deposits in Valles Marineris [Bibring et al. 2005; Gendrin et al. 2005; Mangold et al. 2008b]. The reason for the association of sulfates with Valles Marineris is uncertain but could be due to a combination of  $\text{SO}_2$  gas sourced from nearby Tharsis volcanism, deep basins to concentrate or retain sulfate-rich brines, and hydrothermal or groundwater circulation of sulfur-rich fluids [Gendrin et al. 2005]. One explanation for the concentration of sulfates near Valles Marineris comes from modeling the effect of Tharsis volcano building on the Martian global hydrology [Andrews-Hanna et al. 2007a]. The model shows that Valles Marineris and its outflow channels and Meridiani Planum are locations of prolonged groundwater upwelling and subsequent evaporation would result in accumulation of significant evaporite deposits [Andrews-Hanna et al. 2007a; Murchie et al. 2009b].

Mars Rover Opportunity investigated Meridiani Planum in detail [Squyres and et al. 2004] and supported the aqueous hematite formation mechanism; it uncovered chemical, morphological, and mineralogical evidence of aqueous alteration of basalt and formation of hydrated sulfate-bearing evaporites and hematite concretions [Squyres and Knoll 2005; Grotzinger et al. 2005]. The Mars Rover team has devel-

oped a model for the Terra Meridiani region involving interdune playas and multiple episodes of high water tables, resulting in complex sulfate recrystallization [McLennan et al. 2005]. The hematite concretions at Terra Meridiani are proposed to derive from the breakdown of jarosite (  $\text{Fe}_3 [ (\text{OH})_2 \text{SO}_4 ]_2$  ) or oxidation of a hydrated ferrous sulfate, such as melanterite,  $\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$  [McLennan et al. 2005]. Jarosite is 10% of the outcrop and only stable at  $\text{pH} < 4$ , putting a strong geochemical control on the system [Clark et al. 2005; Klingelhofer et al. 2004]. Melanterite has not been uniquely identified at Meridiani Planum, but has been proposed as one of the original minerals to form the evaporite facies [McLennan et al. 2005]. Melanterite is very soluble and in a fluctuating briny water table, would have dissolved, leaving tabular vugs in the outcrops [McLennan et al. 2005; Peterson and Wang 2006]. This link between iron oxides and hydrated sulfates may be useful in determining environment of formation on Mars, and the relative amounts of sulfate to iron oxide may indicate amount of aqueous dissolution and transport after formation of the evaporite.

It is difficult to tie the genesis of the gypsum near the North Pole to near Valles Marineris events. The gypsum-bearing late Amazonian-aged circumpolar dunes are enigmatic as no source of the gypsum has been identified [Langevin et al. 2005]. The gypsum might be formed by local ice cap melt water altering basaltic sand grains or by modern re-exposure and re-working of the Polar Basal Unit, which may contain variable amounts of gypsum [Langevin et al. 2005; Fishbaugh et al. 2007].

The presence of sulfates in a location does not imply the original weathering of basaltic precursor material occurred there, since the relatively high solubility of sulfates and their mobility in solution complicates our ability to tie sulfate formation to specific volcanic or geologic processes. Present sulfate locations and abundances on the Martian surface are likely a function of how they have been transported, altered or recycled, and preserved since formation. For example, the sulfate deposits at

Meridiani Planum are interpreted as transported sulfate grains, recemented by local groundwater fluctuations [McLennan et al. 2005]. However, regional similarities in the lithology, mineralogy, and relative stratigraphy of sulfate exposures in the Valles Marineris system indicate that similar processes may have formed or modified many sulfate deposits in this region.

### 1.2.2 Sulfate formation mechanisms on Mars

Sulfates can be formed on Mars by: 1) surface weathering of volcanic material from acidic rains or fog [Banin et al. 1997], 2) evaporation of standing bodies of water [Tosca et al. 2005], or 3) oxidation of hydrothermally emplaced pyrite [Pirajno and Van Kranendonk 2005].

In the acidic fog scenario, acidic volcanic aerosols weather rock over  $10^8$  years to produce an amorphous soil rich in silica, sulfur, chloride, and iron oxides [Banin et al. 1997]. The chemistry and mineralogy of the basalt being weathered strongly controls the resulting evaporite salt chemistry [Tosca et al. 2003]. This weathering process does not involve liquid water, so clays and large sulfate crystals do not form. The acidic rain or fog is a very slow process that takes  $10^8$  years to weather just the surface to sulfate [Banin et al. 1997], so it cannot easily explain the several kilometer-thick deposits in Valles Marineris that have sulfate in their bulk. Weathering of repeated ash-fall layers before the next ash deposition would be one way to produce a massively bedded sulfate deposit, however the process would take too long ( $10^9$  years) to be feasible for the ILDs.

The second scenario for sulfate formation is aqueous weathering of basaltic rock and evaporation of those fluids to leave evaporite sequences. Evaporation in a closed system produces a sequence of sulfates and iron oxides as the solubility of each mineral is surpassed in the concentrating brine. This idea of successive chemical divides

Table 1.1: Calculated evaporite sequences from brines with Martian starting chemistries. The first section has the order of appearance of major evaporite phases and the second section lists trace phases that may appear at complete evaporation of the brine.

| Brine A                                              | Brine B                                         | Brine C                                         | Brine D                           | Brine E                                               |
|------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-----------------------------------|-------------------------------------------------------|
| Siderite<br>Calcite, Magnesite<br>Gypsum<br>Epsomite | Siderite<br>Gypsum<br>Epsomite                  | Siderite<br>Gypsum<br>Melanterite<br>Epsomite   | Gypsum<br>Melanterite<br>Epsomite | Gypsum                                                |
| $\text{NaHCO}_3$ ,<br>$\text{KHCO}_3$                | Halite, sylvite,<br>bischofite,<br>antarcticite | Halite, sylvite,<br>bischofite,<br>antarcticite | Halite, sylvite,<br>bischofite    | Bloedite,<br>polyhalite,<br>glauberite,<br>thenardite |

dictates which evaporite sequence forms as the brine evolves geochemically (Fig 1.3). The greater amount of water required for this model than for the acid fog model means the resulting sulfates can be crystalline. A typical evaporite sequence on Mars will derive from brines that have only interacted with basaltic composition rocks, a rare occurrence for terrestrial brines [Tosca and McLennan 2006]. While the type and sequence of sulfates on Mars will be different than expectations for terrestrial sulfates, they can be modeled by experimental acidic leaching of Martian basalt analogs and evaporation of the resulting fluid [Tosca and McLennan 2006]. Table 1.2.2 shows five calculated evaporite sequences from brines with Martian starting chemistries, adapted from [Tosca and McLennan 2006]. The brines, labelled A-E, are different starting proportions of  $\text{CO}_2$  and  $\text{SO}_2$  gases. The linear sequence shown for Brine A is a condensation of four different precipitation pathways.

The third scenario produces massive sulfide deposits as a result of hydrothermal circulation of sulfur-rich groundwater in volcanic environments [Pirajno and Van Kraendonk 2005]. A high sulfidation hydrothermal system is most applicable to Mars

due to its very acidic and oxidized nature [Pirajno and Van Kranendonk 2005], and it might be easy to search for, if well exposed on Mars, because deposits exhibit consistent alteration mineralogy and zoning. In a high sulfidation hydrothermal system, 150-300° C, SO<sub>2</sub> -rich volcanic gases acidify groundwater, strongly leach wall rocks, and deposit pyrite-rich sulfides. When exposed on the surface, these sulfide deposits could oxidize in the presence of water into iron sulfates. Diagnostic alteration minerals from wall rock dissolution include kaolinite, alunite, barite, dickite, pyrophyllite, and diasporite [Pirajno and Van Kranendonk 2005].

Now we must consider the possible sources of sulfur for sulfate formation, and the size of the reservoir available. The sulfur content of Tharsis volcanics has been estimated at a factor of 4 to 7 greater than terrestrial volcanics [Gaillard and Scaillet 2009]. This is because S preferentially partitions with Fe into the magma melt, and since the proportion of Fe in the mantle is higher on Mars than Earth, the proportion of S is correspondingly higher as well. Assuming reducing conditions, the Tharsis basalts would contain significant sulfide abundances; assuming oxidizing conditions, the sulfur would be outgassed as H<sub>2</sub>S and SO<sub>2</sub> [Gaillard and Scaillet 2009]. In the absence of conclusive knowledge of the redox potential of the Martian atmosphere, either environment produces high sulfur content of Tharsis-related volcanics. These volcanics — either pyrite-bearing tephra or settled volcanic aerosols — are logical sources for S to create sulfates within Valles Marineris.

### 1.3 Formation of Valles Marineris

The origin of the Valles Marineris canyon system has been an area of intense research since its discovery (e.g. [McCauley et al. 1972; Sharp 1973; Carr 1974; Nedell et al. 1987; Lucchitta et al. 1992, 1994]). Several mechanisms have been proposed to explain

Figure 1.3: Martian chemical divides in evaporating brines. Figure and caption from [Tosca and McLennan 2006]: Flow chart for the chemical evolution of evaporating fluids derived by basaltic weathering. Evaporative concentration increases downward and the relative amount of  $\text{HCO}_3^-$  to  $\text{SO}_4^{2-}$  decreases to the right. Precipitates causing chemical divides are indicated as are conditions leading to chemical fractionation from mineral precipitation. The resulting brines and their characteristics are described in boxes. The precipitation pathways for the Nakhla (green arrows) and Meridiani Planum (red arrows) evaporite assemblages correspond to two distinct geochemical environments for saline mineral formation on Mars.

its formation, including karst-style collapse, erosional, and tectonic processes (e.g. [McCauley et al. 1972; Blasius et al. 1977; Croft 1989a,b; Tanaka and Golombek 1989; Schultz 1998]). The currently favored model invokes extension due to tectonic stress related to the Tharsis Rise, although the details are under debate [Mege and Masson 1996a,b] and references therein.

The region consists of a megabrecciated basement [Tanaka and Golombek 1989] overlain in the Late Noachian by sequences of horizontally layered lava flows at least several km thick [Lucchitta et al. 1992; Tanaka et al. 1992; McEwen et al. 1999]. These Late Noachian — Early Hesperian lava plains were part of the voluminous Tharsis volcanism [Tanaka et al. 1991] and are interpreted to be cut by multiple volcanic dikes or lithified faults [Lucchitta et al. 1992]. The  $\sim 400$  m thick, uppermost layers of the lava flows are more resistant to erosion than underlying layers and may be evidence of diagenesis or aqueous alteration during the Late Hesperian [Treiman et al. 1995; Fuks et al. 1995; McEwen et al. 1999]. After the thick lava plains, tectonic stresses due to Tharsis loading started opening the Valles Marineris trough system in Early Hesperian [Tanaka 1986]. Both Noachian and Hesperian material is likely exposed in the Valles Marineris wallrock, but the contact between the two units is not easily distinguished.

Valles Marineris formed over a long period from Early to Late Hesperian, and multiple processes likely contributed to its resulting geometry. It is possible that wider, more irregular chasmata, such as Capri and Melas Chasma, formed in subsiding ancestral basins [Lucchitta et al. 1994; Schultz 1998]. Long rectangular troughs, including Ius Chasma, developed as grabens that eventually connected to the wider chasmata [Lucchitta and Bertolini 1989; Peulvast and Masson 1993a,b]. Ius Chasma may have been isolated from Melas Chasma during its earliest stages, but was later connected [Peulvast and Masson 1993a]. The basins within the canyon system empty

into massive outflow channels. The outflow channels may be carved during periods when liquid water was present on the Martian surface or may be the result of catastrophic outbursts of ground water trapped beneath the cryosphere [Clifford 1993]. The large outflow channels debouched at the eastern end of Valles Marineris in Middle Hesperian, but did not leave fluvial features in Ius Chasma. This is either because the bulk of the water was sourced eastward of Ius, or because later deposition and landslides obscured those features. Mass wasting along faults, fluvial erosion, and landslides all modified the canyon walls. There was late stage tectonic activity mostly concentrated along the southern walls, after much of the fluvial and landslide activity had decreased [Peulvast and Masson 1993a,b]. The late stage normal faulting cuts all fluvial and landslide erosional features.

### **1.3.1 Formation of Interior Layered Deposits (ILDs) in Valles Marineris**

The chasmata contain km-thick, light toned, and massively or finely-layered materials that weather into mesas and mounds, known as Interior Layered Deposits (ILDs), of controversial origin. They range from a few 100 m to 5 km thick and often have horizontal layering traceable for 100s of meters. Within the ILD family, there is variability in thickness, tone, and regularity of layering, but individual deposits often show significant lateral continuity [Nedell et al. 1987]. ILDs often have a fluted topography, suggesting they are fine-grained and easily eroded by wind [Nedell et al. 1987]. They have been suggested to form via lacustrine [McCauley 1978; Lucchitta 1982; Nedell et al. 1987; Lucchitta et al. 1992], volcanic [Witbeck 1991; Lucchitta et al. 1992; Weitz 1999], aeolian [Peterson 1981; Nedell et al. 1987], evaporite precipitation [Beyer et al. 2000; Rossi et al. 2008], mass-wasting [Lucchitta 1987a; Lucchitta et al.



1994] or subglacial volcanic [Chapman and Tanaka 2001; Komatsu and Litasov 2002; Komatsu et al. 2004] processes.

ILDs are found in all chasmata except Echus and Ius, with significant central mounds in Candor [Lucchitta et al. 1994; Komatsu et al. 1993], Ganges [Komatsu et al. 1993], Ophir [Lucchitta et al. 1994], Capri [McEwen and Soderblom 1989], Melas [Lucchitta et al. 1994; Quantin et al. 2005b], Candor [Lucchitta et al. 1994; Komatsu et al. 1993], and Hebes Chasmata [Peterson 1981; Hauber et al. 2006, 2008]. ILDs are also present in the linear troughs — Tithonium and Coprates Chasmata — in smaller deposits. Ius Chasma is a linear trough with no mapped ILDs. There is debate as to whether some ILDs formed before Valles Marineris opened or if all postdate the canyon formation [Malin and Edgett 2000a; Lucchitta et al. 1994; Komatsu et al. 1993]. ILDs may have formed in ancestral basins that predate the fully-formed canyon system [Schultz 1998]. In one case, HiRISE digital terrain models have shown the ILDs in Western Candor Chasma formed in a pre-existing depression [Okubo et al. 2008]. Resolving this point has important implications for the timing of sulfate formation within the Martian geologic timeline. MOC imagery [Lucchitta 2001] supports the theory that the ILDs postdate canyon formation, but detailed fieldwork will be needed to lay this controversy to rest.

The age of ILDs cannot easily be estimated by crater counting, as they have few impact craters [Malin and Edgett 2000b]. The absence of many impact craters on ILDs suggests their surfaces are too young to have accumulated craters or that they are eroding away too quickly to retain craters. The canonical age for ILDs is Upper Hesperian-Amazonian [Lucchitta et al. 1992; Lucchitta 1999]. Crater counting studies of specific ILDs found ages of 10 Ma in Hebes to 400 Ma in Juventae [Sowe et al. 2007; Neukum 2007; Rossi et al. 2008]. These ages are complicated by erosion, and may represent the retention age, not the formation age. Alternatively, the ages may

represent the date of deposition of the top-most surface of ILDs (such as a thick aeolian or ash fall layer) [Rossi et al. 2008]. The most recent volcanic surfaces on Mars, dated to  $<100$  Ma, are at least an order of magnitude more cratered than most ILDs [Hartmann et al. 1999; Hartmann and Berman 2000; Malin and Edgett 2000b].

The sulfate detection in Valles Marineris has been limited to ILDs with high thermal inertia [Gendrin et al. 2005]. Dust cover, amount of induration, lamination thickness, albedo, and texture vary among the ILDs [Lucchitta et al. 1992], which complicates the mapping of these features. In addition to determining how the ILDs formed, there are two additional challenges: (1) understanding how they became enriched in sulfate, (2) decoding how they have been modified since formation. We must consider that the period of sulfate enrichment may not have been when the layered deposits first formed, but during later interaction with groundwater. Post-depositional modification such as deformation, mass wasting, and aeolian fluting are common processes on ILDs. Dark areas on the the ILDs, often found in topographic depressions, are interpreted as dunes and debris fans [Weitz et al. 2001, 2008a]. The dark areas contain gray hematite and mafic minerals, including pyroxene and feldspar [Weitz et al. 2008a]. HiRISE imagery has shown significant dust and loose material filling flutes on ILDs, creating dune fields partially covering the deposit, or forming talus cones at the base of ILDs. MOC imagery suggests aeolian, fluvial and mass wasting processes were active in the erosion of the ILDs [Weitz et al. 2001].

### **Sub-ice volcanism or volcanism**

Volcanism or subaqueous volcanism are expected given the canyon's tectonic formation, and may have been a significant source of material for the ILDs [Nedell et al. 1987]. Although vents and caldera have not been identified, if the volcanism was subaqueous, they may have been obscured by settling volcanic material [Nedell et al.

1987].

If the ILDs are volcanic deposits, they are not competent lava flows like the wall rock, since the ILDs erode into a different morphology than the layered volcanics in the canyon walls [Nedell et al. 1987]. The ILDs are more friable, and could be consistent with layered tuff or ash deposits [Lucchitta 1990; Peterson 1981; Witbeck 1991]. Several ILDs have been suggested to be volcanic deposits based on texture, gross morphology, and structural analysis (i.e. [Hauber et al. 2006; Chapman et al. 2007; Hamelin et al. 2008]). These ILDs will be discussed in more detail in Chapter 5.

### **Aeolian deposition of ash and dust**

The model of aeolian deposition of ash and dust into ILDs can explain the finely layered deposits. Cross bedding would be expected in an aeolian process, but possibly the cross-beds are too small scale to be resolved in HiRISE imagery. Loess deposits, which are very thick, weakly indurated deposits of windblown dust, are held together by their angular grains. The ILDs in Valles Marineris cannot be an uncemented loess deposits, since they must have some degree of cementation to explain their moderate thermal inertia values. Thermal inertia, a measure of how well a material holds on to heat, is controlled by grain size, amount of induration, and hydration state [Mellon et al. 2000]. ILDs have thermal inertia values above 200 [Mangold et al. 2008b], which is the cut off between unconsolidated dust ( $<200$ ) and larger grains or more consolidated material [Mellon et al. 2000]. Additionally, loess deposits erode in characteristic "cat step" patterns, not the flutes and yardangs seen in ILDs.

Some have argued that aeolian deposition is not realistic since some of the deposits are too regularly bedded and as a whole the ILDs are too variable in albedo, competence and erosional characteristics [Peterson 1981; Lucchitta 1987b; Nedell et al.

1987]. However, operating under the assumption that multiple processes formed the range of ILDs present in the canyon system, aeolian deposition is a valid method for some of them. Aeolian deposition can bring a significant amount of dust, ash and saltating grains into the canyon. The few km-deep canyon system acts as a global trap for aeolian fines, so significant aeolian deposits would be expected.

Ash from Tharsis volcanism can be transported long distances and is expected to be more voluminous than terrestrial pyroclastic eruptions [Wilson and Head 1994]. The greater volatile content in Martian magmas would create faster eruption speeds and greater areal distribution – pyroclastic deposits up to hundreds of km<sup>2</sup> are expected [Wilson and Head 1994]. The resulting ash deposits are projected to be located east and west of Tharsis and to thin with distance from the eruption epicenter [Hynek et al. 2003]. The bulk of the Interior Layered Deposits may be volcanic ash from explosive Tharsis volcanism.

### **Lacustrine deposition**

The lacustrine model encompasses deposition within a standing body of water (or ice), including both deposition of the suspended load brought into the body and evaporite formations as the basin concentrated. If the water bodies in Valles Marineris were ice covered, sediment could still penetrate the ice cover by foundering or Rayleigh-Taylor instabilities [Nedell et al. 1987]. Deposition in low-energy lacustrine environments could explain the laterally continuous, finely bedded, horizontal layers [Lucchitta 1987b; Nedell et al. 1987; Peterson 1981]. McCauley went further to state that only deposition in standing water could produce such regular and rhythmic features [McCauley 1978]. The newer generation of high resolution imagery has revealed that the fine bedding continues to the sub-meter scale, but that the deposits are not as homogeneously layered as suspected from Viking imagery.

## Mass wasting

Mass wasting of canyon wall rock is not the dominant source for ILD deposits. Not enough material has been eroded from the canyon walls after Tharsis-related graben formation to account for all the interior layered deposit mass [Lucchitta 1990]. However, mass wasting could be one process bringing loose material into the canyons which are redeposited by aeolian or fluvial processes into ILDs.

## 1.4 Visible-Near Infrared Spectroscopy

Visible-Near Infrared (VNIR) reflectance spectroscopy can be used to identify minerals based on the albedo, continuum slope, and absorption features of their spectra [Clark 1999]. The wavelength range of VNIR reflectance spectroscopy is sensitive to crystal field transitions, charge transfers, and vibrational features diagnostic of iron-bearing and hydrated minerals [Burns 1993; Gaffey et al. 1993; Clark 1999]. The specific wavelength of a diagnostic feature is dependent on the type of absorption and excitation, the type of ligands involved and their location within the mineral structure.

### 1.4.1 Crystal field transitions

Crystal field transitions arise in minerals with transition metal ions whose unfilled inner shell electrons absorb photons of a specific energy and jump to an excited energy state, resulting in an absorption feature at that wavelength [Burns 1993]. The wavelength of absorption is determined by the energy difference between the two states and is also affected by crystal symmetry and ligand coordination [Clark 1999; Burns 1993]. For example, goethite has a wide  $0.90\ \mu\text{m}$  minimum while hematite has a narrower  $0.86\text{-}0.87\ \mu\text{m}$  minimum, both due to crystal field transitions of octahedrally

coordinated  $\text{Fe}^{3+}$  [Clark 1999; Morris et al. 1985; Hunt et al. 1971a].

### 1.4.2 Charge transfers

Charge transfer absorptions occur when an electron absorbs a photon (usually at ultraviolet wavelengths) and moves between ions or between an ion and ligand [Clark 1999]. Iron oxides owe their red color to saturated UV charge transfer absorptions that cause very low reflectivity shortward of  $0.55\ \mu\text{m}$  [Morris et al. 1985]. Iron oxides show a variety of  $\sim 0.5\ \mu\text{m}$  absorptions, which are caused by ferric ion charge transfers or crystal field splitting [Hunt et al. 1971a; Hunt and Salisbury 1970; Morris et al. 1985].

### 1.4.3 Vibrational features

Vibrational features in spectra are due to vibrational modes (or their overtones) of molecular species such as  $\text{CO}_3$ ,  $\text{SO}_4$ ,  $\text{OH}$ , or  $\text{H}_2\text{O}$ , within a mineral structure [Clark 1999]. The vibrations are proportional to the bond strength and mass of elements within the vibrating molecule [Clark 1999]. Frequencies of fundamental vibrations are labeled  $\nu^1$ ,  $\nu^2$ ,  $\nu^3$ , overtones are labeled  $2\nu^3$  (second overtone of third fundamental vibration) and combinations are labeled  $\nu^1 + \nu^2$  and are approximately the sum of the fundamental vibrations. For example, hydrated minerals have a combination H-O-H bend and OH stretch at  $1.9\ \mu\text{m}$  ( $\nu^1 + \nu^2$ ) and an overtone OH stretch at  $1.4\ \mu\text{m}$  ( $2\nu^1$  and  $2\nu^3$ ). Mineral structures with hydroxyls but not water molecules only have the  $1.4\ \mu\text{m}$  overtone OH stretch.

Sulfate vibrational features in the VNIR are limited to the previously mentioned hydroxyl vibrations and tentatively identified at  $2.4\ \mu\text{m}$  [Hunt et al. 1971b; Cloutis et al. 2006]. Many sulfates with multiple water molecules are very spectrally similar

in library spectra (absorptions at 1.4, 1.9, and 2.4  $\mu\text{m}$ ), and are indistinguishable in OMEGA or CRISM data. The spectral identification of polyhydrated sulfate in OMEGA and CRISM is admittedly unsatisfactory since the unspecified cation does not allow us to tightly constrain possible paragenetic assemblages or parent brine chemistry. However, the possible cations for "polyhydrated sulfate" are partially restricted, as will be discussed later.

#### 1.4.4 Spectrally Bland Minerals

Some minerals are spectrally bland in the VNIR wavelength region, and thus other wavelength regions or techniques must be employed to identify the mineralogy. Although VNIR spectroscopy can confidently resolve iron oxides, mafic minerals, phyllosilicates, and sulfates, it cannot identify anhydrous quartz and other Fe-free silicates, anhydrous sulfates, or anhydrous chlorides. The common trait in these VNIR-indistinct minerals is the lack of an OH vibrational feature from water or metal-OH ligands. The shape, position, and bonding of OH and H<sub>2</sub>O molecules in mineral structures can produce diagnostic vibrations, which correspond to diagnostic VNIR absorptions.

Since Mars is a dominantly basaltic planet, plagioclase and other spectrally neutral silicates are expected to be a large fraction of every surface. Thus, we need to be cognizant of CRISM's inability to see what might be the dominant mineral and to consider detected minerals in the context of complex mineral assemblages, many phases of which may not be distinguishable. On surfaces with significant alteration minerals, such as phyllosilicate-bearing Noachian units, the hydrated alteration material may be the only spectrally identifiable phase, but unaltered or partially altered basaltic material (such as pyroxenes, feldspars, and olivine) are undoubtedly also present, and may actually be the volumetrically dominant minerals.

Other wavelength ranges, such as mid-infrared (IR), can resolve silicate minerals such as feldspar and quartz, based on the strong fundamental vibrational frequencies of silicates in the thermal IR [Christensen et al. 2001]. Combined studies of thermal IR and VNIR spectra are promising, but generally do not have immediately interpretable results [Michalski et al. 2006; Abrams et al. 1991]. This is because other properties besides mineralogy, like texture and grain size, can have strong effects on the thermal IR and VNIR spectra. The different sensing depth of thermal IR instruments (upper tens of microns of a surface) and VNIR instruments (less than a micron) mean they register different characteristics of the surface of Mars [Wyatt and Mustard 2006; Wyatt 2007]. Differences in the spectral results of thermal IR and VNIR spectrometers do not indicate one is in error, but that details of the surface texture, rinds and coatings, or mineral abundances are having important effects of the spectra in each wavelength regime. Those differences can be exploited to gauge finer-scale surface properties than can be resolved with high resolution orbital imagers and other instruments.

## 1.5 CRISM instrument

The CRISM instrument is a visible-near infrared hyperspectral imaging spectrometer aboard the MRO spacecraft [Murchie et al. 2007a]. It entered Mars orbit on March 10, 2006 and began its primary science phase in November 2006 [Murchie et al. 2009c]. It has two detectors, covering the visible/near infrared (0.392–1.01  $\mu\text{m}$ ) and infrared (1.01–3.92  $\mu\text{m}$ ) wavelength regions in 544 bands. The detectors are on a gimbal which is used to track the surface during observations and prevent image smearing in the downtrack direction.

CRISM has two basic modes: mapping and targeted. In mapping mode, the



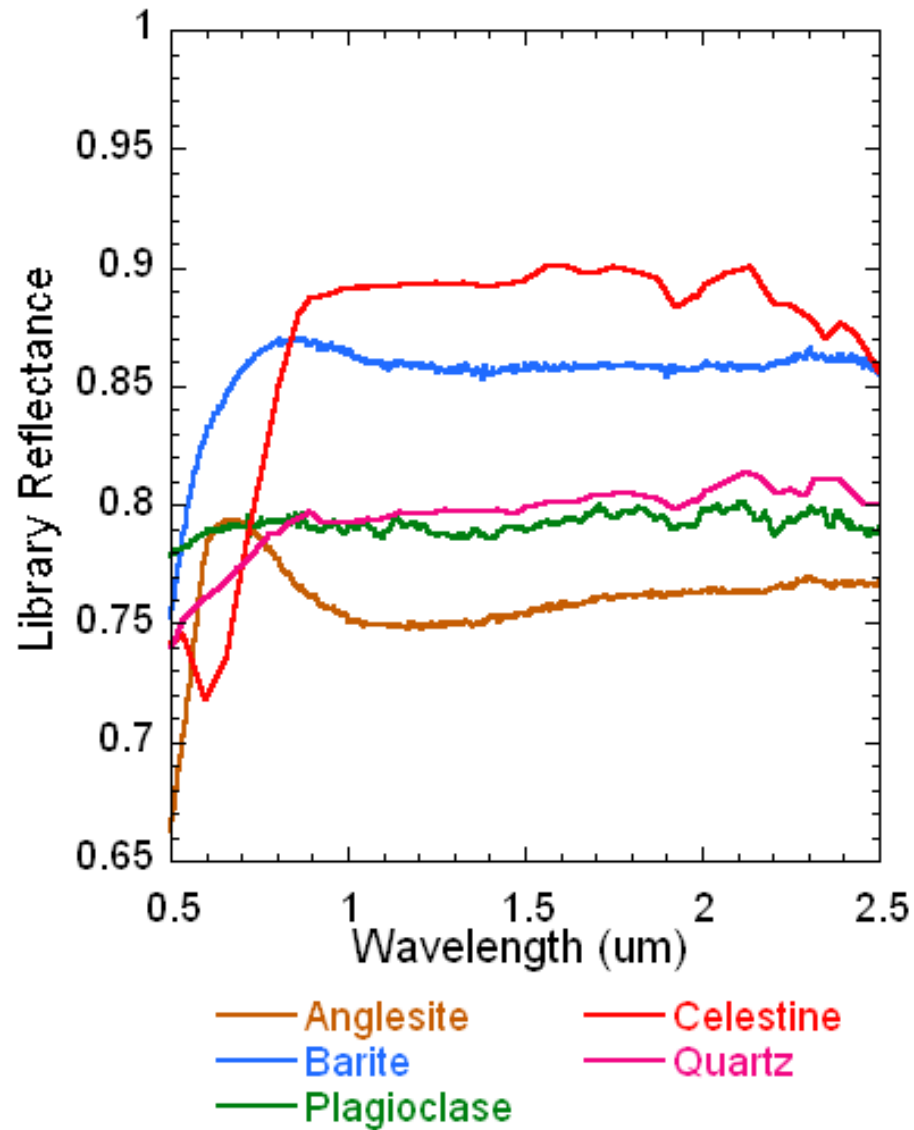


Figure 1.4: Common basaltic component minerals and anhydrous sulfate minerals with no VNIR absorption features. RELAB library spectra plagioclase, quartz, barite ( $\text{BaSO}_4$ ), anglesite ( $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ ), and celestine ( $\text{SrSO}_4$ ).

spectrometer points to the nadir and collects long strips of data at 100 or 200 m/pixel resolution. These strips are several kilometers across and tens of kilometers long. Mapping data is only collected in 72 wavelengths, which are specially selected from the 544 wavelength channels available to capture important absorptions.

In targeted mode, the gimbal allows the spectrometer to track the surface, so higher spatial resolution data can be acquired without smearing in the downtrack direction. The three types of targeted images are full resolution targeted (FRT), half resolution long (HRL), and half resolution short (HRS). The FRT is acquired at  $\sim 18$  m/pixel, while the HRL and HRS observations are 2x binned, or  $\sim 36$  m/pixel. In addition to having higher spatial resolution than the mapping data, the targeted data also has higher spectral resolution since it utilizes all 544 wavelengths.

When acquiring a targeted observation, the CRISM instrument also captures ten to twelve 10x binned observations before and after the main nadir observations. These observations are also centered at the nadir location, but are taken when the spacecraft is relatively far away. These highly gimballed observations provide measurements of the same scene with different atmospheric path lengths, which is called an emission phase function, or EPF. The difference in reflectance between two of these 10x binned observations is due to the difference in amount of aerosols and atmospheric gases and the anisotropic scattering of aerosols. The CRISM team is developing a radiative transfer model that uses these EPFs to remove all aerosol and atmospheric gas absorptions from the central nadir observation [McGuire et al. 2009]. The spectra presented in this thesis do not use this atmospheric correction technique, but instead use the much quicker but possibly less accurate “volcano scan” correction, which is described in more detail in later chapters.

## 1.6 New sulfate types identified with CRISM

The sulfate mineralogy and stratigraphy mapped across Valles Marineris with MRO data is at the crucial scale needed to understand regional structures and interpret them based on local field studies, both on Mars and Earth. CRISM observes at a spatial scale intermediate between MER and MEX, offering the opportunity to scale spectral signatures from the rover (cm-scale) to orbital (10s and 100s of meters) perspectives. The regional views of CRISM mapping tiles and OMEGA spectra allow comparisons and correlations between chasmata. The high resolution targeted CRISM data with CTX and HiRISE imagery are detailed enough for comparison with MER results or to terrestrial sulfate field sites like Rio Tinto, Spain or White Sands, New Mexico. The two CRISM modes together with associated remote sensing datasets are complementary assets in the Valles Marineris-wide survey of sulfate types, locations, and geologic contexts.

OMEGA's discovery paper of sulfates on Mars listed kieserite, gypsum, and epsomite (or another polyhydrated sulfate) as the phases present [Gendrin et al. 2005]. Subsequent investigation with CRISM has confirmed those detections and has revealed new candidate sulfate identification, some of which are as definite as the kieserite and gypsum identification [Swayze et al. 2008] and some of which are spectral classes rather than specific minerals [Bishop et al. 2008b; Mangold et al. 2008c; Roach et al. 2008c]. Identifications are limited to spectral classes in cases where diagnostic differences between related minerals are not sufficient for unique identification. Hydrated iron sulfates are one example of a spectral class that cannot be more definitely resolved.

The mineralogic identification of "polyhydrated sulfate" in OMEGA data cannot be better refined with CRISM data, but more complete spectral libraries have afforded

us a more systematic view of which sulfates are potential matches. Of the multitude of sulfates that have broad, deep 1.4, 1.9, and 2.4  $\mu\text{m}$  absorptions — polyhydrated sulfates — many also have other diagnostic bands, which are not observed. Fig 1.5 shows library spectra of some polyhydrated sulfates together with the uniquely identified kieserite, alunite, and jarosite; of the Mg sulfates, only hexahydrite is plotted, since all other Mg sulfates with 2+ water molecules look very similar spectrally. Fig 1.6 shows CRISM type spectra that most closely match the library spectra. Other polyhydrated sulfates, like copiapite, melanterite, or schwertmannite, have strong ferric or ferrous absorptions in the  $\sim 1 \mu\text{m}$  region, which can be diagnostic. The CRISM type spectra are only shown over 1.0–2.5  $\mu\text{m}$  rather than the whole wavelength region of 0.4–3.92  $\mu\text{m}$  for three reasons: (1) the VNIR wavelength region is not well-aligned with the IR detector so it is difficult to interpret absorptions in the 1  $\mu\text{m}$  region, (2) hydrated sulfates have their most diagnostic absorptions in the 1.0–2.5  $\mu\text{m}$  region, and (3) thermal effects and the strong  $\sim 3 \mu\text{m}$  water absorption overwhelm sulfate-related absorptions and complicate the longer IR wavelengths.

Pure Na sulfates also are not as good a spectral match to Martian polyhydrated sulfates as Mg or Fe sulfates are — their  $\sim 1.4 \mu\text{m}$ ,  $\sim 1.9 \mu\text{m}$ , and 2.4  $\mu\text{m}$  absorptions are all at  $\sim 0.04 \mu\text{m}$  longer wavelengths [Crowley 1991]. At Meridiani Planum, the Opportunity Rover found limited evidence for Na sulfates as Na cation abundance was not correlated to  $\text{SO}_3$  abundance [Clark et al. 2005]. The dominant sulfates were Mg and Ca sulfates, with (Na, K)-jarosite, rather than the expected Al-jarosite [Clark et al. 2005]. In addition, Na sulfates are geochemically less plausible than Fe or Mg sulfate, as experimental weathering of olivine-bearing basaltic rocks is unlikely to produce large amounts of Na sulfates, such as bloedite or eugsterite, without also producing larger amounts of Ca, Mg and Fe sulfates [Tosca et al. 2004]. However, trace substitution of Na in Ca, Mg, and Fe sulfates will occur when Na is also present

in brines derived from weathering basalts, and might not significantly shift band positions.

### 1.6.1 New sulfate phases identified

More recent sulfate detections on Mars include (1) alunite ( $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ) in a Noachian crater in Terra Sirenum [Swayze et al. 2008]; (2) Fe sulfates in small mounds within Noctis Labyrinthus, putatively sourced from very young, post-Valles Marineris opening, volcanism [Mangold et al. 2008c]; (3) dehydrated jarosite with hydrated silica in the plains surrounding Valles Marineris [Milliken et al. 2008a]; and (4) szomolnokite ( $\text{FeSO}_4 \bullet \text{H}_2\text{O}$ ) with kieserite in an ILD in Juventae Chasma [Bishop et al. 2008b].

The alunite is found in layered material near the crater wall of an unnamed 70 km crater, and is associated with kaolinite or halloysite, and montmorillonite or partially hydrated silica [Swayze et al. 2008]. The mineral assemblage and CRISM spectral features is most consistent with alunite formed in low temperature lacustrine environments, rather than a hydrothermal origin.

The iron sulfate in Noctis Labyrinthus cannot be narrowed down to a specific sulfate, but the absence of iron oxides indicate the sulfate cation is iron [Mangold et al. 2008c]. A polyhydrated phase which may be epsomite or another Mg sulfate is also present in Noctis Labyrinthus. The presence of Fe sulfates in Noctis Labyrinthus but not widespread throughout Valles Marineris may mean that the more recent volcanism that hosts these sulfates has a different chemistry, and thus weathers to more Fe-rich sulfates or has not seen as much subsequent alteration by groundwater.

The dehydrated jarosite found with hydrated silica in light-toned layers in the plains around Valles Marineris together indicate alteration by acidic groundwater [Milliken et al. 2008a]. Implications for timing of this acidic aqueous alteration are

discussed in Chapter 3. Other sulfates, such as kieserite and szomolnokite, do not necessarily imply acidic conditions during formation.

Both szomolnokite and kieserite are found in several ILDs in Juventae Chasma [Bishop et al. 2008b]. They likely represent a sequence of monohydrated sulfate with variable amounts of Fe and Mg. However, laboratory spectra of cation mixtures studies for monohydrated sulfates don't exist, and current library spectra of kieserite and szomolnokite may have impurities that contribute to the VNIR spectrum. Taken all together, these recent findings show the sulfate story on Mars is more complex than previously appreciated.

### 1.6.2 Phases associated with sulfates

Other major minerals expected with sulfates would be carbonates, chlorides, phosphates, iron oxides and possibly borates. Carbonates have not been detected within Valles Marineris, and CRISM study shows they may only be present in visible amounts in Nili Fossae due to the high concentration of olivine and abundance of water [Ehlmann et al. 2008]. Carbonates may be present in Valles Marineris at levels below the detection limit, either due to abundance or fine grain size. Chlorides, as mapped by TES by a non-unit emissivity, occur in local lows in cratered plains across Mars [Osterloo et al. 2008]. Allochthonous materials, like clay minerals and zeolites, are also expected to be admixed with sulfates if significant fluvial transport occurred.

Chlorides are expected with sulfates in terrestrial evaporite sequences. Halite, NaCl, is the dominate evaporite in massive terrestrial salt deposits, but the more mafic surface chemistry of Mars is not expected to produce as large volumes. Halite and other dehydrated chlorides are spectrally neutral in the VNIR, so CRISM is not sensitive to their presence. Terrestrial evaporites often contain hydrated chlorides like bischofite in small amounts. Hydrated chlorides have diagnostic H<sub>2</sub>O and OH

absorptions, but are not seen in Valles Marineris.

Previous research noted the association of ferric oxide with sulfate on Mars [Gendrin et al. 2005; Bibring et al. 2007]. The association with ferric oxide has been much studied but was not conclusively resolved: OMEGA generally finds a ferric absorption at the same or lower elevations than the extent of the co-occurring sulfate deposit [Gendrin et al. 2005; Le Deit et al. 2008; Bibring et al. 2007]. Joint analysis of TES hematite distribution and OMEGA sulfate distribution similarly shows that hematite occurs at lower elevations than sulfates, and may be a lag deposit [Chojnacki and Hynek 2008]. Mineral identification in these deposits with OMEGA was confounded by the spectral similarity between ferric sulfates and ferric oxides mixed with another sulfate. Thus, there was a debate of whether the deposits were ferric sulfates or ferric oxide/Mg sulfates mixtures. Chapter 4 discusses the now-confident hematite detection. It has now been determined that the ferric absorption associated with sulfates in CRISM and OMEGA data is a ferric oxide, which can in some cases be further resolved to be hematite.

The hypothesis put forth to explain the presence of hematite with sulfate is analogous to the acid mine drainage model of Meridiani Planum [Clark et al. 2005; Squyres and Knoll 2005] or Rio Tinto, Spain [Fernandez-Remolar et al. 2004, 2005]. In terrestrial acid mine drainage locales, pyrite is exposed to the oxidizing atmosphere and produces a variety of iron oxides and sulfates. The deposits often form mineralogic "bulls eyes," with jarosite and sulfates in the center above the pyrite deposit, and goethite and then hematite with radial distance from the pyrite [Swayze et al. 2000]. This pattern is caused by increased leaching of metals and more neutral pH further away from the source. Jarosite, hematite, and goethite all have strong absorption features in the VNIR, so although pyrite is spectrally neutral, evidence of oxidation of pyrite on the surface would be very apparent.

Maturation and leaching of iron-bearing sulfates produces a collection of ferric oxides from melanterite to schwertmannite and jarosite to goethite to hematite [e.g. [Fernandez-Remolar et al. 2004; Roach et al. 2006]]. The transition from hydrated ferrous sulfates to mixed ferrous/ ferric hydroxysulfates to iron oxides is an unidirectional dehydration/ dehydroxylation process [Fernandez-Remolar et al. 2004]. If the same process holds on Mars in the sulfate- and hematite-bearing ILDs, then hematite is formed by either sulfate weathering or in situ precipitation of iron oxide. It is then concentrated on the surface by differential erosion of hematite concretions from finer-grained sulfates. The hematite collects in channels on the ILD and at the base in a lag deposit.

Of the possible hydrated sulfates CRISM and OMEGA are capable of detecting,  $\text{Fe}^{2+}$  and  $\text{Fe}^{2+}$  sulfates are underrepresented by volume. The ubiquitous and globally distributed dust with its nanophase ferric oxide component may mask some of the ferric or ferrous absorptions in iron sulfates, but cannot completely explain the lack of iron sulfates. Additionally, less variety in the polyhydrated sulfate class has been seen than was expected. Very hydrated sulfates, like epsomite, kornelite, or metavoltine, are spectrally similar. They all have strong hydration bands at 1.4 and 1.9  $\mu\text{m}$  and a roll off at  $>2.3 \mu\text{m}$  (from a very deep  $\sim 3 \mu\text{m}$  water absorption). It is difficult to spectrally distinguish between very hydrated sulfates in Martian data. Less hydrated sulfates, like bassanite, syngenite, or sideronatrite, are underrepresented. This could be due to mineral mixtures of multiple sulfates and/or other hydrated minerals that when combined, deepen the 1.4 and 1.9  $\mu\text{m}$  bands and the roll off at  $>2.3 \mu\text{m}$ . These mixtures may also mute the relative effect of minor but diagnostic absorptions of their constituents. In contrast to the strong water bands, absorptions due to metal-OH vibrations in the 2.2–2.3  $\mu\text{m}$  region or other water overtones in the 1–2.5  $\mu\text{m}$  region may be not confidently resolved from the noise if the mineral is present in



small amounts.

A uniform polyhydrated sulfate chemistry across Valles Marineris is at odds with the very individual style of each chasma's formation and the very path-dependent nature of sequential sulfate precipitation. Mg monohydrated sulfates are found throughout Valles Marineris and together with Fe monohydrated sulfate in Juventae Chasma. Polyhydrated Fe sulfate is identified in Noctis Labyrinthus and dehydrated Fe-bearing jarosite is present in deposits on the plateau surrounding the canyon system. A range of cations may be present in the "polyhydrated sulfate" type that may account for the volumetrically deficient Ca and Fe sulfate phases [Tosca and McLennan 2006].

## 1.7 Thesis Structure

The goal of the thesis is to better understand evolution of the Martian surface through close investigation of equatorial sulfate deposits, as they can be sensitive indicators of past aqueous history. Chapter 1 contains the motivation for the project and a variety of background information. Chapter 2, 3, and 4 discuss more detailed aspects of the Valles Marineris sulfate deposits. Chapters 5 and 6 synthesizes what we have learned about Martian sulfates, and attempts to place the detailed analyses from chapters 2-4 in a more global context.

Chapter 1 presents background information about (1) location and types of sulfate deposits on Mars, (2) how Valles Marineris formed and ideas about how the sulfate-rich Interior Layered Deposits within them formed, and (3) the basics of visible-near infrared spectral analysis that allow us to identify sulfates and ferric oxides from orbit around Mars. A preview of new sulfate types and associated phases identified with CRISM data is also presented.

Chapter 2 addresses how stable sulfates are to alteration under Martian condi-

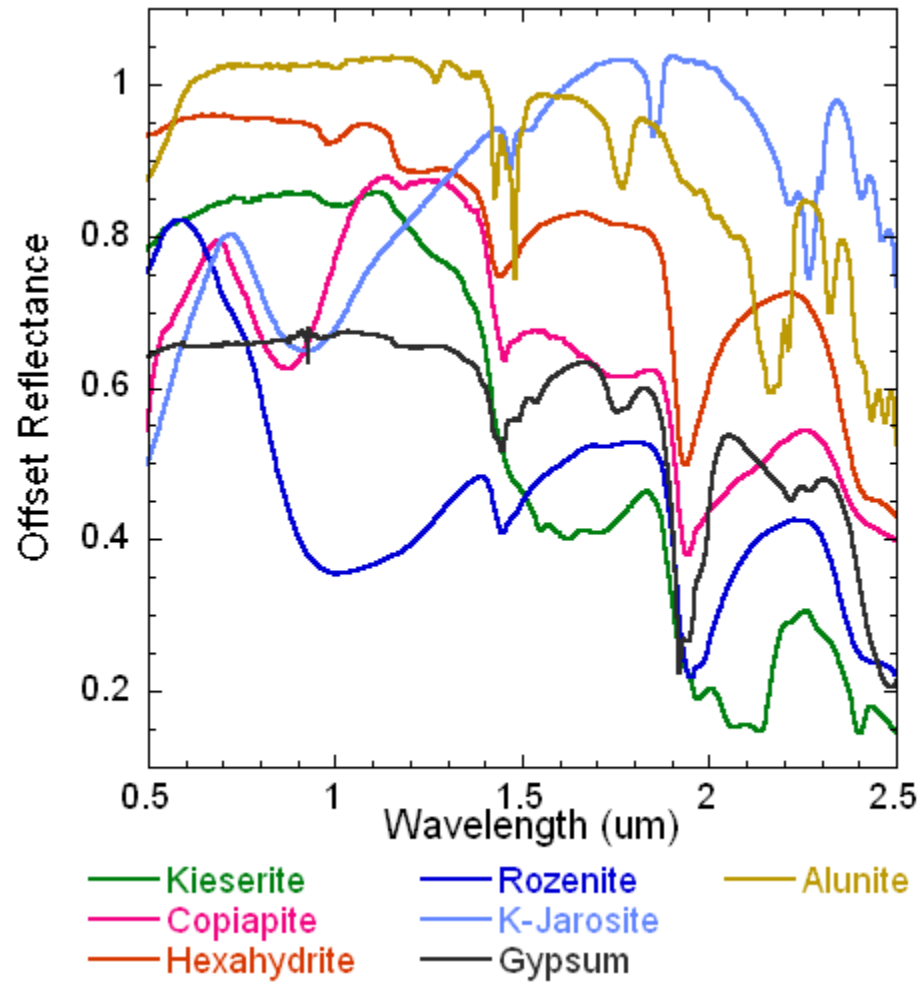


Figure 1.5: RELAB library spectra of polyhydrated sulfates (with alunite and kieserite) that potentially match Martian spectra with  $\sim 1.4$ ,  $1.9$ , and  $2.4 \mu\text{m}$  absorptions. Many sulfates, such as jarosite, have additional diagnostic absorptions that can distinguish them from hexahydrite-like spectra.

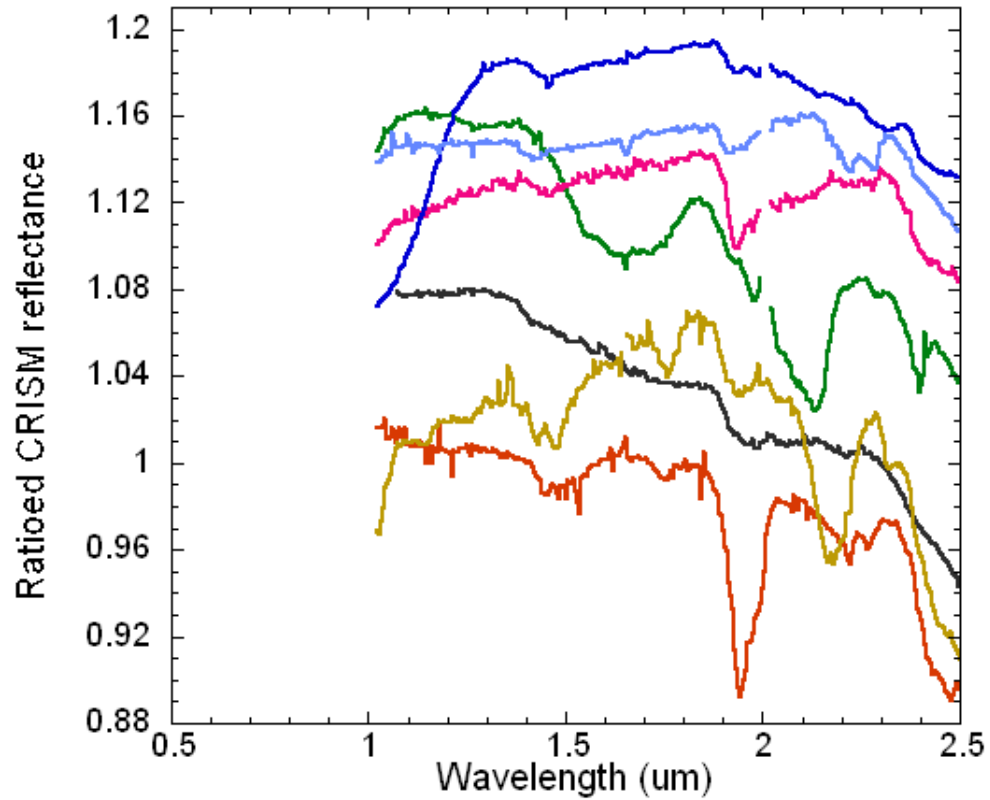


Figure 1.6: CRISM ratioed reflectance type spectra of sulfates that potentially match library spectra with  $\sim 1.4$ ,  $1.9$ , and  $2.4 \mu\text{m}$  absorptions. Some spectra represent mineral mixtures. Color scheme is not the same as in Fig 1.5. VNIR data ( $0.35\text{--}1.0 \mu\text{m}$ ) not shown.

tions, and how much sulfate hydration state reflects past climate. Kieserite, a thermodynamically unstable sulfate phase on the Martian surface today, has widespread presence in Valles Marineris. It would be expected to hydrate to a polyhydrated Mg sulfate, such as epsomite or hexahydrite, relatively quickly. That we still see kieserite on the surface with only some converted to a polyhydrated sulfate gives important clues how the kinetic limitations of this transformation and on past climatic regimes in Valles Marineris. We hypothesize that kieserite is not converting to a polyhydrated Mg sulfate under current Martian conditions but may be metastable currently. The transformation to a polyhydrated Mg sulfate would occur during periods of high obliquity, when Valles Marineris would accumulate ice seasonally and have a higher relative humidity.

Chapter 3 presents a detailed local and regional stratigraphy of sulfates and other alteration minerals within Ius Chasma to test the OMEGA mineralogic timeline. We find kieserite, polyhydrated sulfate, hydrated silica (opal), sedimentary layered Fe/Mg smectite and Fe/Mg smectite in basaltic bedrock, and a hydrated silicate mineral previously undetected on Mars. The hydrated silicate is not exactly matched by any terrestrial sample, but spectral similarities to laboratory and natural leached smectite clays/jarosite mixtures suggests that it could be a phase formed under near neutral conditions that spans the range between acidic sulfates (like jarosite) and alkaline smectite clays as an alteration product. The mineralogy and stratigraphy in Ius Chasma is a key location to test the Bibring mineralogic model, since clay minerals and sulfates are found in adjacent, in situ deposits. Overall, the model hold up, with smectite clays in the Noachian-aged wallrock and hydrated silica and sulfates in younger deposits that postdate the opening of Valles Marineris.

Chapter 4 investigates the stratigraphic relationship between sulfates and hematite (and other ferric oxides) throughout Valles Marineris and theorizes on possible dia-

genetic processes to form them. A detailed stratigraphic study was completed in Capri Chasma that showed hematite was found in kieserite-rich bedrock but not in overlying polyhydrated sulfate-rich bedrock. Hematite and other ferric phases are also found at the bases of sulfate-rich Interior Layered Deposits. Textural differences between kieserite/hematite-rich bedrock and polyhydrated sulfate-rich bedrock are another indication of different processes forming and altering these layers. We propose diagenetic alteration converted the polyhydrated sulfate to kieserite and precipitated hematite or converted goethite and other ferric oxides/sulfates to hematite. Hematite can be created by diagenetic alteration of jarosite [Barron et al. 2006] or a variety of ferric oxides like goethite, magnetite, and ferrihydrite [Schwertmann and Cornell 2003]. The stratigraphy created in Capri Chasma is also consistent with other thick sulfate-rich deposits in other basinal chasma. Chasma such as Melas, Ganges, Hebes, Juventae, and Candor all show several km-thick sulfate-rich deposits with kieserite/hematite in the lower elevations and a polyhydrated sulfate phase at higher elevations. There may be a common genetic mechanism for all basinal chasmata and the Meridiani Planum sulfate and hematite-rich deposits.

Chapter 5 synthesizes the results from chapters 2-4 and other studies of the Interior Layered Deposits. Sulfate deposits throughout Valles Marineris are classified by depositional style and mineralogic stratigraphy to draw broad conclusions about sulfate formation processes. Evidence for any of the multiple possible ILD formation mechanisms are tested throughout Valles Marineris. The complex and individual nature of the chasmata that make up Valles Marineris can complicate connecting the sulfate deposits with the regional geologic history. As multiple processes are responsible for forming Valles Marineris, multiple events — spatially and temporally separated — were likely active in producing the sulfates and associated alteration minerals.

Chapter 6 addresses the implications for Valles Marineris’s aqueous geologic history. Chapter 6 discusses the implications of the findings presented in Chapter 5 — how to compare terrestrial and Martian sulfate deposits and what these sulfates can tell us about past Martian climate. This chapter also describes outstanding questions about ILDs and their formational history, as well as sulfate detection other spectral concerns, and the geologic implications of the hydrated mineralogy. Each of the three issues are discussed in the context of what further research with high resolution orbital or roving landed datasets would be necessary to address them, and what further CRISM analysis could contribute.

The compiled bibliography for all chapters is at the end of the thesis. Appendix A lists the name and ideal chemical formula of many of the most relevant sulfates and related chloride and mixed sulfate/chloride phases. All sulfates mentioned in the text as well as selected additional phases are included. Appendix B lists the 134 CRISM targeted observations in Valles Marineris that show spectral evidence of sulfate and/or ferric phases. Observations of the gypsum dunes near the North Pole are not included. Many times, the same location was imaged twice by CRISM when HIRISE was acquiring stereo-imagery. Duplicate observations in Valles Marineris were occasionally included in the study if they were acquired under periods of more favorable aerosol loading and thus had more clear spectral features. Aside from Valles Marineris, there are several other locations that show evidence for sulfates or have spectral features consistent with sulfate or zeolites in CRISM data. Sulfates or putative sulfates are found in the North Polar dune field [Langevin et al. 2005; Calvin et al. 2009], Meridiani Planum [Arvidson et al. 2005, 2006; Wiseman et al. 2007], Aram Chaos [Lichtenberg et al. 2009], Terra Sirenum [Wray et al. 2008b], and Nili Fossae [Ehlmann et al. 2009].

## Chapter 2

# Stability of Hydrated Mg Sulfates to Changes in Martian Environment

The East Candor Interior Layered Deposit (ILD) has signatures of mono- and polyhydrated sulfate in alternating layers that give insight into the processes which formed these layered deposits and on the environmental conditions acting on them since then. We use orbital data to explore multiple hypotheses for how these deposits formed: (1) sulfate-bearing ILDs experience hydration changes on seasonal to few year time scales under current Mars environmental conditions; (2) the deposits experience hydration under recent Mars conditions but require the wetter climate of high obliquity; and (3) the kieserite could be an original or diagenetic part of a complex evaporite mineral assemblage. Modelled climatology shows recent Mars environmental conditions might pass between multiple sulfate fields. However, comparison of OMEGA (Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activite) and CRISM (Compact Reconnaissance Imaging Spectrometer) observations of the same ILD do not show changes in hydration over 2 Mars years. Low temperatures might slow the kinetics of that transition; it's likely that more clement conditions during periods of high obliquity are needed to overcome mineral metastability and

hydrate kieserite-bearing deposits. We find the alternate model, that the deposit is a cyclic evaporite sequence of mono- and polyhydrated sulfates, also plausible but with an unexplained dearth of Fe sulfates.

## 2.1 Introduction

OMEGA has mapped kieserite ( $\text{MgSO}_4 \bullet \text{H}_2\text{O}$ ) and a polyhydrated sulfate of unknown cation within ILDs in Valles Marineris. Subsequent measurements by CRISM on the Mars Reconnaissance Orbiter (MRO) has elaborated on the distribution and type of sulfate found within the ILDs [Murchie et al. 2007b; Bishop et al. 2007; Parente et al. 2007; Roach et al. 2007b; Murchie et al. 2009b]. CRISM targeted observations show kieserite and polyhydrated sulfate occasionally alternate by layer within an ILD [Roach et al. 2008a]. It is not common to find a locale on Earth with alternating occurrences of multiple hydration states of a sulfate with a single common cation (such as gypsum, bassanite, and anhydrite in alternating layers) since the mineral rapidly converts to the thermodynamically stable phase, which is often kieserite or anhydrite ( $\text{CaSO}_4$ ), with burial diagenesis [e.g. Permian evaporite in [Lowenstein 1988]; Messinian evaporite in [Testa and Lugli 2000]]. However, slower kinetics on Mars could preserve metastable assemblages [Chipera and Vaniman 2007]. If the polyhydrated sulfate identified on Mars has some Mg sulfate component, then the presence of both mono- and polyhydrated forms of Mg sulfate in an outcrop raises questions about environmental conditions since deposition in light of the mineral's thermodynamic stability.

Experimental work on the stability fields of Mg sulfates [e.g. [Chipera and Vaniman 2007]] finds the range of environmental conditions on Mars potentially encompasses several fields in a Mg sulfate phase diagram. It also reveals that Mg sulfates exhibit strong metastable behavior, which affects the kinetics of hydration or dehydra-



tion. Relevant findings are discussed more in section 2.2. Investigating deposits with alternating exposure of monohydrated Mg sulfate and polyhydrated sulfates (possibly Mg-bearing), is one way to better understand hydrated sulfate behavior on Mars and to develop hypotheses for formation and subsequent alteration of these sulfate layers.

The hydration state of a sulfate deposit is a function of its formation process, possible diagenesis or alteration, and subsequent re-exposure to the environment. This paper focuses on an ILD in East Candor Chasma (Fig. 2.1) with a multiple sulfate assemblage in order to look for evidence of changing hydration state. The presence of multiple hydration states of Mg sulfate in a layered deposit is challenging, since Mg sulfate readily changes hydration state on Earth. Many Mg sulfate phases, such as kieserite, are not projected to be stable at Mars conditions. Mangold was the first to suggest kieserite in ILDs might be weathering to polyhydrated sulfate with exposure to the atmosphere [Mangold et al. 2008b]. In an effort to explain the presence of kieserite and of a multi-sulfate suite in Valles Marineris, we put our mineralogic and geomorphic findings in context with experimental stability data and temporal studies. We consider experimental data on the stability of Mg sulfates in various temperature and humidity conditions, which provides constraints to expected phases under current Valles Marineris environments. We also compare OMEGA and CRISM observations of the sulfate deposit spaced one and two Mars years apart to assess sulfate stability and whether seasonal and annual environmental changes in hydration state occur.

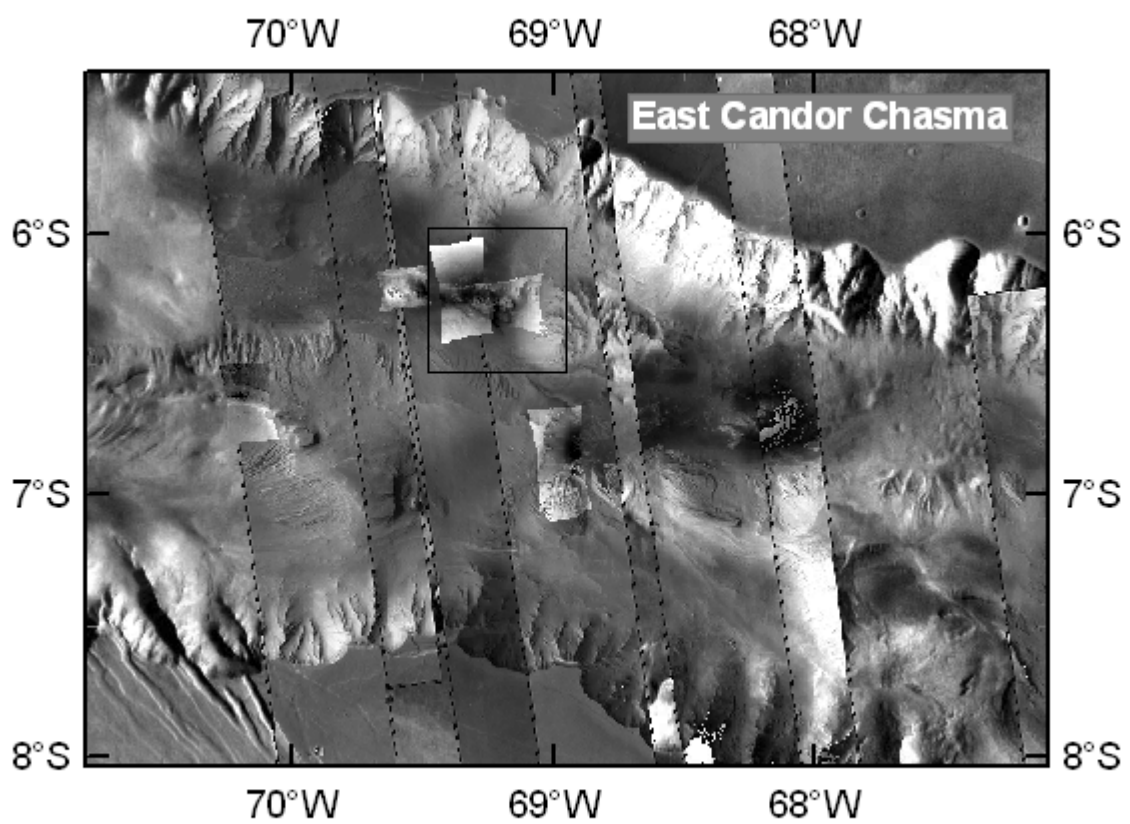


Figure 2.1: Context map of East Candor Chasma. Box indicates extent of Interior Layered Deposit study area, as show in Fig 2.5.

## 2.2 Thermodynamic and kinetic models of hydrated sulfate stability

Much work has been done on the stability of Mg sulfates with respect to hydration and dehydration [Vaniman et al. 2004a; Chipera et al. 2005; Marion and Kargel 2005; Vaniman et al. 2005; Vaniman and Chipera 2006a; Chipera et al. 2006], summarized in Fig. 2.2. In order to speed reaction rates, this wealth of experimental data can only partially imitate the T, P, and RH (relative humidity) conditions of modern Mars. Nonetheless, there is an abundance of data that foremost, speaks forcefully to the complex behavior of Mg sulfates and secondly, gives indications about sulfate stability on Mars. The Mg sulfate system has extensive metastability fields when kinetic limitations prevent phase changes. An example of where Mg sulfate metastable conditions overstep a stability field before they can overcome an activation energy barrier is the possibility of hydrating kieserite to  $\text{MgSO}_4 \bullet 6\text{H}_2\text{O}$  without first forming  $\text{MgSO}_4 \bullet 4\text{H}_2\text{O}$ . Metastability is especially persistent in conditions of rapid crystallization at low RH in concentrated brines [Vaniman et al. 2004b]. The recent discovery of a kieserite pseudomorph that may form under different conditions than typical kieserite [Wang et al. 2008] raises questions about Mg sulfate stability that will require more investigation.

While the most extensive studies on kinetics and stability have been run at temperatures above 273 K, some have been performed under Martian conditions. Vaniman and colleagues [2006] have shown that under Martian temperature conditions (constant 243 K trials) but  $\sim 1$  bar pressure, kieserite hydrates to hexahydrite in  $\sim 1000$  hr at 100 % RH. At 100% RH in lower temperatures (193 K), the water vapor does not hydrate kieserite, but accumulates as surface frost on the mineral [Vaniman and Chipera 2006a]. The rate of hydration on Mars is not necessarily on the same order

of magnitude as on Earth, since the experiments were run under terrestrial pressures, and the kinetics of the reaction are likely to be slower under the thinner Martian pressures. While water ice is not currently present for extended periods today in Valles Marineris, during periods of higher obliquity (conditions of 100% RH and temperatures of at least 243 K), ice was likely stable [Vaniman et al. 2006; Vaniman and Chipera 2006a]. A location with stable ice in the subsurface would more likely produce a microclimate for possible kieserite hydration [Forget et al. 2006; Madeleine et al. 2008]. The experimental results demonstrate that kieserite is not stable anywhere on Mars where water ice is present for long periods of time. While the speed of hydration cannot be constrained, the reaction of kieserite to polyhydrated Mg sulfate in the presence of ice is favorable.

While kieserite is not considered stable on Mars' surface, we should consider kieserite's extensive metastability field, as its actual hydration rate under Martian conditions is unknown. Diurnal fluctuations in temperature and RH on Mars mean kieserite is not held at 100% RH and sufficiently high temperatures for long periods of time, so its hydration rate may be retarded. Additionally, diurnal temperature and RH cycles in equatorial regions may cause polyhydrated Mg sulfate to vary between polyhydrated states or to and from an amorphous, slightly hydrated, state [Vaniman and Chipera 2006a; Chou and Seal 2007]. The speed of this dynamic response to atmospheric water vapor is not well defined, but could occur daily or seasonally. Fig. 2.2 shows experimentally determined stability fields for the Mg sulfate system at temperatures  $>273$  K; metastability can complicate extrapolation to subfreezing temperatures. Further experimental data is needed at subfreezing temperatures to bracket Mg sulfate stability.

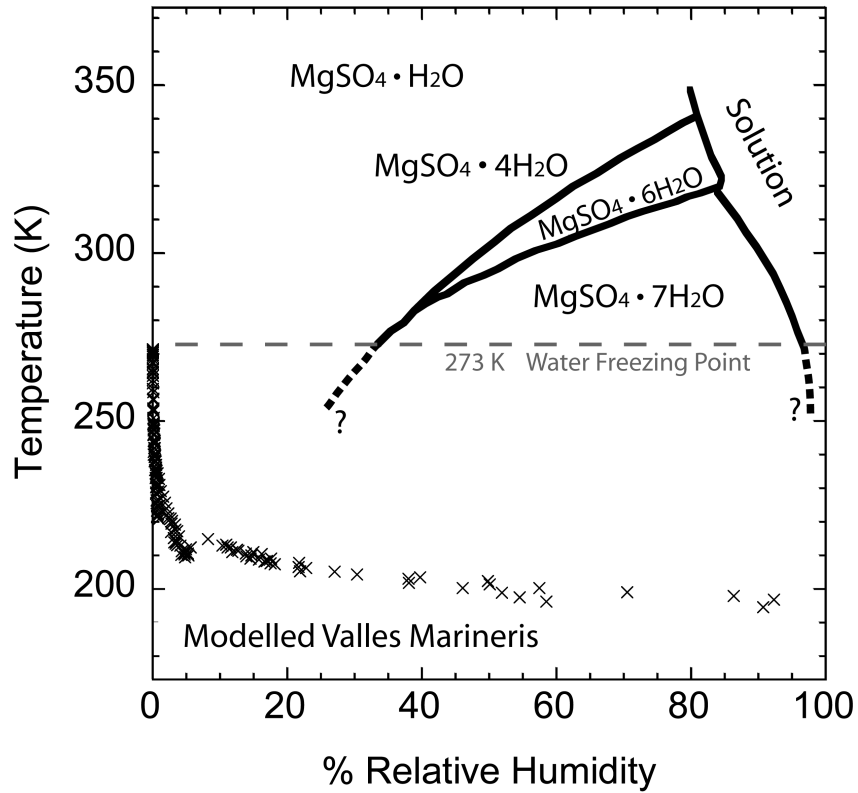


Figure 2.2: Experimental T - % RH stability phase diagram for Mg sulfates. Modelled Mars environmental conditions are also plotted as 'x'. Modelled T, % RH at Capri Chasma serves as proxy for the environmental conditions in Valles Marineris. Dashed gray line delineates the freezing point of pure water at 1 atm P. The extension of Mg sulfate stability fields below freezing is uncertain. The boundary between kieserite and  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  is not well defined so the black dotted line is an approximation of that boundary. The current environment in Valles Marineris might pass between multiple sulfate fields, although the low temperatures would slow the kinetics of that transition.

### 2.2.1 T, P, and RH at Valles Marineris

Pathfinder, Viking, and MER lander data confirm that equatorial regions get warm enough for hours a day in the summer to promote hydration (Fig 2.2) [e.g. [Savijarvi 1995; Spanovich et al. 2006]. The Mini-TES (Thermal Emission Spectrometer) instrument on Opportunity in Meridiani Planum measured a maximum surface temperature of 295K in early afternoon,  $L_s = 339^\circ$ , with surface temperature above freezing for  $\sim 5$  hrs [Spanovich et al. 2006]. While no RH measurements exist from landed missions, modeled RH at the Viking 1 landing site ( $22^\circ$  N) ranges from 100% at night to  $<1\%$  in the afternoon [Savijarvi 1995]. To better understand the environmental conditions in Valles Marineris and how they differ from those at the landing sites, we modelled T and RH values in Capri Chasma throughout the year using a tuned global climate model described in [Forget et al. 1999]. Capri Chasma was chosen because its large size covered more than one  $3.75^\circ$  latitude x  $5.625^\circ$  longitude pixel in the model. Model results from Capri Chasma were considered to confidently represent Valles Marineris conditions with minimal contribution from the surrounding plateaus and can be extrapolated to represent East Candor Chasma. The model's 2 hour temporal resolution allows sensitive tracking of daily variation in RH. While consistent with the extreme T and estimated RH values of the Viking 1 lander, it additionally shows the rapidity of RH decrease with increasing T. The modelled Martian conditions do not pass through experimentally measured Mg sulfate stability fields, and the location of those stability fields under Mars conditions is currently unknown. Yet, for the entire diurnal cycle, kieserite is likely unstable.

The reverse transformation *dehydration* of polyhydrated Mg sulfate to kieserite cannot happen in the ILDs under current Martian surface conditions. In experimental studies at all T, kieserite converts to more hydrated Mg sulfates as humidity increases but does not revert to kieserite on desiccation; instead it becomes amor-

phous and remains more hydrated than kieserite [Vaniman et al. 2004b]. A recently discovered kieserite pseudomorph created by Wang et al. (2008) is formed by direct high temperature precipitation ( $\sim 323$  K). This kieserite pseudomorph also cannot form at Martian temperatures (near freezing) from a polyhydrated Mg sulfate [Freeman et al. 2007]. Conversion of polyhydrated Mg sulfates to kieserite is favored under elevated temperatures [e.g. [Wang et al. 2008], so penecontemporaneous diagenesis is possible. Exhumation after diagenesis is necessary to re-expose the kieserite. Thus, the presence of dominantly kieserite on fresh surfaces indicates that they have not changed hydration state since exposure and that they are either original evaporites or a diagenetic phase after  $\text{MgSO}_4 \bullet n\text{H}_2\text{O}$  and other sulfates.

The Mg sulfate hydration state depends on not just the appropriate T and RH conditions, but also the time spent at those conditions. On Earth, strong kinetic limitations on Mg sulfate equilibrium may prevent kieserite hydration [Vaniman and Chipera 2006a].

### **Other factors affecting hydration**

We briefly consider two, lesser factors than temperature, RH, and presence of liquid water which can affect the hydration state of sulfate on the Martian surface — photodecomposition and texture.

Photodecomposition, where ultraviolet (UV) radiation excites molecules sufficiently to dissociate bonds, would not affect the hydration state of sulfate, per say, but can break up sulfates. Later hydration might create amorphous sulfate. There is some evidence that appreciable photodecomposition of carbonate and Mg-sulfates (at a rate an order of magnitude lower than carbonate) by ultraviolet (UV) radiation is expected under current Martian surface conditions [Mukhin et al. 1996]. Other workers argue that using a more realistic  $\text{CO}_2$  atmosphere implies that carbonate

decomposition measured by Mukhin et al (1996) is the result of decomposition under vacuum, not by photodecomposition [Quinn et al. 2006]. In either case, it would be a small effect on Mg sulfates and would only affect a thin surface layer of a sulfate deposit [Navrotsky et al. 2005].

The surface texture (grain size and surface roughness) affect the surface area to volume ratio, and so can affect the rate of chemical reactions. In addition to changing rates of hydration, textural differences can affect the resulting spectra. Physical weathering of friable sulfate outcrop into fine grained dust would weaken absorption bands. Recementing of these grains in surface crusts would make them more visible to VNIR spectroscopy [Cooper and Mustard 2002]. The effect of physical weathering on Mars would thus affect both our ability to measure changes in hydration state and possibly speed hydration reaction rate by creating smaller particles.

### **2.2.2 Visible-Near Infrared (VNIR) Spectra**

Visible and near infrared spectra are used to identify sulfates and their hydration state. In targeted hyperspectral mode, CRISM acquires observations at 544 wavelengths from 0.392-3.92  $\mu\text{m}$  at  $\sim 20$  m/pixel [Murchie et al. 2007a]. OMEGA observations have 352 wavelengths from 0.35-5.1  $\mu\text{m}$  and a spatial sampling that varies from 300 m to 4.8 km/pixel [Bibring et al. 2004]. Both datasets are calibrated to radiance and divided by the solar spectrum, yielding I/F. An empirical atmospheric correction is performed by division of I/F spectra by an atmospheric transmission spectrum derived over Olympus Mons as in [Pelkey et al. 2007]. The atmospheric transmission spectrum is scaled each OMEGA and CRISM observation by the strength of the 2.0  $\mu\text{m}$   $\text{CO}_2$  absorption. This approximately removes the atmospheric spectral absorptions due to gas bands, but does not account for aerosol effects.

CRISM observations can also be corrected for aerosols using the gimbaled obser-



uations [Murchie et al. 2007a] to solve for the aerosol phase function as in [Vincendon et al. 2007]. After gas band removal, the emission phase function is modelled for mean surface Lambert albedo and aerosol optical depth as a function of wavelength. A smoothed model of aerosol optical depth with wavelength and albedo is then removed from the central CRISM observation. Large differences in topography across the scene can affect optical depth results because there is a change in the relative magnitude of the surface contribution with changing phase angle. Aerosol removal accuracy is also affected by variation in surface illumination due to slopes, since the model assumes a flat, constant albedo surface. These caveats are relevant to the observations in East Candor Chasma, as the ILD covers  $\sim 450$  m in elevation and is steep-sided.

The  $1.0 - 2.6 \mu\text{m}$  VNIR wavelength region of the OMEGA and CRISM detectors is suited to identifying hydrated sulfates. Example library reflectance spectra are shown in Fig 2.4. Spectral band depths for each pixel in a scene are calculated for both OMEGA and CRISM observations to capture spectral features related to both sulfate mineralogy and atmospheric constituents and to map surface mineralogic units [Pelkey et al. 2007]. CRISM ratioed reflectance spectra of the spectral variability of the East Candor ILD are shown in Fig 2.3. CRISM spectra of interest are ratioed to spectra of nearby spectrally neutral materials with similar albedo to accentuate mineral absorption bands and to remove instrumental artifacts and residual calibration effects.

Polyhydrated sulfates, and other hydrated minerals, have an absorption near  $1.9 \mu\text{m}$  due to a combination of water molecule bending and stretching vibrations [Cloutis et al. 2006]. The  $1.9 \mu\text{m}$  band strength measures the average absorption depth within the  $\sim 1.9 \mu\text{m}$  water absorption, compared to the reflectance just outside the absorption at  $1.857 \mu\text{m}$  and  $2.067 \mu\text{m}$ , weighted by their distance from the center of the

absorption Eq. (2.1, where  $R_{1930}$  is the reflectance at  $1.930 \mu\text{m}$ ) [Pelkey et al. 2007]. Amorphous polyhydrated Mg sulfates are spectrally very similar to their crystalline counterparts [Wang et al. 2008]. Monohydrated sulfates as a class have an absorption near  $2.1 \mu\text{m}$  due to water vibrational combinations, with the exact minimum varying by cation [Cloutis et al. 2006]. The  $2.1 \mu\text{m}$  band strength measures the average absorption depth within the  $\sim 2.13 \mu\text{m}$  absorption compared to the reflectance on either side outside the absorption (at  $1.93 \mu\text{m}$  and  $2.25 \mu\text{m}$ ) (Eq. 2.2) [Pelkey et al. 2007]. We identify hydrated sulfates by combining these band depth parameters with a parameter (*SINDEX*) to measure the spectral shape near the  $2.4 \mu\text{m}$  band, which is due to sulfate and water combinations and/or overtones [Cloutis et al. 2006]. The  $2.4 \mu\text{m}$  parameter gauges the convexity at  $2.29 \mu\text{m}$  due to sulfate absorptions at  $1.9$  or  $2.1 \mu\text{m}$  and  $2.4 \mu\text{m}$  (Eq. (2.3) and is modification of  $BD_{2400}$  in [Pelkey et al. 2007].

$$BD_{1900} = 1 - \frac{(R_{1930} + R_{1985}) \times 0.5}{0.52 \times R_{1857} + 0.48 \times R_{2067}} \quad (2.1)$$

$$BD_{2100} = 1 - \frac{(R_{2120} + R_{2140}) \times 0.5}{0.38 \times R_{1930} + 0.62 \times R_{2250}} \quad (2.2)$$

$$SINDEX = 1 - \frac{R_{2100} + R_{2400}}{2 \times R_{2290}} \quad (2.3)$$

The East Candor Chasma ILD hosts a multi-sulfate assemblage, several types of which can be identified by their VNIR spectra. A monohydrated sulfate is identified as kieserite, rather than other monohydrated sulfates, based on its  $2.13 \mu\text{m}$  reflectance minimum, and  $2.4 \mu\text{m}$  absorption. The mineral determination polyhydrated sulfate from OMEGA and CRISM spectra does not refer to a specific cation, as many polyhydrated sulfates have similar VNIR spectral shapes due to their very hydrated state. Possible mineral matches for the OMEGA detection include polyhy-

drated Mg sulfates such as epsomite, hexahydrate or starkeyite,  $\text{Fe}^{2+}$  sulfates such as halotrichite,  $\text{Fe}^{3+}$  sulfates such as botryogen, and mixed  $\text{Fe}^{2+}$  /  $\text{Fe}^{3+}$  sulfates including copiapite group minerals [Gendrin et al. 2005; Mangold et al. 2008b]. Other possible mineral matches include the bloedite  $[\text{Na}_2\text{Mg}(\text{SO}_4)_2 \bullet 4\text{H}_2\text{O}]$ , kainite  $[\text{KMg}(\text{SO}_4)\text{Cl} \bullet 3\text{H}_2\text{O}]$ , and bischofite  $[\text{MgCl}_2 \bullet 6\text{H}_2\text{O}]$ , which are all diagenetic salts often found with kieserite in terrestrial deposits. Fe-bearing sulfates are unlikely matches in this deposit since the ferrous absorption corresponds to the loose pyroxene-bearing dunes overlying the deposit, and not to specific layers within the deposit. Both OMEGA and CRISM datasets also indicate minor phases such as hydrated silicate or gypsum  $[\text{CaSO}_4 \bullet 2\text{H}_2\text{O}]$  may be present based on weak absorptions in the 2.21- 2.26  $\mu\text{m}$  region. This identification is uncertain because of the weak bands, and would correspond to very trace amounts of gypsum, since only a few weight% gypsum is necessary to have discernible bands [Bonello et al. 2004a]. Other possible but less satisfactory mineral matches to the 2.2x  $\mu\text{m}$  region include jarosite group minerals, polyhalite  $[\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \bullet 2\text{H}_2\text{O}]$ , and a clay mineral such as montmorillonite.

### 2.2.3 Geologic setting of East Candor ILD

The study area (Figs. 2.1 and 2.5) is a  $\sim 450$  m high finely layered (meters scale) light-toned deposit exposed below a dusty ridge in the middle of East Candor Chasma. The East Candor Chasma ILD is surrounded to the north, east, and west by wall rock landslides and chaotic terrains [Le Deit et al. 2007]. This obscures the ILD's relationship to chasma wall rock and thus its age relative to Valles Marineris formation. Small bedrock and possibly aeolian drift outcrops of bright mono- and polyhydrated sulfate extend to the south. The regional extent of sulfate-bearing materials is  $\sim 250$   $\text{km}^2$ . The ILD appears to be eroding along layers on its relatively flat top and along one exposed side. Talus and significant landslide material are shedding off the ILD.

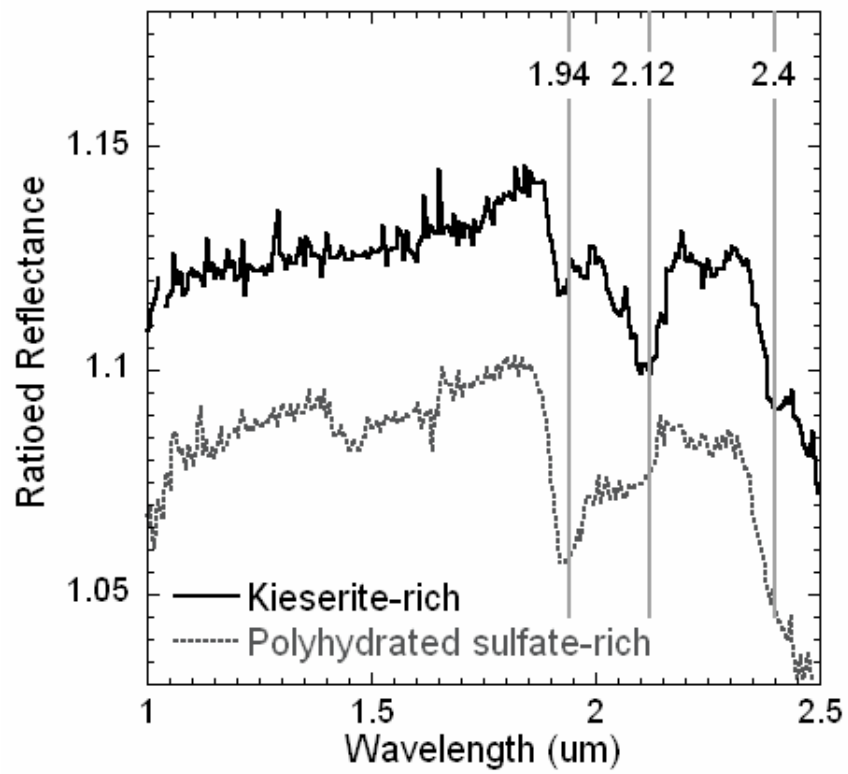


Figure 2.3: Representative kieserite-rich and polyhydrated sulfate-rich spectral ratios from the East Candor Chasma ILD from CRISM observation HRS00002FAF.

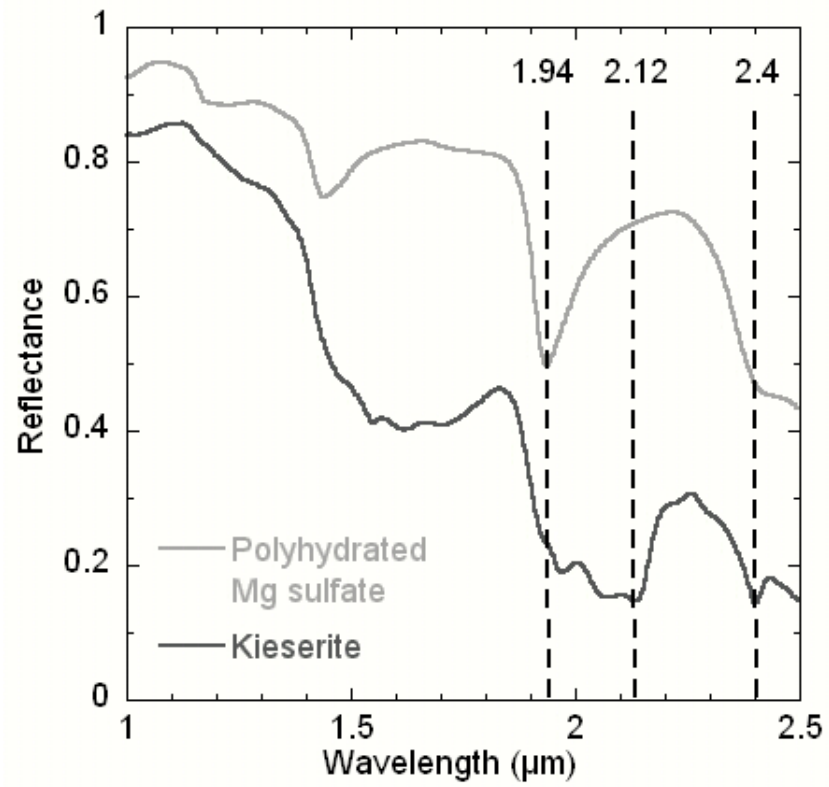


Figure 2.4: CRISM wavelength-resampled RELAB library sulfate spectra with central wavelength locations for 1.9, 2.1, and 2.4  $\mu\text{m}$  band depth parameters.

A HiRISE stereo-derived digital elevation model (DEM) with 1 m post spacing was produced for this region using the method of [Kirk 2008] (Fig. 2.10). HiRISE paired observations PSP\_002076\_1735 and PSP\_002498\_1735 were used in this analysis. Structural measurements were made by fitting planar surfaces to elevation profiles using linear regression. Efforts were made to ensure these measurements adequately constrained a unique orientation by selecting outcrops with natural curvature. The measurements shown in Figure 2.10 all had errors less than 5 degrees in azimuth and 0.5 degrees in dip. The layering within the ILD is subparallel with a  $\sim 10^\circ$  westerly dip toward the western edge and a  $\sim 15^\circ$  dip to the south in the exposed southern flank. The layering is a relatively constant thickness across the ILD, attesting to a lack of slumping during deposition. A schematic cross-section (Fig. 2.10) shows gentle folding of the sulfate-bearing layers.

The HiRISE-derived topographic model, used in conjunction with overlapping CRISM spectral data, shows kieserite-rich material is found on cliff-forming units and polyhydrated sulfate-rich material is more common on flat units. This is consistent with the broader finding of kieserite being more common on steep slopes elsewhere in Valles Marineris, which are interpreted to be more recently exposed by erosion than flat units [Mangold et al. 2008b].

The layers are not mineralogically pure: generally speaking, regions identified as spectrally kieserite-rich also have strong  $1.9\ \mu\text{m}$  absorptions consistent with a polyhydrated sulfate, and taken all together, there is a continuum of kieserite/polyhydrated sulfate spectral strengths across the scene. Spectra in Figure 2.3 show the presence of varying amounts of sulfates with mixed hydration phases. There are two interpretations for these spectral findings. The first interpretation is a difference in the relative amounts of polyhydrated/monohydrated sulfates between layers, which may also have different physiochemical properties that affect their weathering appear-

ance. Kieserite-bearing layers may be better cemented, making them stronger and more likely to form cliffs than the polyhydrated sulfate-bearing layers. Formation of polyhydrated sulfate from kieserite or cyclic hydration and dehydration of polyhydrated sulfates may cause expansion and fracturing, thus weakening polyhydrated sulfate-bearing layers, making them less resistant to erosion than their monohydrated counterparts. The second interpretation is that surfaces with different exposure ages may show varying progress in conversion of kieserite to polyhydrated sulfate. Steeper surfaces, which are undergoing more rapid erosion, would have fresher exposures of kieserite. Flatter surfaces that have been exposed to the atmosphere for longer would have had time to convert to mostly polyhydrated sulfate.

The geologic context under which these sulfates are found is important evidence to argue whether the hydration is recent. Sulfate is restricted to ILD bedrock and bright dunes at the base of the ILD, a distribution in line with previous studies across Valles Marineris [Gendrin et al. 2005; Murchie et al. 2009b]. Dark, pyroxene-bearing dunes collect at the bases of cliffs between layers of the sulfate deposit. CRISM spectra allow a more detailed correspondence of mineralogy with geologic context and indicate that the sulfate mineralogy is relatively uniform within a layer and that it changes between layers (as delineated by morphology). This is easily seen in Figs. 2.7 and 2.8, where layers with different relative amounts of poly- and monohydrated sulfates appear as different colors on a spectral band depth parameter image. Within a layer, the consistent mineralogy is reflected in the fairly uniform strength of the band depth parameter. Slight variation in band strength within a layer could be attributed to differences in surface exposure or layer geometry. Hydrated silica or gypsum is additionally identified in the ILD based on an absorption at 2.21–2.26  $\mu\text{m}$ . This feature is very weak and thus not able to be constrained to specific layers. Dark sulfate-bearing dunes (with strong sulfate signatures) are commonly associated with

ILDs in nearby West Candor Chasma [Murchie et al. 2007b], but are not seen here.

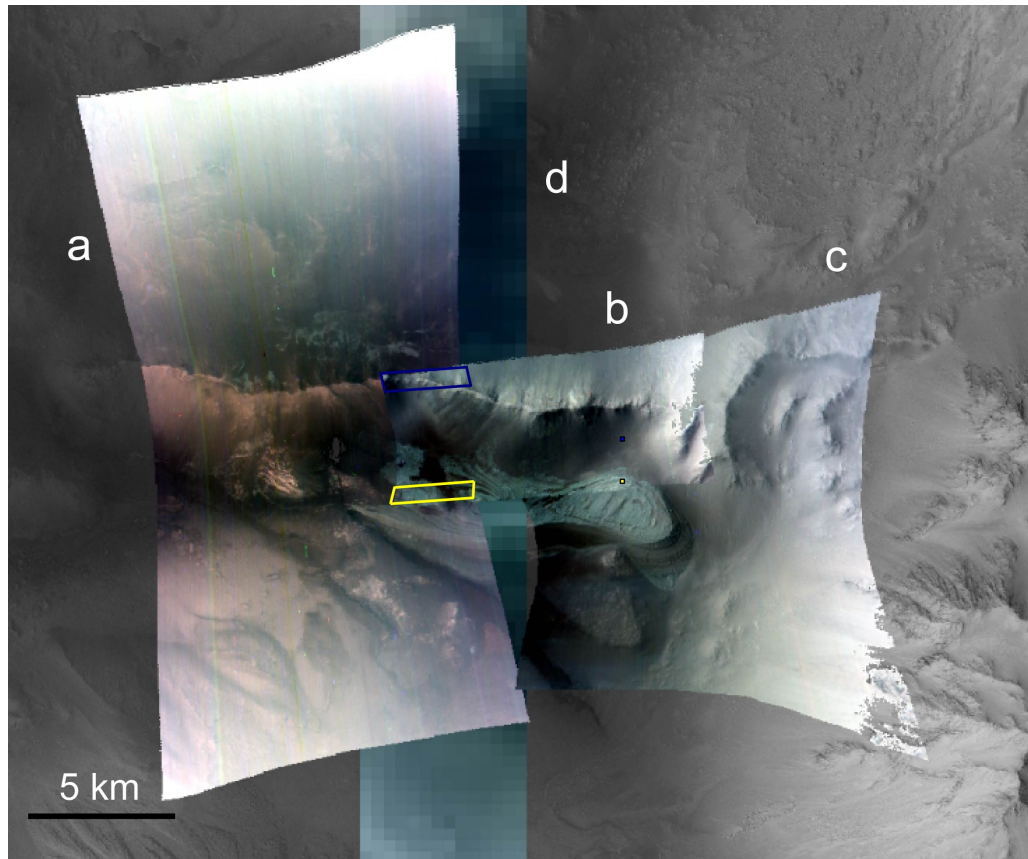


Figure 2.5: CRISM observations (a) HRL00006844 (left) and (b) HRS00002FAF (center) and (c) FRT00009901 (right) over (d) OMEGA observation ORB002050\_6 (center, background). Blue and yellow boxes indicate location of paired reflectance spectra shown in Fig. 2.6.

## 2.3 Temporal observations of sulfates

CRISM has imaged an ILD in East Candor Chasma three times since OMEGA first detected kieserite there (2.3). The images span over one Mars year and are all of sufficient spatial resolution to resolve the ILD and show variation in the relative amounts of polyhydrated and monohydrated sulfate across layering. Correcting for the aerosol loading in the CRISM observations is important as one observation (HRL00006844)



was acquired in the build-up to a global dust storm and had significant aerosol contribution.

We perform two spectral comparisons of the East Candor Chasma ILD. The first comparison is of OMEGA spectra from Northern hemisphere winter (Ls 273°) and co-aligned CRISM spectra from the following late Northern summer and winter (HRS00002FAF (Ls 134°) and HRL00006844 (Ls 271°), respectively) (Fig 5). They cover the same  $\sim 3.7 \text{ km}^2$  location. The spectra from the observations are quite similar and show both a  $1.9 \mu\text{m}$  and a relatively deeper  $2.1 \mu\text{m}$  absorption. The observations were acquired over a range of Ls yet are not significantly different. The second comparison is of CRISM observations HRS00002FAF and FRT00009901 (Ls 20°), taken late Northern summer and the following spring. The OMEGA observation does not overlap this pair. Comparing only CRISM data allows us to compare smaller areas that are likely more homogeneous. Three comparisons of  $7000 \text{ m}^2$  regions, one location of which is shown in Fig. 2.6, record similar sulfate hydration states.

Additionally, two other paired OMEGA and CRISM observations spaced over 2 Mars years have consistent spectra. The first OMEGA and CRISM pair is located in Ius Chasma (ORB0071\_2 and FRT0000A91C, respectively), and were acquired Feb 1, 2004 (Ls 343°) and April 23, 2008 (Ls 62°), respectively. Fig. 2.9 shows region of overlap and paired OMEGA and CRISM spectra of the kieserite deposit. The second pair is over a Capri Chasma kieserite deposit (ORB0061\_3 and FRT0000A23F, respectively), acquired Jan 29, 2004 (Ls 341°) and Feb 27, 2008 (Ls 37°), respectively. These two locations are the first two where OMEGA discovered kieserite, and both show similar kieserite band-depths in OMEGA and CRISM pairs. Multiple paired OMEGA and CRISM spectra have similarities in the relative band depths of the  $1.9 \mu\text{m}$  and  $2.1 \mu\text{m}$  absorptions.

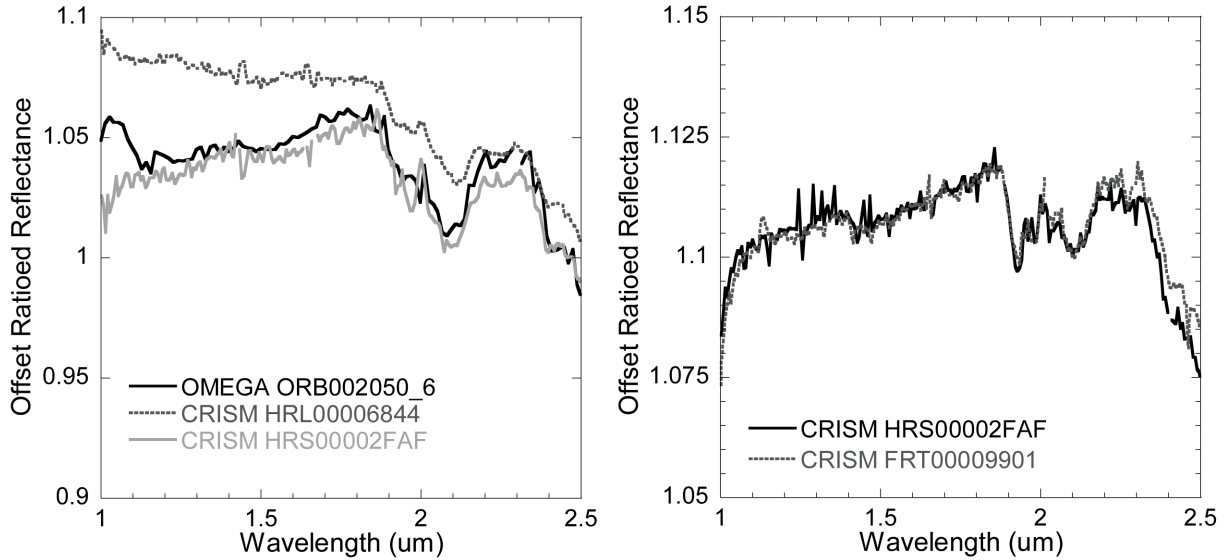


Figure 2.6: Co-aligned sulfate spectra were collected from yellow boxes in Fig. 2.5, and the corresponding bland denominators for spectral ratioing, from blue boxes. The larger polygons indicate locations of co-aligned spectra from images a, b, and d, and the small squares, from images b and c. Left: Comparison of OMEGA ORB002050\_6 spectral ratio with aerosol-removed CRISM HRS00002FAF and HRL00006844 spectral ratios of location shown as large polygon. HRS00002FAF spectrum offset by +0.25. Interpreted as a mixed monohydrated/polyhydrated sulfate assemblage. The relative band depths of mono- and polyhydrated sulfate are similar for all three observations. Right: Comparison of CRISM HRS00002FAF and FRT00009901 spectral ratios of location shown as small square. HRS00002FAF spectrum offset by -0.055. Similar relative band depths of mono- and polyhydrated sulfate in the two observations show no evidence for yearly sulfate hydration state change.

Table 2.1: Targeted observations of East Candor Chasma ILD

| Instrument | Date          | $L_s$ | Observation |
|------------|---------------|-------|-------------|
| OMEGA      | Aug. 21, 2005 | 273°  | ORB002050_6 |
| CRISM      | Nov. 12, 2006 | 134°  | HRS00002FAF |
| CRISM      | July 6, 2007  | 271°  | HRL00006844 |
| CRISM      | Jan. 20, 2008 | 20°   | FRT00009901 |

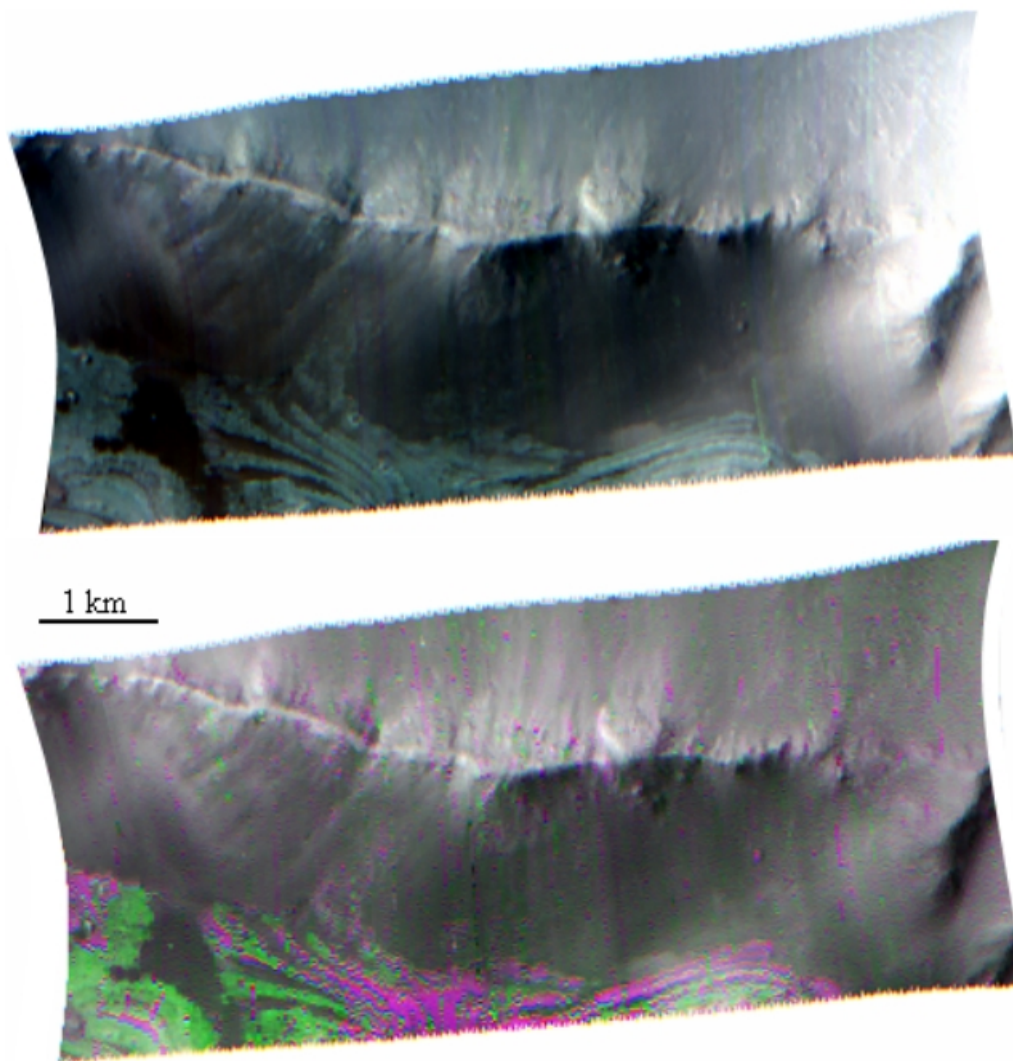


Figure 2.7: Top: CRISM HRS00002FAF false color IR (RGB: 2.5, 1.5, 1.08  $\mu\text{m}$ ). Dusty ridge to north with exposed layering from ILD to south. Bottom: Spectral band depth parameter image (magenta: 1.9  $\mu\text{m}$  band depth, green: 2.1  $\mu\text{m}$  band depth) overlain on false color IR albedo. Magenta areas indicate presence of dominantly polyhydrated sulfates with green areas are mostly kieserite.

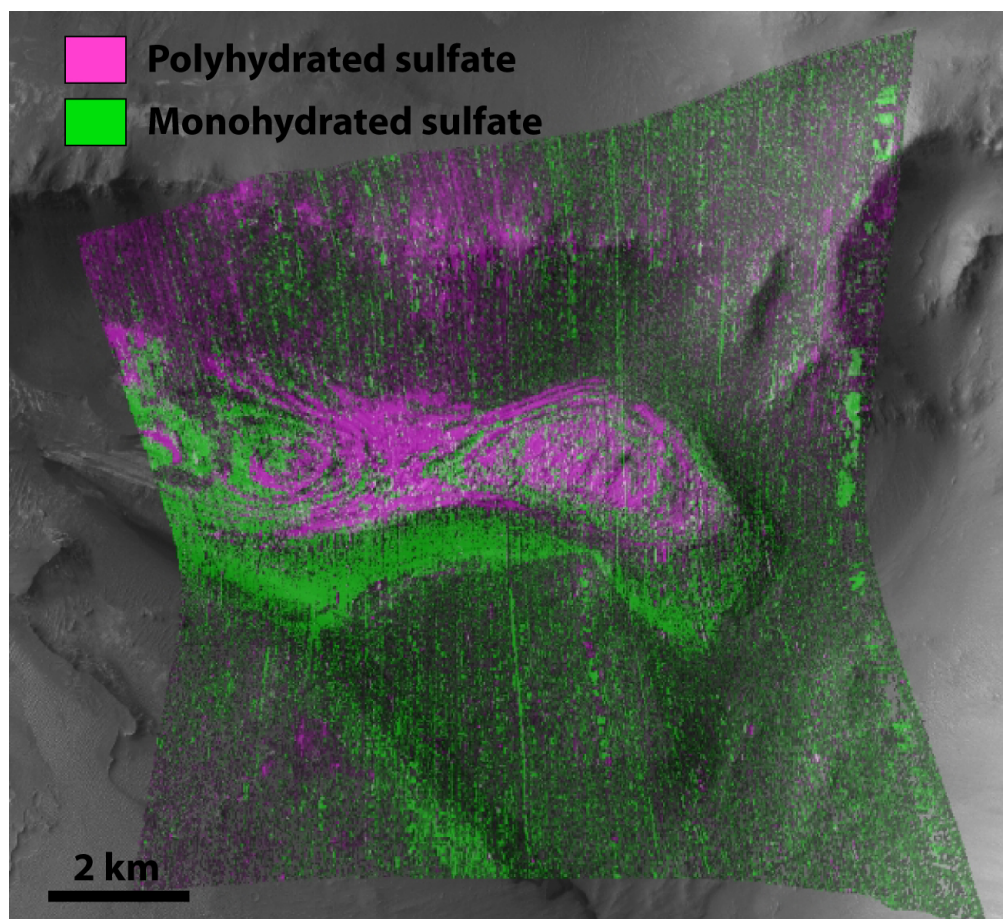


Figure 2.8: HiRISE image PSP\_008088\_1760 colorized with CRISM FRT0000C470 spectral band depth parameters (magenta:  $1.9\ \mu\text{m}$  band depth, green:  $2.1\ \mu\text{m}$  band depth). Magenta areas indicate presence of dominantly polyhydrated sulfates with green areas are mostly kieserite. Same deposit as in Fig 2.7.

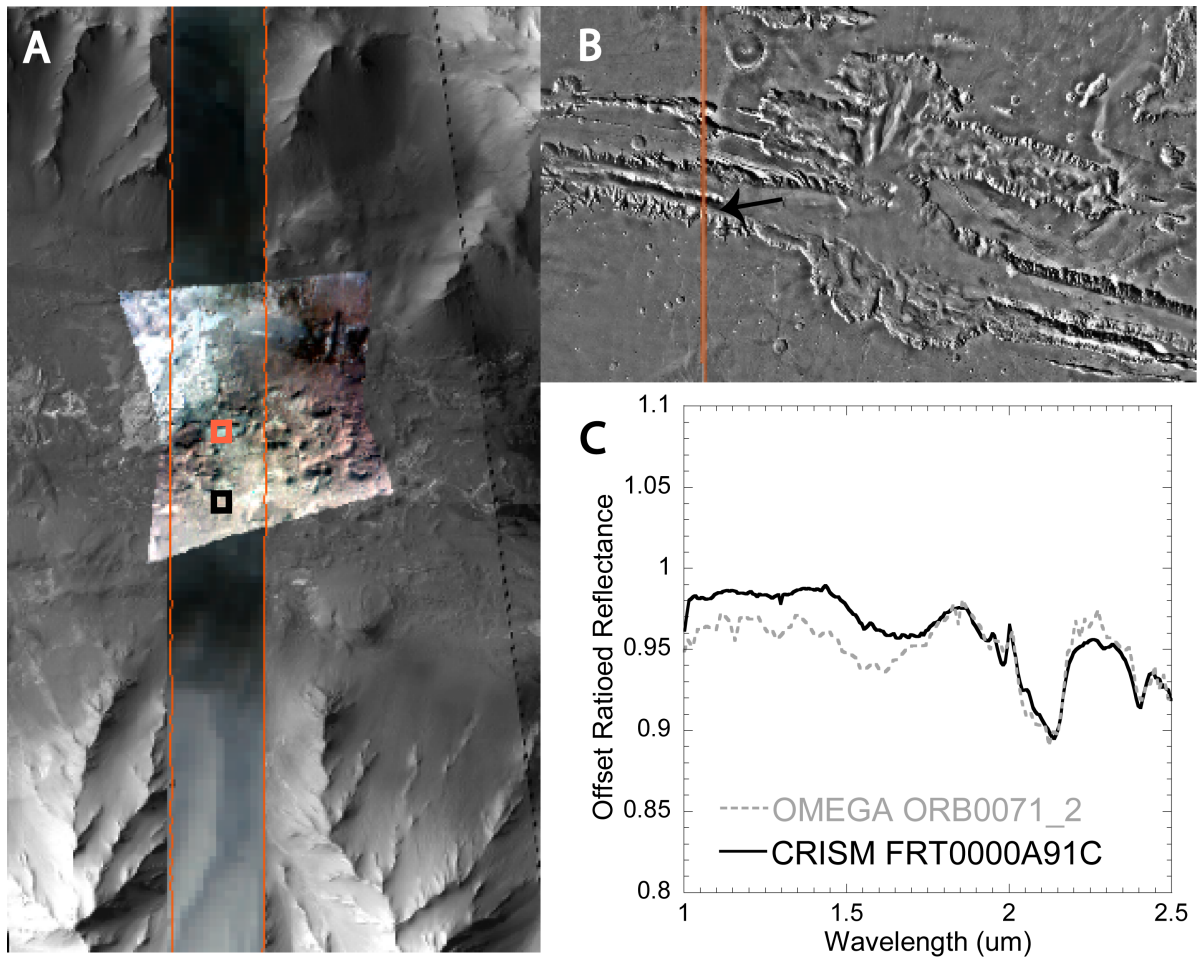


Figure 2.9: Overlapping observations OMEGA ORB0071\_2 and CRISM FRT0000A91C with CTX mosaic in background. Numerators located at light-colored box; denominators at black box. B. Context map of central Valles Marineris. Arrow points to paired observations, located in Ius Chasma. Orange outline is OMEGA ORB0071\_2. C. Comparison of ratioed reflectance spectra, showing similarity of 2.1  $\mu\text{m}$  band depths due to kieserite. OMEGA spectrum offset by -0.22.



## 2.4 Implications and Conclusions

There are three plausible hypotheses for the finding of polyhydrated sulfate and kieserite in the same deposits: (1) kieserite is converting to a polyhydrated state upon exposure to the surface environment under current environmental conditions; (2) kieserite conversion cannot progress under current environmental conditions and requires a warmer and wetter climate, such as periods of high obliquity; and (3) a multi-sulfate evaporite assemblage created by changing brine chemistry during evaporation, altered by diagenesis. Another hypothesis, that the kieserite and polyhydrated sulfate could have formed elsewhere and been transported by aeolian processes to the ILD, is unlikely since the cementing process would probably affect or homogenize the sulfate hydration state and it is implausible that this process occurred at least six or seven times (six alternations in sulfate mineralogy visible in Fig. 2.10). There are complications to these three sulfate formation and alteration mechanisms that should be considered, such as the presence of other phases that are spectrally neutral in the VNIR and the unknown kinetics of sulfate phase change under Martian conditions.

### 2.4.1 Active hydration of kieserite hypothesis

The presence of significant talus at the base of the East Candor Chasma ILD and other ILDs is evidence that they are easily weathered. Steeper surfaces undergo more continual erosion, continually refreshing the surface exposure of kieserite in these strata, which creates layering with the flatter polyhydrated strata, which have been exposed longer at the surface.

The similarity of paired orbital observations indicate the proportionate amounts of polyhydrated sulfate and kieserite have not changed within the resolving capability of these instruments over at least two Mars years, but several other factors must

be considered. Differences in shadows may explain some of the offset in ratioed reflectance. Slight inaccuracies in data co-aligning and differences in instrumental atmospheric calibrations may account for some differences in spectral shape, especially  $<1.3 \mu\text{m}$ . It is possible that there is a slight seasonal or yearly variation in hydration state, but that it is less than CRISM's detection limit. However, CRISM has a signal-to-noise of  $\sim 400$  around  $2 \mu\text{m}$ , which corresponds to a  $3\text{-}\sigma$  detection of a 1% band depth [Murchie et al. 2007a], so non-detection of a real change in hydration state is improbable.

### 2.4.2 High obliquity hydration of kieserite hypothesis

If the hydration is not occurring under current conditions, it could be provoked during obliquity oscillations that bring warmer or more humid conditions to Valles Marineris [Vaniman et al. 2004a; Vaniman and Chipera 2006a]. Numerical models of Martian climate with obliquities of up to  $45^\circ$  show significant seasonal water ice precipitation in Valles Marineris [Forget et al. 2006; Madeleine et al. 2008]. The ease with which these models can create ice in the equatorial regions with a variety of parameters and a high obliquity indicates that kieserite hydration during high obliquity periods is credible. The obliquity of Mars is well constrained for the past 10 million years and during this period there were multiple occurrences of obliquity  $>40^\circ$  [Laskar et al. 2004]. These periods of increased surface and subsurface ice stability seasonally established conditions for kieserite to hydrate to  $\text{MgSO}_4 \bullet 6\text{H}_2\text{O}$  [Vaniman and Chipera 2006a]. The continued presence of kieserite on Mars in conditions outside of its stability field suggests kieserite behaves metastably and that periods of kieserite hydration to polyhydrated sulfate would be episodic and incomplete.

### 2.4.3 Multi-sulfate evaporite deposit hypothesis

A third hypothesis for the multi-sulfate assemblage is alternating mono- and polyhydrated sulfate-rich layers that are metastable under current conditions. These alternating sulfate layers could have been laid down as basinal evaporites from a brine of cyclically changing composition.

Cyclic evaporite sequences have multiple salts precipitated as the brine concentrates and passes through chemical divides [e.g. [Hardie and Eugster 1970; Tosca et al. 2005]]. Evaporites derived from weathering of Martian basalts would produce multiple phases, depending of relative amount of  $\text{HCO}_3^-$  to  $\text{SO}_4^{2-}$  and degree of evaporative concentration, and include the sulfates gypsum, epsomite, and melanterite [Tosca and McLennan 2006]. Total evaporation of the brine in a closed system results in relative proportions of 44% epsomite, 43% Fe sulfates, and 13% gypsum [Tosca and McLennan 2006]. Fe sulfates do not appear in this deposit, and gypsum (or alternatively hydrated silica) does not appear in large concentrations. Multiple cation chemistries for the polyhydrated sulfate are possible, including bloedite [ $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \bullet 4\text{H}_2\text{O}$ ], kainite [ $\text{KMg}(\text{SO}_4)\text{Cl} \bullet 3\text{H}_2\text{O}$ ], and bischofite [ $\text{MgCl}_2 \bullet 6\text{H}_2\text{O}$ ]. Other phases common in massive evaporites, such as anhydrite, halite, or sylvite, may also be present in this deposit, but are not detected because they are either completely dehydrated or otherwise lack bands in the VNIR wavelength region.

Possible formation mechanisms for cyclically alternating sulfate layers include groundwater interaction or original evaporite deposition. Groundwater interaction is less favorable than evaporitic deposition since the layers are on the order of meters thick, and are unlikely to form repeated oscillations between mono- and polyhydrated sulfate over such a small distance. An evaporating closed basin with changing brine chemistry could precipitate first a polyhydrated sulfate, then epsomite or another Mg sulfate as the brine concentrates, then a different polyhydrated sulfate again when



fresher water dilutes the brine [Hardie 1991]. Kieserite could be formed by syndepositional diagenesis of epsomite, and the polyhydrated sulfate currently observed could be converted to bloedite, kainite, and bischofite from the original evaporite. At least six changes in sulfate mineralogy are visible in CRISM imagery of the East Candor Chasma ILD where dust and landslides do not obscure layering (Fig. 2.10). If these layers are evaporitic, it points to a reservoir of relatively concentrated brine in East Candor Chasma that was frequently recharged.

The sulfate composition of the layers could also be related to material properties, such as grain size, porosity, and induration; i.e. the kieserite-bearing units are more resistant units and the softer units are enriched in polyhydrated sulfate. Polyhydrated sulfate-bearing units in West Candor Chasma have generally higher thermal inertia than kieserite-bearing units, arising from their more hydrated state and probably also differences in material properties of each unit [Mangold et al. 2008b]. The additional water in polyhydrated sulfate-rich material might make it structurally weaker and more likely to form slopes.

#### **2.4.4 Discussion**

An alternative hydration scenario is that anhydrous but slowly hydrating sulfates are mixed as a minor phase with the kieserite. A complex mineral assemblage in the ILD of kieserite with other, non-Mg-bearing sulfates is possible. These anhydrous sulfates would have no distinguishing VNIR spectral shape as they lack bonded OH and HOH to form vibrational features [Hunt et al. 1971b]. However, with hydration, these anhydrous sulfates can impart their spectral character to the resulting mixed spectrum. Thus, the steeper slopes could contain kieserite and an anhydrous sulfate while the flatter slopes contain kieserite and a now polyhydrated sulfate that spectrally dominates.

If the polyhydrated sulfate is Mg-bearing, then finding both monohydrated and polyhydrated Mg sulfate on the Martian surface raises questions about the relative stability of the various phases. Kieserite and lower hydrated crystalline and amorphous Mg sulfates are the most stable forms in the warmer areas of the Martian surface, such as Valles Marineris [Chipera and Vaniman 2007]. Kieserite and a polyhydrated Mg sulfate might exist together metastably in Valles Marineris; active conversion between Mg sulfate phases could be limited because excursions into the hexahydrate T-RH stability field are on the order of hours a day in the summer and might not be for long enough to overcome the kinetic limitations.

In the Martian chemical divide model, epsomite is expected to precipitate from brine that has previously precipitated gypsum and melanterite and/or a carbonate [Tosca and McLennan 2006]. The brine resulting from weathering a Martian basalt results in sub-equal amounts of Mg and Fe sulfates with the bulk of the Mg sulfates precipitated last, so it is unrealistic to expect a closed evaporite sequence to contain no appreciable  $\text{Fe}^{2+}$  while showing strong spectral evidence for monohydrated Mg sulfate. Even if the  $\text{Fe}^{2+}$  precipitated as an iron oxide instead of a ferrous or ferric sulfate, the strong Fe charge transfer bands in the VNIR wavelength region [e.g. [Hunt et al. 1971b]] would allow confident detection at low abundances. The lack of a ferrous (or ferric) sulfate detection unfortunately does not allow us to make a strong case for a cyclic evaporite model or to constrain the original brine chemistry. Thus, if this deposit is an evaporite, it precipitated from an evolved brine saturated with only Mg sulfate or experienced significant post-depositional groundwater alteration.

The speed of the proposed active hydration of kieserite to a polyhydrated sulfate in a complex assemblage is not well constrained. Having complex sulfate mixtures may affect sulfate stability fields by creating microenvironments with conditions different from the ambient environment [Freeman et al. 2007]. Paired OMEGA and

CRISM observations over more than one Martian year do not indicate a change in the assemblage's hydration state, and another similar ILD shows no change over more than two Mars years. However, the hydration reaction must have progressed at some point in the past to produce both mono- and polyhydrated sulfates in the same assemblage. Hydration may only be possible during periods of high obliquity and is not presently progressing. Furthermore, the CRISM observations span multiple seasons yet are spectrally similar, which contravenes seasonal changes in hydration.

While we discard the hypothesis that sulfates are hydrating on a seasonal or several year period, we cannot decide between either hydration under periods of high obliquity or exposure of metastable cyclic evaporite sequences as the preferred explanation for the multi-sulfate assemblage at the East Candor ILD. Experimental sulfate stability studies and modelled Mars climate data suggest sulfate hydration is possible and likely rapid under certain (wetter) conditions. The evaporite model is consistent with other sulfate-bearing ILDs, especially those in nearby West Candor Chasma. Both possibilities offer exciting implications for the formation and alteration of layered deposits within Valles Marineris, and future MRO and MEx monitoring of this and similar sites within Valles Marineris will continue to test the two hypotheses.

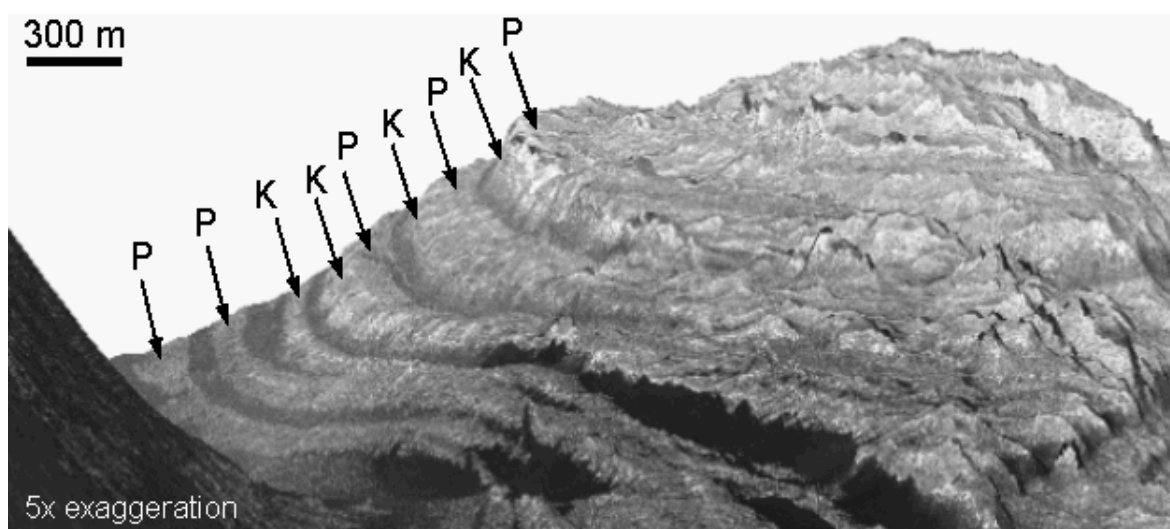


Figure 2.10: Looking east along top of East Candor Chasma ILD in HiRISE PSP\_2076\_1735 orthographically projected and draped on HiRISE-derived digital elevation model. Slope up to ridge is just visible on left. Kieserite-dominated units, labelled K, occur as steeper slopes than polyhydrated sulfate-dominated units, labelled P. Six alternations between kieserite and polyhydrated sulfate are visible.

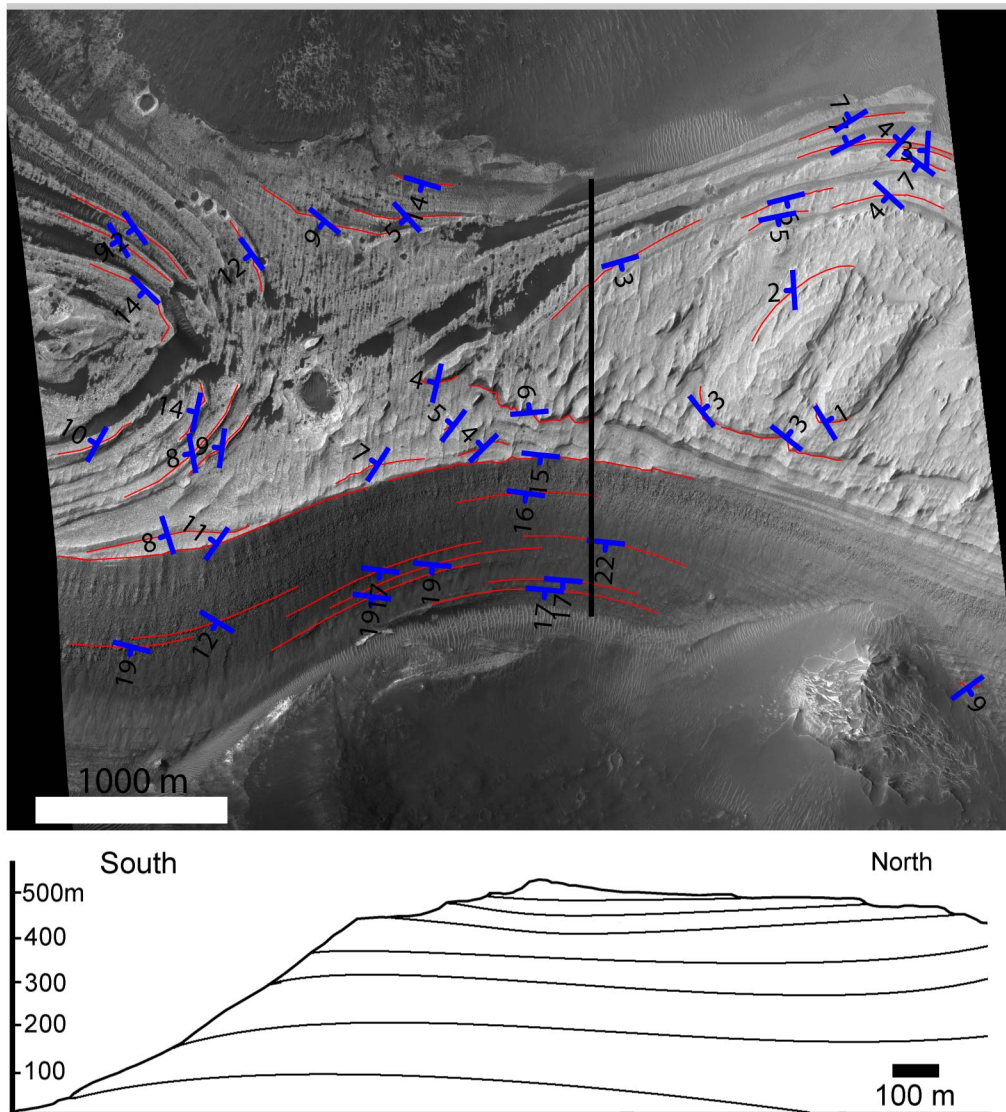


Figure 2.11: A: Strike and dip measurements of layers in East Candor Chasma ILD. The red lines indicate the portion of the layer used to calculate the strike and dip. B: Schematic N-S cross section through middle of ILD showing deformed layering.

## Chapter 3

# Sulfate Stratigraphy in Ius Chasma, Valles Marineris

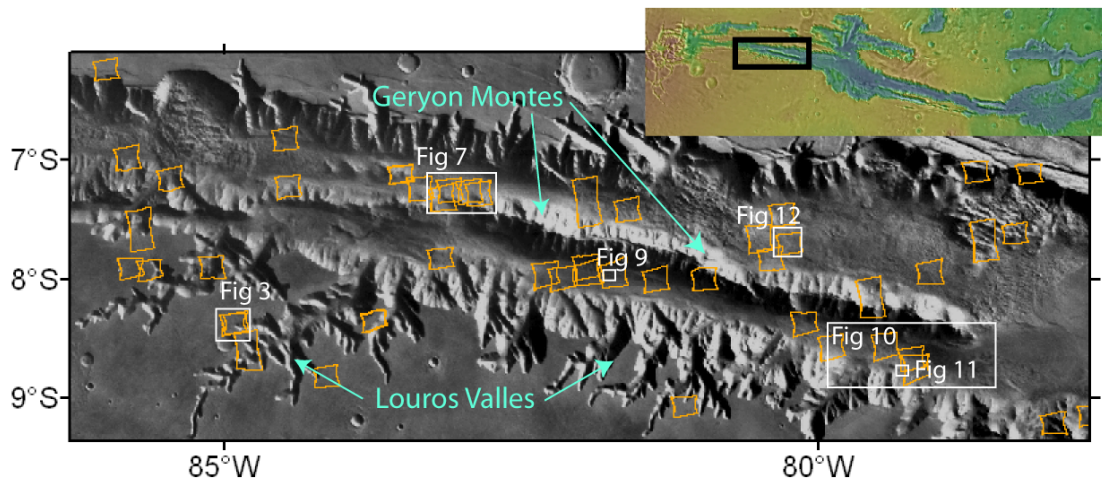


Figure 3.1: MDIM of linear Ius Chasma showing sapping channels, spur-and-gully erosional topography on wallrocks, and structurally controlled fractures. CRISM outlines included in study in orange. White boxes indicate locations of geologic contacts shown in Figures 3.3 (labeled Fig 3), 3.9 (labeled Fig 9), 3.10 (labeled Fig 10), 3.11 (labeled Fig 11), 3.12 (labeled Fig 12) and 3.13 (labeled Fig 7). Inset: Location of Ius Chasma within Valles Marineris (colored MOLA).

New high-resolution spectral and morphologic imaging of deposits on walls and floor of Ius Chasma extend previous geomorphic mapping, and permit a new interpretation of aqueous processes that occurred during the development of Valles Marineris. Multiple episodes formed and transported hydrated minerals within Ius Chasma. A closed basin at the lowest elevations in the chasma hosted a brine that precipitated polyhydrated sulfate then kieserite, a monohydrated sulfate, as it evaporated. Fluvial or aeolian processes then deposited layered Fe/Mg smectite clays and hydrated silicate on the chasma floor, postdating the sulfates. The smectite clay apparently was weathered out of Noachian-age wallrock and transported to the depositional sites. The overlying hydrated silicate is interpreted to be an acid-leached phyllosilicate transformed from the underlying smectite clay unit, or a smectite/jarosite mixture. The finely layered smectite clay and massive hydrated silicate units have an erosional unconformity between them, that marks a change in surface water chemistry. Landslides transported large blocks of wallrock, some altered to contain Fe/Mg smectite, to the chasma floor. After the last episode of normal faulting and subsequent landslides, opal was transported short distances into the chasma from a  $\sim 10$  s m-thick light toned layer near the top of the wall rock, by sapping channels in Louros Valles. The superposition of different types of hydrated minerals and the different fluvial morphologies of the units containing them indicate sequential, distinct aqueous environments, characterized by alkaline, then neutral/acidic, and finally very acidic surface or groundwater chemistry.

### 3.1 Introduction

Valles Marineris is a dominant feature in the western hemisphere of Mars — 4000 km long and up to 7 km deep — that has inspired many hypotheses for its formation (e.g.

[McCauley et al. 1972; Tanaka and Golombek 1989; Lucchitta et al. 1992]). Orbiting spectrometers have discovered large exposures of a variety of minerals within Valles Marineris, from olivine and other basaltic components [Christensen et al. 2003, 2005] to alteration minerals including sulfate [Gendrin et al. 2005], hematite [Christensen et al. 2001], and other ferric phases [Bibring et al. 2007]. Recent OMEGA and CRISM results have also found opal [Milliken et al. 2008a] and phyllosilicates [Poulet et al. 2005; Murchie et al. 2009a] within and surrounding Valles Marineris. Water played an important role in both the formation of Valles Marineris and its associated outflow channels and in creating these alteration minerals [Gendrin et al. 2005; Murchie et al. 2009a,b]. However, the different chemical alteration products within Valles Marineris are newer discoveries (e.g. [Gendrin et al. 2005; Milliken et al. 2008a; Murchie et al. 2009a,b; Bishop et al. 2009; Roach et al. 2009c]) and their relative timing is not well understood.

Exposures of different geologic units within Ius Chasma are ideal for probing the possible occurrence of different chemical environments during the formation of Valles Marineris. Studying the mineralogy of materials in Ius Chasma can help shed more light onto fluvial processes and constrain the timing of phyllosilicate alteration. Examining the close spatial relationship between sulfate and smectite clays can also help resolve questions about their relative timing and respective formation processes. With geomorphic and mineralogic evidence, we build on previous structural and surficial geologic mapping to construct a more detailed history of aqueous alteration in this area of Mars.



## 3.2 Background

### 3.2.1 Geologic history

The origin of the Valles Marineris canyon system has been an area of intense research since its discovery (e.g., [McCauley et al. 1972; Sharp 1973; Carr 1974; Lucchitta et al. 1992, 1994]). Several mechanisms have been proposed to explain its formation, including karst-style collapse, erosional, and tectonic processes (e.g., [McCauley et al. 1972; Tanaka and Golombek 1989; Blasius et al. 1977; Croft 1989b; Lucchitta 1990; Schultz 1998]). The currently favored model invokes extension due to tectonic stress related to the Tharsis Rise, although the details are under debate ([Mege and Masson 1996a] and references therein).

The structural control of landform development is striking in Ius Chasma (Fig. 3.1), where several features are evidence of the repeated tensional and erosional events. First, the wall rock often exhibits triangular faceted spurs where linear fault scarps cut the spur-and-gully topography [Hamblin 1976; Blasius et al. 1977]. Secondly, the central ridge, Geryon Montes, is interpreted as a horst between the two grabens of north and south Ius Chasma [Peulvast and Masson 1993a]. Finally, the sapping channels that comprise Louros Valles along the southern wall have two preferred orientations [Kochel and Piper 1986]. These orientations demonstrate the structural control that influences both the sapping channels and fracturing along the chasma [Kochel and Piper 1986]. The creation of structural weaknesses exploited by sapping channels and other fracturing is thought to predate the formation of Valles Marineris [Tanaka 1986].

A detailed geologic history of Ius Chasma has been established from imaging and topographic data (e.g., [Tanaka 1986; Peulvast and Masson 1993a,b; Peulvast et al. 2001], SchultzLin2001). The region consists of a megabrecciated basement [Tanaka

and Golombek 1989] overlain during the Late Noachian period by lava flows that accumulated to several km in thickness [Lucchitta et al. 1992; Tanaka et al. 1992; McEwen et al. 1999; Williams et al. 2003]. The elevation of the contact between Hesperian and Noachian materials is uncertain, but the Hesperian volcanics are at least several km thick in Ius Chasma. These Late Noachian — Early Hesperian lava plains were part of the voluminous Tharsis volcanism [Tanaka et al. 1991] and are interpreted to be cut by multiple dikes or lithified faults [Lucchitta et al. 1992]. The  $\sim 400$  m thick, uppermost layer of the lava flows is more resistant to erosion than underlying layers and may be evidence of diagenesis or aqueous alteration during the Late Hesperian period [Treiman et al. 1995; McEwen et al. 1999].

Valles Marineris formed over a long period from Early to Late Hesperian following the accumulation of the thick lavas [Tanaka 1986], and multiple processes likely contributed to its geometry. It is possible that wider, more irregular chasmata, such as Capri and Melas Chasma, formed in subsiding ancestral basins [Lucchitta et al. 1994; Schultz 1998]. Long rectangular troughs, including Ius Chasma, developed as grabens that eventually connected to the wider chasmata [Lucchitta and Bertolini 1989; Peulvast and Masson 1993a,b]. Ius Chasma may have been isolated from Melas Chasma to the east during its earliest stages [Peulvast and Masson 1993a]. Mass wasting of wallrock widened the chasma. Large outflow channels debouched at the eastern end of Valles Marineris during the middle Hesperian period, but did not leave fluvial features in Ius Chasma either because the bulk of the water originated eastward of Ius, or because later deposition, faulting, and landslides obscured those features.

Geryon Montes divided Ius Chasma into northern and southern sub-basins early in the chasma's history, yet retains possible evidence for how the horst and graben topography initiated. Geryon Montes has several linear ridges  $\sim 10$ -20 km in length along its crest, variously interpreted as mafic dikes [Ernst et al. 2001], the result of slow

mass wasting [Peulvast et al. 2001], or fault zones cemented by groundwater [Treiman 2008]. Dike formation is the most likely explanation. Mass wasting of a narrow horst would not obviously create multiple linear ridges, but would tend to form one crest, and in cases of asymmetry in horst geometry or rainfall, create arcuate crests [Ellis et al. 1999]. Water-deposited mineral cements in fault zones also do not satisfactorily explain the linear ridges. These ridges are 5.5 km above the trough floor and 2.5 km below the surrounding plateau; an enormous amount of water would be necessary to have groundwater cementation of these faults. Additionally, the texture and albedo of these linear ridges do not differ from other wall rock ridges, and, though not dust covered, lack evidence of hydrated mineralogy in CRISM spectra. The ridges are similar in character to the rest of the layered volcanic rocks in Geryon Montes. The major volcano-building activity in Tharsis Rise created multiple radial dike swarms, and the linear ridges in Geryon Montes may be part of a Noachian-aged swarm [Ernst et al. 2001]. The putative dikes also align with the sapping channel orientations and are nearly parallel with the trough’s strike. Thus, the fractures controlling these features formed before Valles Marineris opened and could be part of the tectonic stress regime that predated Tharsis as well [Tanaka 1986; Lucchitta et al. 1992]. Dike intrusion into the future Geryon Montes may have locally strengthened that rock by filling fractures or partially annealing the layered volcanic flows and underlying regolith. A similar linear ridge runs along the crest of the central horst in Coprates Chasma [Treiman 2008]. It is possible that dike intrusions help facilitate horst and graben formation under extensional stress [McKenzie and Nimmo 1999].

After initial rifting, the walls of Ius Chasma were extensively modified by fluvial erosion and mass wasting — forming spur-and-gully morphology, sapping channels, and landslide scars. The “spur-and-gully” morphology in Ius Chasma was developed by streams cutting across fault scarps [Lucchitta et al. 1992]. The spur-and-gully

morphology is visible on the interior ridge of Geryon Montes and on wall material not later cut by sapping channels and landslides. It is not found re-developing on landslide scars, so either the landslides were too recent to allow spur-and-gully erosion, or the spur-and-gully morphology was developed in an early, possibly wetter, environment [Lucchitta et al. 1992]. The level of dissection is dependent on rock strength and amount of fluvial erosion (Ellis et al., 1992). Normal faulting during spur-and-gully formation resulted in hanging triangular facets along the north wall of north Ius Chasma, eroded by continued incision of the catchments. Later normal faulting after spur-and-gully formation ceased preserved those triangular facets [Hamblin 1976; Ellis et al. 1999]. In addition to spur-and-gully morphology, fluvial erosion also formed sapping channels on both the northern and southern chasma walls. It is most noticeable in Louros Valles, which is interpreted as a collection of sapping channels each 30 to 130 km long. The sapping channels were active into the early Amazonian period [Craddock and Howard 2002], and they uniformly cut spur-and-gully features [Peulvast et al. 2001]. Finally, landslide deposits cover much of the trough floor. Crater counting of five landslides in eastern Ius Chasma produced dates ranging from 60 to >1000 My, suggesting episodic landslide activity from the initial rifting until the present [Quantin et al. 2004].

Normal faulting in Ius Chasma continued from the late Hesperian through early Amazonian periods, and the cross-cutting relations of these faults with mineral deposits and erosional features can determine the relative timing and duration of different processes [Peulvast et al. 2001]. Landslides and sapping channels both transect and are transected by faults. Faulting in Ius can generally be divided into “earlier” and “later” faulting, occurring either during spur-and-gully formation or after it had ceased. The “later” faulting caused preferentially more slip along the base of northern walls than southern walls in both the northern and southern sub-basins [Peulvast

et al. 2001]. This could be due to an asymmetric graben. Although “later” faulting only accounts for  $\sim 10\%$  of the total canyon wall relief, it was an important period that likely widened the connection between Ius and Melas Chasmata [Peulvast et al. 2001]. There is also evidence for aqueous processes on the plateau around Ius Chasma. Opal deposits on the plateau south of Ius Chasma formed between the late Hesperian and early Amazonian periods [Milliken et al. 2008b,a]. The drainage networks on the plains south west of Ius and within Melas Chasma may be caused by Hesperian-aged precipitation and surface runoff [Weitz et al. 2003; Mangold et al. 2004].

### 3.2.2 Mars Reconnaissance Orbiter (MRO) datasets

The Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument is a visible-infrared hyperspectral imaging spectrometer capable of acquiring observations in both targeted and mapping modes. Targeted observations are taken in 544 wavelengths from  $0.392\text{--}3.92\ \mu\text{m}$  at  $\sim 20\ \text{m/pixel}$  [Murchie et al. 2007a]. Mapping observations at 72 wavelengths and  $100\text{--}200\ \text{m/pixel}$  are acquired in the multispectral survey mode [Murchie et al. 2007a]. Both spatial scales are useful in mapping spectral units and making connections to geologic and morphologic features. The spectra include compositional information due to charge transfer and electronic transition absorptions due to transition metal elements (especially Fe) in materials, and vibrational overtones and combination tones of anions including  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$  in coordination with cations of Si, Mg, Fe, etc. [Burns 1993; Clark et al. 1990].

Two cameras are coaligned with CRISM on the MRO spacecraft: the High Resolution Imaging Science Experiment (HiRISE) and the Context imager (CTX). HiRISE acquires very high resolution (up to  $25\ \text{cm/pixel}$ ) imagery, sufficient to resolve the fine layering and polygonal fracturing in many of the hydrated materials [McEwen et al. 2005, 2007]. CTX images are  $\sim 6\ \text{m/pixel}$  and  $\sim 30\ \text{km}$  across, well-suited for

compiling high resolution mosaics covering large areas [Malin et al. 2007]. Many of the CRISM observations are accompanied by simultaneous HiRISE and CTX images for coordinated analysis of surface composition and morphology.

### **3.2.3 MOLA topography**

The Mars Orbiter Laser Altimeter (MOLA) on the MGS spacecraft collected shot data with a 160 m surface spot size and 300 m spacing between shots [Zuber et al. 1992]. These data were aggregated into a global 128 pixel/degree grid with a vertical accuracy of  $<30$  m [Zuber et al. 1992]. This gridding results in 460 m / pixel spacing near the equator. In regions with rapid elevation changes and with dense shot distribution, such as Ius Chasma, shot data is preferable for its higher accuracy than gridded data, but is limited to the acquired orbital tracks. MOLA shot data is ideal for creating detailed stratigraphy and cross sections of the surface deposits in Ius Chasma.

## **3.3 Methods**

### **3.3.1 CRISM data reduction**

CRISM data are reduced to atmospherically corrected surface reflectance via a standard calibration pipeline. First the instrumental dark current is subtracted from the data to remove the detector background noise. The data are then converted to radiance by dividing by the signal measured from an onboard calibration standard, and multiplying by a ground-based radiance model of the calibration standard [Murchie et al. 2007a, 2009c]. Dividing the radiance data by the solar spectrum scaled to the top of Mars' atmosphere yields an estimate of  $I/F$ .

Next, the atmospheric and surface components of the data need to be separated. An atmospheric transmission spectrum is derived from a single CRISM observation over the flank and top of Olympus Mons as in [Mustard et al. 2008]. An averaged spectrum from the base is ratioed to an averaged spectrum from the summit to create an atmospheric transmission spectrum. This computation is performed for each detector column, to account from cross-track variation in wavelength calibration [Murchie et al. 2007a, 2009c]. Assuming similar surface radiances at the base and summit of Olympus Mons (which is a good approximation, since both are very dusty) and a lack of clouds, the difference between the base and summit is due to the difference in atmospheric pathlength, i.e. atmospheric absorptions alone. For each CRISM observation of interest, this transmission spectrum is scaled by the CRISM observation’s atmospheric pathlength, as estimated by the strength of the  $2.011\ \mu\text{m}$   $\text{CO}_2$  absorption, and the I/F spectrum is divided by the scaled transmission spectrum to approximately remove atmospheric gas bands. The data are then divided by the cosine of the incidence angle to approximate Lambert albedo. An optional further step is to “clean” the data in the spectral and spatial dimensions to remove instrumental noise and column-to-column variation [Parente and Bishop 2008].

### **3.3.2 Spectral interpretation of minerals**

Spectral summary parameters are calculated from diagnostic absorptions to aid preliminary identification of minerals and atmospheric components as described in [Pelkey et al. 2007]. Parameters for hydrated sulfate and phyllosilicate minerals were particularly useful (see Equations 3.1 – 3.5 for formulations). Summary parameters used in this study include the  $1.9\ \mu\text{m}$  band depth, due to combinations of  $\text{H}_2\text{O}$  bending and stretching vibrations (BD1900); the  $2.1\ \mu\text{m}$  band depth, due to  $\text{H}_2\text{O}$  vibrational combinations (BD2100); the  $2.21\text{--}2.26\ \mu\text{m}$  band depth, due to Si-OH vibrations

(BD2210); the 2.3  $\mu\text{m}$  band depth, due to metal-OH vibrations (D2300); and the convexity around 2.3  $\mu\text{m}$  in very hydrated phases due to strong  $\text{H}_2\text{O}$  absorptions at 1.9 and 3  $\mu\text{m}$  (SINDEX). These summary parameters are useful for sifting through large amount of spectral data to identify areas that warrant more detailed analysis, and for mapping out regions with aqueous minerals, but they are not sufficient by themselves to for mineral identification.

$$BD1900 = 1 - \frac{R1908 + R1914 + R1921 + R1928 + R1934 + R1941}{R1862 + R1869 + R1875 + R2112 + R22120 + R2126} \quad (3.1)$$

1.9  $\mu\text{m}$  absorption due to combinations of  $\text{H}_2\text{O}$  bending and stretching vibrations

$$BD2100 = 1 - \frac{(R2120 + R2140) \times 0.5}{b \times R1930 + a \times R2250} a = \frac{(R2120 - R1930)}{R2250 - R2140} b = 1 - a \quad (3.2)$$

2.1  $\mu\text{m}$   $\text{H}_2\text{O}$  vibrational combinations in monohydrated sulfates

$$BD2210 = 1 - \frac{R2210}{b \times R2140 + a \times R2250} a = \frac{(R2210 - R2140)}{R2250 - R2140} b = 1 - a \quad (3.3)$$

Si-OH vibrations around 2.21  $\mu\text{m}$

$$D2300 = 1 - \frac{\frac{R2290}{CR2290} + \frac{R2320}{CR2320} + \frac{R2330}{CR2330}}{\frac{R2120}{CR2120} + \frac{R2170}{CR2170} + \frac{R2210}{CR2210}} \quad (3.4)$$

Metal-OH vibrations around 2.3  $\mu\text{m}$

$$SINDEX = 1 - \frac{R2100 + R2400}{2 \times R2290} \quad (3.5)$$



Convexity around  $2.3\ \mu\text{m}$  due to  $\text{H}_2\text{O}$  absorptions at  $1.9$  and  $3\ \mu\text{m}$

In Equations 3.1 – 3.5, R1908 indicates the reflectance at  $1.908\ \mu\text{m}$  and CR2290 indicates the calculated continuum reflectance at  $2.29\ \mu\text{m}$  from a fit to a line from  $1.80$ – $2.53\ \mu\text{m}$ .

Further analysis including at least the  $0.4$ – $2.6\ \mu\text{m}$  wavelength range in both corrected I/F and ratioed spectra is necessary to determine the presence of a specific mineralogy. Typically, corrected I/F spectra are averaged into at least  $3\times 3$  or  $5\times 5$  pixel aggregates to reduce instrumental noise. A spectrum of interest is also divided by a spectrum of a spectrally neutral (i.e. dusty) region to accentuate subtle mineral absorption bands and to remove residual instrumental artifacts. If ratioing is performed, the spectrally neutral denominator spectrum should come from the same column(s) as the spectrum of interest to account for column-dependent wavelength calibration [Murchie et al. 2007a, 2009c]. A spectrally neutral denominator is best, as mineral absorptions in the denominator show up as inverse features in ratioed spectra and can complicate mineral identification. Ratioed spectra then are compared to the laboratory data of pure minerals for potential matches.

Hydrated minerals, including hydrated silica, sulfates, phyllosilicates, and carbonates, all show a pronounced  $\sim 1.9\ \mu\text{m}$  absorption [Hunt et al. 1971b, 1973], so other absorptions are necessary to resolve which class of hydrated mineral is present (Fig. 3.2). Monohydrated sulfates, such as kieserite and szomolnokite, have an absorption near  $2.1\ \mu\text{m}$  (with the exact minimum varying by cation) and near  $2.4\ \mu\text{m}$  [Cloutis et al. 2006]. The  $2.1\ \mu\text{m}$  absorption, which is due to a combination of  $\text{H}_2\text{O}$  stretch and rotation vibrations, is closer to  $2.13\ \mu\text{m}$  in kieserite (Mg monohydrate) and  $2.09\ \mu\text{m}$  in szomolnokite ( $\text{Fe}^{2+}$  monohydrate) [Cloutis et al. 2006; Crowley et al. 2003]. Szomolnokite also has a broad ferrous crystal field absorption at  $0.94\ \mu\text{m}$  [Crowley et al. 2003]. Polyhydrated sulfates, such as hexahydrite, have strong  $\text{H}_2\text{O}$  vibrations

at 1.45 and 1.95  $\mu\text{m}$  as well as a drop off in reflectance near 2.45  $\mu\text{m}$  attributed to SO or OH/H<sub>2</sub>O combinations and/or overtones [Cloutis et al. 2006].

Multiple hydrated minerals have diagnostic absorptions in the 2.2–2.3  $\mu\text{m}$  region. Hydrated silica is identified by minima at 1.37–1.46 and 2.20–2.26  $\mu\text{m}$ , which are attributed to a combination of the OH stretching fundamental with an Si-OH bending mode [Anderson and Wischersheim 1964]. The 2.20  $\mu\text{m}$  feature is due to Si-OH vibrations, while the 2.26  $\mu\text{m}$  is due to hydroxyls bound to free waters of hydration [Anderson and Wischersheim 1964]. Hydrated silica without free water will only have an absorption will only have a 2.20  $\mu\text{m}$  absorption, while more hydrated samples show a broad absorption between 2.20–2.26  $\mu\text{m}$ . The 2.20  $\mu\text{m}$  absorption is always stronger than the 2.26  $\mu\text{m}$  absorption [Anderson and Wischersheim 1964].

In addition to classifying by the presence/absence of free water, hydrated silica can be classified into opal-A (disordered), opal-C, and opal-CT, which contain ordered domains of crystalline cristobalite or cristobalite and tridymite [Smith 1998]. Spectral signatures are similar between opal subtypes with excess waters of hydration [Goryniuk et al. 2004; Milliken et al. 2008a], and for clarity with other minerals discussed in this paper, we refer in this paper to all hydrated silica phases as “opal.”

Jarosite and gypsum also have absorptions in the 2.2  $\mu\text{m}$  region, but are distinguished by other VNIR absorptions. Jarosite has absorptions at 1.47 and 1.85  $\mu\text{m}$  due to hydroxyl vibrations, and a doublet at 2.21 and 2.26  $\mu\text{m}$  due to Fe-OH vibrations [Crowley et al. 2003]. Gypsum has a distinctive triplet absorption between 1.44 and 1.54  $\mu\text{m}$ , absorptions at 1.75 and 1.9  $\mu\text{m}$ , and a doublet at 2.25 and 2.265  $\mu\text{m}$ , all due to combinations and overtones of H<sub>2</sub>O vibrations and librations [Hunt et al. 1971b; Cloutis et al. 2006]. Smectite clays have a narrow metal-OH absorption in the 2.3  $\mu\text{m}$  region, whose minimum moves from 2.31  $\mu\text{m}$  for Mg-rich saponite to 2.28  $\mu\text{m}$  for Fe-rich nontronite to 2.20  $\mu\text{m}$  for Al-rich montmorillonite [Bishop et al. 1994, 2008a].

In this paper we focus on the presence, not the abundance, phases with visible-infrared spectral signatures. Spectrally neutral minerals, like quartz or plagioclase, may also be present in any abundance. Variations in grain size, texture, and admixture with darkening agents or other minerals can all complicate retrieving abundances. Abundance calculations are not yet available for CRISM mineral identifications, although preliminary modeling efforts with OMEGA data are promising (e.g. [Poulet et al. 2009a,b]).

## 3.4 Results

### 3.4.1 Spectral results

Fe/Mg smectite clay minerals, opal, and sulfates, including kieserite ( $\text{MgSO}_4 \bullet \text{H}_2\text{O}$ ) and a polyhydrated sulfate with an unspecified cation, are all identified in light-toned deposits within Ius Chasma (Fig. 3.2, Table 3.3.2). The Fe/Mg smectite clay was identified by its hydration bands at 1.40–1.44 and 1.91–1.92  $\mu\text{m}$ , and a narrow minimum between 2.28 and 2.31  $\mu\text{m}$  indicative of metal-OH vibrations. The Fe/Mg smectite clay signature in Ius Chasma has a minimum near 2.29  $\mu\text{m}$ , which is more consistent with Fe-bearing nontronite than Mg-bearing saponite and indicates an Fe-rich smectite clay. Opal is identified by absorptions at 1.42, 1.92, and a broad asymmetric-right absorption centered at 2.20  $\mu\text{m}$ . Kieserite is distinguished by its broad 1.65  $\mu\text{m}$ , strong asymmetric-left 2.13  $\mu\text{m}$ , and 2.39  $\mu\text{m}$  absorptions. Polyhydrated sulfate has distinct absorptions at 1.43–1.45 and 1.91–1.95  $\mu\text{m}$  and a drop off in reflectance around 2.4  $\mu\text{m}$ . Pyroxene-bearing sand dunes (identified from broad 1- and 2- $\mu\text{m}$  absorptions) and dust partially overlie some of these light-toned deposits. The wall rock, which shows mafic signatures elsewhere, is generally dusty and lacks strong spectral features. No oxide separate from that in the globally-homogeneous

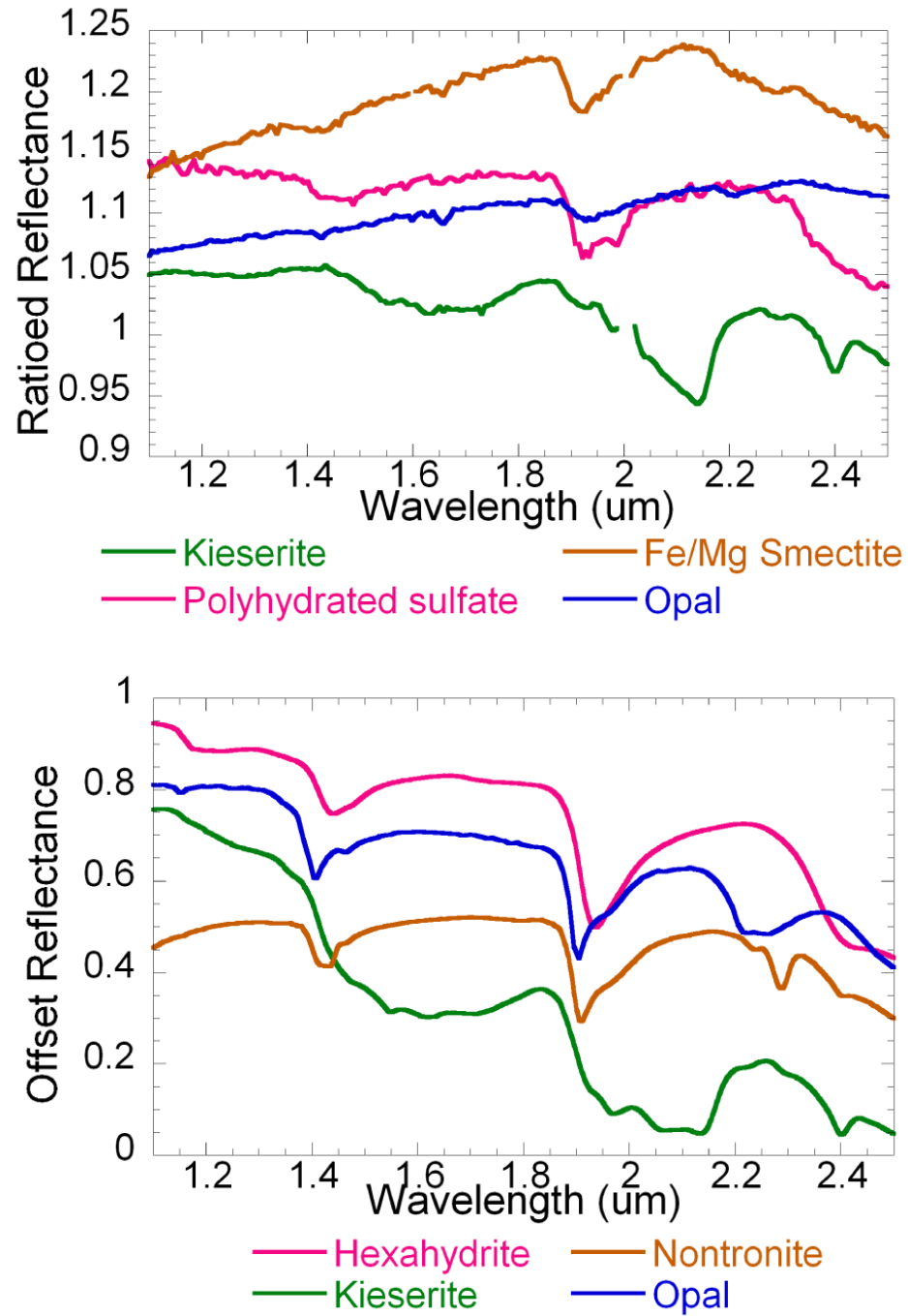


Figure 3.2: A. CRISM ratioed spectra of hydrated minerals identified within Ius Chasma. B. RELAB library reflectance spectra of relevant hydrated minerals: hexahydrite ( $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$ ), nontronite and opal.

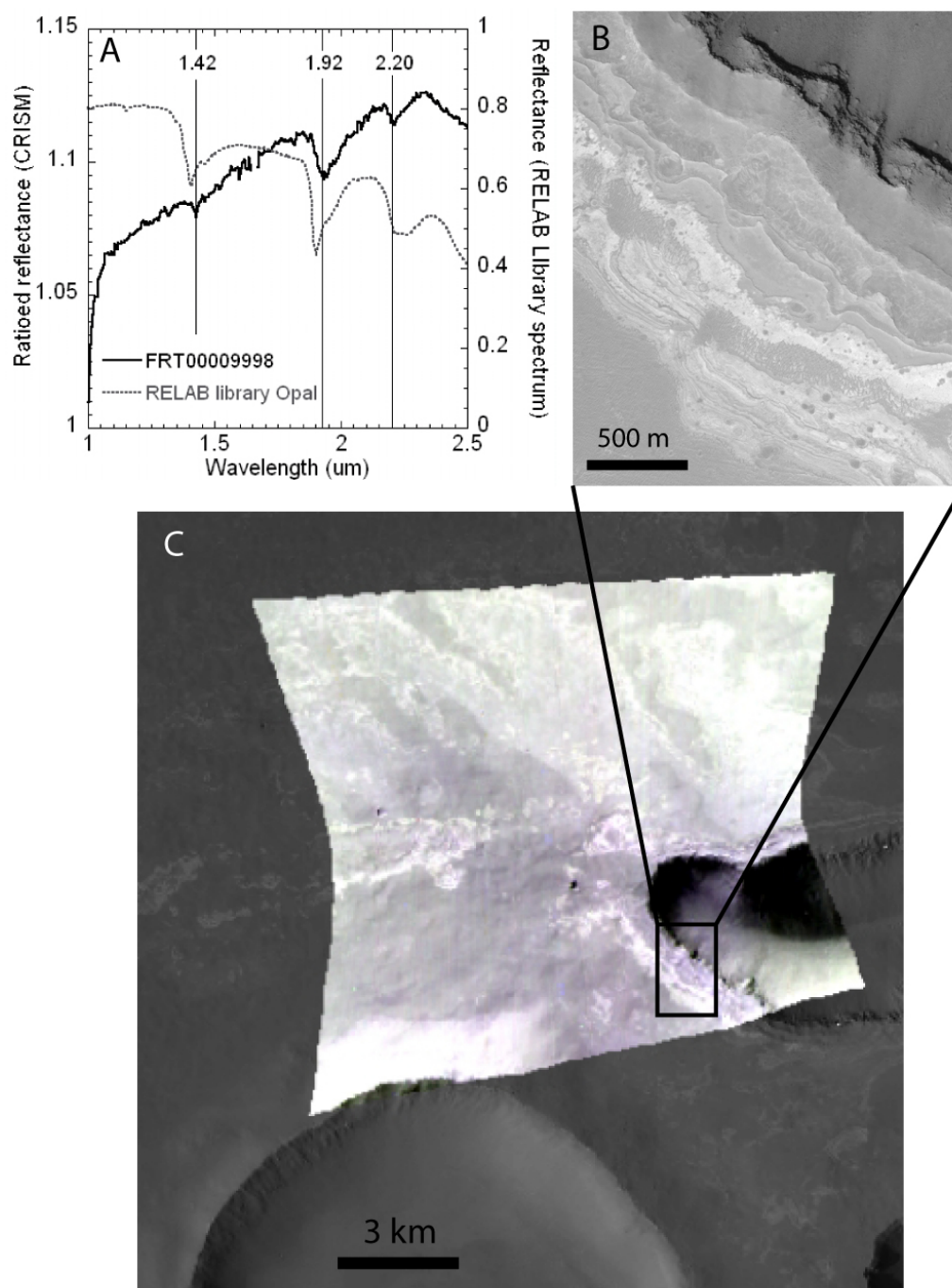


Figure 3.3: A. CRISM ratioed spectrum from FRT00009998 and RELAB library spectrum of opal. Both show the  $2.21\ \mu\text{m}$  absorption due to silanol vibrations. Library spectrum has an additional absorption at  $2.26\ \mu\text{m}$  due to free waters of hydration which the CRISM spectrum lacks. B. HiRISE PSP\_005215\_1715 subset showing fine layering in hydrated silica. C. CRISM FRT00009998 of Louros Valles over CTX P06\_003237\_1734. Part of  $\sim 10\ \text{km}$  diameter crater visible in SW part of image.

Table 3.1: Geologic units in Ius Chasma, Valles Marineris

| Geologic unit                        | Spectral absorptions                                                                                 | Description                                                                                                           |
|--------------------------------------|------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Kieserite                            | Broad 1.65, 2.13, 2.39 $\mu\text{m}$                                                                 | Light-toned, massive unit, >200 m thick                                                                               |
| Polyhydrated sulfate                 | 1.43-1.45, 1.91-1.95, drop off $\sim 2.4 \mu\text{m}$                                                | Light-toned, massive unit, polygonal meter-scale fracturing, >500 m thick                                             |
| Massive hydrated silicate            | 1.40-1.42, 1.91-1.92, sharp doublet at 2.205-2.218 and 2.265-2.278, sometimes $\sim 2.4 \mu\text{m}$ | Light-toned, massive unit, weathers into rough, orange peel-like texture, <few meters thick                           |
| Layered sedimentary Fe/Mg smectite   | 1.40-1.44, 1.91-1.92, 2.29 $\mu\text{m}$                                                             | Finely layered to HiRISE resolution, meter-scale polygonal fracturing                                                 |
| Opal                                 | 1.42, 1.92, broad absorption between 2.17 and 2.30 $\mu\text{m}$ centered at 2.20 $\mu\text{m}$      | Intermediate to light-toned, 10s m thick, meter-scale polygonal fracturing, sometimes lobate features in HiRISE       |
| Landslide with hydrated silicates(s) | 1.40-1.42, 1.91-1.92, sharp doublet at 2.205-2.218 and 2.265-2.278, sometimes $\sim 2.4 \mu\text{m}$ | Breccia blocks up to 100m across. Hydrated silicate in both breccia and cement                                        |
| Landslides                           | Spectrally neutral                                                                                   | Morphologically similar to above, but without hydrated silicate signatures                                            |
| Wallrock                             | Spectrally neutral                                                                                   | Layered, intermediate toned material exposed on sides of chasma and central ridge, with fluted spur and gully erosion |
| Undivided floor material             | Pyroxene (broad $\sim 1$ and $\sim 2 \mu\text{m}$ ) or dust                                          | Pyroxene-bearing dark dunes, or dusty capping material                                                                |

dust was identified using CRISM data from 0.4 to 1.0  $\mu\text{m}$ .

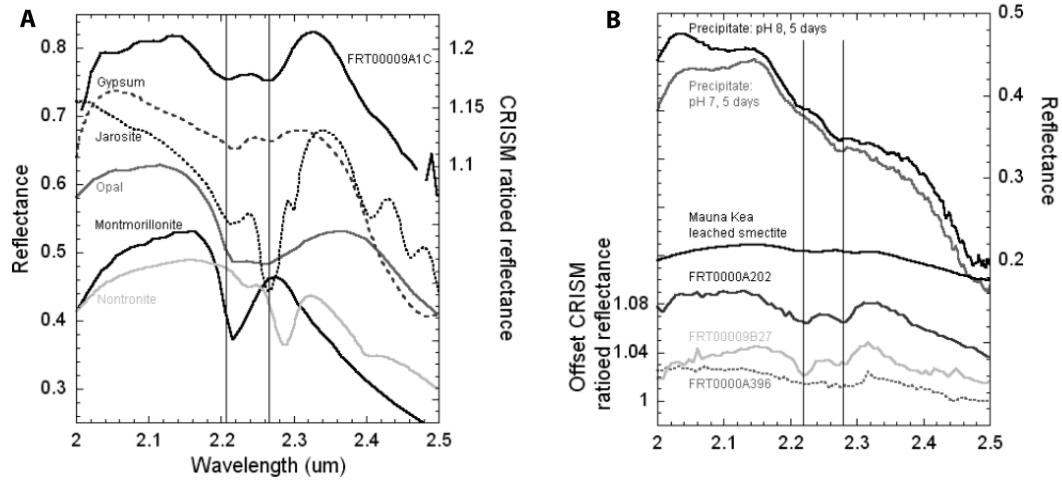


Figure 3.4: A. Cleaned spectrum from CRISM FRT00009A1C of 5387 pixels with RE-LAB library spectra of possible mineral components gypsum, jarosite, opal, montmorillonite, and nontronite. Vertical lines at 2.207 and 2.266  $\mu\text{m}$ . B. Spectra of two precipitated phases created by Nick Tosca [Tosca et al. 2008b,a] and leached smectite clay from Mauna Kea compared to three representative CRISM spectra (FRT0000A202, FRT00009B27, and FRT0000A396) with 2.21 and 2.27  $\mu\text{m}$  doublet. Vertical lines at 2.219 and 2.276  $\mu\text{m}$ . C. Same spectra as in B, with continuum removal.

A hydrated mineral phase not previously seen on Mars was also detected and mapped in this region using CRISM data (Fig. 3.4). It has molecular  $\text{H}_2\text{O}$  absorptions at 1.40–1.42 and 1.91–1.92  $\mu\text{m}$  and a sharp doublet at 2.205–2.218 and 2.265–2.278  $\mu\text{m}$ , unassigned but attributed to metal-OH vibrations. The relative depths of the 2.21 and 2.27  $\mu\text{m}$  absorptions vary, but both absorptions are always present and have similar widths. Spectra of this phase can also exhibit a step or minor absorption near 2.4  $\mu\text{m}$ . This phase is found in light-toned deposits elsewhere in Valles Marineris (the floors of southern Melas Chasma, Coprates Chasma, and Noctis Labyrinthus, and the central horst in Coprates Chasma), often in association with other hydrated minerals such as Fe/Mg smectite clays.

This new hydrated mineral phase does not correspond to any single mineral whose

spectra are available in the RELAB or USGS spectral libraries [Clark et al. 2007]. Mineral types investigated include sulfates, phyllosilicates, carbonates, chlorides, zeolites, phosphates, and opal. The closest spectral matches are jarosite, gypsum, opal, or a combination of hydrated phases such as smectite clay plus jarosite (Fig. 3.4). There are four hypotheses for the mineralogy that causes these absorptions: (1) sulfates structurally similar to gypsum or jarosite, perhaps in a mixture, (2) opal plus smectite clay, (3) a combination of smectite clays, and (4) poorly crystalline mixed Al-ferric clay formed from acid alteration of Fe/Al smectite clay.

Gypsum- or jarosite-group sulfates are close matches to the new hydrated mineral phase, but their multiple absorptions in the  $2.2\ \mu\text{m}$  region do not perfectly correspond. Cloutis et al. (2006) attributes the  $2.21\text{--}2.26\ \mu\text{m}$  doublet in jarosites to a combination of OH stretch and OH out-of-plane bend, and the  $2.25\text{--}2.265\ \mu\text{m}$  doublet in gypsum to S-O bending overtones. Jarosites have infinite sheet structures and gypsum has alternating chains of edge-sharing  $\text{SO}_4$  tetrahedra and polyhedra [Hawthorne et al. 2000], so other sulfates with similar structures would be the most likely candidates to have a doublet near  $2.21$  and  $2.27\ \mu\text{m}$ . Other Ca-sulfates such as bassanite and anhydrite are structurally similar to gypsum, but neither matches spectrally. Bassanite has absorptions at  $1.42$  and  $1.91\ \mu\text{m}$ , a shoulder at  $2.25\ \mu\text{m}$ , and a drop of longward of  $\sim 2.4\ \mu\text{m}$  [Crowley 1991]. Anhydrite has no absorptions in the VNIR since it lacks hydroxyls and  $\text{H}_2\text{O}$  in this structure. Na, K, and H-bearing jarosites do not match exactly and more exotic jarosites (e.g. Ag and Pb) are geologically unlikely. The doublet in K-jarosite is significantly deeper at  $2.267$  than at  $2.21\ \mu\text{m}$ , natrojarosite has a single absorption at  $2.267$ , and hydronium jarosite has no clear absorptions that match the  $2.2\ \mu\text{m}$  region [Bishop and Murad 2005].

Opal has a broad absorption with a minimum at  $2.21\ \mu\text{m}$  due to Si-OH (silanol) groups and a shoulder at  $2.26\ \mu\text{m}$ , depending on how much  $\text{H}_2\text{O}$  is attached to the



silanol groups [Milliken et al. 2008a,b]. However, the shape of the two features seen in the CRISM spectra is different from the bands observed in opal. Also the relative strengths of the two bands in the CRISM spectra can vary, whereas the 2.21  $\mu\text{m}$  band is always stronger than the 2.26  $\mu\text{m}$  band in opal. It is plausible that admixture with a smectite clay such as nontronite with its 2.28  $\mu\text{m}$  minimum could recreate the 2.21–2.27  $\mu\text{m}$  doublet. However, the Si-OH bands in opal are broader than the metal-OH bands in phyllosilicates, and the doublet in CRISM spectra is too narrow to be fit by a large component of hydrated silica.

A mixture of smectite clays could produce overlapping narrow absorptions in the 2.2  $\mu\text{m}$  region that reproduce the 2.21–2.27  $\mu\text{m}$  doublet in the CRISM spectra. ferromagnesian smectites have a range of Fe/Mg overtones at 2.28–2.31  $\mu\text{m}$  and montmorillonite as an Al-OH overtone at 2.21  $\mu\text{m}$ . The variable relative band depths in the CRISM spectra are consistent with a mixture of varying composition. Both montmorillonite and Fe-rich smectite have been found in separate deposits elsewhere on Mars (e.g. [Poulet et al. 2005; Mustard et al. 2008; Wray et al. 2008a]), and Al-rich phyllosilicate is found above Fe/Mg smectite in wallrock in Coprates Chasm [Murchie et al. 2009a]. An intimate mixture of jarosite and montmorillonite would have a similar spectral shape to a mixture of Fe-rich smectite and montmorillonite. Its doublet would be at 2.20–2.21 and 2.267  $\mu\text{m}$ , which is a close match, but still does not fully explain the range in the longer absorption. Jarosite forms at  $\text{pH} < 3$ , so this mixture would indicate very acidic conditions [Bigham et al. 1996].

The last hypothesis is an neutral- to acid-leached smectite. In Mauna Kea, acidic vapors or fluids leach Fe/Mg smectite-rich areas producing an alteration product with a doublet at 2.23 and 2.29  $\mu\text{m}$  (Fig. 3.4) (G. Swayze, unpublished data). The 2.29  $\mu\text{m}$  band is due to saponite-rich smectite that varies in abundance perhaps depending on the degree of acid alteration. As the saponite is consumed by acidic

fluids, a new phase of unknown mineralogy forms with an absorption at  $2.23\ \mu\text{m}$ . The  $2.23\ \mu\text{m}$  absorption is due to  $\text{AlFeOH}$  vibrations [Frost et al. 2002], so the new phase is suspected to be poorly crystalline ferruginous smectite. While this is not an exact match to the CRISM spectra's doublet, a difference in common smectite cation chemistry between Earth and Mars may produce a  $2.21\ \mu\text{m}$  absorption rather than  $2.23\ \mu\text{m}$ . Laboratory studies of smectite or silicate neoformation from chemical weathering of simulated Martian basalt [Tosca et al. 2008b,a] have produced an XRD amorphous phase with a possible doublet at  $2.21$  and  $2.27\ \mu\text{m}$ . The laboratory neoformed phase appears in experiments run under oxidizing conditions and pH 8. Its continuum-removed spectrum matches the CRISM spectra (Fig. 3.4) and suggests that a mildly acidic alteration process could replicate the new hydrated phase given a Martian starting composition for the basalt at moderate pH. While the Mauna Kea smectite is transformed by acidic leaching and the synthetic silicate is precipitated under circum-neutral conditions, together they offer a good model for neutral to acidic leaching of Martian smectites to cause transformation into multiple smectites or hydrated silicates.

These laboratory and terrestrial examples of altered smectite or silicate have absorptions at wavelengths that are close to the CRISM spectrum, however, continuum removal is necessary to accentuate those absorptions (Fig. 3.4). Typically, laboratory spectra have much stronger absorption features than those collected from orbit around Mars. The weaker features in Mars spectra may be due to reduced spectral contrast due to aerosols, mineral mixing, and dust cover. It is inappropriate that laboratory spectra require continuum removal in order to match non-continuum-removed Martian spectra. Perhaps the difference between laboratory and terrestrial phases and the Martian spectral type is due to amount of crystallinity. Perhaps the Martian phase is more crystalline than the laboratory and terrestrial examples and thus

has stronger metal-hydroxyl vibration bands in the 2.25  $\mu\text{m}$  region. The neoformed phase was created in five days in a laboratory setting and would perhaps become more crystalline with maturity and dehydration.

Of the four possible mineralogies of the hydrated mineral phase, we favor three: a neutral- to acid-leached phyllosilicate, a montmorillonite/jarosite mixture, or a montmorillonite/ferromagnesian smectite mixture. Both are satisfactory but not perfect spectral matches and are geologically feasible with the other alteration minerals found in Ius Chasma. In subsequent mapping, this phase is called hydrated silicate, although it may in fact represent or include another mineral class.

### 3.4.2 Stratigraphic results

The spectral identifications in individual CRISM observations have been classified into geologic units (Table 3.3.2) and extended into a regional unit map 3.5. First, CRISM targeted and multispectral mapping data were used to identify the locations of different hydrated phases. HiRISE and CTX images of those regions were examined to see if units have a characteristic morphology and to determine superposition relationships with adjacent geologic units. Many of the hydrated units are high-albedo, massive deposits that are indistinguishable in HiRISE or CTX imagery. For example, the polyhydrated sulfate and massive hydrated silicate-bearing units are morphologically very similar, and in locations lacking spectral coverage, they cannot be confidently distinguished by imagery alone. Thus, detailed stratigraphic analysis is limited to locations covered by CRISM targeted observations. In places where the geologic unit identification and stratigraphy is clear in CTX data, those morphologic indicators are used for geologic mapping outside the extent of CRISM observations. The resulting regional unit map (Fig. 3.5) shows the broad extent of hydrated mineralogy on the Ius Chasma floor. Three inferred stratigraphic cross-sections show the

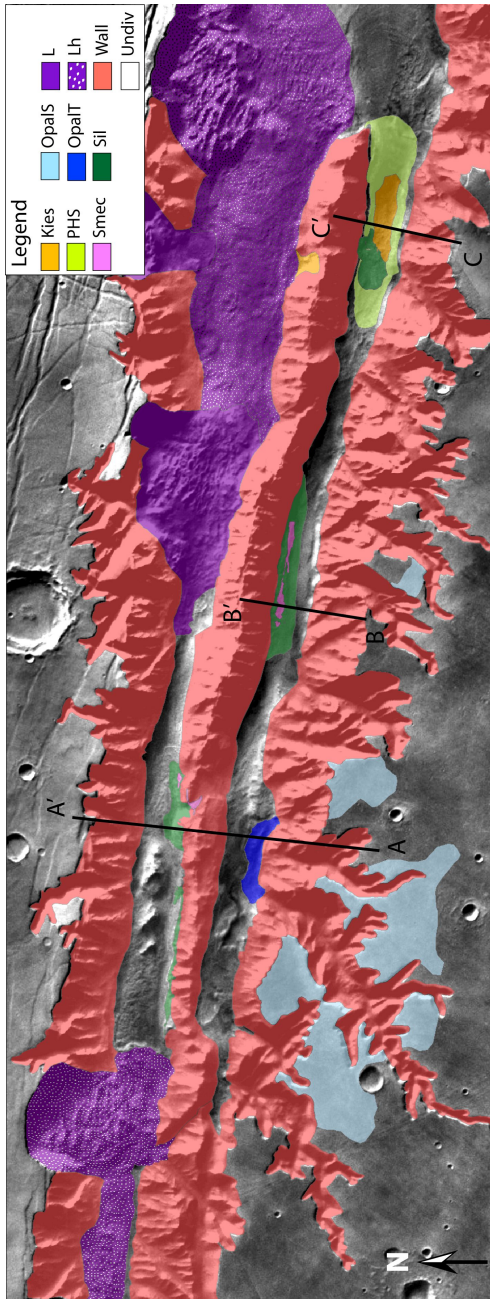


Figure 3.5: Regional geologic map of Ius Chasma. Unit descriptions in Table 3.3.2, from spectral analysis of targeted CRISM observations and morphologic contact mapping of CTX and HiRISE data. Kies: kieserite, PHS: polyhydrated sulfate, Smec: Fe/Mg smectite, OpalS: sedimentary opal, OpalT: transported opal, Sil: massive hydrated silicate, L: landslide, Lh: landslide with hydrated mineralogy, Wall: wallrock, Undiv: undivided floor units. Locations of three cross-sections (Figures 3.6 and 3.7) are labeled.

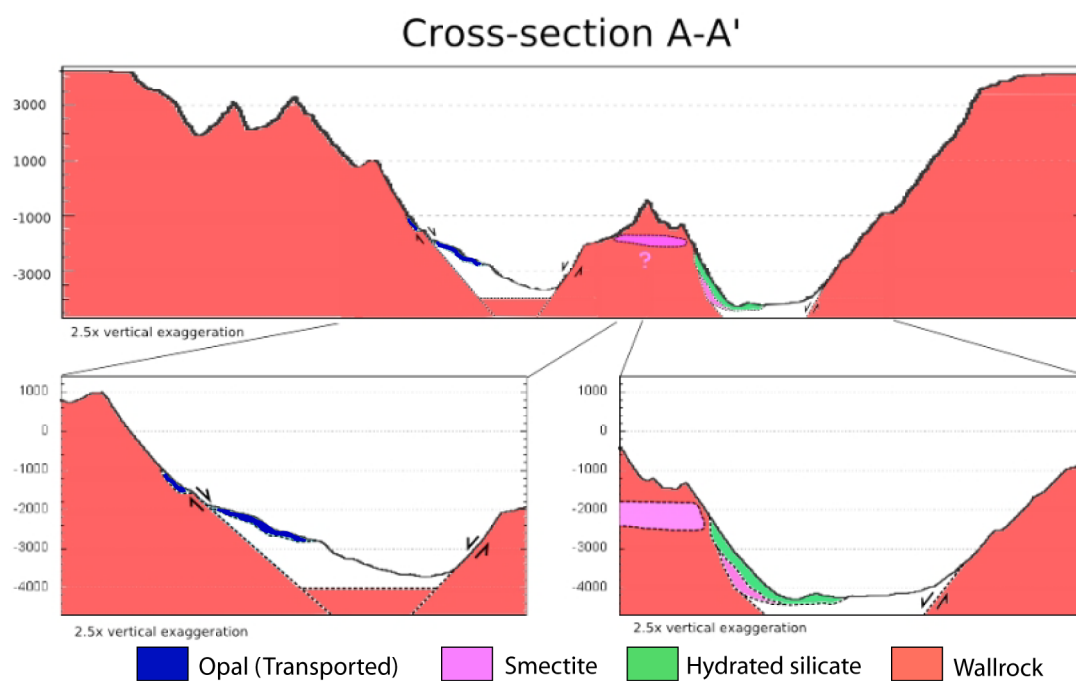


Figure 3.6: Cross-section A-A' covering opal at base of sapping channels and hydrated silicate unit overlaying layered smectite clay unit on chasma floor.\* indicates location of Figure 3.3b. Colors of geologic units same as Figure 3.5.

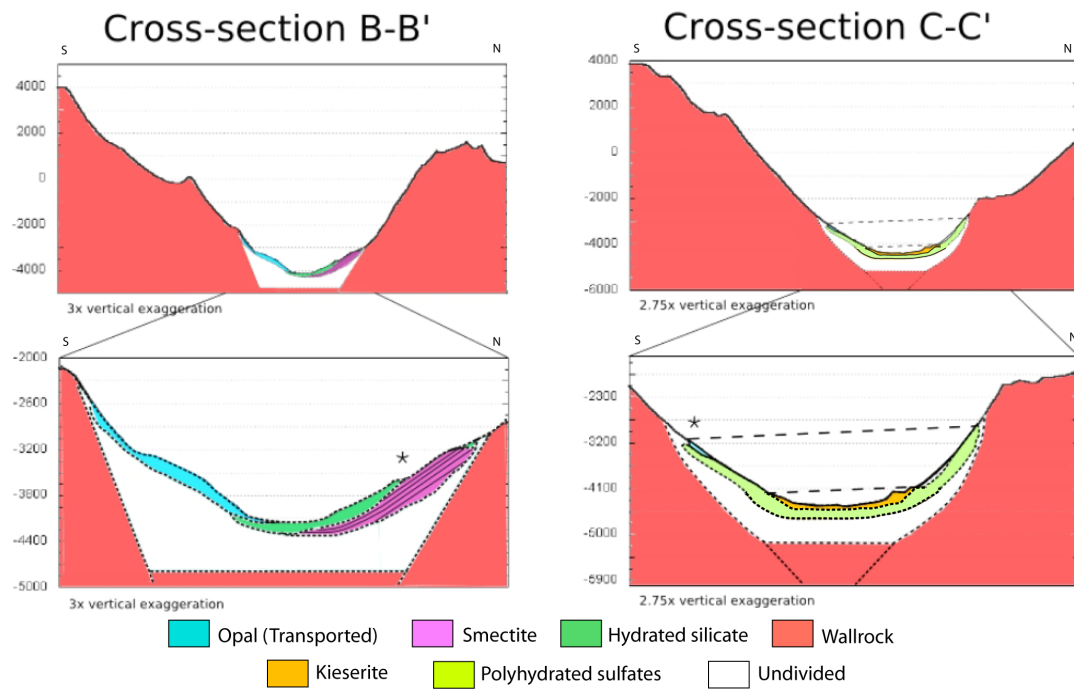


Figure 3.7: A. Cross-section B-B' covering stratigraphic contacts of hydrated silica, hydrated silicate, and Fe/Mg smectite clay units. \* indicates location of Figure 3.9. B. Cross-section C-C' detailing stratigraphy of closed evaporite basin with kieserite and polyhydrated sulfate, overlain by thin opal layer derived from the sapping channels. \* indicates location of Figure 3.11. Colors of geologic units same as Figure 3.5.

relationships between the different geologic units.

Cross-section A-A' (Fig 3.6) shows the relationship of the hydrated silica, Fe/Mg smectite, and hydrated silicate with the wall rock and plains material. In the southern sub-basin, the opal-bearing material at the base of the sapping channels has been transported from the light-toned opal-bearing deposits on the surrounding plateau. The opal-bearing deposits have an overlapping, lobate morphology consistent with viscous flow. The floor deposits are cut by normal faulting, interpreted to be continued faulting of a graben underlying the floor of the southern Ius Chasma sub-basin. On the plateau, a thin layer of opal is found in the headwall of one sapping channel of Louros Valles [Milliken et al. 2008a], and in transported material at its base (Fig 3.3). Trace amounts of opal are also seen at the base of another sapping channel, 240 km away, overlying a polyhydrated sulfate deposit. There are about a dozen other observations of Louros Valles headwalls showing a similar thin, light-toned layer in the top few meters of the wall rock, but small exposures and dust cover complicate retrieving clean spectra. Several show weak hydration bands, although none of them have spectra clearly identifiable as hydrated silica. We interpret the entire region cut by the Louros Valles sapping channels to be capped by a thin deposit that contains opal, of unknown amount [Milliken et al. 2008a]. The opal has been transported into southern Ius as a thin deposit that thins to less than the detection limit further away from Louros Valles.

Based on topography, the Fe/Mg smectite and overlying hydrated silicate are interpreted to be weathering out of the northern side of Geryon Montes wallrock and being deposited in fine layers downslope at the foot of the ridge. The Geryon Montes wallrock shows Fe/Mg smectite alteration in layered material near -2000 m elevation (Fig 3.8). At the base of this outcrop is a finely layered sedimentary Fe/Mg smectite deposit that drapes the lowest elevations. A massive hydrated silicate unit

unconformably overlays the sedimentary Fe/Mg smectite unit. The northern part of cross-section A-A' (Fig 3.6) is located slightly to the west of Fig 3.8 and the surface expression of Fe/Mg smectite alteration in Geryon Montes is likely obscured by mass-wasting. The “?” in Fig 3.6 beneath Geryon Montes expresses the uncertainty of the depth of smectite alteration in Noachian basement rocks. Unlike in the southern sub-basin, scars from “recent” normal faulting of the graben underlying the northern sub-basin are not visible; the hydrated deposits are not cut by late stage tectonic activity.

Cross-section B-B' (Fig 3.7) details the relative stratigraphy of the opal, layered sedimentary Fe/Mg smectite clay, and massive hydrated silicate units. Layered sedimentary Fe/Mg smectite clays comprise the lowest exposed stratigraphy in the central region of Ius Chasma. The layers dip at the same angle as the current surface,  $\sim 10^\circ$ . The fine layering favors a transport origin over in situ neoformation. The Fe/Mg smectite layers are eroded and unconformably overlain by the massive hydrated silicate unit (Fig 3.9). These units are exposed on the north side of southern Ius Chasma. They may have been emplaced as a drape or been originally flat-lying but tilted down to the south during late stage normal faulting that occurred preferentially on the southern part of the graben [Peulvast and Masson 1993a]. Thin opal deposits were transported into Ius Chasma by Louros Valles and overlay both the Fe/Mg smectite clay and hydrated silicate units.

Cross-section C-C' (Fig 3.7) shows the kieserite and polyhydrated sulfate are restricted to specific elevation ranges suggestive of a closed evaporite deposit. Sulfates are found in the lowest region within Ius Chasma, in an enclosed basin in the easternmost part of the trough (Fig 3.10). Kieserite is found at elevations less than -4175 m and corresponds to a closed basin. Polyhydrated sulfate is found at higher elevations (-3700 to -4175 m) overlying the kieserite. While the polyhydrated sulfate occurrences



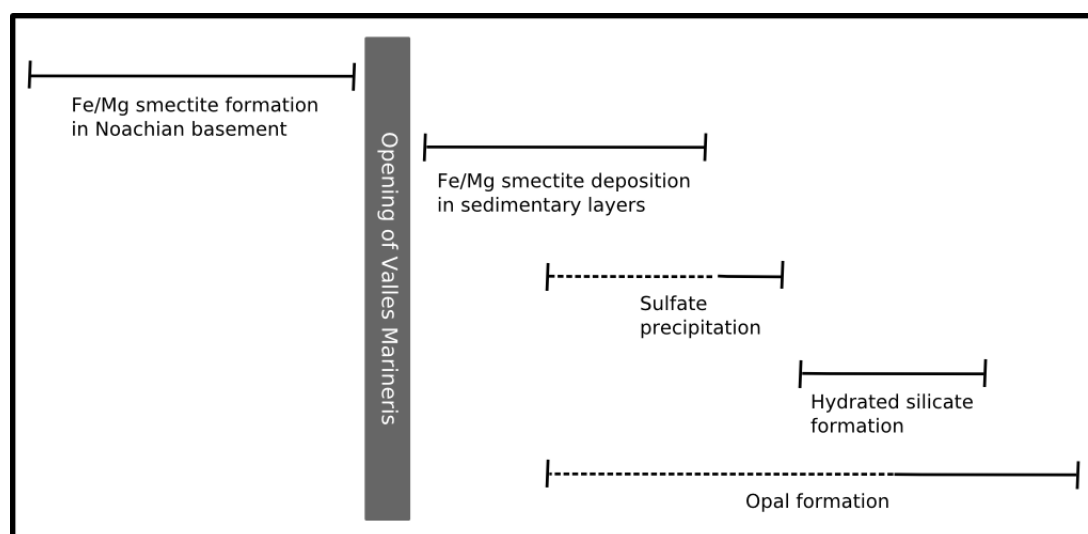


Figure 3.8: Relative timeline of hydrated mineral formation in Ius Chasma, Valles Marineris.

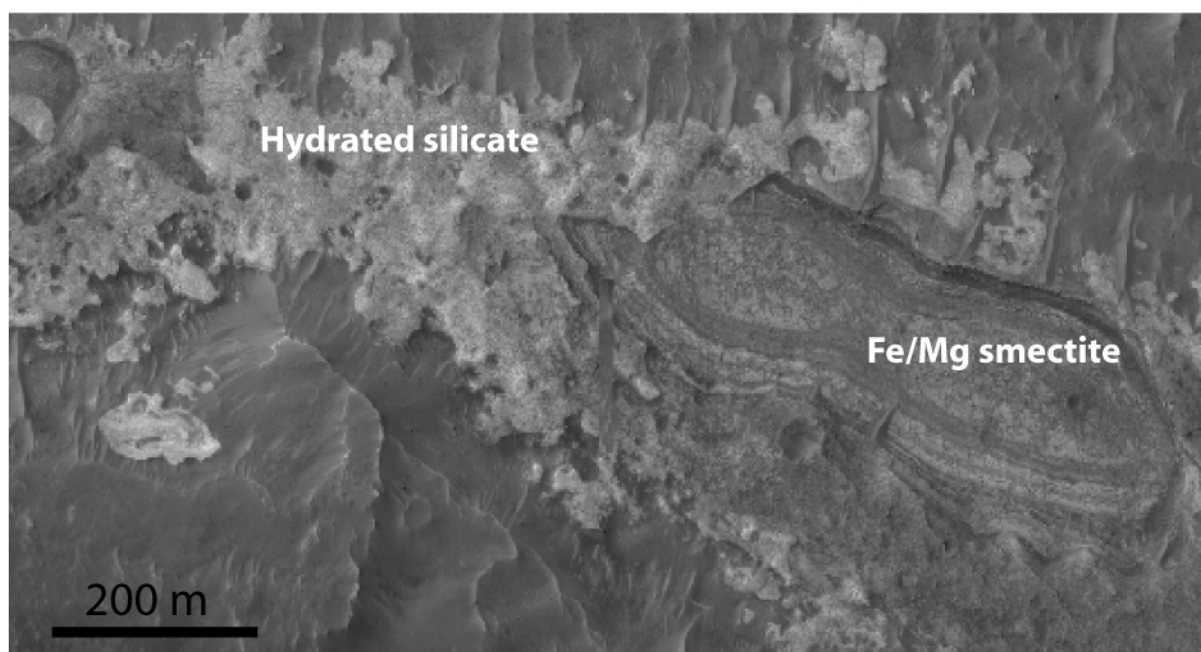


Figure 3.9: Contact between layered sedimentary Fe/Mg smectite with massive hydrated silicate showing erosional unconformity (HiRISE PSP\_006718\_1720). Pyroxene-rich dunes and spectrally neutral capping material overlie hydrated minerals.

lie at a roughly consistent elevation and surround the kieserite, CRISM coverage is not complete enough to resolve if they lie within a closed basin. Like the layered sedimentary Fe/Mg smectite unit, there is a  $\sim 10^\circ$  southerly dip to the contact between kieserite and polyhydrated sulfate. The eastern portion of the -3700 m contour which would define a closed basin for the polyhydrated sulfate is unfortunately covered by dunes and thick dust deposits, mapped as undivided floor material in this study.

Massive hydrated silicate deposits also appear over the same elevation range as the polyhydrated sulfate (not shown in Fig 3.7, but visible in Fig 3.10). However, sufficient HiRISE imagery does not exist to discern the stratigraphic relationship between massive hydrated silicate and polyhydrated sulfate within Ius Chasma. At the eastern edge of the evaporite deposit, in western Melas Chasma and thus outside the scope of this study, CRISM targeted observations show a massive deposit containing hydrated silicate overlying the polyhydrated sulfate. The chasma floor between this outcrop and the mapped sulfate evaporite deposit in Ius is covered by undivided floor materials. However, we infer the relationship between massive hydrated silicate and polyhydrated sulfate to be the same in both chasmata, and extrapolate that the hydrated silicate probably overlies the sulfate units in Ius Chasma.

There is a slight southerly dip to the planes described by the contacts between the kieserite and polyhydrated sulfate and at the uppermost elevations of polyhydrated sulfate exposure. The dip of these sulfate units may be due to late-stage preferential faulting on the southern part of graben(s) underlying the southern Ius Chasma floor, as is suggested above for the Fe/Mg smectite and hydrated silicate deposits in Cross-section B-B'. A very thin opal-bearing deposit overlies the evaporite deposit in the south (Fig 3.11). The polyhydrated sulfate and opal have cross-cutting fractures, suggesting they were in place at the time stresses acted to form the fractures. Those stresses may have been due to tectonic processes or dehydration. The opal is found

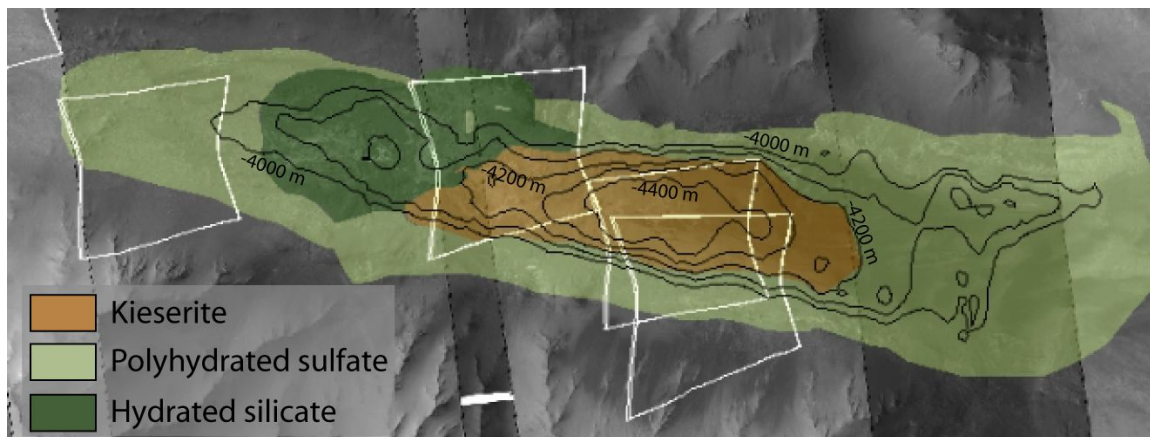


Figure 3.10: Kieserite and polyhydrated sulfate deposit showing topographic restriction of kieserite as outlined in MOLA 100 m contours. White outlines of CRISM targeted observations over CTX mosaic. Kieserite (orange) is within a closed basin and polyhydrated sulfate (light green) occurs over a limited elevation range, but insufficient imagery to determine if it is within a closed contour. Hydrated silicate (dark green) overlies both.

on the plateau eroded by Louros Valles and in lobate deposits at the base of Louros Valles (Fig 3.11). Thus, we theorize that the opal was transported from the plateau by Louros Valles, either as a precipitate or suspended particle.

Massive hydrated silicate and Fe/Mg smectite also appear in the breccia and cementing material of many, but not all landslides (Fig 3.12 shows landslide material with hydrated mineralogy). The bluish tones in Fig 3.12 are associated with hydrated mineral-rich breccia blocks and matrix, while the redder tones are associated with material that both underlies and overlies the bluish toned rocks interpreted to be unhydrated material from the same landslide. HiRISE imagery (Fig 3.12b, c) shows that breccia blocks with hydrated materials are extensively folded and fractured. Hydrated materials are not seen in any of the landslide scars or in any wall rock. Two plausible explanations are that the hydrated minerals come from lower layers in the wallrock now completely covered by later landslides, or that dust cover obscures the composition of the wall rock. Landslides may contain both hydrated, Noachian-

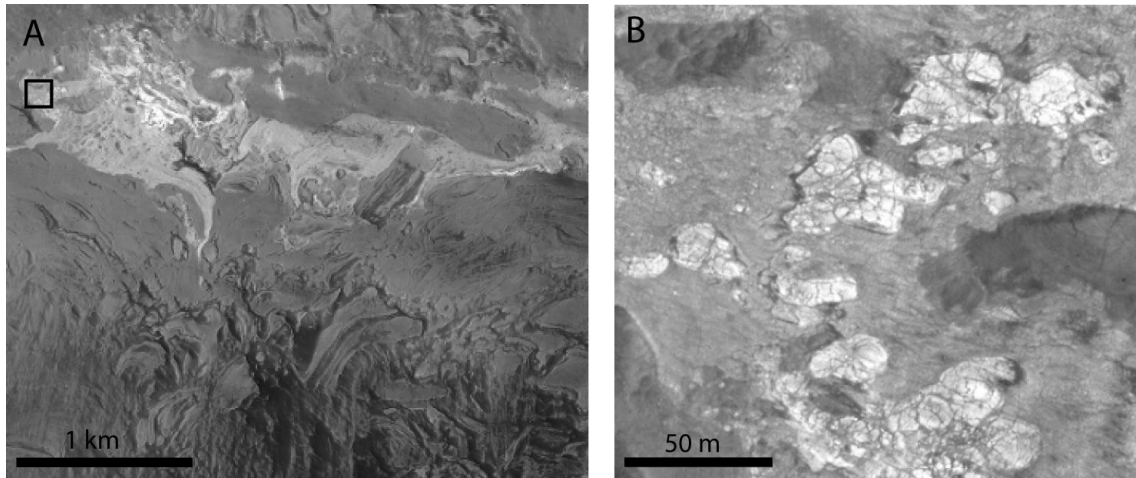


Figure 3.11: HiRISE image PSP\_005940\_1710. A. Lobate morphology of opal (intermediate toned) and non-hydrated dark material at base of Louros Chasma. Box indicates location of B. B. Polyhydrated sulfate (brighter) and opal (intermediate) units have cross-cutting fractures, suggesting desiccation at the same time. Opal overlies polyhydrated sulfate in a thin layer. Overlain by loose, non-hydrated dark material thin enough to only partially fill fractures.

aged material and non-hydrated, Hesperian-aged material.

### 3.5 Discussion

Fitting these hydrated mineral deposits into the previously proposed stratigraphy of Ius Chasma gives new insight into the intersection of its aqueous and structural history. Previous morphologic and structural mapping efforts [Tanaka 1986; Lucchitta and Bertolini 1989; Lucchitta et al. 1992; Peulvast and Masson 1993a,b; Peulvast et al. 2001], combined with the mineralogic results presented in this paper, reveal the following updated geologic history:

1. Formation of the early Noachian basement
2. Alteration of basement to Fe/Mg smectite

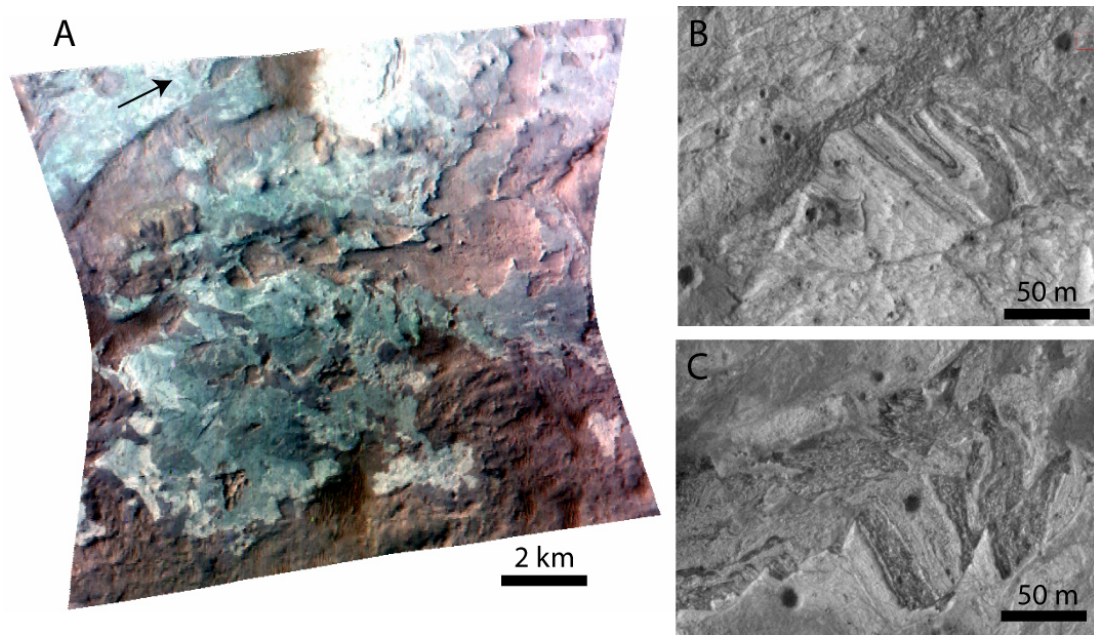


Figure 3.12: A. CRISM FRT0000A396 false color (RGB: 2.5, 1.5, 1.08  $\mu\text{m}$ ) of hydrated silicate material (bluish tones) and non-hydrated material (reddish tones) in landslide on Ius Chasma floor, both in breccia blocks and cementing material. Arrow points to location of B. and C., subsets of HiRISE PSP\_006652\_1725. Both show folds, fractures, and megabreccia blocks.

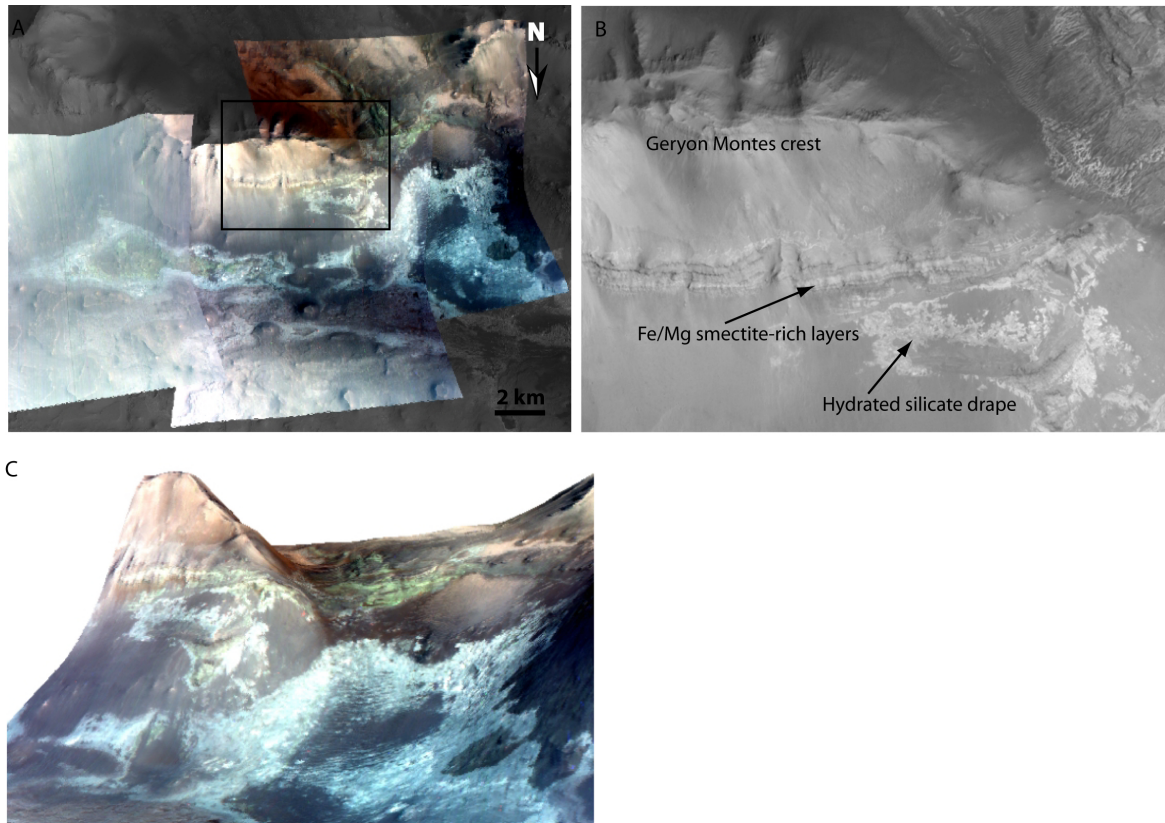


Figure 3.13: Fe/Mg smectite-rich layers in Geryon Montes wallrock. A. CRISM false color (RGB: 2.5, 1.5, 1.08  $\mu\text{m}$ ) over CTX mosaic. Fe/Mg smectite-rich materials in the wallrock and redeposited on the chasma floor appear greenish and hydrated silicate-rich materials draping the deposits are bluish. Black box in location of panel B. North is down. B. CTX P16\_007430\_1727 showing continuity of layering in Fe/Mg smectite-rich bedrock, traceable around Geryon Montes. North is down and sun illumination from the bottom. C. CRISM FRT00009B27 false color draped over MOLA topography.

3. Late-Noachian to Hesperian lava flows over basement/regolith create several km of layered basalts
4. Valles Marineris forms by repeated tectonic extension in late Hesperian, forming horst and grabens in Ius Chasma. Erosion creates spur-and-gully morphology on wallrock. Both Hesperian and Noachian materials may be exposed in wallrock.
5. Continuous mass wasting transports altered wallrock rich in Fe/Mg smectite into Ius Chasma as sedimentary fines and breccia blocks. Fines accumulate into layered deposits on chasma floor
6. The layered sedimentary Fe/Mg smectite is eroded by fluvial or aeolian processes
7. Surface water geochemistry changes to more acidic conditions, and sulfate precipitates from evaporating brines at the lowest elevations
8. Hydrated silicate is deposited as massive layer on top of layered sedimentary Fe/Mg smectite and sulfate deposits and as matrix material cementing (altered) megabreccia
9. The uppermost layer of basaltic wall rock is altered to opal-bearing material
10. Fluvial processes along Louros Valles bring opal into Ius Chasma as sedimentary particles or precipitates. Louros Valles may predate opal transport. Louros Valles morphology controlled by fractures related to Valles Marineris or to older Noachian stresses
11. “Recent” tectonism cuts Louros Valles and possibly widens connection between Ius and Melas Chasmata. Differential slip along southern walls tilts the chasma floor



12. Landslides without hydrated material partially cover landslides containing hydrated silicate

From this geologic history, we interpret the aqueous geochemistry to be first neutral to alkaline, resulting in alteration of crustal material to Fe/Mg smectite; then neutral to very acidic, resulting in sulfate precipitation and possibly alteration of smectite to a leached phyllosilicate or jarosite/smectite mixture; and then very acidic, resulting in extensive precipitation of opal on the plateau (Fig 3.8). This opal co-occurs with a dehydrated jarosite elsewhere on the plateau surrounding Valles Marineris, indicating low pH conditions [Milliken et al. 2008a; Weitz et al. 2008b]. Jarosite forms most commonly under low temperature, low pH ( $<4$ ) conditions [Stoffregen et al. 2000]. While jarosite has not been found with the opal on the plateau south of Ius Chasma, we interpret the presence of sedimentary opal as indicative of acidic geochemistry demonstrated by the opal and jarosite mineralogy elsewhere on the plateau [Milliken et al. 2008a; Weitz et al. 2008b; Bishop et al. 2009]. This interpreted trend in aqueous geochemistry is consistent with other OMEGA and CRISM studies suggesting widespread change in the character of aqueous mineral assemblages in late Noachian to Hesperian time, from ones consistent with a neutral or alkaline environment to ones indicating a relatively acidic and saline environment [Bibring et al. 2006; Murchie et al. 2009a]. Details of the timing of that environmental change, from phyllosilicate formation in Noachian terrains to sulfate formation in Hesperian terrains, may be captured in Ius Chasma.

### 3.5.1 Formation and transportation of Fe/Mg smectite

The Geryon Montes wallrock is altered to Fe/Mg smectite near -2000 m elevation (Fig. 3.13); that elevation may be early Hesperian lavas or Noachian basement,



although faulting may have displaced Geryon Montes upwards from its original elevation. Geryon Montes is a central horst bracketed to the north and south by graben, and stratigraphically deeper (Noachian) section may have been elevated by tectonism and exposed in the ridge. Other outcrops of Noachian-aged wallrock in Capri and Coprates Chasmata also expose Fe/Mg smectite-rich layers [Murchie et al. 2009a]. Fe/Mg smectite or other hydrated alteration products are not found in the bulk of the Hesperian-aged lava flows; the upper, Hesperian-aged wallrock and many landslides sourced from there do not exhibit a signature of hydrated or hydroxylated phases. The opal deposits on the uppermost surface of the Hesperian lava flows probably correspond to acidic surface alteration rather than to older crustal alteration that formed the smectite clays.

The tectonism, mass-wasting, and fluvial erosion associated with the opening of Ius Chasma is expected to have mobilized Fe/Mg smectite-rich fines and redeposited them in sedimentary materials on the trough floor. Layered, sedimentary Fe/Mg smectite is visible in the western and both the northern and southern sub-basins of central Ius, but are not exposed in eastern Ius. The stratigraphic relationship between the sulfates and smectite units is unclear: the layered smectite deposits may be covered by later sulfate evaporites or they may postdate the sulfates. The layered sedimentary smectites are also themselves eroded by subsequent fluvial or aeolian processes.

### **3.5.2 Evidence for sulfate evaporites in a paleobasin**

Kieserite and polyhydrated sulfate are both found within a closed topographic basin in eastern Ius Chasma (Fig 3.10). The polyhydrated sulfate is found at higher elevations, and kieserite at lower elevations, and the deposits together span  $\sim 700$  m in elevation. This sulfate deposit in a local depression is unlike any other sulfate

deposit in Valles Marineris. Elsewhere in Valles Marineris, sulfate is found in mound-shaped, friable, layered deposits that can reach several km in thickness (e.g. [Gendrin et al. 2005]). There are several hypotheses for how distinct monohydrated and polyhydrated sulfates formed in those areas: by sequential deposition in an evaporating basin, through dehydration of a polyhydrated Mg sulfate to kieserite by heating after burial, or through dehydration of an existing polyhydrated sulfate deposit by upwelling, hydrophillic chloride-rich brines within a tectonically active fault basin (as in [Hardie 1991]). We will briefly discuss each one and point out questions that remain.

The elevation distribution of the sulfate phases is consistent with concentration of an evaporating brine that first precipitated polyhydrated phases and then precipitated monohydrated sulfates at the near-terminal stage of evaporation ([Spencer 2000]. The sulfate deposits are thin enough that they would conform to the preexisting basin topography rather than completely fill the basin. Thus, the kieserite is stratigraphically higher than the polyhydrated sulfate even though it is exposed at lower elevations (Fig. 3.7). Ius Chasma may have been somewhat isolated from Melas Chasma at that time, which would make it easier for water to pond and evaporate. However, there are several uncertain aspects of the evaporite model. First, if the kieserite is from terminal evaporation of a brine and kieserite is exposed over 200 m, that implies a relatively large volume of water for an end stage evaporite mineral. Second, the polyhydrated sulfate unit beneath the kieserite unit is not exposed in erosional windows, so the continuity of the polyhydrated sulfate unit is uncertain.

The second hypothesis is that the kieserite is a diagenetic phase formed from polyhydrated Mg sulfate. The bulk of the sulfate detected in Valles Marineris is within light-toned, layered deposits that range in size from 10s–100s kilometers wide and 100s meters to 4 kilometers thick [Gendrin et al. 2005; Bishop et al. 2009; Murchie et al. 2009b; Roach et al. 2009a]. Kieserite units are typically found beneath polyhydrated

sulfate-rich units, especially in large deposits several kilometers in thickness, and may be diagenetic products formed by dehydration of polyhydrated Mg sulfates, like epsomite ( $\text{MgSO}_4 \bullet 7\text{H}_2\text{O}$ ) [Roach et al. 2009a]. This diagenesis requires burial to a few km to reach high enough temperatures for sulfate conversion [Roach et al. 2009a]. The deposit in Ius Chasma is too thin to convert to kieserite via diagenesis, barring a very localized, unusually high geothermal gradient beneath the basin.

The third hypothesis also involves conversion of a sulfate sequence to Mg-rich sulfates, like kieserite, and includes aspects of both previous hypotheses. The sulfate is originally precipitated as an evaporite in an extensional fault basin.  $\text{CaCl}_2$  brines produced hydrothermally during periods of tectonic or magmatic activity upwell and percolate through the sulfates [Hardie 1991]. The brines are very hydrophilic and readily convert more polyhydrated sulfates to kieserite. Perhaps the upwelling brines only permeated the lower 400 m of exposed sulfates, such that the overlying polyhydrated sulfates remained unaltered. This hypothesis is a controversial hypothesis to explain massive Mg sulfate-rich evaporite deposits on Earth, and the implications for its application to a Martian evaporite sequence (i.e. [Tosca and McLennan 2006]) are not yet worked out.

We consider the evaporite basin with successive draped layers of sulfates as the parent brine concentrated to be the most feasible interpretation, but the relative importance of low temperature diagenesis and later Cl-rich brine recirculation is unknown.

### 3.5.3 Relationships between smectites, sulfates, and hydrated silicate

Fe/Mg smectite clays and sulfate are not found together in any CRISM image of Valles Marineris. The location of the expected contact between the two units in central Ius Chasma has not yet been imaged with CRISM, but CTX images suggest that the contact would be obscured by mafic mineral-rich dunes and other mobile material. However, the relative timing of the sulfate deposition and the unconformity between Fe/Mg smectite and massive hydrated silicate can be partially constrained. The Fe/Mg smectite clays were deposited, then eroded, then capped by hydrated silicate. The sulfate evaporite sequence is capped by the same massive hydrated silicate unit, so the sulfates must have formed before the clay minerals were covered by the hydrated silicate.

The contact between the finely layered sedimentary Fe/Mg smectite and the massive hydrated silicate marks a change in regional aqueous geochemistry to more acidic conditions. Neutral to acidic surface water or groundwater would have partially leached Fe/Mg smectite fines, which were then deposited over the length of Ius Chasma, in a few meter-thick layer and as matrix material within landslides. Alternatively, very acidic surface water could have partially dissolved smectite materials and precipitated a few meter-thick layer of jarosite-cemented smectite particles. A third option is that the hydrated silicate is a multiple smectite mixture (containing Al, Mg, and Fe cations) perhaps formed by further alteration of the Noachian-aged Fe/Mg smectite. Landslides with hydrated minerals have Fe/Mg smectite and hydrated silicate in both matrix material and the megabreccia blocks. The Fe/Mg smectite-bearing megabreccia from Noachian wallrock was likely deposited on the trough floor by landslide. More recent landslides sourced from dominantly Hesperian

wallrock do not show hydrated mineralogy, consistent with the model of decreasing water availability with time [Jakosky and Phillips 2001].

Several relationships between the hydrated silicate material and other minerals can help constrain the relative stratigraphy. First, the hydrated silicate material is found in three types of locations within Ius Chasma: in landslides from the wall rock, unconformably overlying layered Fe/Mg smectite clays, and overlying sulfates. It is found in both the breccia and cementing material of many, but not all landslides. Second, smectite clays are found in several places within the chasma in deposits that appear finely layered at HiRISE resolution, and they are unconformably overlain by the hydrated silicate material (Fig 3.9). The hydrated silicate material does not show layering and has an apparent thickness of a few meters. Third, in the sulfate deposit at the eastern end of Ius Chasma, the hydrated silicate is found at a higher elevation than kieserite and possibly at the same elevation as polyhydrated sulfate. Further east in Melas Chasma, the eastern edge of the polyhydrated sulfate unit in the evaporite deposit is overlain by hydrated silicate. HiRISE imagery shows the hydrated silicate has a lobate, hummocky morphology, which previous studies have suggested is caused by landslide movement [Weitz et al. 2003; Pelkey et al. 2003].

The stratigraphic relations between hydrated mineralogies can also help us resolve the relative timing of aqueous alteration and the last tectonic activity. The opal deposits are found at the base of Louros Valles sapping channels, but not in northern Ius Chasma which has less prevalent sapping morphology. If the opal-bearing material was transported onto the chasma floor as particles or dissolved precipitates by the groundwater sapping that formed Louros Valles, then the opal would be most concentrated close to the source. The thin opal-bearing deposit superposes a polyhydrated sulfate unit. Thus the latest sapping event(s) are posited to postdate the evaporation of the closed sulfate-rich basin. Nearby, opal-rich material at the bottom of a sapping

channel is cut by a basal scarp formed by late tectonic activity. Since opal is the last of the hydrated alteration materials to be emplaced in Ius Chasma, this suggests that deposition of alteration phases occurred before the most “recent” tectonism, such as the southerly slip of the southern Ius Chasma graben(s). The “recent” tectonism, as described by Peulvast and Masson (1993a, 1993b), cannot be precisely dated, but it postdates deposition of all hydrated phases and much of the mass wasting activity in Ius Chasma.

### 3.6 Conclusion

The superposition of different hydrated phases and the different morphologies of units containing them suggest a series of several distinct aqueous events in Ius Chasma. In the central region, Fe/Mg smectite clays are found in finely layered deposits, which favors a transportation and deposition model rather than in situ alteration. Subsequent erosion of the Fe/Mg smectite and their unconformable superposition by massive hydrated silicate points to multiple fluvial events sculpting the floor of Ius Chasma. If the hydrated silicate material is an acid-leached phyllosilicate, then its presence indicates a change from alkaline to more neutral or acidic groundwater. In this scenario, acidic surface or ground water partially altered the Fe/Mg smectite clay to a less crystalline, leached smectite, which was deposited in a thin layer along Ius Chasma. If the hydrated silicate material is instead a jarosite/smectite mixture, it indicates an aqueous environment with  $\text{pH} < 3$  where partial smectite dissolution is followed by precipitation of jarosite as a cement for Al-rich smectite. Fe/Mg smectite-bearing breccia blocks in landslide deposits on the floor of Ius were also partially altered to hydrated silicate. If the hydrated silicate in the landslide deposits was a mixture of smectite clays, then either the Fe/Mg smectite further altered to a new smectite mix-

ture, or the Noachian-aged material contains multiple domains of smectite alteration. Deposition of opal by sapping channels was a late stage event which overlaid the sulfate sequence to the east. Similar aqueous activity was reported in western Candor Chasma, where fluvial erosion and redeposition of sulfates following formation of sulfate-bearing deposits [Murchie et al. 2009b]. Perhaps fluvial activity persisted for a significant time after sulfate deposition and after erosion of the sulfate host material in both Ius and Candor Chasma. Tectonic activity continued after the last hydrated minerals were formed.

The hydrated silicate found throughout Valles Marineris could indicate either a complex smectite mineral assemblage or acidic alteration of crustal phyllosilicate. Regardless of the exact mineralogy of the hydrated silicate, this material is a marker for “intermediate” conditions in between the neutral-to-alkaline smectite units and the acidic opal-jarosite plateau deposits. Fe/Mg smectites have been found in Noachian-aged crust throughout Mars [Mustard et al. 2008], but the hydrated silicate is restricted to Valles Marineris. If Mars did undergo a global transition from alkaline to acidic conditions, then similar “intermediate” mineralogies should be expected where phyllosilicate-bearing Noachian crust was in contact with acidic groundwater to an extended period of time. Global hydrologic modelling has shown Valles Marineris, its outflow channels, and Meridiani Planum to be locations of sustained upwelling that would have supported the deposition of large volumes of acidic minerals [Andrews-Hanna et al. 2007b; Murchie et al. 2009b]. However, several large highland craters outside these locations (Columbus, “Alunite,” Gale, and Schiaparelli craters) also host significant sulfates [Wray et al. 2008b; Swayze et al. 2008; Milliken et al. 2009; Wiseman et al. 2009]. The transition from alkaline to more acidic groundwater was temporal and may be widespread in location.

Ius Chasma is a superb location for future landed missions as it has extensive

expression of a diversity of hydrated alteration minerals, shows a variety of geologic processes—volcanic, tectonic, and fluvial, and contains excellent exposures of Hesperian and Noachian-aged materials. It is an ideal location to study the transition in global aqueous geochemistry in the mineralogy, morphology, and geologic relationships of a collection of diverse hydrated minerals.



## Chapter 4

# Diagenetic hematite and sulfate assemblages in Valles Marineris

**Abstract:** Previous orbital mapping of crystalline gray hematite, ferric oxides, and sulfates has shown an association of this mineralogy with light-toned, layered deposits on the floor of Valles Marineris, in chaos terrains in the canyon's outflow channels, and in Meridiani Planum. The exact nature of the relationship between ferric oxides and sulfates within Valles Marineris is uncertain. The Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activite (OMEGA) spectrometer identified kieserite and a polyhydrated sulfate type in the light-toned, layered deposits in Valles Marineris and a ferric oxide phase in or at the base of these deposits. The Thermal Emission Spectrometer (TES) has also mapped gray hematite in or at the base of these deposits. We use orbital data from the Mars Reconnaissance Orbiter (MRO) to explore the mineralogy and morphology of the large layered deposit in central Capri Chasma, part of the Valles Marineris canyon system which has large, clear exposures of sulfate and hematite. We find kieserite ( $\text{MgSO}_4 \bullet \text{H}_2\text{O}$ ) and ferric oxide (often crystalline red hematite) in the lower bedrock exposures and a polyhydrated sulfate type without ferric oxides in the upper bedrock. This stratigraphy is duplicated in many of the other basinal chasmata, suggesting a common genesis. We propose the hematite and monohydrated sulfate formed by diagenetic alteration of a sulfate-rich

sedimentary deposit, where the upper polyhydrated sulfate-rich, hematite-poor layers either were not buried sufficiently to convert to a monohydrated sulfate or were part of a later depositional phase. Based on the similarities between the Valles Marineris assemblages and the sulfate and hematite-rich deposits of Meridiani Planum, we hypothesize a common evaporite and diagenetic formation process for the Meridiani Planum sediments and the sulfate-bearing basinal interior layered deposits.

## 4.1 Introduction

The discovery of crystalline gray hematite [Christensen et al. 2000] and sulfates [Gendrin et al. 2005] in the equatorial regions from orbital data was a revolution in our understanding of Martian geologic history (e.g. [Christensen et al. 2001; Bibring et al. 2006]). These important alteration minerals provide direct evidence of liquid water on the surface and are clues to the evolution of the Martian surface. The first detection was crystalline gray hematite by the TES instrument [Christensen et al. 2000; Christensen et al. 2001]. Follow up in situ investigation by the Mars Exploration Rover (MER) Opportunity discovered significant jarosite and other sulfates with the gray hematite and shed more light on the aqueous origins of the assemblage [Squyres and Knoll 2005; McLennan et al. 2005]. Hematite and sulfate has also been mapped from orbit in specific locations throughout Valles Marineris and the chaos regions between Valles Marineris and Meridiani Planum [Christensen et al. 2001; Gendrin et al. 2005; Glotch and Christensen 2005; Weitz et al. 2008a; Lichtenberg et al. 2009], suggesting that aqueous alteration is widespread.

TES identified crystalline gray hematite by the presence of fundamental Fe-O stretching vibrations at 33.3, 22.2, and  $<19\text{ }\mu\text{m}$  [Christensen et al. 2000]. A lack of Si-O stretching vibrations ruled out the presence of significant silicate minerals. The material has grain diameters  $>10\text{ }\mu\text{m}$  and a surface abundance in Meridiani Planum

of 25-60% [Christensen et al. 2000]. Christensen et al. (2000) suggested multiple formation mechanisms, four out of five which required significant aqueous activity. These processes include: (1) precipitation from oxygenated, Fe-rich bodies of water (like terrestrial banded iron formations), (2) precipitation in hydrothermal systems, (3) low temperature groundwater leaching and deposition (like terrestrial pedogenic processes), and (4) surface weathering and coating formation [Christensen et al. 2000].

MER Opportunity landed in Meridiani Planum and confirmed the gray hematite detection and an implied aqueous formation process [Squyres and Knoll 2005; McLennan et al. 2005]. The leading hypotheses for the formation of the hematite and sulfate-rich stratigraphy in Meridiani Planum are (1) aeolian deposition with cementation by a fluctuating groundwater table [Squyres and Knoll 2005; Andrews-Hanna et al. 2007b] and (2) pyrite-rich pyroclastic ash flows and air fall [Hynek et al. 2002; McCollom and Hynek 2005]. Both models are consistent with the regional geology [Hynek and Phillips 2008], and more importantly for this study, require aqueous alteration to form the hematite and sulfates. Under the first hypothesis, iron oxides would have formed by dissolution of Fe sulfates like jarosite by surface or groundwater with changing geochemistry [Bingham and Nordstrom 2000; Clark et al. 2005; McLennan et al. 2005; Barron et al. 2006]. The second hypothesis invokes hydrothermal precipitation of hematite in fumaroles [McCollom and Hynek 2005].

TES has also detected crystalline gray hematite within Valles Marineris [Christensen et al. 2001] and in several of the chaos terrains [Glotch and Christensen 2005; Glotch and Rogers 2007].

Ferric minerals have been previously identified in basinal chasmata throughout Valles Marineris with OMEGA data, but could not be definitively resolved as ferric oxide plus sulfate or ferric sulfate [Bibring et al. 2007]. The OMEGA team used multiple spectral parameters to characterize the ferric absorption in the visible-near in-

frared (VNIR), since spectral matching to library spectra proved inconclusive [Poulet et al. 2007, 2008b]. These parameters are indicative of mineralogy but require further spectral analysis to confirm. The 0.55  $\mu\text{m}$  band depth measured the strength of the ferric absorption edge near 0.55  $\mu\text{m}$ . The ratio of reflectance at 0.97  $\mu\text{m}$  to the reflectance at 0.80  $\mu\text{m}$  characterizes the width and depth of the  $\sim 0.90$   $\mu\text{m}$  ferric absorption. The ratio of reflectance at 1.35  $\mu\text{m}$  to the reflectance at 1.0  $\mu\text{m}$  can indicate the degree of crystallinity in a monomineralic, anhydrous ferric oxide [Morris et al. 1989]. More details on the causes of ferric oxide absorptions captured in these parameters is found in section 4.3.2. These parameters were coupled with Modified Gaussian Models, linear mixing, and nonlinear mixing models to interpret the ferric minerals in Valles Marineris and Meridiani Planum as ferric oxides [Bibring et al. 2007; Le Deit et al. 2008; Poulet et al. 2008a].

Hydrated sulfates, including monohydrated Mg sulfate and a polyhydrated sulfate of unknown cation composition, were detected in light toned deposits throughout Valles Marineris [Gendrin et al. 2005]. The light toned, layered deposits are characterized as Interior Layered Deposits (ILDs) [Lucchitta et al. 1992]. A general correlation of ferric oxide with sulfates was noted [Gendrin et al. 2005; Hutchison et al. 2005; Bibring et al. 2007; Le Deit et al. 2008; Poulet et al. 2008b; Mangold et al. 2008b], but detailed stratigraphic mapping needed higher resolution spectral data. Ferric oxides were often found downslope or at lower elevations than hydrated sulfates, but sometimes the extent of hydrated sulfates and ferric oxides overlapped on the slope of the outcrop. In those cases, it was unclear if the spectral signature represented a hydrated ferric sulfate (or sulfate assemblage including kieserite and a ferric sulfate) or kieserite plus an ferric oxide. Where the ferric signature was separated from sulfate signatures, as at the base of ILDs, it was interpreted as a ferric oxide (e.g. [Mangold et al. 2008b]).

The TES albedo of the interpreted ferric oxides at the base of ILDs is 0.12 and 0.17 on the bright ILDs. ILD surfaces without ferric signatures can have an albedo up to 0.20 [Mangold et al. 2008b]. The darkening effect of the ferric oxides on both the ILD and the chasma floor around ILDs indicates the ferric oxide is fairly large grained. The albedo of the ferric oxide was too low to be a thin veneer of dust with ferric components, since dust often has an albedo above 0.25 [Putzig et al. 2005]. While the ferric phase in Valles Marineris is not the globally homogeneous dust, care must be taken to spectrally distinguish the two.

There have been numerous telescopic, orbital, and landed spectral studies of the globally homogeneous dust on Mars (e.g. [McCord et al. 1977; Pinet and Chevrel 1990; Mustard and Bell 1994; Bell et al. 2000; Morris et al. 2000; Bandfield and Smith 2003; Yen et al. 2005]). It is spectrally dominated by a nanophase ferric oxide component and has minor contributions from crystalline ferric oxide and ferrous phases [Morris et al. 2006; Yen et al. 2005]. This dust is present both as a ubiquitous coating on the surface and as an aerosol particulate in the atmosphere [McCord et al. 1977; Wolff et al. 1997]. Understanding the spectral signature of Martian dust is crucial to being able to resolve other ferric oxide phases, like crystalline hematite, on the surface.

There is a need to make a strong connection between thermal infrared and VNIR detections of ferric oxide to explain what phases are present, how they were created, and their geologic context. The definitive VNIR identification of the ferric oxide and its spatial and geologic relationship to the gray hematite and sulfate deposits are outstanding questions. Is the ferric phase a surface coating or an alteration product? Another question is if there are genetic relationships between the Valles Marineris deposits and the hematite and sulfate-rich sedimentary sequences in Meridiani Planum. The sulfate and ferric oxide deposits cover 1000s km<sup>2</sup> on the floors of Valles Marineris and associated chaos regions. We would like to test the applicability of the Meridiani

Planum model to the ILDs in Valles Marineris. If we can apply the detailed geologic and chemical evidence from the Opportunity rover in Meridiani Planum toward an understanding of these deposits, that is a large step forward in our knowledge of the Valles Marineris geologic history.

We use data from Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), a VNIR spectrometer aboard MRO, to better resolve the variety of ferric mineralogy present in Valles Marineris. Geologic and mineralogic mapping of all of the ILDs reveal a regionally consistent, repeatable stratigraphy: monohydrated sulfate and ferric oxide (often red hematite) are found in the lower bedrock layers while polyhydrated sulfate without ferric oxides are found in the upper bedrock layers. A detailed spectral and stratigraphic study in Capri Chasma is presented as a type locality, as Capri Chasma has strong spectral signatures and abundant exposed bedrock. The geologic implications for this stratigraphy are discussed, which have parallels to the Meridiani Planum model.

## 4.2 Background

### 4.2.1 Datasets

The CRISM instrument on the MRO spacecraft is a VNIR hyperspectral imaging spectrometer capable of acquiring observations in both targeted and mapping mode. Targeted observations are taken in 544 wavelengths from 0.392–3.92  $\mu\text{m}$  at  $\sim 20$  m/pixel [Murchie et al. 2007a]. The wavelength range is acquired with two independent spectrometers. The “S” detector covers 0.392–1.02  $\mu\text{m}$  in the VNIR while the “L” detector covers 1.02–3.92  $\mu\text{m}$  in the infrared (IR) [Murchie et al. 2007a]. Observations at 72 wavelengths and 100–200 m/pixel are acquired in the multispectral survey mode [Murchie et al. 2007a]. The multispectral wavelengths are chosen as a

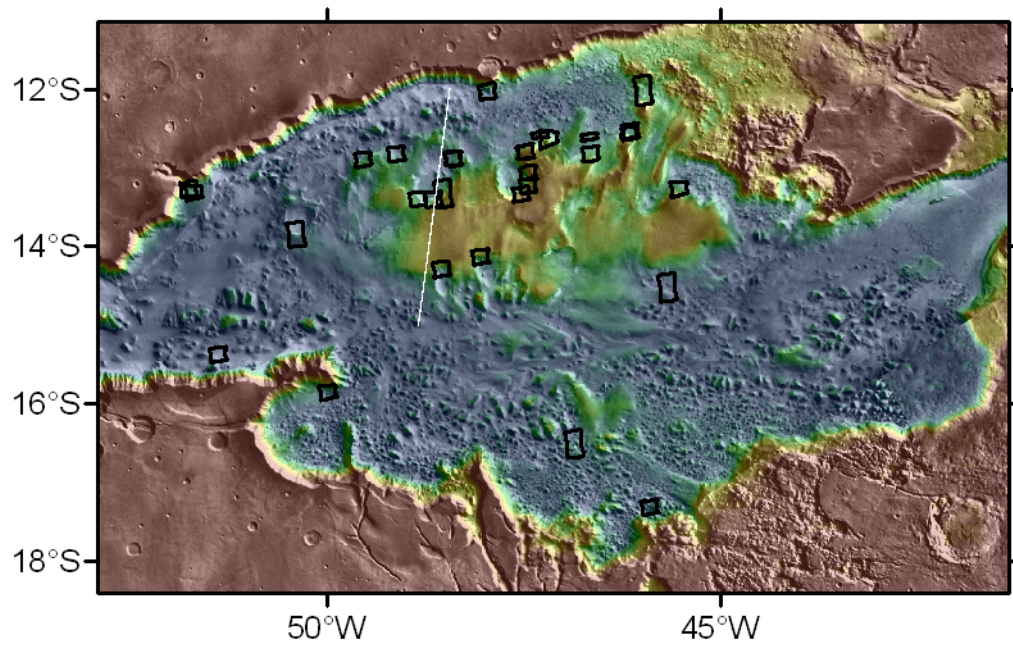


Figure 4.1: Central mound and surrounding knobs in Capri Chasma, in eastern Valles Marineris. CRISM observations analyzed for this study in black. MOLA colored elevation over MDIM.

subset of the targeted observation wavelengths to cover important absorption bands. VNIR spectroscopy is ideal to detecting minerals that have electronic transition absorptions from iron and vibrational overtones and combination tones from anions such as  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$  [Burns 1993; Clark et al. 1990].

Two high resolution cameras are coaligned with CRISM on MRO and can take coordinated observations with the spectrometer. The High Resolution Imaging Science Experiment (HiRISE) camera acquires imagery at 25 cm/pixel in strips  $\sim 5$  km across (McEwen et al. 2005). HiRISE data is useful when examining fine layering or detailed stratigraphic relationships. The Context imager (CTX) captures images at  $\sim 6$  m/pixel and  $\sim 30$  km across [Malin et al. 2007]. Multiple CTX scenes can be mosaicked together to create high resolution base maps useful for correlating unit morphologies across long distances.

The OMEGA hyperspectral spectrometer covers a similar wavelength range as CRISM (352 spectral channels between 0.35–5.1  $\mu\text{m}$ ) with broader spatial coverage. The spatial sampling that varies from 300 m (at pericenter) to 4.8 km (at 4000 km altitude) [Bibring et al. 2004; Bibring et al. 2005]. OMEGA data will be used for spectral analysis in regions without targeted or mapping CRISM data. OMEGA data are calibrated to reflectance using the standard steps (as described in [Bibring et al. 2005; Mustard et al. 2005]).

### 4.2.2 Study locale

Capri Chasma, in eastern Valles Marineris, consists of a large layered sedimentary mound in the center of the canyon surrounded by knobs and other collapse features (Fig 4.1). The mound is one of many similar features in Valles Marineris that have been classified as ILDs [Lucchitta et al. 1992]. The 300 km across, up to 4 km tall mound in Capri Chasma shows a bright-toned, massive unit at the lower elevations



capped by a dustier, more finely textured unit above. The massive lower unit shows erosional fluting on exposed faces, while much of the upper unit has been eroded away. A  $\sim 15$  km wide mound to the northeast may be an aeolian redeposition of the upper unit, as it differs in morphology and has a lower thermal inertia [Putzig and Mellon 2007] than surfaces with a similar mineralogy. The ILD has been suggested to form by aeolian [Lucchitta et al. 1992; Peterson 1981; Nedell et al. 1987], lacustrine [McCauley 1978; Lucchitta 1982; Nedell et al. 1987], sub-ice volcanic [Chapman and Tanaka 2001; Komatsu and Litasov 2002; Komatsu et al. 2004], or volcanic processes [Lucchitta 1981; Witbeck 1991; Lucchitta et al. 1992; Weitz 1999].

This ILD is representative of other ILDs located in the centers of the broad, basinal chasmata. Capri Chasma was chosen for detailed mapping of ferric oxides and sulfates because TES, OMEGA, and CRISM data show strong spectral signatures indicative of good bedrock exposure over a large area. More regional (coarser scale) mapping of ferric oxide and sulfate distribution was performed throughout Valles Marineris.

## 4.3 Methods

### 4.3.1 CRISM data reduction

CRISM data are converted from instrumental data to atmospherically corrected surface reflectance through a series of steps as in Mustard et al. (2008). First, the data is converted to radiance by subtracting the instrumental dark current and dividing by the internal instrumental calibration standard [Murchie et al. 2007a]. This standard was calibrated in pre-flight ground testing. Dividing the radiance data by the solar spectrum at the top of Mars' atmosphere yields an estimate of I/F.

The I/F data contains contributions from both the Martian surface and atmosphere. We model the contribution from atmospheric gases via an atmospheric trans-

mission spectrum and remove it from the IR portion of the I/F spectrum. An atmospheric transmission spectrum is derived from a single CRISM observation over the flank and top of Olympus Mons as in [Mustard et al. 2008]. The ratio in reflectance at the top and the base is assumed due to the shorter pathlength to the summit and thus the reduced effect of atmospheric absorptions. An averaged spectrum from multiple lines at the summit of the volcano is divided by an average spectrum from multiple lines near the base to create an atmospheric transmission spectrum. A transmission spectrum is calculated for each detector column, since each column has slightly different wavelength positions [Murchie et al. 2007a]. This atmospheric transmission spectrum is scaled to the amount of atmospheric absorptions in the CRISM spectrum to be atmospherically corrected by matching the strengths of the  $2.011\text{ }\mu\text{m}$   $\text{CO}_2$  absorption. Dividing the CRISM IR spectrum by the scaled transmission spectrum approximately removes the atmospheric spectral absorptions due to gas bands, but does not account for aerosol effects. There are no prominent atmospheric gas bands in the visible region, so the CRISM visible spectrum is not divided by the scaled transmission spectrum. The potential presence of aerosols in the atmospherically corrected CRISM data is most important when analyzing CRISM VNIR data, since aerosols have their greatest contribution to spectra at the shortest wavelengths. Caution must be employed in visible wavelength spectral interpretation, as aerosols dampen surface reflectance features and may add their own dust-like absorptions.

After removing an approximation of the gas absorptions from the IR data, both the VNIR and IR CRISM data are divided by the cosine of the incidence angle to convert to Lambert albedo. This step accounts for variations in viewing geometry and illumination between observations.

### 4.3.2 VNIR spectroscopy of sulfates and ferric oxides

Analyses of atmospherically corrected I/F spectra and ratios of those spectra over the whole VNIR wavelength range are necessary to determine the specific mineralogy present in a CRISM observation. Spectra are often averaged over 10s or 100s of pixels to improve the signal to noise. A spectrum of interest is also often divided by a spectrum of a spectrally neutral (i.e. dusty) region to accentuate mineral absorption bands and to remove instrumental artifacts and residual calibration effects. The spectrally neutral denominator spectrum should come from the same column(s) as the spectrum of interest to account for column-dependent variations in the detector's wavelength array [Murchie et al. 2007a]. A spectrally neutral denominator is best, as mineral absorptions in the denominator show up as inverse features in ratioed spectra and can complicate mineral identification. In practice, the denominator is from dusty terrain, which can convolve dust-related spectral features in the resulting ratio spectra.

The atmospherically corrected I/F and ratioed spectra are then compared to a spectral library resampled to CRISM wavelengths. The VNIR and IR spectra are analyzed independently. This is because the two detectors' radiances do not align at the 1  $\mu\text{m}$  join, possibly because of uncorrected effects of the beamsplitter temperature [Murchie et al. 2009c]. Thus, it is not possible to calculate a reasonable continuum across the full wavelength region. More details on the continuum removal process are given after the discussion of relevant spectral features.

The two spectral classes discussed in this paper are hydrated sulfates and ferric oxides. Hydrated sulfates have an absorption near 2.4  $\mu\text{m}$  due to  $\text{H}_2\text{O}$  and OH combinations and sulfate bending overtones (Fig 4.2) [Cloutis et al. 2006]. Kieserite,  $\text{MgSO}_4 \bullet \text{H}_2\text{O}$ , and szomolnokite,  $\text{FeSO}_4 \bullet \text{H}_2\text{O}$ , are structurally similar and thus have similar combination  $\text{H}_2\text{O}$  stretch and rotation vibrations at  $\sim 2.1 \mu\text{m}$ . They can

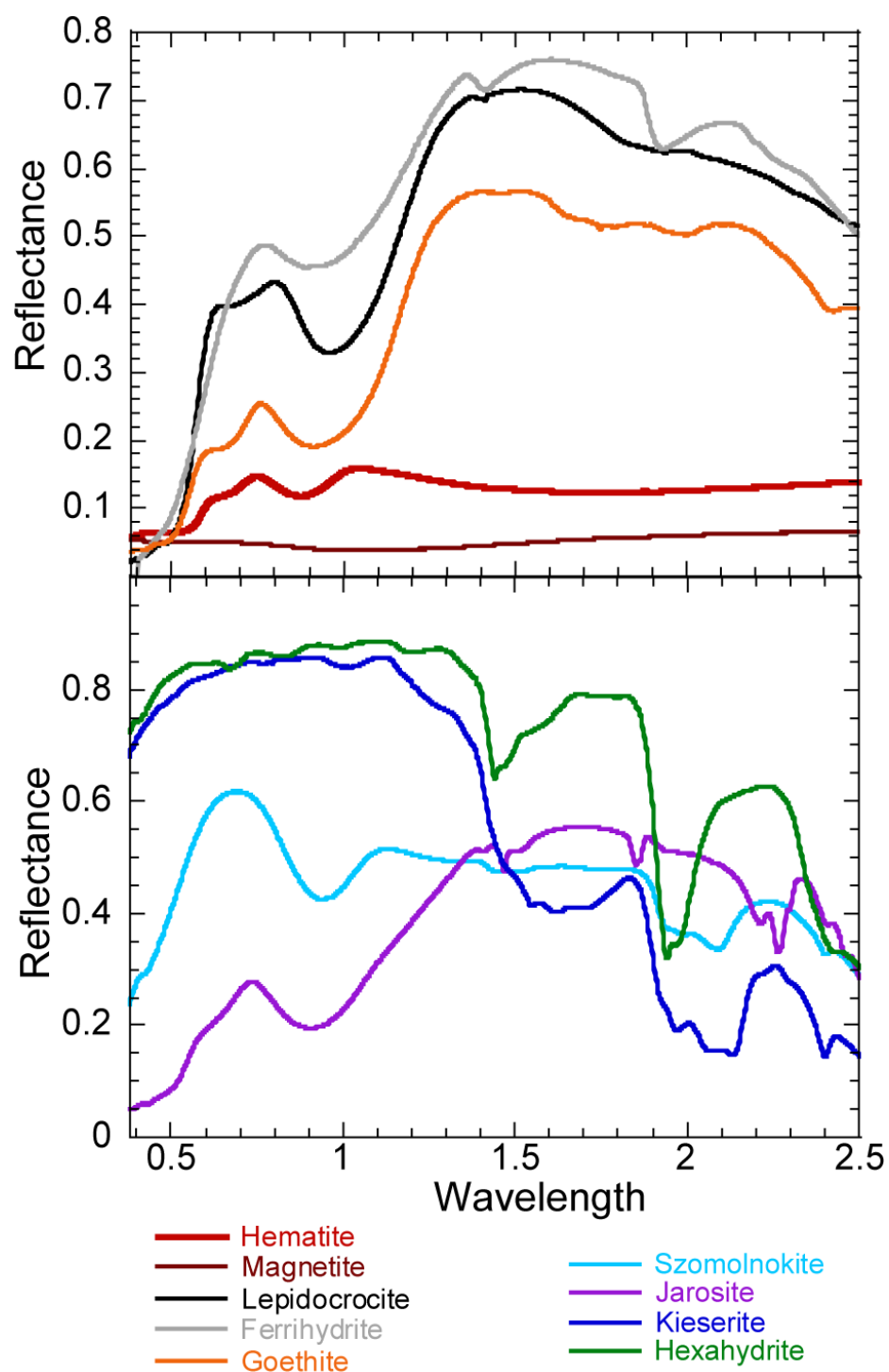


Figure 4.2: RELAB library spectra 0.38–2.5  $\mu\text{m}$ . Ferric oxides on top and  $\text{Fe}^{3+}$  and Mg sulfates on bottom.

be distinguished from each other in natural samples since the first absorption moves from 2.13 in kieserite to 2.10  $\mu\text{m}$  in szomolnokite. Szomolnokite has an additional broad absorption near 0.9  $\mu\text{m}$  due to  $\text{Fe}^{2+}$  crystal field transitions [Cloutis et al. 2006]. Polyhydrated sulfates, such as epsomite and bloedite, have strong  $\text{H}_2\text{O}$  vibrations at 1.45 and 1.95  $\mu\text{m}$  as well as a drop off in reflectance near 2.45  $\mu\text{m}$  attributed to SO or OH/ $\text{H}_2\text{O}$  combinations and/or overtones [Cloutis et al. 2006].

Ferric oxides have a variety of very distinctive absorption features due to the iron in their structures. Ferric oxides such as hematite, goethite, magnetite, lepidocrocite, and ferrihydrite have strong iron crystal field transitions in the 0.9  $\mu\text{m}$  region (Fig 4.2) [Morris et al. 1985, 1997]. Two Fe sulfates, szomolnokite and jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), are also included for comparison. Iron oxides owe their red color to saturated UV charge transfer absorptions that cause very low reflectivity shortward of 0.55  $\mu\text{m}$  [Morris et al. 1985]. Iron oxides show a variety of  $\sim 0.5$   $\mu\text{m}$  absorptions, which are caused by ferric ion charge transfers or crystal field splitting [Hunt et al. 1971a; Hunt and Salisbury 1970; Morris et al. 1985]. Fig 4.3 shows RELAB library spectra of ferric oxides and sulfates after continuum removal. Crystalline red hematite (thick red line in Fig 4.3a) is distinguishable from all other ferric oxides and sulfates since it has a 0.53  $\mu\text{m}$  minimum at distinctly longer wavelengths than other minerals. The presence of two minima (0.53 and 0.88  $\mu\text{m}$ ), a 0.62  $\mu\text{m}$  shoulder, and 0.74  $\mu\text{m}$  relative peak also provide many features in the visible wavelengths to fit to and thus the possibility of a confident spectral match.

Identification of iron oxide or sulfate species is attempted after continuum removal. The continuum is removed from CRISM visible spectra over the 0.41–0.97  $\mu\text{m}$  region to better resolve ferric absorptions in the presence of Martian dust. Globally homogeneous dust on Mars also has a nanophase ferric oxide component in addition to minor crystalline ferric oxide and ferrous phases [McCord et al. 1977; Pinet and

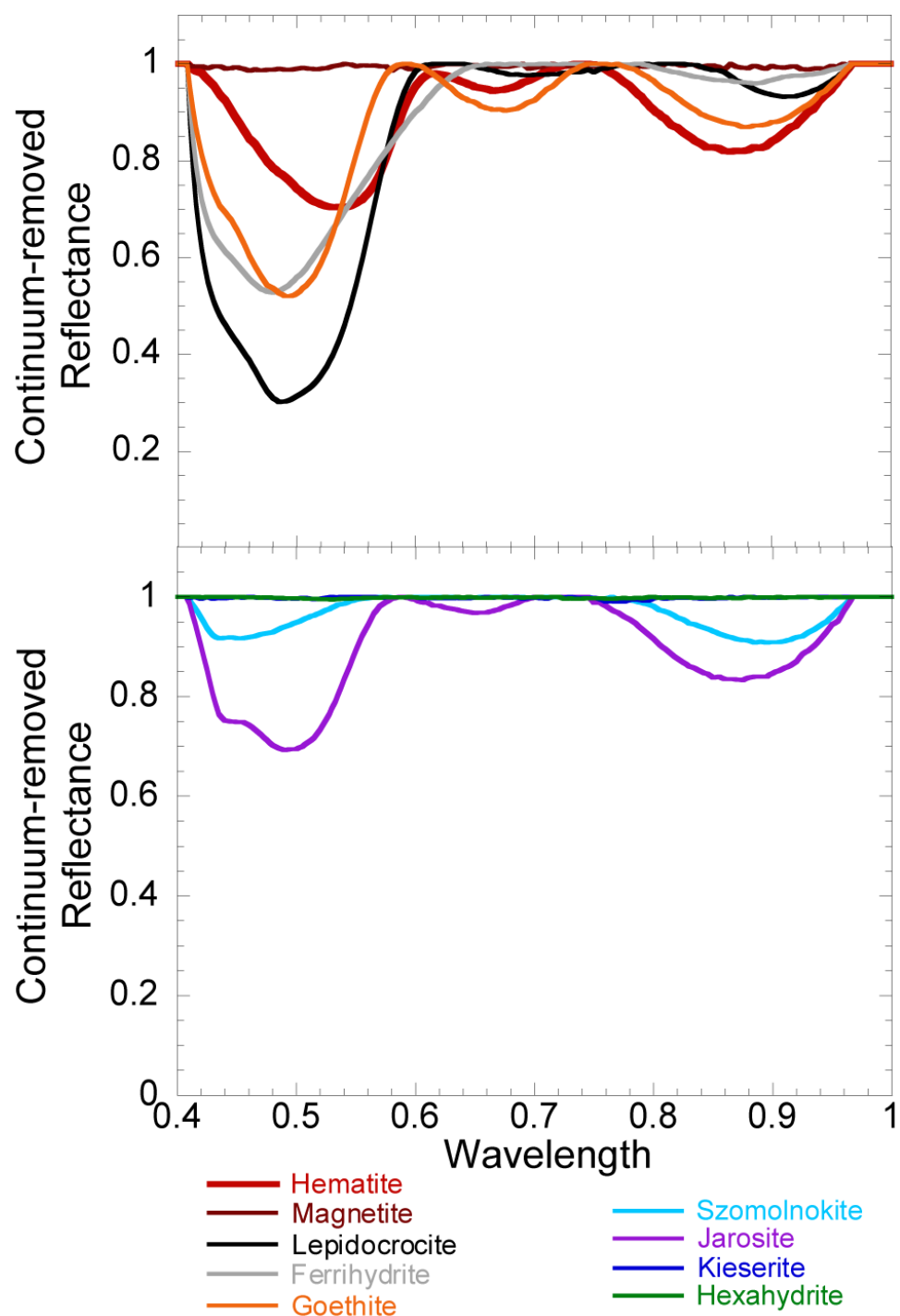


Figure 4.3: Continuum-removed RELAB library spectra 0.41–0.97  $\mu\text{m}$ . Ferric oxides on top and  $\text{Fe}^{3+}$  and Mg sulfates on bottom.

Chevrel 1990; Bell et al. 2000; Bandfield and Smith 2003; Yen et al. 2005]. Martian dust is characterized by a broad, shallow ferric absorption centered near  $0.9\ \mu$ , a local maximum near  $0.75\ \mu$ m, and an absorption edge shortward of  $\sim 0.5\ \mu$ m [Bell et al. 2000; Morris et al. 2000; Yen et al. 2005]. Since dusty regions in CRISM images are used in spectral ratioing to reduce instrumental noise, the absorptions due to iron in the dust need to be distinguished from crystalline ferric phases in the spectrum of interest.

The continuum removal computation fits a convex hull over the spectrum using straight segments connecting local spectral maxima [ITT Visual Information Solutions 2007]. The first and last value in the wavelength region undergoing continuum removal is set to 1.0. Two different continua are computed over the VNIR and IR spectral ranges. We determine ferric oxide mineralogy in CRISM ratioed and continuum-removed ratioed spectra over  $0.41\text{--}0.97\ \mu$ m. We categorize hydrated sulfates based on absorption in CRISM ratioed and continuum-removed ratioed spectra over  $1.01\text{--}2.5\ \mu$ m. The CRISM short wavelength channels between  $0.644$  and  $0.684\ \mu$ m, less than  $0.41\ \mu$ m, and greater than  $0.97\ \mu$ m are routinely excluded from analysis. The wavelengths  $<0.41\ \mu$ m are degraded due to artifacts from the scattered light correction, and the region between  $0.644\text{--}0.684\ \mu$ m has a detector artifact [Murchie et al. 2009c]. However, the remaining channels can fully capture the hematite and other ferric oxide absorption features. In the IR spectra, the continuum is fit over  $1\text{--}2.5\ \mu$ m because that is the wavelength region of interest for hydrated mineralogy.

## 4.4 Spectral Results

### 4.4.1 Minerals identified in Capri Chasma

Kieserite is identified in Capri Chasma based upon characteristic H<sub>2</sub>O vibrational absorption features at 2.13 and 2.4  $\mu\text{m}$  (dark gray line in Fig 4.4a). See Table 4.7 for a description of where the CRISM type spectra are located. The CRISM spectrum lacks the broad 1.6  $\mu\text{m}$  in the library kieselite spectrum (dark blue in Fig 4.4a). However, the broad 1.6  $\mu\text{m}$  absorption is not visible in all terrestrial kieselite samples or in all Martian spectra. The continuum-removed CRISM spectrum is more consistent with kieselite (2.13  $\mu\text{m}$  minimum) than szomolnokite (2.09  $\mu\text{m}$ ) (Fig 4.4b). The VNIR region of the CRISM kieselite type spectrum is the red spectrum in Fig 4.5. The VNIR absorptions are consistent with hematite, not szomolnokite. Thus the best monohydrated sulfate match is kieselite not szomolnokite. Polyhydrated sulfates (PHS), such as hexahydrite and bloedite, are identified by absorptions near 1.4 and 1.9  $\mu\text{m}$  due to H<sub>2</sub>O (Fig 4.4). The PHS are probably iron-poor, since they lack iron electronic transitions near 0.9  $\mu\text{m}$ .

A variety of ferric absorptions occur in materials associated with the sulfate-bearing ILDs. We class them as “red hematite,” “probable hematite,” “ferric phases,” and “dust” based on their features in CRISM continuum removed spectra (Fig 4.5b). Fig 4.5a shows ratioed CRISM type spectra of “red hematite,” “probable hematite,” and “ferric phases.” Well-crystalline red hematite can be resolved from other ferric oxides and from ferric sulfates by absorptions at 0.53 and 0.88  $\mu\text{m}$ , and a peak at 0.76  $\mu\text{m}$  with a shoulder near 0.62  $\mu\text{m}$  (Morris 1985). Continuum removed ratioed CRISM spectra that only have three of the four hematite features in the right position or all four features but at slightly shifted wavelengths (within 0.02  $\mu\text{m}$ ) are classified as “probable hematite.” Spectra with visible wavelength absorptions different from



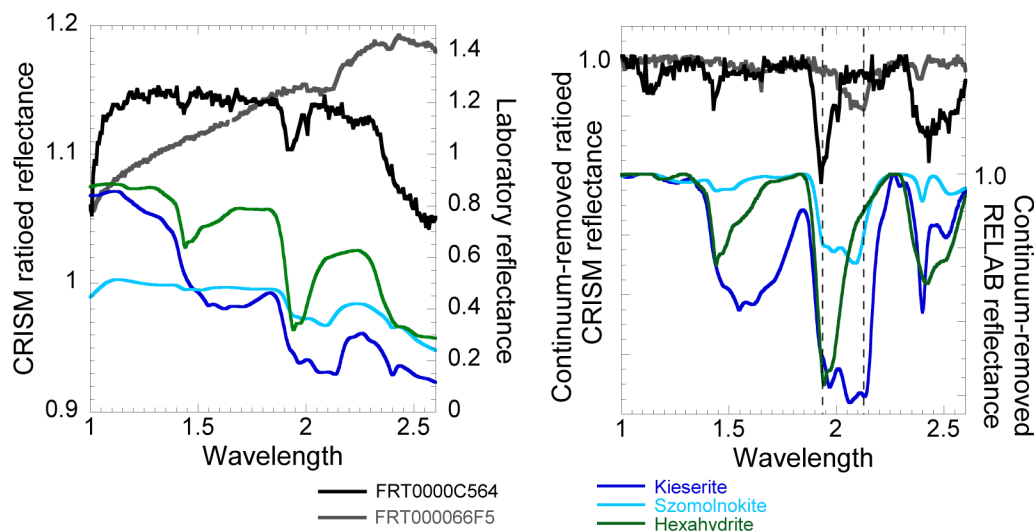


Figure 4.4: CRISM ratioed (left) and continuum-removed ratioed (right) spectra of typical kiserite/hematite location (gray) and of hematite-poor PHS (black) location in Capri Chasma. The kiserite/hematite spectrum has IR absorptions that match the RELAB library natural kiserite spectrum (dark blue) while VNIR absorptions are characteristic of hematite (red spectrum in Fig 4.3.) rather than szomolnokite (light blue in Fig 4.3). PHS is an approximate fit to RELAB library hexahydrite (green).

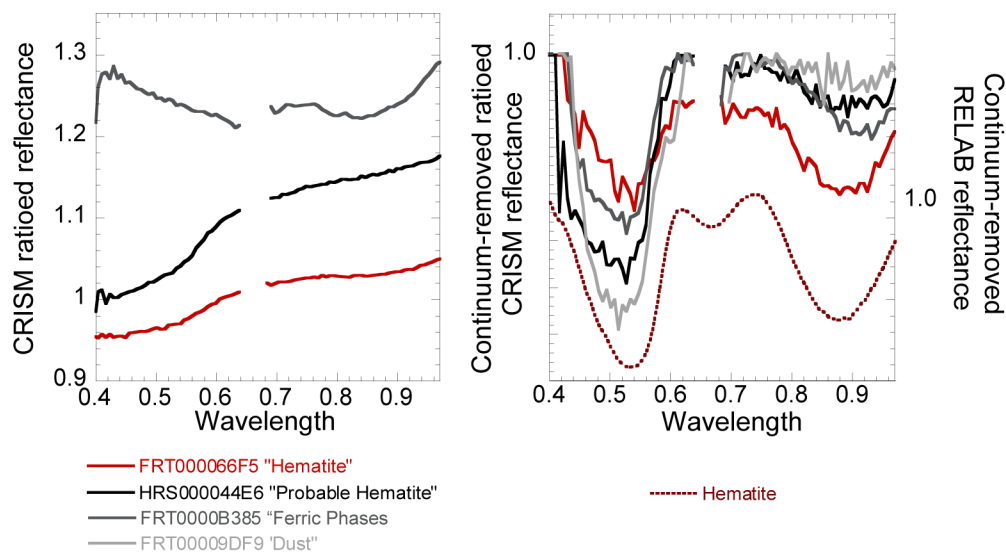


Figure 4.5: A. Ratioed CRISM spectra of typical “red hematite,” “probable hematite,” and “ferric phases” over 0.4–1.1  $\mu\text{m}$ . Denominator for ratioing in all is similar to “dust” spectral type. B. Continuum removed ratioed CRISM spectra of “red hematite,” “probable hematite,” “ferric phases,” and “dust” spectral types.

the nanophase ferric oxide in the dust are classified as “ferric phases.” The “dust” spectral class in Fig 4.5b is an unratiod continuum-removed spectrum. “Dust” is not shown as a ratioed spectrum, since similar spectra are used as denominators for the other spectral types. Overall its spectral features match those reported from previous studies (e.g. [Bell et al. 2000; Morris et al. 2000; Yen et al. 2005]).

Ferrous minerals like olivine and pyroxene can be excluded based on the position and width of the 1.0 and 2.0  $\mu\text{m}$  absorptions. Although these mafic minerals are a dominant phase in the chasma walls and in volcanic plains across Mars, they are not present in measurable amounts in ILDs.

The ability to classify a spectrum as “red hematite” or as “probable hematite” is predicated on the image’s data quality. A CRISM observation with high quality spectra and a large spectrally neutral (dusty) region in the same columns as the spectra of interest is much more likely to resolve all four hematite spectral features than one that has high aerosol loading, small exposures of the spectra of interest, and/or no suitable spectrally neutral region for ratioing. Similarly, further imaging of a location classified as containing “ferric phases” may reveal the spectra are actually consistent with “red hematite” or “probable hematite.” Thus, this study is a conservative estimation of the locations of hematite deposits in CRISM data.

It is common for observations with “red hematite” or “probable hematite” to also have other ferric phases present in the scene. The “red hematite” may be in the bedrock or collecting in channels on the bedrock, while the “ferric phases” are more commonly found in loose deposits at the base of the ILD. The spectra classified as “ferric phases” may contain other ferric oxides, ferric sulfates, or a mixture of ferric phases.

Previous studies with OMEGA data [Le Deit et al. 2008; Bibring et al. 2007] identified ferric phases in the same locations we find red hematite with CRISM data,

but they were not able to resolve all the hematite spectral features. One of the challenges of interpreting sulfate and ferric oxide stratigraphy from OMEGA data is that the spectral identifications are on too coarse a scale to tie to specific geologic units identified in high resolution imagery (such as Mars Orbiter Camera (MOC) or High Resolution Stereo Camera (HRSC) data). The 400 m to 4 km-sized footprint of the OMEGA instrument could cover an entire, mineralogically complex outcrop with a handful of pixels. Sulfate absorptions at 1.9 or 2.1  $\mu\text{m}$  and at 2.4  $\mu\text{m}$  (for poly- and monohydrated sulfate, respectively) often partially spatially overlap ferric absorptions in OMEGA data. With the lack of well crystalline red hematite features, the ferric absorption could be interpreted as due to ferric sulfates, such as copiapite or schwertmannite or a variety of ferric oxides. TES identified gray hematite in many of the same locations that showed ferric absorptions in OMEGA data [Christensen et al. 2000; Weitz et al. 2008b]. So although the VNIR spectra were ambiguous, red hematite was a reasonable interpretation.

CRISM's higher spatial resolution allows for the collection of spectra from distinct units within an outcrop and thus spectra have less spatial mixing. The higher spatial resolution also allows selection of just the strongest spectral signatures within unit, for more robust spectral identification.

The above criteria for sulfate and ferric oxide spectral identifications were also applied to CRISM spectra across Valles Marineris (including Tithonium, Ius, Melas, Candor, Ophir, Coprates, Ganges, Juventae and Hebes Chasmata). Appendix B lists 134 CRISM observations in Valles Marineris that show sulfate or ferric oxide features; a total of 299 CRISM observations were examined as part of this study. Duplicate observations were occasionally included if they were acquired under periods of more favorable aerosol loading and thus had more clear spectral features. There are 24 observations in Capri/Eos Chasma that show sulfate or ferric oxide mineralogy.

#### 4.4.2 Ferric oxide variability throughout Valles Marineris

Many Interior Layered Deposits (ILDs) in Valles Marineris show absorptions due to iron electronic transitions. Those in Capri Chasma show clear spectral features for crystalline red hematite, but many other ILDs show more ambiguous ferric oxide spectra in addition to crystalline red hematite. A complete list of CRISM targeted observations showing ferric oxide are given in Appendix B.

Appendix B includes the location within Valles Marineris, the type of sulfate and ferric phase detected, and the geologic setting of the ferric phase within the CRISM observation. The “sulfate” category is classified as -1: long wavelength imagery not acquired, 0: no sulfate detected, 1: PHS, 2: kieserite, 3: PHS and kieserite, and 4: sulfate and another hydrated phase. The “ferric phase” category is classified as -1: short wavelength imagery not acquired, 0: no ferric phase detected, 1: red crystalline hematite, 2: probable hematite, 3: ferric phase, and 4: multiple ferric phases present. Multiple ferric phases could include red hematite plus another deposit with a different ferric absorption, perhaps due to another ferric oxide or sulfate. The location of ferric phases was classified as 1: in bedrock only, 2: in loose material only, or 3: in both bedrock and loose material. In observations where multiple ferric phases were detected, often one type would be in bedrock and the other in loose material.

Differences in continuum-removed, ratioed VNIR spectra are subtle due to the ubiquitous, muting presence of dust. Diffuse deposits often have weak spectral features where hematite absorptions cannot be differentiated from other ferric oxides or ferric phases. Thus, concentrated deposits of ferric oxide are needed to be able to confidently identify them as red hematite. One example is in West Candor Chasma, where Murchie et al. (2009b) have shown a concentration of red hematite in the braided channels eroding into Candor Mensa and a concentration of “ferric oxide” at the base of the ILD. This “ferric oxide” corresponds spatially to a TES detection

of gray crystalline hematite. Gray hematite is spectrally neutral in the VNIR, but perhaps the gray hematite deposit at the base of the ILD contains some abraded pieces displaying ferric absorption features. These feature may not be sharp enough to resolve as red hematite but are spectrally different from dusty spectra used in ratioing. Concentration of the material into channels on the ILD and as a lag at the base may have been necessary to get strong enough spectral features for identification with CRISM data. We recognize an identification bias toward ferric phases concentrated into lags and realize the true iron-bearing mineral diversity in ILDs is likely much higher than presented here.

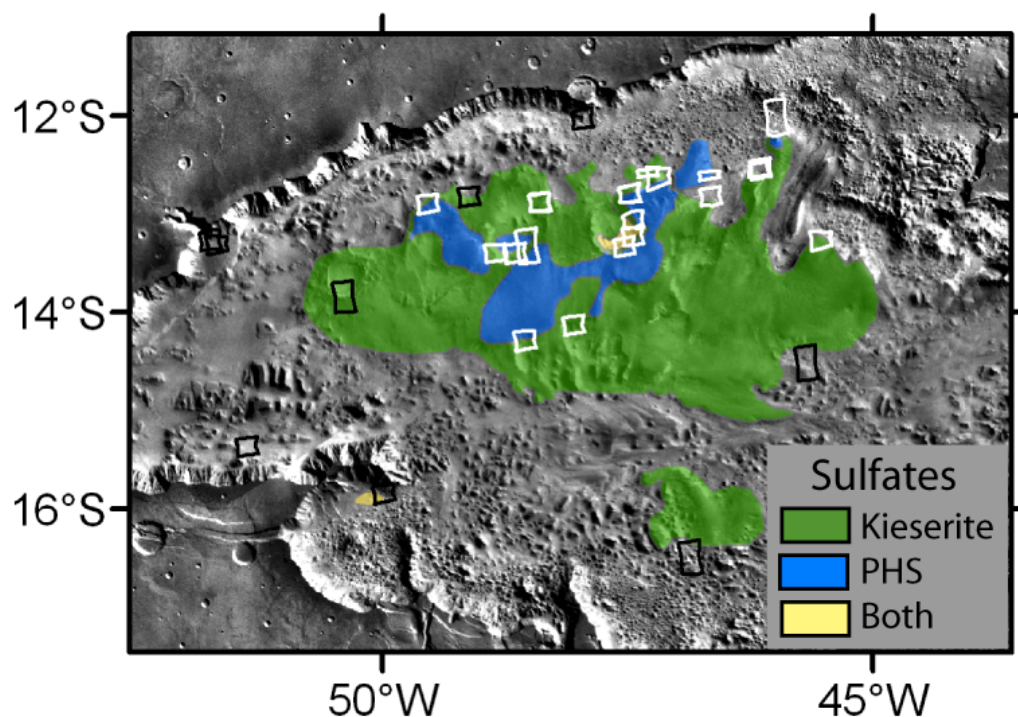


Figure 4.6: Regional unit map of sulfate distribution in Capri Chasma. Kieserite (green), PHS (blue) and mixed mono- and polyhydrated sulfate (yellow). CRISM targeted observations containing ferric phases are shown in white while those without ferric phases are black. Geologic contacts are determined by CRISM spectral analysis and extended over areas of morphologic similarity and along areas with similar elevation.

## 4.5 Stratigraphic Results

### 4.5.1 Stratigraphic section and regional unit map of Capri Chasma

The spectral identifications from individual CRISM targeted and mapping observations and OMEGA observations in Capri Chasma are extended into a regional unit map (Fig 4.6). The entire central ILD is interpreted to be sulfate rich. First, detailed spectral analysis of CRISM targeted and multispectral mapping data and OMEGA data identified locations with kieserite and/or PHS. Then HiRISE and CTX data were examined to determine the association of sulfate mineralogy to morphologic units.

In Capri Chasma, kieserite-bearing units tend to be bright, massive deposits that weather into fluted shapes, while PHS-bearing units tend to be dustier, slightly lower albedo, and easily erodible into blocky material (Fig 4.7). The lower albedo of PHS may be due to intrinsic properties or may be an effect of the greater dust cover on flatter PHS-bearing units. These units have a rougher texture and thus would trap more aeolian material than the smooth kieserite-bearing units (Fig 4.8b). The smoother texture of kieserite-bearing units may prevent aeolian material from collecting so uniformly over the surface and may restrict aeolian deposits to local depressions, some of which can be seen in the upper left of Fig 4.8c. Aeolian material collects along the PHS-rich slope in the center of Fig 4.8c. Mangold et al. (2008a) noted that PHS were systematically darker than kieserite in West Candor Chasma and similarly suggested either an intrinsic or dust-related cause. The PHS is also often on shallower slopes than kieserite here and elsewhere in Valles Marineris [Mangold et al. 2008b], which would contribute to its dustiness.

The kieserite-rich material and PHS-rich material show very different erosional styles. Large fluted erosional structures cut across both units in the ILD in Fig 4.8,

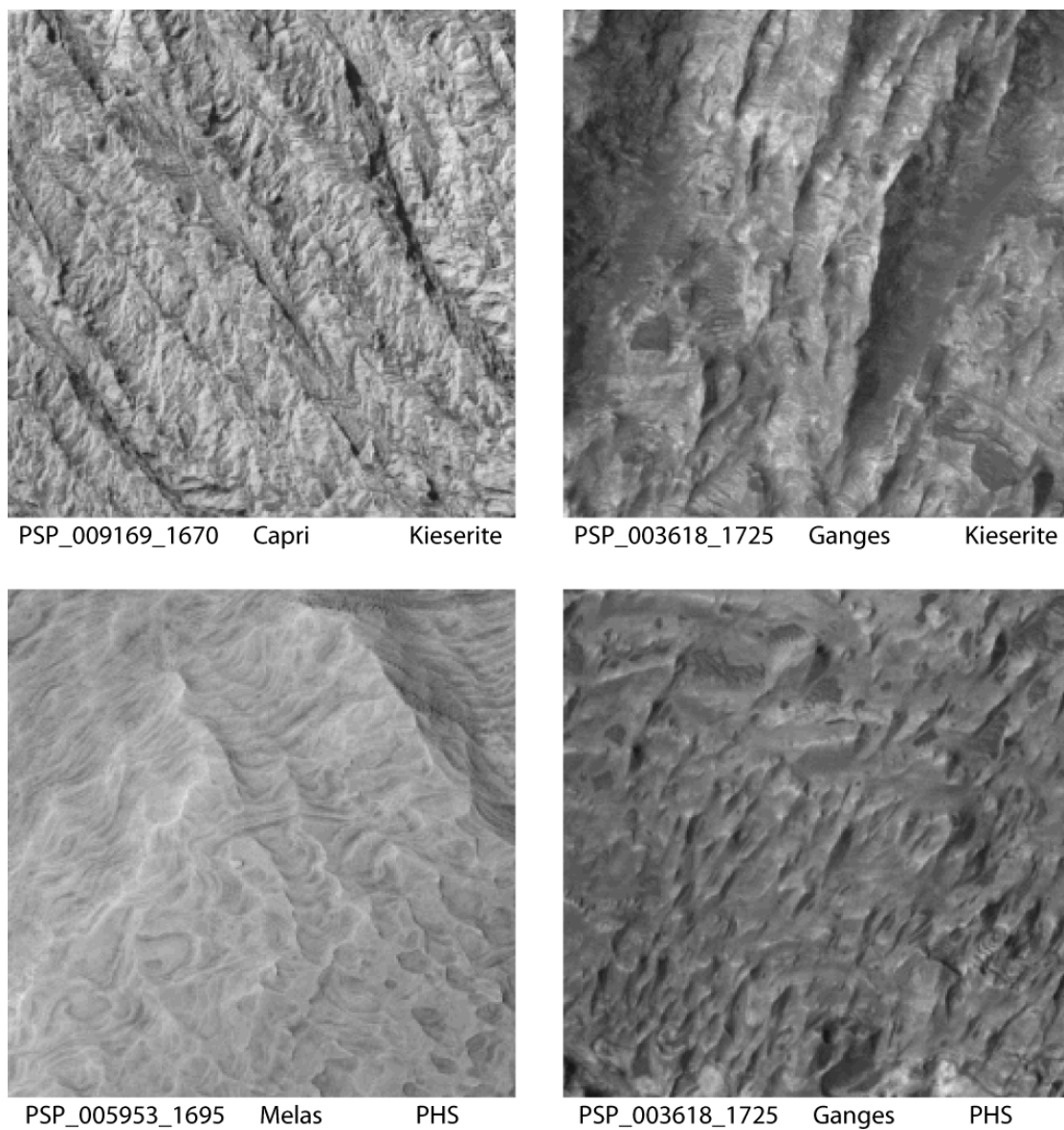


Figure 4.7: Example textures of units with kieserite (top row) and PHS (bottom row). All HiRISE images are 1 km across.

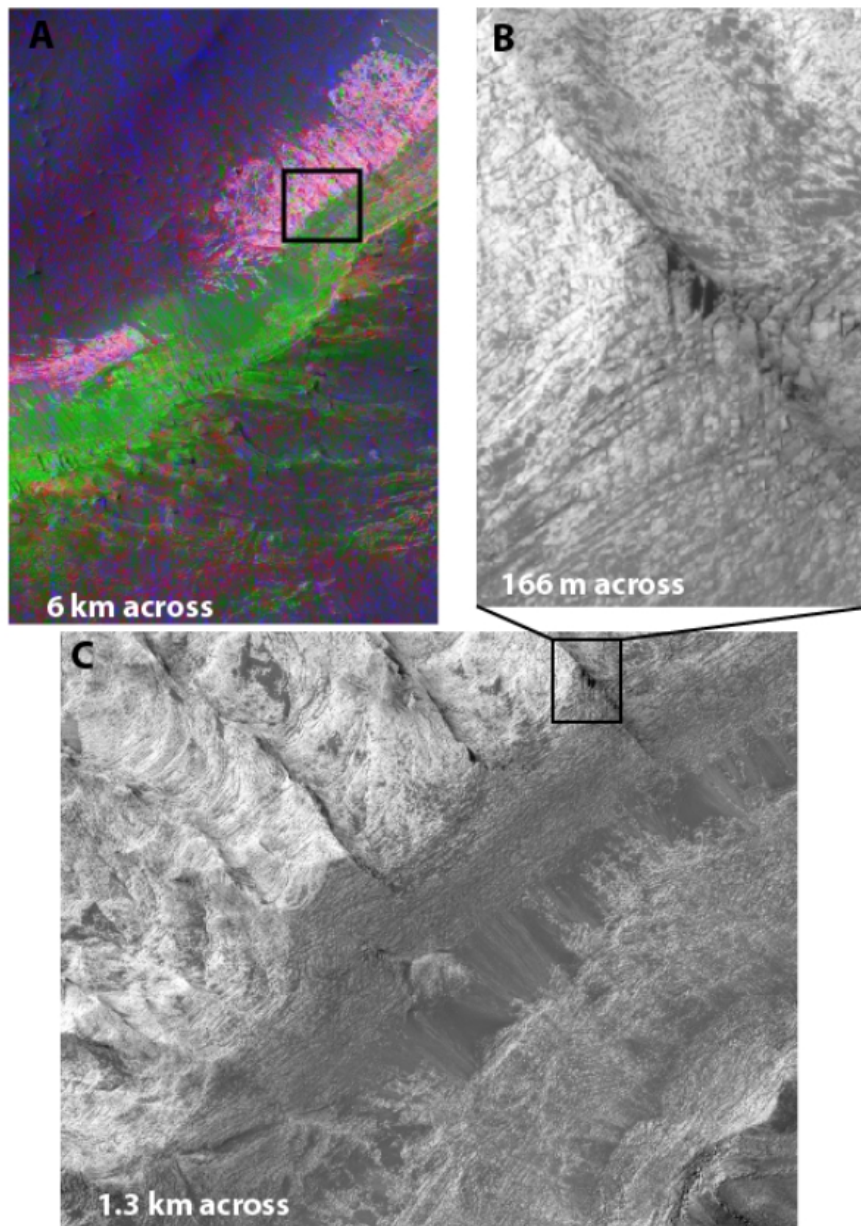


Figure 4.8: A. Contact between kieserite/hematite and PHS in subset of HiRISE PSP\_008088\_1760 colorized with CRISM FRT0000A82E. R: shoulder at  $0.60\ \mu\text{m}$ , G:  $1.90\ \mu\text{m}$  band depth, B:  $2.10\ \mu\text{m}$  band depth, indicative of hematite, PHS, and kieserite-bearing material respectively. Box shows extent of C. B. Detail showing different erosional texture of brighter, smoother kieserite and rougher PHS. C. Closeup of contact between kieserite/hematite (bright, fluted material to NW) and overlying PHS (darker, more debris-covered material to SE). Box indicates location of B.



but detailed imagery shows that the flute ridge in the kieserite-rich material is smooth and in the PHS-rich material is fractured and breaking into meter-scale blocks (Fig 4.8b).

In addition to morphologic characteristics, units were delineated by elevation data. MOLA shot and gridded data was used to determine elevations of the sulfate-bearing layers. The kieserite and PHS units were extended from the CRISM and OMEGA identifications to regions with similar morphology and topography. In regions with incomplete CRISM or OMEGA coverage and/or obscuration by a dusty, spectrally neutral mantle, the sulfate units were mapped with the morphology and elevation constraints.

PHS lies stratigraphically above kieserite throughout Capri Chasma (Fig 4.6). CRISM targeted data in 10 locations and MOLA shot data on both the northern and southern part of the ILD were used to determine the elevation of the contact between kieserite and PHS. The elevation of the contact between the sulfates is between -2550 and -850 m in CRISM observations that span 120 km across the deposit, with systematically lower elevations toward the west. Assuming the PHS and kieserite layers are continuous across the ILD, that corresponds to a long-range dip of the contact of  $<1^\circ$  westward. MOLA shot data have 150 m footprints, which is much larger than the contact between the two sulfates. This adds uncertainty to the elevation data, especially as the contact occurs on slopes ranging from  $25\text{--}35^\circ$ . Fig 4.10 shows the slope of ILD flanks and the dip of the contact between kieserite and PHS units. In regions with multiple adjacent CRISM observations that resolve the contact between kieserite and PHS units, the local dip of the contact is  $<2^\circ$  (as in Fig 4.9). The contact between the kieserite and PHS unit is horizontal both over 125 km and at the scale of a CRISM observation, within the measurement error for the elevation data.

The bottom of the kieserite-rich layer is not exposed anywhere in Capri Chasma

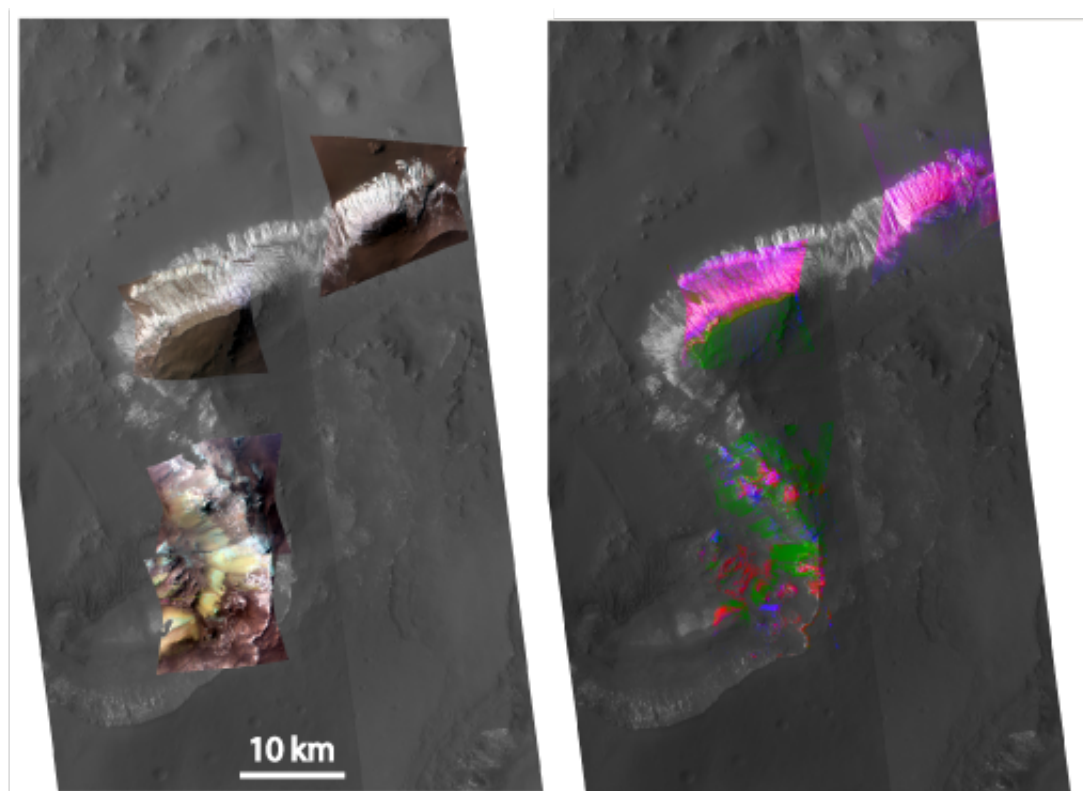


Figure 4.9: A. False color CRISM observations FRT0000B776, FRT0000BB25, FRT0000C564, and FRT0000B385 top to bottom (RGB: 2.5, 1.5, 1.08  $\mu\text{m}$ ) covering contact between kieserite and PHS on the northern edge of Capri Chasma ILD. Putative 30 km impact crater in southwest of image. B. RGB: band depths at 0.86, 1.9, and 2.1  $\mu\text{m}$ , in this case indicating hematite, PHS, and kieserite, respectively. Kieserite and hematite-bearing locations (magenta) are common, while PHS and hematite-bearing locations (yellow) are absent.

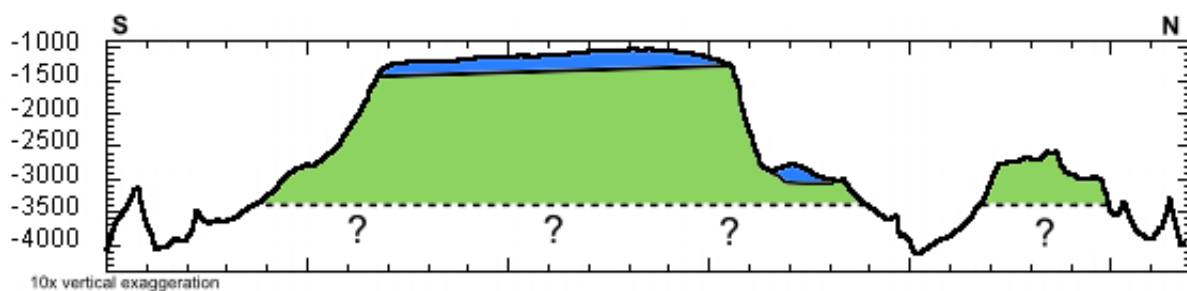


Figure 4.10: Stratigraphic cross-section of sulfates within the central mound in Capri Chasma, from MOLA orbit 16830. Kieserite is green and PHS is blue. Lower extent of kieserite uncertain.

and loose materials mantle the bottom of ILD slopes and surrounding chasma floor. As a result, the total thickness of the kieserite layer cannot be assessed. It is also unknown if the kieserite-rich unit has uniform thickness. The maximum thickness of exposed kieserite-rich material is 2000 m. The PHS-rich unit varies in thickness due to aeolian stripping of the top of the ILD; in some parts of the ILD it is entirely removed. The PHS-rich unit has a maximum thickness of 400 m.

### 4.5.2 Hematite and sulfate association in Capri Chasma

Hematite and other ferric oxides are generally associated with sulfate in the Capri Chasma ILD. The spectral signatures of hematite or ferric phases cannot be tied to a unique morphologic unit in HiRISE or CTX data, nor are they widespread in CRISM imagery. This is in contrast to the sulfates which have both a clear identification in CRISM imagery and an association with specific surface textures and albedos that make it possible to map them as regional units. Thus, ferric phases are not mapped as continuous units; rather, outlines of CRISM targeted observations that show the presence of red hematite, probable hematite, or ferric phases are all shown in white, while other CRISM observations lacking ferric spectral signatures are shown in black in Fig 4.6. The details of the relationship between sulfates and ferric phases are best seen in individual CRISM observations.

The northern edge of the central ILD is a key outcrop that clearly shows the contact between underlying the kieserite- and hematite-bearing unit and the overlying PHS-bearing, ferric oxide-poor unit. The stratigraphy of the PHS-bearing unit above the kieserite/hematite-bearing unit is consistent throughout the chasma but is best expressed in CRISM observation FRT0000BB25 and nearby observations (Fig 4.9). The northern part of Fig 4.9 has an undisturbed stratigraphy while the southern part covers a 30 km diameter putative impact crater and has a jumbled mineral

stratigraphy. The sulfate-rich material within the putative crater was previously interpreted to be brecciated bedrock [Roach et al. 2007c]. The contrast in mineral stratigraphy between the two parts indicates the sulfates are a bulk component of the bedrock that are redistributed by impact processes and not due to a surface-atmospheric interaction.

Fig 4.9b shows band depths indicative of hematite in red ( $0.86\ \mu\text{m}$ ), PHS in green ( $1.9\ \mu\text{m}$ ) and kieserite in blue ( $2.1\ \mu\text{m}$ ). Thus, regions with  $0.86\ \mu\text{m}$  and  $2.1\ \mu\text{m}$  absorptions (colored magenta) contain both kieserite and hematite. Along the northern part of Fig 4.9 where the sulfate stratigraphy is undisturbed, all kieserite-bearing bedrock materials have a ferric oxide component. Spectral analysis shows it is due to red crystalline hematite. The base of the kieserite/hematite unit where it meets the canyon floor does not have either  $0.86$  or  $2.1\ \mu\text{m}$  absorptions. The spectral signature of the PHS overlying the kieserite lacks significant admixture with crystalline red hematite – it has a  $1.9\ \mu\text{m}$  absorption but not a strong  $0.86\ \mu\text{m}$  absorption. This association of hematite with kieserite-bearing bedrock units but not with the overlying PHS-bearing bedrock is seen in CRISM observations across Capri Chasma.

Impact cratering can disturb the general stratigraphy of PHS above kieserite (SW portion of Fig 4.9). The cratering and slumping process has reworked the mineral stratigraphy. The  $0.86\ \mu\text{m}$  absorption characteristic of hematite is found alone (red in Fig 4.9b) and with mono- and polyhydrated sulfates in regions disturbed by cratering. Regions that have a  $2.1\ \mu\text{m}$  absorption from kieserite but no  $0.86\ \mu\text{m}$  absorption (blue in Fig 4.9b) are also common within the crater.

Another example of the strong correlation of hematite with kieserite but not PHS is found in the northwest part of the central ILD (Fig 4.8). HiRISE image PSP\_008088\_1760 is colorized with CRISM false color. Similar to Fig 4.9b, Fig 4.8a

has a false color RGB indicating hematite, PHS, and kieserite-bearing units respectively. The red channel is the 0.6  $\mu\text{m}$  hematite shoulder rather than the 0.86  $\mu\text{m}$  hematite absorption, because in this scene the 0.6  $\mu\text{m}$  absorption is a more robust indicator of pixels with the spectral properties of red hematite. However, the red channel also shows pixels with a 0.6  $\mu\text{m}$  feature due to the nanophase ferric oxide in the dust. Spectral analysis is necessary to identify pixels with red hematite or with dust. Thus, the reddish pixels at the base and on the top of the ILD show spectral features indicative of dust rather than of red hematite or other ferric phases. The green (1.9  $\mu\text{m}$ ) and blue (2.1  $\mu\text{m}$ ) channels remain the same as Fig 4.9b, and indicates PHS and kieserite mineralogy, respectively. The lower part of the ILD has 0.6 and 2.1  $\mu\text{m}$  absorptions from hematite and kieserite (colored magenta), while the upper part of the ILD has only a 1.9  $\mu\text{m}$  absorption from PHS (colored green). The lack of PHS/hematite units can be seen visually by the lack of yellow hues.

The hematite is concentrated in the kieserite-bearing bedrock and at the base of some, but not all, kieserite-bearing ILDs. This variation in hematite distribution at the base of ILDs may be due to differences in aeolian transport of hematite fines from the base of the ILD. Some locations with hematite in loose material at the base of an ILD also show a PHS signature in the loose material. This may be aeolian deposition of the stripped upper layers plus the hematite-rich lag from erosion of the lower layers. Kieserite is not found in loose material in Capri Chasma.

A map of gray crystalline hematite as detected by TES (Fig 4.11) shows that the phase concentrates at the base and the lower flanks of the northern (well-exposed) wall of the central ILD, but not in the PHS-rich upper unit. It is also found in the slumped material in the putative impact crater discussed previously. Red crystalline hematite in CRISM data is located in the bedrock of the central ILD and also sometimes at the base of the ILD. The spatial correlation between red and gray hematite is not

exact, but generally, locations with red hematite overlap areas with gray hematite. The areal coverage of gray hematite is greater, if only because TES has more spatial coverage in Capri Chasma than CRISM targeted observations.

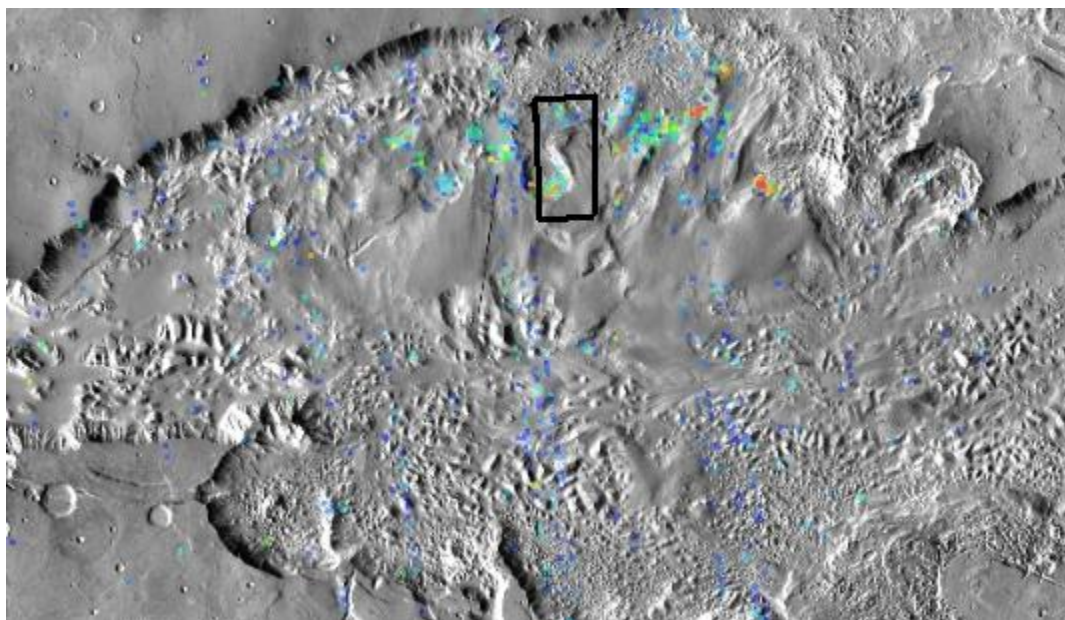


Figure 4.11: Gray hematite distribution in Capri Chasma from TES data. Box indicates extent of Fig 4.9.

### 4.5.3 Interpreted stratigraphic section across Valles Marineris basins

Regional maps of sulfate distribution in Western and Eastern Valles Marineris (Figs 4.12 and 4.13) from CRISM and OMEGA data follow the general distribution shown by previous maps of OMEGA data [Gendrin et al. 2005]. Mapping was first performed with CRISM targeted and mapping observations, and then gaps were filled with OMEGA data. Where OMEGA and CRISM data overlap, they show consistent results for sulfate distribution, but the higher resolution CRISM data is better able to distinguish between mono- and polyhydrated sulfate.

Sulfate is concentrated in bright-toned mounds in the basinal chasma but is also found in a few small and low relief floor deposits in the linear chasma. In the maps, kieserite-rich deposits are colored green, PHS-rich deposits are blue, units with both kieserite and PHS or with uncertain sulfate mineralogy are yellow. Bright, light-toned ILDs that appear relatively dust-free in HiRISE imagery but which do not have sulfate signatures in CRISM or OMEGA are colored with white dots on a light gray background. These locations may be sulfate-free, have dehydrated sulfates, have sulfate in too low concentrations for detection, or may have enough dust cover to completely mask any spectral signatures from the bedrock. Similar muting mechanisms were proposed for the weak spectral signatures of sulfate in Meridiani Planum from orbital spectrometers [Arvidson et al. 2006]. The other possible interpretation for ILDs lacking hydration signatures is that they host a spectrally neutral evaporite, like halite or anhydrite. CRISM observations showing ferric mineralogy are outlined in white boxes, and CRISM observations without ferric mineralogy are outlined in black boxes.

The large basinal chasma in Juventae, Ganges, Melas, and West Candor all have similar sulfate stratigraphy to the central ILD in Capri Chasma. These basinal chasma have bright, mound-like central ILDs 2–4.5 km in thickness. The lower exposures are kieserite- and red crystalline hematite-rich, and the upper exposures contain PHS with no ferric phases. In all chasma, the ferric phase associated with kieserite is red crystalline hematite, but in some locations within the chasma, the ferric absorption is less diagnostic of red hematite and is instead assigned to a more generic “probable hematite” or “ferric phase” interpretation. The degree of layering and the amount of admixture with basaltic sand varies between the ILDs. However, the erosional style of the basinal ILDs are broadly similar — a fluted or channeled morphology with few boulders on the slopes or at the base, suggesting a fine-grained composition. These

ILDs are similar in shape, morphology, location within their respective chasma, and sulfate and hematite stratigraphy; they may share a common geologic history.

## 4.6 Discussion

### 4.6.1 Implications for formation

There are five key elements to the sulfate stratigraphy: (1) PHS on top of kieserite with a horizontal contact; (2) crystalline red hematite associated with kieserite-bearing bedrock but not with PHS; (3) other ferric oxides may be present in loose material at base of ILDs; (4) crystalline gray hematite in a lag deposit at the base of ILDs but sometimes on the ILD flank; and (5) stratigraphy is consistent and repeated across 120 km in Capri and in other basinal chasmata. Fig. 4.14 shows a schematic of how the basinal ILDs could have formed and been enriched in sulfates. These elements together suggest that the kieserite and crystalline red and gray hematite could have formed by diagenesis of sulfate-bearing sediments as a consequence of burial and/or a higher heat flow early in the chasma's history. This diagenetic process would be active in the lower parts of any ILDs thicker than a couple of km; upper units would remain unaltered. The gray hematite weathers out of the ILD and collects as a lag at the base, while the red crystalline hematite is most concentrated in the bedrock. The red hematite could be either an erosional product of gray hematite or also formed by diagenesis. There are several possibilities for the formation of the overlying PHS: (1) it could have been the original sulfate precipitated which never altered to kieserite, (2) it could have formed from kieserite by later interaction with near-surface groundwater or snow/water ice or by sulfate dissolution and re-precipitation, or (3) it could be a later precipitate after the kieserite and hematite were emplaced.

The difference in the erosional style of the more competent kieserite and the more



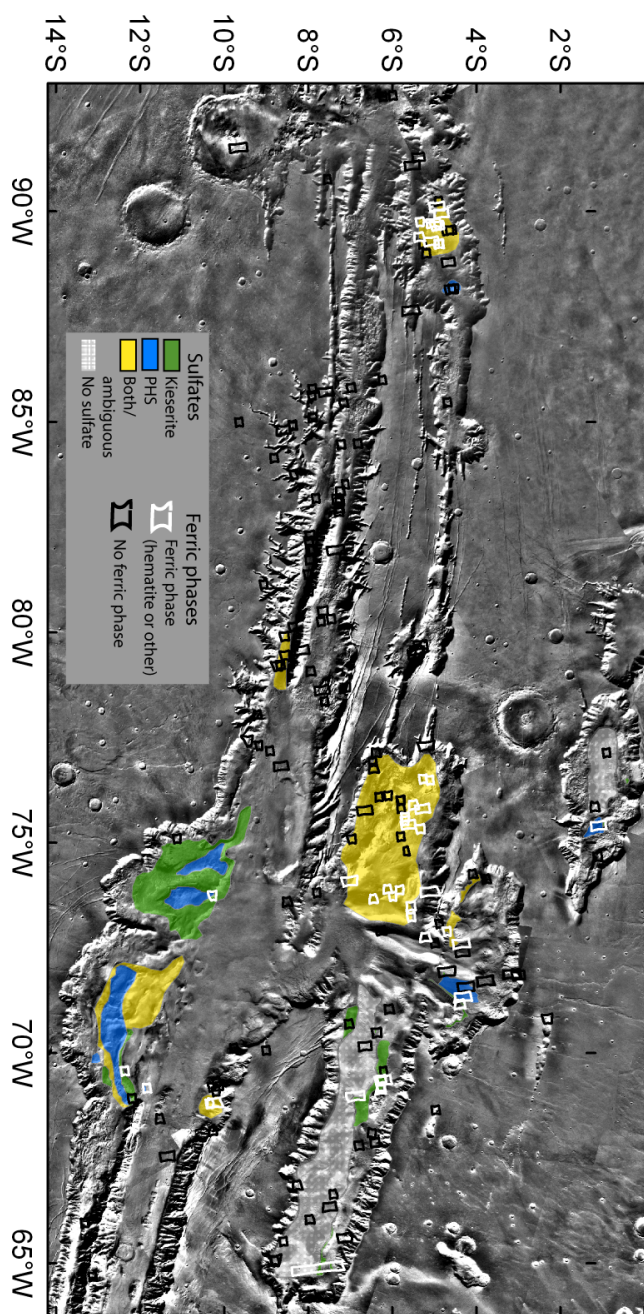


Figure 4.12: Sulfate occurrences in Western Valles Marineris in CRISM data. Kieserite-rich deposits are colored green, PHS-rich deposits are blue, units with both kieserite and PHS or with uncertain sulfate mineralogy are yellow. Bright, light-toned ILDs that appear relatively dust-free but which do not have sulfate signatures are colored with white dots on a light gray background. Outlines of CRISM observations showing ferric mineralogy in white boxes, and CRISM observations without ferric mineralogy shown in black boxes.

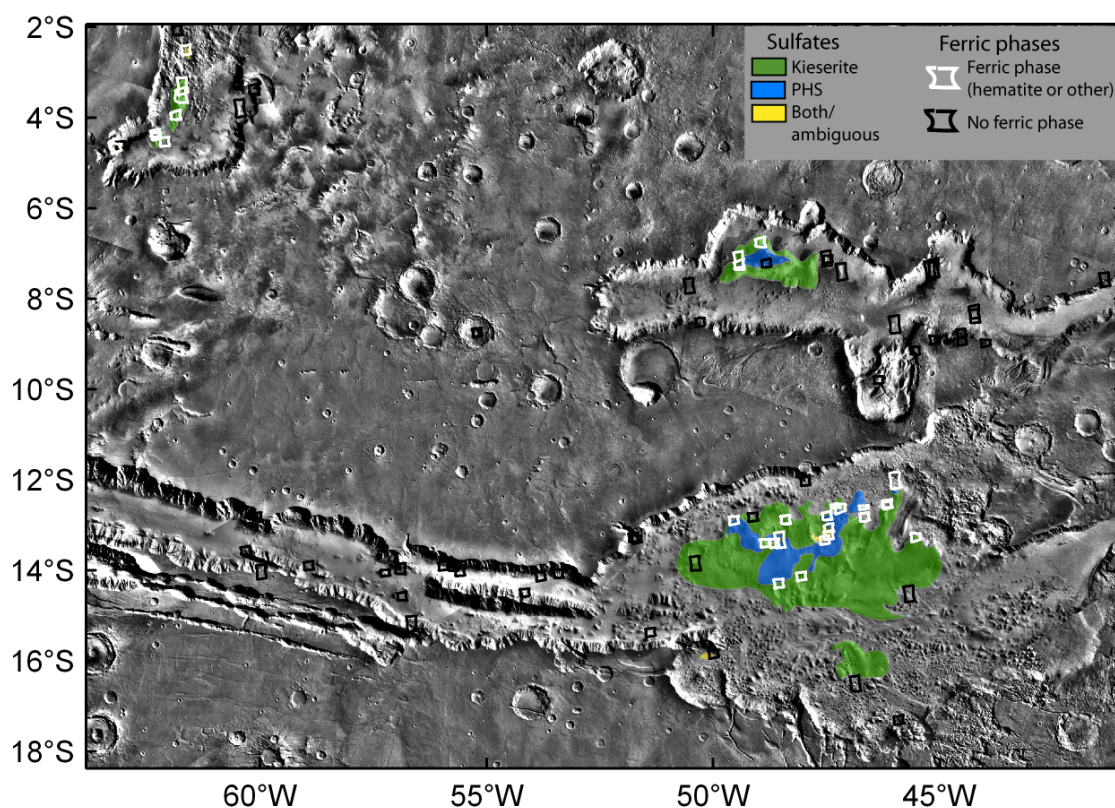


Figure 4.13: Sulfate occurrences in Eastern Valles Marineris in CRISM data. Kieserite-rich deposits are colored green, PHS-rich deposits are blue, units with both kieserite and PHS or with uncertain sulfate mineralogy are yellow. Bright, light-toned ILDs that appear relatively dust-free but which do not have sulfate signatures are colored with white dots on a light gray background. Outlines of CRISM observations showing ferric mineralogy in white boxes, and CRISM observations without ferric mineralogy shown in black boxes.

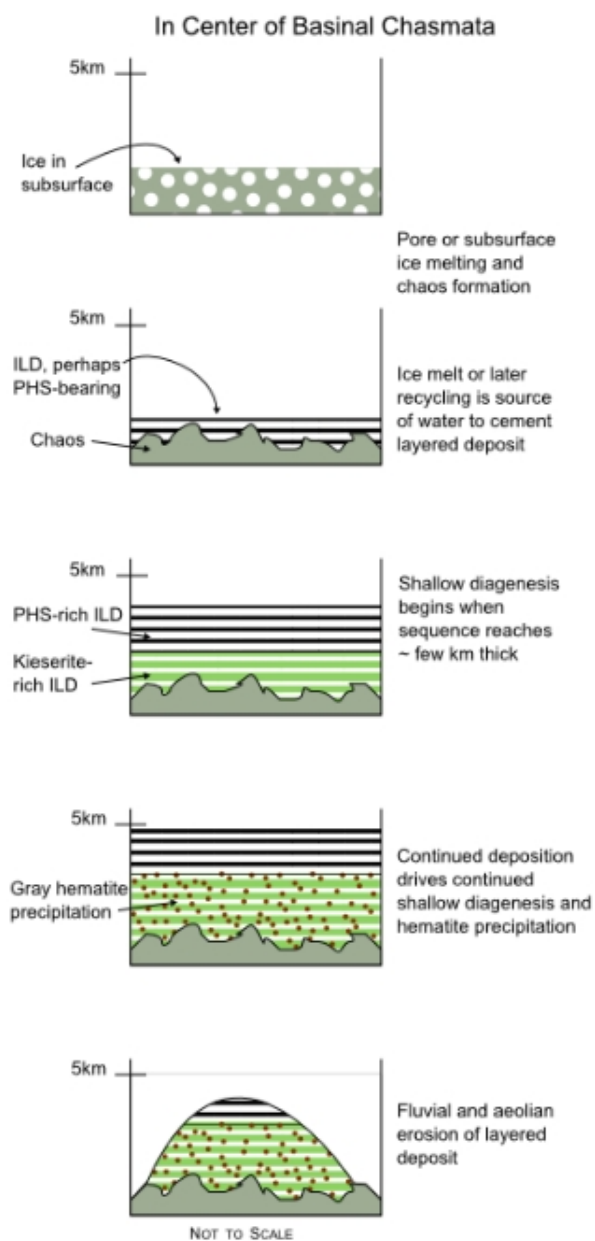


Figure 4.14: Schematic of ILD formation and sulfate enrichment in basinal chasmata. Chasma walls not shown. Sulfate enrichment could postdate early ILD formation.

friable PHS may be a clue about how the PHS formed – rehydrated kieserite or primary precipitation. Polyhydrated Mg sulfates, such as epsomite ( $\text{MgSO}_4 \bullet 6\text{H}_2\text{O}$ ) or an amorphous, hydrated Mg sulfate are expected to be the stable phases on Mars, not kieserite [Vaniman and Chipera 2006b]. Elsewhere in Valles Marineris, we have seen evidence that the outermost surface of kieserite can hydrate to a polyhydrated (Mg) sulfate [Roach et al. 2009b]. This hydration layer must be very thin, since it is eroded away on steeper slopes to reveal the underlying kieserite signature. The volume expansion of pure kieserite to crystalline polyhydrated Mg sulfates can result in expansion by 10–38%. The 35–40% sulfate abundance in Meridiani Planum [McLennan et al. 2005] may be a reasonable estimate for the sulfate abundance in ILDs. If so, then complete hydration of the kieserite in an ILD could create  $\sim 10\%$  volume expansion. Hydration of a thin surface layer of the ILD to a polyhydrated Mg sulfate would not cause enough expansion to fracture the surface into 3–4 meter-scale blocks, as is seen in Capri Chasma. Thus, if the fracturing is due to rehydration, the PHS in Capri Chasma is present in more than a thin surface layer of the unit. This PHS is more likely formed by primary precipitation or dissolution and reprecipitation, rather than atmospheric rehydration. However, the friable nature of PHS-containing units may be due to other factors than sulfate hydration state; physical properties such as grain size, packing, and differential stress between layers could also account for the difference between the blocky PHS unit and smooth kieserite unit.

The strong correlation between kieserite and hematite suggest that a common mechanism was responsible for forming them. Meridiani Planum has a similar association of gray hematite ( $\sim 10\%$ ) and jarosite and other sulfates (35–40%) [McLennan et al. 2005]. The hematite concretions are thought to form by shallow groundwater interactions in a sulfate-rich basaltic sedimentary sequence [McLennan et al. 2005]. Variations in hematite spherule size and shape over the 6 km course of the MER Op-

portunity traverse suggests a changing depositional or diagenetic environment [Calvin et al. 2008]. Similar mechanisms that created that mineral assemblage in Meridiani Planum may also be at work in Valles Marineris. One hypothesis for the Meridiani mineralogy is direct dehydration in a water limited environment of jarosite to hematite [Barron et al. 2006]. In terrestrial settings, intermediates like goethite and ferrihydrite are common in the dehydration and dehydroxylation of ferric sulfates to hematite [Cornell and Schwertmann 1996]. Another potential source of iron for diagenetic formation of hematite is melanterite ( $\text{Fe}^{2+}\text{SO}_4 \bullet 7\text{H}_2\text{O}$ ) [McLennan et al. 2005; Sefton-Nash and Catling 2008]. In Valles Marineris, low temperature syndepositional diagenesis of a km-thick sulfate sequence could dehydrate a polyhydrated Mg sulfate to kieserite, and could transform ferric sulfates or oxides to hematite as interstitial cement or concretions.

#### 4.6.2 Evaporite diagenesis

The general distinction between kieserite at lower elevations and polyhydrate at higher elevations in basinal chasmata could be due to changes in climate or groundwater discharge rate or due to post-depositional diagenesis. The sulfates could be an evaporite sequence with significant aeolian material contribution or an ash and aeolian deposit possibly altered and then cemented by sulfates through groundwater interaction. The source of sulfur could be either igneous pyrite in the deposit or atmospheric  $\text{SO}_2$  from volcanic outgassing [Burns and Fisher 1990; Chevrier et al. 2006]. Changes in aqueous chemistry, such as the freshening of the interstitial brine composition in the upper layers due to meteoritic water input, could partially explain the enhancement of polyhydrated sulfate at the higher elevations and monohydrated sulfate at lower. However, in a multi-km thick deposit, syngenetic and diagenetic alteration is unavoidable and can also produce stratified secondary mineralization.

Once sulfate is precipitated, it is susceptible to dissolution or reaction with brines of many different chemistries [Sonnenfeld 1984]. Syngenetic brines derived from the same reservoir that precipitated the sulfates may become more concentrated and sink, percolating through unconsolidated evaporites and causing recrystallization [Stewart 1956; Sonnenfeld 1984]. When the deposits are sufficient thickness, lower portions are lithified by the overburden pressure and increased temperatures. Many of the basinal ILDs on Mars are many km thick, and diagenetic processes were likely active at the lower layers. Brines released by diagenesis are expelled upward by the lithostatic pressure and can alter overlying evaporites to secondary precipitates [Sonnenfeld 1984]. Mineral pseudomorphs, relict crystals, and recrystallization textures all indicate diagenetic alteration. After the sulfates became lithified by diagenesis, they are still subject to brine interactions; epigenetic brines, which are groundwaters unrelated to the evaporite deposit, may percolate through the ILD and affect the hydration state or chemistry of the evaporites.

While the effect of recrystallization is most easily seen at the microscopic scale (i.e. [Lowenstein and Hardie 1985], some effects may be visible on the macroscopic scale (i.e. in HiRISE imagery). Shallow diagenesis can completely overprint the original crystalline texture and bedding [Lowenstein 1986], but evidence of diagenetic recrystallization may be interpretable on a macroscopic scale. It is possible more recrystallized sulfate cements or crystals are more competent and well-aligned and thus weather into a smoother texture than the original evaporite.

The influence of syngenetic, diagenetic, and epigenetic brines is felt whether the ILD is dominantly evaporites or only contains minor amounts of evaporites in an aeolian or ash matrix. The 35–40% sulfate abundance in Meridiani Planum may be an appropriate estimate for the Valles Marineris ILDs. Distinguishing the mineralogic alterations caused by each type of brine is difficult even in terrestrial evaporites with

the aid of microscopic analysis. Orbital detection of sulfate deposits on Mars cannot reproduce the inherently complicated history of evaporite formation, but general mineralogic trends can point to the relative importance of alteration processes after formation.

The exact diagenetic temperature needed to convert from epsomite and other polyhydrated sulfates to kieserite in a multi-sulfate assemblage is complicated by mineral and groundwater chemistry. One study of a terrestrial seawater-composition brine finds epsomite would convert to kieserite between 25 and 40 °C [Borchert and Muir 1964]. Figure 4.15 shows the equilibrium from the system  $K_2-Na_2-Mg-Cl_2-SO_4$  at 25° and 40° C. For a given chemistry (position on the ternary diagram), raising the temperature changed which mineral phase was stable. In the region on the ternary diagram where epsomite and hexahydrite are stable at 25°, the stable mineral phase at 40° is kieserite; epsomite and hexahydrite would transform to kieserite with rising temperature. Assuming thermodynamic equilibrium processes, the changing mineral stability fields with increasing temperature would promote recrystallization and transformation of the lower layers of the evaporite to a different sulfate assemblage.

Assuming a geothermal gradient of about 10K/km for the Valles Marineris region inclusive of the residual Tharsis volcanic thermal pulse [Schultz and Lin 2001; Hoffman 2001], diagenetic conversion to kieserite only requires burial to a few km. Since many of the basinal ILDs are several km thick, the kieserite stability field may be easily reached in the lower parts of those ILDs. The increased temperature at the base of ILDs would not just have converted more hydrated sulfates to kieserite, it also would prevent that monohydrate from becoming polyhydrated by potential late stage flushing with more diluted brines.

In sulfate-bearing ILDs where groundwater precipitation and diagenesis formed hematite, the same process could form kieserite from epsomite or other polyhydrated



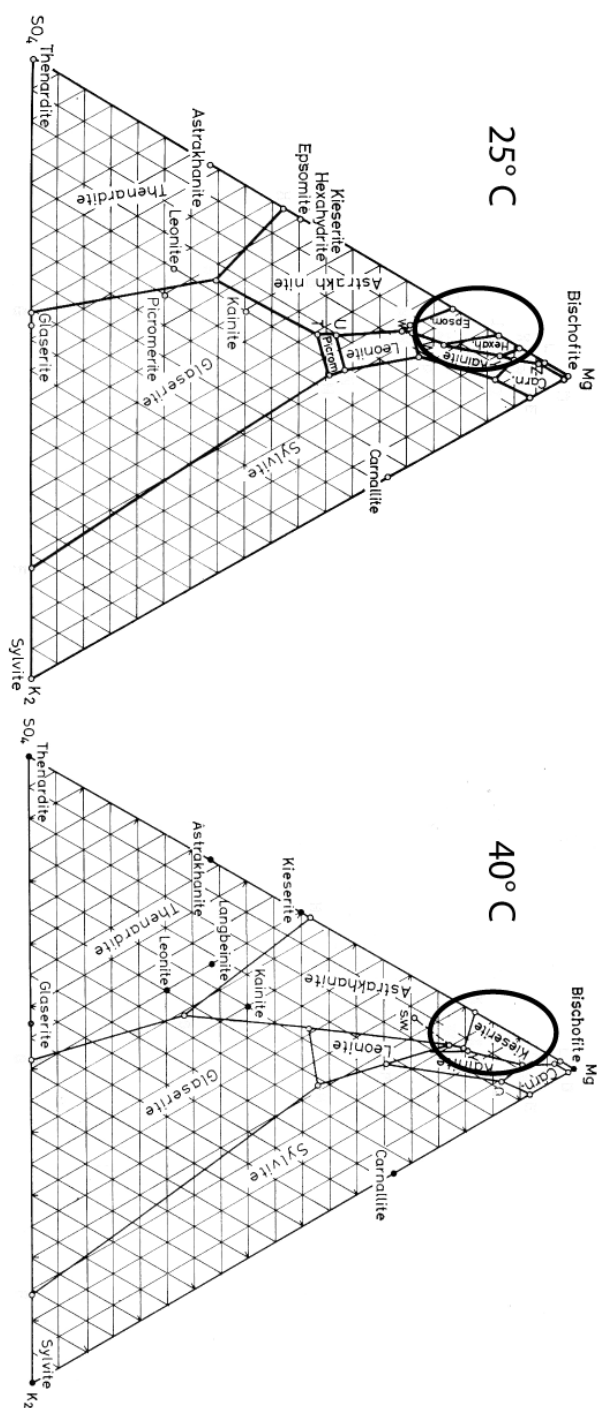


Figure 4.15: Equilibrium mineralogy in a system containing  $\text{K}_2\text{-Na}_2\text{-Mg-Cl}_2\text{-SO}_4$  solutes at 25° and 40° C. Adapted from [Borchert and Muir 1964]. Epsomite and hexahydrate are thermodynamically stable at 25°, while kieserite is stable at 40°.



sulfates.

Hematite in terrestrial evaporites likely originated as goethite-bearing deposits that were subsequently dehydroxylated by later, more concentrated brines [Sonnenfeld 1984]. These more concentrated, end stage brines are hygroscopic and will also dehydrate sulfate phases. Epsomite dehydration to kieserite or gypsum dehydration to anhydrite are common transformations in terrestrial evaporite deposits. There are many other processes for hematite formation. Given enough time, goethite also converts to hematite without requiring highly saline waters or high temperatures [Berner 1970]. Jarosite and melanterite are other possible precursors to hematite [Barron et al. 2006; Sefton-Nash and Catling 2008]. Pyrite could also oxidize to hematite in terrestrial deposits, but only in the absence of biologic reduction [Sonnenfeld 1984].

Several of the deposits, such as in Juventae and Melas Chasmata, have very sharp and traceable contacts between kieserite and polyhydrated sulfate. These contacts often have a tonal difference, but not unconformities or other physical disruptions. The lack of a gradational diagenetic boundary, with co-occurring poly- and monohydrated sulfates, suggests the alteration process was not just burial and dewatering, but that groundwater table fluctuations may have had a strong imprint of resulting mineralogy.

Other ILDs show alteration between poly- and monohydrated sulfate with stratigraphic section (e.g. eastern and western Candor) that cannot be explained by diagenesis alone. The upper layers of Ceti Mensa in Candor Chasma shows sharp contacts between two polyhydrated sulfate layers within a mostly monohydrated sulfate-rich deposit [Murchie et al. 2009b]. It is proposed to be due to either sequential evaporation events or partial diagenesis [Murchie et al. 2009b]. The polyhydrated sulfate layers are proposed to be evaporites formed under the wettest conditions. Perhaps the elevated temperatures at the bottom of thick ILDs could have prevented that mono-

hydrate from becoming polyhydrated during late stage flushing with more diluted brines that could deposit polyhydrated sulfate in the upper stratigraphic sections.

### 4.6.3 Connections to Meridiani Planum

The layered sulfates at Meridiani Planum have seen similar processes, with multiple generations of groundwater fluctuations alternately precipitating, recrystallizing, and dissolving evaporite minerals and precipitating hematite spherules [Squyres and Knoll 2005; McLennan et al. 2005; Squyres et al. 2006]. The Whatanga contact of the Burns Formation at Meridiani Planum is interpreted as the terminal height of a water table fluctuation and thus as a diagenetic boundary [McLennan et al. 2005; Grotzinger et al. 2005]. The Whatanga contact is physically different than adjacent layers, with a darker albedo and overprinted texture from recrystallization [McLennan et al. 2005; Grotzinger et al. 2005], and chemically different, as represented by variation in Br and Cl concentrations above and below the contact [Clark et al. 2005]. The Whatanga contact is  $\sim 10$  cm thick, so it is reasonable to expect sharp diagenetic contacts between poly- and monohydrated sulfates at HiRISE and CRISM scales.

Studies of the regional geology [Hynek and Phillips 2008] and mineralogy [Poulet et al. 2008a] in Meridiani Planum suggest the sedimentary structures and minerals seen by the MER Opportunity are representative of a much larger geologic unit that covers  $2 \times 10^5$  km<sup>2</sup> [Hynek et al. 2004].

If the Meridiani Planum model is also applicable to the sulfate-rich Interior Layered Deposits in Valles Marineris, then the region affected by acidic, aqueous processing is extended by 1000s of km. A common genesis for the Meridiani and Valles Marineris sulfate- and hematite-bearing deposits suggests a regional aqueous environment rich in sulfate with a complex water geochemistry with time.

## 4.7 Conclusions

Mapping of the mono- and polyhydrated sulfate distribution in ILDs across Valles Marineris based on CRISM targeted and mapping observations shows remarkable consistency in relative mineralogic stratigraphy and trends in mineralogy and deposit texture and erosional style. To first order, kieserite is often found in layers that are stratigraphically below polyhydrated sulfate-rich layers, especially in ILDs less than several km thick. Hematite is often associated with kieserite in the ILD bedrock, and other ferric oxides are found in either ILD bedrock or in loose material at its base. This mineralogic grouping at the lowest exposed elevations of many ILDs in the broad basins within Valles Marineris leads us to hypothesize a regional diagenetic process emplacing hematite and kieserite in previously polyhydrated sulfate-bearing sedimentary deposits (see Fig. 4.14).

The ILDs in Valles Marineris are Hesperian-aged sedimentary deposits that occur over a range of elevations. Taking into account the ILD morphology and the common mineral stratigraphy indicating diagenetic alteration of the hydrated phases, we propose a model for the aqueous geologic history acting on these deposits. They may have originally started accumulating in isolated ancestral basins and rifts predating the present Valles Marineris configuration [Schultz 1998; Lucchitta et al. 1994]. Many of the basinal ILDs sit unconformably on chaotic terrain. The chaotic terrain may be the result of collapse from ground ice. That released melt water (or recycling of that water) may be the source of water for cementing the ILDs. The ILD deposition and lithification processes could either have pre-dated or been coincident with original sulfate enrichment. As the basinal ILDs grew in thickness to a couple kilometers by aeolian, lacustrine, or volcanic processes, diagenetic alteration of sulfate within the sedimentary structure was unavoidable. The increased temperature (10s of degrees)

and overburden pressure would convert polyhydrated sulfate to kieserite and promote low-temperature alteration of iron oxides to hematite. Gradation of the upper portions of ILDs have since exhumed the lower, kieserite- and hematite-bearing layers. Physical erosion has also concentrated hematite and ferric oxide as a lag deposit at the base of many ILDs. The PHS-rich units on top of the kieserite-rich units may be the remnants of upper layers that were not buried sufficiently to convert to kieserite or they may be part of a later depositional event.

This model explains many of the thick ILDs located in the Valles Marineris basins, like Melas, Capri, and Candor Chasmata but cannot explain all sulfate-bearing outcrops. Several unique sulfate deposits in a linear trough may be due to different processes; for example the character of the  $\sim 100$ s meters thick ILD in Ius Chasma is consistent with near-complete evaporation within a closed basin [Roach et al. 2009c]. However, the thick ILDs in the basinal chasma show a repeated mineral stratigraphy and may all be formed by low temperature diagenesis.

The OMEGA team has put forth a mineralogic timeline [Bibring et al. 2006] complementary to the global geologic timeline based on crater counting and superposition relationships. The proposed mineralogic timeline rests on the OMEGA results that phyllosilicates are in the oldest terrains (Phyllosian), sulfates are within younger terrains in Valles Marineris and westward outflow channels and Meridiani Planum (Theiikian), and ferric oxide-bearing dust is globally distributed on the surface (Siderikian). The Phyllosian and Theiikian eras are well separated in Valles Marineris as Noachian-age bedrock-hosted phyllosilicate [Murchie et al. 2009b; Roach et al. 2009c] and Hesperian-age sulfate-enriched ILDs. The Siderikian era is less clearly separated from the Theiikian, as hematite and other ferric oxides occur as a diagenetic product with kieserite throughout Valles Marineris. The co-precipitation of hematite and kieserite and the large expanses of red hematite and other ferric oxides

(OMEGA and CRISM) and gray hematite (TES) show aqueous formation of ferric oxides is an important process that should be included in a mineralogic timeline. The Siderikian was proposed as the terminal alteration period on Mars, where anhydrous nanophase ferric oxides form by oxidation of the surface [Bibring et al. 2006]. While surface oxidation undoubtedly played a role in formation of the ferric oxides that comprise part of the global dust, comminution of hematite (and their sulfate-rich host rock) in Valles Marineris and Meridiani Planum may have also been a large source. It is possible that the Amazonian period has been even less mineralogically active, if the bulk of the ferric oxide in the dust is from abrasion of Hesperian-age hematite and not slow surface-atmospheric interactions.

We hypothesize that the sulfate-bearing ILDs in Valles Marineris are genetically related to the sulfate and hematite mineralogy in Meridiani Planum. The layered sulfates at Meridiani Planum have seen multiple generations of groundwater fluctuations alternately precipitating, recrystallizing, and dissolving evaporite minerals and precipitating hematite spherules [Squyres and Knoll 2005; McLennan et al. 2005; Squyres et al. 2006]. Diagenetic contacts similar to the one seen in the Burns Formation, Meridiani Planum may appear as sharp mineralogy contacts at HiRISE and CRISM scales.

Light toned deposits across Valles Marineris show a consistent mineral stratigraphy. Kieserite and crystalline red hematite are found in the lower bedrock exposures of basinal ILDs and PHS without ferric oxide phases are found in the upper bedrock exposures. The detailed mineral stratigraphy identified in Capri Chasma is repeated in Melas, West Candor, Ganges, Juventae, and Hebes Chasmata. These basinal chasmata may have formed from ancestral basins that predated the final, interconnected configuration of Valles Marineris [Schultz 1998; Lucchitta et al. 1994]. Regardless of how the ILDs originally formed and were enriched in sulfates, the several-km thick-

Table 4.1: Location of CRISM type spectra

| Mineral type spectrum | CRISM observation | Detector Location                                                                                                                               |
|-----------------------|-------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|
| Kieserite             | FRT000066F5       | L detector, 5x5 pixel average centered at (68, 258) divided by 5x5 average at (68, 39)                                                          |
| Polyhydrated sulfate  | FRT0000C564       | L detector, 5x5 pixel average centered at (150, 334) divided by 5x5 average at (150, 391)                                                       |
| Hematite              | FRT000066F5       | S detector, 5x5 pixel average centered at (64, 258) divided by 5x5 average at (64, 39). Coaligned with “kieserite” type spectrum in L detector. |
| Probable hematite     | HRS000044E6       | S detector, 5x5 pixel average centered at (30, 62) divided by 5x5 average at (30, 120)                                                          |
| Ferric phase          | FRT0000B385       | S detector, 15x15 pixel average centered at (149, 378) divided by 15x15 average at (149, 157)                                                   |
| Dust                  | FRT00009DF9       | S detector, 15x15 pixel average centered at (40, 32)                                                                                            |

ness of these ILDs would have inevitably promoted low temperature diagenesis of the lower, sulfate-bearing layers. The Theiikian was a period not only of sulfate precipitation but also of hematite formation. The similar mineral stratigraphy across Valles Marineris, in Aram Chaos, and in Meridiani Planum suggests regionally similar aqueous geochemistry and formation processes.

## Chapter 5

# Synthesis of sulfate distribution and formation mechanisms throughout Valles Marineris

### 5.1 Introduction

This chapter presents a synthesis of the mineralogy, stratigraphy, and aqueous geologic history of sulfate-bearing Interior Layered Deposits (ILDs) across Valles Marineris. This chapter summarizes the current literature on ILDs and sulfates within Valles Marineris together with new sulfate mapping and interpretations presented in this thesis. It can be broken into four main themes. Briefly, the themes are (1) how the ILDs formed, (2) how the ILDs became enriched in sulfate, (3) details of sulfate and ferric oxide distribution within each chasma, and (4) post-depositional weathering of sulfate.

In the first theme, I discuss the timing of ILD formation relative to the opening of Valles Marineris. Then I discuss the plausible ILD formation mechanisms with their diagnostic morphologies. A summary section presents the most probable ILD formation mechanism.

Next, I address how the ILDs may have been enriched in sulfates. This includes a

generalization of the sulfate stratigraphy in Valles Marineris and a discussion of the thermodynamic stability of various Mg sulfates. I present a general theory of ILD formation and sulfate-enrichment based on the results presented in these two themes.

The third theme details the sulfate and ferric oxide distribution by chasma. The sulfate stratigraphy in Ius and Capri Chasmata are covered in detail in Chapters 3 and 4 and are not presented again here. The mapping of the sulfate distribution in each chasma is an original effort. A literature review is also presented for each chasma, including previous research with MOC, HRSC, TES, OMEGA, and CRISM data.

The last theme in the chapter is a discussion of post-depositional weathering of sulfate. Chapter 2 discussed one ILD in East Candor Chasma that shows evidence for partial hydration of kieserite-bearing surfaces to a polyhydrated state. This theme describes other ILDs that show similar kieserite hydration and suggests it is a regional process caused by exposure to the atmosphere during periods of higher obliquity.

## 5.2 Timing of ILD formation

ILDs postdate Valles Marineris canyon formation [Lucchitta 2001] and chaotic terrain formation [Sowe et al. 2007]. Malin and Edgett originally interpreted ILDs as sedimentary fill in craters that predated the widespread Hesperian lavas [Malin and Edgett 2000b]. These sedimentary deposits would have been covered by Hesperian lavas and then cut by Valles Marineris formation. Subsequent work has shown that the superposition and relationships of volcanic wallrock and ILDs are not consistent with ILD formation before Valles Marineris formation [Lucchitta 2001; Weitz et al. 2001]. Part of this confusion is because ILDs against wallrock often dip at the slope of the wallrock, obscuring any clear stratigraphic relationships. Since we now know



that many ILDs are enriched in sulfates and other associated alteration products, additional geologic arguments can be made against ILD formation predating Valles Marineris formation. Any tectonic activity or physical erosion that would strip away overlying competent basaltic lavas would preferentially erode the much softer, altered ILD material, rather than leaving them to stand in relief, surrounded by eroded basaltic material. The very friable nature of the ILDs is indicated by their aeolian fluting, fine-grained composition, and lack of retained craters. Also, wallrock erodes into meter-scale boulders while ILDs weather into fine-grained talus with occasional boulders [Beyer et al. 2007]. The difference in erosional style is consistent with volcanic wallrock and sedimentary ILD compositions. Thus, mineralogic arguments can be added to the morphologic arguments for post-Valles Marineris ILD formation.

One hypothesis to explain how km-thick ILDs form in the basinal chasmata invokes ancestral basins that predated the opening of Valles Marineris [Schultz 1998; Schultz and Lin 2001]. These basins may have been preexisting impact basins or other depressions that formed during or after the bulk of Tharsis volcanism. As they fill with sediments (that will later be called interior layered deposits), the basins subside [Schultz 1998]. The isolated basins may have different sediment thicknesses and rates of subsidence. The sedimentation and subsidence are contemporaneous events. If the sediments are lacustrine in nature, the lake can be shallow but still accumulate a significant thickness of sediments. After a period of active basin subsidence, extensional stresses due to regional tectonic stresses opened a graben system that connected the previously isolated basins [Schultz 1998; Lucchitta et al. 1994]. Linear troughs like Ius and Coprates were created by that normal faulting; basinal chasma like Candor and Melas may have widened as a result [Schultz 1998]. Basin subsidence continued after graben formation. This can be best seen in East Candor Chasma, where the ILD deposits are in the southern, high-standing portion of the chasma [Schultz

1998]. These ILDs may have been deposited within an ancestral depression, while the northern, ILD-poor part of the chasma was lowered by subsequent graben extension [Schultz 1998]. Erosion of the ILDs and mass-wasting of wallrock have since made the basinal chasmata deeper and wider.

There are several aspects to consider when determining how sulfates formed within Valles Marineris. The first is to consider possible ILD formation mechanisms (section 5.3). Multiple formation processes are likely across Valles Marineris, as the ILDs vary widely in morphology, texture, and geologic relationships with nearby features. The ILDs host most of the sulfate in Valles Marineris. However, the mechanism(s) that originally formed them may not have been the same that enriched some ILD with sulfate. The second to consider is how surface and groundwater interacted with the ILDs, and either deposited sulfates or altered the pre-existing sulfates. Syngenetic and diagenetic alteration of sulfate-bearing ILDs was likely an important process in the redistribution of hydrated sulfates. The third aspect to consider is how physical erosion and exposure to the atmosphere has changed the sulfates (section 5.4).

### 5.3 Plausible ILD formation mechanisms

Of the many possible formation mechanisms for ILDs (e.g. [Lucchitta 1990; Lucchitta et al. 1992; Beyer et al. 2000; Chapman and Tanaka 2001; Komatsu et al. 2004; Nedell et al. 1987; Peterson 1981]), analysis of HiRISE imagery and mineralogic stratigraphy suggest that some mechanisms are more plausible than others. Below we briefly address the major formation mechanisms that may be active in each chasma. The majority of thick ILD deposits have features consistent with aeolian or lacustrine deposition due to their flat-lying layers, friable (fine grained) composition, and possible evidence for cross-bedding. Aeolian yardangs and fluvial channels (distinguished by

their curvature and spacing) are common on ILDs, [Weitz and Parker 2000], so even if aeolian or fluvial processes did not form the ILDs, they definitely have modified the ILDs since formation.

Not all sulfates deposits are within ILDs: one sulfate deposit in Ius Chasma has features characteristic of an evaporite basin. Chapter 3 discusses how that sulfate deposit is found within a closed basin at the lowest elevation within the chasma. It also has a bulls-eye mineral distribution interpreted to be from consecutive brine concentration to first precipitate polyhydrated sulfate and then kieserite. The sulfate-bearing layers line 400 meters of elevation within the basin. This deposit is unlike ILDs, which are mounds reaching kilometers in thickness.

The lack of one-to-one correlation between sulfate exposures and ILDs suggests multiple sulfate enrichment processes. One ILD may be volcanic in origin, and another ILD may be either volcanic or a spring mound deposit. These non-sedimentary interpretations are based on unique structural measurements of normal faulting and dipping layers in ILDs (e.g. [Fueten et al. 2005; Hauber et al. 2008; Stesky et al. 2006; Zegers et al. 2006] and similar papers). The interpretation of these structural measurements do not exclusively support a volcanic origin for the ILDs, as will be discussed below.

### **5.3.1 Aeolian or lacustrine deposition of dust and ash**

The majority of ILDs have features consistent with deposition and erosion by aeolian and/or lacustrine processes. The ILDs of the basinal chasmata (e.g. Capri, Melas, Candor, Ganges, Juventae) could all be formed this way. Fig. 5.1 shows a mosaic of basinal ILDs at the same scale to facilitate comparison. They share similar gross-scale morphology (mounds that are hundreds of meters to a few kilometers thick and tens to hundreds of kilometers long), are light toned, friable, erode into flutes or channels,

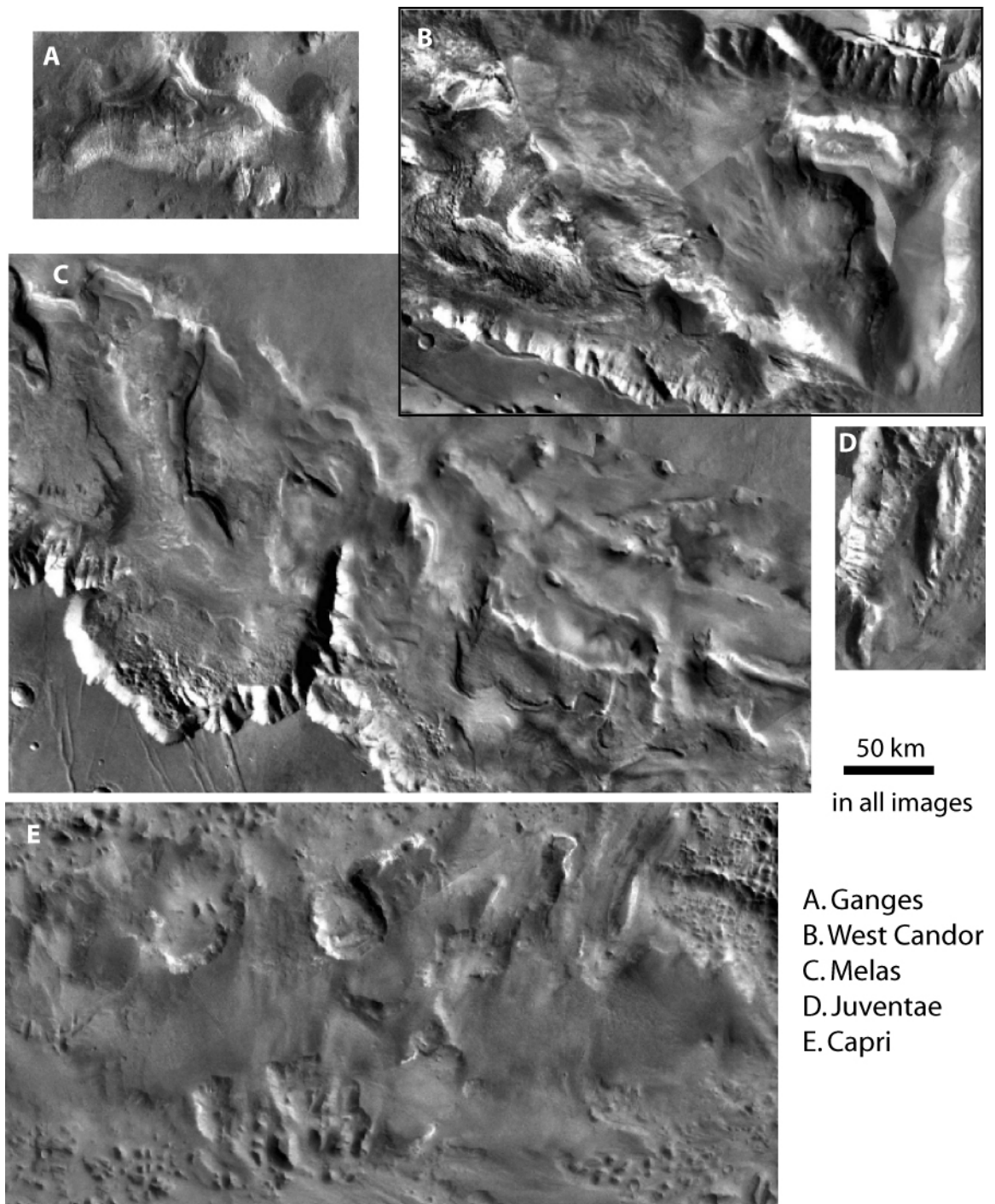


Figure 5.1: MDIM mosaic of basinal chasma with central ILDs - Ganges, West Candor, Melas, Juventae, and Capri Chasmata. All figures to same scale.

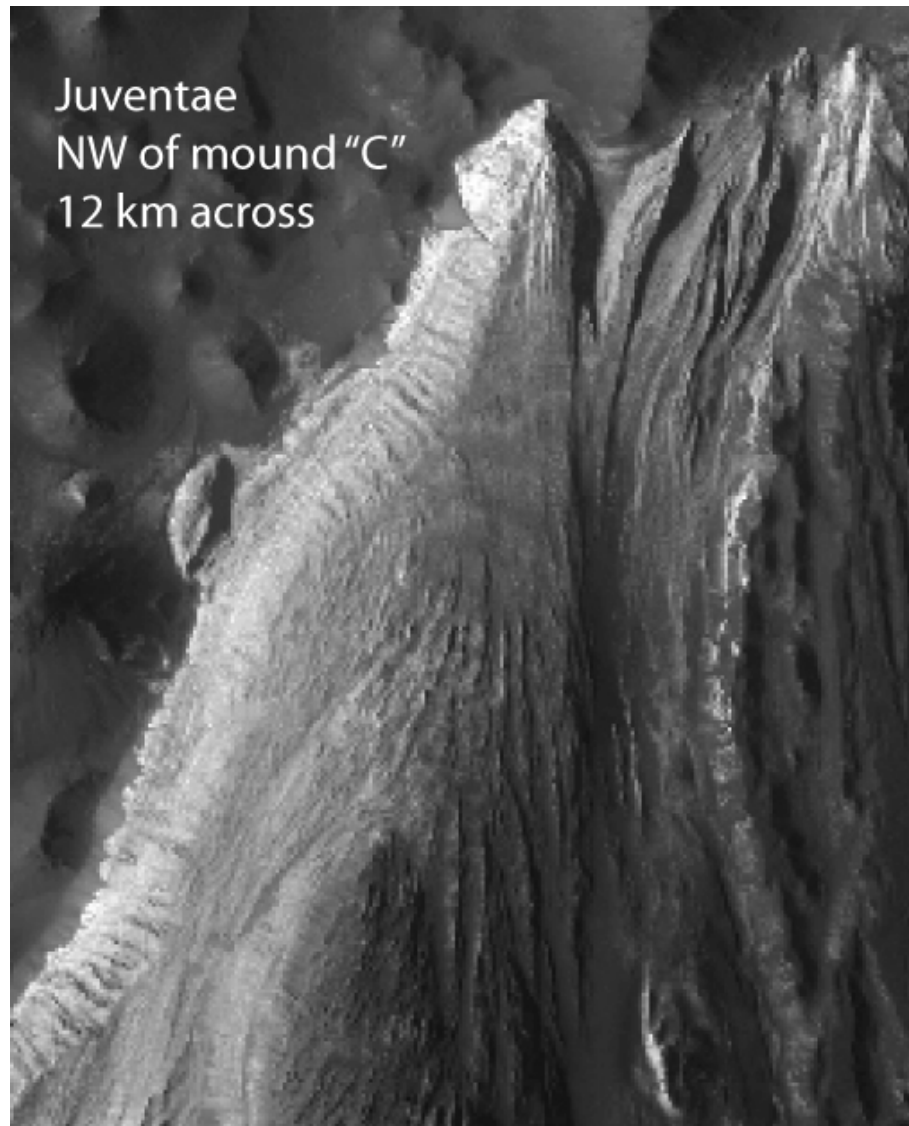


Figure 5.2: Detail of CTX image of Juventae Chasma, showing fluted texture of ILDs.

have layered or massive or both layered and massive bedding, and are found isolated from the chasma walls. Several ILDs have putative cross-bedding in HiRISE imagery [Beyer et al. 2007]. The friable nature of ILDs, seen from their low crater retention, rounded shape, and aeolian fluting, suggests a fine-grained, weakly to moderately competent material. They lack recognizable volcanic vents [Nedell et al. 1987] and are not landslide deposits from wallrock [Lucchitta et al. 1992, 1994].

An example of the bright-toned, fluted nature of most ILDs is shown in Fig. 5.2. This figure shows the NW portion of the “mound C” ILD in Juventae Chasma. The ILD is bright-toned and weathers into a mound shape. Its lower surfaces and the contact with surrounding canyon floor are always covered with darker mobile material, which is visible in the upper left of Fig. 5.2.

The floor of Valles Marineris is 3–9 km below the surrounding plateau, which makes the canyon system a net sink for aeolian materials. Seasonal dust storms and ash from nearby Tharsis volcanism would both be abundant sources of fine-grained material for building aeolian or lacustrine sequences. Tharsis volcanism is expected to generate more ash and transport it further than terrestrial pyroclastic eruptions [Wilson and Head 1994], and thick ash deposits have been recognized both east and west of the Tharsis province [Hynek et al. 2003]. Periodic cementation by surface or groundwater would be enough to generate potentially very thick deposits.

Both aeolian and lacustrine deposition of dust and ash can produce the finely bedded morphology seen in many ILDs. Sediment transport in a fluid (water or air) can form cross-bedding structures as sediment ripples prograde [Boggs 2001]. Cross-bedding features are interpreted in ILDs in Juventae [Komatsu et al. 2004; Catling et al. 2006] and Melas Chasmata [Dromart et al. 2007; Bourgeois and Som 2007] from MOC imagery. These researchers variously attribute the cross-bedding features to sub-ice volcanic ash flows, fluvial transport, aeolian transport, or a coincidence of

lighting and image resolution. The subtle differences between each type of deposition is difficult to assess from orbit. Tell-tale morphologic differences between the aeolian and lacustrine depositional methods, such as scale and number of cross-beds, grain size, and zonal differences in ripple thickness [Boggs 2001], are not visible at MOC and HiRISE scales. In situ investigation of ILD layering will be necessary to distinguish the relative importance of each depositional method.

Morphologic markers such as cross-bedding, scale of ripples, and gradational surfaces may only be visible at rover scales (mm to cm resolution). Alternatively, the morphologic markers may be more subtle than expected due to low temperature diagenetic reprocessing that can compact and recrystallize sulfate-bearing sedimentary sequences. The MER Opportunity found abundant evidence for cross-bedding and diagenetic fronts in sediments exposed in the walls of the Burns Formation, in Endurance Crater [Grotzinger et al. 2005; Grotzinger 2007]. The scale of cross-bedding was in the 1–10 cm range, and the scale of the albedo change at the diagenetic front in the Burns Formation was 10–15 cm [Grotzinger et al. 2005]. HiRISE imagery of Endurance Crater in Meridiani Planum shows layered materials in the crater walls but does not resolve cross-bedding or other features that would indicate a sedimentary process. Extending this to the ILDs in Valles Marineris, the absence of abundant cross-bedding observed in the layered materials should not be taken as evidence of a non-aeolian or lacustrine deposition, but as a lack of sufficiently high resolution imagery to test that morphologic indicator.

In the lacustrine model, water may be sourced from either precipitation and/or groundwater flow. While one is subaerial and the other subaqueous deposition, aeolian and lacustrine models represent endmembers in a continuum of depositional processes, involving varying water to sediment ratios. Lacustrine and fluvial activity alone were not sufficient to source all of the sediment in the ILDs; the channels draining into

Valles Marineris are too small to have carried enough sediments [Lucchitta et al. 1992]. Aeolian deposition is also necessary. There is a significant global reservoir of dust, and Tharsis volcanism may have contributed a large volume ash to the Valles Marineris region [Hynek et al. 2003]. Individual ILDs probably formed under a range of water to sediment ratios, and aeolian- and lacustrine-derived material are likely interbedded.

Aeolian materials collect in local lows within Valles Marineris and can then be lithified by groundwater, frost interaction, or precipitation. Aeolian deposits can have significant thickness; on Earth, the Loess Plateau in China can be up to 350 m thick [Liansheng and Zheng 2007]. However, ILDs are not loose loess deposits – their thermal inertia is consistent with coarse or partially indurated surfaces [Pelkey et al. 2003; Mangold et al. 2008b] and they lack the jagged, steep erosional morphology from shearing of unconsolidated angular loess particles. Additionally, cementation by sulfate is indicated by the sulfate spectral signature of many basinal ILDs.

Similarly, lacustrine deposits can be cemented by sulfate or hydrated silicate mineral precipitation. Cementation of aeolian dust or ash in Valles Marineris by sulfate-bearing groundwater has been suggested as the result of a global evaporation/precipitation model [Andrews-Hanna et al. 2007a,b, 2008; Murchie et al. 2009b]. This global hydrologic model calculates the effect of Tharsis volcano building and geothermal flux on the regional groundwater table over 400 Ma. It encompasses the lacustrine and aeolian deposition models, and can produce dirty evaporite deposits up to 5 km thick in roughly the same areas where the ILDs are located [Murchie et al. 2009b]. It predicts significant deposits in Tithonium, Ophir, Candor, Melas, Capri/Eos and Ganges Chasmata. This hydrologic model also explains the sulfate precipitates and hematite concretions in Terra Meridiani [Squyres et al. 2006; Arvidson et al. 2006]. If the hydrologic model is correct and there was sufficient aeolian or



lacustrine sediment available to lithify into km-thick sedimentary sequences, then the large ILDs in the “basinal” chasma may have been formed and enriched in sulfate by that process.

### 5.3.2 Evaporite

The sulfates in Ius Chasma (discussed in chapter 3) are not located in a unit traditionally classified as an ILD. The deposit is light toned and covers  $\sim 700$  m in elevation, but the surface expression of the sulfate-bearing material does not exceed 100 m in height. The deposit does not weather into a mound shape and lacks the fine to massive layering characteristic of other typical ILD deposits. It is interpreted as a closed evaporite basin, where concentrating brines precipitated first polyhydrated sulfate(s) and then monohydrated sulfate. Other evaporite minerals may also have been precipitated, but they are not distinguishable in VNIR spectra (such as halite and other dehydrated chlorides, or anhydrite).

Other linear chasmata, such as Tithonium or Coprates, do not show evaporite sulfate deposits with existing data. It may be because the Ius Chasma floor is at -4400 m, the lowest elevation of the linear chasmata, and so the focus of regional ponding and evaporation. Ius Chasma hosts the only evaporite ILD identified within Valles Marineris, although there is insufficient CRISM imagery of the Coprates Chasma floor to rule out evaporite deposits there; the Coprates floor is also at a lower elevation than most of the canyon system.

### 5.3.3 Volcanic

#### Types of Volcanic Features

The tuya is one class of volcanic structure that may be present in Valles Marineris. Tuyas, or subice volcanoes, are characterized by steeply dipping pyroclastic flows that form under ice, capped by a subaerial sequence of flat-lying ash and lava layers [Chapman and Tanaka 2001]. Sometimes a friable ash cone caps the flat-lying layers. The pyroclastic flows and pillow basalts are emplaced underwater and quickly cooled. These pyroclastic layers flow underwater until they reach the angle of repose [Chapman 2007]. These steeply dipping pyroclastic layers dip outward at  $\sim 30^\circ$  in a radial direction [Allen 1979]. A key measurement to identify tuyas in Valles Marineris would be to see an angular unconformity with steeply outward-dipping layers capped by flat-lying volcanic layers.

Tuyas are common in Iceland, where volcanic and glacial processes are both very active. On Mars, tuya structures would require hundreds of meters to kilometers of ice to form, since ice confinement of the volcanic structure is important to shape a tall, narrow edifice. In gross-scale morphology, tuyas are similar to ILDs: they are flat-topped, layered deposits with significant friable material and cusped margins and ridges [Chapman 2007]. However, more detailed morphologic study reveals differences. The ridges in tuyas are tephra or lava dikes, while ridges in ILDs are erosional features. Glacial erosional forms are common on tuyas, but only occasionally seen in ILDs (see sections 5.6.4 and 5.6.6 on Ophir and Candor Chasmata for more details about glacial erosion). Tuyas are composed of both tephra and competent volcanic layers, while the ILDs have a texture and erosional style consistent with friable, fine-grained material throughout.

The other class of volcanoes that may form ILDs are pyroclastic subaerial con-

structs. ILDs are more likely to be composed of pyroclastics than of basaltic lavas. The ILDs have a bright, fine-grained nature consistent with tephra, and they have erosional and morphologic differences from the Hesperian volcanic lavas in the wallrock (see section 5.2 for more details about differences between wallrock and ILDs). Sub-aerial volcanism is expected in magmatically active regions undergoing extension, such as Valles Marineris.

### **ILDs interpreted to be Volcanic**

Several ILDs have been suggested to be volcanic in origin because of dark deposits on their flanks or at their bases that could be pyroclastic materials or dark ridges on the crest that could be mafic dikes (e.g. [Chapman and Tanaka 2001; Komatsu and Strom 1990]). However, higher resolution imagery shows, in many cases, that the putative dark mafic dikes and volcanic ridges on the bright-toned ILDs are a partially eroded, indurated dark mantling material [Beyer et al. 2007]. The mantling material is suggested to be fine-grained since it erodes without breaking into boulders [Beyer et al. 2007]. The dark deposits at the base of ILDs would then be the erosional product of the remobilized mantling material. This mantling material is found throughout Valles Marineris at the uppermost surface, and may be regional ash fall from Tharsis volcanism. Thus, the presence of a dark mantle on top of an ILD and dark deposits at the base do not directly imply the ILD is volcanic.

There is only one ILD with a convincing argument that it is volcanic, the central mound in Hebes Chasma [Weitz 1999; Hauber et al. 2006, 2008]. The central ILD is surrounded by a “moat” of smooth floor materials that mask the total depth of the ILD. Light-toned material is found on the northern chasma wall on the other side of the “moat,” suggesting the deposit has been extensively eroded since formation [Weitz 1999]. HRSC digital elevation models have shown that the layers in the Hebes ILD dip

outward in all directions at  $10^{\circ}$ – $20^{\circ}$  [Hauber et al. 2006]. This has been confirmed by qualitative estimates of the dip of layers by tracing the exposure of dark and bright layers on the Hebes Mensa slopes in MOC imagery [Beyer and McEwen 2005]. The layers have a dip near  $20^{\circ}$ , and are consistent with either flat-lying or shallowly dipping layers (either radially inward or outward) [Beyer and McEwen 2005]. The volcanic construct is not likely a tuya, since the lowermost layers do not have the features of sub-ice deposition — they do not dip steeply enough ( $\sim 30^{\circ}$ ) and do not have an unconformity with overlying flatter layers. A sub-aerial pyroclastic deposit is consistent with the layering and texture seen in Hebes Chasma, and a pyroclastic eruption can create an edifice several km high within a closed basin.

Another ILD that might be volcanic is a 12 km-long mound-shaped ILD perched on the northern wall of Coprates Chasma (Fig. 5.19). It shows some morphologic similarities with other ILDs, but its location and structure indicate a different depositional process. The ILD's layers dip  $<20^{\circ}$  in the direction of the topographic slope of the wallrock, suggesting it is a drape that postdates chasma formation [Hamelin et al. 2008]. The layers also dip away from the central axis, which is consistent with a volcanic morphology. However, the central axis of the Coprates ILD has a fault structure that was active both before and during ILD formation [Hamelin et al. 2008]. There are two possibilities for its formation: subaerial volcanic ash deposits sourced from along a fault plane or spring deposits due to preferential groundwater flow and mineralization along a fault plane.

Neither of these ILDs have features consistent with tuyas, but may be sub-aerial volcanic constructs. As more detailed structural measurements are made with HiRISE or HRSC (High Resolution Stereo Camera) stereo-imagery (e.g. [Fueten et al. 2005; Hauber et al. 2008]), the number of ILDs with layering consistent with a volcanic or tuya origin may increase.

## Questions about HRSC structural analyses

Two ILDs have been convincingly argued to be volcanic in nature, and other ILDs may also have morphologies and structural relationships consistent with a volcanic origin. However, these volcanic interpretations are predicated on accurate structural analysis of the ILDs. A critical measurement in arguing that an ILD is sub-ice or sub-aerial volcanic in origin is the strike and dip of layering across the entire ILD. Most of the literature presenting structural analyses of ILDs are conference abstracts based on HRSC data. The limited space in conference abstracts creates some uncertainty as to how and where those structural measurements were taken and makes it impossible to reproduce the work. The paper presenting the general methodology of HRSC structural analysis [Fueten et al. 2005] reveals several issues with the method.

The first issue is that layers almost always dip in the same direction as the regional slope and strike parallel to the local surface exposure. This finding should throw a warning flag about the precision and robustness of structural measurements. This is true of both ILDs and of the nearly flat-lying chasma wallrock. Three measurements of the attitude of a traceable layer in the Northern Capri Chasma wallrock within 50 km of each other give dips of 14, 0.8, and 0.5° [Fueten et al. 2005]. In each case, the strike is nearly parallel to the local wallrock exposure, but the range of values in absolute strike among the three measurements is 45° [Fueten et al. 2005]. It seems the orientation of the local exposure of a bed strongly affects the structural measurements of the bedding plane. These measurements in Northern Capri Chasma are not an isolated occurrence: structural measurements of wallrock across Valles Marineris show a similar slight dipping of wallrock into the chasma [Fueten et al. 2005].

Also, if measurements are not collected over a range of aspects along a layer (across at least 90° and preferably 180° along a bedding plane), the resulting strike and dip

may not fully capture the attitude of the bed. With the exception of the West Candor Chasma analyses [Fueten et al. 2005], the HRSC literature does not provide enough information to assess the accuracy of the results. Incidentally, HiRISE structural mapping of West Candor confirms HRSC results [Okubo et al. 2008]. HRSC-based conference abstracts have reported outward dipping layers in Ophir [Zegers et al. 2006], southwestern Candor [Stesky et al. 2006], Ceti Mensa in West Candor [Fueten et al. 2007, 2008], Hebes [Hauber et al. 2006, 2008], and Northern Coprates [Hamelin et al. 2008]. A rare analysis shows flat-lying layering in an ILD; the broad ILD in southern Melas dips at less than  $6^\circ$  [Racher et al. 2009].

The outward dipping layers is a robust determination in places where HRSC layer attitude measurements are backed up by other analysis (e.g. Hebes as in [Beyer and McEwen 2005]). However, it should be kept in mind that outward dipping layers is not exclusively diagnostic of volcanism. The presence of vents, dikes, and mafic mineralogy may all be further evidence supporting a volcanic interpretation. Also, other geologic features besides volcanoes have outward dipping layers. A salt diapir is also characterized by radially outward dipping beds [Schultz-Ela et al. 1993].

### 5.3.4 Spring mounds

Spring mounds have been proposed as a source of ILDs [Rossi et al. 2008]. Spring mounds are composed dominantly of chemical precipitates from hydrothermal or groundwater flow onto the surface. Because the bulk of a spring deposit is precipitated material, on Earth spring mounds usually only reach tens of meters in thickness [Rossi et al. 2008]. Scaling this to the size of even small Martian ILDs, with 100s of meters of relief, is troublesome. Spring-cemented aeolian fines could increase deposit thicknesses dramatically and would be one way to form thick mounds as a ready source of cementing agents. However, then the spring mound model gets

intertwined with the aeolian/lacustrine model; the main source of water and precipitable solutes may be the same in spring and lacustrine settings, just with varying water/precipitate/transported sediment ratios. Additionally, we cannot trace the relative importance of groundwater and surface water flow in ILD formation. We prefer to consider spring mounds as mostly chemical precipitates, and thus do not consider them plausible as the only process creating ILDs. Spring activity may contribute to all of the above formation mechanisms and be an auxiliary source of dissolved compounds for sedimentary cementation.

We hypothesize that the Coprates Chasma ILD may be one such deposit. The central axis of the oblong, finely layered deposit is cut by a fault structure that was active both before and during ILD formation [Hamelin et al. 2008]. That fault may have been an ideal conduit for hydrothermal or groundwater flow to the surface, where a spring mound or fissure ridge could develop as sulfates and other (spectrally neutral) minerals are precipitated on the surface [Pentecost 2005]. Characteristic spring mound morphology includes sedimentary structures indicative of draping or progradation, textural variations over short distances, systematic compositional variations, and fault or fracture-controlled deposition [Rossi et al. 2008]. We propose a volcanic or spring mound formation mechanism for the Coprates Chasma ILD both because it has geomorphic similarities to those models and because aeolian or lacustrine deposition near the top of the wallslope are not viable processes. However, in situ microscopic and geologic investigation would be necessary to confirm this hypothesis. Other ILDs lack this axial faulting and are not perched on the wallrock like this ILD; thus, a spring mound origin is not preferred for all ILDs.

## 5.4 General sulfate stratigraphy and diagenesis

There are several possibilities for how some ILDs became sulfate-rich: the sulfate within ILDs may have been emplaced during the deposits' formation or may be a secondary enrichment after formation. The bulk of ILDs may be pyrite-rich ash, which weather to sulfates in the presence of atmospheric water vapor. However, sulfate is found as an evaporate on the floor and as a thin layered deposit on the side of the central ridge in Ius Chasma, suggesting that at least some sulfate is formed by surface groundwater processes, not in situ atmospheric alteration of ash deposits. Regardless of how sulfate originally concentrated in ILDs and not in surrounding features, there is evidence for transformation of sulfate within the deposits. Kieserite is generally found at lower elevations than polyhydrated sulfate [Mangold et al. 2008b; Quantin et al. 2005b], and often is stratigraphically below polyhydrated sulfate in an outcrop.

The general distinction between kieserite at lower elevations and polyhydrate at higher elevations could be due to changes in climate or groundwater discharge rate or due to post-depositional diagenesis. In sulfate-bearing ILDs where groundwater precipitation and diagenesis formed hematite, the same process could form kieserite from epsomite or other polyhydrated sulfates. The exact diagenetic temperature needed to convert from epsomite to kieserite in a multi-sulfate assemblage is complicated by mineral and groundwater chemistry. One study of a terrestrial seawater-composition brine finds epsomite would convert to kieserite between 25 and 40°C [Borchert and Muir 1964; Garrett 1995]. Figure 4.15 shows the equilibrium from the system  $K_2$ - $Na_2$ - $Mg$ - $Cl_2$ - $SO_4$  at 25° and 40° C. The epsomite/hexahydrite stability fields become the kieserite stability field with a temperature increase from 25° to 40° C. Assuming thermodynamic equilibrium processes, the changing stability fields with increasing



temperature would promote recrystallization and transformation to a different sulfate assemblage.

Assuming a geothermal gradient of about 10° K per km depth for the Valles Marineris region inclusive of the residual Tharsis volcanic thermal pulse [Schultz and Lin 2001; Hoffman 2001], diagenetic conversion to kieserite only requires burial to a few km. If the mineral assemblage started in the epsomite or hexahydrate stability fields on the surface of Mars and was then buried to several km, it would be expected to convert to kieserite from a thermodynamic standpoint. Since many of the basinal ILDs are several km thick, the kieserite stability field would be easily reached in the lower parts of those ILDs.

Several of the deposits, such as in Juventae and Melas Chasmata, have very sharp and traceable contacts between kieserite and polyhydrated sulfate. These contacts often have a tonal difference, but not unconformities or other physical disruptions. The lack of a gradational diagenetic boundary suggests the alteration process was not just burial and dewatering, but that coeval groundwater table fluctuations may have had a strong imprint in the resulting mineralogy.

Other ILDs show alteration between poly- and monohydrated sulfate within stratigraphic sections (e.g. eastern and western Candor) that can't be explained by diagenesis alone. One possibility is that there were multiple sulfate precipitation events, some of which may have occurred after early diagenesis converted the lower layers of the ILD to monohydrated sulfate. Perhaps the elevated temperatures at the bottom of thick ILDs could have prevented the monohydrate sulfate there from becoming polyhydrated during late stage flushing with more diluted brines. These brines could be sourced from a rising groundwater table, precipitation, or overland flow. Flushing by more dilute brines could have precipitated polyhydrated sulfate within the upper stratigraphic section but left the lower layers largely unaffected.

### 5.4.1 Non-sulfate bearing ILDs

Study of non-sulfate bearing ILDs is also instructive in understanding the processes that enriched some ILDs with sulfate. Two chasmata have ILDs without significant hydrated spectral features. The deposits may be devoid of sulfate, have trace amounts of sulfate not discernible in VNIR spectra, or be covered with enough dust to completely mask any spectral signature from the bedrock.

Ganges Chasma, in eastern Valles Marineris, has several  $\sim 10$  km ILDs exhibiting classic morphology: bright-toned and massive with a fluted erosional style. The mounds, which are directly to the east of the central, sulfate-rich mound, do not contain sulfate but one has an iron oxide component. These mounds are also within a few km of outcrops of unaltered mafics (high- and low-Ca pyroxene and olivine) on the floor of the chasma. The mounds in Ganges may truly lack sulfates or they may have a minor component of sulfates in a matrix covered with sufficient dust to mask their spectral signatures. Thermal inertia values are consistent with a very low dust cover [Putzig et al. 2005]. However, very thin dust coatings (10s of  $\mu\text{m}$ ) could obscure the VNIR spectral signature but not greatly affect the material's measured thermal inertia.

Similarly, the upper levels of the ILD stretching the length of East Candor Chasma are also spectrally neutral. The lower levels show kieserite with the occasional presence of hematite or another ferric oxide. The upper portion of the ILD has the same bright, fluted morphology as the kieserite-rich unit but does not have any hydrated spectral features. In this case, there is a thick dust cover on the upper surfaces [Putzig et al. 2005] which is likely obscuring any potential sulfate signatures. Whether or not bright toned ILDs that lack sulfate signatures in OMEGA or CRISM data are actually sulfate-poor is an open question that can be studied with in situ exploration.

In other parts of Valles Marineris, such as Capri Chasma, dust cover on the top of

broad ILDs masks the sulfate signatures from the bedrock. However, along scarps and steep slopes, sulfates and hematite are visible. The ILDs in Ganges discussed above do not show hydrated mineralogy along scarps or on steep slopes; in East Candor hydrated mineralogy is not visible on steeper slopes at the upper elevations.

These findings can be interpreted in two very different ways. The first interpretation is that the ILDs really are composed of sulfate-poor materials. It is possible that they are the primary dust and ash which comprise the bulk of the ILD and have not been altered to sulfate or been cemented by evaporite minerals. The second interpretation is that they are evaporite minerals, but are anhydrous or covered by an optically thick layer of dust which obscures their hydrated mineralogy.

If these ILDs are sulfate-poor while other ILDs formed by similar processes are sulfate-rich, then regional variations in aqueous geochemistry or in degree of alteration are implied. Connecting the secondary mineralogy with the primary mineralogy and morphology gives a window into the active geologic processes that drove the changing aqueous geochemistry. The close spatial association of unaltered pyroxene and olivine-rich outcrops in Ganges Chasma to bright-toned fluted ILDs without sulfate signatures suggests a lack of acidic surface water or groundwater altering the primary lithology and precipitating sulfates. Perhaps this region of Valles Marineris saw less acidic upwelling groundwater [Andrews-Hanna et al. 2007b, 2008] due its greater distance from the putative source of sulfur, the Tharsis volcanic complex.

The other possibility for ILDs lacking hydration signatures is that they host a spectrally neutral evaporite, like halite or anhydrite. Halite and anhydrite are often the dominant component(s) of terrestrial evaporite assemblages [Schreiber and El Tabakh 2000; Schreiber 1988; Borchert and Muir 1964]. For example, complete evaporation of terrestrial seawater would produce 90.0 % chlorides (78 % halite) where the total salt content is 35 parts per thousand [Borchert and Muir 1964]. The remain-

ing minerals precipitated are mostly sulfates with trace amounts of borates, nitrates, and phosphates. In more concentrated brines, like the Great Salt Lake, the total amount of chlorides produced is 92.2 %, with 20% total salt content [Borchert and Muir 1964].

Martian evaporites will undoubtedly differ from terrestrial continental or marine evaporites due to the different parent rock chemistry, activity of water, and amount of flushing. Geochemical modelling of weathering of synthetic Martian basalts shows that carbonates and sulfates dominate the alteration minerals produced [Tosca et al. 2005]. Cl is more abundant in marine evaporite sequences on Earth because Cl has become concentrated in the ocean over time. On Mars, such Cl concentration is not expected. Only in the very terminal stages of evaporation is Cl concentrated enough to precipitate chlorides [Tosca and McLennan 2006].

However, anhydrous phases may be volumetrically significant on Mars; gypsum or anhydrite is 15 to 30% of the mineral precipitates from a synthetic Martian basalt fluid, depending on if backreaction of products is allowed or not [Tosca et al. 2005]. If the Ca sulfate is present as only anhydrite, it could account for the large volumes of spectrally neutral ILDs in regions where other sulfates are found. Even though Ca sulfates are an expected product from thermodynamic modelling, they have not been confidently identified in Valles Marineris. One way to explain the lack of VNIR detection of Ca sulfate in Valles Marineris is that the Ca sulfate is present as anhydrite rather than gypsum. However, if the deposits in Ganges and East Candor are anhydrite, then a model needs to be created that explains the absence of other expected evaporite minerals. Anhydrite is probably only part of an evaporite sequence including other sulfates, chlorides, and possibly carbonates.

## 5.5 Summary of ILD formation and sulfate enrichment

When grouping ILDs based on their most probable formation mechanism, we find the majority have features consistent with aeolian or lacustrine deposition. A handful show evidence for evaporitic, volcanic, or spring mound morphologies. We have mapped the mono- and polyhydrated sulfate distribution in ILDs across Valles Marineris based on CRISM targeted and mapping observations. This mapping shows remarkable consistency in relative mineralogic stratigraphy and trends in mineralogy and deposit texture and erosional style. To first order, kieserite is often found in layers that are stratigraphically below polyhydrated sulfate-rich layers, especially in ILDs greater than several km thick. Hematite is often associated with kieserite in the ILD bedrock, and other ferric oxides are found in either ILD bedrock or in loose material at its base. This mineralogic grouping at the lowest exposed elevations of many ILDs in the broad basins within Valles Marineris leads us to hypothesize a regional diagenetic process emplacing hematite and kieserite in previously polyhydrated sulfate-bearing sedimentary deposits.

We propose a model for the aqueous geologic history acting on ILDs. ILD morphology indicates that they are likely formed by lacustrine or aeolian processes. The common mineral stratigraphy across most large basinal ILD indicates a regional diagenetic alteration of the hydrated phases. The ILDs are Hesperian-aged sedimentary deposits that occur over a range of elevations [Lucchitta et al. 1994]. They may have originally started accumulating in isolated ancestral basins and rifts predating the present Valles Marineris configuration [Schultz 1998; Lucchitta et al. 1994]. Their deposition and lithification processes could either have pre-dated or been coincident with original sulfate enrichment. As the basinal ILDs grew in thickness to a couple

kilometers, diagenetic alteration of sulfate in the lowest part of the sedimentary structure was unavoidable. The increased temperature (10s of degrees) and overburden pressure would convert polyhydrated sulfate to kieserite and promote low-temperature alteration of iron oxides, jarosite, or other Fe sulfates to hematite. Gradation of the upper portions of ILDs has since exhumed the lower, kieserite- and hematite-bearing layers. Physical erosion has also concentrated hematite and ferric oxide as a lag deposit at the base of many ILDs. In some locations, subsequent atmospheric exposure has rehydrated a thin rind of the kieserite to polyhydrated sulfates like starkeyite or epsomite.

The model of diagenetic hematite and sulfate formation within layered sedimentary layers proposed here is similar to previous models of gray hematite and sulfate formation in Valles Marineris [Weitz et al. 2008a], Aram Chaos [Glotch and Christensen 2005; Noe Dobrea et al. 2008], and Meridiani Planum [Squyres and et al. 2004; McLennan et al. 2005]. All three locations show morphologic and mineralogic similarities, and may have been created by an aqueous event spanning a quarter of the globe.

This model explains many of the thick ILDs located in the Valles Marineris basins, like Melas, Capri, and Candor Chasmata but cannot explain all sulfate-bearing outcrops. Several unique sulfate deposits in the linear troughs can be due to volcanic, spring mound, or evaporative processes, as is discussed below. The disparity in texture, degree of layering, and surface albedo in large sulfate-bearing ILDs across Valles Marineris does not necessarily imply that those ILDs formed by different processes. Variations in the bulk lithology of ILDs (more fines or more ash), in groundwater chemistry, and in the amount of groundwater interaction can all cause the observed differences within an aeolian/lacustrine evaporite model.

## 5.6 Sulfate Distribution by Chasma

This section summarizes the state of knowledge about sulfates in Valles Marineris on a chasma by chasma basis, and includes both research from others using CRISM, OMEGA, HRSC, and HiRISE data, and research completed as part of this thesis. This is a first cut at mapping of sulfates on the sub-kilometer scale across Valles Marineris and is by definition preliminary. This new mapping effort is based on CRISM and OMEGA spectral identifications by the author. It is a stand alone effort, but extends previous mapping efforts (e.g. [Gendrin et al. 2005; Gendrin et al. 2006]).

Of course, detailed mineralogic mapping is restricted by the locations of OMEGA and CRISM observations. Many CRISM targets were acquired in Valles Marineris because those locations were deemed mineralogically interesting in OMEGA analyses. Thus, there is a CRISM sampling bias toward sulfate deposits already imaged by OMEGA. Additionally, morphologically interesting places targeted by HiRISE are also acquired by CRISM as a “ride-along” effort. These HiRISE targets in Valles Marineris are often light-toned and layered, and analysis with CRISM data often reveals a hydrated mineralogy. An example is the hydrated silica-rich layers on the plains cut by Louros Valles, south of Ius Chasma [Weitz et al. 2007a]. Sometimes this hydrated mineralogy escaped detection in OMEGA data, perhaps because of a small areal exposure or because it was not yet acquired with higher resolution OMEGA imagery. As more CRISM and OMEGA data are collected, our understanding of the locations of sulfates will expand. Future work could include more detailed analyses of each chasma examining the specifics of sulfate mineralogy, texture, stratigraphy, elevation, and amount of atmospheric hydration. Ius and Capri are treated in detail in Chapters 3 and 4. Sulfate and iron oxide mineralogy in Tithonium, Melas/Coprates, Juventae, Ganges, East Candor, West Candor, Ophir, and Hebes Chasmata are all

summarized here.

There were several steps to creating this mineralogic map. First, kieserite and PHS detections in targeted and mapping CRISM data were mapped. In cases where the two units had distinct morphology or albedo in CTX or HiRISE data, the sulfate units were extended beyond the CRISM imagery to regions with similar morphology and albedo. Similarly, where the units were characterized by distinct elevations, MOLA gridded data was used to extend the unit to nearby deposits with a similar elevation (and morphology and albedo). OMEGA data was used to fill the gaps in CRISM mineralogic interpretation, but contacts between sulfates in OMEGA data is understandably less certain.

In the following subsections, a context map of each chasma shows the extent of kieserite (green), polyhydrated sulfate (blue), and mixed mono- and polyhydrated sulfate (yellow) VNIR spectral signatures from CRISM targeted and mapping observations and OMEGA observations studied as part of this thesis. Bright ILDs that do not show hydrated spectral signatures are colored with a white/gray pattern. The sulfate distributions presented here are broadly consistent with previous sulfate mapping (i.e. [Gendrin et al. 2005; Gendrin et al. 2006]).

The yellow color in each map can refer to: (1) intimate mixtures of kieserite and PHS, (2) kieserite and PHS alternating on too fine a scale to be resolved in regional mapping, or (3) a hydrated sulfate that cannot be determined as mono- or polyhydrated. Some OMEGA data shows the presence of a convex shape 2-2.4  $\mu\text{m}$  indicative of hydrated sulfates but instrumental noise and imperfect atmospheric removal around 2  $\mu\text{m}$  make it difficult to distinguish sulfate hydration state. If such areas are not also covered by CRISM mapping or targeted data, the ILD is colored yellow.

Southeastern Melas Chasma is an example of a large deposit determined to be



hydrated sulfate in OMEGA data (yellow) (Fig. 5.5). In some places, CRISM mapping and targeted data can resolve the hydrated sulfate as kieserite or PHS, so those regions are colored green or blue respectively. Those “hydrated sulfate” regions in Melas Chasma that are not covered by CRISM cannot be reliably classified as either kieserite or PHS with OMEGA data alone. However, it is probable that the sulfate stratigraphy in southeastern Melas is similar to that seen in southwestern Melas.

CRISM observations with evidence of hematite or another ferric phase (as determined in Chapter 4) are shown as white outlines. The ferric phase is located somewhere within the CRISM outline. CRISM observations included in this study that do not contain ferric phases are outlined in black. Mapping the surface expression of specific ferric phases, like the hydrated sulfate mapping, was not attempted. This is because the ferric phases do not have clear and consistent morphologies, elevation constraints, and albedos as the sulfates often do. Sulfates often have morphologic differences that allow them to be distinguished in CTX images that span the isolated CRISM identifications. Ferric phases do not have those same morphologic flags that allow interpretive mapping between CRISM observations. Appendix B lists all CRISM targeted observations included in this thesis that have sulfate or ferric phases present.

### 5.6.1 Tithonium

Western Tithonium Chasma is a linear trough with a very complicated central ILD complex ~40 km in length. Multiple mounds with different erosional textures and amounts of spectrally neutral dust/aeolian cover sit adjacent to each other. The sulfate mineralogy is no less complex — kieserite and polyhydrated sulfate are found alternating within the same deposit or grading from one to the other [Roach et al. 2008b]. This alternation is attributed to sulfate hydration state change. Section 5.7

discusses in more detail the evidence for kieserite hydration to polyhydrated sulfate.

The textures of the sulfate-bearing ILDs are also very interesting. Fig. 5.4 shows one example in HiRISE image PSP\_003158\_1745 which overlaps the northern part of FRT0000510D. A mixed kieserite/PHS deposit is found at this location. There is little topographic relief here and no apparent textural differences between the more kieserite-rich or more PHS-rich parts of this bedrock. The HiRISE image show this mixed sulfate-bearing bedrock region is weathering into 3–4 m blocks. Is the blocky fracturing due to bulk dehydration or rehydration of Mg sulfate? Dehydration of epsomite to kieserite would result in a volumetric change of 38%, and changes between other polyhydrated Mg sulfates would result in significant loss of water and thus change in the sulfate volume [Vaniman and Chipera 2006b]. Is the fracturing due to dehydration? Where is the kieserite and PHS physically located within the blocks?

The mounds in Tithonium Chasma have been suggested to be the expression of salt diapirism [Popa et al. 2007]. The sulfate-rich ILDs are elongated in the direction of the trough and are proposed to undergo diapirism when disrupted by extensional graben formation [Popa et al. 2007]. However, a detailed morphologic study of the ILD textures to see if diapir-related features were present (as in [Milliken et al. 2007]) was not attempted in Tithonium Chasma. A calculation to determine if there is necessary overburden and the scale of expected diapiric features (as in [Schultz-Ela et al. 1993]) would also be necessary to support this hypothesis. Also, the timing of the graben formation creating Tithonium Chasma and the ILD accumulation may be contemporaneous, or may be separated in time. Overall, a diapiric model is not supported in Tithonium Chasma from existing research, but further modelling and morphologic study may show that diapirism is active in sulfate deposits in Tithonium and other chasma. A better understanding of the volumetric concentration of sulfate or other salt within the ILDs would help numerical modelling of diapir movement.

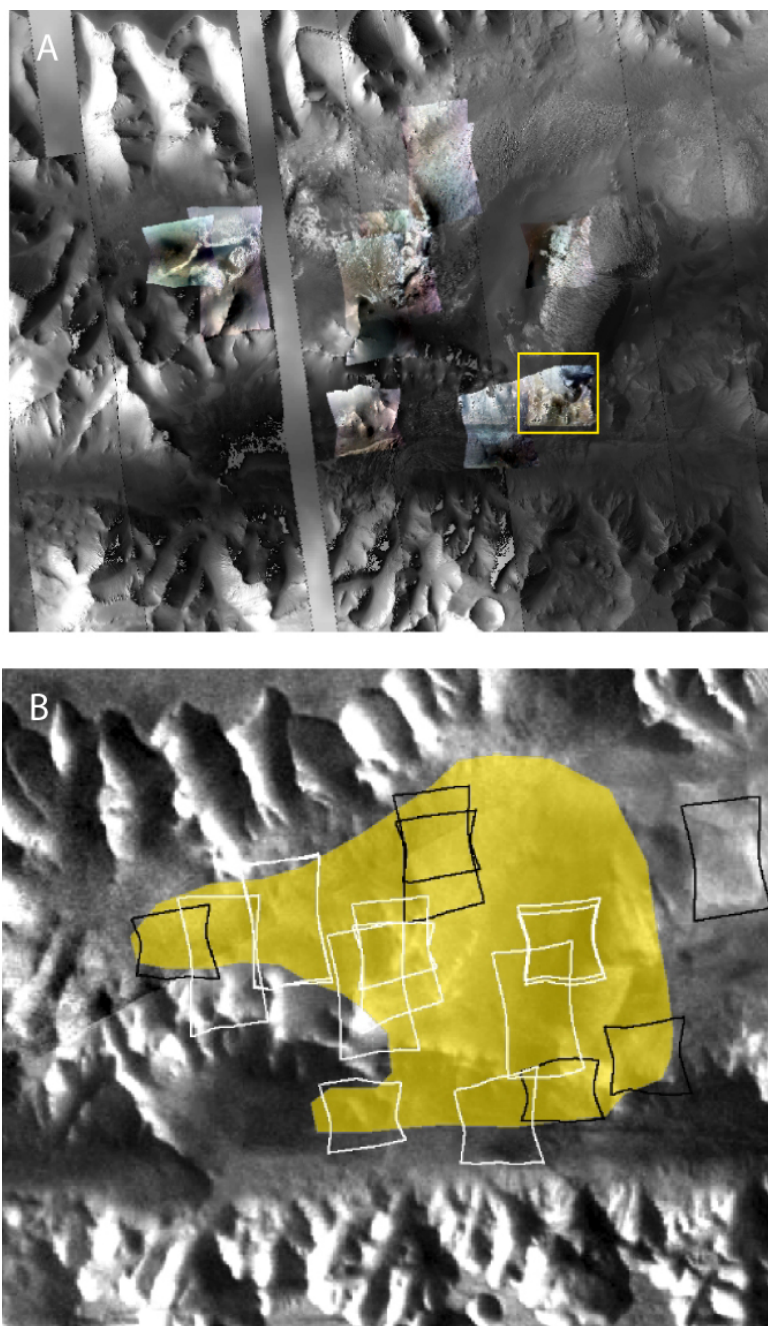


Figure 5.3: A. Tithonium Chasma targeted CRISM observations as false color RGB (2.5, 1.5, and 1.08  $\mu\text{m}$ ) over CTX mosaic over MDIM. Yellow box indicates location of Fig. 5.4. B. Yellow delineates location of mixed mono- and polyhydrated sulfates. White CRISM outlines have ferric phases, while black boxes do not.

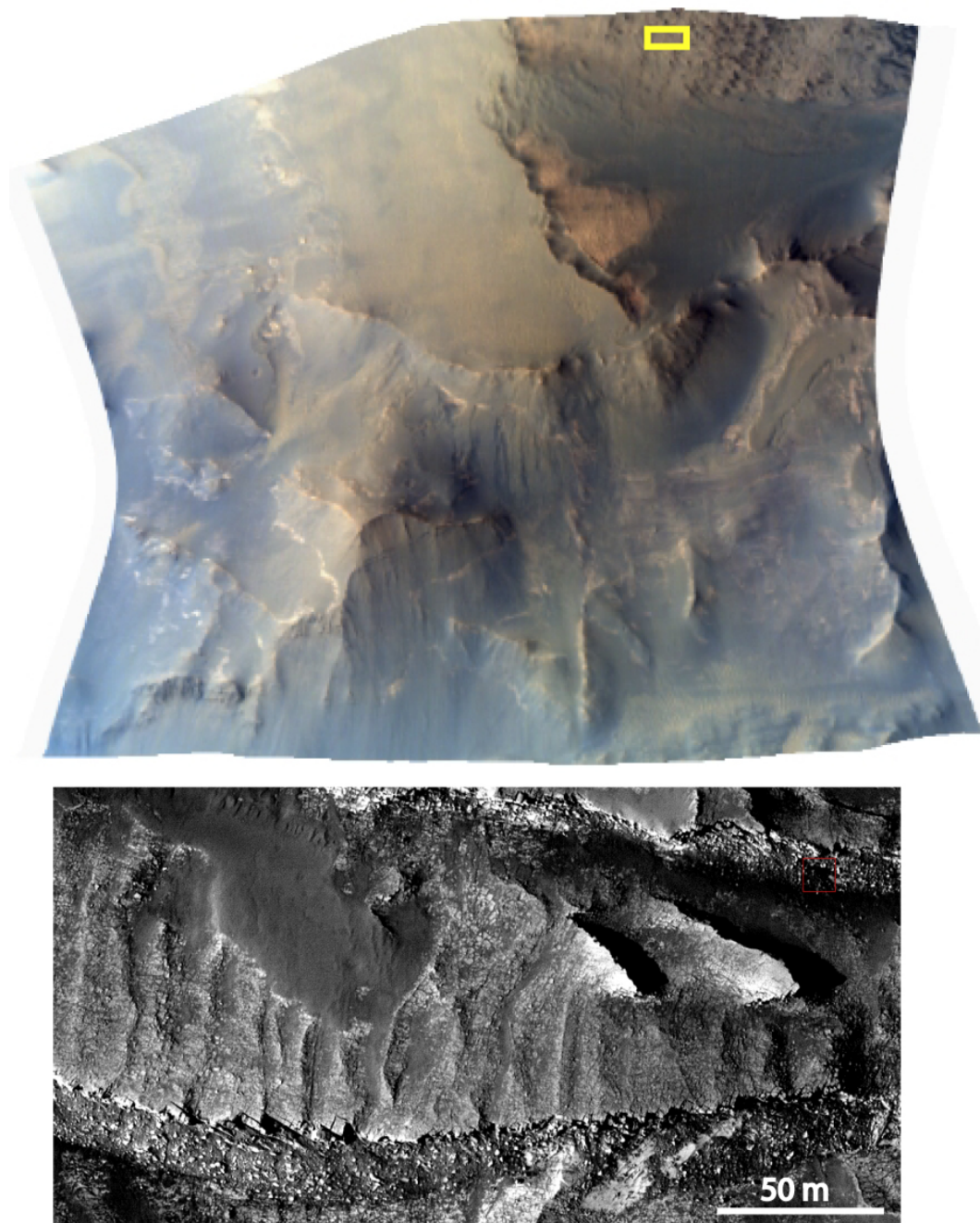


Figure 5.4: Top. Tithonium Chasma CRISM observation FRT00000510D in false color RGB (2.5, 1.5, and 1.08  $\mu\text{m}$ ). Yellow box indicates location of subset HiRISE image. Bottom: subset of HiRISE image PSP\_003158\_1745 over a mixed mono- and polyhydrated sulfate deposit.

### 5.6.2 Melas/Coprates

Sulfate identifications in southern Melas Chasma are limited because of the lack of targeted CRISM observations (note only four targeted observations to date in the entire chasma!). Great liberties have been taken in extending CRISM targeted and mapping detections of mono- and polyhydrated sulfates into regional units. OMEGA observations were also looked at, but were more useful as a presence/absence test than for mapping the distribution of specific sulfates. The 2.4  $\mu\text{m}$  absorption due to  $\text{SO}_4$  vibrations is present in OMEGA spectra. Spectra often show enhanced noise between 1.9–2.1  $\mu\text{m}$  due to inaccuracies in the atmospheric removal, so confident labeling of spectra as monohydrated or polyhydrated was impossible. These regions were colored yellow in the context map. Future CRISM observations will help determine the extent of sulfate units in this important chasma.

Fig 5.5 shows the key observation in Melas Chasma exhibiting PHS (pink in Fig. 5.5c) above kieserite (yellow in Fig. 5.5c). Examining the contact between the kieserite and PHS with HiRISE data (Fig. 5.6) reveals a difference in albedo, but not in texture, across the contact. Similar albedo banding is visible in the kieserite-only unit as well. Whether the albedo banding is indicative of a diagenetic boundary or is a spatial coincidence is an open question. In the absence of spectral information, there does not seem to be a large difference in erosional texture or amount of layering in the upper or lower units of Melas Chasma. Future CRISM and HiRISE observations will help constrain the mineralogic and stratigraphic relationships.

Extensive work has been done on the geomorphology of layered deposits within Melas Chasma (e.g. [Weitz et al. 2003; Quantin et al. 2005b; Pelkey et al. 2003]). Multiple landing sites within Melas Chasma have been proposed for in situ investigation of the layered deposits [Weitz et al. 1999, 2003]. A basin in southwestern Melas Chasma, adjacent to the southern wallrock, shows a closed topography, precipitation-sourced

valley networks, and sedimentary structures indicative of a lacustrine environment [Weitz et al. 2003; Quantin et al. 2005a; Dromart et al. 2007]. Ductile deformation (possibly diapiric) is also seen within the lacustrine basin [Weitz et al. 2003; Quantin et al. 2005b]. Aside from this unique closed basin, southern Melas Chasma also has layered deposits on a broad, raised bench that runs most of its length. This bench is enriched in sulfate, as is shown in Fig. 5.5 (also in [Gendrin et al. 2005; Quantin et al. 2005b]).

HiRISE image analysis has detected possible evidence of cross-bedding in Melas Chasma [Weitz et al. 2007b], but the structural relationship is not clear due to partial obscuration by overlying loose material. The southern bench in Melas Chasma is covered by one of the largest ILDs in the canyon system, yet there is still much to learn about the distribution of sulfate within the ILD, and the origin of both the sedimentary materials and the sulfate enrichment. Future HiRISE and CRISM imagery will be key to investigating this large and complex ILD.

### 5.6.3 Ganges

Like the other basinal chasmata, Ganges Chasma hosts a thick central ILD with a kieserite- and hematite-rich unit on the bottom and a hematite-poor, PHS-rich unit on the top (Fig. 5.7). The ILD unconformably overlies chaotic terrain [Komatsu et al. 1993]. Kieserite and hematite are present in the lower  $\sim 1.6$  km out of the 3.5 km total thickness of the central ILD [Sowe et al. 2008, 2006]. The transition zone between kieserite and PHS is characterized by a discrete layer at an elevation of about -1.9 km. Above that boundary, the upper unit shows weak PHS signatures. The deposit is finely layered (Fig. 5.7b and c) and shows typical aeolian fluting on its flanks.

Others have suggested the central ILD in Ganges is a tuya (subice volcano) based on its flat top capped by knobs and flanked by steep slopes [Lucchitta et al. 1994].



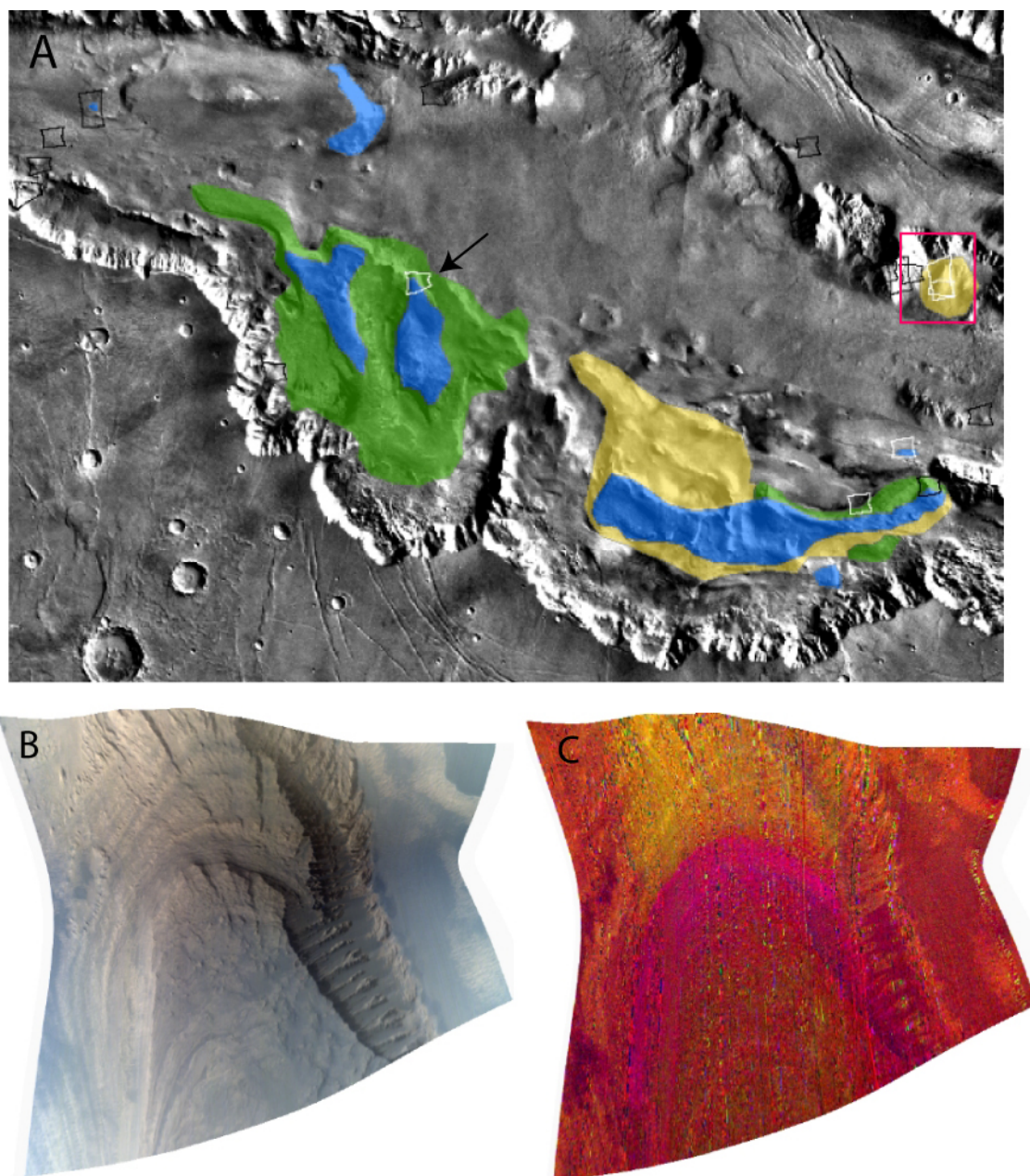


Figure 5.5: A. Location of sulfate and ferric oxides within Melas Chasma. White CRISM outlines have ferric phases, while black boxes do not. Black arrow points to FRT000062BD shown in B and C. Pink box indicates extent of Fig 5.19. B. False color RGB (2.5, 1.5, and 1.08  $\mu\text{m}$ ). C. R:1.9  $\mu\text{m}$  band depth, G:2.1  $\mu\text{m}$  band depth, B:convexity around 2-2.4  $\mu\text{m}$ .

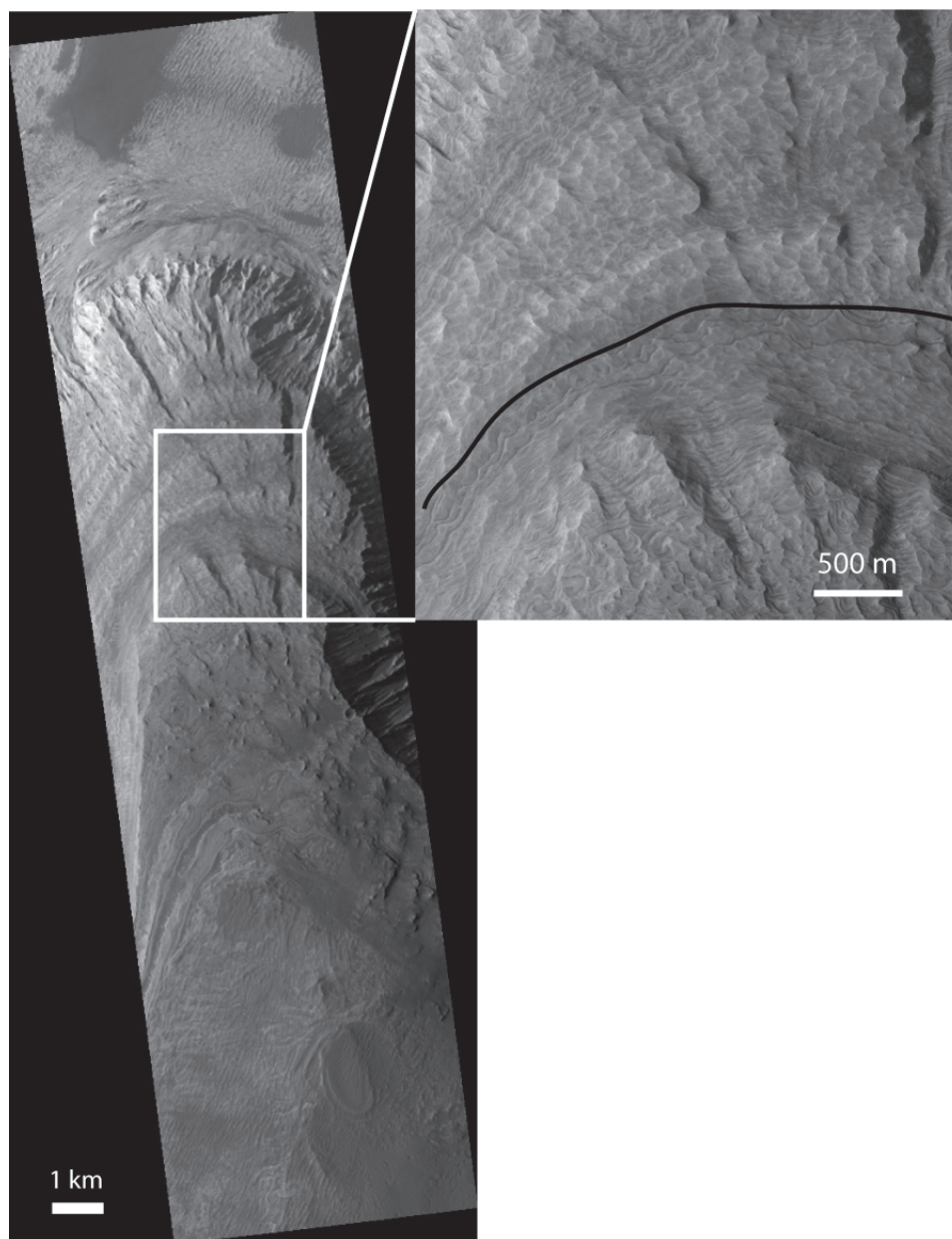


Figure 5.6: HiRISE imagery over contact between sulfates in Melas Chasma. Black line in inset shows approx. location of contact between upper PHS and lower kieserite.



However, structural analysis with HRSC has shown that the steep slopes are composed of relatively flat-lying layers [Sowe et al. 2008] and thus not consistent with the  $\sim 30^\circ$  slopes of sub-ice pyroclastic flows of a tuya (see section 5.3.3 for more details about tuyas).

Ganges Chasma is unusual among chasmata in Valles Marineris for its extensive olivine and pyroxene exposures on the floor. Eastern Capri Chasma also shows primary, unaltered mafic mineralogy, but those minerals are  $\sim 100$  km away from the sulfate minerals in the central ILD. In Ganges Chasma, the olivine and pyroxene exposures are within a few kilometers of the sulfate-rich ILD. Does the primary mineralogy in such close proximity thus indicate less flushing of acidic ground or surface water through Ganges Chasma? Or that more of the Noachian basement is exposed from under the spectrally neutral floor deposits in Ganges Chasma than in any other chasma? Is sulfate less abundant in the central ILD of Ganges Chasma than in other chasma?

There are also two 10-15 km wide, bright, spectrally neutral ILDs adjacent to the central, sulfate-rich ILD and the primary mafic exposures (Fig. 5.8). These ILDs have a similar morphology, texture, and albedo to ILDs elsewhere, but do not share the sulfate mineral signatures. Fig 5.9 shows the two spectrally neutral ILDs (HRL0000843E and HRL000089A2) with a kieserite and PHS bearing ILD (HRL0000633F). HRL0000633F is the long observation on the SW edge of the central Ganges ILD (shown as a white CRISM outline in Fig. 5.7 partially overlapped by the white outline for FRT0000A0F0). HRL0000943E appears very dusty, and so may not have hydrated spectral signatures because of a dust coating. However, HRL000089A2 appears as dust free as HRL0000633F, but does not show similar hydration features. Does the lack of visible sulfate absorption features indicate a lack of sulfate? The Meridiani Planum deposits are 40% sulfate but the OMEGA and CRISM spectra

show much weaker sulfate features than expected. One hypothesis is that the outer surface of the sulfate deposits are dehydrated and thus do not have a prominent sulfate signature [Arvidson et al. 2005]. However, if the central Ganges ILD is sulfate poor, does the lack of sulfate in an otherwise typical ILD indicate that ILD formation and sulfate enrichment were not linked processes?

#### 5.6.4 Ophir

Ophir Chasma has sulfates in a variety of settings - in floor units overlain by spectrally neutral landslides, in the lowest levels of a thick ILD, and as a drape from Ophir Mensa onto the SW wallrock [Chojnacki and Hynek 2008; Chojnacki et al. 2006]. Fig. 5.10 shows updated sulfate mapping from that previously presented [Chojnacki and Hynek 2008; Gendrin et al. 2005]. The excellent exposure of multiple sulfate deposits may be due to wind scouring effects; the thermal inertia of the Ophir Chasma floor is higher than other chasma [Chojnacki et al. 2006]. Sulfates in two locations — the west exposure of the easternmost ILD and the southern wall of Ophir Chasma — are discussed in more detail.

In one observation, sulfate is found in a curious geometry — it is present at the base of an ILD but not in the ILD itself. FRT0000BB63 covers the lower half of an ILD in Ophir Chasma as well as the floor materials (Fig. 5.11). Kieserite is found in bright competent material (possibly fragments of bedrock?) at the base of the ILD. The ILD may be sulfate-rich but covered with an optically thick coating of dust, or it may be spectrally neutral.

The ILD surface in Fig. 5.11 is also morphologically interesting. The fluted upper unit and smoother lower unit in the ILD have been interpreted to be caused by glacial scouring of the lower portion [Chapman 2007; Chapman et al. 2007; Thaisen et al. 2008]. The correspondence of kieserite with putative glacial features is tantalizing,

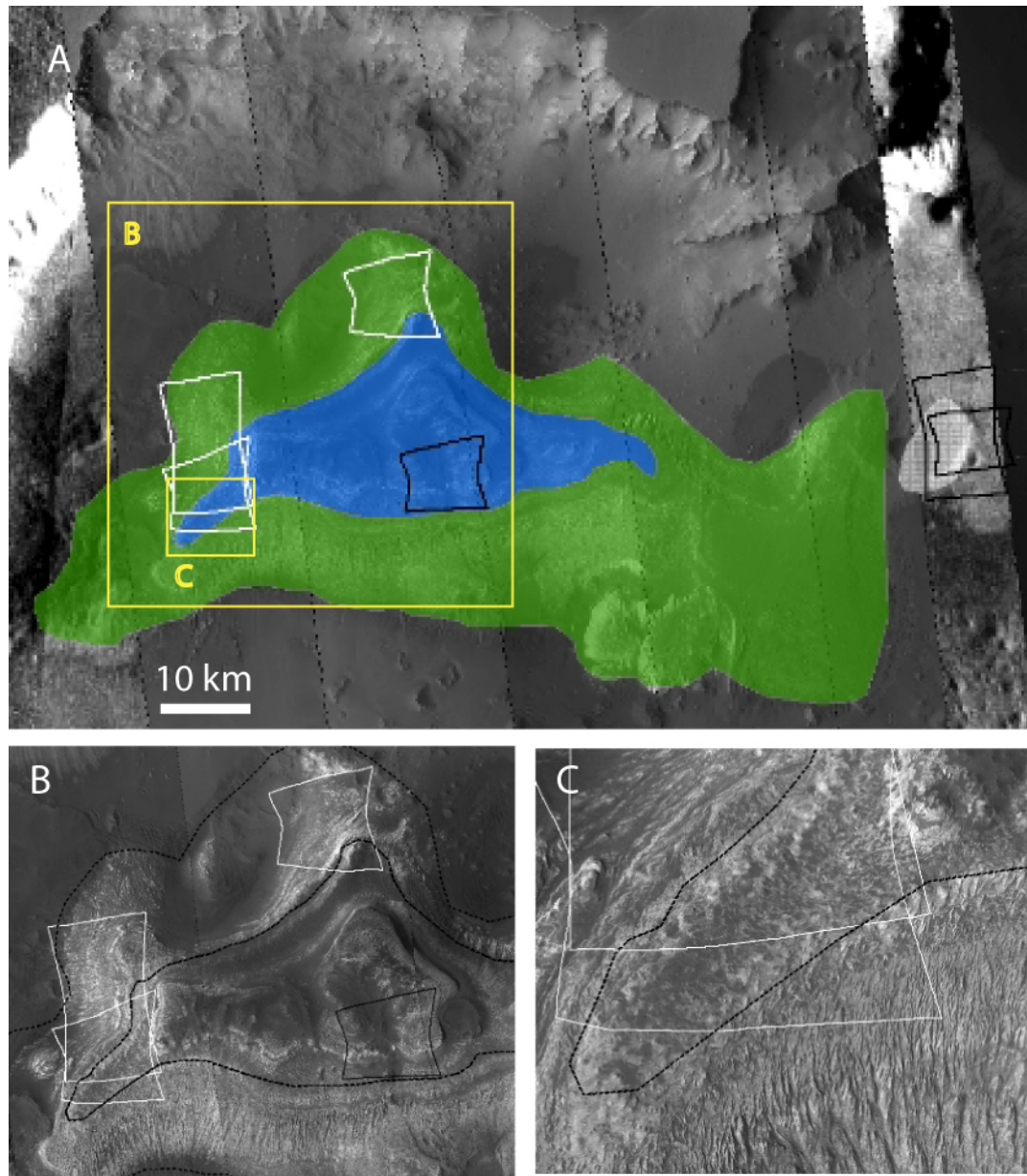


Figure 5.7: A. Location of sulfate and ferric oxides within Ganges Chasma. Targeted CRISM observations. White CRISM outlines have ferric phases, while black boxes do not. Yellow boxes indicate location of B and C, which are CTX mosaics of the ILD, showing textural and albedo differences between the lower kieserite and upper PHS. Dotted lines in B and C are boundaries between sulfate phases.

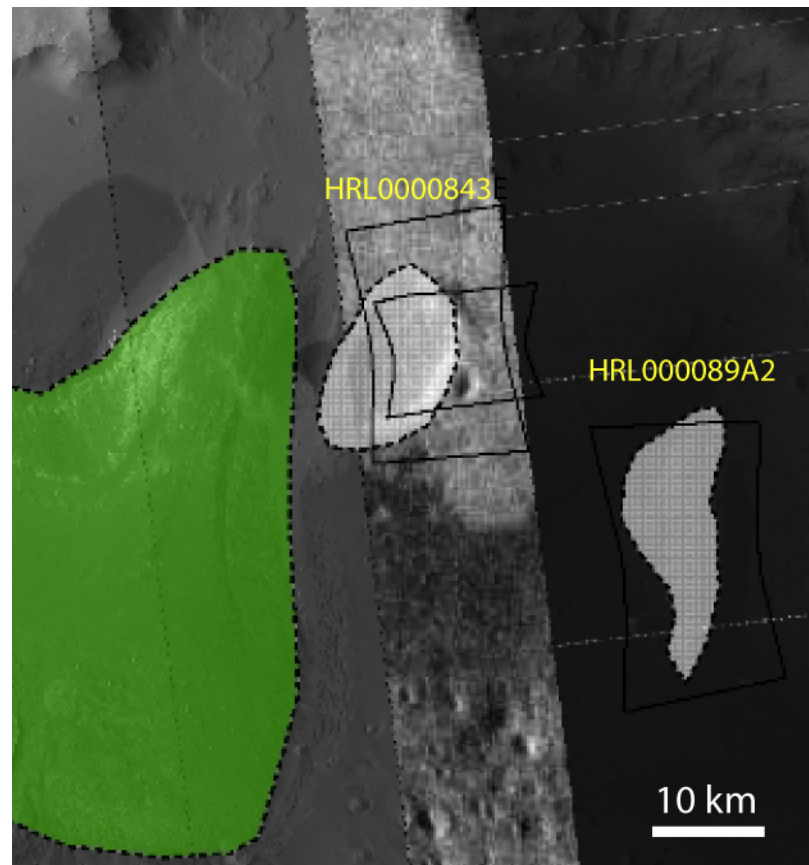


Figure 5.8: Spectrally neutral ILDs (white/gray pattern) adjacent to the sulfate-rich central ILD to the west. CRISM targeted observations HRL0000843E and HRL000089A2 shown in Fig. 5.9.

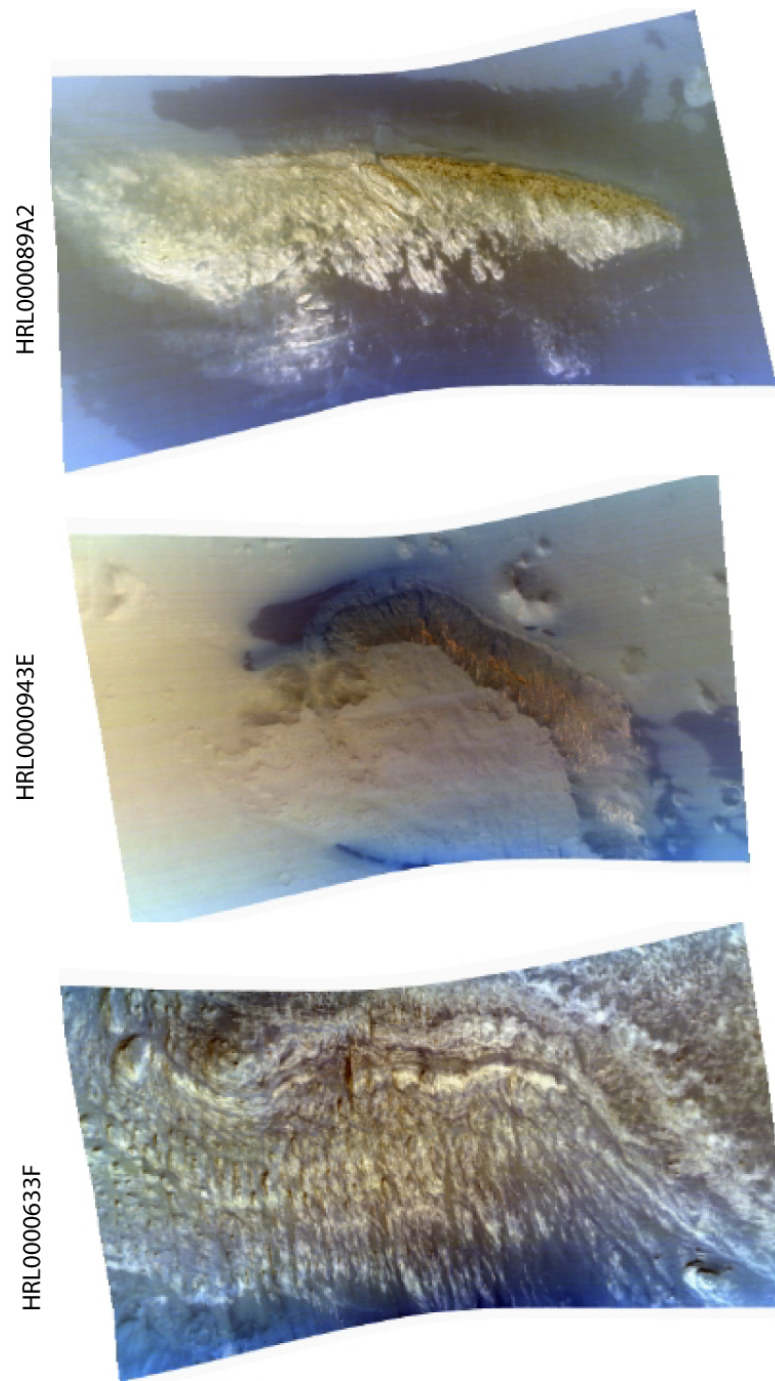


Figure 5.9: CRISM targeted observations in Ganges Chasma of ILDs lacking spectral signatures (HRL0000843E and HRL000089A2) and having strong kieserite signatures (HRL0000633F). HRL0000943E appears very dusty; HRL000089A2 is at least as dusty as HRL0000633F but still spectrally neutral.

and may indicate glacial meltwater to be one source of water important in the regional geochemistry and sulfate formation.

The sulfates and hematite draped on the southern wall of Ophir are in layers that are continuous in dip with those within the Ophir Mensa and are interpreted to be the erosional remnants of Ophir Mensa when it originally filled all of southern Ophir [Weitz et al. 2008a; Chojnacki and Hynek 2008; Chojnacki et al. 2006]. Very strong ferric signatures are also found within these deposits [Murchie et al. 2009b], which have since been determined to be strong red crystalline hematite (see Chapter 4).

Strong gray hematite signatures have also been seen in the same location [Christensen et al. 2001; Weitz et al. 2008a]. The gray crystalline hematite is concentrated at the base of ILDs in semi-indurated dark deposits or in ILDs partially covered by dark debris, and is not seen in the clean, bright ILD slopes [Weitz et al. 2008a]. Not all dark debris has gray hematite spectral signatures. The hematite may have originally formed as part of the ILD but have since eroded out and collected as a lag at the base [Weitz et al. 2008a]. The hematite volume in the ILD may be too small to be spectrally visible; concentration in lag deposits or on lower albedo surfaces may be necessary to resolve the hematite.

### 5.6.5 East Candor

East Candor Chasma has extensive layered deposits, especially in its southern part. The trough has a relatively simple stratigraphy and consistent ILD morphology and mineralogy along its length. A small ILD ( $\sim 15$  km across) shows evidence for kieserite hydration to a polyhydrated Mg sulfate [Roach et al. 2007a, 2009b], but the clear layering and erosional morphology of that deposit is very different from the main ILD.

Fig. 5.12 shows the extent of the southern ILD. Much of the upper layers are



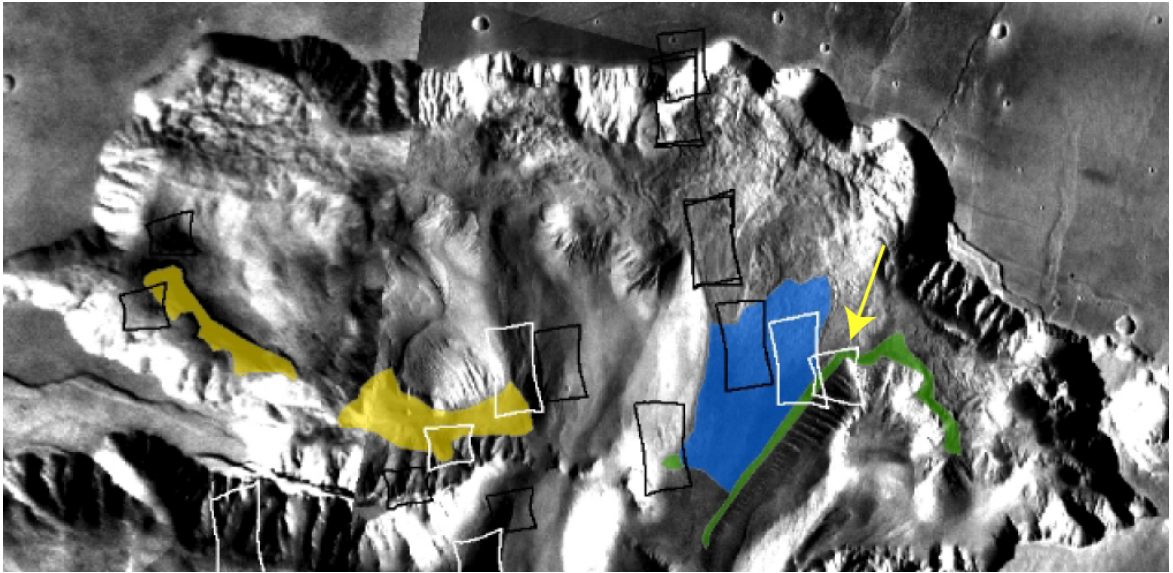


Figure 5.10: A. Location of sulfates and ferric oxides within Ophir Chasma. White CRISM outlines have ferric phases, while black boxes do not. Yellow arrow indicates location of FRT0000BB63 shown in Fig. 5.11.

spectrally neutral (white/gray pattern in Fig. 5.12) while the lowermost exposures of the ILD are kieserite-rich. There is also a difference in erosion style in the kieserite-rich ILD materials (Fig. 5.13). Sulfate-bearing materials weather into a fluted morphology with a smooth texture. The thermal inertia (and visual appearance) of the upper portion of this ILD is consistent with a thick dust cover [Chojnacki and Hynek 2008] that may also mask the underlying erosional fluting. It is possible that the entire ILD may be sulfate-rich, which is consistent with the ILDs in West Candor that show sulfate signatures over all elevations.

The kieserite on the chasma floor at the base of the northern chasma wall (Fig. 5.13) may have once been contiguous with the kieserite to the south, but was down-dropped by graben extension in the northern part of the chasma. Graben extension is popularly believed to have widened East Candor Chasma [Lucchitta et al. 1994; Peulvast et al. 2001]. Knobs of light toned material in the central part of the chasma

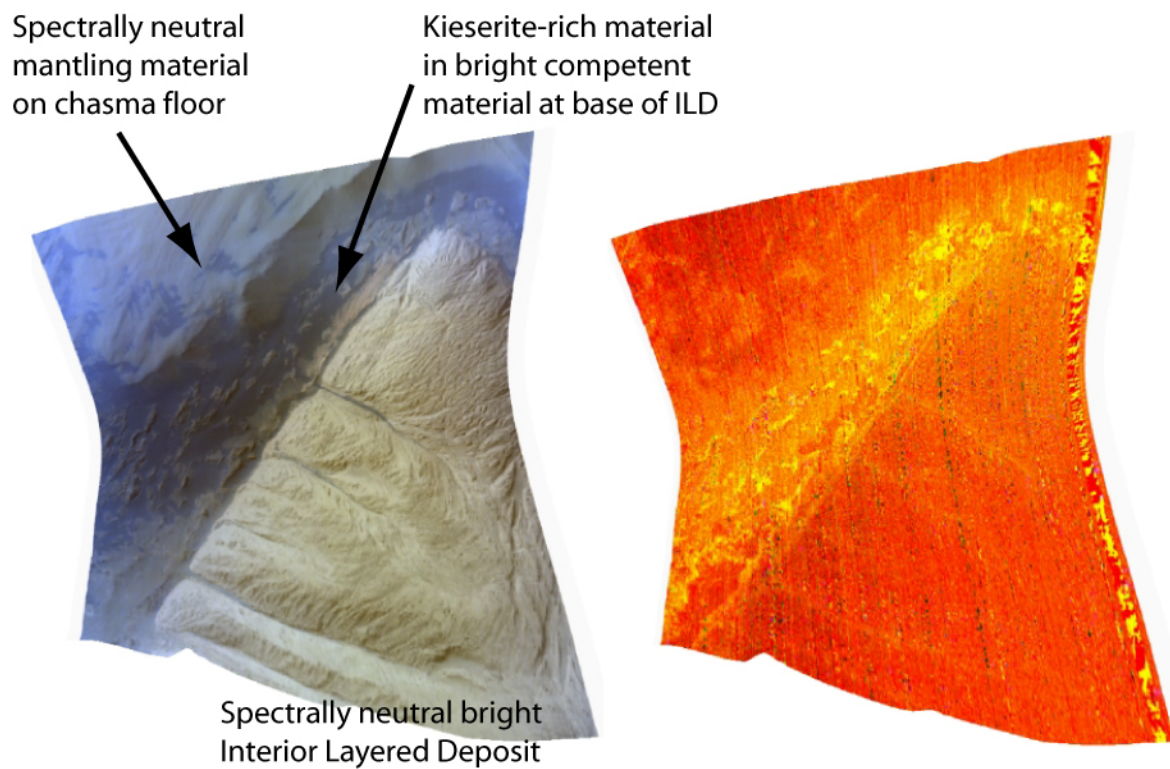


Figure 5.11: A. CRISM FRT0000BB63 in Ophir Chasma showing kieserite in bright competent material at the base of an ILD, but not in the deposits' bulk. A. False color RGB (2.5, 1.5, and 1.08  $\mu\text{m}$ ). B. R:1.9  $\mu\text{m}$  band depth, G:2.1  $\mu\text{m}$  band depth, B:convexity around 2-2.4  $\mu\text{m}$ .



seem to connect the two sulfate deposits, but the knobs do not have hydrated spectral signatures. This could be due to obscuration by dust or sand, which is visibly more prevalent in the center of the chasma.

Probable ferric oxide is found associated with kieserite in bedrock of ILDs in East Candor Chasma. Gray crystalline hematite is also found in smooth, dark material at the base of the kieserite-rich ILD in the southern half of the trough [Weitz et al. 2008a]. The association of gray hematite at the base of ILDs and ferric oxide within the bedrock of ILDs suggests an erosional process may be linking the two (see Chapter 4 for more details).

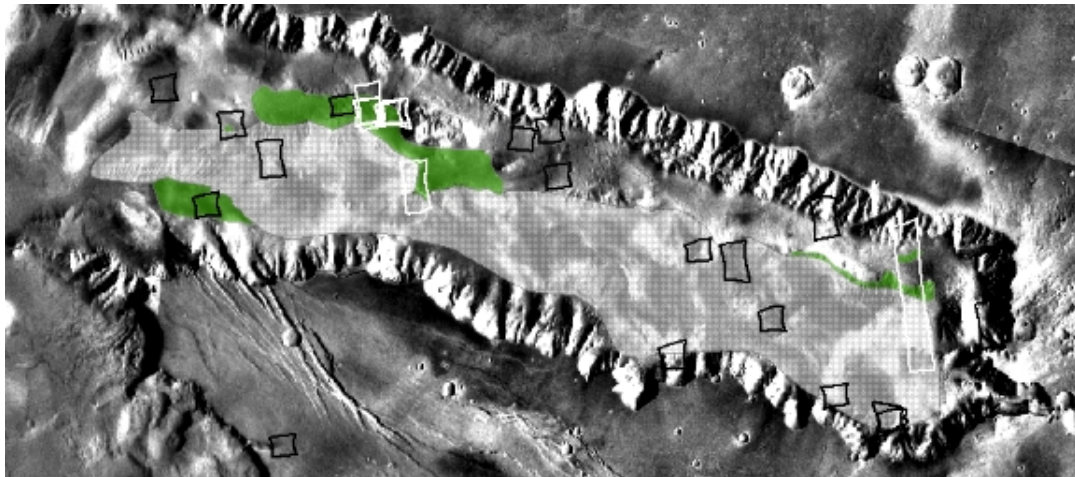


Figure 5.12: A. Location of sulfate and ferric oxides within East Candor Chasma. White CRISM outlines have ferric phases, while black boxes do not. Long observation in the east is described in Fig. 5.13.

### 5.6.6 West Candor

West Candor is a thick, well-exposed central ILD. The deposit is spectrally dominated by monohydrated sulfate and dust, with discrete layers of PHS in the upper section [Murchie et al. 2009b]. Interbedded in the layered deposit are monohydrated sulfate-bearing basaltic sands, which erode out of the ILD into dark toned dunes [Murchie

HRL00004F38

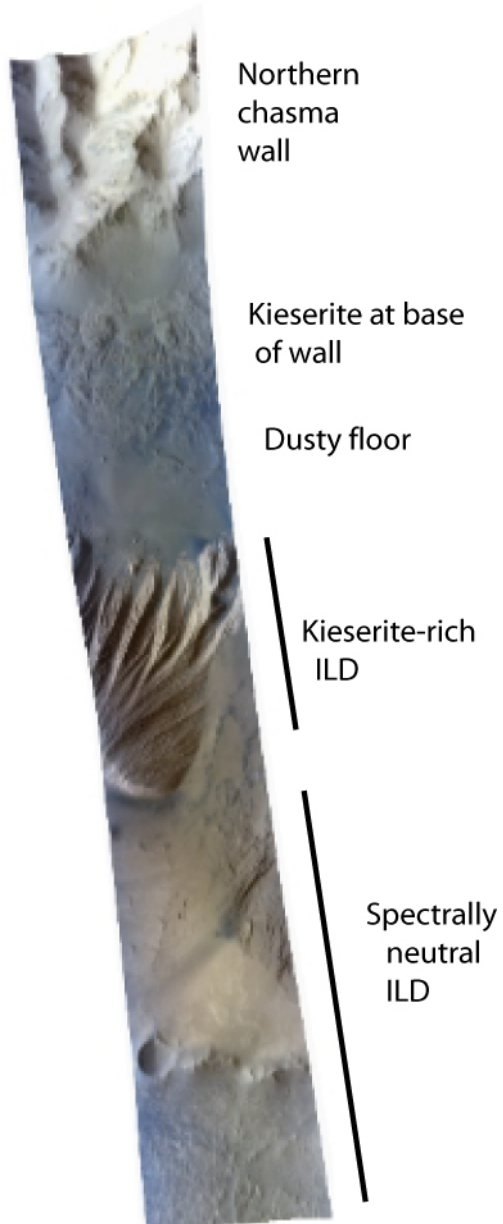


Figure 5.13: CRISM exceptionally long HRL00004F38 in East Candor Chasma.

et al. 2009b].

The PHS-bearing unit are generally, but not always, at higher elevations than the kieserite-bearing units. The PHS layers are at 2450 m and 2200 m elevation, and are within 400 m of those elevations over 70 km in distance [Murchie et al. 2009b]. However, PHS are also found at the base of Ceti Mensa at 0 km and at -2 km elevation. Fig. 5.14 shows the sulfate-rich extent of the central ILD in yellow, indicating mixed poly- and monohydrated sulfate exposures at the scale of this image. The deposits are interpreted to be lithified sequences of aeolian dust and sand, cemented by sulfate evaporites. Diagenesis during formation could have precipitated the crystalline hematite and modified sulfate phases to kieserite [Murchie et al. 2009b].

Hematite is associated with most of the kieserite exposures. Color analysis of Viking orbiter data first suggested high red hematite concentrations in West Candor [Komatsu et al. 1993]. CRISM finds red crystalline hematite is concentrated in channels in the fluted kieserite-rich ILD, while TES detections of gray crystalline hematite are located at the base of the ILD. If the red hematite is from abrasion of gray hematite, is it removed from the ILD base by winds but preserved in the sheltering ILD channels? Locations with gray hematite also show VNIR features indicative of an unidentified ferric phase. The VNIR features cannot be from gray hematite, but may be from other ferric oxide or sulfate. These deposits undoubtedly host a complex mineral assemblage, and other ferric oxides or sulfates would be expected.

There is abundant evidence of ductile and brittle deformation of the ILDs after deposition. West Candor has very intricate sulfate-rich layering, which has been folded and faulted in places [Weitz et al. 2007b]. The dip of many of these beds is not horizontal [Weitz et al. 2007b; Beyer et al. 2007], suggesting ductile deformation of the layered material after deposition. This deformation may be associated with further extension in Valles Marineris [Beyer et al. 2007]. Many fractures in West Candor

ILDs have lighter-colored halos, which could be due to mineralization by fluid flow along those fractures [Okubo and McEwen 2007].

The different erosional processes acting on ILDs may be most evident in West and Central Candor Chasma. The ILDs in Central Candor show meter-scale ventifacts from erosion within a dominant wind regime [Beyer et al. 2007]. The scalloped morphology is caused by aeolian erosion [Beyer et al. 2007] but may also be shaped by diagenetic fluid flow prior to aeolian stripping [Beyer et al. 2007; Okubo and McEwen 2007]. Like Ophir Chasma, there are erosional features on some ILDs that are attributed to glacial processes [Thaisen et al. 2008]. Putative glacial features identified include glacial moraines, hanging valleys, and troughs with a parabolic cross-section [Thaisen et al. 2008]. However, that study and others also find abundant evidence for fluvial activity, often on the opposite sides of ILDs with glacial features. Perhaps the fluvial and glacial features were formed at different times, or perhaps alternate explanations, such as a combination of ductile deformation, diagenesis, and aeolian erosion, need to be considered.

### 5.6.7 Hebes

Hebes Chasma is an isolated, closed basin north of the main canyon system. The origin of the thick ILD mound in the center of the closed basin is an enigma [Pelkey et al. 2005; Weitz 1999]. Most of the central ILD is spectrally neutral, with the only sulfate outcrops on the chasma floor and at the lowest elevations of the ILD. A volcanic origin for Hebes is discussed in section 5.3.3. The layering dips at less than  $10^\circ$  in a radial direction [Hauber et al. 2008; Beyer and McEwen 2005].

The sulfate-bearing layers are at the lowest stratigraphic level in Hebes Mensa, at very low elevations within Hebes Chasma. Sulfate is found on the chasma floor at an elevation of -3400 m to -1600 m, while the central ILD reaches +3400 m in eleva-

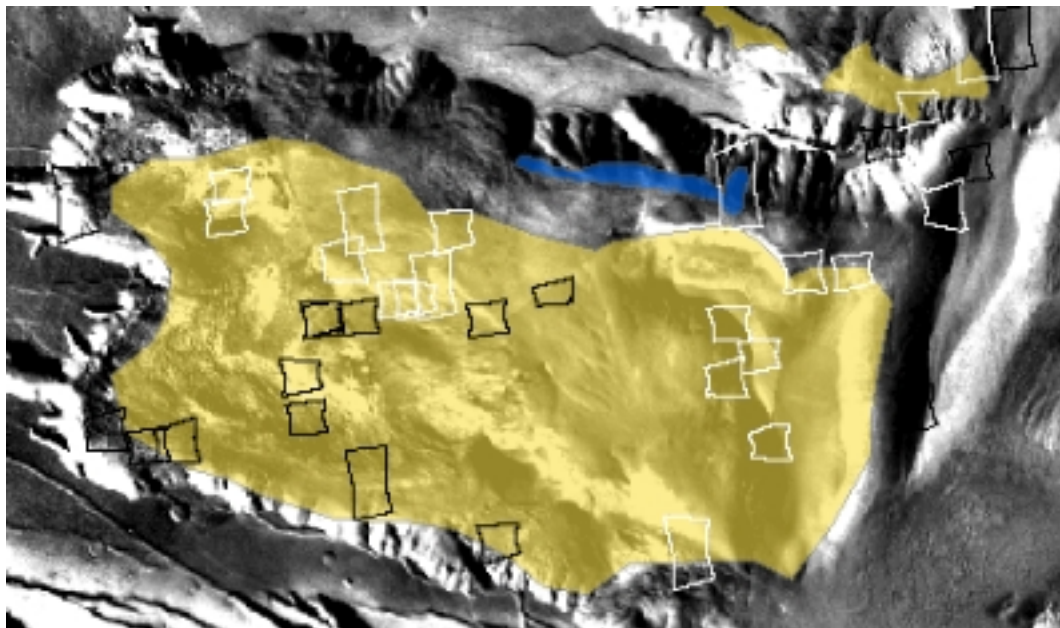


Figure 5.14: Location of sulfate and ferric oxides within West Candor Chasma. White CRISM outlines have ferric phases, while black boxes do not.

tion. The lowest elevations within the chasma floor are covered by dark, presumably basaltic sand dunes. Sulfate may be beneath those dark dune, but is not exposed for observation. The distribution of sulfate in the lowest portions of the chasma and not in the bulk of the central ILD suggests sulfate formation via surface or groundwater circulation and not as a direct consequence of the volcanic structure. The source of sulfur for sulfate precipitation may be from this volcanic construct or from a more regional volcanic sulfur inventory.

### 5.6.8 Juventae

Juventae Chasma consists of four separated mound-shaped ILDs along its western edge [Catling et al. 2006]. The ILDs unconformably overlie chaotic terrains [Komatsu et al. 1993]. The geography of the ILDs within the chasma is a little different from other chasmata — mound “A” sits on the wallrock and the top of mound “C” is higher

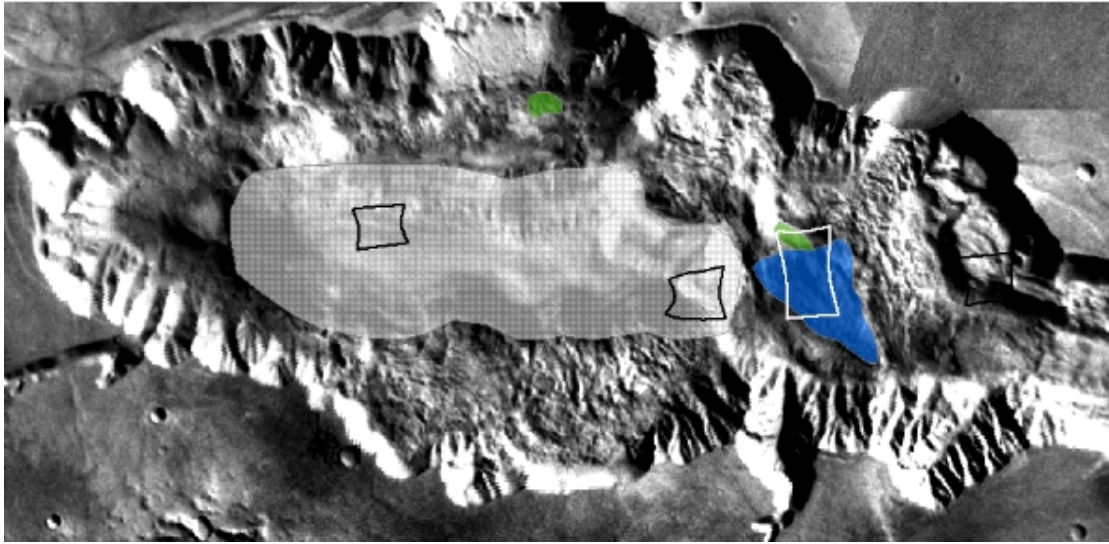


Figure 5.15: A. Location of sulfate and ferric oxides within Hebes Chasma. White/gray patterned areas are spectrally neutral ILDs, green areas are kieserite-bearing, and blue areas are PHS-bearing. White CRISM outlines have ferric phases, while black boxes do not.

than the surrounding chasma walls. Mounds “A” and “B” have similar textures, albedos, and kieserite elevations, so they are interpreted to have been once connected as one ILD [Bishop et al. 2009]. The spectral character, elevation, and stratigraphy of sulfate minerals on mounds “C” and “D” are distinct enough to suggest they formed as separate mounds from mound “A-B.”

There are three main hypotheses for the formation of the ILDs within Juventae Chasma: (1) formation of the chasma then infilling the depression with sulfate-rich sediments, (2) formation of smaller depressions that infilled with sulfate-rich sediment and then the surrounding volcanic material was eroded away to create a larger depression [Catling et al. 2006], and (3) a extensive sulfate deposit that predated the formation of Juventae Chasma and has been exposed through the opening and erosion of the chasma [Malin and Edgett 2000b]. The interpretation that the ILDs predated the volcanic wall rock comes from MOC imagery showing the light-toned ILDs ex-

posed beneath dark wallrock or chaotic material derived from wallrock [Catling et al. 2006]. However, in some cases, that dark material is part of the spectrally neutral mantling unit that caps sulfate-rich deposits here and elsewhere in Valles Marineris. In other cases, light-toned material appears at a constant elevation on three sides of a ridge of wallrock. The light-toned material could either be deposited at a constant elevation on the pre-existing wallrock or compose the lower layers of that wallrock. The differential erosional style of sulfate-rich ILD material and basaltic wallrock, however, suggest that the bright-toned ILD material is not part of the wallrock. The third hypothesis can be discarded because the sulfate-rich ILD would completely physically or chemically erode away before the much more competent basaltic lavas were physically eroded. A pre-existing sulfate deposit covered by basaltic lavas would cause significant karsting [Montgomery and Gillespie 2005] but would not leave behind sulfate-rich ILDs after erosion of the basaltic lavas. Infilling of the Juventae Chasma depression by one or more sedimentary deposits is much more consistent with the physical properties of sulfate and basaltic materials and the stratigraphic relationships between the chaotic terrain, ILDs, and wallrock.

This infilling could be from aeolian, lacustrine, or volcanic deposition of fines. The ILDs have a moderate amount of dark sand filling fractures which serve to better delineate their topography. The ILDs tend to erode along joints into semi-rounded boulders, which is consistent with a fine-grained sedimentary origin [Beyer et al. 2007].

All four ILDs are sulfate-rich, as is shown in Fig. 5.16. The spectral interpretations are based on work included in this thesis and in [Bishop et al. 2009]. Mounds “A” and “C” have spectral signatures of monohydrated sulfate (kieserite and szomolnokite or mixtures). Mound “B” has monohydrated sulfate in the lower layers and polyhydrated sulfate(s) in the upper layers. Mound “D” is partially covered by mantling material, but both monohydrated (more consistent with kieserite than szomolnokite) and PHS

are present. Kiserite is generally found at higher elevations than szomolnokite, but the mineral stratigraphy is less clear than the PHS-kiserite stratigraphy elsewhere. PHS in bedrock in mound “B” is stratigraphically above both monohydrates. Dark, spectrally neutral mantling material caps the sulfate-rich material. It erodes into a dark, finely grained deposit that collects in topographic lows in the bright, sulfate-rich layers. This alternation of dark and bright material was previously interpreted to be cross-bedding [Komatsu et al. 1993; Catling et al. 2006].

All four deposits also show hematite, probable hematite, or ferric phases in the ILD bedrock and collected in local hollows on the flanks and at the base. The ferric signature is not correlated to just the kiserite. The presence of szomolnokite complicates visible wavelength spectral analysis since the Fe sulfate also has strong features in the visible. It is possible that the ferric phases are polyhydrated ferric sulfates rather than (or in addition to) ferric oxides.

The layered materials containing polyhydrated sulfate from CRISM mapping as part of this thesis and from [Bishop et al. 2009] were previously interpreted to be gypsum-rich from OMEGA data [Gendrin et al. 2005]. More detailed analysis with CRISM data has shown the gypsum identification to be a by-product of spectral ratioing with a denominator that was not spectrally neutral. When dividing a spectrum by another spectrum in the scene to reduce instrumental noise and exaggerate spectral differences, using a spectrally neutral denominator spectrum is important. Otherwise, the denominator spectrum’s absorption features can appear as inverted features in the resulting ratioed spectrum. In this case, a kiserite-rich denominator spectrum had been used which added extra features to the resulting ratioed spectrum.

Joint analysis by the author and Janice Bishop confirmed that in CRISM data, when using isolated dusty surfaces as denominator spectra, the 2.2  $\mu\text{m}$  region absorptions reminiscent of gypsum do not appear in the resulting ratio spectra. Recent



OMEGA analysis of Juventae Chasma also found no gypsum [Kuzmin et al. 2009]. However, the presence of szomolnokite in this chasma and not in other chasmata does suggest a different mineralogic composition. Perhaps the aqueous chemistry was different here from elsewhere and created a different mineral assemblage. Is the PHS the same here as elsewhere? Ganges Chasma, which is nearby, also differs from other basinal chasma in that it has so little sulfate enrichment. Are Ganges and Juventae Chasmata somehow genetically linked?

### 5.6.9 Aram Chaos

Aram Chaos is one of the large collapse regions cut by the Valles Marineris outflow channels on their way to Chryse Planitia. TES data analysis has shown large extents of gray crystalline hematite at abundances between 2-16% [Glotch and Christensen 2005; Noe Dobrea et al. 2008]. This high concentration of gray hematite is more comparable to the abundances in Meridiani Planum [Christensen and Ruff 2004] than in Valles Marineris [Weitz et al. 2008b]. Unlike the hematite in Valles Marineris, the gray crystalline hematite in Aram Chaos is associated with a specific layer [Glotch and Christensen 2005].

Regional unit maps of mineralogy from CRISM targeted image analysis shows regionally extensive sulfate-bearing units (Fig. 5.17, from [Lichtenberg et al. 2009]). Red hematite is found as a dark, lag deposit associated with sulfate-bearing units [Lichtenberg et al. 2009]. Aram has a complicated stratigraphic stack (from youngest to oldest) of: (1) loose crystalline hematite and polyhydrated sulfate, (2) nanophase ferric oxide and monohydrated sulfate-rich cap material, (3) monohydrated sulfate, and (4) hydroxylated ferric sulfate all on top of (5) basaltic chaotic surfaces [Lichtenberg et al. 2009]. The sulfates and hematite are proposed to be precipitated by a rising groundwater table [Lichtenberg et al. 2009; Noe Dobrea et al. 2008]. Multiple

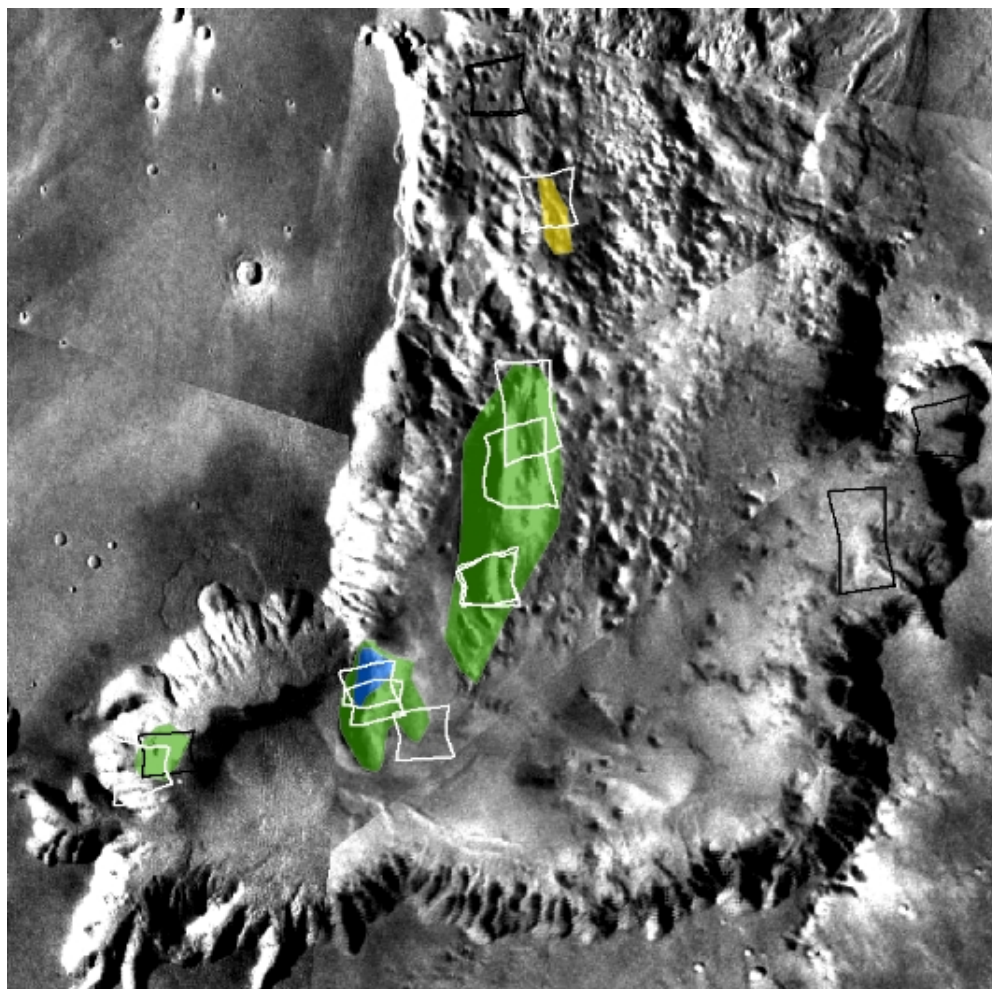


Figure 5.16: A. Location of sulfate and ferric oxides within Juventae Chasma. Green areas are kieserite-bearing, blue areas are PHS-bearing, and yellow areas are mixed mono- and polyhydrated sulfates. White CRISM outlines have ferric phases, while black boxes do not.

evaporation and groundwater flushing events could have precipitated multiple sulfates and hematite.

The diagenetic model is less satisfactory in Aram Chaos than in the basinal chasma since the total thickness of ILD material does not exceed 500 m. That is insufficient depth for low temperature diagenesis of polyhydrated Mg sulfates to convert to kieserite [Borchert and Muir 1964]. More work needs to be done connecting the sulfate deposits and stratigraphy in Aram Chaos (and the other chaos) with the sulfate and hematite stratigraphy of Valles Marineris.

## 5.7 Post-depositional weathering of sulfate

The ILDs show multiple evidences of physical erosion, from fluted morphologies to braided channels to debris aprons. Physical weathering or atmospheric conditions may also affect the hydration state of sulfates within the ILDs. As shown in Chapter 2, equatorial sulfate deposits may change hydration state upon exposure to the atmosphere. We find evidence that multiple sulfate-rich ILDs have changed hydration state in the past, lending more credence to an atmospheric phenomenon.

This process may be especially favored during periods of high obliquity, when there would be higher relative humidity (RH) in equatorial regions and thus more favorable kinetics for sulfate hydration. Kieserite is not projected to be the thermodynamically stable Mg sulfate phase on Mars [Vaniman et al. 2005; Vaniman and Chipera 2006b], but slow kinetics may prevent its hydration to epsomite or other polyhydrated Mg sulfate except under periods of high obliquity. Physical weathering of sulfate deposits may then uncover the evidence of atmospheric alteration of sulfates and the resulting sulfate hydration state change.

The ILD in East Candor Chasma with alternating poly- and mono-hydrated sul-

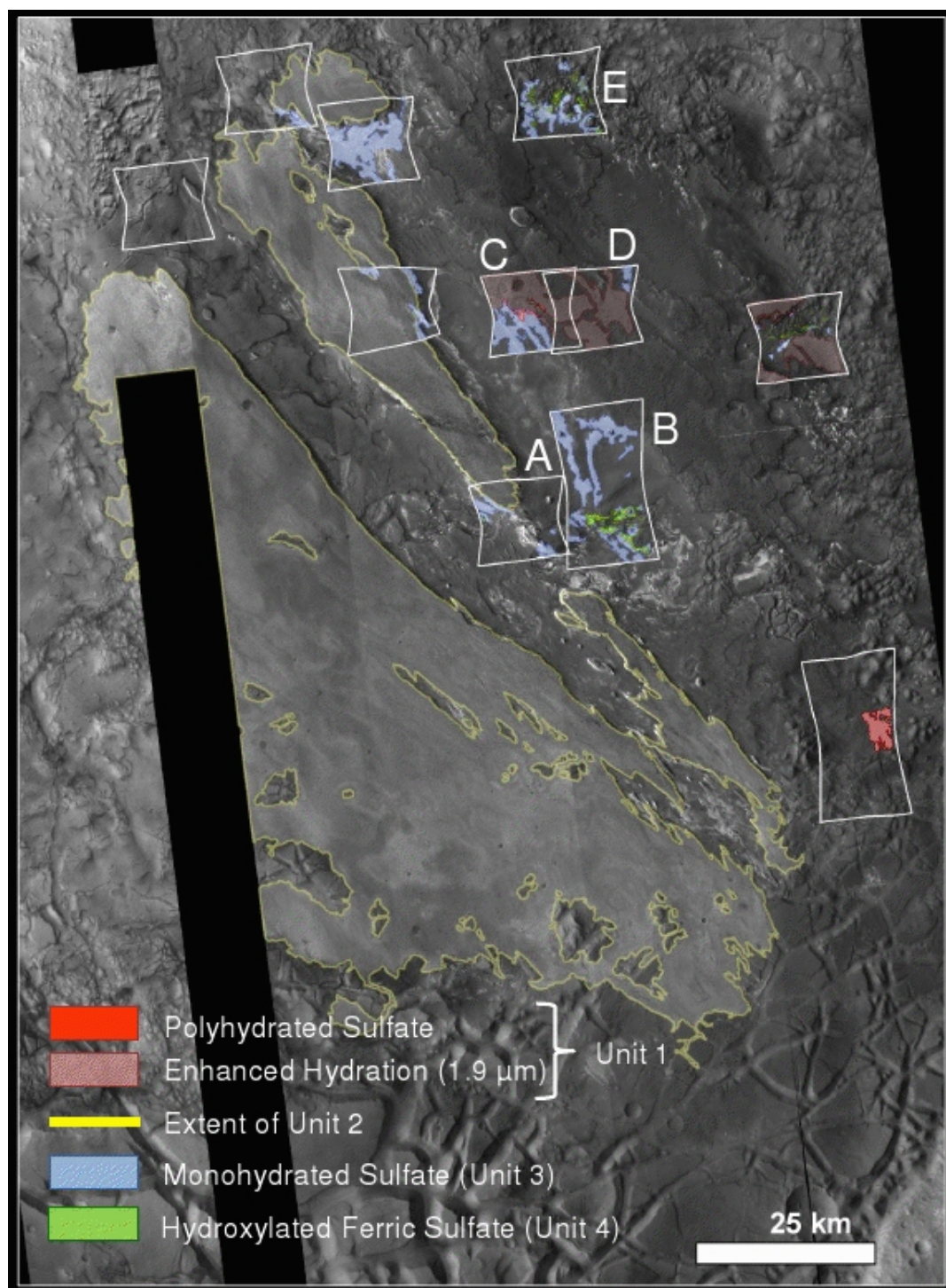


Figure 5.17: Aram Chaos ILDs: location of hydrated mineralogy, from [Lichtenberg et al. 2009], Fig. 2. Unit 2 is a cap unit consisting of monohydrated sulfate and nanophase ferric oxide with significant basaltic sand cover.

fate exposures is not the only instance of sulfate alteration by physical or atmospheric processes. Another type example of erosion or atmospheric conditions changing hydration state of sulfate is in the dominantly kieserite-bearing ILD in western Tithonium Chasma which stretches  $\sim 40$  km in length. There is a transition from kieserite to PHS where the ILD is weathering out from underneath a spectrally bland, smooth mantle and abutted by a dark dune field (Fig. 5.18). There is little topographic relief across the transition. Layering is not apparent, but the PHS-bearing material appears rougher, darker, and with more dark aeolian material on it. The polyhydrated spectra cannot be explained by intimate or areal mixing of kieserite with the aeolian material.

There are several potential explanations for the transition between hydration states. 1) The ILD adjacent to the dunes has a rougher texture and perhaps the greater surface area promotes more rapid hydration than the smoother ILD material above it. Alternately, the PHS could be a type of “desert varnish” from aeolian erosion of sand grains in the dust field. 2) Shallow groundwater or collected melt water from interstitial ice in the dune field alters the ILD adjacent to the dunes. 3) Kieserite overlies PHS here from original evaporite deposition or later groundwater alteration and is coincidentally eroded so the PHS-bearing material is just visible. The first two hypotheses require hydration under current conditions while the third relies on a coincidence of exhumation. Since two different parts of the deposit show PHS-kieserite contacts near the erosional front, we discount the spatial coincidence and believe this is more evidence of erosional and atmospheric processes converting kieserite to PHS.

A third example of rehydration of kieserite with exposure to the atmosphere is in the perched ILD in western Coprates Chasma (Fig 5.19). Steeper, and presumably fresher, surfaces show kieserite spectral signatures, while flatter surfaces are enriched



in PHS. The western (left) side of the ILD has bright, loose material at its base that contains both poly- and monohydrated sulfate. This loose material may represent a more recent aeolian erosional process stripping material from the ILD. It is posited to be a more recent event since the kieserite has not yet converted to PHS.

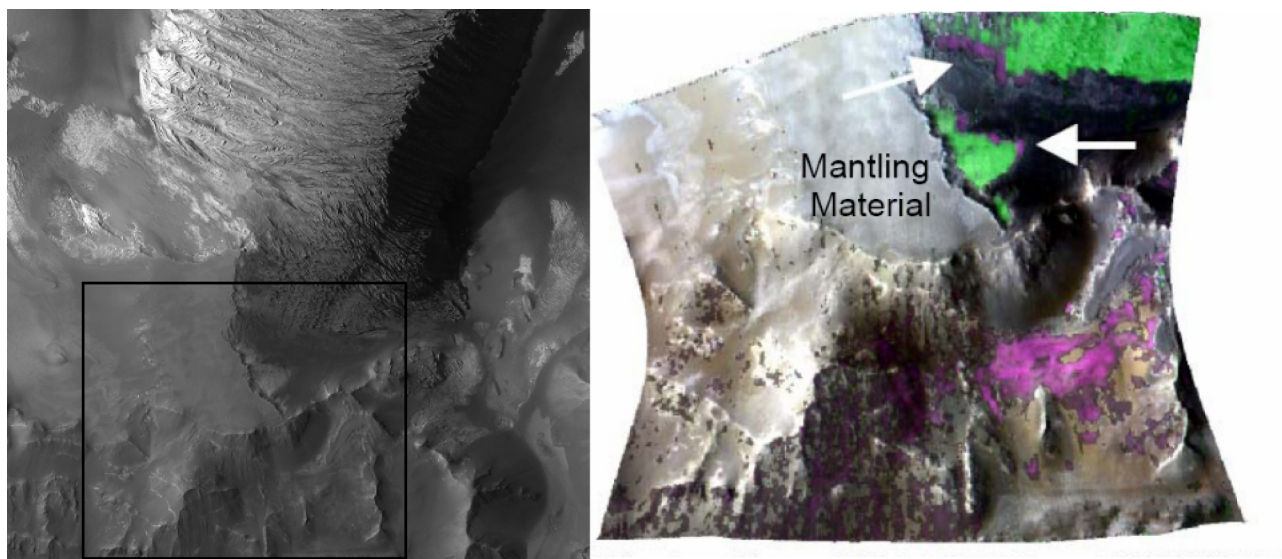


Figure 5.18: Left: CTX background showing kieserite-rich ILD in Tithonium Chasma partially covered to the south by a dust mantle. Black box indicates location of CRISM observation. Right: CRISM targeted observation FRT0000510D. CRISM parameters indicating kieserite (green) and polyhydrated sulfate (purple) overlain on false color (RGB: 2.33, 1.5, 1.08  $\mu\text{m}$ ). White arrows point to hydration state transition. Observation  $\sim 10$  km across the middle.

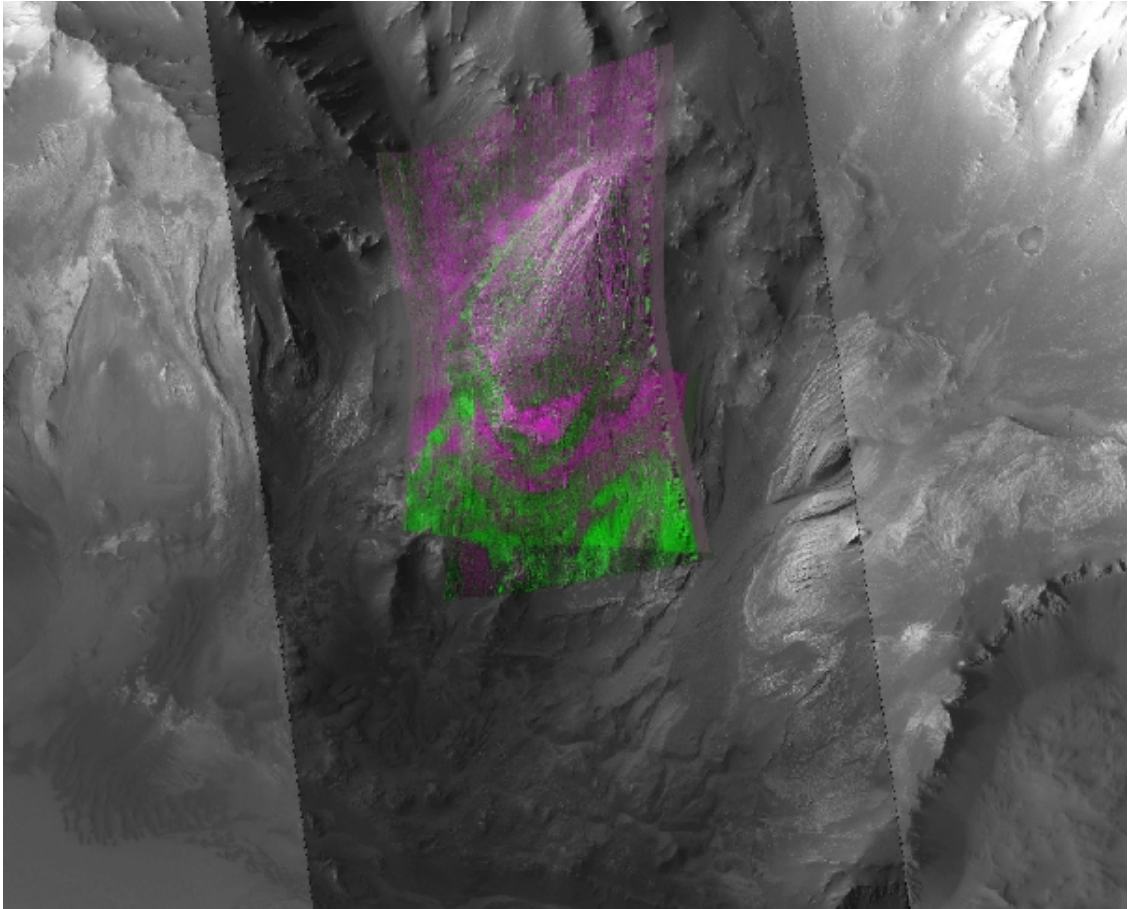


Figure 5.19: Coprates Chasma ILD with kieserite and polyhydrated sulfate indicating hydration state transition. Parameter maps from CRISM targeted observations FRT0000B64A and HRL00003752. Kieserite in green and polyhydrated sulfate in purple. Kieserite on steeper slopes and polyhydrated sulfate in loose material and flat-lying layers. CTX background.

# Chapter 6

## Implications for Valles Marineris's aqueous geologic history

### 6.1 Introduction

This chapter presents a synthesis of the mineralogy, stratigraphy, and aqueous geologic history of sulfate-bearing Interior Layered Deposits (ILDs) across Valles Marineris. The previous synthesis chapter summarized the current state of knowledge about the sulfate-bearing ILDs within Valles Marineris. This chapter talks about the implications of those findings — how to compare terrestrial and Martian sulfate deposits and what these sulfates can tell us about past Martian climate.

This second synthesis chapter is a little more free-ranging. There are four main themes in this chapter: (1) comparing the salt giants on Earth to Martian sulfate-rich deposits, (2) the relative timing of aqueous alteration events in Valles Marineris, (3) implications for the Martian mineralogic timeline, and (4) outstanding questions related to this thesis.

The first theme compares the ILDs to ancient salt giants on Earth and contemporary terrestrial sulfate evaporites. Many questions remain about how the ancient salt giants formed, and study of the Martian deposits may give new insight into the problem. Specifically, the lack of widespread biology on Mars may allow the biologic



and abiologic processes in evaporite formation to be decoupled.

The second theme addresses the multiple aqueous alteration events observed in Valles Marineris. A range of alteration minerals — from alkaline to near neutral to acidic — are found in and around Valles Marineris. This section presents the case that changing regional aqueous geochemistry had a strong influence on the secondary minerals precipitated.

The third theme places our aqueous alteration history in Valles Marineris in a more global context. The new global mineralogic timeline proposed by the OMEGA team [Bibring et al. 2006] has not been carefully tested with CRISM-derived mineralogies. This thesis is one of the ongoing efforts to validate this new timeline. Connections between Valles Marineris and Meridiani Planum and the importance of hematite in the global mineral timeline are emphasized.

This part concludes with outstanding questions and further research as suggested by this thesis. The questions can be broken into three categories: spectral uncertainties, unknown mineralogy and mineral assemblages, and thermodynamic and kinetic issues.

## **6.2 Comparing salt giants on Earth to Martian sulfate-rich deposits**

Currently forming salt and sulfate evaporite deposits are at least an order of magnitude smaller than evaporites preserved in the rock record. These ancient “salt giants” are enigmatic in their composition, volume, and formation history. The ancient salt giants may have formed by a similar mechanism as current evaporites — evaporation of a shallow marine brine — but under different tectonic settings. Just as we must extrapolate from current terrestrial evaporative settings to the ancient salt giants, we

must also extend the logic to Martian sulfate deposits. Interpretation of Martian sulfate deposits has several added complications: neither the sulfate abundance nor the complete mineral assemblage present in Martian ILDs are well constrained. Knowing the abundance of sulfate(s) and the presence of auxiliary minerals are critical to understanding how any sulfate deposit formed. However, in some respects, Martian sulfate deposits may be simpler than their terrestrial counterparts, since they presumably lack the influence of biology.

The geologic setting for salt giants has been proposed to be salterns [Schreiber 1988; Warren 1991]. Salterns are shallow subaqueous evaporite beds that form extensive deposits across 100s–1500 km in inland seas or large continental lakes on Earth [Schreiber 1988; Warren 1991]. These deposits have no modern counterparts in scale or mineralogy. Ancient evaporite deposits on Earth are at least an order of magnitude larger in aerial extent than modern evaporites and cumulative evaporite materials are two to three orders of magnitude greater [James and Kendall 1992]. Salt giants often contain higher percentages of terminal evaporite phases, like kieserite and carnallite. Their general mineral assemblages are “ $\text{MgSO}_4$ -deficient” compared to normal equilibrium evaporation of seawater, while modern evaporites follow equilibrium evaporation trends [Lowenstein 1989]. The salt giants have also seen latter diagenetic processes not active in current salt or sulfate deposits due to their large size and sulfate-rich chemistry.

There are three factors that may have promoted salt giant deposition in the geologic past. (1) Periods of warmer global climate would create larger latitudinal belts where evaporites could form [Borchert and Muir 1964; Gordon 1975]. (2) Plate tectonics had created supercontinents that could support enormous inland seaways into arid intercontinental regions [Borchert and Muir 1964]. (3) Tectonic and climatic conditions were stable over large depositional basins for long enough to accumulate

thick sedimentary sequences [Borchert and Muir 1964; Hsu et al. 1973]. Frequent introduction of more dilute brines without loss of more concentrated brines is necessary to construct a thick evaporite sequence. Currently there are no large, shallow bodies periodically separated from the ocean of the same size as those that may have formed the salt giants.

One of the mysteries about salt giants is why they are so depleted in sulfates relative to modern evaporites. There are three main theories to explain the paucity of Mg sulfates [Garrett 1995]. They require biologic intervention, coincidences of sulfate remobilization, or major changes in ocean chemistry between the ancient salt giant precipitation and today. All three are controversial, but the last theory is gaining traction among sedimentologists.

One theory is that sulfate-reducing bacteria in the brine convert the sulfate to pyrite or otherwise remove it from the system [Borchert and Muir 1964]. A balanced reaction is given in Eq. 6.1.



Bacteria use organic matter to reduce sulfate to create hydrogen sulfide and carbon dioxide gases and carbonate. Bacterial sulfate reduction would create an equal volume of carbonate for each sulfate ion removed from the brine. Thermodynamics predicts that a typical terrestrial evaporite sequence contains first carbonates, then gypsum, then halite, and lastly Mg sulfates. Carbonate is only found in appreciable amounts in the first stage. Bacterial sulfate reduction is a controversial hypothesis because it requires the bacteria to only be active in the window of carbonate deposition but not in later gypsum or halite depositional phases. Bacterial sulfate-reduction could only have been active in the sulfate precipitating phases since they lack carbonate.

Another hypothesis is that sulfate has all been remobilized from the ancient evaporite deposits by leaching. However, leaching of sulfates from an evaporite deposit would also leach significant chlorides, since halite has an intermediate solubility between Mg and Ca sulfates. Also, evaporite textures and pseudomorph structures in many ancient salt giants do not indicate the presence and then exsolution of large amounts of sulfate [Garrett 1995].

The last theory involves changing the major ion composition of the oceans over time. Recent work analyzing trapped fluid inclusions within ancient and modern evaporites has shown that the major-ion chemistry of terrestrial oceans has changed dramatically over time [Lowenstein et al. 2003, 2005]. These trapped brines record the chemistry of the host brine when the crystal first formed. These fluid inclusions can survive diagenesis and recrystallization, and can give information about the original brine chemistry when the precipitated minerals from that brine have since been altered multiple times [Lowenstein et al. 2003, 2005]. The ocean chemistry has fluctuated between  $\text{CaCl}_2$  seas ( $m\text{Ca}^{2+} > m\text{SO}_4^{2-}$ ) and  $\text{MgSO}_4$  seas ( $m\text{Ca}^{2+} < m\text{SO}_4^{2-}$ ) four times in the past 400 Ma [Lowenstein et al. 2003]. There is now growing acceptance for secular changes in seawater composition, which creates evaporates that either lack Mg sulfates or have abundant Mg sulfates relative to KCl evaporites [Hardie 1996; Lowenstein et al. 2005; Bridge and Demicco 2008]. The presence of thick KCl sequences (and absence of large amounts of Mg sulfates) in ancient salt giants may be simply because the ocean was more enriched in chloride when they formed. The secular change in marine chemistry to a more Cl-rich constitution was caused by rapid seafloor spreading and high influxes of mid-ocean-ridge brines rich in  $\text{CaCl}_2$  and elevated sea levels [Lowenstein et al. 2003]. High sea levels also created large shallow continental seas, prime locations for evaporite deposition [Lowenstein et al. 2003].

The sulfate-rich deposits on Mars, if they are large evaporites in the mode of the

salt giants, may be able to shed light on how these salt giants formed, and where the “missing” sulfate goes. Of primary importance is understanding the abundance and types of minerals present in the Martian evaporite. Then, we can make comparisons between the expected Martian mineralogy from models of Martian basalt dissolution and evaporation (e.g. [Tosca and McLennan 2006; Bullock and Moore 2007]), the expected terrestrial mineralogy from ocean chemistry (e.g. [Borchert and Muir 1964]), and observed terrestrial mineralogy in the salt giants.

Biology on Earth plays an unavoidable role in modulating the sulfur cycle and in shaping the landscape in aqueous environments (through features such as stromatolites, carbonate platforms, and possibly banded iron formations). Carbonate platforms may have played a very important role in creating shallow marginal basins where the salt giants could accumulate. Without that biologic intervention, would the evaporite deposits be as thick? It is also unclear how much bacterial sulfate-reduction and -oxidation have affected terrestrial evaporites, both by altering the brine composition during evaporation and the evaporite deposit after formation. The effects of life on both the physical and chemical configuration of aqueous deposits can overwhelm abiologic processes. These effects complicate separating out biologically-mediated and abiologic processes. Mars lacks evidence for widespread biology, so aqueous environments may be simpler and evaporite sequences only affected by equilibrium thermodynamics. Models for how large sulfate deposits formed on Mars may let us probe how ancient terrestrial salts giants were emplaced.

### **6.3 Relative timing of crustal alteration**

The relative timing of sulfate formation and other alteration events can enlighten us on regional geochemistry of Valles Marineris from the Noachian to Early Amazonian.

The timeline of Fe/Mg smectite, hydrated silica, and sulfate formation can be pieced together with reference to regional geologic events in Ius Chasma. Ius Chasma has abundant exposures of all three hydrated mineral types, and the geologic timeline derived from Ius Chasma is assumed applicable to all of Valles Marineris.

Fe/Mg and Al-rich smectite clays have been found in the Noachian basement exposed on the lower wallrock in the deepest chasmata, but not in the overlying Hesperian-aged lava flows [Murchie et al. 2009a]. However, the contact between Noachian and Hesperian lavas in canyon wallrock is not well-defined, so some Hesperian-aged lavas may also be altered. Generally, the lowest elevations of exposed wallrock in the deepest chasma (like Coprates and Ius) show smectite clay alteration. This neutral to alkaline groundwater alteration occurred prior to the Tharsis volcanism, and thus before Valles Marineris opened up. Fe/Mg smectite has been physically eroded from wallrock, redeposited in sedimentary layers on the canyon floors, and in some cases, possibly altered by later, more acidic groundwater (see Chapter 3).

Sulfate deposition postdates phyllosilicate formation and likely occurred in the Early to Late Hesperian, the age of many ILDs. The time of sulfate enrichment in ILDs cannot be dated, and the sulfate may have been precipitated, dissolved, transported, and precipitated again over the course of geologic history. Putative sulfates are only rarely found in Noachian terrains [Ehlmann et al. 2009]. It may be that sulfates did precipitate but have all been remobilized by later aqueous activity. Some sulfates in Valles Marineris show evidence of diagenetic alteration, from burial and groundwater fluxing. Others deposits in Valles Marineris show the effects of interaction with an intermittently moist atmosphere from periods when obliquity excursions deposited ice at the Martian equator during Amazonian times.

The thin layers of hydrated silica on the plateaus around Valles Marineris are dated to the Late Hesperian or Early Amazonian period [Weitz et al. 2008b; Milliken

et al. 2008a], and they further constrain the aqueous alteration to neutral or acidic pH conditions [Milliken et al. 2008a]. Hydrated silica deposits in the light-toned layers on the plains near Juventae Chasma are associated with dehydroxylated jarosite, a phase that only forms at  $\text{pH} < 3$  [Milliken et al. 2008a].

In addition to the opaline phases on the plateau, the  $\sim 400$  m thick, uppermost layers of the Hesperian lava flows that make up the plateaus also show evidence of alteration. The layers at the top of Valles Marineris walls are more resistant to erosion than underlying layers [Treiman et al. 1995]. These layers extend the length of Valles Marineris, are at a consistent depth below the surface, and cut across both Noachian and Hesperian materials [Treiman et al. 1995; Fuks et al. 1995; McEwen et al. 1999]. The layers are interpreted as evidence of diagenesis or aqueous alteration during the Late Hesperian by near subsurface groundwater [Treiman et al. 1995], however it is unclear how diagenetically altered basalt would be more resistant to weathering than unaltered basalt. It is possible the aqueous alteration that formed a few meters of hydrated silica layers on the uppermost surface also altered hundreds of meters of basalts beneath the silica coating. This wallrock does not show evidence for phyllosilicate or sulfate enrichment, indicating a possibly less active alteration period than existed in the Noachian or Hesperian.

Formation of hydrated silica on the plateau may have been contemporaneous with sulfate formation; the only constraint is that the last episode of sapping channel transport of hydrated silica into Ius Chasma postdates sulfate precipitation there. The connection between hydrated silica and sapping channels, which are caused by groundwater rather than overland flow, point to an acidic, drying environment, which is also consistent with evaporite sulfate formation in regional lows within the trough. The overall stratigraphic relationships between alkaline smectite to poorly crystalline leached smectite/sulfate under circum-neutral conditions to acidic jarosite within and

around Valles Marineris points to a general decrease in ground and surface water pH with time (Fig 6.1).

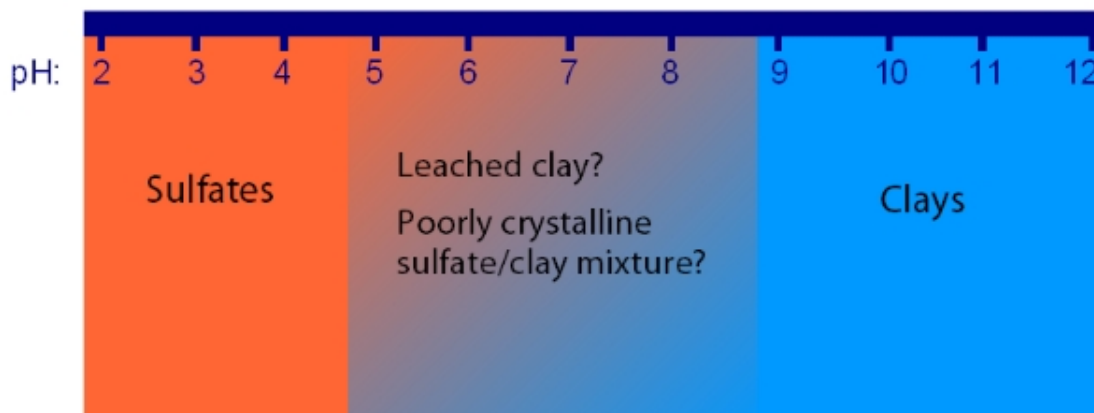


Figure 6.1: Hydrated mineralogy in Valles Marineris covers a range in pH conditions

## 6.4 Implications for mineralogic timeline

The OMEGA team has put forth a new, mineralogic timeline [Bibring et al. 2006] to augment the established geologic time based on crater counting statistics and extrapolation from lunar crater statistics and rock ages (see Fig 1.2). The proposed mineralogic timeline rests on the OMEGA results that phyllosilicates are in the oldest terrains, sulfates are within younger terrains in Valles Marineris and westward outflow channels, and ferric oxide-bearing dust is globally distributed on the surface.

The association of phyllosilicates with Noachian bedrock (e.g. [Poulet et al. 2005; Mustard et al. 2008]) is taken to represent Noachian-era aqueous alteration of the subsurface or surface. Orbital remote sensing rarely finds sulfates in Noachian terrains, with or without phyllosilicate mineralogy. The exception is alunite in one crater central peak in Sirenum Planum [Swayze et al. 2008]; several spectra in Lybia Montes and Nili Fossae has spectral similarities to both sulfate and zeolite, so the exact min-



eral class is not yet determined. The lack of sulfate detection in the oldest rocks that saw pervasive aqueous alteration is surprising, since a balanced whole-rock reactions could include carbonates and/or sulfates as precipitates of excess cations (e.g. [Tosca and McLennan 2006; Bullock and Moore 2007]). In the absence of complete bedrock dissolution, a partial-rock reaction in the presence of volcanic  $\text{SO}_2$  would still likely include sulfate phases.

Sulfates undoubtedly were forming in the Noachian too, as volcanism was active and regions of acidic groundwater were probably unavoidable. However, the ionic sulfate bonds are more susceptible to physical and chemical weathering than the covalent bonds of phyllosilicates and their basaltic precursors, and thus the sulfates may have been largely eroded or dissolved from Noachian materials and reworked into Hesperian-aged surfaces by aeolian transport and groundwater cementation.

The Phyllosian and Theiikian eras are well separated in Valles Marineris as Noachian bedrock-hosted phyllosilicate and Hesperian sulfate-enriched ILDs. The Siderikian era is less clearly separated from the Theiikian, as hematite and other ferric oxides occur as a diagenetic product with kieserite throughout Valles Marineris. The co-precipitation or recrystallization of hematite and kieserite and the large expanses of red hematite and other ferric oxides (OMEGA and CRISM) and gray hematite (TES) show aqueous formation of ferric oxides is an important process that should be included in a mineralogic timeline. The Siderikian was proposed as the terminal alteration period on Mars, where anhydrous nanophase ferric oxides form by oxidation of the surface [Bibring et al. 2006]. While surface oxidation undoubtedly played a role in formation of the ferric oxides that comprise part of the global dust, comminution of hematite (and their sulfate-rich host rock) may have also been a large source.

The general mineralogic timeline and the minerals present in Valles Marineris are similar to those in Meridiani Planum. The layered sulfates at Meridiani Planum have

seen complementary processes, with multiple generations of groundwater fluctuations alternately precipitating, recrystallizing, and dissolving evaporite minerals and precipitating hematite spherules [Squyres and Knoll 2005; McLennan et al. 2005; Squyres et al. 2006]. The Whatanga contact of the Burns Formation at Meridiani Planum is interpreted as the terminal height of a water table fluctuation and thus as a diagenetic boundary [McLennan et al. 2005; Grotzinger et al. 2005]. The Whatanga contact is physically different than adjacent layers, with a darker albedo and overprinted texture from recrystallization [McLennan et al. 2005; Grotzinger et al. 2005], and chemically different, as represented by variation in Br and Cl concentrations above and below the contact [Clark et al. 2005]. The Whatanga contact is  $\sim 10$  cm thick, so it is reasonable to expect sharp diagenetic contacts between poly- and monohydrated sulfates at HiRISE and CRISM scales. Groundwater precipitation of hematite in Valles Marineris has previously been proposed [Weitz et al. 2008b]. We suggest the mechanism is diagenetic recrystallization of ferric oxides/sulfates to hematite along with recrystallization of polyhydrated sulfates to kieserite within the ILDs.

## 6.5 Outstanding questions

The newer generation of higher resolution imagers and spectrometers around Mars have answered some questions raised by previous missions, but have also raised many more questions that require more detailed orbital or in situ investigations to address. The unanswered questions can be broken into three categories: spectral uncertainties, unknown mineral assemblages and the abundance of sulfates, and thermodynamic and kinetic issues.

### 6.5.1 Spectral uncertainties

First are the spectral uncertainties encountered in this study. The exact cation chemistry of the “polyhydrated sulfate” type remains a mystery. Does the “polyhydrated sulfate” type have uniform cation chemistry across Valles Marineris? Is it monomineralic, or does the spectral type include many polyhydrated sulfate phases? Since monohydrated Mg sulfate is so ubiquitous, does that make it more or less likely from a geochemical perspective that the polyhydrated sulfate is Mg-bearing?

There is a spectral difference between natural and synthetic kieserite. In a natural kieserite sample containing 90% kieserite and 10% halite (spectrally neutral in VNIR) as determined by XRD, the spectrum has a broad, boxy absorption with a minimum at  $2.13\ \mu\text{m}$  [Cloutis et al. 2006]. Synthetic kieserite, created by dissolving reagent-grade Mg sulfate in water and heating to dryness at  $150^\circ\text{C}$ , has a narrower, more rounded absorption centered near  $2.09\text{--}2.11\ \mu\text{m}$ . The reason for this discrepancy is not understood. There are two steps that need to be taken: (1) measure spectra of more natural samples, and (2) dissolve and re-precipitate those natural samples to create synthetic kieserite and collect spectra. These measurements will help determine if the spectral difference is due to trace sulfates and other evaporites in the natural kieserite sample, or due to minor differences in how water is held in natural kieserite formed at low temperatures (near  $40\text{--}55^\circ\text{C}$ ) and in synthetic kieserite formed at higher temperatures (near  $150^\circ\text{C}$ ).

In many cases, we can argue against a significant iron sulfate component since most polyhydrated sulfate deposits lack extra features in the visible wavelength region not present in dusty spectra. It is possible, but unlikely, that the nanophase ferric oxide and other Fe-bearing phases in dust would obscure absorptions from Fe in sulfates. There are isolated locations in Noctis Labyrinthus that show Fe sulfates, which highlights the lack of conclusive Fe sulfate identifications elsewhere in Valles

Marineris. What is the Fe sulfate phase in Noctis Labyrinthus and why is it only found there? The Fe sulfate is found in pits in Noctis Labyrinthus that are also interpreted to be centers of more recent volcanism [Mangold et al. 2008a]. Is its presence due to alteration of a different composition lava?

We can now better resolve the crystalline red hematite deposits in Valles Marineris, but there are a host of other ferric oxides or sulfates present in many deposits that cannot be uniquely identified. What is the total diversity of ferric oxides? Is the pathway to hematite formation from goethite, magnetite, or ferric sulfate? What is the composition of the non-hematite ferric minerals concentrated at the bases of ILDs? The minerals typically have a red spectral slope with a broad minimum near 0.85–0.90  $\mu\text{m}$ , and sometimes have absorptions at 1.9 and 2.2  $\mu\text{m}$ . Possible minerals fitting these spectral features include copiapite (a hydrated ferric sulfate), ferrihydrite (a hydrated ferric oxyhydroxide), or hematite, possibly in combination with one or more other hydrated sulfates [Roach et al. 2007b; Murchie et al. 2007b; Bishop et al. 2009].

The “hydrated silicate” unit identified in Chapter 3 could be either: (1) a poorly crystalline leached smectite, or (2) a jarosite/montmorillonite or hydrated silica mixture. Further laboratory spectral mixture studies of sulfates and phyllosilicates or hydrated silica will provide more information on how the 2.2–2.3  $\mu\text{m}$  region is affected by mineral mixtures. In addition, further laboratory work on refining the origin of sulfate vibrational overtones in the 2–2.5  $\mu\text{m}$  region is necessary to help extrapolate the crystalline structure of the “hydrated silicate” unit. While extensive work has been completed on the vibrational band assignments of phyllosilicates (e.g. [Bishop et al. 1994, 2002b,a, 2008a]), similar studies of the vibrational band assignments of sulfates are more limited (e.g. [Bishop and Murad 2005; Cloutis et al. 2006]). In situ investigation of the “hydrated silicate” unit may be necessary to ultimately determine

its mineral chemistry.

### 6.5.2 Unknown mineral assemblages and abundance of sulfates

The next questions deal with understanding the mineral assemblage as a whole and the abundance of the various phases present. Sulfates are only part of the mineral assemblage present in these ILDs. Other minerals that are spectrally neutral or subtle are very likely present. These phases could even be a major or dominant phase by volume in the deposit. We must think of the sulfates as being a (potentially minor) component of the lithology. Are sulfates 1% , 10% , or 50% of the outcrop?

Knowing what other minerals that are present is an important step in reconstructing the aqueous history of the ILDs. Complex mineral assemblages are ubiquitous in evaporite, hydrothermal/solfatar, or acid mine drainage settings (e.g. [Schreiber 1988; Bishop et al. 2005, 2006; Sarrazin et al. 2007; Baldrige et al. 2008]). Trace mineralogy, such as bromides, may be critical to understand the aqueous evolution of the deposit, as the Cl/Br ratios in Meridiani Planum illustrated [McLennan et al. 2005]. The entire mineral assemblage must be identified to understand how the sulfate was formed.

Mineral abundance goes hand in hand with cataloging the entire suite of minerals present. CRISM data are not yet able to give abundance estimates, but preliminary modelling with OMEGA data shows the promise of producing abundance calculations for phases with well-determined optical constants [Bonello et al. 2004b; Poulet et al. 2008b]. The abundance modelling has only been attempted for basaltic or phyllosilicate-rich terrains; sufficiently high quality optical constants have not been determined for even the most common sulfates (i.e. gypsum), so sulfate abundances in

Valles Marineris will await those measurements. Knowing the abundance of sulfates within an ILD could help with the reconstruction of how the ILD became enriched in sulfate — is the deposit mostly an evaporite with small amounts of foreign matter like the terrestrial salt giants or is it mostly dust and ash cemented with very small amounts of sulfate? This has implications for the distribution of the sulfur budget on the Martian surface (e.g. [Gaillard and Scaillet 2009]).

Kieserite-bearing units tend to be higher albedo, more massively layered, and with a fluted or polished erosional style, while polyhydrated sulfate-bearing units often have a more intermediate albedo, are finely layered, and portray a more blocky erosional style [Roach et al. 2007c; Mangold et al. 2008b]. This trend is not universal across Valles Marineris but as a first order observation, is consistent with the majority of the ILDs. Is this relationship between ILD albedo and sulfate composition due to albedo differences in the minerals or to textural differences? The rougher textured PHS-rich layers would be more efficient at trapping darker sands than the smoother kieserite-rich layers. What causes the textural difference between the two units?

The global dust has a 5–10% sulfate component [Pollack et al. 1990; Bandfield et al. 2003; Hamilton et al. 2005; Glotch et al. 2006]. Viking lander X-ray fluorescence data showed elevated and correlated abundances of S, Cl, and Br in the dust, suggestive of sulfates and chlorides [Baird et al. 1976; Toulmin et al. 1976, 1977; Clark and van Hart 1981]. Pathfinder alpha proton X-ray spectrometry data is broadly consistent with the Viking results [McSween et al. 1999]. The MER Opportunity at Meridiani has found Al-rich opaline silica, Mg-, Ca-, and Fe-bearing sulfates, plagioclase feldspar, nontronite, and hematite in light-toned (dusty) surfaces [Glotch et al. 2006].

While the global dust is enriched in sulfate, very few areas on the surface show sulfate enrichment. The only large areal occurrences of sulfate are in the north polar

dune field and in light-toned deposits within Valles Marineris, its outflow channels, and nearby Meridiani Planum. Is crystalline sulfate present at other locations in small volumes or beneath a thin cover? Or is it restricted to equatorial regions? Was sulfate only formed during warmer and wetter periods in the Noachian and Hesperian, or is it still forming in soils? Banin et al. has suggested that the sulfate in the Martian dust and soil is not from a warmer and wetter era, but that it is due to geologically recent acid fog weathering of the surface by volcanic volatiles [Banin et al. 1997]. Is the genesis of the sulfate in the global dust the same as the sulfate-bearing ILDs? How has sulfate been remobilized since formation? Among alteration products, sulfates (and associated chlorides) are much more soluble than phyllosilicates, iron oxides, or hydrated silica. This is because sulfate has ionic bonding while the others have stronger covalent or covalent-ionic bonding. Was sulfate formed in the Noachian at the same time as the widespread crustal alteration to phyllosilicate, but then removed from Noachian terrains by relatively minor groundwater flushing?

### **6.5.3 Thermodynamic and kinetic concerns**

Finally, thermodynamic models for sulfate stability are at odds with the sulfates CRISM and OMEGA see on the surface. Kieserite, one of the few specific sulfate phases identified on Mars, is not thermodynamically stable under Mars' currently cold and dry conditions [Vaniman and Chipera 2006b]. Thermodynamic modelling has shown that epsomite rather than kieserite would be the expected phases at equilibrium with the surface [Wang et al. 2006; Vaniman and Chipera 2006a,b]. In conditions where kieserite would be exposed to surface or ground ice for part of the year (where there is sufficient humidity available), thermodynamics would predict that kieserite would convert to a polyhydrated sulfate (epsomite) [Vaniman and Chipera 2006b]. There is abundant evidence for fluvial erosion of ILDs after sulfate enrichment (i.e.

[Murchie et al. 2009b]) and climate models predict significant ice accumulation within Valles Marineris during periods of high obliquity [Madeleine et al. 2008]. Yet, there are many large kieserite deposits within Valles Marineris. It is unlikely that the relative humidity in Valles Marineris has remained below the threshold for kieserite hydration to  $\text{MgSO}_4 \bullet x\text{H}_2\text{O}$  since kieserite was originally formed. More likely, sulfates in Mars are not in thermodynamic equilibrium. The sulfate phases present may rely more on the kinetics of hydration and dehydration reactions rather than the thermodynamically expected phases.

Experimental data shows the kinetics for Mg sulfate hydration and dehydration are slow and are often path dependent. Kieserite will readily hydrate to epsomite, but in a vacuum at temperatures  $< 323\text{K}$  epsomite dehydrates to an amorphous phase ( $\sim 1.25$   $\text{H}_2\text{O}$  molecules) rather than kieserite [Vaniman and Chipera 2006b]. Slow kinetics of sulfate hydration and dehydration have been proposed as a mechanism to slow sulfate hydration and retain metastable sulfate phases over geologic time on Mars [Vaniman and Chipera 2006b]. Mg sulfates are unique in this respect; other hydrated phases, like zeolites and smectites, readily gain and lose waters of hydration under Martian conditions [Bish et al. 2003]. Exactly how slow is sulfate hydration and dehydration on Mars? How important is sulfate metastability at the low temperatures and relative humidities on Mars?

Modeled thermodynamic values for sulfate stability at Martian (below freezing) temperatures may not be realistic, and existing laboratory experiments are not long-term enough to see changes in hydration state between Mg sulfates (e.g. up to 1000s of hours in [Vaniman et al. 2006; Vaniman and Chipera 2006a; Wang et al. 2007]). Calculating the relative humidity (RH) at below freezing temperatures is complicated, as one must consider gaseous, liquid, and solid water phases [Hardy 1998]. The various theoretical formulas to compute RH at subfreezing temperatures can vary by 50% at



230 K. Since RH is a basic measurement needed in both kinetic and thermodynamic models of sulfate hydration/dehydration rates, those models are subject to significant uncertainty. That translates into an uncertainty in how Mg sulfates fare in Martian conditions. Further work needs to be done to constrain the kieserite stability field at Martian temperatures (both with long time, low temperature experiments and long time, oscillatory temperature and RH experiments), and to understand rates of kieserite-epsomite hydration under Martian conditions.

## 6.6 Future Directions

This thesis presents a summary of what is known about sulfate deposits within Valles Marineris. The Interior Layered Deposits (ILDs) are enigmatic mounds that post-date the opening of Valles Marineris in the late Hesperian period. These sedimentary or volcanic deposits have seen extensive aqueous activity, either during their formation or by later erosional events. The recent orbital spectrometers (TES, OMEGA, CRISM) have discovered hematite and a variety of hydrated sulfates in these ILDs. These early detections have revolutionized how we understand the geologic history of Valles Marineris, and of Mars as a whole. The hydrated mineralogy and evidence of sedimentary diagenesis suggest that Mars was still very active in the late Hesperian period.

The most important data to collect next about these sulfate deposits is the sulfate abundance and the complete mineral assemblage in each deposit. Quantifying mineral abundance will help us choose between the various hypotheses for sulfate enrichment. Sulfate enrichment possibilities range from a trace sulfate cement, to a minor sulfate component transported from elsewhere, to a pure sulfate evaporite. Knowing the complete mineral assemblage will similarly help resolve how the sulfate was formed,

if it was altered after formation, and what is the relationship between the sulfates and unaltered primary materials.

The “polyhydrated sulfate” spectral type probably represents a mixture of multiple sulfates, and may be variable across the canyon system. Understanding that variability might help trace how localized sulfate formation was. If Noctis Labyrinthus and Tithonium Chasma in western Valles Marineris have the same “polyhydrated sulfates” as Capri Chasma in eastern Valles Marineris, for example, that might suggest an integrated canyon-wide aqueous geochemistry.

Trace minerals in the ILDs — whether chlorides, sulfates, or carbonates — and trace elements, like Cl and Br, can be fingerprints of different aqueous events. A complete evaporation sequence of a brine derived from weathering a Martian basalt would be expected to precipitate carbonates, sulfates, and chlorides [Tosca and McLennan 2006]. The complete mineral assemblage of an ILD can tell us if it is consistent with an evaporation sequence, and how concentrated or “evolved” the brine was.

While orbital spectrometers are ideal for mapping hydrated mineralogy across 100s of meters to 1000s of kilometers, the next step in exploration needs to be landed assets that characterize deposits at the outcrop scale. The MER rovers transformed our understanding of Meridiani Planum and Gusev Crater with their microscopic imaging, high resolution spectroscopy, and studies of physical properties. A similar rover to one of the sulfate deposits in Valles Marineris would be enlightening.

The rover would need to have the following abilities:

1. Rove for several kilometers
2. Be able to climb up rocky surfaces on a 15° slope
3. A sampling arm
4. Thermogravimetric measurement of amount of water in samples

5. Resolve different types of polyhydrated sulfates (XRD)
6. Identify wide range of sulfates, carbonates, chlorides, bromides, phosphates, iron oxides, etc... (XRD)
7. Resolve variations in trace elemental composition (XRF or APXS)
8. Abundance of mineral phases present (XRD, XRF)
9. Scrap/grind/ablate off outer surface to reveal dust-free, fresh exposures
10. Microscopic imager to look at crystalline texture, possible recrystallization or diagenetic features, and fine scale bedding (and possible cross-bedding).

It is difficult to pick just one location to send a rover. Leaving aside engineering considerations, the best landing site would have spatially concentrated occurrences of multiple hydrated minerals in an interpretable stratigraphy. The sulfate evaporite basin in eastern Ius Chasma qualifies. Ius Chasma also has hydrated silicate, opal, and Fe/Mg smectite deposits on its floor. CRISM identifies hydrated silicate and opal on top of sulfate deposits, so a rover would definitely be able to investigate those phases as well. Fe/Mg smectite is not seen adjacent to the sulfate in Ius Chasma in OMEGA or CRISM data, but may be present in the sulfate-bearing basin in amounts detectable by a landed mission.

However, the Ius Chasma sulfate basin probably formed by different processes than the sulfate-bearing ILDs elsewhere in Valles Marineris. Thus a more typical ILD would be applicable to understanding the canyon-wide mineral stratigraphy. Juventae Chasma has several typical ILD deposits with kieserite, szomolnokite, polyhydrated sulfate, red hematite, and other probable ferric phases. There are undoubtedly other minerals present as well. The plateau to the west of Juventae Chasma also hosts thin opaline and dehydrated jarosite deposits. These phases may have been transported

into the chasma by fluvial processes and may be available for study by a rover. While Ius and Juventae Chasmata have specific charms, almost any of the sulfate deposits are worthy of further landed investigation.

# Appendix A

## Sulfate mineral names and formulas

Sulfate minerals are categorized in the table by cation and hydration state. First are hydrated Mg, Ca, and  $\text{Fe}^{2+}$  sulfates; then hydrated chlorides and Fe-poor sulfates; hydrated mixed iron sulfates; anhydrous hydroxylated sulfates; and finally anhydrous sulfates and chlorides. The list is not exhaustive but includes all sulfates mentioned in the text as well as selected related sulfates.

|                  |                                                                 |
|------------------|-----------------------------------------------------------------|
| kieserite        | $\text{MgSO}_4 \bullet \text{H}_2\text{O}$                      |
| sanderite        | $\text{MgSO}_4 \bullet 2\text{H}_2\text{O}$                     |
| starkeyite       | $\text{MgSO}_4 \bullet 4\text{H}_2\text{O}$                     |
| hexahydrite      | $\text{MgSO}_4 \bullet 6\text{H}_2\text{O}$                     |
| epsomite         | $\text{MgSO}_4 \bullet 7\text{H}_2\text{O}$                     |
| meridianiite     | $\text{MgSO}_4 \bullet 11\text{H}_2\text{O}$                    |
| anhydrite        | $\text{CaSO}_4$                                                 |
| bassanite        | $\text{CaSO}_4 \bullet 0.5\text{H}_2\text{O}$                   |
| gypsum           | $\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$                     |
| syngenite        | $\text{K}_2\text{Ca}(\text{SO}_4)_2 \bullet \text{H}_2\text{O}$ |
| szomolnokite     | $\text{FeSO}_4 \bullet \text{H}_2\text{O}$                      |
| rozenite         | $\text{FeSO}_4 \bullet 4\text{H}_2\text{O}$                     |
| siderotil        | $\text{FeSO}_4 \bullet 5\text{H}_2\text{O}$                     |
| ferrohexahydrite | $\text{FeSO}_4 \bullet 6\text{H}_2\text{O}$                     |
| melanterite      | $\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$                     |
| antarcticite     | $\text{CaCl}_2 \bullet 6\text{H}_2\text{O}$                     |
| bischofite       | $\text{MgCl}_2 \bullet 6\text{H}_2\text{O}$                     |
| carnallite       | $\text{KMgCl}_3 \bullet 6\text{H}_2\text{O}$                    |
| sinjarite        | $\text{CaCl}_2 \bullet 2\text{H}_2\text{O}$                     |
| kainite          | $\text{KMg}(\text{SO}_4)\text{Cl} \bullet 3\text{H}_2\text{O}$  |

|                    |                                                                                                                    |
|--------------------|--------------------------------------------------------------------------------------------------------------------|
| polyhalite         | $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \bullet 2\text{H}_2\text{O}$                                        |
| leonite            | $\text{K}_2\text{Mg}_2(\text{SO}_4)_2 \bullet 4\text{H}_2\text{O}$                                                 |
| picromerite        | $\text{K}_2\text{Mg}_2(\text{SO}_4)_2 \bullet 6\text{H}_2\text{O}$                                                 |
| pickeringite       | $\text{MgAl}_2(\text{SO}_4)_4 \bullet 22\text{H}_2\text{O}$                                                        |
| alunogen           | $\text{Al}_2(\text{SO}_4)_3 \bullet 17\text{H}_2\text{O}$                                                          |
| bloedite           | $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \bullet 4\text{H}_2\text{O}$                                                  |
| schwertmannite     | $\text{Fe}_{16}^{3+} \text{O}_{16}(\text{OH}, \text{SO}_4)_{12-13} \bullet 10-12\text{H}_2\text{O}$                |
| copiapite          | $\text{Fe}^{2+} \text{Fe}_4^{3+} [(\text{OH})_2 (\text{SO}_4)_3]_2 \bullet 20\text{H}_2\text{O}$                   |
| ferricopiapite     | $\text{Fe}_5^{3+} (\text{SO}_4)_6 \text{O}(\text{OH}) \bullet 20\text{H}_2\text{O}$                                |
| coquimbite         | $\text{Fe}_2^{3+} (\text{SO}_4)_3 \bullet 9\text{H}_2\text{O}$                                                     |
| bilinite           | $\text{Fe}^{2+} \text{Fe}_2^{3+} (\text{SO}_4)_4 \text{O} \bullet 22\text{H}_2\text{O}$                            |
| halotrichite       | $\text{Fe}^{2+} \text{Al}_2 (\text{SO}_4)_4 \bullet 22\text{H}_2\text{O}$                                          |
| metavoltine        | $(\text{K}, \text{Na})_8 \text{Fe}^{2+} \text{Fe}_6^{3+} (\text{SO}_4)_1 2\text{O}_2 \bullet 20\text{H}_2\text{O}$ |
| sideronatriite     | $\text{Na}_2 \text{Fe}^{3+} (\text{SO}_4)_2 \text{OH} \bullet 3\text{H}_2\text{O}$                                 |
| kornelite          | $\text{Fe}_2^{3+} (\text{SO}_4)_3 \bullet 6\text{H}_2\text{O}$                                                     |
| lausenite          | $\text{Fe}_2^{3+} (\text{SO}_4)_3 \bullet 7\text{H}_2\text{O}$                                                     |
| romerite           | $\text{Fe}^{2+} \text{Fe}_2^{3+} (\text{SO}_4)_4 \bullet 14\text{H}_2\text{O}$                                     |
| rhomboclase        | $\text{HFe}^{3+} (\text{SO}_4)_2 \bullet 4\text{H}_2\text{O}$                                                      |
| alunite            | $\text{KAl}_3 [(\text{OH})_3 \text{SO}_4]_2$                                                                       |
| jarosite           | $\text{Fe}_3 [(\text{OH})_2 \text{SO}_4]_2$                                                                        |
| natrojarosite      | $\text{NaFe}_3^{3+} [(\text{OH})_3 \text{SO}_4]_2$                                                                 |
| hydronium jarosite | $(\text{H}_3\text{O})\text{Fe}_3^{3+} [(\text{OH})_3 \text{SO}_4]_2$                                               |
| anglesite          | $\text{Na}_2\text{Ca}(\text{SO}_4)_2$                                                                              |
| thenardite         | $\text{Na}_2\text{SO}_4$                                                                                           |
| vanthoffite        | $\text{Na}_6\text{Mg}(\text{SO}_4)_4$                                                                              |
| langbeinite        | $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$                                                                             |
| arcanite           | $\text{K}_2\text{SO}_4$                                                                                            |
| mercallite         | $\text{KHSO}_4$                                                                                                    |
| barite             | $\text{BaSO}_4$                                                                                                    |
| celestine          | $\text{SrSO}_4$                                                                                                    |
| glaserite          | $(\text{K}, \text{Na})_3 \text{Na}(\text{SO}_4)_2$                                                                 |
| glauberite         | $\text{Na}_2\text{Ca}(\text{SO}_4)_2$                                                                              |
| halite             | $\text{NaCl}$                                                                                                      |
| sylvite            | $\text{KCl}$                                                                                                       |

# Appendix B

## CRISM targeted observations in Valles Marineris with sulfate and/or ferric phases

This appendix lists all targeted CRISM observations in Valles Marineris that show either hydrated sulfates, ferric oxides, or both. “Latitude” and “Longitude” are the central latitude and longitude of the observation. The “sulfate” category is classified as -1: long wavelength imagery not acquired, 0: no sulfate detected, 1: PHS, 2: kieserite, 3: PHS and kieserite, and 4: sulfate and another hydrated phase. The “ferric phase” category is classified as -1: short wavelength imagery not acquired, 0: no ferric phase detected, 1: red crystalline hematite, 2: probable hematite, 3: ferric phase, and 4: multiple ferric phases present. Multiple ferric phases could include red hematite plus another deposit with a different ferric absorption, perhaps due to another ferric oxide or sulfate. The location of ferric phases was classified as 1: in bedrock only, 2: in loose material only, or 3: in both bedrock and loose material. In observations where multiple ferric phases were detected, often one type would be in bedrock and the other in loose material.

| Latitude | Longitude | Observation | Chasma    | Sulfate | Ferric phase | Loc. |
|----------|-----------|-------------|-----------|---------|--------------|------|
| -12.66   | -47.28    | FRT0000282F | Eos       | 1       | 1            | 1    |
| -12.6    | -46.68    | FRT00003050 | Capri     | 3       | 3            | 1    |
| -12.88   | -48.41    | FRT000035BD | Capri     | 3       | 1            | 1    |
| -4.89    | -89.24    | FRT00003EEF | Tithonium | 3       | 1            | 3    |
| -5.7     | -75.6     | FRT00004694 | Candor    | 3       | 2            | 1    |
| -13.1    | -64.7     | FRT0000474F | Coprates  | 4       | 0            |      |
| -5.29    | -89.24    | FRT0000510D | Tithonium | 3       | 0            |      |
| -5.79    | -75.83    | FRT00005350 | Candor    | 1       | 0            |      |
| -5.26    | -76.53    | FRT00005521 | Candor    | 3       | 4            | 3    |
| -4.53    | -62.13    | FRT00005633 | Juventae  | 3       | 1            | 1    |
| -4.6     | -63.1     | FRT00005C2B | Juventae  | 2       | -1           |      |

| Latitude | Longitude | Observation | Chasma    | Sulfate | Ferric phase | Loc. |
|----------|-----------|-------------|-----------|---------|--------------|------|
| -5.79    | -75.16    | FRT00005D17 | Candor    | 1       | 1            |      |
| -11.83   | -69.18    | FRT00005D59 | Melas     | 1       | 3            | 2    |
| -10.26   | -73.76    | FRT000061BD | Melas     | 3       | 1            | 1    |
| -12.17   | -68.94    | FRT000061F3 | Melas     | 3       | 0            |      |
| -6.11    | -73.91    | FRT00006470 | Candor    | 3       | 4            | 3    |
| -8.58    | -65.54    | FRT00006622 | Candor    | 1       | 0            |      |
| -13.39   | -48.66    | FRT000066F5 | Capri     | 3       | 1            | 1    |
| -4.9     | -90.26    | FRT0000679F | Tithonium | 3       | 0            |      |
| -12.53   | -46.16    | FRT0000681A | Capri     | 1       | 1            | 1    |
| -2.06    | -17.59    | FRT00007E16 | Iani      | 1       | 0            |      |
| -4.64    | -89.57    | FRT00007EC9 | Tithonium | 3       | 0            |      |
| -15.86   | -50       | FRT00007F63 | Eos       | 3       | 0            |      |
| -12.51   | -46.19    | FRT00007FAA | Capri     | 3       | 1            | 1    |
| -4.68    | -63.2     | FRT0000803B | Juventae  | 2       | 2            | 1    |
| -8.26    | -66.87    | FRT000081A4 | Candor    | 1       | 0            |      |
| -4.92    | -89.68    | FRT0000835F | Tithonium | 3       | 3            | 3    |
| -6.21    | -69.58    | FRT0000849B | Candor    | 3       | 0            |      |
| -12.89   | -48.39    | FRT000085F9 | Capri     | 2       | 1            | 1    |
| -7.39    | -66.66    | FRT0000869B | Candor    | 1       | 0            |      |
| -6.44    | -67.88    | FRT00008849 | Candor    | 0       | 2            | 3    |
| -8.72    | -79.21    | FRT00008950 | Ius       | 4       | 0            |      |
| -10.19   | -69.34    | FRT00008A02 | Coprates  | 2       | 0            |      |
| -4.65    | -26.94    | FRT00008C71 | Aureum    | 3       | 1            | 3    |
| -14.15   | -48.06    | FRT00008CC0 | Capri     | 2       | 1            | 1    |
| -9.2     | -78.05    | FRT00008E66 | Ius       | 1       | 0            |      |
| -5.36    | -89.76    | FRT00009390 | Tithonium | 1       | 2            | 1    |
| -8.66    | -79.24    | FRT00009445 | Ius       | 3       | 0            |      |
| -10.44   | -98.47    | FRT000096EE | Noctis    | 4       | 4            | 3    |
| -3.95    | -61.88    | FRT000097A8 | Juventae  | 2       | 1            | 1    |
| -5.37    | -89.41    | FRT000097B1 | Tithonium | 3       | 1            | 3    |
| -6.45    | -73.68    | FRT000098BB | Candor    | 2       | 1            | 3    |
| -6.26    | -69.15    | FRT00009901 | Candor    | 3       | 1            | 1    |
| -6.75    | -48.97    | FRT00009A1B | Ganges    | 1       | 2            | 1    |
| -5.81    | -76.02    | FRT00009A20 | Candor    | 3       | 4            | 3    |
| -6.35    | -70.49    | FRT00009A67 | Candor    | 3       | 2            | 3    |
| -3.95    | -61.88    | FRT00009ADC | Juventae  | 2       | 1            | 1    |
| -4.42    | -62.31    | FRT00009C0A | Juventae  | 3       | 4            | 3    |
| -5.85    | -73.89    | FRT00009CB6 | Candor    | 2       | 4            | 3    |
| -13.89   | -58.95    | FRT00009D64 | Coprates  | 4       | 0            |      |
| -4.32    | -27.04    | FRT00009DAD | Aureum    | 3       | 3            | 1    |
| -5.81    | -76.02    | FRT00009DF9 | Candor    | 3       | 3            | 3    |



| Latitude | Longitude | Observation | Chasma    | Sulfate | Ferric phase | Loc. |
|----------|-----------|-------------|-----------|---------|--------------|------|
| -4.37    | -26.8     | FRT0000A0B2 | Aureum    | 1       | 0            |      |
| -7.24    | -49.44    | FRT0000A0F0 | Ganges    | 3       | 2            | 1    |
| -9.77    | -70.13    | FRT0000A131 | Melas     | 4       | 0            |      |
| -3.92    | -26.61    | FRT0000A38B | Aureum    | 3       | 3            | 1    |
| -11.12   | -75.11    | FRT0000A3E9 | Melas     | 1       | 0            |      |
| -5.56    | -73.48    | FRT0000A5B6 | Candor    | -1      | 2            | 1    |
| -12.88   | -49.55    | FRT0000A82E | Eos       | 3       | 3            | 1    |
| -4.69    | -72.91    | FRT0000A86A | Ophir     | 3       | 4            | 3    |
| -8.56    | -79.46    | FRT0000A91C | Ius       | 3       | 0            |      |
| -6.96    | -75.1     | FRT0000A938 | Candor    | 1       | 0            |      |
| -12.35   | -69.59    | FRT0000A95B | Melas     | 3       | 3            | 2    |
| -8.91    | -77.19    | FRT0000AA51 | Ius       | 1       | 0            |      |
| -6.1     | -76.13    | FRT0000B0F2 | Candor    | 3       | 0            |      |
| -4.08    | -74.27    | FRT0000B27B | Ophir     | 3       | 0            |      |
| -13.22   | -47.46    | FRT0000B385 | Eos       | 3       | 4            | 3    |
| -6.07    | -71.05    | FRT0000B3C0 | Candor    | 2       | 0            |      |
| -5.54    | -73.25    | FRT0000B4D2 | Candor    | 2       | 2            | 1    |
| -10.36   | -68.81    | FRT0000B64A | Coprates  | 3       | 4            | 3    |
| -12.61   | -47.2     | FRT0000B776 | Eos       | 3       | 1            | 1    |
| -12.77   | -47.5     | FRT0000BB25 | Capri     | 3       | 1            | 1    |
| -5.34    | -75.34    | FRT0000BB2A | Candor    | 1       | 2            | 1    |
| -4.37    | -71.18    | FRT0000BB63 | Ophir     | 2       | 1            | 2    |
| -5.21    | -72.77    | FRT0000BD02 | Ophir     | 2       | 4            | 3    |
| -6.27    | -69.36    | FRT0000BE68 | Candor    | 3       | 4            | 3    |
| -12.77   | -47.5     | FRT0000C152 | Capri     | 3       | 1            | 1    |
| -6.27    | -72.92    | FRT0000C433 | Ophir     | 0       | 2            | 2    |
| -6.28    | -69.21    | FRT0000C470 | Candor    | 3       | 4            | 3    |
| -13.06   | -47.46    | FRT0000C564 | Capri     | 3       | 2            | 3    |
| -14.3    | -48.56    | FRT0000C678 | Capri     | 3       | 1            | 1    |
| -4.35    | -62.33    | FRT0000C72A | Juventae  | 3       | 4            | 3    |
| -13.24   | -45.55    | FRT0000C81D | Eos       | 2       | 1            | 1    |
| -6.26    | -69.38    | FRT0000C87C | Candor    | 3       | 4            | 3    |
| -6.26    | -69.36    | FRT0000CCB5 | Candor    | 3       | 4            | 3    |
| -5.19    | -89.02    | FRT0000CE25 | Tithonium | 3       | 1            | 1    |
| -13.39   | -48.86    | FRT0000D117 | Capri     | 2       | 1            | 1    |
| -5.99    | -73.74    | FRT0000D272 | Candor    | 3       | 1            | 3    |
| -13.33   | -47.53    | FRT0000D3A4 | Capri     | 3       | 4            | 3    |
| -8.55    | -79.92    | FRT0000D5F8 | Ius       | 1       | 0            |      |
| -12.82   | -46.51    | FRT0000D62D | Capri     | 2       | 1            | 1    |
| -5.7     | -75.41    | HRL00002831 | Candor    | 1       | 2            | 1    |
| -3.55    | -61.75    | HRL000028A6 | Juventae  | 2       | 2            | 1    |

| Latitude | Longitude | Observation | Chasma    | Sulfate | Ferric phase | Loc. |
|----------|-----------|-------------|-----------|---------|--------------|------|
| -6.67    | -75.77    | HRL000033B7 | Candor    | 1       | 3            | 3    |
| -10.23   | -68.82    | HRL00003752 | Coprates  | 2       | 4            | 3    |
| -3.28    | -61.73    | HRL0000444C | Juventae  | 2       | 2            | 1    |
| -4.64    | -89.57    | HRL00004893 | Tithonium | 3       | 3            | 3    |
| -7.81    | -64.89    | HRL00004F38 | Candor    | 2       | 4            | 3    |
| -4.25    | -71.58    | HRL0000508A | Ophir     | 1       | 0            |      |
| -4.37    | -72.61    | HRL00005B82 | Ophir     | 2       | 1            | 1    |
| -3.61    | -26.27    | HRL00006181 | Aureum    | 3       | 3            | 1    |
| -7.13    | -49.44    | HRL0000633F | Ganges    | 2       | 2            | 1    |
| -7.35    | -45.15    | HRL0000638C | Ganges    | 1       | 0            |      |
| -5       | -89.74    | HRL000063F1 | Tithonium | 3       | 3            | 3    |
| -6.85    | -68.99    | HRL0000648F | Candor    | 3       | 1            | 1    |
| -6.23    | -69.36    | HRL00006844 | Candor    | 4       | 1            | 3    |
| -4.92    | -89.68    | HRL00007692 | Tithonium | 3       | 3            | 3    |
| -4.92    | -90.13    | HRL00008F8E | Tithonium | 3       | 1            | 2    |
| -4.67    | -88.81    | HRL0000A1BA | Tithonium | 1       | 0            |      |
| -13.83   | -50.41    | HRL0000A23F | Capri     | 3       | 2            | 3    |
| -4.32    | -71.35    | HRL0000A432 | Ophir     | 1       | 3            | 2    |
| -2.51    | -61.66    | HRL0000A4CF | Juventae  | 3       | 2            | 3    |
| -7.02    | -74.1     | HRL0000AB7A | Candor    | 2       | 1            | 1    |
| -12.01   | -46       | HRL0000AF21 | Capri     | 0       | 4            | 3    |
| -4.72    | -71.94    | HRL0000B7D4 | Ophir     | 2       | 0            |      |
| -5.14    | -73.85    | HRL0000C03D | Candor    | 3       | 1            | 1    |
| -10.23   | -69.22    | HRL0000C194 | Coprates  | 1       | 0            |      |
| -8.64    | -76.83    | HRL0000C2BA | Melas     | 1       | 0            |      |
| -4.82    | -89.97    | HRL0000C72F | Tithonium | 3       | 3            | 3    |
| -8.13    | -79.59    | HRL0000C7C6 | Ius       | 2       | 0            |      |
| -4.82    | -89.97    | HRL0000CBC8 | Tithonium | 3       | 3            | 3    |
| -5.07    | -89.3     | HRL0000D1BE | Tithonium | 2       | 1            | 3    |
| -1.1     | -75.41    | HRL0000D632 | Hebes     | 3       | 3            | 1    |
| -13.33   | -48.52    | HRL0000D770 | Capri     | 3       | 1            | 1    |
| -12.36   | -69.26    | HRS0000285D | Coprates  | 3       | 2            | 1    |
| -12.28   | -45.99    | HRS00002F87 | Capri     | 1       | 3            | 3    |
| -6.23    | -69.23    | HRS00002FAF | Candor    | 3       | 3            | 4    |
| -10.26   | -73.76    | HRS000044E6 | Melas     | 3       | 1            | 1    |
| -5.49    | -75.89    | FRT0000BE37 | Candor    | 3       | 3            | 2    |
| -5.71    | -75.52    | FRT0000C9E8 | Candor    | 2       | 2            | 1    |
| -5.11    | -76.48    | FRT0000CD9C | Candor    | 2       | 4            | 3    |
| -4.89    | -89.22    | FRT0000ACC1 | Tithonium | 3       | 1            | 3    |
| -2.51    | -61.64    | FRT0000A4CF | Juventae  | 3       | 2            | 3    |
| -5.29    | -75.8     | HRL00007C86 | Candor    | 2       | 3            | 2    |

# Bibliography

- M. Abrams, E. Abbot, and A. Kahle. Combined use of visible, reflected infrared, and thermal infrared images for mapping hawaiian lava flows. *Journal of Geophysical Research (Planets)*, 96:475–484, 1991.
- C. C. Allen. Volcano-ice interactions on Mars. *Journal of Geophysical Research (Planets)*, 84:8048–8059, 1979.
- J. H. Anderson and K. A. Wischersheim. Near infrared characterization of water and hydroxyl groups on silica surfaces. *Surface Science*, 2:252–260, 1964.
- J. C. Andrews-Hanna, M. T. Zuber, and R. J. Phillips. Meridiani Planum: Implications for the Hydrologic and Climatic Evolution of Mars. *LPI Contributions*, 1353: 3173, July 2007a.
- J. C. Andrews-Hanna, M. T. Zuber, and R. J. Phillips. Early Mars Hydrology: Valley Networks and Evaporites. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Institute Conference Abstracts*, page 1993, March 2008.
- J. H. Andrews-Hanna, R. Phillips, and M. Zuber. Meridani Planum and the global hydrology of Mars. *Nature*, 446:163–168, 2007b.
- R. E. Arvidson, F. Poulet, J.-P. Bibring, M. Wolff, A. Gendrin, R. V. Morris, J. J. Freeman, Y. Langevin, N. Mangold, and G. Bellucci. Spectral Reflectance and Morphologic Correlations in Eastern Terra Meridiani, Mars. *Science*, 307:1591–1594, March 2005. doi: 10.1126/science.1109509.
- R. E. Arvidson, F. Poulet, R. V. Morris, J.-P. Bibring, J. F. Bell, S. W. Squyres, P. R. Christensen, G. Bellucci, B. Gondet, B. L. Ehlmann, W. H. Farrand, R. L. Fergason, M. Golombek, J. L. Griffes, J. Grotzinger, E. A. Guinness, K. E. Herkenhoff, J. R. Johnson, G. Klingelhöfer, Y. Langevin, D. Ming, K. Seelos, R. J. Sullivan, J. G. Ward, S. M. Wiseman, and M. Wolff. Nature and origin of the hematite-bearing plains of Terra Meridiani based on analyses of orbital and Mars Exploration rover data sets. *Journal of Geophysical Research (Planets)*, 111:12, November 2006. doi: 10.1029/2006JE002728.

- A. K. Baird, P. Toulmin, III, H. J. Rose, Jr., R. P. Christian, B. C. Clark, K. Keil, and J. L. Gooding. Mineralogic and petrologic implications of Viking geochemical results from Mars - Interim report. *Science*, 194:1288–1293, December 1976. doi: 10.1126/science.194.4271.1288.
- A. M. Baldridge, J. Michalski, J. Kargel, S. Hook, G. Marion, J. Crowley, N. Bridges, A. Brown, B. Ribeiro da Luz, C. R. de Souza Filho, and B. Thomson. Using Australian Acidic Playa Lakes as Analogs for Phyllosilicate and Sulfate Depositional Environments on Mars. *AGU Fall Meeting Abstracts*, page A6, December 2008.
- J. L. Bandfield and M. D. Smith. Multiple emission angle surface-atmosphere separations of Thermal Emission Spectrometer data. *Icarus*, 161:47–65, 2003. doi: doi:10.1016/S0019-1035(02)00025-8.
- J. L. Bandfield, T. D. Glotch, and P. R. Christensen. Spectroscopic Identification of Carbonate Minerals in the Martian Dust. *Science*, 301:1084–1087, August 2003. doi: 10.1126/science.1088054.
- A. Banin, F. X. Han, I. Kan, and A. Cicelsky. Acidic volatiles and the Mars Soil. *Journal of Geophysical Research (Planets)*, 102:13341–13356, June 1997. doi: 10.1029/97JE01160.
- V. Barron, J. Torrent, and J. P. Greenwood. Transformation of jarosite to hematite in simulated Martian brines. *Earth and Planetary Science Letters*, 251:380–385, 2006. doi: 10.1016/j.epsl.2006.09.022.
- J. F. Bell, H. Y. McSween, J. A. Crisp, R. V. Morris, S. L. Murchie, N. T. Bridges, J. R. Johnson, D. T. Britt, M. P. Golombek, H. J. Moore, A. Ghosh, J. L. Bishop, R. C. Anderson, J. Brückner, T. Economou, J. P. Greenwood, H. P. Gunnlaugsson, R. M. Hargraves, S. Hviid, J. M. Knudsen, M. B. Madsen, R. Reid, R. Rieder, and L. Soderblom. Mineralogic and compositional properties of Martian soil and dust: Results from Mars Pathfinder. *J. Geophys. Res.*, 105:1721–1756, January 2000. doi: 10.1029/1999JE001060.
- R. A. Berner. *Handbook of Geochemistry II-2*, chapter Iron behavior during weathering sedimentation and diagenesis, page Section 26. Springer-Verlag, 1970.
- R. A. Beyer and A. S. McEwen. Constraints on the Origin of Fine Layers in Ganges Mensa and Hebes Mensa, Mars. In S. Mackwell and E. Stansbery, editors, *36th Annual Lunar and Planetary Science Conference*, volume 36 of *Lunar and Planetary Institute Science Conference Abstracts*, page 1070, March 2005.
- R. A. Beyer, H. J. Melosh, A. S. McEwen, and R. D. Lorenz. Salt Diapirs in Candor Chasma, Mars? In *Lunar and Planetary Institute Conference Abstracts*, volume 31 of *Lunar and Planetary Institute Conference Abstracts*, page 2022, March 2000.

- R. A. Beyer, C. M. Weitz, B. J. Thompson, J. M. Moore, A. S. McEwen, and Hirise Team. HiRISE Observations of Valles Marineris Layering. *LPI Contributions*, 1353: 3310, July 2007.
- J.-P. Bibring, A. Soufflot, M. Berthé, Y. Langevin, B. Gondet, P. Drossart, M. Bouyé, M. Combes, P. Puget, A. Semery, G. Bellucci, V. Formisano, V. Moroz, V. Kottsov, G. Bonello, S. Erard, O. Forni, A. Gendrin, N. Manaud, F. Poulet, G. Poulleau, T. Encrenaz, T. Fouchet, R. Melchiori, F. Altieri, N. Ignatiev, D. Titov, L. Zasova, A. Coradini, F. Capacionni, P. Cerroni, S. Fonti, N. Mangold, P. Pinet, B. Schmitt, C. Sotin, E. Hauber, H. Hoffmann, R. Jaumann, U. Keller, R. Arvidson, J. Mustard, and F. Forget. OMEGA: Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité. In A. Wilson and A. Chicarro, editors, *Mars Express: the Scientific Payload*, volume 1240 of *ESA Special Publication*, pages 37–49, August 2004.
- J. P. Bibring, Y. Langevin, A. Gendrin, B. Gondet, F. Poulet, M. Berthe, A. Soufflot, R. Arvidson, N. Mangold, J. Mustard, P. Drossart, and Omega Team. Mars surface diversity as revealed by the OMEGA/Mars Express observations. *Science*, 307(5715):1576–1581, 2005. ISSN 0036-8075.
- J. P. Bibring, Y. Langevin, J. F. Mustard, F. Poulet, R. Arvidson, A. Gendrin, B. Gondet, N. Mangold, P. Pinet, F. Forget, and Omega team. Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data. *Science*, 312(5772):400–404, 2006. ISSN 0036-8075.
- J.-P. Bibring, R. Arvidson, A. Gendrin, B. Gondet, Y. Langevin, S. Le Louelic, N. Mangold, R. Morris, J. Mustard, F. Poulet, C. Quantin, and C. Sotin. Coupled ferric oxides and sulfates on the Martian surface. *Science*, 317:1206–1210, 2007.
- J. Bigham, U. Schwertmann, and G. Pfab. Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. *Applied Geochemistry*, 11:845–849, 1996.
- J. M. Bingham and D. K. Nordstrom. *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance, Reviews in Mineralogy and Geochemistry*, chapter Iron and aluminum hydroxysulfates from acid sulfate waters, pages 351–403. Mineralogical Society of America, 2000.
- D. L. Bish, J. William Carey, D. T. Vaniman, and S. J. Chipera. Stability of hydrous minerals on the martian surface. *Icarus*, 164:96–103, July 2003. doi: 10.1016/S0019-1035(03)00140-4.
- J. Bishop and E. Murad. The visible and infrared spectral properties of jarosite and alunite. *American Mineralogist*, 90:1100–1107, 2005.
- J. Bishop, C. Pieters, and J. Green. Infrared spectroscopic analysis on the nature of water in montmorillonite. *Clay and Clay Minerals*, 42(6):702–716, 1994.

- J. Bishop, M. Lane, M. D. Dyar, and A. J. Brown. Reflectance and emission spectroscopy study of four groups of phyllosilicates: smectites, kaolinite-serpentines, chlorites and mica. *Clay Minerals*, 43:35–54, 2008a.
- J. L. Bishop, J. Madejova, P. Komadel, and H. Froschl. The influence of structural Fe, Al and Mg on the infrared OH bands in spectra of dioctahedral smectites. *Clay Minerals*, 37:607–616, 2002a.
- J. L. Bishop, E. Murad, and M. D. Dyar. The influence of octahedral and tetrahedral cation substitution on the structure of smectites and serpentines as observed through infrared spectroscopy. *Clay Minerals*, 37:617–628, 2002b.
- J. L. Bishop, P. Schiffman, M. D. Lane, and M. D. Dyar. Sulfatization Alteration in Hawaii as a Mechanism for Formation of the Sulfates Observed on Mars by OMEGA and the MER Instruments. In S. Mackwell and E. Stansbery, editors, *36th Annual Lunar and Planetary Science Conference*, volume 36 of *Lunar and Planetary Institute Conference Abstracts*, page 1456, March 2005.
- J. L. Bishop, A. J. Brown, M. Parente, M. D. Lane, M. D. Dyar, P. Schiffman, E. Murad, and E. Cloutis. VNIR spectra of sulfates formed in sulfatization and aqueous acid sulfate environments and applications to Mars. *Workshop on Martian Sulfates as Recorders of Atmospheric-Fluid-Rock Interactions*, 1331:14, 2006.
- J. L. Bishop, E. Noe Dobrea, S. L. Murchie, C. M. Weitz, W. M. Calvin, L. A. Roach, S. M. Pelkey, A. J. Brown, J. F. Mustard, J.-P. Bibring, and MRO CRISM Team. Sulfates and Mafic Minerals in Juventae Chasma as Seen by CRISM in Coordination with OMEGA, HiRISE and Context Images. *LPI Contributions*, 1353:3350, July 2007.
- J. L. Bishop, M. Parente, C. M. Weitz, E. Z. Noe Dobrea, W. M. Calvin, R. E. Milliken, L. H. Roach, S. L. Murchie, N. K. McKeown, J. F. Mustard, and CRISM Team. Characterization of Light-toned Sulfate and Hydrated Silica Layers at Juventae Chasma Using CRISM, OMEGA, HiRISE and CTX Images. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Institute Technical Report*, page 2334, March 2008b.
- J. L. Bishop, M. Parente, C. Weitz, E. Dobrea, L. H. Roach, S. L. Murchie, P. McGuire, N. McKeown, C. Rossi, A. J. Brown, W. M. Calvin, R. E. Milliken, and J. F. Mustard. Mineralogy of Juventae Chasma: sulfates in the light-toned mounds, mafic minerals in the bedrock, and hydrated silica and hydroxylated ferric sulfate on the plateau. *Journal of Geophysical Research (Planets)*, 2009.
- K. R. Blasius, J. A. Cutts, J. E. Guest, and H. Masursky. Geology of the Valles Marineris - First analysis of imaging from the Viking 1 orbiter primary mission. *Journal of Geophysical Research (Planets)*, 82:4067–4091, September 1977.

- S. Boggs. *Principles of Sedimentology and Stratigraphy*. Prentice Hall, 2001.
- G. Bonello, J.-P. Bibring, F. Poulet, A. Gendrin, B. Gondet, Y. Langevin, and S. Fonti. Visible and infrared spectroscopy of minerals and mixtures with the OMEGA/MARS-EXPRESS instrument. *Planet. Space Sci.*, 52:133–140, January 2004a. doi: 10.1016/j.pss.2003.08.014.
- G. Bonello, F. Poulet, J. Bardinzeff, S. Erard, L. d’Hendecourt, and B. Platevoet. Unmixing basalt composition from laboratory reflectance spectroscopy. *Geophysical Research Abstracts*, 6:07119, 2004b.
- H. Borchert and R. O. Muir. *Salt Deposits: The Origin, Metamorphism, and Deformation of Evaporites*. D. Van Nostrand Co, Ltd., 1964.
- J. Bourgeois and S. Som. Stratigraphic architectures spotted in southern Melas Chasma, Valles Marineris, Mars: Comment. *Geology*, 2007. doi: 10.1130/G24181C.1.
- J. Bridge and R. Demicco. *Earth surface processes, landforms and sediment deposits*. Cambridge University Press, 2008.
- M A. Bullock and J. M. Moore. Atmospheric conditions on early Mars and the missing layered carbonates. *Geophys. Res. Lett.*, 34, 2007. doi: 10.1029/2007GL030688.
- R. G. Burns. *Remote Geochemical Analysis: Elemental and Mineralogical Composition*, chapter Origin of electronic spectra of minerals in the visible to near-infrared region, pages 3–29. Cambridge University Press, 1993.
- R. G. Burns and D. S. Fisher. Iron-sulfur mineralogy of Mars - Magmatic evolution and chemical weathering products. *J. Geophys. Res.*, 95:14415–14421, August 1990. doi: 10.1029/JB095iB09p14415.
- W. M. Calvin, J. D. Shoffner, J. R. Johnson, A. H. Knoll, J. M. Pockock, S. W. Squyres, C. M. Weitz, R. E. Arvidson, J. F. Bell, P. R. Christensen, P. A. de Souza, W. H. Farrand, T. D. Glotch, K. E. Herkenhoff, B. L. Jolliff, A. T. Knudson, S. M. McLennan, A. D. Rogers, and S. D. Thompson. Hematite spherules at Meridiani: Results from MI, Mini-TES, and Pancam. *Journal of Geophysical Research (Planets)*, 113:12, December 2008. doi: 10.1029/2007JE003048.
- W. M. Calvin, L. H. Roach, F. P. Seelos, K. D. Seelos, S. L. Murchie, and J. F. Mustard. CRISM observations of northern Martian latitudes in summer. *Journal of Geophysical Research (Planets)*, 2009.
- M. H. Carr. Tectonism and volcanism of the Tharsis region of Mars. *Journal of Geophysical Research (Planets)*, 79:3943–3949, 1974.

- D. C. Catling, S. E. Wood, C. Leovy, D. R. Montgomery, H. M. Greenberg, C. R. Glein, and J. M. Moore. Light-toned layered deposits in Juventae Chasma, Mars. *Icarus*, 181:26–51, March 2006. doi: 10.1016/j.icarus.2005.10.020.
- M. Chapman. *The geology of Mars: evidence from Earth-based analogs*. Cambridge University Press, New York, 2007.
- M. G. Chapman and K. L. Tanaka. Interior trough deposits on Mars: Subice volcanoes? *Journal of Geophysical Research (Planets)*, 106:10087–10100, May 2001. doi: 10.1029/2000JE001303.
- M. G. Chapman, A. Dumke, G. Michaels, and G. Neukum. Possible glacial erosion of Interior Layered Deposit mounds in Central Candor Chasma. *AGU Fall Meeting Abstracts*, 2007.
- V. Chevrier, P.-E. Mathé, P. Rochette, O. Grauby, G. Bourrié, and F. Trolard. Iron weathering products in a CO<sub>2</sub> and (H<sub>2</sub>O or H<sub>2</sub>O<sub>2</sub>) atmosphere: Implications for weathering processes on the surface of Mars. *Geochim. Cosmochim. Acta*, 70:4295–4317, August 2006. doi: 10.1016/j.gca.2006.06.1368.
- S. J. Chipera and D. T. Vaniman. Experimental stability of magnesium sulfate hydrates that may be present on Mars. *Geochim. Cosmochim. Acta*, 71:241–250, January 2007. doi: 10.1016/j.gca.2006.07.044.
- S. J. Chipera, D. T. Vaniman, D. L. Bish, J. W. Carey, and W. C. Feldman. Experimental Stability and Transformation Kinetics of Magnesium Sulfate Hydrates that may be Present on Mars. In S. Mackwell and E. Stansbery, editors, *36th Annual Lunar and Planetary Science Conference*, volume 36 of *Lunar and Planetary Institute Conference Abstracts*, page 1497, March 2005.
- S. J. Chipera, D. T. Vaniman, and J. W. Carey. Dehydration and Metastable States of Mg-Sulfate Hydrates that May be Present on Mars. In S. Mackwell and E. Stansbery, editors, *37th Annual Lunar and Planetary Science Conference*, volume 37 of *Lunar and Planetary Institute Conference Abstracts*, page 1457, March 2006.
- M. Chojnacki and B. Hynek. Geological context of water-altered minerals in Valles Marineris, Mars. *Journal of Geophysical Research (Planets)*, 113, 2008. doi: 10.1029/2007JE003070.
- M. Chojnacki, B. M. Jakosky, and B. Hynek. Surficial properties of landslides and surrounding units in Ophir Chasma, Mars. *Journal of Geophysical Research (Planets)*, 111, 2006. doi: 10.1029/2005JE00302601.
- I.-M. Chou and R. R. Seal. Magnesium and calcium sulfate stabilities and the water budget of Mars. *Journal of Geophysical Research (Planets)*, 112(E11):11004, November 2007. doi: 10.1029/2007JE002898.



- P. R. Christensen and S. Ruff. Formation of the hematite-bearing unit in Meridiani Planum: Evidence for deposition in standing water. *Journal of Geophysical Research (Planets)*, 109, 2004. doi: 10.1029/2003JE002233.
- P. R. Christensen, J. L. Bandfield, R. N. Clark, K. S. Edgett, V. E. Hamilton, T. Hoefen, H. H. Kieffer, R. O. Kuzmin, M. D. Lane, M. C. Malin, R. V. Morris, J. C. Pearl, R. Pearson, T. L. Roush, S. W. Ruff, and M. D. Smith. Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: Evidence for near-surface water. *Journal of Geophysical Research-Planets*, 105(E4): 9623–9642, 2000. ISSN 0148-0227.
- P. R. Christensen, J. L. Bandfield, V. E. Hamilton, S. W. Ruff, H. H. Kieffer, T. N. Titus, M. C. Malin, R. V. Morris, M. D. Lane, R. L. Clark, B. M. Jakosky, M. T. Mellon, J. C. Pearl, B. J. Conrath, M. D. Smith, R. T. Clancy, R. O. Kuzmin, T. Roush, G. L. Mehall, N. Gorelick, K. Bender, K. Murray, S. Dason, E. Greene, S. Silverman, and M. Greenfield. Mars Global Surveyor Thermal Emission Spectrometer experiment: Investigation description and surface science results. *Journal of Geophysical Research (Planets)*, 106:23823–23872, October 2001. doi: 10.1029/2000JE001370.
- P. R. Christensen, J. L. Bandfield, J. F. Bell, N. Gorelick, V. E. Hamilton, A. Ivanov, B. M. Jakosky, H. H. Kieffer, M. D. Lane, M. C. Malin, T. McConnochie, A. S. McEwen, H. Y. McSween, G. L. Mehall, J. E. Moersch, K. H. Nealson, J. W. Rice, M. I. Richardson, S. W. Ruff, M. D. Smith, T. N. Titus, and M. B. Wyatt. Morphology and Composition of the Surface of Mars: Mars Odyssey THEMIS Results. *Science*, 300:2056–2061, June 2003. doi: 10.1126/science.1080885.
- P. R. Christensen, H. Y. McSween, J. L. Bandfield, S. W. Ruff, A. D. Rogers, V. E. Hamilton, N. Gorelick, M. B. Wyatt, B. M. Jakosky, H. H. Kieffer, M. C. Malin, and J. E. Moersch. Evidence for magmatic evolution and diversity on Mars from infrared observations. *Nature*, 436:504–509, July 2005. doi: 10.1038/nature03639.
- B. C. Clark and D. C. van Hart. The salts of Mars. *Icarus*, 45:370–378, February 1981. doi: 10.1016/0019-1035(81)90041-5.
- B. C. Clark, R. V. Morris, S. M. McLennan, R. Gellert, B. Jolliff, A. H. Knoll, S. W. Squyres, T. K. Lowenstein, D. W. Ming, N. J. Tosca, A. Yen, P. R. Christensen, S. Gorevan, J. Bruckner, W. Calvin, G. Dreibus, W. Farrand, G. Klingelhofer, H. Waenke, J. Zipfel, J. F. Bell, J. Grotzinger, H. Y. McSween, and R. Rieder. Chemistry and mineralogy of outcrops at Meridiani Planum. *Earth and Planetary Science Letters*, 240(1):73–94, 2005. ISSN 0012-821X.
- R. Clark, T. King, M. Klejwa, G. Sqayze, and N. Vergo. High resolution reflectance spectroscopy of minerals. *Journal of Geophysical Research (Planets)*, 95:12653–12680, 1990.

- R. Clark, G. Swayze, R. Wise, K. Livo, T. Hoefen, R. Kokaly, and S. Sutley. USGS Digital Spectral Library splib06a, 2007.
- R.N. Clark. *Manual of Remote Sensing*, chapter Spectroscopy of rocks and minerals, and principles of spectroscopy, pages 3–58. John Wiley and Sons, Inc, 1999.
- S. M. Clifford. A model fo the hydrologic and climatic behavior of water on Mars. *Journal of Geophysical Research Planets*, 98:10973–11016, 1993.
- E. A. Cloutis, F. C. Hawthorne, S. A. Mertzman, K. Krenn, M. A. Craig, D. Marcino, M. Methot, J. Strong, J. F. Mustard, D. L. Blaney, J. F. Bell, and F. Vilas. Detection and discrimination of sulfate minerals using reflectance spectroscopy. *Icarus*, 184:121–157, September 2006. doi: 10.1016/j.icarus.2006.04.003.
- C. D. Cooper and J. F. Mustard. Spectroscopy of loose and cemented sulfate-bearing soils: Implications for duricrust on Mars. *Icarus*, 158(1):42–55, 2002. ISSN 0019-1035.
- R. M. Cornell and U. Schwertmann. *The Iron Oxides: structure, properties, occurrence and uses*. VCH, 1996.
- R. A. Craddock and A. D. Howard. The case for rainfall on a warm, wet early Mars. *Journal of Geophysical Research (Planets)*, 107:5111, November 2002. doi: 10.1029/2001JE001505.
- S. K. Croft. Canyon Structure in the Hebes-Juventae-Gangis Area, Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 20 of *Lunar and Planetary Institute Conference Abstracts*, page 203, March 1989a.
- S. K. Croft. Spelunking on Mars: the carbonate-tectonic hypothesis for the origin of Valles Marineris. In *Tectonic Features on Mars*, pages 21–24, 1989b.
- J. Crowley. Visible and near-infrared (0.4-2.5  $\mu\text{m}$ ) reflectance spectra of playa evaporite minerals. *Journal of Geophysical Research (Planets)*, 96:16231–16240, 1991.
- J. Crowley, D. Williams, J. Hammarstrom, N. Piatak, I. M. Chou, and J. Mars. Spectral reflectance properties (0.4-2.5  $\mu\text{m}$ ) of secondary fe-oxide, fe-hydroxide, and fe-sulphate-hydrate minerals associated with sulphide-bearing mine wastes. *Geochemistry: Exploration and Environmental Analysis*, 3:219–228, 2003.
- G. Dromart, C. Quantin, and O. Broucke. Stratigraphic architectures spotted in southern Melas Chasma, Valles Marineris, Mars. *Geology*, 35:363–366, 2007. doi: 10.1130/G23350A.1.
- B. Ehlmann, J. Mustard, S. Murchie, F. Poulet, J. Bishop, A. Brown, W. Calvin, R. Clark, D. Des Marais, R. Milliken, L. H. Roach, T. Roush, G. Swayze, and J. Wray. Orbital identification of carbonate-bearing rocks on Mars. *Science*, 322:1828–1832, 2008.

- B. L. Ehlmann, J. F. Mustard, G. A. Swayze, R. N. Clark, J. L. Bishop, F. Poulet, D. Des Marais, L. H. Roach, R. E. Milliken, J. J. Wray, O. Barnouin-Jha, and S. L. Murchie. Identification of hydrated silicate minerals on Mars using MRO-CRISM: geologic context near Nili Fossae and implications for aqueous alteration. *Journal of Geophysical Research (Planets)*, 2009.
- M. Ellis, A. Densmore, and R. Anderson. Development of mountainous topography in the basin ranges, usa. *Basin Research*, 11(1):21–41, 1999.
- R. E. Ernst, E. B. Grosfils, and D. Mège. Giant Dike Swarms: Earth, Venus, and Mars. *Annual Review of Earth and Planetary Sciences*, 29:489–534, 2001. doi: 10.1146/annurev.earth.29.1.489.
- D. Fernandez-Remolar, J. Gomez-Elvira, F. Gomez, E. Sebastian, J. Martiin, J. A. Manfredi, J. Torres, C. Gonzalez Kesler, and R. Amils. The Tinto River, an extreme acidic environment under control of iron, as an analog of the Terra Meridiani hematite site of Mars. *Planet. Space Sci.*, 52:239–248, January 2004. doi: 10.1016/j.pss.2003.08.027.
- D. C. Fernandez-Remolar, R. V. Morris, J. E. Gruener, R. Amils, and A. H. Knoll. The Rio Tinto Basin, Spain: Mineralogy, sedimentary geobiology, and implications for interpretation of outcrop rocks at Meridiani Planum, Mars. *Earth and Planetary Science Letters*, 240:149–167, November 2005. doi: 10.1016/j.epsl.2005.09.043.
- K. E. Fishbaugh, F. Poulet, V. Chevrier, Y. Langevin, and J. P. Bibring. On the origin of gypsum in the mars north polar region. *Journal of Geophysical Research-Planets*, 112(E7), 2007. ISSN 0148-0227.
- F. Forget, F. Hourdin, R. Fournier, C. Hourdin, O. Talagrand, M. Collins, S. R. Lewis, P. L. Read, and J.-P. Huot. Improved general circulation models of the Martian atmosphere from the surface to above 80 km. *Journal of Geophysical Research (Planets)*, 104:24155–24176, October 1999. doi: 10.1029/1999JE001025.
- F. Forget, R. M. Haberle, F. Montmessin, B. Levrard, and J. W. Heads. Formation of glaciers on mars by atmospheric precipitation at high obliquity. *Science*, 311(5759):368–371, 2006. ISSN 0036-8075.
- J. J. Freeman, A. Wang, and B. L. Jolliff. Pathways to Form Kieserite from Epsomite at Mid to Low Temperatures, with Relevance to Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 38 of *Lunar and Planetary Institute Conference Abstracts*, page 1298, March 2007.
- R. L. Frost, J. T. Klopogge, and Z. Ding. Near-infrared spectroscopic study of nontronites and ferruginous smectites. *Spectrochimica Acta Part A*, 58:1657–1668, 2002.

- F. Fueten, R. M. Stesky, and P. MacKinnon. Structural attitudes of large scale layering in Valles Marineris, Mars, calculated from Mars Orbiter Laser Altimeter data and Mars Orbiter Camera imagery. *Icarus*, 175:68–77, May 2005. doi: 10.1016/j.icarus.2004.11.010.
- F. Fueten, R. Stesky, P. MacKinnon, E. Hauber, K. Gwinner, F. Scholten, T. Zegers, G. Neukum, and HRSC Co-Investigator Team. Faulting of ILD Deposits on Ceti Mensa, Western Candor Chasma, Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 38 of *Lunar and Planetary Institute Conference Abstracts*, page 1388, March 2007.
- F. Fueten, R. Stesky, P. MacKinnon, E. Hauber, K. Gwinner, F. Scholten, and T. E. Zegers. Structural Relations of a Sulfate-bearing Unit near Ceti Mensa, Candor Chasma, Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Institute Conference Abstracts*, page 1428, March 2008.
- K. H. Fuks, A. H. Treiman, and S. Murchie. Layering in the Upper Walls of Valles Marineris, Mars: A Diagenetic Origin. In *Lunar and Planetary Institute Conference Abstracts*, volume 26 of *Lunar and Planetary Institute Conference Abstracts*, page 431, March 1995.
- S. J. Gaffey, L. A. McFadden, D. Nash, and C. M. Pieters. *Remote Geochemical Analysis: Elemental and Mineralogical Composition*, chapter Ultraviolet, Visible, and Near-infrared Reflectance Spectroscopy: Laboratory spectra of Geologic Materials, pages 43–78. Cambridge University Press, 1993.
- F. Gaillard and B. Scaillet. The sulfur content of volcanic gases on mars. *Earth and Planetary Science Letters*, 279:34–43, 2009. doi: 10.1016/j.epsl.2008.12.028.
- D. E. Garrett. *Potash: Deposits, Processing, Properties, and Uses*. Kluwer Academic Publishers, 1995.
- A. Gendrin, J.-P. Bibring, J. F. Mustard, N. Mangold, C. Quantin, B. Gondet, Y. Langevin, F. Poulet, C. Sotin, S. Le Mouélic, J.-P. Combe, and L. E. Hutchison. Identification of predominantly ferric signatures in association to the Martian sulfate deposits. In *Lunar and Planetary Institute Conference Abstracts*, volume 36 of *Lunar and Planetary Institute Conference Abstracts*, page 1378, March 2005.
- A. Gendrin, N. Mangold, J. P. Bibring, Y. Langevin, B. Gondet, F. Poulet, G. Bonello, C. Quantin, J. Mustard, R. Arvidson, and S. LeMouelic. Sulfates in martian layered terrains: the OMEGA/Mars Express view. *Science*, 307(5715):1587–1591, 2005. ISSN 0036-8075.
- A. Gendrin, J.-P. Bibring, C. Quantin, N. Mangold, S. Le Mouelic, E. Hauber, B. Gondet, Y. Langevin, F. Poulet, and R. E. Arvidson. Two Years of Sulfate

- Mapping in Valles Marineris and Terra Meridiani as Seen by OMEGA/Mars Express. In S. Mackwell and E. Stansbery, editors, *37th Annual Lunar and Planetary Science Conference*, volume 37 of *Lunar and Planetary Institute Conference Abstracts*, page 1872, March 2006.
- T. Glotch and P. R. Christensen. Geologic and mineralogic mapping of Aram Chaos: evidence for a water-rich history. *Journal of Geophysical Research*, 110, 2005. doi: 10.1029/2004JE002389.
- T. D. Glotch and A. D. Rogers. Evidence for aqueous deposition of hematite- and sulfate-rich light-toned layered deposits in Aureum and Iani Chaos, Mars. *Journal of Geophysical Research (Planets)*, 112, 2007. doi: 10.1029/2006JE002863.
- T. D. Glotch, J. L. Bandfield, P. R. Christensen, W. M. Calvin, S. M. McLennan, B. C. Clark, A. D. Rogers, and S. W. Squyres. Mineralogy of the light-toned outcrop at Meridiani Planum as seen by the Miniature Thermal Emission Spectrometer and implications for its formation. *Journal of Geophysical Research (Planets)*, 111:12, September 2006. doi: 10.1029/2005JE002672.
- W.A. Gordon. Distribution by latitude of Phanerozoic evaporite deposits. *Journal of Geology*, 83:671–684, 1975.
- M. C. Goryniuk, B. A. Rivard, and B. Jones. The reflectance spectra of opal-A (0.5–25  $\mu\text{m}$ ) from the Taupo Volcanic Zone: Spectra that may identify hydrothermal systems on planetary surfaces. *Geophysical Research Letters*, 31, 2004. doi: 10.1029/2004GL021481.
- J. Grotzinger. Depositional model for the Burns Formation, Meridiani Planum. *LPI Contributions*, 1353:3292, July 2007.
- J. P. Grotzinger, R. E. Arvidson, J. F. Bell, W. Calvin, B. C. Clark, D. A. Fike, M. Golombek, R. Greeley, A. Haldemann, K. E. Herkenhoff, B. L. Jolliff, A. H. Knoll, M. Malin, S. M. McLennan, T. Parker, L. Soderblom, J. N. Sohl-Dickstein, S. W. Squyres, N. J. Tosca, and W. A. Watters. Stratigraphy and sedimentology of a dry to wet eolian depositional system, burns formation, meridiani planum, mars. *Earth and Planetary Science Letters*, 240(1):11–72, 2005. ISSN 0012-821X.
- W. K. Hamblin. Patterns of displacement along the wasatch fault. *Geology*, 4:619–622, 1976.
- N. Hamelin, H. Racher, F. Fueten, R. Stesky, P. MacKinnon, E. Hauber, K. Gwinner, F. Scholten, and T. E. Zegers. Structural Analysis of an Interior Layered Deposit in Northern Coprates Chasma, Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Inst. Technical Report*, page 1424, March 2008.

- V. E. Hamilton, H. Y. McSween, and B. Hapke. Mineralogy of Martian atmospheric dust inferred from thermal infrared spectra of aerosols. *Journal of Geophysical Research (Planets)*, 110:12006, December 2005. doi: 10.1029/2005JE002501.
- L. A. Hardie. On the significance of evaporites. *Annuals Reviews in Earth and Planetary Science*, 19:131–168, 1991.
- L. A. Hardie. Secular variation in seawater chemistry: an explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites of the past 600 My. *Geology*, 24:279–283, 1996.
- L. A. Hardie and H. P. Eugster. The evolution of closed basin brines. *Mineral Society of America Special Publication 3*, pages 273–290, 1970.
- B. Hardy. ITS-90 formulations for vapor pressure, frostpoint temperature, dewpoint temperature, and enhancement factors in the range -100 to +100 C. *Third International Symposium on Humidity and Moisture*, 1:214–222, 1998.
- W. K. Hartmann and D. C. Berman. Elysium Planitia lava flows: Crater count chronology and geological implications. *Journal of Geophysical Research (Planets)*, 105:15011–15026, June 2000. doi: 10.1029/1999JE001189.
- W. K. Hartmann, M. Malin, A. McEwen, M. Carr, L. Soderblom, P. Thomas, E. Danielson, P. James, and J. Veverka. Evidence for recent volcanism on Mars from crater counts. *Nature*, 397:586–589, February 1999. doi: 10.1038/17545.
- E. Hauber, K. Gwinner, A. Gendrin, F. Fueten, R. Stesky, S. Pelkey, H. Wulf, D. Reiss, T. Zegers, P. MacKinnon, G. Michael, R. Jaumann, J.-P. Bibring, G. Neukum, and HRSC Co-Investigator Team. An Integrated Study of Interior Layered Deposits in Hebes Chasma, Valles Marineris, Mars, Using MGS, MO, and MEX Data. In S. Mackwell and E. Stansbery, editors, *37th Annual Lunar and Planetary Science Conference*, volume 37 of *Lunar and Planetary Inst. Technical Report*, page 2022, March 2006.
- E. Hauber, K. Gwinner, A. Gendrin, F. Fueten, R. Stesky, S. Pelkey, D. Reiss, T. E. Zegers, P. MacKinnon, R. Jaumann, J.-P. Bibring, and G. Neukum. Hebes Chasma, Mars: Slopes and Stratigraphy of Interior Layered Deposits. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Inst. Technical Report*, page 2375, March 2008.
- F.C. Hawthorne, S. Krivovichev, and P. Burns. *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance*, *Reviews in Mineralogy and Geochemistry*, chapter The crystal chemistry of sulfate minerals, pages 1–112. Mineralogical Society of America, 2000.

- N. Hoffman. Modern geothermal gradients on mars and implications for subsurface liquids. *Conference on the Geophysical Detection of Subsurface Water on Mars*, 2001.
- K. J. Hsu, W. B. F. Ryan, and M. B. Cita. Late Miocene desiccation of the Mediterranean. *Nature*, 242:240–244, 1973.
- G. R. Hunt and J. W. Salisbury. Visible and near infrared spectra of minerals and rocks. I. Silicate minerals. *Modern Geology*, 1:283–300, 1970.
- G. R. Hunt, J. W. Salisbury, and C. J. Lenhoff. Visible and near infrared spectra of minerals and rocks. III. Oxides and hydroxides. *Modern Geology*, 2:195–205, 1971a.
- G. R. Hunt, J. W. Salisbury, and C. J. Lenhoff. Visible and near infrared spectra of minerals and rocks. IV. Sulfides and Sulfates. *Modern Geology*, 3:1–14, 1971b.
- G. R. Hunt, J. W. Salisbury, and C. J. Lenhoff. Visible and near infrared spectra of minerals and rocks. VI. Additional silicates. *Modern Geology*, 4:85–106, 1973.
- L. Hutchison, J. F. Mustard, A. Gendrin, J.-P. Bibring, Y. Langevin, B. Gondet, N. Mangold, and The Omega Science Team. Mafic Polyhydrated Sulfates and Kieserite in Capri Chasma. In S. Mackwell and E. Stansbery, editors, *36th Annual Lunar and Planetary Science Conference*, volume 36 of *Lunar and Planetary Institute Science Conference Abstracts*, page 1404, March 2005.
- B. M. Hynek and R. J. Phillips. The stratigraphy of Meridiani Planum, Mars, and implications for the layered deposits’ origin. *Earth and Planetary Science Letters*, 274:214–220, September 2008. doi: 10.1016/j.epsl.2008.07.025.
- B. M. Hynek, R. E. Arvidson, and R. J. Phillips. Geologic setting and origin of Terra Meridiani hematite deposit on Mars. *Journal of Geophysical Research (Planets)*, 107:5088, October 2002. doi: 10.1029/2002JE001891.
- B. M. Hynek, R. J. Phillips, and R. E. Arvidson. Explosive volcanism in the tharsis region: Global evidence in the martian geologic record. *Journal of Geophysical Research (Planets)*, 108:5111, 2003. doi: 10.1029/2003JE002062.
- B. M. Hynek, B. M. Jakosky, N. T. Putzig, and M. T. Mellon. Extensive Bedrock Throughout Terra Meridiani, Mars: Implications for Regional Hydrologic Processes. In S. Clifford, J. Farmer, R. Haberle, H. Newsom, and T. Parker, editors, *Second Conference on Early Mars: Geologic, Hydrologic, and Climatic Evolution and the Implications for Life*, page 8058, October 2004.
- ITT Visual Information Solutions. Using continuum removal. ENVI 4.4 Help File, 2007.

- B. M. Jakosky and R. J. Phillips. Mars' volatile and climate history. *Nature*, 412: 237–244, July 2001.
- N. P. James and A. C. Kendall. Introduction to carbonate and evaporite facies models. *Geological Association of Canada*, pages 265–275, 1992.
- J. R. Johnson, J. F. Bell, E. Cloutis, M. Staid, W. H. Farrand, T. McCoy, M. Rice, A. Wang, and A. Yen. Mineralogic constraints on sulfur-rich soils from pancam spectra at gusev crater, mars. *Geophysical Research Letters*, 34(13), 2007. ISSN 0094-8276.
- D. M. Kass and Y. L. Yung. Loss of atmosphere from Mars due to solar wind-induced sputtering. *Science*, 268:697–699, 1995. doi: 10.1126/science.7732377.
- R. L. Kirk. Ultrahigh resolution topographic mapping of mars with mro hirise stereo images: Meter-scale slopes of candidate phoenix landing sites. *Journal of Geophysical Research (Planets)*, 113:E00A24, 2008.
- G. Klingelhofer, R. V. Morris, B. Bernhardt, C. Schroder, D. S. Rodionov, P. A. de Souza, A. Yen, R. Gellert, E. N. Evlanov, B. Zubkov, J. Foh, U. Bonnes, E. Kankleit, P. Gutlich, D. W. Ming, F. Renz, T. Wdowiak, S. W. Squyres, and R. E. Arvidson. Jarosite and Hematite at Meridiani Planum from Opportunity's Mössbauer Spectrometer. *Science*, 306:1740–1745, December 2004. doi: 10.1126/science.1104653.
- L. P. Knauth, D. M. Burt, and K. H. Wohletz. Impact origin of sediments at the opportunity landing site on mars. *Nature*, 438:1123–1128, 2005. doi: 10.1038/nature04383.
- R. C. Kochel and J. F. Piper. Morphology of large valleys on Hawaii - Evidence for groundwater sapping and comparisons with Martian valleys. *Journal of Geophysical Research (Planets)*, 91:175, November 1986. doi: 10.1029/JB091iB13p0E175.
- G. Komatsu and Y. Litasov. Subice Volcanism on the Azas Plateau: A Comparison with Possible Martian Tuyas. In *Lunar and Planetary Institute Conference Abstracts*, volume 33 of *Lunar and Planetary Institute Conference Abstracts*, page 1262, March 2002.
- G. Komatsu and R. G. Strom. Layered Deposits with Volcanic Instructions in Gangis Chasma, Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 21 of *Lunar and Planetary Inst. Technical Report*, page 651, March 1990.
- G. Komatsu, P. E. Geissler, R. G. Strom, and R. B. Singer. Stratigraphy and erosional landforms of layered deposits in Valles Marineris, Mars. *Journal of Geophysical Research (Planets)*, 98:11105, June 1993.



- G. Komatsu, G. G. Ori, P. Ciarcelluti, and Y. D. Litasov. Interior layered deposits of Valles Marineris, Mars: analogous subice volcanism related to Baikal Rifting, Southern Siberia. *Planet. Space Sci.*, 52:167–187, January 2004. doi: 10.1016/j.pss.2003.08.003.
- R. O. Kuzmin, M. V. Mironenko, and N. A. Evdokimova. Spectral and thermodynamic constraints on the existence of gypsum at Juventae Chasma on Mars. *Planetary and Space Science*, 2009. doi: 10.1016/j.pss/2008/1012/1008.
- M. D. Lane, J. L. Bishop, M. D. Dyar, P. L. King, and B. C. Hyde. Iron Sulfate and Sulfide Spectroscopy at Thermal Infrared Wavelengths for Application to Mars. *AGU Fall Meeting Abstracts*, page B1398, December 2008.
- Y. Langevin, F. Poulet, J. P. Bibring, and B. Gondet. Sulfates in the north polar region of Mars detected by OMEGA/Mars Express. *Science*, 307(5715):1584–1586, 2005. ISSN 0036-8075.
- J. Laskar, A. C. M. Correia, M. Gastineau, F. Joutel, B. Levrard, and P. Robutel. Long term evolution and chaotic diffusion of the insolation quantities of Mars. *Icarus*, 170:343–364, August 2004. doi: 10.1016/j.icarus.2004.04.005.
- L. Le Deit, D. Mège, O. Bourgeois, S. Le Mouélic, C. Sotin, N. Mangold, E. Hauber, A. Gendrin, and J.-P. Bibring. Morphological and Mineralogical Analysis of East Candor Chasma in Valles Marineris on Mars. *LPI Contributions*, 1353:3227, July 2007.
- L. Le Deit, S. Le Mouélic, O. Bourgeois, J.-P. Combe, D. Mège, C. Sotin, A. Gendrin, E. Hauber, N. Mangold, and J.-P. Bibring. Ferric oxides in East Candor Chasma, Valles Marineris (Mars) inferred from analysis of OMEGA/Mars Express data: Identification and geological interpretation. *Journal of Geophysical Research (Planets)*, 113:7001, July 2008. doi: 10.1029/2007JE002950.
- J. Liansheng and L. Zheng. High-precision gravity correction methods for loess plateau areas, a case study. *Applied Geophysics*, 4:89–93, 2007.
- K. A. Lichtenberg, R. E. Arvidson, R. V. Morris, S. L. Murchie, J. L. Bishop, D. Fernandez-Remolar, T. D. Glotch, E. Z. Noe Dobrea, J. F. Mustard, J. C. Andrews-Hanna, and L. H. Roach. Stratigraphy of hydrated sulfates in the sedimentary deposits of Aram Chaos, Mars. *Journal of Geophysical Research Planets*, 2009.
- T. K. Lowenstein. Evaporite depositional fabrics in the deeply buried Jurassic Buchner Formation, Alabama. *Journal of Sedimentary Petrology*, 57:108–116, 1986.
- T. K. Lowenstein. Origin of depositional cycles in a Permian saline giant: The Salado (McNutt zone) evaporites of New Mexico and Texas. *Geological Society of America Bulletin*, 100:592–608, 1988.

- T. K. Lowenstein. Origin of ancient potash evaporites: clues from the modern non-marine Qaidam Basin of Western China. *Science*, 245:1090–1092, 1989.
- T. K. Lowenstein and L. A. Hardie. Criteria for the recognition of salt-pan evaporites. *Sedimentology*, 32:627–644, 1985.
- T. K. Lowenstein, L. A. Hardie, M. N. Timofeeff, and R. V. Demicco. Secular variation in seawater chemistry and the origin of calcium chloride basinal brines. *Geology*, 31:857–860, 2003.
- T. K. Lowenstein, M. N. Tomofeeff, V. M. Kovalevych, and J. Horita. The major-ion composition of Permian seawater. *Geochimica et Cosmochimica Acta*, 69:1701–1719, 2005.
- B. K. Lucchitta. Valles Marineris - faults, volcanic rocks, channels, basin beds. Technical report, United State Geological Survey, 1981.
- B. K. Lucchitta. Lakes or playas in Valles Marineris. In *Reports of Planetary Geology Program*, NASA TM-85127:233–234, 1982.
- B. K. Lucchitta. Valles Marineris, Mars - Wet debris flows and ground ice. *Icarus*, 72:411–429, November 1987a. doi: 10.1016/0019-1035(87)90183-7.
- B. K. Lucchitta. History of Valles Marineris. In *Lunar and Planetary Institute Conference Abstracts*, volume 18 of *Lunar and Planetary Inst. Technical Report*, page 572, March 1987b.
- B. K. Lucchitta. Young volcanic deposits in the Valles Marineris, Mars? *Icarus*, 86: 476–509, August 1990. doi: 10.1016/0019-1035(90)90230-7.
- B. K. Lucchitta. Geologic map of Ophir and Central Candor Chasmata (MTM - 05072) of Mars: USGS Miscellaneous Investigation Series Map I-2568. *United States Geological Survey*, 1999.
- B. K. Lucchitta. Moc images confirm layered deposits formed within valles marineris, mars. *Lunar and Planetary Institute Conference Abstracts*, 2001.
- B. K. Lucchitta and L. M. Bertolini. Interior Structures of Valles Marineris, Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 20 of *Lunar and Planetary Inst. Technical Report*, page 590, March 1989.
- B. K. Lucchitta, A. S. McEwen, G. D. Clow, P. E. Geissler, R. B. Singer, R. A. Schultz, and S. W. Squyres. *Mars*, chapter The canyon system on Mars, pages 453–492. Arizona Press, 1992.
- B. K. Lucchitta, N. K. Isbell, and A. Howington-Kraus. Topography of Valles Marineris: Implications for erosional and structural history. *Journal of Geophysical Research (Planets)*, 99:3783–3798, February 1994.

- J.-B. Madeleine, F. Forget, J. Head, B. Levrard, F. Montmessin, and E. Millour. Amazonian northern mid-latitude glaciation on Mars: A proposed climate scenario. *Journal of Geophysical Research (Planets)*, 2008.
- M. C. Malin and K. S. Edgett. Evidence for recent groundwater seepage and surface runoff on mars. *Science*, 288(5475):2330–2335, 2000a. ISSN 0036-8075.
- M. C. Malin and K. S. Edgett. Sedimentary rocks of early Mars. *Science*, 290(5498):1927–1937, 2000b. ISSN 0036-8075.
- M. C. Malin, J. F. Bell, B. A. Cantor, M. A. Caplinger, W. M. Calvin, R. T. Clancy, K. S. Edgett, L. Edwards, R. M. Haberle, P. B. James, S. W. Lee, M. A. Ravine, P. C. Thomas, and M. J. Wolff. Context Camera Investigation on board the Mars Reconnaissance Orbiter. *Journal of Geophysical Research (Planets)*, 112:5, May 2007. doi: 10.1029/2006JE002808.
- N. Mangold, C. Quantin, V. Ansan, C. Delacourt, and P. Allemand. Evidence for Precipitation on Mars from Dendritic Valleys in the Valles Marineris Area. *Science*, 305:78–81, July 2004. doi: 10.1126/science.1097549.
- N. Mangold, A. Gendrin, B. Gondet, S. Le Mouélic, C. Quantin, J.-P. Bibring, Y. Langevin, F. Poulet, V. Ansan, P. Masson, E. Hauber, and G. Neukum. Mineralogy of West Tithonium-Noctis Labyrinthus, Mars: Putative Volcanism on Noctis Canyons Floors. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Institute Conference Abstracts*, page 1592, March 2008a.
- N. Mangold, A. Gendrin, B. Gondet, S. Lemouelic, C. Quantin, V. Ansan, J.-P. Bibring, Y. Langevin, P. Masson, and G. Neukum. Spectral and geological study of the sulfate-rich region of West Candor Chasma, Mars. *Icarus*, 194:519–543, April 2008b. doi: 10.1016/j.icarus.2007.10.021.
- N. Mangold, R. Milliken, L. Roach, F. Poulet, S. Lemouelic, D. Loizeau, V. Ansan, J. Bibring, Y. Langevin, B. Gondet, S. Murchie, and J. F. Mustard. Local Sulfate-rich Layered Deposits in Noctis Labyrinthus, Mars, and Their Chronological Consequences. *AGU Fall Meeting Abstracts*, page A3, December 2008c.
- G. M. Marion and J. S. Kargel. Stability of Magnesium Sulfate Minerals in Martian Environments. In S. Mackwell and E. Stansbery, editors, *36th Annual Lunar and Planetary Science Conference*, volume 36 of *Lunar and Planetary Institute Conference Abstracts*, page 2290, March 2005.
- J. F. McCauley. USGS Miscellaneous Investigation Series Map I-897. *United States Geological Survey*, 1978.
- J. F. McCauley, M. H. Carr, J. A. Cutts, W. K. Hartmann, H. Masursky, D. J. Milton, R. P. Sharp, and D. E. Wilhelms. Preliminary Mariner 9 Report on the Geology of Mars (A 4. 3). *Icarus*, 17:289, October 1972.

- T. M. McCollom and B. M. Hynek. A volcanic environment for bedrock diagenesis at Meridiani Planum on Mars. *Nature*, 438:1129–1131, December 2005. doi: 10.1038/nature04390.
- T. B. McCord, R. L. Huguenin, D. Mink, and C. Pieters. Spectral reflectance of Martian areas during the 1973 opposition - Photoelectric filter photometry 0.33-1.10 microns. *Icarus*, 31:25–39, May 1977. doi: 10.1016/0019-1035(77)90069-0.
- A. McEwen and L. Soderblom. Mars color/albedo and bedrock geology. *Fourth Int. Conf. Mars.*, pages 138–139, 1989.
- A. McEwen, E. Eliason, J. Bergstrom, N. Bridges, C. Hansen, W. A. Delamere, J. Grant, V. Gulick, K. Herkenhoff, L. Keszthelyi, R. Kirk, M. Mellon, S. Squyres, N. Thomas, and C. Weitz. Mars Reconnaissance Orbiter’s High Resolution Imaging Science Experiment (HiRISE). *AGU Fall Meeting Abstracts*, page A171, December 2005.
- A. S. McEwen, M. C. Malin, M. H. Carr, and W. K. Hartmann. Voluminous volcanism on early Mars revealed in Valles Marineris. *Nature*, 397(6720):584–586, 1999. ISSN 0028-0836.
- A. S. McEwen, E. M. Eliason, J. W. Bergstrom, N. T. Bridges, C. J. Hansen, W. A. Delamere, J. A. Grant, V. C. Gulick, K. E. Herkenhoff, L. Keszthelyi, R. L. Kirk, M. T. Mellon, S. W. Squyres, N. Thomas, and C. M. Weitz. Mars Reconnaissance Orbiter’s High Resolution Imaging Science Experiment (HiRISE). *Journal of Geophysical Research (Planets)*, 112, May 2007. doi: 10.1029/2005JE002605.
- P. McGuire, M. Wolff, M. Smith, R. Arvidson, S. Murchie, R. Clancy, T. Roush, S. Cull, K. Lichtenberg, S. Wiseman, R. Green, T. Martin, R. Milliken, P. Cavanaugh, D. Humm, K. Seelos, H. Taylor, B. Ehlmann, J. Mustard, S. Pelkey, T. Titus, C. Hash, and E. Malaret. CRISM Retrieval of Surface Lambert Albedos for Multi-spectral Mapping of Mars with DISORT-based Radiative Transfer Modeling: Phase 1 – Using Historical Climatology for Temperatures, Aerosol Optical Depths, and Atmospheric Pressures. *Transactions on Geoscience and Remote Sensing*, 2009.
- D. McKenzie and F. Nimmo. The generation of martian floods by the melting of ground ice above dykes. *Nature*, 397:231–233, January 1999. doi: 10.1038/16649.
- S. M. McLennan, J. F. Bell, W. M. Calvin, P. R. Christensen, B. C. Clark, P. A. de Souza, J. Farmer, W. H. Farrand, D. A. Fike, R. Gellert, A. Ghosh, T. D. Glotch, J. P. Grotzinger, B. Hahn, K. E. Herkenhoff, J. A. Hurowitz, J. R. Johnson, S. S. Johnson, B. Jolliff, G. Klingelhofer, A. H. Knoll, Z. Learner, M. C. Malin, H. Y. McSween, J. Pockock, S. W. Ruff, L. A. Soderblom, S. W. Squyres, N. J. Tosca, W. A. Watters, M. B. Wyatt, and A. Yen. Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars. *Earth and Planetary Science Letters*, 240(1):95–121, 2005. ISSN 0012-821X.

- H. Y. McSween, S. L. Murchie, D. T. Britt, J. Brückner, G. Dreibus, T. Economou, A. Ghosh, M. P. Golombek, J. P. Greenwood, J. R. Johnson, H. J. Moore, T. J. Parker, R. Rieder, R. Singer, and H. Wänke. Chemical, multispectral, and textural constraints on the composition and origin of rocks at the Mars Pathfinder landing site. *Journal of Geophysical Research (Planets)*, 104:8679–8716, April 1999. doi: 10.1029/98JE02551.
- D. Mege and P. Masson. Stress models for Tharsis formation, Mars. *Planet. Space Sci.*, 44:1471–1497, December 1996a.
- D. Mege and P. Masson. A plume tectonics model for the Tharsis province, Mars. *Planet. Space Sci.*, 44:1499–1546, December 1996b.
- M. T. Mellon, B. M. Jakosky, H. H. Kieffer, and P. R. Christensen. High-Resolution Thermal Inertia Mapping from the Mars Global Surveyor Thermal Emission Spectrometer. *Icarus*, 148:437–455, December 2000. doi: 10.1006/icar.2000.6503.
- J. R. Michalski, M. D. Kraft, T. G. Sharp, and P. R. Christensen. Effects of chemical weathering on infrared spectra of Columbia River Basalt and spectral interpretations of martian alteration. *Earth and Planetary Science Letters*, 248:822–829, 2006.
- R. E. Milliken, J. Grotzinger, R. A. Beyer, S. Murchie, and A. McEwen. Evidence for salt tectonics in Valles Marineris, Mars. *Seventh International Conference on Mars*, page 3383, 2007.
- R. E. Milliken, G. Swayze, R. Arvidson, J. Bishop, R. Clark, B. Ehlmann, R. Green, J. Grotzinger, R. Morris, S. Murchie, J. Mustard, and C. Weitz. Opaline silica in young deposits on Mars. *Geology*, 36(11):847–850, 2008a.
- R. E. Milliken, G. Swayze, R. E. Arvidson, J. L. Bishop, R. N. Clark, B. L. Ehlmann, J. Grotzinger, R. V. Morris, S. L. Murchie, J. F. Mustard, C. M. Weitz, and Crism Science Team. Spectral Evidence for Sedimentary Silica on Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Inst. Technical Report*, page 2025, March 2008b.
- R. E. Milliken, K. S. Edgett, G. Swayze, R. N. Clark, B. J. Thompson, R. Anderson, and J. F. Bell. Clay and sulfate-bearing rocks in a stratigraphic sequence in Gale Crater. In *Lunar and Planetary Institute Conference Abstracts*, volume 40 of *Lunar and Planetary Inst. Technical Report*, page 1479, March 2009.
- D. R. Montgomery and A. Gillespie. Formation of Martian outflow channels by catastrophic dewatering of evaporite deposits. *Geology*, 33:625–628, 2005. doi: 10.1130/G21270.1.

- R. V. Morris, C. A. Lawson, E. K. Gibson, Jr., H. V. Lauer, Jr., G. A. Nace, and C. Stewart. Spectral and other physicochemical properties of submicron powders of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), goethite ( $\alpha$ -FeOOH), and lepidocrocite ( $\gamma$ -FeOOH). *Journal of Geophysical Research (Planets)*, 90:3126–3144, March 1985.
- R. V. Morris, D. G. Agresti, H. V. Lauer, J. A. Newcomb, T. D. Shelfer, and A. V. Murali. Evidence for pigmentary hematite on Mars based on optical, magnetic, and Moessbauer studies of superparamagnetic (nanocrystalline) hematite. *J. Geophys. Res.*, 94:2760–2778, March 1989. doi: 10.1029/JB094iB03p02760.
- R. V. Morris, D. C. Golden, and J. F. Bell. Low-temperature reflectivity spectra of red hematite and the color of Mars. *J. Geophys. Res.*, 102:9125–9134, April 1997. doi: 10.1029/96JE03993.
- R. V. Morris, D. C. Golden, J. F. Bell, T. D. Shelfer, A. C. Scheinost, N. W. Hinman, G. Furniss, S. A. Mertzman, J. L. Bishop, D. W. Ming, C. C. Allen, and D. T. Britt. Mineralogy, composition, and alteration of Mars Pathfinder rocks and soils: Evidence from multispectral, elemental, and magnetic data on terrestrial analogue, SNC meteorite, and Pathfinder samples. *J. Geophys. Res.*, 105:757, January 2000. doi: 10.1029/1999JE001059.
- R. V. Morris, G. Klingelhöfer, C. Schröder, D. S. Rodionov, A. Yen, D. W. Ming, P. A. de Souza, T. Wdowiak, I. Fleischer, R. Gellert, B. Bernhardt, U. Bonnes, B. A. Cohen, E. N. Evlanov, J. Foh, P. Gütlich, E. Kankeleit, T. McCoy, D. W. Mittlefehldt, F. Renz, M. E. Schmidt, B. Zubkov, S. W. Squyres, and R. E. Arvidson. Mössbauer mineralogy of rock, soil, and dust at Meridiani Planum, Mars: Opportunity’s journey across sulfate-rich outcrop, basaltic sand and dust, and hematite lag deposits. *Journal of Geophysical Research (Planets)*, 111:12, December 2006. doi: 10.1029/2006JE002791.
- L. M. Mukhin, A. P. Koscheevi, Y. P. Dikov, J. Huth, and H. Wänke. Experimental simulations of the photodecomposition of carbonates and sulphates on Mars. *Nature*, 379:141–143, January 1996. doi: 10.1038/379141a0.
- S. Murchie, R. Arvidson, P. Bedini, K. Beisser, J.-P. Bibring, J. Bishop, J. Boldt, P. Cavender, T. Choo, R. T. Clancy, E. H. Darlington, D. Des Marais, R. Espiritu, D. Fort, R. Green, E. Guinness, J. Hayes, C. Hash, K. Heffernan, J. Hemmler, G. Heyler, D. Humm, J. Hutcheson, N. Izenberg, R. Lee, J. Lees, D. Lohr, E. Malaret, T. Martin, J. A. McGovern, P. McGuire, R. Morris, J. Mustard, S. Pelkey, E. Rhodes, M. Robinson, T. Roush, E. Schaefer, G. Seagrave, F. See-los, P. Silverglate, S. Slavney, M. Smith, W.-J. Shyong, K. Strohbehn, H. Taylor, P. Thompson, B. Tossman, M. Wirzbarger, and M. Wolff. Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on Mars Reconnaissance Orbiter

- (MRO). *Journal of Geophysical Research (Planets)*, 112(E11):5, May 2007a. doi: 10.1029/2006JE002682.
- S. Murchie, R. Milliken, L. Roach, J.-P. Bibring, J. Mustard, S. Pelkey, F. Seelos, J. Bishop, J. Grotzinger, A. McEwen, and Crism Science Team. CRISM Mapping of Layered Deposits in Western Candor Chasma. *LPI Contributions*, 1353:3238, July 2007b.
- S. Murchie, J. Mustard, B. Ehlmann, R. Milliken, J. Bishop, N. McKeown, E. Noe Dobrea, F. Seelos, D. Buczkowski, S. Wiseman, R. Arvidson, J. Wray, G. Swayze, R. Clark, J.-P. Bibring, and A. McEwen. A synthesis of Martian aqueous mineralogy after one Mars year of observations from the Mars Reconnaissance Orbiter. *Journal of Geophysical Research (Planets)*, 2009a.
- S. Murchie, L. H. Roach, F. Seelos, R. Milliken, J. Mustard, R. Arvidson, S. Wiseman, K. Lichtenberg, J. Andrews-Hanna, J.-P. Bishop, J. and Bibring, M. Parente, and R. Morris. Compositional Evidence for the Origin of Layered Deposits in Valles Marineris, Mars. *Journal of Geophysical Research (Planets)*, 2009b.
- S. L. Murchie, F. P. Seelos, C. D. Hash, D. C. Humm, E. Malaret, J. A. McGovern, T. H. Choo, K. D. Seelos, D. L. Buczkowski, M. F. Morgan, O. S. Barnouin-Jha, H. Nair, H. W. Taylor, G. W. Patterson, C. A. Harvel, J. F. Mustard, R. E. Arvidson, P. McGuire, M. D. Smith, M. J. Wolff, T. N. Titus, J. P. Bibring, F. Poulet, and the CRISM science team. The CRISM investigation and data set for the Mars Reconnaissance Orbiter’s Primary Science Phase. *Journal of Geophysical Research (Planets)*, 2009c.
- J. F. Mustard and J. F. Bell. New composite reflectance spectra of Mars from 0.4 to 3.14 micron. *Geophys. Res. Lett.*, 21:353–356, March 1994. doi: 10.1029/94GL00198.
- J. F. Mustard, F. Poulet, A. Gendrin, J.-P. Bibring, Y. Langevin, B. Gondet, N. Mangold, G. Bellucci, and F. Altieri. Olivine and Pyroxene Diversity in the Crust of Mars. *Science*, 307:1594–1597, March 2005. doi: 10.1126/science.1109098.
- J. F. Mustard, S. L. Murchie, S. M. Pelkey, B. L. Ehlmann, R. E. Milliken, J. A. Grant, J.-P. Bibring, F. Poulet, J. Bishop, E. N. Dobrea, L. Roach, F. Seelos, R. E. Arvidson, S. Wiseman, R. Green, C. Hash, D. Humm, E. Malaret, J. A. McGovern, K. Seelos, T. Clancy, R. Clark, D. D. Marais, N. Izenberg, A. Knudson, Y. Langevin, T. Martin, P. McGuire, R. Morris, M. Robinson, T. Roush, M. Smith, G. Swayze, H. Taylor, T. Titus, and M. Wolff. Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter CRISM instrument. *Nature*, 454: 305–309, July 2008. doi: 10.1038/nature07097.
- A. Navrotsky, F. L. Forray, and C. Drouet. Jarosite stability on mars. *Icarus*, 176 (1):250–253, 2005. ISSN 0019-1035.

- S. S. Nedell, S. W. Squyres, and D. W. Andersen. Origin and evolution of the layered deposits in the Valles Marineris, Mars. *Icarus*, 70:409–441, June 1987. doi: 10.1016/0019-1035(87)90086-8.
- G. et al. Neukum. Episodicity in the geological evolution of Mars: Resurfacing events and ages from cratering analysis of image data and correlation with radiometric ages of Martian meteorites. *7th International Mars Conference*, 2007.
- P. B. Niles and J. Michalski. Meridiani planum sediments on mars formed through weathering in massive ice deposits. *Nature Geoscience*, 2:215–220, 2009. doi: 10.1038/ngeo438.
- E. Z. Noe Dobrea, F. Poulet, and M. C. Malin. Correlations between hematite and sulfate in the chaotic terrain east of Valles Marineris. *Icarus*, 193:516–534, 2008. URL 10.1016/j.icarus/2007.06.029.
- C. H. Okubo and A. S. McEwen. Fracture-controlled paleo-fluid flow in Candor Chasma, Mars. *Science*, 315:983–985, 2007. doi: 10.1126/science.1136855.
- C. H. Okubo, K. W. Lewis, A. S. McEwen, and R. L. Kirk. Relative age of the Interior Layered Deposits in southwestern Candor Chasma based on high-resolution structural mapping. *Journal of Geophysical Research*, 113, 2008. doi: 10.1029/2008JE003181.
- M.M. Osterloo, V.E. Hamilton, J.L. Bandfield, T.D. Glotch, A.M. Baldridge, P.R. Christensen, L.L. Tornabene, and F.S. Anderson. Chloride-bearing materials in the Southern Highlands of Mars. *Science*, 319(5870):1651–1654, 2008.
- M. Parente and J L. Bishop. A new technique for identification of minerals in hyperspectral images: application to robust characterization of phyllosilicate deposits at Mawrth Vallis using CRISM images. *AGU Fall Meeting Abstracts*, 89, 2008.
- M. Parente, J. L. Bishop, E. Noe Dobrea, W. Calvin, L. Roach, and S. Murchie. Characterization of Sulfate Minerals in Juventae Chasma from CRISM images. *AGU Fall Meeting Abstracts*, page A1091, December 2007.
- S. M. Pelkey, B. M. Jakosky, and P. R. Christensen. Surficial properties in Melas Chasma, Mars, from Mars Odyssey THEMIS data. *Icarus*, 165:68–89, September 2003. doi: 10.1016/S0019-1035(03)00152-0.
- S. M. Pelkey, A. Gendrin, J. F. Mustard, N. Mangold, J.-P. Bibring, Y. Langevin, B. Gondet, and The Omega Science Team. An Integrated Study of OMEGA-Identified Mineral Deposits in Eastern Hebes Chasma, Mars. In S. Mackwell and E. Stansbery, editors, *36th Annual Lunar and Planetary Science Conference*, volume 36 of *Lunar and Planetary Institute Science Conference Abstracts*, page 1891, March 2005.



- S. M. Pelkey, J. F. Mustard, S. Murchie, R. T. Clancy, M. Wolff, M. Smith, R. Milliken, J. P. Bibring, A. Gendrin, F. Poulet, Y. Langevin, and B. Gondet. CRISM multispectral summary products: Parameterizing mineral diversity on Mars from reflectance. *Journal of Geophysical Research-Planets*, 112(E8), 2007. ISSN 0148-0227.
- A. Pentecost. *Travertine*. Springer-Verlag, 2005.
- C. M. Peterson. Hebes Chasma - Martian Pyroclastic Sink. In *Lunar and Planetary Institute Conference Abstracts*, volume 12 of *Lunar and Planetary Institute Conference Abstracts*, pages 828–829, March 1981.
- R. C. Peterson and R. Wang. Crystal molds on Mars: Melting of a possible new mineral species to create Martian chaotic terrain. *Geology*, 11:957–960, 2006.
- J. P. Peulvast and P. L. Masson. Erosion and tectonics in central valles marineris (mars) - a new morpho-structural model. *Earth Moon and Planets*, 61(3):191–217, 1993a. ISSN 0167-9295.
- J. P. Peulvast and P. L. Masson. Melas chasma - morphology and tectonic patterns in central valles marineris (mars). *Earth Moon and Planets*, 61(3):219–248, 1993b. ISSN 0167-9295.
- J. P. Peulvast, D. Mege, J. Chiciak, F. Costard, and P. L. Masson. Morphology, evolution and tectonics of Valle Marineris wallslopes (Mars). *Geomorphology*, 37: 329–352, 2001.
- P. Pinet and S. Chevrel. Spectral identification of geological units on the surface of Mars related to the presence of silicates from earth-based near-infrared telescopic charge-coupled device imaging. *J. Geophys. Res.*, 95:14435–14446, August 1990. doi: 10.1029/JB095iB09p14435.
- F. Pirajno and M. J. Van Kranendonk. Review of hydrothermal processes and systems on earth and implications for martian analogues. *Australian Journal of Earth Sciences*, 52(3):329–351, 2005. ISSN 0812-0099.
- J. B. Pollack, T. Roush, F. Witteborn, J. Bregman, D. Wooden, C. Stoker, and O. B. Toon. Thermal emission spectra of Mars (5.4-10.5 microns) - Evidence for sulfates, carbonates, and hydrates. *Journal of Geophysical Research (Planets)*, 95: 14595–14627, August 1990. doi: 10.1029/JB095iB09p14595.
- C. I. Popa, F. Esposito, G. G. Ori, L. Marinangeli, and L. Colangeli. Tithonium Chasma domes: a result of salt diapirism by means of thin-skinned extension? *LPI Contributions*, 1353:1848, July 2007.

- F. Poulet, J.-P. Bibring, J. F. Mustard, A. Gendrin, N. Mangold, Y. Langevin, R. E. Arvidson, B. Gondet, and C. Gomez. Phyllosilicates on Mars and implications for early martian climate. *Nature*, 438:623–627, December 2005. doi: 10.1038/nature04274.
- F. Poulet, C. Gomez, J.-P. Bibring, Y. Langevin, B. Gondet, P. Pinet, G. Bellucci, and J. Mustard. Martian surface mineralogy from Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité on board the Mars Express spacecraft (OMEGA/MEx): Global mineral maps. *Journal of Geophysical Research (Planets)*, 112:8, July 2007. doi: 10.1029/2006JE002840.
- F. Poulet, R. E. Arvidson, C. Gomez, R. V. Morris, J.-P. Bibring, Y. Langevin, B. Gondet, and J. Griffes. Mineralogy of Terra Meridiani and western Arabia Terra from OMEGA/MEx and implications for their formation. *Icarus*, 195:106–130, May 2008a. doi: 10.1016/j.icarus.2007.11.031.
- F. Poulet, N. Mangold, D. Loizeau, J. P. Bibring, Y. Langevin, J. Michalski, and B. Gondet. Abundance of minerals in the phyllosilicate-rich units on Mars. *Astronomy and Astrophysics*, 487:41–44, 2008b.
- F. Poulet, J. P. Bibring, Y. Langevin, J. F. Mustard, N. Mangold, M. Vincendon, B. Gondet, P. pinet, J. M. Bardintzeff, and B. Platevoet. Quantitative compositional analysis of Martian mafic regions using MEx/OMEGA reflectance data: 1. Methodology, uncertainties and examples of application. *Icarus*, 2009a.
- F. Poulet, N. Mangold, B. Platevoet, J. M. Bardintzeff, V. Sautter, J. F. Mustard, J. P. Bibring, P. Pinet, Y. Langevin, B. Gondet, and A. Aleon-Toppani. Quantitative compositional analysis of Martian mafic regions using the MEx/OMEGA reflectance data: 2. Petrological implications. *Icarus*, 2009b.
- N. E. Putzig and M. T. Mellon. Apparent thermal inertia and the surface heterogeneity of Mars. *Icarus*, 191:68–94, November 2007. doi: 10.1016/j.icarus.2007.05.013.
- N. E. Putzig, M. T. Mellon, K A. Kretke, and R. E. Arvidson. Global thermal inertia and surface properties of Mars in the MGS mapping mission. *Icarus*, 173:325–341, 2005.
- C. Quantin, P. Allemand, N. Mangold, and C. Delacourt. Ages of valles marineris (mars) landslides and implications for canyon history. *Icarus*, 172:555–572, 2004.
- C. Quantin, P. Allemand, N. Mangold, G. Dromart, and C. Delacourt. Fluvial and lacustrine activity on layered deposits in Melas Chasma, Valles Marineris, Mars. *Journal of Geophysical Research (Planets)*, 110:12, October 2005a. doi: 10.1029/2005JE002440.

- C. Quantin, A. Gendrin, N. Mangold, J.-P. Bibring, F. Poulet, P. Allemand, and The Omega Team. Sulfate Deposits Identified by OMEGA in Melas Chasma. In S. Mackwell and E. Stansbery, editors, *36th Annual Lunar and Planetary Science Conference*, volume 36 of *Lunar and Planetary Inst. Technical Report*, page 1789, March 2005b.
- R. Quinn, A. P. Zent, and C. P. McKay. The photochemical stability of carbonates on Mars. *Astrobiology*, 6(4):581–591, 2006. ISSN 1531-1074.
- H. Racher, M. Slingerland, F. Fueten, R. Stesky, P. MacKinnon, E. Hauber, K. Gwinner, and T. Zegers. Structural analysis of interior layered deposit in Southern Coprates Chasma, Mars. *40th Annual Lunar and Planetary Science Conference*, 40:1472, March 2009.
- L. H. Roach, J. Mustard, A. Gendrin, D. Fernández-Remolar, R. Amils, and L. Amaral-Zettler. Finding mineralogically interesting targets for exploration from spatially coarse visible and near IR spectra. *Earth and Planetary Science Letters*, 252:201–214, November 2006. doi: 10.1016/j.epsl.2006.09.044.
- L. H. Roach, J. F. Mustard, S. Murchie, C. M. Weitz, B. L. Ehlmann, S. Pelkey, F. P. Seelos, K. Seelos, J.-P. Bibring, and Crism Team. Sulfate Identification in East Candor, Valles Marineris with CRISM Visible-Infrared Spectra. In *Lunar and Planetary Institute Conference Abstracts*, volume 38 of *Lunar and Planetary Institute Conference Abstracts*, page 2106, March 2007a.
- L. H. Roach, J. F. Mustard, S. L. Murchie, J. L. Bishop, R. E. Arvidson, R. V. Morris, R. E. Milliken, and K. A. Lichtenberg. Multi-sulfate and Iron Oxide Assemblages Within the Valles Marineris Interior Layered Deposits. *AGU Fall Meeting Abstracts*, page C5, December 2007b.
- L. H. Roach, J. F. Mustard, S. L. Murchie, J. L. Bishop, C. M. Weitz, A. T. Knudson, J.-P. Bibring, S. M. Pelkey, B. L. Ehlmann, and Crism Science Team. Magnesium and Iron Sulfate Variety and Distribution in East Candor and Capri Chasma, Valles Marineris. *LPI Contributions*, 1353:3223, July 2007c.
- L. H. Roach, J. F. Mustard, S. L. Murchie, O. Aharonson, T. Lowenstein, C. M. Weitz, R. E. Arvidson, J. L. Bishop, K. W. Lewis, K. Lichtenberg, F. P. Seelos, and Crism Science Team. Sulfate Mineral Stratigraphy in Valles Marineris Interior Layered Deposits. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Inst. Technical Report*, page 1891, March 2008a.
- L. H. Roach, J. F. Mustard, S. L. Murchie, J.-P. Bibring, R. E. Arvidson, J. L. Bishop, R. E. Milliken, F. P. Seelos, and Crism Science Team. Constraints on the Rate of Sulfate Phase Changes in Valles Marineris Interior Layered Deposits. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Inst. Technical Report*, pages 1823–+, March 2008b.

- L. H. Roach, J. F. Mustard, S. L. Murchie, R. E. Milliken, J. K. Crowley, J. L. Bishop, and R. E. Arvidson. Sulfates and Other Hydrated Minerals in Ius Chasma, Valles Marineris and Implications for Water Geochemistry. *AGU Fall Meeting Abstracts*, page B1394, December 2008c.
- L. H. Roach, J. F. Mustard, S. L. Murchie, J. L. Bishop, B. L. Ehlmann, K. Lichtenberg, and M. Parente. Sulfate and iron oxide stratigraphy in Capri Chasma, Valles Marineris. In *Lunar and Planetary Institute Conference Abstracts*, volume 40 of *Lunar and Planetary Inst. Technical Report*, page 1823, March 2009a.
- L. H. Roach, J. F. Mustard, S. M. Murchie, J.-P. Bibring, F. Forget, K. W. Lewis, O. Aharonson, M. Vincendon, and J. L. Bishop. Testing evidence of recent hydration state change in sulfates on Mars. *Journal of Geophysical Research (Planets)*, 2009b. doi: 10.1029/2008JE003245.
- L. H. Roach, J. F. Mustard, G. Swayze, R. E. Milliken, J. L. Bishop, B. L. Ehlmann, S. L. Murchie, and K. Lichtenberg. Hydrated mineral stratigraphy of Ius Chasma, Valles Marineris. *in prep*, 2009c.
- L. A. Rossbacher and S. Judson. Ground ice on Mars: Inventory, distribution, and resulting landforms. *Icarus*, 45:39–59, 1981. doi: 10.1016/0019-1035(81)90005-1.
- A. P. Rossi, G. Neukum, M. Pondrelli, S. van Gasselt, T. Zegers, E. Hauber, A. Chicarro, and B. Foing. Large-scale spring deposits on Mars? *Journal of Geophysical Research (Planets)*, 113:8016–8033, August 2008. doi: 10.1029/2007JE003062.
- P. Sarrazin, D. W. Ming, R. V. Morris, D. Fernández-Remolar, R. Amils, R. E. Arvidson, D. Blake, and D. L. Bish. Mineralogical In-Situ Investigation of Acid-Sulfate Samples from the Rio Tinto River, Spain, with a Portable XRD/XRF Instrument. In *Lunar and Planetary Institute Conference Abstracts*, volume 38 of *Lunar and Planetary Institute Conference Abstracts*, page 2147, March 2007.
- H. Savijarvi. Mars boundary-layer modeling - diurnal moisture cycle and soil properties at the viking-lander-1 site. *Icarus*, 117(1):120–127, 1995. ISSN 0019-1035.
- B. C. Schreiber. *Evaporites and Hydrocarbons*. Columbia University Press, 1988.
- B. C. Schreiber and M. El Tabakh. Deposition and early alteration of evaporites. *Sedimentology*, 47:215–238, 2000. ISSN 0037-0746.
- R. A. Schultz. Multiple-process origin of Valles Marineris basins and troughs, Mars. *Planet. Space Sci.*, 46:827–834, June 1998.
- R. A. Schultz and J. Lin. Three-dimensional normal faulting models of the Valles Marineris, Mars, and geodynamical implications. *Journal of Geophysical Research (Planets)*, 106:16549–16566, 2001.

- D. D. Schultz-Ela, M. P. A. Jackson, and B. C. Vendevillie. Mechanics of active salt diapirism. *Tectonophysics*, 228:275–312, 1993.
- U. Schwertmann and R. M. Cornell, editors. *The Iron Oxides: Structure, properties, reactions, occurrences and uses*. Wiley, 2003.
- E. Sefton-Nash and D. C. Catling. Hematitic concretions at Meridiani Planum, Mars: Their growth timescale and possible relationship with iron sulfates. *Earth and Planetary Science Letters*, 269:366–376, 2008. doi: 10.1016/j.epsl.2008.02.009.
- M. Settle. Formation and deposition of volcanic sulfate aerosols on Mars. *Journal of Geophysical Research*, 84:8343–8354, 1979. ISSN 0148-0227.
- R. P. Sharp. Mars: Troughed Terrain. *Journal of Geophysical Research (Planets)*, 78:4063–4083, July 1973.
- D. K. Smith. Opal, cristobalite, and tridymite: noncrystallinity versus crystallinity, nomenclature of the silica minerals and bibliography. *Powder Diffraction*, 13:2–19, 1998.
- P. Sonnenfeld. *Brines and Evaporites*. Academic Press, 1984.
- M. Sowe, E. Hauber, R. Jaumann, K. Gwinner, F. Fueten, R. Stesky, and G. Neukum. Geological analysis of Interior Layered Deposits occurring in chaotic terrains from Ganges Chasma to Iani Chaos on Mars. In *European Planetary Science Congress 2006*, page 418, 2006.
- M. Sowe, E. Hauber, R. Jaumann, K. Gwinner, F. Fueten, R. Stesky, and G. Neukum. Interior Layered Deposits in the Eastern Valles Marineris and Chaotic Terrains on Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 38 of *Lunar and Planetary Inst. Technical Report*, page 1568, March 2007.
- M. Sowe, L. H. Roach, E. Hauber, R. Jaumann, J. F. Mustard, and G. Neukum. Interior Layered Deposits on Mars: Insights from elevation, image- and spectral data of Ganges Mensa. In *European Planetary Science Congress 2008*, page 510, 2008.
- N. Spanovich, M. D. Smith, P. H. Smith, M. J. Wolff, P. R. Christensen, and S. W. Squyres. Surface and near-surface atmospheric temperatures for the Mars Exploration Rover landing sites. *Icarus*, 180:314–320, February 2006. doi: 10.1016/j.icarus.2005.09.014.
- R.J. Spencer. *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance, Reviews in Mineralogy and Geochemistry*, chapter Sulfate Minerals in Evaporite Deposits, pages 173–192. Mineralogical Society of America, 2000.

- S. W. Squyres and et al. The spirit rover's athena science investigation at gusev crater, mars. *Science*, 305(5685):794–799, 2004. ISSN 0036-8075.
- S. W. Squyres and A. H. Knoll. *Sedimentary geology at Meridiani Planum, Mars*. Sedimentary geology at Meridiani Planum, Mars / ed. by Steven W. Squyres and Andrew H. Knoll. Amsterdam : Elsevier, 2005. ISBN: 0444522506, 2005.
- S. W. Squyres, R. E. Arvidson, J. F. Bell, J. Brückner, N. A. Cabrol, W. Calvin, M. H. Carr, P. R. Christensen, B. C. Clark, L. Crumpler, D. J. Des Marais, C. d’Uston, T. Economou, J. Farmer, W. Farrand, W. Folkner, M. Golombek, S. Gorevan, J. A. Grant, R. Greeley, J. Grotzinger, L. Haskin, K. E. Herkenhoff, S. Hviid, J. Johnson, G. Klingelhöfer, A. H. Knoll, G. Landis, M. Lemmon, R. Li, M. B. Madsen, M. C. Malin, S. M. McLennan, H. Y. McSween, D. W. Ming, J. Moersch, R. V. Morris, T. Parker, J. W. Rice, L. Richter, R. Rieder, M. Sims, M. Smith, P. Smith, L. A. Soderblom, R. Sullivan, H. Wänke, T. Wdowiak, M. Wolff, and A. Yen. The Opportunity Rover’s Athena Science Investigation at Meridiani Planum, Mars. *Science*, 306:1698–1703, December 2004. doi: 10.1126/science.1106171.
- S. W. Squyres, R. E. Arvidson, D. Bollen, J. F. Bell, J. Brückner, N. A. Cabrol, W. M. Calvin, M. H. Carr, P. R. Christensen, B. C. Clark, L. Crumpler, D. J. Des Marais, C. d’Uston, T. Economou, J. Farmer, W. H. Farrand, W. Folkner, R. Gellert, T. D. Glotch, M. Golombek, S. Gorevan, J. A. Grant, R. Greeley, J. Grotzinger, K. E. Herkenhoff, S. Hviid, J. R. Johnson, G. Klingelhöfer, A. H. Knoll, G. Landis, M. Lemmon, R. Li, M. B. Madsen, M. C. Malin, S. M. McLennan, H. Y. McSween, D. W. Ming, J. Moersch, R. V. Morris, T. Parker, J. W. Rice, L. Richter, R. Rieder, C. Schröder, M. Sims, M. Smith, P. Smith, L. A. Soderblom, R. Sullivan, N. J. Tosca, H. Wänke, T. Wdowiak, M. Wolff, and A. Yen. Overview of the Opportunity Mars Exploration Rover Mission to Meridiani Planum: Eagle Crater to Purgatory Ripple. *Journal of Geophysical Research (Planets)*, 111:12, December 2006. doi: 10.1029/2006JE002771.
- R. Stesky, F. Fueten, P. MacKinnon, E. Hauber, K. Gwinner, F. Scholten, T. E. Zegers, G. Neukum, and HRSC Co-Investigator Team. Layering Attitudes in Southwestern Candor Chasma from HRSC Image Data and Stereo-derived DTM. In S. Mackwell and E. Stansbery, editors, *37th Annual Lunar and Planetary Science Conference*, volume 37 of *Lunar and Planetary Institute Conference Abstracts*, page 2013, March 2006.
- F. H. Stewart. Replacements involving early carnallite in the postassium-bearing evaporites of Yorkshire. *Mineralogical Magazine*, 31:127–135, 1956. doi: 10.1180/minmag.1956.031.233.02.
- R. E. Stoffregen, C. N. Alpers, and J. L. Jambor. *Alunite-jarosite crystallography, thermodynamics, and geochemistry*, *Reviews in Mineralogy and Geochemistry*,

- chapter Sulfate Minerals in Evaporite Deposits, pages 453–479. Mineralogical Society of America, 2000.
- G. A. Swayze, K. S. Smith, R. N. Clark, S. J. Sutley, R. M. Pearson, J. S. Vance, P. L. Hageman, P. H. Briggs, A. L. Meier, M. J. Singleton, and S. Roth. Using imaging spectroscopy to map acidic mine wastes. *Environmental Science and Technology*, 34:47–54, 2000. doi: 10.1021/es990046w.
- G. A. Swayze, B. L. Ehlmann, R. E. Milliken, F. Poulet, J. J. Wray, R. O. Rye, R. N. Clark, G. A. Desborough, J. K. Crowley, B. Gondet, J. F. Mustard, K. D. Seelos, and S. L. Murchie. Discovery of the Acid-Sulfate Mineral Alunite in Terra Sirenum, Mars, Using MRO CRISM: Possible Evidence for Acid-Saline Lacustrine Deposits? *AGU Fall Meeting Abstracts*, page A4, December 2008.
- K. L. Tanaka. The stratigraphy of Mars. *Journal of Geophysical Research (Planets)*, 91:139, November 1986. doi: 10.1029/JB091iB13p0E139.
- K. L. Tanaka and M. P. Golombek. Martian tension fractures and the formation of grabens and collapse features at Valles Marineris. In G. Ryder and V. L. Sharpton, editors, *Lunar and Planetary Science Conference*, volume 19 of *Lunar and Planetary Science Conference*, pages 383–396, 1989.
- K. L. Tanaka, M. P. Golombek, and W. B. Banerdt. Reconciliation of stress and structural histories of the Tharsis region of Mars. *Journal of Geophysical Research (Planets)*, 96:15617, August 1991. doi: 10.1029/91JE01194.
- K. L. Tanaka, D. H. Scott, and R. Greeley. *Mars*, chapter Global Stratigraphy, pages 345–382. Arizona Press, 1992.
- G. Testa and S. Lugli. Gypsum-anhydrite transformations in Messinian evaporites of central Tuscany (Italy). *Sedimentary Geology*, 130(3):249–268, 2000.
- K. G. Thaisen, J. Schieber, A. Dumke, E. Hauber, and G. Neukum. Geomorphic Evidence for Significant Glacial and Fluvial Activity in Candor Chasma, Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Institute Conference Abstracts*, page 2358, March 2008.
- N. J. Tosca and S. M. McLennan. Chemical divides and evaporite assemblages on Mars. *Earth and Planetary Science Letters*, 241:21–31, January 2006. doi: 10.1016/j.epsl.2005.10.021.
- N. J. Tosca, S. M. McLennan, D. H. Lindsley, and M. A. A. Schoonen. Acid-Sulfate Weathering of Synthetic Martian Basalt: The Acid Fog Model Revisited. In S. Mackwell and E. Stansbery, editors, *Lunar and Planetary Institute Conference Abstracts*, volume 34 of *Lunar and Planetary Institute Conference Abstracts*, page 1325, March 2003.

- N. J. Tosca, S. M. McLennan, D. H. Lindsley, and M. A. A. Schoonen. Acid-sulfate weathering of synthetic Martian basalt: The acid fog model revisited. *Journal of Geophysical Research (Planets)*, 109:5003, May 2004. doi: 10.1029/2003JE002218.
- N. J. Tosca, S. M. McLennan, B. C. Clark, J. P. Grotzinger, J. A. Hurowitz, A. H. Knoll, C. Schroder, and S. W. Squyres. Geochemical modeling of evaporation processes on mars: Insight from the sedimentary record at meridiani planum. *Earth and Planetary Science Letters*, 240(1):122–148, 2005. ISSN 0012-821X.
- N. J. Tosca, R. E. Milliken, and F. M. Michel. Smectite formation on early mars: Experimental constraints. In *Martian Phyllosilicates: Records of Aqueous Processes*, 2008a.
- N. J. Tosca, R. E. Milliken, and M. B. Wyatt. An experimental approach to clay mineral formation on Mars. *Geochimica et Cosmochimica Acta Supplement*, 72: 952, July 2008b.
- P. Toulmin, III, H. J. Rose, Jr., B. C. Clark, A. K. Baird, and K. Keil. Preliminary results from the Viking X-ray fluorescence experiment - The first sample from Chryse Planitia, Mars. *Science*, 194:81–84, October 1976. doi: 10.1126/science.194.4260.81.
- P. Toulmin, III, H. J. Rose, Jr., R. P. Christian, A. K. Baird, P. H. Evans, B. C. Clark, K. Keil, and W. C. Kelliher. Geochemical and mineralogical interpretation of the Viking inorganic chemical results. *Journal of Geophysical Research (Planets)*, 82: 4625–4634, September 1977. doi: 10.1029/JS082i028p04625.
- A. H. Treiman. Ancient groundwater flow in the Valles Marineris on Mars inferred from fault trace ridges. *Nature Geoscience*, 1, 2008.
- A. H. Treiman, K. H. Fuks, and S. Murchie. Diagenetic layers in the upper walls of Valles Marineris, Mars: Evidence for drastic climate change since the mid-Hesperian. *Journal of Geophysical Research (Planets)*, 100:26339–26344, 1995. doi: 10.1029/95JE03223.
- D. T. Vaniman and S. J. Chipera. Rates and Modes of Hydration in Mg- and Ca-Sulfates on Mars. *LPI Contributions*, 1331:73, October 2006a.
- D. T. Vaniman and S. J. Chipera. Transformations of Mg- and Ca-sulfate hydrates in Mars regolith. *American Mineralogist*, 91:1628–1642, 2006b.
- D. T. Vaniman, D. L. Bish, S. J. Chipera, C. I. Fialips, J. William Carey, and W. C. Feldman. Magnesium sulphate salts and the history of water on Mars. *Nature*, 431: 663–665, October 2004a. doi: 10.1038/nature02973.



- D. T. Vaniman, S. J. Chipera, D. L. Bish, J. W. Carey, C. I. Fialips, and W. C. Feldman. Sulfate Salts, Regolith Interactions, and Water Storage in Equatorial Martian Regolith. In S. Mackwell and E. Stansbery, editors, *Lunar and Planetary Institute Conference Abstracts*, volume 35 of *Lunar and Planetary Institute Conference Abstracts*, page 1690, March 2004b.
- D. T. Vaniman, S. J. Chipera, D. L. Bish, J. W. Carey, and W. C. Feldman. Martian Relevance of Dehydration and Rehydration in the Mg-Sulfate System. In S. Mackwell and E. Stansbery, editors, *36th Annual Lunar and Planetary Science Conference*, volume 36 of *Lunar and Planetary Institute Conference Abstracts*, page 1486, March 2005.
- D. T. Vaniman, S. J. Chipera, and J. W. Carey. Hydration Experiments and Physical Observations at 193 K and 243 K for Mg-Sulfates Relevant to Mars. In S. Mackwell and E. Stansbery, editors, *37th Annual Lunar and Planetary Science Conference*, volume 37 of *Lunar and Planetary Institute Conference Abstracts*, page 1442, March 2006.
- M. Vincendon, Y. Langevin, F. Poulet, J.-P. Bibring, and B. Gondet. Recovery of surface reflectance spectra and evaluation of the optical depth of aerosols in the near-IR using a Monte Carlo approach: Application to the OMEGA observations of high-latitude regions of Mars. *Journal of Geophysical Research (Planets)*, 112 (E11):8, July 2007. doi: 10.1029/2006JE002845.
- A. Wang, J. F. Freeman, and B. L. Jolliff. Hydration State of Magnesium Sulfates on Mars. *LPI Contributions*, 1331:75, October 2006.
- A. Wang, J.J. Freeman, and B.L. Jolliff. Formation Rate of Amorphous Magnesium Sulfates at Low Temperatures Approaching the Current Surface Conditions on Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 38 of *Lunar and Planetary Institute Conference Abstracts*, page 1195, March 2007.
- A. Wang, J.J. Freeman, and R.E. Arvidson. Study of Two Structural Polymorphs of  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  by Raman, IR, XRD, and Humidity Buffer Experiments - Implication for Martian Kieserite. In *Lunar and Planetary Institute Conference Abstracts*, volume 39 of *Lunar and Planetary Institute Conference Abstracts*, page 2172, 2008.
- J. K. Warren. Tepees, modern and ancient (Permian) - a comparison. *Sedimentary Geology*, 34:1–19, 1991.
- C. M. Weitz. A Volcanic Origin for the Interior Layered Deposits in Hebes Chasma, Mars. In *Lunar and Planetary Institute Conference Abstracts*, volume 30 of *Lunar and Planetary Inst. Technical Report*, page 1277, March 1999.
- C. M. Weitz and T. J. Parker. New evidence that the Valles Marineris Interior Layered Deposits formed in standing bodies of water. In *Lunar and Planetary Institute*

- Conference Abstracts*, volume 31 of *Lunar and Planetary Institute Conference Abstracts*, page 1693, March 2000.
- C. M. Weitz, B. K. Lucchitta, and M. G. Chapman. Potential 2001 landing sites in Melas Chasma, Mars. *Second Mars Surveyor Landing Site Workshop*, 1999.
- C. M. Weitz, T. J. Parker, F. S. Anderson, and J. A. Grant. The Interior Layered Deposits of Valles Marineris: Layering, Erosional Processes, and Age Relationships. In *Lunar and Planetary Institute Conference Abstracts*, volume 32 of *Lunar and Planetary Inst. Technical Report*, page 1629, March 2001.
- C. M. Weitz, T. J. Parker, M. H. Bulmer, F. Scott Anderson, and J. A. Grant. Geology of the Melas Chasma landing site for the Mars Exploration Rover mission. *Journal of Geophysical Research (Planets)*, 108:8082, October 2003. doi: 10.1029/2002JE002022.
- C. M. Weitz, A. S. McEwen, R. E. Milliken, J. A. Grant, and HiRISE Team. MRO Observations of Light-toned Layered Deposits along the Plains Adjacent to Valles Marineris. *AGU Fall Meeting Abstracts*, page D4, December 2007a.
- C. M. Weitz, A. S. McEwen, C. H. Okubo, P. Russell, J. A. Grant, C. Dundas, N. Bridges, and Hirise Team. Early HiRISE Observations of Light-toned Layered Deposits. In *Lunar and Planetary Institute Conference Abstracts*, volume 38 of *Lunar and Planetary Institute Conference Abstracts*, page 1442, March 2007b.
- C. M. Weitz, M. D. Lane, M. Staid, and E. Noe Dobrea. Gray hematite distribution and formation in Ophir and Candor chasmata. *Journal of Geophysical Research (Planets)*, 113, 2008a. doi: 10.1029/2007je002930.
- C. M. Weitz, R. E. Milliken, J. A. Grant, A. S. McEwen, R. M. E. Williams, and J. L. Bishop. Light-toned strata and inverted channels adjacent to Juventae and Ganges chasmata, Mars. *Geophysical Research Letters*, 35:19202, October 2008b. doi: 10.1029/2008GL035317.
- J. P. Williams, D. A. Paige, and C. E. Manning. Layering in the wall rock of valles marineris: intrusive and extrusive magmatism. *Geophysical Research Letters*, 30: 1623, 2003.
- L. Wilson and J. W. Head. Mars: review and analysis of volcanic eruption theory and relationships to observed landforms. *Reviews of Geophysics*, 32:221–263, 1994.
- R. E. Wiseman, K. S. Edgett, G. Swayze, R. N. Clark, B. J. Thompson, R. Anderson, and J. F. Bell. Clay and sulfate-bearing rocks in a stratigraphic sequence in Gale Crater. In *Lunar and Planetary Institute Conference Abstracts*, volume 40 of *Lunar and Planetary Inst. Technical Report*, page 1798, March 2009.

- S. M. Wiseman, R. E. Arvidson, S. Murchie, F. Poulet, R. V. Morris, A. S. McEwen, J. C. Andrews-Hanna, and The CRISM Science Team. Juxtaposition of Layered Sulfate and Phyllosilicate Deposits, Meridiani Planum, Mars. *AGU Fall Meeting Abstracts*, December 2007.
- N. E. Witbeck. USGS Miscellaneous Investigation Series Map I-2020. *United States Geological Survey*, 1991.
- M. J. Wolff, S. W. Lee, R. T. Clancy, L. J. Martin, J. F. Bell, III, and P. B. James. 1995 observations of Martian dust storms using the Hubble Space Telescope. *J. Geophys. Res.*, 102:1679–1692, January 1997. doi: 10.1029/96JE03417.
- J. J. Wray, B. L. Ehlmann, S. W. Squyres, J. F. Mustard, and R. L. Kirk. Compositional stratigraphy of clay-bearing layered deposits at Mawrth Vallis, Mars. *Geophysical Research Letters*, 35, 2008a.
- J. J. Wray, R. E. Milliken, S. L. Murchie, G. A. Swayze, C. M. Dundas, F. P. Seelos, and S. W. Squyres. Clays and Sulfates in a Potential Lacustrine Evaporite Sequence at Columbus Crater, Mars. *AGU Fall Meeting Abstracts*, page B1446, December 2008b.
- M. Wyatt. Chemically altered basalt at high-latitudes on Mars: TES, OMEGA, and GRS integrated data sets. *Goldschmidt Conference Abstracts*, 2007.
- M. B. Wyatt and J. F. Mustard. Constraints on mineral-phase abundances and compositions in the low-albedo northern plains of Mars using MGS-TES, OMEGA, and laboratory spectral data. *Eos. Transactions AGU Fall Meeting Abstracts*, 87, 2006.
- A. S. Yen, R. Gellert, C. Schröder, R. V. Morris, J. F. Bell, A. T. Knudson, B. C. Clark, D. W. Ming, J. A. Crisp, R. E. Arvidson, D. Blaney, J. Brückner, P. R. Christensen, D. J. Desmarais, P. A. de Souza, T. E. Economou, A. Ghosh, B. C. Hahn, K. E. Herkenhoff, L. A. Haskin, J. A. Hurowitz, B. L. Joliff, J. R. Johnson, G. Klingelhöfer, M. B. Madsen, S. M. McLennan, H. Y. McSween, L. Richter, R. Rieder, D. Rodionov, L. Soderblom, S. W. Squyres, N. J. Tosca, A. Wang, M. Wyatt, and J. Zipfel. An integrated view of the chemistry and mineralogy of martian soils. *Nature*, 436:49–54, July 2005. doi: 10.1038/nature03637.
- T. E. Zegers, W. Dabekaussen, E. Hauber, K. Gwinner, F. Scholten, F. Fueten, R. Stesky, P. MacKinnon, G. Neukum, and HRSC Co-Investigator Team. 3D Structural Analysis of Ophir Chasma Based on HRSC Image Data and Stereo-derived DTM. In S. Mackwell and E. Stansbery, editors, *37th Annual Lunar and Planetary Science Conference*, volume 37 of *Lunar and Planetary Institute Conference Abstracts*, page 1605, March 2006.

M. Zuber, D. Smith, S. Solomon, D. Muhleman, J. Head, J. Garvin, J. Abshire, and J. Bufton. The mars observer laser altimeter investigation. *Journal of Geophysical Research (Planets)*, 97:7781–7797, 1992.