

Water-Rock Reactions on Earth and Mars: Insights from Remote Sensing, Meteorites, and Subsurface Exploration

by

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A dissertation

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Conferences and Presentations

Conference Papers or Presentations

- Abiotic CH₄ Production in the Subsurface of Terrestrial Planets, Goldschmidt 2020, JUN 2020, Presented, **Tarnas, J.**; Mustard, J.; Sherwood Lollar, B.; Stamenkovic, V.; Warr, O.

- Constraining the origin of hydrated silica in Jezero crater and its accessibility by NASA's Mars 2020 rover, 51st Lunar and Planetary Science Conference, MAR 2020, Meeting cancelled, **Tarnas, J.D.**; Mustard, J.F.; Parente, M.; Seelos, F.P.; Itoh, Y.; Saranathan, A.M.
- Abiotic H₂, CH₄, and SO₄ production on Earth and Mars: atmospheric warming agents and redox energy sources for ancient and modern subsurface martian life, 51st Lunar and Planetary Science Conference, MAR 2020, Meeting cancelled, **Tarnas, J.D.**; Mustard, J.F.; Sherwood Lollar, B.; Stamenkovic, V.; Warr, O.; Cannon, K.M.; Palumbo, A.M.; Plesa, A.-C.
- Bridge to the stars: a mission concept to an interstellar object, 51st Lunar and Planetary Science Conference, MAR 2020, Meeting cancelled, Moore, K.;...; **Tarnas, J.**;...Mitchell, K.
- Mars' subsurface environment: where to search for groundwater? , 51st Lunar and Planetary Science Conference, MAR 2020, Meeting cancelled, Plesa, A.-C.; Stamenkovic, V.; Breuer, D.; Hauber, E.; **Tarnas, J.D.**; Mustard, J.F.; Mischna, M.; and the TH₂OR and VALKYRIE Teams
- Hyperspectral target detection and application to low abundance serpentine mapping, 51st Lunar and Planetary Science Conference, MAR 2020, Meeting cancelled, Wu, X.; Mustard, J.F.; Zhang, X.; **Tarnas, J.D.**
- Laboratory testing of mineral detection algorithms for minerals at low abundance using visible-infrared hyperspectral data, 51st Lunar and Planetary Science Conference, MAR 2020, Meeting cancelled, Das, E.; **Tarnas, J.D.**; Mustard, J.F.; Wu, X.
- Laboratory testing of mineral detection and abundance algorithms: factor analysis detection and nonlinear mixture modeling, 51st Lunar and Planetary Science Conference, MAR 2020, Meeting cancelled, Mustard, J.F.; **Tarnas, J.D.**; Wu, X.; Das, E.; Parente, M.
- "Mars Extant Life: What's Next?" conference report, 51st Lunar and Planetary Science Conference, MAR 2020, Meeting cancelled, Carrier, B.L.;...**Tarnas, J.D.**; Webster, K.D.
- Abiotic CH₄ flux from the Precambrian Shield on Earth and during the Noachian Hesperian and Amazonian periods on Mars, 2019 AGU Fall Meeting, San Francisco, CA, DEC 2019, Presented, **Tarnas, J.D.**; Mustard, J.F.; Sherwood Lollar, B. Warr, O.; Cannon, K.M.; Palumbo, A.M., Plesa-A.C.

- Water-rock Alteration and Geochemical Conditions in the Hawai'i Scientific Drilling Program Core: Implications for Understanding the 3-D architecture of Volcanic Subsurface, 2019 AGU Fall Meeting, San Francisco, CA, DEC 2019, Presented, Mustard, J.F.; **Tarnas, J.D.**; Wu, X.
- Deep groundwaters on Earth as analogs for modern martian habitat, Mars Extant Life: What's Next?, Carlsbad, NM, NOV 2019, Presented, **Tarnas, J.D.**; Mustard, J.F.; Sherwood Lollar, B.; Warr, O.; Palumbo, A.M.; Plesa, A.-C
- A Sparsity Divergence Constrained Factor Analysis and Target Transformation Method and Application to Hydrous Minerals Detection of Hyperspectral Imagery, 2019 AGU Fall Meeting, San Francisco, CA, SEP 2019, Presented, Wu, X.; **Tarnas, J.D.**; Zhang, X.; Mustard, J.F.
- Mars could have been warmed by eccentricity variations or a subsurface biosphere, Ninth International Mars Conference, Pasadena, CA, JUL 2019, Presented, **Tarnas, J.D.**; Mustard, J.F.; Sherwood Lollar, B.; Cannon, K.M.; Palumbo, A.M.; Plesa, A.-C.
- Mineral detections over Jezero crater using advanced data processing techniques for CRISM data—the CRISM “Fandango”, Ninth International Conference on Mars, Pasadena, CA, JUL 2019, Presented, Parente, M.; Arvidson, R.; Itoh, Y.; Lin, H.; Mustard, J.F.; Saranathan, A.M.; Seelos, F.P.; **Tarnas, J.D.**
- A geologic record of the first billion years of Mars history at the Mars 2020 landing site, Ninth International Conference on Mars, Pasadena, CA, JUL 2019, Presented, Mustard, J.F.; Bramble; M.S., Kremer, C.H.; **Tarnas, J.D.**; Pascuzzo, A.; Head, J.W.
- Is Abiotic Methane Production Sufficient for Warming Noachian and Hesperian Mars?, 2019 Astrobiology Science Conference, Bellevue, WA, JUN 2019, Presented, **Tarnas, J.D.**; Mustard, J.F.; Sherwood Lollar, B.; Cannon, K.M.; Palumbo, A.M.; Plesa, A.-C.
- An insufficient methane budget for warming Noachian and Hesperian Mars, 50th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2019, Presented, **Tarnas, J.D.**; Mustard, J. F., Sherwood Lollar, B.; Cannon, K. M.; Palumbo, A. M., Plesa, A.-C.; Bramble, M.S.

- Convergence on Mineral Detections over Gale Crater, NE Syrtis and Jezero Crater using Advanced Data Processing Techniques for CRISM Hyperspectral Imaging Data, 50th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2019, Presented, Parente M., Arvidson, R.E., Itoh, Y., Lin, H., Mustard, J.F., Saranathan, A.M., Seelos, F.P., **Tarnas, J.D.**
- Hydrated silica in the Jezero deltas, 50th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2019, Presented, **Tarnas, J.D.**; Mustard, J.F.; Lin, H.; Goudge, T.A.; Amador, E.S.; Bramble, M.S.; Zhang, X.
- Laboratory Testing of the Factor Analysis-Target Transformation Method for Mineral Detection at Low Abundance from Visible-Infrared Hyperspectral Data, 50th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2019, Presented, Mustard, J.F.; **Tarnas, J.D.**; Parente, M.
- Scientific Exploration of Mare Imbrium with OrbitBeyond Inc.: Characterizing the Regional Volcanic History of the Moon, 50th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2019, Presented, Tokle, L.; Palumbo, A.; Deutsch... **Tarnas, J.**; ... Vatsal, V
- VNIR Characterization of the Martian North Polar Ice Cap 2): Constraining the Surface Compositions, 50th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2019, Presented, Pascuzzo, A.C.; **Tarnas, J.D.**; Mustard, J.F.; Lin, H.
- H₂ and CH₄ Production, Storage, and Release over ~4.5 Gyr of Martian History: Implications for Atmospheric Warming, Habitability, and ISRU, American Geophysical Union Fall Meeting, Washington, D.C., DEC 2018, Presented, **Tarnas, J.D.**; Mustard, J. F., Sherwood Lollar, B.; Bramble, M.S.; Cannon, K. M.; Palumbo, A. M., Plesa, A.-C.
- Production of H₂ on Mars Through Radiolysis and Implications for Habitability, Goldschmidt 2018, Boston, MA, AUG 2018, Presented, **Tarnas, J. D.**; Mustard, J. F., Sherwood Lollar, B.; Bramble, M.S.; Cannon, K. M.; Palumbo, A. M., Plesa, A.-C.
- Target Transformation Constrained Sparse Unmixing (TTCSU) Algorithm for Retrieving Hydrated Minerals on Mars: Application to Southwest Melas Chasma, International Archives of the Photogrammetry, Remote Sensing & Spatial Information Sciences; ISPRS

TC III Mid-term Symposium “Developments, Technologies and Applications in Remote Sensing”, Beijing, China, MAY 2018, Presented, Lin, H.; Zhang, X.; Wu, X.; **Tarnas, J.D.**; Mustard, J.F.

- Characterization of serpentine and carbonate in Mars 2020 landing site candidates using Integrated Dynamic Aperture Target Transformation and Sparse Unmixing (IDATTSU), 49th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2018, Under Review, **Tarnas, J.D.**; Lin, H.; Mustard, J.F.; Zhang, X.
- Dynamic Aperture Target Transformation (DATT): A Novel and Valuable Method for Mineral Detection on Mars, 49th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2018, Presented, Lin, L.H.; **Tarnas, J.D.**; Mustard, J.F.; Zhang, X.; Wu, X.
- Hydrated silicates and carbonates mapping in candidate Mars 2020 rover landing sites with integration of Dynamic Aperture Target Transformation and Sparse Unmixing (IDATTSU), 49th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2018, Presented, Zhang, X.; Lin, H.; Mustard, J.F.; **Tarnas, J.D.**
- Radiolytic H₂ Production, Transport, and Dissolution on Noachian Mars, 49th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2018, Presented, **Tarnas, J.D.**; Mustard, J.F.; Sherwood Lollar, B.; Bramble M.S.; Cannon, K.M.; Palumbo, A.M.; Plesa, A.-C.
- Radiolytic H₂ Production on Noachian Mars: Implications for Subsurface Habitability, 4th International Conference on Early Mars, Flagstaff, AZ, OCT 2017, Presented, **Tarnas, J. D.**; Mustard, J. F.; Sherwood Lollar, B.; Bramble, M.S.; Cannon, K. M.; Palumbo, A. M.
- Radiolytic Hydrogen Production on Noachian Mars, 2017 Astrobiology Science Conference, Mesa, AZ, APR 2017, Presented, Tarnas, J. D.; Mustard, J. F.; Sherwood Lollar, B.; Bramble, M. S.
- Hydrogen production from the upper 15 km of martian crust via serpentinization: implications for habitability, 48th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2017, Presented, Mustard, J. F.; **Tarnas, J. D.**

- Radiolytic Hydrogen Production on Noachian Mars, 48th Lunar and Planetary Science Conference, Woodlands, TX, MAR 2017, Presented, **Tarnas, J. D.**; Mustard, J. F.; Sherwood Lollar, B.; Bramble, M. S.
- HOMER: A smallsat ground penetrating radar sounding fleet to map planetary surfaces at high resolution, 47th LPSC, Woodlands, TX, MAR 2016, Presented, Persaud, D.; Wu, T.; **Tarnas, J.**; Preudhomme, M.; Jurg, M.; Chalumeau, C.; Buckley, H.; Lombard- Poirot, N
- Transit, Secondary Eclipse, and Phase Curve Modeling to Characterize Kepler Exoplanet Candidates, 227th Meeting of the American Astronomical Society, Kissimmee, FL, JAN 2016, Presented, **Tarnas, J.**, Redfield, S.
- Subsurface Feature Mapping of Mars using a High Resolution Ground Penetrating Radar System, 2015 AGU Fall Meeting, San Francisco, CA, DEC 2015, Presented, Wu, T.; Persaud, D.; Preudhomme, M.; Jurg, M.; Smith, M.K.; Buckley, H.; **Tarnas, J.**; Chalumeau, C.; Poirot-Lombard, N.; Mann, B.
- Determination of the amount of peroxy in granite rock using the Seebeck Effect, 2015 AGU Fall Meeting, San Francisco, CA, DEC 2015, Presented, Tregloan-Reed, J.; **Tarnas, J.**, Plante, Z.; Freund, F.

Workshop Papers or Presentations

- CRISM “Fandango” Progress Report: Validated Derived Products for the Perseverance Jezero Mapping Team, Perseverance Science Team Meeting, Virtual, MAR 2020, Presented, Arvidson, R.; Seelos, F.; Parente, M.; **Tarnas, J.**; Christian, J.; Itoh, Y.; Mustard, J.; O’Sullivan, J.; Pollite, D.; Saranathan, A.; Frizzell, K.
- Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT) application to CRISM data, APL CRISM Mapping Meeting, Laurel, MD, JAN 2019, Presented, **Tarnas, J.D.**; Lin, H.; Mustard, J.F.; Zhang, X.

- Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT) analysis of CRISM data, CRISM virtual meeting, Providence, RI, SEP 2018, Presented, **Tarnas, J.D.**; Lin, H.; Mustard, J.F.; Zhang, X.;

Chaired Conference Sessions

- Astrobiology I: Looking for Life on Mars, Microbial Impact of Human Exploration, Curation Contamination Measurements. 49th Lunar and Planetary Science Conference (2018). Co-chair Amy Williams, Research Associate NASA Goddard Space Flight Center.

Fellowships and Awards

External Honors and Awards

- RI Space Grant Travel Grant, NASA RI Space Grant, 1800, 04/30/2019
- Mars Student Travel Grant for 4th Landing Site Workshop for the Mars 2020 Rover Mission, Mars Exploration Program at NASA Headquarters, 1000, 09/19/2018
- SSERVI SEEED Grant for 2017 Sudbury Field Camp, SSERVI, 1273, 08/22/2017

Brown University Honors and Awards

- Research Matters Semi-Finalist 2020. Finalist selection postponed.
- Brown University Doctoral Research Grant, Brown University, \$1800, 05/08/2019, 05/08/2019
- Brown University Graduate Conference Travel Grant, Brown University, \$650, 11/16/2018, 11/16/2018
- Brown University Graduate Conference Travel Grant, Brown University, \$650, 04/22/2017, 04/28/2017
- Sigma Xi, member 2019-present

Teaching and Mentoring

Teaching

<i>Appointment Type</i>	<i>Instructor</i>	<i>Term</i>	<i>Course</i>	<i>Section</i>	<i>Title</i>	<i>Enrollment</i>	<i>Supervised</i>
<i>Teaching Assistant</i>	Fischer, Karen Tullis, Jan	Fall 2018	GEOL 0220	S01	Physical Processes in Geology	47	47
<i>Teaching Assistant</i>	Milliken, Ralph	Spring 2017	GEOL 0810	S01	Planetary Geology	76	76

Mentoring

Undergraduate, Summer 2019, Lab

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Publications

Articles

- The global distribution and outcrop characteristics of serpentine on Mars as seen by the Mars Reconnaissance Orbiter, **J.D. Tarnas**, J.F. Mustard, In Preparation
- Successes and challenges of factor analysis target transformation applications to visible-to-near-infrared hyperspectral data, **J.D. Tarnas**, J.F. Mustard, X. Wu, E. Das, M. Parente, In Preparation
- Abiotic and microbial CH₄ production in the Precambrian lithosphere's deep subsurface, **J.D. Tarnas**, J.F. Mustard, B. Sherwood Lollar, V. Stamenkovic, O. Warr, In Preparation
- Earth-like habitable environments in the subsurface of Mars, **J.D. Tarnas**, J.F. Mustard, B. Sherwood Lollar, V. Stamenkovic, O. Warr, K.M. Cannon, A.M. Palumbo, A.-C. Plesa, J.-P. Lorand, T.C. Onstott, In Preparation
- Bridge to the stars: A mission concept to an interstellar object, *Planetary and Space Science*, K. Moore, S. Courville,...**J.D. Tarnas**,..., C., Budney, Peer Review, Under Review

- Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT) for serpentine and Mg-carbonate mapping on Mars with CRISM near-infrared data, *Icarus*, Honglei Lin, **J. D. Tarnas**, J. F. Mustard, Xia Zhang, Yong Wei, Weixing Wan, F. Klein, and J.R. Kellner, Peer Review, Under Review
- Mars Extant Life: What's Next? Conference Report, *Astrobiology*, 20, 6, 2020, B.L. Carrier, D.W. Beaty, M.A. Meyer,...**J.D. Tarnas**,..., J. Xu, Peer Review, Published
- Abiotic Sources of Molecular Hydrogen on Earth, *Elements*, 16, 19-24, 2020, F. Klein, **J.D. Tarnas**, W. Bach, Peer Review, Published
- Orbital identification of hydrated silica in Jezero crater, Mars, *Geophysical Research Letters*, 46, 22, 2019, **J.D. Tarnas**, J.F. Mustard, H. Lin, T.A. Goudge., E.S. Amador-French, M.S. Bramble, C.H. Kremer, X. Zhang, Y. Itoh, M. Parente, Peer Review, Published
- Scientific Exploration of Mare Imbrium with OrbitBeyond, Inc.: Characterizing the Regional Volcanic History of the Moon, *New Space*, 7, 3, 2019, A.M. Palumbo, A.N. Deutsch, M.S. Bramble, **J.D. Tarnas**,..., V. Vatsal, Peer Review, Published
- The next frontier for planetary and human exploration, *Nature Astronomy*, 3, 116-120, 2019, V. Stamenković, L. W. Beegle, K. Zacny,..., **J. D. Tarnas**,..., R. Woolley, Peer Review, Published
- Radiolytic H₂ production on Noachian Mars: Implications for habitability and atmospheric warming, *Earth and Planetary Science Letters*, 502, 133-145, 2018, **Tarnas, J. D.**; Mustard, J. F.; Sherwood Lollar, B.; Bramble, M. S.; Cannon, K. M.; Palumbo, A. M.; Plesa, A.-C., Peer Review, Published
- Universal heating curve of damped Coulomb plasmas in a Paul trap, *Physical Review A*, 88, 041401(R), 2013, **Tarnas, J. D.**; Nam, Y. S.; Blümel, R., Peer Review, Published

Professional Development

Other Skill Building Opportunities

- Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) “Fandango” Advanced Data Analysis Working Group, 11/2018-present. I am the lead participant from Brown University in the CRISM “Fandango” group, which is a team composed of

members from Brown University, Washington University in St. Louis, Johns Hopkins University Applied Physics Lab, University of Massachusetts at Amherst, Planetary Science Institute, and other institutions. We test advanced methods for processing and analyzing CRISM hyperspectral data by determining if these different approaches can reach consensus regarding spectral signals and compositional interpretations from those signals. We have developed hyperspectral image and mineral map products, validated by the teams within this group, for delivery to the Perseverance rover Science Team and Mapping Team.

- JPL Planetary Science Summer Seminar, Pasadena, CA, 05/20/2019, 08/09/2019, In this NASA-sponsored program that takes place via 11 weeks of webinars, culminating in a week at NASA's Jet Propulsion Laboratory (JPL), we were taken through the entire process of designing a robotic space mission. This included working one-on-one with JPL's A-Team (space mission architecture team) and Team-X (space mission design team) and presenting the mission design to a panel of NASA scientists, engineers, and administrators. Many successful NASA mission leaders have gone through this program. We designed a mission to intercept an interstellar object passing through the Solar System.
- NASA Volcanology Workshop, Big Island, HI, 07/11/2019, 07/17/2019, NASA-sponsored, fully funded workshop to study volcanism on the Big Island of Hawaii. It is designed to allow planetary scientists to develop a better understanding of field volcanology on Earth, which improves our interpretive capabilities regarding volcanic processes on other planets, observed in images and other forms of remote sensing data.
- Short Course and Field School at Sudbury Impact Structure, Sudbury, Ontario, 09/23/2017, 09/30/2017, I received funding from NASA's Solar System Exploration Research Virtual Institute (SSERVI) to participate in this Sudbury field camp, where we studied field geology of one of the largest impact structures on Earth. Studying affects of impacts on Earth rocks allows us to understand how they affect other planetary (sub)surfaces.

- Subsurface science fieldwork in Kidd Creek Mine, Ontario through Stable Isotope Laboratory at University of Toronto. We sampled and studied the geochemistry of the longest-isolated groundwater discovered to-date by humans, and how this geochemistry affects Earth's subsurface biosphere (February 2019).
- Remote sensing fieldwork in Nanyuki Kenya, through the Institute at Brown for Environment and Society SEED grant to Kartzinel and Kellner labs (July 2018).

Service

Professional Organizations and Committees including Peer Reviews, Journals, Books, etc.

- Planetary and Space Science, Manuscript Reviewer. Manuscript published. Methane release on Early Mars by atmospheric collapse and atmospheric reflation, Planetary and Space Science, 181, 104820, E.S. Kite, M.A. Mischna, P. Gao, Y.L. Yung, M. Turbet.
- Geophysical Research Letters, Manuscript Reviewer.
- Nature Scientific Reports, Manuscript Reviewer.
- Journal of Geophysical Research: Planets, Manuscript Reviewer

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E Nihi Ka Hele I Ka Uka O Puna

*E nihi ka hele i ka uka o Puna
Mai 'ako i ka pua
O lilo i ke ala o ka hewahewa
Ua hūnā 'ia ke kino o ka pōhaku
'O ka pua na'e ke ahu nei i ke alanui
Alanui hele o ka unu kupukupu ē
Ka uila
A kaunu nō anei 'oe 'o ke aloha lā
Hele a'e a komo i ka hale o Pele
Ua huahua'i i Kahiki, lapa uila
Pele ē, hua'ina ho'i!*

Walk carefully in the upland trail of Puna
Don't pick the flowers
Or the path will become unrecognizable
The tricky ones are hidden in the rocks
The thriving flowers distract from the path
The roadway full of growth covers the stones
If there is a sudden accident
Would you not be yearning for compassion
Go forward and enter the house of Pele
She bursts forth to Kahiki, lightning flashing
Ever growing Pele!

Chant recorded and translated by
Pualani Kanaka'ole Kanahele
in *Ka Honua Ola 'Eli'eli kau mai*
Published in 2011
by Kamehameha Schools

INTRODUCTION

The concept of cosmic pluralism, the philosophical belief that Earth is one of many different inhabited worlds, manifested in mythology and religion millennia before its establishment as a scientific ponderance. It was postulated by pre-Socratic Greek philosophers—including Anaximander and Democritus—in the 4th and 5th centuries BCE and as a concept in Jainism predating the 5th century BCE. The scientific manifestation of cosmic pluralism is the search for evidence of extraterrestrial life. This has been a main scientific driver of space exploration by the National Aeronautics and Space Administration (NASA) and international space organizations, with the first instruments designed for life-detection reaching Mars onboard the Viking landers in 1976. Decades of space exploration have demonstrated that Earth-like life is uncommon on planetary surfaces in the modern-day Solar System, with Earth being the only object to host a habitable surface environment. It is likely that Mars hosted transiently habitable environments on its surface billions of years ago. Planetary subsurfaces are now highlighted as better targets for extant life detection, from the deep subsurface of Mars, to oceans beneath the ice shells of Europa and Enceladus, to brine reservoirs in dwarf planets such as Ceres. The next frontier of maximally scientifically compelling astrobiological exploration is therefore largely in planetary subsurfaces.

Deep subsurface life on Earth

The spatial expanse, metabolic diversity, and total biomass of microbial life in Earth's deep subsurface was underappreciated until the 1990s, when studies first presented evidence

for widespread microbial presence at greater than kilometer depths (Gold, 1992; Whitman et al., 1998). Recent estimates of subsurface biomass ranges from $[2-52] \times 10^{29}$ cells in the continental subsurface (23-135 Pg carbon) (Bar-On et al., 2018; Magnabosco et al., 2018; McMahon and Parnell, 2014), $2.9-50 \times 10^{29}$ cells in subseafloor sediments (4-90 Pg carbon) (Bar-On et al., 2018; Kallmeyer et al., 2012; Lipp et al., 2008; Parkes et al., 1994), and $0.2-100 \times 10^{29}$ cells in the oceanic crust (0.55-210 Pg carbon) (Bar-On et al., 2018; Heberling et al., 2010), which equates to $5.1-202 \times 10^{29}$ cells and 27.5-435 Pg carbon total. This compares to microbial biomass estimates for Earth's continental surface and near-surface soil of ~ 20 Pg carbon and ~ 470 Pg carbon including plants and animals (Bar-On et al., 2018). As such, the total biomass in Earth's deep subsurface likely exceeds the total microbial biomass on the subaerial surface, and is comparable to Earth's total subaerial surface and near-surface biomass. Constraining the physical architectures and geochemical processes that sustain deep subsurface life is critical to understanding the controls on this major sector of Earth's system, as well as for determining the likelihood that such life could exist on other planetary objects.

In the deep subsurface of Earth's Precambrian crust, groundwater is primarily confined to compartmentalized fracture networks within crystalline rock, which are estimated to contain $\sim 30\%$ of Earth's total groundwater inventory (Warr et al., 2018). These networks can be stochastically interconnected via large-scale regional stress variations that induce more fracturing (Sleep and Zoback, 2007). Compartmentalized groundwaters on Earth can vary widely in their mean residence times, meaning the average amount of time that the water molecules within a specific groundwater pocket have existed without surface water input. Near-surface groundwater is often meteoric, only transiently existing in the shallow subsurface

before reentering the hydrologic cycle (e.g. Markovich et al., 2019). Deeper groundwater can become isolated from the surface for millions to billions of years (Heard et al., 2018; Holland et al., 2013; Lippmann et al., 2003; Lippmann-Pipke et al., 2011; Warr et al., 2018). The groundwater reservoir with the longest mean residence time currently known is found in Kidd Creek Mine, and has remained largely isolated from surface substrate input for $>10^9$ years (Holland et al., 2013; Warr et al., 2018). Nonphotosynthetic chemolithotrophic microbial communities exist even in these longest isolated currently known subsurface fluids (Lollar et al., 2019), driving their metabolisms using oxidants and reductants produced by water-rock interactions (Sherwood Lollar et al., 2007; Li et al., 2016; Warr et al., 2019).

Radiolysis—the breaking of neutral H_2O molecules into their constituent oxidants and reductants by α , β , and γ radiation—is a water-rock interaction that provides life-sustaining redox energy in millions to billions year old groundwater. In natural settings, radiolysis occurs via breakdown of water in pore and fracture spaces by radiation released from decay of K, Th, and U within the host rock matrix (Li et al., 2016; Lin et al., 2005b, 2005a; Onstott et al., 2006; Sherwood Lollar et al., 2014; Warr et al., 2019). This process produces H_2 —a reductant—and complementary oxidants, including H_2O_2 , which are typically too oxidizing for direct metabolic usage by microorganisms. These radiolytically-derived oxidants will oxidize sulfides present in the rock matrix, forming sulfate (Lefticariu et al., 2010), which coupled with H_2 is consumable by microorganisms via the reaction $4H_2 + H^+ + SO_4^{2-} \rightarrow HS^- + 4H_2O$. This process generates a sustained redox energy source for microbial communities in ancient groundwaters in Earth's deep subsurface, one that does not require surface nutrient input. Sulfate-reducing bacteria are commonly found in these ancient groundwaters (Chivian et al., 2008; Lin et al., 2006; Lollar et

al., 2019), and in some settings such as Kidd Creek, it has been demonstrated that radiolytically-derived primary H_2 and secondary sulfate are the primary feedstocks for these organisms (Li et al., 2016).

Other water-rock interactions produce biosustaining gases in Earth's deep subsurface, including abiotic Fischer-Tropsch Type (FTT) reactions that reduce CO or CO_2 with H_2 to form CH_4 via the reactions $3H_2 + CO \rightarrow CH_4 + H_2O$ and $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$. Abiotic CH_4 produced via this method can sustain methanotrophic microbial communities. Methanogens in the deep subsurface harness metabolic energy derived from reduction of CO_2 by H_2 to form CH_4 via the reaction $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$. While methanogens and methanotrophs sometimes comprise a small fraction of total biomass in oligotrophic subsurface microbial ecosystems, their metabolic activity generates redox products that remove thermodynamic bottlenecks from the overall ecosystem (Lau et al., 2016). Additional microbial metabolisms found in Earth's deep subsurface include aerobic respiration, sulfide and Fe^{2+} oxidation, nitrate and Fe^{3+} reduction, fermentation, and acetogenesis (Onstott et al., 2019). The prominence of any given metabolism with respect to total energy consumption by a deep subsurface microbial ecosystem varies depending on the predominantly available redox compounds, including the energetic framework established by other microbes within the ecosystem. Chapter 1 of this dissertation focuses on constraining the rates and mechanisms for redox compound production in Earth's deep subsurface.

The subsurface of Mars

The low temperature, low pressure, desiccating, highly oxidizing, and heavily irradiated surface of Mars is not conducive to the existence of Earth-like life. The subsurface of Mars, however, has long been postulated to be the most habitable environment for Earth-like life on the planet (Jakosky et al., 2003; Sagan and Lederberg, 1976), and the most likely refugia for any martian life (Michalski et al., 2018; National Academies of Sciences, Engineering, and Medicine et al., 2018). Reducing compounds such as H_2 and CH_4 could be generated in the martian subsurface via processes similar to those in Earth's subsurface (Onstott et al., 2006; Tarnas et al., 2018). Such abiotic gas formation processes may explain detection of CH_4 by telescopic (Mumma et al., 2009), orbital (Giuranna et al., 2019), and landed (Webster et al., 2018) observations. In Chapter 2 of this dissertation, we demonstrate that sulfate required for microbially-facilitated redox coupling to these reductants is likely present in sufficient quantities to support martian life wherever groundwater exists.

The Mars Advanced Radar for Subsurface and Ionosphere Sounding (MARSIS) and the Shallow Radar (SHARAD) instruments have not found definitive evidence of groundwater on Mars, though a reflector near the South Polar Cap has been controversially interpreted as a ~1.5 km depth brine pocket (Orosei et al., 2018). The penetration depth of radar at the wavelengths of these instruments is maximized in pure ice, and therefore they are able to measure deeper depths of the crust in polar regions (Orosei et al., 2018). Because polar regions of Mars are colder than mid-latitudes, any groundwater there would likely be several kilometers deeper compared to mid-latitude regions (Clifford et al., 2010), which partially negates the advantage of greater radar penetration depth at the poles. At mid-latitudes, SHARAD and MARSIS can penetrate <3 kilometers depth (Fois et al., 2007), which is not a

sufficient to detect any widespread groundwater table—if such a table is present—as this would likely be deeper (Clifford et al., 2010). While the presence, distribution, and geochemical characteristics of groundwater on Mars is an open question that necessitates new missions and data to answer, the total water budget for Mars indicates that some reservoir likely still exists in the crust, as D/H isotopic ratios and modeling indicate that not all of the original martian water budget could have escaped the planet (Grimm et al., 2017; Grimm and Painter, 2009). The critical next step in Mars subsurface exploration is to constrain the presence, distribution, and characteristics of groundwater there.

Bulk subsurface physical properties in the Tharsis and Elysium volcanic bulges are likely similar to basaltic volcanic formations such as Hawaii, Iceland, and/or Large Igneous Provinces, as is estimated by orbital gravimetry (Broquet and Wieczorek, 2019; Goossens et al., 2017). In other locations, like the Noachian-aged southern highlands that compose ~50% of Mars' crust, no comparable analog is preserved in Earth's geologic record. Orbital gravimetry estimates indicate that the Noachian crust has a bulk average density of $\sim 1600 \text{ kg m}^{-3}$ (Goossens et al., 2017). Rover gravimetry estimates for the top 300 meters of the Gale crater sedimentary mound—loosely age constrained to Late Noachian-Early Hesperian (Milliken et al., 2010)—indicate a density of $1680 \pm 180 \text{ kg m}^{-3}$ (Lewis et al., 2019). Orbital gravimetry density estimates are notably dependent on assumed crustal thickness (Goossens et al., 2017). These estimated densities are substantially lower than densities of lithologies on Earth that are predominantly rock rather than dispersed rock within an ice matrix. For the Noachian crust, this may stem from a remarkably different geologic history compared to Earth's modern crust. Impact processes have shaped the surface and subsurface of the Noachian crust to an extent

unmatched in any part of Earth's preserved geologic record. The lunar highlands are similarly shaped predominately by impact processes and have estimated surface densities of ~2300-2500 kg m⁻³ (Besserer et al., 2014). The Noachian crust, however, is substantially altered to clay (Ehlmann and Edwards, 2014), in contrast to the lunar crust which is predominantly anorthosite-rich material (Lucey, 2004). The formation of subsurface clay in the Noachian crust via alteration of primary volcanic minerals by a supercritical steam atmosphere immediately following magma ocean crystallization, and simultaneous burial of those clays by impacts (Cannon et al., 2017), would impart characteristics on the Noachian crust that are not preserved in Earth's geologic record. This combination of an alteration-mineral-rich composition and heightened fracturing/porosity due to impact bombardment may explain the uniqueness of the Noachian crust's density relative to Earth's modern crust. These physical parameters will affect both the physical and chemical architecture of the martian subsurface, including the locations at which groundwater can permeate to.

Ancient habitable environments on the surface of Mars

Investigation by NASA's Curiosity rover demonstrated the presence of an ancient transient lacustrine environment in Gale crater, which was likely habitable (Grotzinger et al., 2014). NASA's Spirit rover observed evidence for hot spring environments in Columbia Hills (Ruff et al., 2019; Ruff and Farmer, 2016), and these settings are often habitable on Earth. Observations using the Context Camera (CTX) and High Resolution Imaging Science Experiment (HiRISE) have revealed the presence of paleolakes of a variety of ages in the southern highlands of Mars (Fassett and Head, 2008; Goudge et al., 2012, 2015a, 2016). Some of these interpreted

paleolakes host deltaic deposits, with the best-preserved deposit existing in western Jezero crater, Mars. The mineralogy of this deltaic deposit, determined using the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), includes clays (Ehlmann et al., 2008) and carbonates (Goudge et al., 2015b, 2017; Horgan et al., 2020), which may have formed in a habitable aqueous environment and also have relatively high biosignature preservation potential. As such, there is both orbital and landed evidence for ancient habitable environments on Mars that might preserve biosignatures. NASA's Perseverance rover will investigate rocks in Jezero crater to evaluate whether they contain biosignatures, then will cache samples for return to Earth for in-depth laboratory biosignature evaluation. Chapter 3 of this dissertation develops and tests advanced hyperspectral image analysis methods, which in Chapter 4 are applied to CRISM data of Jezero crater to characterize minerals with high biosignature preservation potential.

Dissertation structure

Chapter 1 focuses on quantifying abiotic and microbial CH₄ production rates in Earth's deep subsurface, how they vary regionally and at individual mine/borehole sites, and what the physical and chemical mechanisms are that induce these variations. This work builds on past studies demonstrating the presence of both abiotic and microbial CH₄ in deep subsurface groundwaters (Sherwood Lollar et al., 1993b, 1993a; Ward et al., 2004; Onstott et al., 2006; Sherwood Lollar et al., 2006; Kietäväinen and Purkamo, 2015; Kietäväinen et al., 2017; Young et al., 2017; Young, 2019). It shows that the rate of abiotic CH₄ production is two orders of magnitude higher in sampled Fennoscandian and Canadian Shield groundwater compared to

groundwater sampled in Witwatersrand Basin. It also demonstrates that microbial CH₄ production rates are typically maximized at depths shallower than ~1 km, vary considerably at individual sites, and show no conclusive trend with depth at sites deeper than ~1 km. Lithology and hydrology are shown to be the most important factors influencing the variability in abiotic and microbial CH₄ production rates between regions and individual sites.

Chapter 2 uses data from martian meteorites, orbital gravimetry of Mars, and biogeochemical processes in Earth's deep subsurface to constrain the number of sulfate-reducing bacteria that could be supported in the martian subsurface solely via radiolysis. This work shows that the source lithologies for the martian meteorites can sustain measurable sulfate-reducing cell densities, and that the sustainable cell densities vary by seven orders of magnitude between the different source lithologies. The regolith breccia source lithology, which is in the southern highlands (Agee et al., 2013; Humayun et al., 2013; Cassata et al., 2018), can sustain the highest sulfate-reducing cell densities –up to millions of cells per kg rock. More sulfide-rich regions of Mars could sustain higher sulfate-reducing cell densities than the 4 lithologies of martian meteorites investigated here, and this work establishes the different settings in which sulfides would likely be concentrated on Mars. This work contributes to a growing body of evidence that the martian subsurface could have previously been habitable and may still be habitable today wherever groundwater exists (Michalski et al., 2013, 2018; Tarnas et al., 2018; Onstott et al., 2019).

Chapter 3 tests different applications of factor analysis/target transformation (FA/TT) methods to hyperspectral data using hyperspectral images of well-characterized mineral mixtures acquired in a laboratory setting. We test full-image FA/TT, the methodology employed

in Thomas and Bandfield, 2017 and Amador et al., 2018; Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT), the methodology developed in Lin et al., 2018 and employed in Chapter 4 of this dissertation; and develop/test a modified application of factor analysis termed guided factor analysis, which builds on concepts from previous studies (Schostack and Malinowski, 1993; Malinowski, 1996; Bandfield et al., 2000, 2002; Glotch and Bandfield, 2006; Amador et al., 2018). We apply R-mode factor analysis and the Hyperspectral Signal Subspace Estimation (HySIME) algorithm to calculate eigenvectors. We find that full-image FA/TT is highly susceptible to false positive detections in laboratory and CRISM data. We find that DAFA/TT can produce false negative results and some false positive results in the presence of structured noise that overlaps with absorption features, but overall performs better than full-image FA/TT. Guided factor analysis is, in some cases, a viable alternative to spectral ratioing to remove image noise—as partly demonstrated by Thomas and Bandfield, 2017—and can also be used to unmix spectral signals contributing variance to a given set of spectra. Overall, this study demonstrates the challenges and successes of factor analysis/target transformation applications to hyperspectral images, and provides a roadmap for scenarios where different versions of these methods do or do not work.

Chapter 4 covers the detection of hydrated silica and Al-phylosilicate in Jezero crater, the landing site of NASA's Perseverance rover. Hydrated silica and Al-phylosilicate are detected via application of DAFA/TT to CRISM data in Jezero crater. Hydrated silica has high biosignature preservation potential on Earth, and its location in Jezero crater implies that it possibly formed in a habitable environment. This study evaluates all the different possible formation environments for hydrated silica in Jezero crater, including detrital versus authigenic origins.

We also report detections of Al-phyllosilicate and hydrated silica in the Nili Fossae basement unit and possible hydrated silica mixed with phyllosilicate, olivine, and carbonate in the Nili Fossae olivine-rich unit. The fluvial channels that feed into Jezero crater incise both of these units (Goudge et al., 2015), therefore it is possible that detected hydrated silica is detrital in origin, though an authigenic origin is not ruled out. The hydrated silica outcrops lie immediately above the olivine-rich unit in Jezero crater, which can be seen protruding through it in multiple locations. Hydrated silica detections reported in this study, and outcrops of this material at spatial scales too small to be resolved in CRISM data, are good targets for biosignature investigation by NASA's Perseverance rover. We published this study in *Geophysical Research Letters* (Tarnas et al., 2019).

Chapter 5 presents a synthesis of the work reported in Chapters 1-4 and suggests future directions for astrobiologically-oriented planetary science in the coming decades. In concert, these chapters advance the search for extinct and extant extraterrestrial life via application of various data analysis and modelling techniques to multiple relevant datasets.

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CHAPTER 1: Quantification of abiotic and microbial CH₄ production rates in the Precambrian crust

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Abstract

Both abiotic and microbial sources contribute to CH₄ documented in saline fracture fluids in the deep subsurface of the Precambrian crust in localities including the Canadian Shield, Fennoscandian Shield, and Witwatersrand Basin. Unlike H₂, estimates of global CH₄ production rates from these settings have not been quantified. Here a database of dissolved gas measurements from kilometers-deep groundwaters in these three regions is used to estimate the relative contribution of abiotic and microbial CH₄, showing that some sites are dominated by microbial CH₄ production, while others are dominated by abiotic CH₄ production via low temperature water-rock reactions. Low-temperature abiotic CH₄ production rates are two orders of magnitude higher in the Canadian and Fennoscandian Shields compared to Witwatersrand Basin. In the Canadian Shield, Kidd Creek fluids contain predominantly abiotic CH₄, but there is significant variability in microbial/abiotic CH₄ contributions within the fracture fluids sampled by these same boreholes. Some Witwatersrand Basin mines are also dominated by abiotic CH₄ (e.g. Mponeng, Kloof), while others are predominantly microbial CH₄ (e.g. Beatrix, Evander, Dreifontein, Masimong, Merriespruit). Witwatersrand Basin sites typically show higher relative microbial/abiotic CH₄ contribution ratios compared to Canadian sites at similar depths. The results of this study are consistent with previous interpretations of CH₄ origins at these sites based on multiple lines of evidence that include geochemical, isotopic, and microbiological data. Estimated abiotic CH₄ production rates in the Precambrian crust range from $[0.02-1.8] \times 10^{-9} \text{ M CH}_4 \text{ year}^{-1}$, equating to $[0.08-7.1] \times 10^9 \text{ moles CH}_4 \text{ year}^{-1}$ from the top 10 km of the entire Precambrian lithosphere. Estimates of microbial CH₄ production rates in the Precambrian crust range from $<10^{-12} \text{ M CH}_4 \text{ year}^{-1}$ to $2.0 \times 10^{-8} \text{ M CH}_4 \text{ year}^{-1}$ at depths $>1 \text{ km}$, to

$[0.02-100] \times 10^{-8} \text{ M CH}_4 \text{ year}^{-1}$ at depths $<1 \text{ km}$. Microbial CH_4 production does not linearly decrease with depth globally, but appears to decrease with depth locally in Witwatersrand Basin, which is consistent with the results of previous studies. Microbial CH_4 production is particularly enhanced at depths $<1 \text{ km}$. Some of the shallowest sites—Fennoscandian Shield sites Ylivieska and Enonkoski, and Beatrix in Witwatersrand Basin—show the highest rates of microbial CH_4 production in the sample set, likely related to the infiltration of paleometeoric groundwaters in these areas.

1.0 Introduction

The majority of CH₄ on Earth is produced by extant biological systems or thermal decomposition of organic matter. Earth's deep subsurface, however, contains a significant amount of CH₄ produced via abiotic, non-thermogenic processes (Sherwood Lollar et al., 1993b; Sherwood Lollar et al., 2002; 2006; Young et al., 2017). Groundwaters in which abiotic CH₄ is detected can have mean residence times—calculated from noble gas abundance and isotopic compositions—of 10⁶-10⁹ years (Lippmann et al., 2003; Lippmann-Pipke et al., 2011; Holland et al., 2013; Kietäväinen et al., 2014; Warr et al., 2018; Heard et al., 2018), indicative of extended hydrogeologic isolation from near-surface processes. These deep groundwaters have primarily been sampled to date in the crystalline rock cratons of Canada, South Africa, and Finland (Fig. 1). Chemolithotrophic microbial communities in these groundwaters drive their metabolisms by facilitating redox reactions using oxidants and reductants produced through water-rock reactions independent of surface nutrient input (Kieft et al., 2005; Moser et al., 2005; Lin et al., 2006a; Onstott et al., 2006a; Lin et al., 2006b; Pfiffner et al., 2007; Chivian et al., 2008; Simkus et al., 2016; Magnabosco et al., 2016; Lollar et al., 2019). The use of CH₄ as a reductant has been identified in several different microbial communities in the subsurface of the Precambrian crust in South Africa and Finland (Kotelnikova, 2002; Moser et al., 2005; Nyssönen et al., 2014; Bomberg et al., 2015; Kietäväinen and Purkamo, 2015; Purkamo et al., 2015; Simkus et al., 2016; Magnabosco et al., 2016; Kietäväinen et al., 2017). Estimates of the relative contribution of abiotic versus microbial methanogenesis have typically been made to date based primarily on mixing curves calculated from carbon and hydrogen isotope values and in some cases CH₄/C₂+ (C₂H₆, C₃H₈, etc...; hereby referred to as C₂+) ratios (Etiope and Sherwood Lollar, 2013

and references therein). Onstott et al., (2006b) used dissolved He concentration, dissolved CH₄ concentration, $\delta^2\text{H-CH}_4$ ‰ VSMOW (Vienna Standard Mean Ocean Water), $\delta^{13}\text{C-CH}_4$ ‰ VPDB (Vienna Pee Dee Belemnite), and radionuclide concentration estimates from deep Witwatersrand Basin groundwaters and rock to model microbial CH₄ production rates from H₂ derived via radiolysis of pore water, assuming that all abiotic CH₄ came from a deeper crustal source. Noble gas studies have discounted the presence of any significant magmatic or mantle-derived gas component in fractures fluids in any of the three cratons evaluated in this study, though they do not definitely rule out a deeper crustal source (Sherwood Lollar et al., 1993; Lippmann et al., 2003; Holland et al., 2013; Kietavainen et al., 2014; Warr et al., 2018). Other lines of evidence, including a potential association between lithology and presence of abiotic CH₄ (Ward et al., 2004), imply that a significant quantity of abiotic CH₄ may be produced *in-situ*. Therefore, modeling undertaken in this work seeks to determine the contribution of abiotic and microbial CH₄ produced *in-situ* at multiple localities within the Precambrian crust (Canadian Shield, Fennoscandian Shield, and Witwatersrand Basin)—based on dissolved He concentrations, dissolved CH₄ concentrations, $\delta^2\text{H-CH}_4$ ‰ VSMOW, $\delta^{13}\text{C-CH}_4$ ‰ VPDB, and radionuclide concentrations measured in these three settings—via an adaptation of the model presented in Onstott et al., (2006b) (Section 2.5). This is necessary to determine the relative rates of these subsurface processes and how they vary based on regional setting. The results from this analysis establish a framework for comparative continental deep subsurface aqueous geochemistry, permitting hypothesis generation and testing regarding the factors controlling variations in abiotic and microbial CH₄ production rates between cratons, as well as between individual sites within the same craton.

Abiotic CH₄ has been detected in seafloor hydrothermal systems (Welhan and Craig, 1983; Botz et al., 1996; Kelley and Fröh-Green, 2001; Proskurowski et al., 2008; Kawagucci et al., 2010; Konn et al., 2015; McDermott et al., 2015; Kawagucci et al., 2016; McDermott et al., 2018; Kawagucci et al., 2018; Sciarra et al., 2019; Sissmann et al., 2019; Klein et al., 2019; Grozeva et al., 2020) and in continental surface seepages/hydrothermal systems (Abrajano et al., 1988; Lyon et al., 1990; Fritz et al., 1992; Sano et al., 1993; Lyon and Giggenbach, 1994; Potter et al., 2004; Taran et al., 2010; Etiope et al., 2011; Tassi et al., 2012; Boschetti et al., 2013; G. Etiope et al., 2013; Giuseppe Etiope et al., 2013; Suda et al., 2014; Cao et al., 2014; Etiope et al., 2015; Etiope et al., 2016; Suda et al., 2017; Etiope et al., 2017; Vacquand et al., 2018; Etiope et al., 2018; Marques et al., 2018). Abiotic CH₄ in most of these settings is proposed to form by water-rock interactions, with a possible magmatic CH₄ component in active hydrothermal settings that is less likely in tectonically quiescent settings. It has been recognized that abiotic CH₄ is more prevalent in seafloor hydrothermal systems hosted in ultramafic rocks compared to mafic rocks (Klein et al., 2019). It has also been demonstrated that abiotic CH₄ formation and hydrothermal fluid convection are decoupled at the Von Damm submarine hydrothermal field (McDermott et al., 2015), leading to suggestions that abiotic CH₄ may be derived via release from fluid inclusions (Vanko and Stakes, 1991; Kelley and Fröh-Green, 2001; McDermott et al., 2015; Klein et al., 2019; Grozeva et al., 2020). A recent study found abiotic CH₄ in olivine-hosted pore fluids in 100% of 43 gabbro samples and 77% of 117 peridotite samples from submarine settings (Klein et al., 2019). The formation of this CH₄ was attributed to pore-fluid-scale serpentinization, which produces H₂ within the pore and serpentinite assemblage minerals in its walls, followed by closed-system CO₂ reduction over

Myr timescales as H_2 activity increases. Myr timescales are apparently sufficient for the kinetic barrier to CO_2 reduction to be overcome in such closed systems. The 23% of peridotite lithologies devoid of olivine-hosted abiotic CH_4 -bearing fluid inclusions lack available magmatically-derived CO_2 for reduction (Klein et al., 2019).

CH_4 is thermodynamically stable throughout most of Earth's crust (McCollom, 2013) (Fig. 2). However, its formation via reduction of CO_2 is kinetically inhibited, typically requiring metal catalysts on which H_2 and CO_2 can adsorb to facilitate the reaction. Serpentine-hosted awaruite (Sleep et al., 2004) and chromite-hosted ruthenium (Etiope et al., 2018) are examples of rock-hosted metal catalysts demonstrated to facilitate CH_4 formation in natural crustal systems at low temperatures. Despite this, experimental evidence from McCollom (2016) suggests that abiotic CH_4 formation via CO_2 reduction is sluggish in closed systems on laboratory timescales (McCollom, 2016). Subsurface systems preserved on long geologic timescales provide settings in which products of such abiotic production can accumulate, even if reaction rates are slow.

Research on CH_4 formation mechanisms is currently heightened given the studies on Earth outlined above, discoveries of CH_4 in the martian atmosphere by telescopic (Mumma et al., 2009), orbital (Giuranna et al., 2019), and landed (Webster et al., 2018) observations, detection of CH_4 in martian meteorites (Blamey et al., 2015), and in the plumes of Enceladus (Waite et al., 2006). These findings necessitate development and application of effective methods to differentiate CH_4 of abiotic, microbial, or thermogenic origin. There is no single "silver bullet" method for determining the origin of CH_4 due to major overlaps in both carbon and hydrogen isotopic signatures for CH_4 of different provenance, and the complexities

introduced by secondary alteration processes. Recent reviews all emphasize the necessity of integrating multiple lines of evidence (Etiope and Sherwood Lollar, 2013; Schrenk et al., 2013; Young, 2019) including:

1. Clumped isotopes. Recent advances in mass spectroscopy have allowed for detection and differentiation of multiply-substituted $^{13}\text{CH}_3\text{D}$ species in CH_4 gas. This permits estimation of formation temperature of CH_4 , as well as differentiation of microbial CH_4 that departs from isotopic bond-order equilibrium (Young et al., 2017). Mixing lines can thus be drawn between microbial, thermogenic, and abiotic endmember CH_4 isotopologues to determine the relative contributions of each source to bulk measured CH_4 (Young et al., 2017; Giunta et al., 2019; Young, 2019).
2. $\text{CH}_4/\text{C}_{2+}$. The amount of CH_4 relative to higher order hydrocarbons (C_{2+}) can be used to assess microbial versus abiogenic sources of CH_4 . If CH_4 is predominantly microbial, typically it is of significantly higher abundance relative to C_{2+} molecules ($\text{CH}_4/\text{C}_{2+} \sim 10^3\text{-}10^4$) (Bernard et al., 1978; Sherwood Lollar et al., 2006). In contrast, CH_4 of a low temperature abiotic origin is typically associated with lower $\text{CH}_4/\text{C}_{2+}$ values ($\sim 10^0\text{-}10^2$), as the same low temperature polymerization reactions that produce CH_4 also produce C_{2+} (McCollom and Seewald, 2007).
3. Schulz-Flory distribution. While not uniquely diagnostic of abiotic processes, the molecular distribution of hydrocarbon alkanes controlled by the chain growth probability factor for abiotic stepwise polymerization, can produce a pattern whereby $\text{C}_{n+1}/\text{C}_n$ is approximately constant (Etiope and Sherwood Lollar, 2013). While found in gas produced by abiotic synthesis (Sherwood Lollar et al., 2002; Sherwood Lollar et al.,

2008), this pattern is also observed in thermogenic CH₄-bearing gas (Giggenbach, 1997), as the size distribution from formation of polymers via random bonding of smaller hydrocarbons is the same as random breaking of larger hydrocarbons. This distribution thus cannot distinguish between thermogenic and abiotic gas, but can typically rule out a predominantly microbial origin for CH₄.

4. The $\delta^2\text{H-CH}_4$ ‰ VSMOW and $\delta^{13}\text{C-CH}_4$ ‰ VPDB values for CH₄ (Fig. 3) have been used to differentiate CH₄ of microbial, thermogenic, and abiotic origins (Etiope and Sherwood Lollar, 2013). There are potential issues with this metric, specifically that the final isotopic values of the CH₄ depend on the isotopic values of precursor material (Sherwood Lollar et al., 1993b; Sherwood Lollar et al., 2006) and thus can vary widely from site to site. Additionally, such empirically based interpretational frameworks are inherently limited by the samples and processes that have been investigated to date. Within individual sites, however, the trend in these isotopes is typically consistent with the trend of microbial and abiotic CH₄ mixing (Sherwood Lollar et al., 2006). Experiments have shown that microbial CH₄ produced in high-pH fluids can develop high $\delta^{13}\text{C-CH}_4$ ‰ VPDB values (Miller et al., 2018), but the additional aforementioned lines of evidence employed at the field sites used in this study supports the interpretation that CH₄ in these localities is a mix of abiotic and microbial CH₄ (Sherwood Lollar et al., 2006; Onstott et al., 2006b; Etiope and Sherwood Lollar, 2013; Kietäväinen and Purkamo, 2015; Kietäväinen et al., 2017; Young et al., 2017), not microbial CH₄ formed at high pH.

Low bulk porosity and permeability in the Precambrian lithosphere means free fluids are constrained to fracture networks that are hydrogeologically isolated from one another, typically with increasing isolation with depth (Sherwood Lollar et al., 2014; Warr et al., 2018). Residence times for these fluids vary from a few thousand to millions of years (typically closer to the surface) (Lippmann et al., 2003; Lippmann-Pipke et al., 2011; Kietäväinen et al., 2014; Heard et al., 2018; Borgonie et al., 2019) to hundreds of millions or even more than a billion years at >2-3 km depth (Lippmann-Pipke et al., 2011; Holland et al., 2013; Warr et al., 2018).

Compartmentalized fracture networks in the subsurface of the Precambrian Shield can directly connect with each other via fracturing induced by large, regional-scale stress variations (Sleep and Zoback, 2007; Warr et al., 2018). These individual compartmentalized fracture networks may host distinct biogeochemical processes compared to proximal, but hydrogeologically separated fracture networks (Ward et al., 2004; Sherwood Lollar et al., 2006). When boreholes are drilled either from the surface or from mine shafts at depth, they intersect with multiple individual fluid-bearing fracture networks (Warr et al., 2018). The fluids flowing from these boreholes are therefore an integration of multiple individual fluid-bearing fractures.

1.1 Abiotic CH₄ on other planetary objects

CH₄ has been invoked to explain a variety of observed phenomena in the Solar System. CH₄ release from clathrate hydrates has been suggested as an explanation for how Mars' ancient climate could have sustained surface temperatures above the freezing point of water for geologically brief periods of time (Kite et al., 2017; Kite et al., 2020). Also, present-day detections of martian CH₄—in particular seasonally variable background levels in the order of 1

ppb volume, as well as short lived spikes about one order of magnitude larger than the background level—from telescopic (Mumma et al., 2009), rover (Webster et al., 2018), and orbital (Giuranna et al., 2019) observations are compatible with various subsurface sources, abiotic and possibly also biotic in origin. CH₄ has also been detected in the plumes of Enceladus, albeit in much smaller quantities than H₂ (Waite et al., 2006). Clathrate hydrates have thermally-insulating and convection inhibiting properties (Waite et al., 2007) and thus have been invoked to explain many observed planetary phenomena in further reaches of the Solar System. A thin, but continuously resupplied, CH₄ clathrate hydrate layer would provide sufficient thermal insulation to stabilize Pluto’s subsurface ocean given its thin crust (Kamata et al., 2019) and ≥ 35 vol % CH₄ clathrate hydrates in Ceres’ crust would stabilize deep brine reservoirs that explain recent cryovolcanic activity (Nathues et al., 2020), crustal strength observations (Castillo-Rogez et al., 2019), negative gravity anomalies (Raymond et al., 2020), spectroscopic evidence for recent or active surface brine emplacement (De Sanctis et al., 2020), and surface morphological expressions of recent surface/near-surface liquid (Schenk et al., 2020; Schmidt et al., 2020; Scully et al., 2020). CH₄ clathrate hydrates could similarly stabilize potential subsurface oceans on heat-deprived objects such as Triton, Callisto, and Ganymede (Sohl et al., 2010). Titan’s atmosphere contains $\sim 1.2 \times 10^{19}$ moles of CH₄, and noble gas data suggests an endogenous source for this CH₄ from the moon’s interior (Glein, 2015). These planetary studies generally all assume that CH₄ was generated via thermogenic decay of organic matter, hydrothermal alteration of ultramafic rock, and/or Fischer-Tropsch Type (FTT) reactions. Thus, quantification of low-temperature abiotic CH₄ production involving FTT reactions should be explored to assess the capability of these processes to explain the

aforementioned planetary phenomena. The results presented in this study provide a quantification for low-temperature abiotic CH₄ production in Earth's subsurface that may be appropriately scalable to other planetary objects.

1.2 Geologic setting

Witwatersrand Basin, South Africa: The Witwatersrand Basin hosts substantial economic deposits including gold, platinum, and diamonds. It lies within the Kaapvaal Craton, which formed between ~3.7-2.5 Ga (Robb and Meyer, 1995; Robb et al., 1997; Poujol et al., 2003) due to episodic tectonomagmatic processes. The oldest rocks in this craton, with ages >3.6 Gyr, are found in the Swaziland-Barberton areas (Poujol et al., 2003). The basin hosts the Vredefort impact structure, which is the oldest (2.023 ± 0.004 Ga; (Reimold and Gibson, 1996)) and perhaps largest (original rim diameter estimated to be 300 km; Therriault et al., 1997) known preserved impact structure on Earth and its formation caused significant uplift, thermal alteration (Ivanov, 2005), fracturing (Collins, 2014), and shock metamorphism (Reimold and Gibson, 1996) of the surrounding country rock. An estimated 5-11 km of vertical erosion has likely occurred since the Vredefort impact (McCarthy, 1990; Gibson and Wallmach, 1995; Stevens et al., 1997; Gibson and Reimold, 1999; Gibson, 2002). Some studies attribute the ore-forming hydrothermal activity in Witwatersrand Basin, and preservation of the basin itself, to the Vredefort impact event (Therriault et al., 1997), though this interpretation is controversial (Minter et al., 1993; Minter, 1999; Meier et al., 2009; Heinrich, 2015).

The Archean basement rocks in the Kaapvaal Craton consist of typical granite-greenstone lithologies, with tonalite-trondhjemite-granodiorite gneisses, mafic-to-ultramafic

volcanic sequences of both lithic clast-bearing tuffs and lava flows, and sediments associated with these source lithologies (Wilson and Adrian Versfeld, 1994; Robb et al., 1997). The Witwatersrand Basin itself formed between 3.074-2.714 Ga in multiple distinct episodes (Robb and Meyer, 1995) and is significantly less ultramafic-rich. The metasedimentary sequences in the basin (the Witwatersrand Supergroup) overly the mafic-volcanic Ventersdorp Supergroup, Archean granite-greenstone basement, and nearby Dominion volcano-sedimentary group, formed up to 3.074 Ga (Robb and Meyer, 1995). The schist, shale, and sedimentary quartzite of the Witwatersrand Supergroup metasediments consist of terrestrial and marginal submarine mudstones, sandstones, and a relatively low-volume amount of conglomeratic gold-bearing reefs. Most of the highest-grade gold ore occurs in organic-rich layers comprising relatively thin veins (so called “carbon leaders”), and mining activity focuses on following these veins, often to great depths, making the mines in Witwatersrand Basin among the deepest on Earth. From this geologic setting, data was used from Mponeng, Dreifontein, Kloof, Beatrix, Merrispruit, Masimong, and Evander Mines in this study. Details of the geologic settings for each individual site are provided in (Robb and Meyer, 1995; van Heerden, 1998; Onstott et al., 2006a; Dankert and Hein, 2010; Grové and Harris, 2010; Manzi et al., 2012; Manzi et al., 2013; Manzi et al., 2015; Frimmel, 2019).

Timmins, Ontario, Canada Kidd Creek Mine is situated 24 km from the city of Timmins, ON within a ~2.7 Ga Archean Volcanogenic Massive Sulfide (VMS) deposit (Thurston et al., 2008). It is within the Kidd-Munro assemblage of the Southern Volcanic Zone of the Abitibi greenstone belt in the Superior Province of the Canadian Shield (Bleeker and Parrish, 1996). The Kidd-

Munro assemblage is composed of steeply dipping interlayered felsic, mafic, ultramafic, and associated metasedimentary lithologies. The VMS deposit was likely formed where metal-rich hydrothermal fluids mixed with Archean seawater (Bleeker et al., 1997; Jamieson et al., 2013). Carbonaceous chert horizons exist within the Kidd-Munro assemblage, which were deposited during periods of low volcanic activity. The entire Kidd-Munro assemblage was metamorphosed to greenschist facies during the last major regional-scale metamorphic event at 2.67-2.69 Ga, with the last known metasomatism episode occurring at 2.64 Ga (Bleeker and Parrish, 1996; Thurston et al., 2008). The steeply dipping nature of the originally roughly horizontal VMS deposit necessitates mining this particularly high-quality ore deposit to depths > 3 km. Kidd Creek is the only sampling site from Timmins used in this study.

Thompson, Manitoba, Canada: The city of Thompson is located in the Thompson Nickel Belt in Manitoba, Canada, on the boundary between the Churchill and Superior provinces. This belt consists of interleaved granitic, mafic-to-ultramafic volcanic, and sedimentary sequences that have been metamorphosed up to granulite facies (Paktunc, 1984). The rocks in this area formed via deposition of Proterozoic Ospwagan sediments above the Superior Archean basement in a continental rift margin ~2.1-2.0 Ga, followed by formation of the Thompson Nappe during a deformation event ~1.9 Ga, and episodic tectonic deformation (Bleeker et al., 1990; White et al., 2000). Samples used in this study were collected from a set of two co-located mines, Birchtree and Thompson, both hosted within the Ospwagan pelitic sediments.

Outokumpu, Finland: The Outokumpu region of Finland hosts the Outokumpu rock complex, part of the Karelian Supracrustals that formed ~1.95-2.2 Ga (Park, 1988). This complex consists of granitic, carbonate, and mafic to ultramafic lithologies (Park, 1988; Loukola-Ruskeeniemi et al., 1991). Rock containing mica and graphite gneiss with black schist interlayers was formed during the Svecofennian orogeny 1.87-1.91 Ga (Juhava et al., 1989; Nironen, 1997). These rocks have been metamorphosed to amphibolite to granulite facies (Korsman et al., 1984). Much of the Ni and Cu produced in Finland is mined from an intrusive body consisting of peridotites, serpentized ultramafics, and quartz diorites that exists in this region. The Outokumpu and Juuka boreholes are the sampling sites from the Outokumpu rock complex that are used in this study. Enonkoski Mine, used as a sampling site in this study, is located in Svecokarelian region. The Ylivieska borehole, used as sampling site in this study, is located in a Svecofennian-aged layered sequence of serpentized ultramafics and gabbroic intrusions (Makkonen et al., 2008).

2.0 Methods

2.1 Groundwater and gas sampling methods

The Canadian and South African gas and fracture water samples were collected at borehole collars following the methods of Sherwood Lollar et al., (2002) and Ward et al., (2004). Briefly, a packer was inserted into the opening of each borehole, below the water level, and inflated to seal it against the inner rock walls, to isolate fluids from the atmosphere. Prior to sampling, the inflated packer apparatus was flushed with flowing gas and water to ensure representative fluids were sampled. A Tygon tube was attached to the end of the packer and gas/water flow from the borehole was then directed into a water-filled, submerged, inverted graduated beaker with a Luer attachment at the base pointing upwards. A rubber stopper was used to block the Luer attachment, allowing for gas to accumulate for collection. These gases were then extracted through the rubber stopper using a gas-tight syringe with a 22-g syringe needle. Gases were transferred from the syringe into pre-evacuated 160 mL borosilicate glass serum vials sealed with air-tight butyl blue rubber stoppers following the method of Oremland and Des Marais (1983). The vials were fixed with 100 µg of saturated HgCl₂ solution to prevent microbial activity post-sampling altering the gas composition and isotopic signatures. Previous studies using these sampling methods for gases in solution at depth have shown that exsolution of the hydrocarbon gases does not alter their composition and isotopic signatures (Sherwood Lollar et al., 1993b; Sherwood Lollar et al., 1994). Water flow rates were measured by placing the tube in a graduated beaker and using a stopwatch to measure the length of time required for 500 mL water to flow out. Gas flow rates were estimated by measuring the length of time required for a water-filled inverted graduated beaker to fill with gas.

The samples from boreholes in Finland were collected using the pressurized-downhole-sampling probes developed by Sherwood Lollar et al. (1994). In these collection vessels, the samples are kept at their *in-situ* pressure by sealing the fluid and its dissolved gases in clamped-off copper tubes or stainless steel vessels fitted with valves. Degassed and dissolved gas phases, along with their associated fluid, were quantitatively extracted by vacuum degassing during which their concentrations were measured in units of cc gas per kg fluid. This method of Sherwood Lollar et al., (1994), allows direct determination of the dissolved gas component, rather than the additional steps outlined in Section 2.3.

2.2 Compositional gas analysis

Compositional analyses of gas samples were performed at the Stable Isotope Laboratory at the University of Toronto. These methods are outlined in Ward et al. (2004) and Sherwood Lollar et al., (2006). A Varian 3400 Gas Chromatograph (GC) equipped with a flame ionization detector (FID) was used to measure concentrations of CH₄, C₂H₆, C₃H₈, and C₄H₁₀. Hydrocarbons were separated on a J&W Scientific GS-Q column (30 m × 0.32 mm ID) with He gas flow and temperature program: hold at 60 °C for 2.5 min, then increase to 120 °C at 5 °C/min intervals. A Varian 3800 GC with a micro-thermal conductivity detector (μTCD) and a Varian Molecular Sieve 5A PLOT column (25 m × 0.53 mm ID) were used to measure concentrations of inorganic gas components (H₂, He, Ar, O₂, CO₂, and N₂). The He gas flow rate while measuring concentrations of Ar, O₂, and N₂ was 3 mL/min and the temperature program was: hold 6 min at 30 °C, then increase to 80 °C at 15 °C/min intervals, then holding at 80 °C for 4 min. To measure CO₂ concentrations, the He gas flow rate was 50 mL/min and the temperature

program was: start at 60 °C, increase to 250 °C at 20 °C/min intervals, then hold at 250 °C for 6 min. To measure concentrations of H₂ and He, the Ar carrier gas flow rate was 2 mL/min and the temperature program was: hold for 10 min at 10 °C, then increase to 80 °C at 25 °C/min intervals, then hold at 80 °C for 7 min. Analyses were run in triplicate and mean values are reported in Tables 1-3. Reproducibility for triplicate analyses was $\pm 5\%$.

2.3 Determining dissolved gas concentrations

Mole fraction solubility constants for each gas, as well as the relative flow rates of water and total gas, were used to calculate the dissolved gas concentration for each chemical species from the measured gas volumes via the equation

$$D = \left(\frac{F_g \times g_v \times \epsilon \times K_{H,g}}{F_w} \right)$$

where D is the dissolved gas concentration, F_g is the gas flow rate, g_v is the measured gas volume, ϵ is the number of moles gas per liter at standard temperature and pressure (STP), $K_{H,g}$ is the mole fraction solubility constant for the chemical species in units of

$\frac{\text{moles dissolved gas}}{\text{moles free gas}}$ at STP, and F_w is the water flow rate. Mole fraction solubilities at STP for each

relevant chemical species at STP are $K_{H,H_2} = 1.411 \times 10^{-5}$ (Young, 1981), $K_{H,CH_4} =$

2.552×10^{-5} (Clever, 1987), $K_{H,He} = 6.997 \times 10^{-6}$ (Clever, 1979), $K_{H,C_2H_6} = 3.401 \times 10^{-5}$

(Hayduk, 1982), $K_{H,C_3H_8} = 2.732 \times 10^{-5}$ (Hayduk, 1986). ϵ is calculated as

$$\epsilon = \frac{P}{RT} \times 10^{-3}$$

where P is standard pressure (10^5 Pa), R is the ideal gas constant ($0.082 \frac{L \cdot atm}{mol \cdot K}$), and T is

standard temperature (298.15 K).

2.4 Isotopic analysis

Stable carbon and hydrogen isotopic analysis for CH₄ were performed at the University of Toronto Stable Isotope Laboratory following the methodology of Sherwood Lollar et al., (2006; 2007). $\delta^{13}C_{CH_4}$ was measured by continuous flow compound specific carbon isotope ratio mass spectrometry using a Finnigan MAT 252 mass spectrometer interfaced with a Varian 3400 capillary gas chromatograph (GC). Total error incorporating both accuracy and reproducibility is $\pm 0.5\%$ with respect to the IAEA international standard V-PDB. $\delta^2H_{CH_4}$ was measured using a continuous flow compound specific hydrogen isotope mass spectrometer consisting of a HP 6890 gas chromatograph (GC) interfaced with a micropyrolysis furnace on line with a Finnigan MAT Delta⁺-XL isotope ratio mass spectrometer. Total error incorporating both accuracy and reproducibility is $\pm 5\%$ with respect to V-SMOW.

2.5 Biogeochemical model

The biogeochemical model of Onstott et al., (2006b) is modified to model *in-situ* abiotic CH₄ production and is applied in a Bayesian framework to calculate the total and relative contributions of abiotic and microbial CH₄ sources in the sampled Canadian, South African, and Fennoscandian groundwaters. The Onstott et al., (2006b) study calculates the total dissolved CH₄ in the groundwaters as

$$CH_4^{total} = He_t \left(\frac{J_{CH_4}}{\theta \rho_w Z} + [P_{CH_4}] \right) \quad (1)$$

where CH_4^{total} is the dissolved concentration of CH_4 in the groundwater (M), ^{He}t is the He-derived residence time of the groundwater (years), J_{CH_4} is the CH_4 flux from a deeper source within the crust $\text{mol dm}^{-2} \text{ year}^{-1}$, θ is the porosity (unitless), ρ_w is the density of water (kg dm^{-3}), z is depth (dm), and $[P_{CH_4}]$ is the rate of methanogenesis (M year^{-1}), where all CH_4 is in the dissolved phase within the pore water. Equation (1) assumes a depth dependency for abiotic CH_4 concentration. ^{He}t is calculated as

$$^{He}t = \frac{[He]}{\frac{J_{He}}{\theta \rho_w z} + \gamma_{He} \frac{(1 - \theta) \rho_r}{\theta \rho_w} P_{He}} \quad (2)$$

where $[He]$ is the dissolved He concentration in the sampled groundwater, J_{He} is the flux of He from depth, γ_{He} is the fraction of He produced in the minerals that is released into the pore water, ρ_w is the density of rock, and P_{He} is the in situ production rate of He. Onstott et al., (2006b) use γ_{He} values from 0.6-100%. Other comparable studies that calculate ^{He}t also use $\gamma_{He} = 100\%$ (Lippmann et al., 2003; Holland et al., 2013; Warr et al., 2018; Heard et al 2018). We elect to use $\gamma_{He} = 100\%$ following these studies, which also gives residence times which are consistent with studies of other noble gases (Lippmann et al., 2003; Holland et al., 2013; Warr et al., 2018; Heard et al., 2018). In accordance with previous some noble gas approaches (Holland et al., 2013; Kietäväinen et al., 2014; Warr et al., 2018; Heard et al., 2018), this model considers each craton as a closed system, with no gas input from deeper crustal sources. This means that Equation 1 can be rewritten and total dissolved CH_4 in the groundwaters is calculated as

$$CH_4^{total} = ^{He}t(P_{CH_4A} + P_{CH_4B}) \quad (3)$$

where P_{CH_4A} is the rate of *in-situ* abiotic CH_4 production and P_{CH_4B} is the rate of *in-situ* methanogenesis, where all microbial and abiotic CH_4 is produced in dissolved phase within the pore water. Equation (3) assumes constant production rates for abiotic and microbial CH_4 over time. Because our model considers the cratons as closed systems, $J_{He} = 0$ in Equation 2 and thus *in-situ* helium accumulation occurs simply as a function of time. All the input parameter values for the biogeochemical model used in this study are shown in Table 1.

The Onstott et al., (2006b) model uses values of $\delta^2H_{CH_4}$ and $\delta^{13}C_{CH_4}$ to differentiate between abiotic and microbial CH_4 . Within individual sites, the trend in these isotopes is typically consistent with the trend of microbial and abiotic CH_4 mixing (Sherwood Lollar et al., 2006). It is on the scale of individual sites within Witwatersrand Basin that the Onstott et al., (2006b) model uses these isotopic values to assess microbial versus abiotic CH_4 contributions, and thus this is a viable metric for the estimation. To perform this estimation, Onstott et al., (2006b) use the following expressions:

$$\delta^2H_{CH_4} = \frac{He_t \left(\delta^2H_{CH_4A} \times \frac{J_{CH_4}}{\theta \rho_w Z} + \delta^2H_{CH_4B} \times P_{CH_4} \right)}{CH_4^{total}} \quad (4)$$

$$\delta^{13}C_{CH_4} = \frac{He_t \left(\delta^{13}C_{CH_4A} \times \frac{J_{CH_4}}{\theta \rho_w Z} + \delta^{13}C_{CH_4B} \times P_{CH_4} \right)}{CH_4^{total}} \quad (5)$$

where $\delta^2H_{CH_4A}$ and $\delta^{13}C_{CH_4A}$ are the abiotic isotopic endmember and $\delta^2H_{CH_4B}$ and $\delta^{13}C_{CH_4B}$ are the microbial isotopic endmembers for hydrogen and carbon respectively. Onstott et al., (2006b) use values of $\delta^2H_{CH_4A} = -360$ and $\delta^2H_{CH_4B} = -220$, and $\delta^{13}C_{CH_4A} = -30$

and $\delta^{13}C_{CH_4B} = -65$. As the model presented in this study considers these groundwaters to be closed systems in terms of gas production, these equations are revised to

$$\delta^2H_{CH_4} = \frac{He_t(\delta^2H_{CH_4A} \times P_{CH_4A} + \delta^2H_{CH_4B} \times P_{CH_4B})}{CH_4^{total}} \quad (6)$$

and

$$\delta^{13}C_{CH_4} = \frac{He_t(\delta^{13}C_{CH_4A} \times P_{CH_4A} + \delta^{13}C_{CH_4B} \times P_{CH_4B})}{CH_4^{total}} \quad (7)$$

All gas production variables are in units of moles $L^{-1} year^{-1}$, meaning these values represent production in fluids within pore/fracture space. These can be converted to units of moles $m^{-3} rock year^{-1}$, by multiplying by $\left(\frac{1-\theta}{\theta}\right) \frac{\rho_r}{\rho_w}$. We assume that $\rho_w = 1000 \text{ kg } m^{-3}$, $\rho_r = 2670 \text{ kg } m^{-3}$, and $\theta = 1\%$, which are values consistent with past studies (Stober, 1997; Aquilina et al., 2004; Onstott et al., 2006b; Stober and Bucher, 2007; Bucher and Stober, 2010; Sherwood Lollar et al., 2014; Warr et al., 2019). A Markov Chain Monte Carlo approach is applied to iteratively solve for 6 unknown parameter values ($\delta^2H_{CH_4A}$, $\delta^2H_{CH_4B}$, $\delta^{13}C_{CH_4A}$, $\delta^{13}C_{CH_4B}$, P_{CH_4A} , and P_{CH_4B}) using 3 equations (equations 3, 6, and 7), data from each groundwater sample (dissolved He concentration, dissolved CH_4 concentration, $\delta^2H_{CH_4}$, and $\delta^{13}C_{CH_4}$), and radionuclide concentrations measured in host rock from each site (Table 1). This allows for a robust assessment of the uncertainty when computing unknown parameter values. The model is fit separately to data from Canadian Shield, Witwatersrand Basin, and the Fennoscandian Shield to determine if there are differences in the abiotic CH_4 production rates between these different regions of Earth's subsurface. This process allows for quantitative determination of

the statistical significance of variations in abiotic and microbial CH₄ production rates between different cratons.

The modeled abiotic-microbial CH₄ mixing ratios are cross-validated by verifying that model results are consistent with studies of each individual target site employing multiple lines of evidence to determine abiotic and microbial CH₄ mixing ratios (Sherwood Lollar et al., 1993b; Sherwood Lollar et al., 1993a; Sherwood Lollar et al., 2002; Ward et al., 2004; Sherwood Lollar et al., 2006; Onstott et al., 2006a; Sherwood Lollar et al., 2008; Kietäväinen and Purkamo, 2015; Simkus et al., 2016; Kietäväinen et al., 2017; Young et al., 2017; Telling et al., 2018). The model is only applied to sites that have previously been suggested to contain simple abiotic-microbial CH₄ mixing, without additional complicating factors such as thermogenic CH₄ production, based on multiple independent lines of evidence.

2.6 Calculation of P_{He}

The radiolytic He production model described in (Lin et al., 2005a; Lin et al., 2005b; Tarnas et al., 2018; Warr et al., 2019) is used to calculate P_{He} . This calculates radiogenic dose rate as

$$E_{net,i} = \frac{E_i \times W \times S_i}{1 + W \times S_i} \quad (8)$$

where i is α , β , or γ radiation, E_{net} is the net dosage absorbed by pore water (eV kg⁻¹ s⁻¹), E is the apparent dosage from radioactive element decay (eV kg⁻¹ s⁻¹), W is the weight ratio of pore water to rock, and S is the stopping power of minerals within the rock matrix with respect to each type of radiation particle/ray, where $S_\alpha = 1.5$, $S_\beta = 1.25$, $S_\gamma = 1.14$ (Lin et al., 2005a; Lin

et al., 2005b; Tarnas et al., 2018; Warr et al., 2019). The stopping power of minerals is estimated using Bragg's law (Bragg and Kleeman, 1905) and for silicate minerals typically varies by <0.5 (Nogami and Hurley, 1948).

W , the weight ratio of pore water to rock, primarily depends on rock matrix porosity. Values from Adamiec & Aitken (1998) are used for E for 1 wt. % K, 1 ppm Th, and 1 ppm U for α , β , and γ radiation, which are $E_{K,\alpha} = 0$ (Gy ka⁻¹), $E_{K,\beta} = 0.782$ (Gy ka⁻¹), $E_{K,\gamma} = 0.243$ (Gy ka⁻¹), $E_{Th,\alpha} = 0.061$ (Gy ka⁻¹), $E_{Th,\beta} = 0.027$ (Gy ka⁻¹), $E_{Th,\gamma} = 0.048$ (Gy ka⁻¹), $E_{U,\alpha} = 0.218$ (Gy ka⁻¹), $E_{U,\beta} = 0.146$ (Gy ka⁻¹), $E_{U,\gamma} = 0.113$ (Gy ka⁻¹). 1 Gy = 6.2415 × 10¹⁸ eV kg⁻¹. He production is calculated as

$$P_{He} = \sum \frac{E_{net,\alpha}}{W \times c^2 \times M \times \rho_w} \quad (9)$$

where $E_{net,\alpha}$ is the net radiogenic alpha dose, c is the speed of light, M is the molar mass of He, and ρ_w is the density of water. The radionuclide concentrations for each sampled rock unit, and associated calculated P_{He} values used in the biogeochemical model, are displayed in Table 1.

2.7 Markov Chain Monte Carlo approach

The biogeochemical model employs a MATLAB implementation of the Goodman and Weare Markov chain Monte Carlo (GWMCMC) (Goodman and Weare, 2010) written by Aslak Grinsted (<https://github.com/grinsted/gwmcmc>). Broadly, MCMC methods utilize walkers to probabilistically explore multidimensional parameter spaces and converge on optimal solutions that achieve the best fit to a given dataset via an applied forward model. Through this, the MCMC process defines the best fit values for all free parameters in the forward model, as well as the range of possible functional values for these free parameters. This process avoids biasing

model results via the arbitrary and subjective selection of endmembers without quantitative exploration of all possible permutations of model parameter combinations. The GWMCMC method also improves upon the classic MCMC approach, which requires specific attunement of variables such as walker step-size, by implementing an affine invariant approach (Goodman and Weare, 2010). Goodman and Weare (2010) provide a detailed description of the benefits of an affine invariant approach.

The ranges for each free parameter estimated via the MCMC are $-500 < \delta^2 H_{CH_4A} < -150$, $-500 < \delta^2 H_{CH_4B} < -150$, $-75 < \delta^{13} C_{CH_4A} < -15$, $-75 < \delta^{13} C_{CH_4B} < -15$, 10^{-17} moles dm^{-3} year $^{-1}$ $< P_{CH_4A} < 10^{-5}$ moles dm^{-3} year $^{-1}$. This range of values encompasses the parameter values from Onstott et al., (2006b), but also provides the MCMC flexibility in selecting values for these free parameters, since none of the true values are definitively known. The MCMC is applied separately to the datasets from the Canadian Shield, Witwatersrand Basin, and the Fennoscandian Shield. The average abiotic CH₄ production rate is modeled for each craton, meaning that, for example, there is a single average abiotic CH₄ production rate value for Witwatersrand Basin rather than different abiotic CH₄ production values for each individual site within Witwatersrand Basin (Masimong, Beatrix, Kloof, etc...). This allows the model to extract information regarding large-scale similarities and differences between abiotic CH₄ production processes between cratons. The MCMC results show that for each individual craton there are statistically significant variations in isotopic endmember values that achieve the best fit via the forward model to the dissolved gas concentration and isotopic datasets (Fig. 4). The results also demonstrate that the average abiotic CH₄ production rate is approximately two orders of

magnitude lower in Witwatersrand Basin compared to the Canadian and Fennoscandian Shields (Fig. 5).

Equation 3 is solved to determine the microbial CH₄ production rate for each site by using difference between the estimated abiotic CH₄ contribution and the total measured CH₄ concentration. This analysis reveals the relationship between microbial CH₄ production rates and depth, variations in microbial CH₄ production rates from measurements within the same mines/boreholes, as well as variations in the relative contribution of abiotic versus microbial CH₄ at each site.

2.8 Model sensitivities and key assumptions

Sensitivities and key assumptions of the model employed in this study are discussed and justified below.

1) The model relies solely on $\delta^2\text{H-CH}_4$ ‰ VSMOW and $\delta^{13}\text{C-CH}_4$ ‰ VPDB values to distinguish the relative contribution of abiotic versus microbial CH₄ for each site. These stable isotopes have been demonstrated to effectively distinguish between abiotic versus microbial CH₄ at *individual* sites if supported by additional lines of evidence including isotopic characterization of DIC and H₂O isotopes, gas compositional ratios, and in some cases clumped isotopologue signatures (Etiope and Sherwood Lollar 2013 and references therein). Such abiotic-microbial CH₄ mixing lines have been used by previous studies (Ward et al., 2004; Sherwood Lollar et al., 2006; Onstott et al., 2006b) and where they show good agreement with other mixing assessment methods, such as CH₄/C₂+ versus $\delta^{13}\text{C-CH}_4$ ‰ VPDB (Sherwood Lollar et

al., 2006) and clumped isotopes (Young et al., 2017), can be used as a functional approximation for quantification of microbial-abiotic CH₄ mixing.

2) The model is sensitive to the calculated P_{He} (He production rate) value, which is primarily a function of the radionuclide content of the rock unit in which a borehole was drilled. The measured radionuclide concentrations for the rock units in which each of the individual boreholes were drilled were used to calculate P_{He} , meaning this parameter is more representative of the specific properties of each site. If radionuclide concentration measurements did not exist for the host rock units of a specific borehole, as was the case for Ylivieska, Juuka, and Enonkoski, we assume that the radionuclide concentration is the same as proximal and similar rock units within that craton. This is different from the modeling method previously employed by Onstott et al., (2006b), where the He production rate, and therefore the radionuclide content of all sampled rock units, was assumed to be the same for each borehole. The mean residence time estimates derived from the He production rate and measured He concentration are also consistent with mean residence times calculated for many of the sampled sites by more intensive noble gas studies (Lippmann et al., 2003; Holland et al., 2013; Kietäväinen et al., 2014; Warr et al., 2018; Heard et al., 2018).

3) Anaerobic oxidation of CH₄ is assumed to not change its isotopic values. Anaerobic CH₄ oxidation negligibly affects $\delta^{13}C\text{-CH}_4$ ‰ VPDB and $\delta^2H\text{-CH}_4$ ‰ VSMOW values for CH₄, particularly if sulfate concentrations are less than 0.5 mM (Yoshinaga et al., 2014), which is the case for the majority of our sample sites (Onstott et al., 2006a; Kietäväinen et al., 2013; Li et al., 2016). Whiticar, (1999) demonstrated that more than ~80% of CH₄ must be oxidized to impart a

significant shift in $\delta^{13}\text{C}\text{-CH}_4$ ‰ VPDB. Therefore, anaerobic CH_4 oxidation is not expected to significantly affect the results presented here.

4) The model assumes that abiotic CH_4 is produced in-situ and does not come from a deeper crustal or mantle source. A mantle source is ruled out by noble gas evidence (Sherwood Lollar et al., 1993; Lippmann et al., 2003; Holland et al., 2013; Kietavainen et al., 2014; Warr et al., 2018). Many past noble gas studies also consider these cratonic subsurface environments as closed systems of gas production (Holland et al., 2013; Kietäväinen et al., 2014; Warr et al., 2018; Heard et al., 2018), which is the approach followed in the model presented here. Additionally, because of previous correlations between abiotic versus microbial CH_4 production and lithology (Ward et al., 2004), it is reasonable to assume that abiotic CH_4 forms in-situ, otherwise lithology could not be impactful.

2.9 Empirical effects of dataset

Datasets from Witwatersrand Basin, the Canadian Shield, and the Fennoscandian Shield used in this study possess very different depth distributions. 5/5 of the Fennoscandian Shield measurements are from depths <1 km, while 16/16 of the Canadian Shield measurements are from depths >1 km, and 13/16 of them are from Kidd Creek. The Witwatersrand Basin data sample depths from ~0.8-3.5 km with a relatively even distribution of datapoints with respect to depth. Still, only 5/36 of the samples from Witwatersrand Basin are from depth <1 km, all of which were collected in Beatrix Mine. 100% of the datapoints from depths >2.5 km are from Witwatersrand Basin sites, while the deepest Canadian Shield samples were collected at 2.4 km depth. The empirical effects induced via application of the biogeochemical model to

inconsistently distributed datasets will certainly affect the results presented here and the interpretations for each region derived from those results. Therefore, it is acknowledged that many of the controls on microbial-versus-abiotic CH₄ formation discussed here may result from the depth distribution of the samples used in this study.

It is likely that lower measured He concentrations and heightened microbial CH₄ production rates at the Fennoscandian Shield sample sites is simply due to their shallower depths relative to the majority of Canadian Shield and Witwatersrand Basin sample sites (Figs. 5c, 8). The increased prevalence of younger fluids at shallower depths is reflected in the lower He concentrations at these shallower depths (Fig. 9). However, Ylivieska and Enonkoski groundwaters do not appear to be meteoric (Fig. 6). Regardless, the sampling of the Fennoscandian Shield used here is heavily biased by the lack of measurements at depths >1 km, while the sampling of the Canadian Shield and Witwatersrand Basin is likely biased by the relative paucity of measurements at depths <1 km. Sampling of Fennoscandian Shield groundwaters at depths >1 km may provide valuable insight regarding the diversity of groundwater geochemistry at depths >1 km and could potentially help constrain the underlying processes that control gas production in Earth's subsurface.

3. Results

3.1 Variations in abiotic CH₄ production rates between cratons

Results from the MCMC application of the biogeochemical model are summarized in Table 3. Average rates of abiotic CH₄ production are found to vary between Witwatersrand Basin versus the Canadian and Fennoscandian Shields (Fig. 5), with the Canadian and Fennoscandian Shields having the highest rates ($\sim 1.7\text{--}1.8 \times 10^{-9} \text{ M year}^{-1}$), and Witwatersrand Basin having two orders of magnitude lower a rate ($\sim 1.9 \times 10^{-11} \text{ M year}^{-1}$). The 2σ uncertainty around the best fit value for the Fennoscandian Shield abiotic CH₄ production rate estimate is $\sim 8.7 \times 10^{-10} \text{ M year}^{-1}$. The 2σ uncertainty for the Canadian Shield abiotic CH₄ production rate estimate is $\sim 1.1 \times 10^{-9} \text{ M year}^{-1}$. The 2σ uncertainty for the Witwatersrand Basin abiotic CH₄ production estimate value distribution is $\sim 8.0 \times 10^{-12} \text{ M year}^{-1}$.

It is notable that the abiotic CH₄ production rate for the Canadian Shield somewhat deviates from a true Gaussian distribution due to the existence of a smaller (<10% the probability density of the best fit peak) probability density distribution value maximum for this parameter in the MCMC (Fig. 5a). This is possibly due to differences in abiotic CH₄ production rates between Thompson, Ontario and Timmins, Ontario, which represent different parts of the Canadian Shield in terms of lithology, formation age, and hydrogeologic properties. The significantly higher (>1000% higher) probability density of the larger peak provides sufficient justification for using this value as a best estimate for the average abiotic CH₄ production rate in the Canadian Precambrian lithosphere.

3.2 Comparison to analysis of individual sites

The results of the global estimates for abiotic and microbial CH₄ production rates at each individual site, as well as abiotic and microbial CH₄ ratios, can be compared to the results for each region and site individually, as shown in Fig. 5. These are now reviewed:

3.2.1 Canadian Shield

The results presented here largely agree with independent studies of the Canadian Shield sample sites Kidd Creek Mine, Birchtree Mine, and Thompson Mine. Kidd Creek CH₄ is known to be predominantly abiotic based on CH₄/C₂+ versus $\delta^{13}C_{CH_4}$, $\delta^{13}C_{CH_4}$ versus $\delta^2H_{CH_4}$ for C₁-C₄ hydrocarbons, and clumped isotope measurements (Sherwood Lollar et al., 1993c; Sherwood Lollar et al., 2006; Young et al., 2017; Warr et al. 2020). 13/16 of the samples from the Canadian Shield used in this study are from Kidd Creek Mine, therefore the properties of this site majorly impact the overall Canadian Shield results in terms of estimated abiotic CH₄ production rates, and the agreement of abiotic-microbial CH₄ mixing ratios with the findings of previous studies. The results for Kidd Creek agree with past studies indicating a largely abiotic origin for the CH₄, with differing microbial CH₄ mixing contributions varying between ~4-30%, with one outlier sample having a ~50% microbial CH₄ component (Fig. 5b) (Sherwood Lollar et al., 1993c; Sherwood Lollar et al., 2006; Young et al., 2017; Warr et al. 2020). The single Birchtree Mine groundwater sample with a previously characterized microbial-abiotic CH₄ mixing ratio showed predominantly microbial CH₄ (Young et al., 2017). However, that sample was derived from a different borehole, with different hydrogeologic properties, than the Birchtree Mine sample used in this study. Based on model results presented here, the Birchtree Mine sample used in this study has a ~50% microbial CH₄ contribution (Fig. 5b). The Thompson

Mine samples used in this study do not have previously characterized microbial-abiotic CH₄ mixing ratios, but Telling et al., 2018 do detect methanogenic activity in one of the Thompson samples used here, in addition to other H₂-utilizing metabolisms. The model results presented here estimate that the CH₄ in these Thompson samples is likely purely abiotic in origin (Fig. 5b), but it is acknowledged that increased uncertainty in the water and gas flow rates for these samples, compared to others used in this study, may induce uncertainties in the model results.

3.2.1.1 Kidd Creek, Canada

Overall, the very high abiotic versus microbial CH₄ production ratio estimates for Kidd Creek agree well with past studies of these fluids (Fig. 5b). Differences in mixing ratios between microbial and abiotic CH₄ gases have previously been reported in Kidd Creek samples (Sherwood Lollar et al., 2002; Sherwood Lollar et al., 2006). While methanogens have been cultivated from Kidd Creek fluids (Doig et al., 1995), evidence from stable isotopes (Sherwood Lollar et al., 1993c), CH₄/C₂+ distributions (Sherwood Lollar et al., 2006), $\delta^{13}\text{C-CH}_4$ ‰ VPDB and $\delta^2\text{H-CH}_4$ ‰ VSMOW values for C₁-C₄ hydrocarbons (Sherwood Lollar et al., 2006), and clumped isotope analysis of CH₄ (Young et al., 2017; Warr et al., 2020) indicate that the CH₄ in these fluids is formed dominantly through abiotic processes. After borehole 6070 was drilled, microbial CH₄ gradually increased in that borehole by 10-25% of the total gas content (Sherwood Lollar et al., 2002; Sherwood Lollar et al., 2008; Warr et al., 2020), perhaps as methanogenic microorganisms adapted to inhabit it (Young et al., 2017). This process is consistent with the variability in abiotic versus microbial CH₄ production rate ratios shown in the results of the present study (Fig. 5b, 5c). The variability could also be due to draining of

groundwater predominantly from different intersected fracture networks into the borehole over time –where some of these fracture networks contained more microbial CH₄ than others.

The model results estimate a non-negligible microbial CH₄ contribution to all the measured Kidd Creek samples (Fig. 5c). It was acknowledged by Sherwood Lollar et al. (2006) that even the most abiotic endmember for Kidd Creek CH₄ could contain a minor contribution of microbial CH₄. This conclusion is therefore supported by the results presented here, which show that microbial methanogenesis likely occurred in these fluids at some point during their ~10⁸-10⁹ year residence times (Holland et al., 2013; Warr et al., 2018).

3.2.1.2 Birchtree, Canada

Previously analyzed samples from a separate borehole at the Birchtree Mine have indicated a predominance of microbial CH₄ (Young et al., 2017). The findings presented here show that while the Birchtree Mine sample is predominantly microbial, it contains a substantial amount of abiotic CH₄ (Fig. 5b). However, the sample used in this study is from a different borehole with substantially different hydrogeological properties compared to the borehole in Young et al., 2017, as it was the only sampled borehole with a steady water flow, which is required to calculate the dissolved gas concentrations in these waters.

3.2.1.3 Thompson, Canada

Samples from the Thompson Mine used in this study are estimated to have little to no CH₄ contribution from microbial sources (Fig. 5b, 5c). This is in contrast with the results of (Telling et al., 2018), who find evidence for methanogenic activity in one of the Thompson Mine

samples used in this study. It is noted that there is lower confidence in the water and gas flow rate measurements for these two samples, so it is possible that this uncertainty affected the model results for this specific site. There is also the possibility of some microbial CH₄ production in these groundwater samples within the 1 σ and 2 σ uncertainties in the model estimates (Fig. 5b-c, Fig. S6).

3.2.2 Witwatersrand Basin, South Africa

Previous studies of Witwatersrand Basin's subsurface have demonstrated a notable diversity in the abiotic-microbial CH₄ mixing ratios between different sample sites, with the Mponeng and Kloof Mines containing predominantly abiotic CH₄, and the Beatrix, Evander, Driefontein, Merriespruit, and Masimong Mines containing predominantly microbial CH₄ (Ward et al., 2004; Sherwood Lollar et al., 2006; Onstott et al., 2006b; Young et al., 2017). The results presented here are consistent with these past studies, and even replicate known variations in microbial-abiotic CH₄ mixing within individual mines, for example Driefontein, which is known to contain some samples with particularly high concentrations of microbial CH₄ (Sherwood Lollar et al., 2006) (Fig. 5b). As Witwatersrand Basin is the largest and most diverse regional sample set used in this study (Fig. 1), the agreement between the model results for Witwatersrand Basin and the results from multiple studies of these individual sites using independent methods confirms the accuracy of the modeling approach implemented here.

3.2.2.1 Beatrix, South Africa

Previous investigations have demonstrated that CH₄ in the Beatrix Mine groundwaters is predominantly of microbial origin (Ward et al., 2004; Sherwood Lollar et al., 2006; Young et al., 2017) produced from a radiocarbon dead dissolved inorganic carbon source over geologic timescales (Slater et al., 2006). The results presented here support that CH₄ in Beatrix Mine groundwaters is predominantly microbial (Fig. 5b). The model results show that microbial CH₄ production in groundwaters from Beatrix boreholes drilled into the Upper Witwatersrand Formation is substantially higher than in groundwaters from boreholes drilled into the Lower Witwatersrand Formation (Fig. 5c). This may be because the Upper Witwatersrand Formation has higher radionuclide content, and therefore is likely to produce more H₂ via radiolysis, which can then reduce CO₂ to form CH₄. It is also possible that shallower groundwaters sampled by boreholes in Beatrix Mine are less saline, and therefore methanogens have less of an energetic barrier to activity. Beatrix groundwaters with enhanced microbial CH₄ production have $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ values that fall close to the paleometeoric water line (Fig. 6), and there appears to be no significant isotopic difference between groundwaters with microbial CH₄ production rates $>10^{-8} \text{ M year}^{-1}$ compared to those with microbial CH₄ production rates $<10^{-8} \text{ M year}^{-1}$ (Fig. 6b). This therefore favors a lithologic control on the microbial CH₄ production rate in sampled Beatrix Mine groundwaters—whereby the H₂ production rate dictated by variations in host-rock radionuclide concentrations dominates microbial CH₄ production rates—rather than a hydrologic control.

Estimates for microbial CH₄ production rates in groundwaters sampled by boreholes in Beatrix Mine from this study mostly agree with those of Onstott et al., (2006b). However, the results presented here also show that estimated microbial CH₄ production rates are ~1-2 orders

of magnitude higher in two Beatrix Mine samples compared to the rates reported in Onstott et al., (2006b) (Fig. 5c).

3.2.2.2 Masimong and Merriespruit, South Africa

Previous investigations have demonstrated that CH₄ in Masimong Mine and Merriespruit Mine groundwaters is predominantly of microbial origin (Ward et al., 2004; Sherwood Lollar et al., 2006; Young et al., 2017), and Ward et al. (2004) and Sherwood Lollar et al. (2006) have even used these sample as microbial CH₄ endmembers in their abiotic and microbial CH₄ mixing estimations based primarily on the highly elevated CH₄/C₂+ ratios (~10³)

3.2.2.3 Driefontein, South Africa

Driefontein Mine contains the second widest range of abiotic versus microbial CH₄ ratios of any of the sample sites used in this study, in that all samples have a substantial (>65%) microbial CH₄ contribution, but one sample in particular (DR938 H3 071202) is ~100% microbial CH₄ and shows the highest microbial CH₄ production rate estimated for depths >1 km (Fig. 5c). This agrees with the findings of Sherwood Lollar et al. (2006), who report one Driefontein Mine sample to be very similar in its $\delta^{13}\text{C-CH}_4$ ‰ VPDB and CH₄/C₂+ values to Masimong and Merriespruit Mines, which are used as microbial endmembers. The Driefontein sample found by Sherwood Lollar et al. (2006) to be dominated by microbial CH₄ is different from the estimated ~100% microbial CH₄ sample from the present study, and the sample they used did not have measured gas and water flow rates required for the model used here. Despite the notably high microbial CH₄ production rate estimates and overall contribution to total CH₄ in

one Driefontein sample, no methanogens were found here via 16S rRNA gene amplification (Sherwood Lollar et al., 2006). It is possible that methanogens once inhabited this groundwater, but no longer survive there. As pointed out by Sherwood Lollar et al. (2006), the wide variability in microbial CH₄ production rates at Driefontein Mine (Fig. 5b, 5c) highlights the heterogeneity and isolation of physically proximal fracture networks in Earth's deep subsurface. It is possible that the particularly enhanced microbial CH₄ production rate in one Driefontein sample used here is tied to hydrological variations induced by the nearby presence of the Spotted Dick Dyke, which could allow for enhanced infiltration of meteoric water. Simkus et al., (2016) similarly reported that enhanced microbial CH₄ production in a Tau Tona Mine sample was tied to enhanced paleometeoric water infiltration through a nearby dyke. The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ values of the Driefontein groundwater sample with enhanced microbial CH₄ production lies between isotopic values of Driefontein groundwaters near the paleometeoric water line and a Driefontein groundwater sample with highly depleted isotopic values (Fig. 6b, 6c). Mixing between a deeper, H₂-rich, saline fluid and moderately saline paleometeoric water could be causing enhanced methanogenic activity, as was proposed by (Sherwood Lollar et al., 2007) for Witwatersrand Basin.

3.2.2.4 Mponeng, South Africa

Mponeng is considered to be one of the most abiotic CH₄-dominated sample sites in Witwatersrand Basin (Sherwood Lollar et al., 2006), which might be attributed to the mafic Ventersdorp Supergroup lithologies into which boreholes were drilled (Ward et al., 2004). Sulfate-reducing bacteria dominate the groundwaters sampled in Mponeng Mine (Lin et al.,

2006b; Chivian et al., 2008; Labonté et al., 2015). The results presented here agree with past studies, finding CH₄ at Mponeng to be predominantly abiotic (Fig. 5b).

3.2.2.5 Kloof, South Africa

The results from this study are consistent with past work that indicates Kloof Mine is dominated by abiotic CH₄ rather than microbial CH₄ (Ward et al., 2004; Sherwood Lollar et al., 2006) (Fig. 5b). However, this model estimates that the microbial CH₄ contribution at Kloof Mine is slightly higher than these past studies. This is because the global context provided by the approach here allows identification of a modest microbial CH₄ component in the most abiotic CH₄ endmember used in the earlier studies of Witwatersrand Basin by Ward et al (2004) and Sherwood Lollar et al. (2006).

16 rRNA gene amplifications have not revealed the extant presence of methanogens at this site (Ward et al., 2004; Kieft et al., 2005), but this does not preclude the past existence of methanogens over the $\sim 10^6$ - 10^8 year mean residence times of these fluids (Lippmann et al., 2003), the existence of methanogens at low biomasses, nor biovariability between fracture networks at this locality.

Ward et al. (2004) found that the most saline and isotopically enriched ($\delta^{18}\text{O-H}_2\text{O}$ and $\delta^2\text{H-H}_2\text{O}$ ‰ VSMOW) water at Kloof Mine also contained the most enriched $\delta^{13}\text{C-CH}_4$ ‰ VPDB. According to Ward et al. (2004), the most microbial CH₄ dominated Kloof sample has $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^2\text{H-CH}_4$ ‰ VSMOW isotopic values closest to meteoric water line, while the other samples lie in between (Ward et al., 2004). They argue that this indicates that mixing between deep, saline fluids and meteoric water might control the prevalence of methanogenesis at this site.

This is inconsistent with the results presented in the present study, where the Kloof groundwater with the highest ratio of microbial CH₄ has intermediate $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^2\text{H-CH}_4$ ‰ VSMOW isotopic values compared to other Kloof groundwaters (Fig. 6c). This indicates that microbial CH₄ production might actually be enhanced by fluid mixing, rather than simply being predominant in paleometeoric waters.

3.2.2.6 Evander, South Africa

Ward et al. (2004) found that the most saline and isotopically enriched ($\delta^{18}\text{O-H}_2\text{O}$ and $\delta^2\text{H-H}_2\text{O}$ ‰ VSMOW) at Evander Mine also contained the most enriched $\delta^{13}\text{C-CH}_4$ ‰ VPDB. The most microbial CH₄ dominated Evander sample has $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^2\text{H-CH}_4$ ‰ VSMOW isotopic values closest to meteoric water line, while the other samples lie in between (Ward et al., 2004). They argue that this indicates that mixing between deep, saline hydrothermal fluids and meteoric water might control the prevalence of methanogenesis at this site. The results presented here show variability in microbial versus abiotic CH₄ ratios in Evander samples similar to that reported by Ward et al., (2004) (Fig. 5b), but find that the most microbial CH₄-dominated samples are isotopically between the most paleometeoric water and most isotopically depleted water in Evander in terms of $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^2\text{H-H}_2\text{O}$ ‰ VSMOW (Fig. 6c). This is similar to findings presented here for Kloof and Driefontein Mines.

3.2.3 Fennoscandian Shield

Previous investigations have shown that CH₄ in Enonkoski Mine and the Ylivieska borehole is predominantly microbial, while CH₄ in the Juuka borehole and the Outokumpu

borehole sample used in this study is predominantly abiotic (Sherwood Lollar et al., 1993b; Sherwood Lollar et al., 1993a; Kietäväinen and Purkamo, 2015). The results presented here notably agree with these past studies, as the two Enonkoski samples and one Ylivieska sample are estimated to contain >~80% microbial CH₄, while the Juuka and Outokumpu samples used in this study are found to contain ~0% microbial CH₄. The present model therefore accurately reaches the same conclusions for these individual sites as are found by multiple independent lines of evidence from previous studies.

3.2.3.1 Enonkoski, Finland

Microbially-generated CH₄ has been found by multiple studies to be dominant in Enonkoski Mine groundwaters (Burruss, 1993; Sherwood Lollar et al., 1993a). The results presented here confirm these results (Fig. 5b, 5c). Enonkoski notably has the most depleted ¹³C isotopic values of any of samples used in this study (Fig. 3). Sherwood Lollar et al. (1993a) find that CH₄ at Enonkoski cannot be entirely microbial, stating that a 6-25% abiotic shield gas endmember likely contributes to generate the variable CH₄/C₂₊ ratio at this site. This is consistent with the results presented here, where microbial CH₄ represents 80% and 90% of the total CH₄ in the two Enonkoski samples used in this study, with the other 20% and 10%, respectively, being abiotic CH₄ (Fig. 5b).

3.2.3.2 Ylivieska, Finland

Previous work has estimated the CH₄ in Ylivieska borehole groundwater to be 30-50% microbial in origin (Sherwood Lollar et al., 1993a). The results presented here estimate that the

CH₄ in the Ylivieska borehole groundwater sample is ~88% microbial in origin (Fig. 5b), which disagrees with this previous work. However, it is possible that microbial CH₄ was present in the abiotic endmember selected by Sherwood Lollar et al., (1993), which would explain this discrepancy.

3.2.3.3 Juuka and Outokumpu, Finland

A predominantly abiotic origin has been suggested for CH₄ in groundwaters sampled by the Juuka and Outokumpu boreholes (Sherwood Lollar et al., 1993b). The similarity in isotopic composition of CH₄ measured >25 years ago (Sherwood Lollar et al., 1993b) and CH₄ measured recently (Kietäväinen et al., 2018) at both Outokumpu and Juuka boreholes show that the source for CH₄ has likely remained constant over this time period. The $\delta^2\text{H-CH}_4$ ‰ VSMOW value for Outokumpu and Juuka is significantly more enriched than other sites dominated by abiotic CH₄ (Fig. 5b, 5c). This may be due to the existence of a distinct abiotic CH₄ isotopic endmember at these sites, which was proposed by (Sherwood Lollar et al., 1993b).

The Outokumpu borehole has been studied significantly more extensively than the Juuka borehole in terms of its biogeochemistry. Mixing of 5 distinct water types has been observed in the Outokumpu borehole (Kietäväinen et al., 2013). Methanogens comprise the primary active community at depths of 0.5 km, 0.967 km (Purkamo et al., 2016), and 2.26 km (Purkamo et al., 2013) and are present in measurable abundances throughout the borehole (Itävaara et al., 2011a; Nyysönen et al., 2014; Purkamo et al., 2015). However, considering the $\delta^{13}\text{C-CH}_4$ ‰ VPDB, $\delta^2\text{H-CH}_4$ ‰ VSMOW, and CH₄/C₂+ values measured for Juuka and Outokumpu, (Kietäväinen et al., 2017) consider these to be predominantly abiotic CH₄ with some amount of

microbial CH₄ mixing that differs between individual samples. The results from the model presented here largely support the conclusions of these previous studies, finding the CH₄ in Juuka and Outokumpu to be entirely abiotic (Fig. 5b).

3.3 Extrapolation of CH₄ production rates to the global Precambrian lithosphere

Using the Sherwood Lollar et al. (2014) Precambrian lithosphere top-10-km volume estimate of $1.06 \times 10^9 \text{ km}^3$ and the maximum (Fennoscandian Shield; $\sim 1.8 \times 10^{-9} \text{ M year}^{-1}$) and minimum (Witwatersrand Basin; $\sim 1.9 \times 10^{-11} \text{ M year}^{-1}$) abiotic CH₄ production rate estimates from the best fit models presented here, the range of abiotic CH₄ production globally in the Precambrian lithosphere is calculated as:

$$\sim [0.08-7.1] \times 10^9 \text{ moles CH}_4 \text{ year}^{-1}$$

Assuming that 4 H₂ molecules are consumed to produce 1 CH₄ molecule via abiotic CO₂ reduction by H₂ ($4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), per the reasoning of Onstott et al., (2006b) and Warr et al. (2019), this equates to:

$$\sim [0.3-28.4] \times 10^9 \text{ moles H}_2 \text{ year}^{-1}$$

This compares to previous H₂ production estimates from the top 10-km of Precambrian lithosphere (Sherwood Lollar et al. 2014) of:

$$\sim[4-23] \times 10^{10} \text{ moles H}_2 \text{ year}^{-1}$$

And to previous H₂ production estimates from the top 10-km of Precambrian lithosphere (Warr et al. 2019) of:

$$\sim[0.4-5.4] \times 10^{10} \text{ moles H}_2 \text{ year}^{-1}$$

The calculated amount of H₂ consumed to form CH₄ in the Precambrian subsurface equates to ~0.8-12% of the global Precambrian lithosphere H₂ production estimate of Sherwood Lollar et al. (2014). This also equates to ~8-53% of the global Precambrian lithosphere H₂ production estimate of Warr et al. (2019). While both Sherwood Lollar et al. (2014) and Warr et al. (2019) provide two independent methods for quantifying global H₂ production in the Precambrian lithosphere, these models do not attempt to quantify rates of H₂ consumption via formation of other gases. CH₄ is known to be a significant sink for H₂ in Earth's subsurface (e.g. Lin et al., 2005; Sherwood Lollar et al., 2006; Onstott et al., 2006b; Warr et al., 2019), but the rate at which H₂ is consumed to form CH₄ has been uncharacterized until this point, other than for microbial CH₄ production in Witwatersrand Basin specifically (Onstott et al., 2006b). Here the different rates at which H₂ is consumed via abiotic and microbial CH₄ formation are quantified for Witwatersrand Basin, the Canadian Shield, and the Fennoscandian Shield, which allows for determination of its global significance as an H₂-sink, based on extrapolation from the 3 regions used in this study. The results presented here quantitatively support the hypothesis that abiotic

CH₄ production is a significant H₂ sink the subsurface of the Precambrian crust and falls within the range of given estimates for available H₂ in the Precambrian crust.

A significant quantity of CH₄ in the Precambrian lithosphere subsurface is also formed microbially, in many cases by CO₂ reduction. Taking the maximum (Evander, SA; $\sim 1.0 \times 10^{-9}$ M year⁻¹) and minimum resolvable (Kloof, SA; $\sim 8 \times 10^{-12}$ M year⁻¹) microbial CH₄ production rates at depths > 1 km that are not outliers from the overall microbial CH₄ production rate versus depth trend, the global microbial CH₄ production rate at depths > 1 km in the Precambrian lithosphere is calculated as

$$\sim [0.03-4] \times 10^9 \text{ moles CH}_4 \text{ year}^{-1}$$

Assuming again that 4 H₂ molecules are consumed to produce 1 CH₄ molecule via microbial reduction of CO₂ by H₂ ($4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), this equates to:

$$\sim [0.1-16] \times 10^9 \text{ moles H}_2 \text{ year}^{-1}$$

This calculated amount of H₂ equates to $\sim 0.3-7\%$ of the global Precambrian lithosphere H₂ production estimate of Sherwood Lollar et al. (2014) being consumed by microbial CH₄ production via CO₂ reduction by H₂. This also equates to 3-30% of the global Precambrian lithosphere H₂ production estimate of Warr et al. (2019). Combining the estimates for H₂ consumption by both abiotic and microbial CH₄ production via CO₂ reduction by H₂ equates to

4-19% the H₂ production estimates from Sherwood Lollar et al. (2014) and 11-83% the H₂ production estimates from Warr et al. (2019). The results presented here provide the first quantitative confirmation that both abiotic and microbial CH₄ production are significant global H₂ sinks in Earth's subsurface. These results show a remarkable agreement and consistency between these three completely independent and methodologically distinct approaches, especially considering that H₂ is also consumed by other reactions in Earth's deep subsurface not considered here, including sulfate reduction, acetogenesis, iron reduction, and nitrate reduction. Determining the relative size of these various H₂ sinks, and how they vary regionally within Earth's subsurface is an important next step in improving understanding of subsurface geochemical processes.

3.3.1 Comparison to CH₄ production rate from mid-ocean ridges

Previous estimates for H₂ and CH₄ production rates in continental and oceanic crustal settings on Earth are compiled in Table 2. Sherwood Lollar et al., 2014 previously estimated that the global H₂ production rate from the top 10 km of the Precambrian lithosphere from radiolysis and other water-rock interactions is $\sim[4-23] \times 10^{10}$ moles H₂ per year. Via an empirical method, Warr et al., (2019) estimated H₂ production in the top 10-km of the Precambrian lithosphere is $[0.4-5.4] \times 10^{10}$ moles H₂ year⁻¹. Recent estimates for the current rate of H₂ production from mid-ocean ridge settings range from $\sim 10^{12}$ moles H₂ per year via the numerical modeling approach of (Worman et al., 2016) and 7×10^{11} moles H₂ per year via the different numerical modeling approach of (Merdith et al., 2020). Previous estimates of H₂ flux from the entire oceanic crust range from $0.3-2.0 \times 10^{11}$ moles H₂ per year (Canfield et al., 2006; Sleep and

Bird, 2007; Kasting and Canfield, 2012), to $\sim 4.5 \pm 3.0 \times 10^{11}$ moles H_2 per year (Bach and Edwards, 2003), to 1.67×10^{11} moles H_2 per year from slow spreading ridges alone (Cannat et al., 2013), and $6.1\text{-}10.7 \times 10^{11}$ moles H_2 per year from transform offset faults alone (Rüpke and Hasenclever, 2017). (Merdith et al., 2020) assume that 10-100% of the H_2 in their calculations will abiotically become CH_4 , which in their model would equate to a CH_4 flux of $[7\text{-}12] \times 10^{10}$ moles CH_4 per year from mid-oceanic ridges. (Emmanuel and Ague, 2007) estimate that the CH_4 flux from mid-ocean ridges is 1.6×10^{11} moles CH_4 per year, while (Cannat et al., 2013) estimate CH_4 fluxes of 2.4×10^{11} moles CH_4 per year. The estimates presented here for abiotic CH_4 production in the top ~ 10 km of Earth's Precambrian lithosphere equate to 0.1-6% of the (Merdith et al., 2020) estimate of CH_4 from slow spreading ridges. Including the estimated rates of microbial CH_4 production in Earth's deep (> 1 km) subsurface, this equates to 0.2-9% of CH_4 flux estimates from slow spreading ridges. However, if microbial CH_4 production rates at depths < 1 km are included, $[0.02\text{-}100] \times 10^{-8}$ M year^{-1} , this equates to 0.2-300% of the estimate of (Merdith et al., 2020) from slow spreading ridges, assuming the microbial CH_4 production rates at < 1 km depth occur from 0-1 km depths. This demonstrates that, relative to other geological sources, abiotic and microbial CH_4 production within tectonically quiescent crustal settings represents a significant source of this greenhouse gas and biochemical energy source that is independent of plate tectonics. This contrasts with spreading ridges which are inherently dependent on plate tectonic processes. Just as abiotic CH_4 production in spreading ridge environments is explored as a CH_4 production mechanism capable of producing greenhouse hazes during the Archean, abiotic CH_4 formation in continental settings may provide an

additional mechanism for generating greenhouse atmospheres during the Archean, but one that is independent of the onset of plate tectonics.

3.4 Comparison with past Precambrian crust abiotic CH₄ production models

The results presented here show that resolvable microbial CH₄ production at depths from 0.2-3.5 km ranges from $\sim 8 \times 10^{-12}$ M year⁻¹ to $\sim 1 \times 10^{-6}$ M year⁻¹. This is consistent with reports by Onstott et al., 2006b; Onstott et al., 2006a, who also find that methanogenesis in Witwatersrand Basin is negatively correlated with depth. The agreement of results presented here with the findings of Onstott et al., 2006b; Onstott et al., 2006a is actually rooted in differences between their modeling approaches and the approach undertaken in the present study.

The model presented here assumes negligible He flux from deeper within the crust while Onstott et al., (2006b) assume a range of values for this flux from depth. The earlier model also assumed that different amounts of He will be introduced into groundwaters via this deeper flux as a function of depth (Equation 2), where more He would be dissolved in groundwaters at shallow depth. This reduces the He residence time estimates for shallower fluids, meaning the same amount of CH₄—i.e. the measured quantity of dissolved CH₄—would have to be produced in these fluids over a shorter period of time, thus increasing the estimates for methanogenesis at shallower depths, leading to the production of a negative correlation trend between methanogenesis and depth. In the model presented here, it is assumed that there is no depth-dependent He flux. P_{He} (He production rate) values for each sample are calculated based on the radionuclide concentration of the rock unit in which the individual

boreholes were drilled. This means that the P_{He} value, and thus the residence time estimate from dissolved He concentrations, will be lower for the samples collected from boreholes drilled into the Ventersdorp Supergroup (Kloof and Mponeng), which consists of mafic lithologies, compared to samples collected from the Upper (5 Beatrix samples) and Lower (3 Beatrix samples, Evander, Driefontein, Masimong, and Merriespruit) Witwatersrand Supergroups, which are composed of schist, sedimentary quartzite, and shale layers. These 3 different rock units are known to have different radionuclide concentrations, and thus different P_{He} values (Lin et al., 2005a; Heard et al., 2018). In contrast to this outlined modelling approach, Onstott et al., (2006b) use a single P_{He} value for each site in the Witwatersrand system.

At depths <1 km, microbial CH_4 production is significantly greater, as exemplified by Beatrix, South Africa; Enonkoski, Finland; and Ylivieska, Finland (Fig. 5c). This is consistent with the results of (et al., 2006b; Onstott et al., 2006a. Two of the Beatrix samples used in the present study show significantly higher (1-2 orders of magnitude) calculated microbial CH_4 production compared to that of Onstott et al., (2006b) (Fig. 5c).

3.5 Relationship between microbial CH_4 production and depth

Cell concentrations are negatively correlated with depth in rock and sediment cores from the continental crust, though there is roughly 4-5 orders of magnitude variability in cell concentrations measured at the same depths (Magnabosco et al., 2018; Onstott et al., 2019). This correlation has typically been proposed and/or shown via power-law fits to cell concentrations versus depth in both the continental crust (Onstott et al., 1999; Magnabosco et

al., 2018; Onstott et al., 2019) and submarine sediments (Parkes et al., 1994; Kallmeyer et al., 2012; Parkes et al., 2014). Onstott et al., (2006b) also proposed that microbial CH₄ production was negatively correlated with depth in Witwatersrand Basin. The results from the model presented here are broadly in agreement with these past studies, whereby microbial CH₄ production in Witwatersrand Basin, the Canadian Shield, and the Fennoscandian Shield are very weakly negatively correlated with depth. This trend is largely dependent on the low microbial CH₄ production rates at Kloof and Mponeng Mines—two deep sites in Witwatersrand Basin—and the high microbial CH₄ production rates at Enonkoski Mine and Ylivieska borehole, Finland, as well as Beatrix Mine, South Africa—all of which are at <1 km depth (Fig. 6c). Similar to cell concentration versus depth data for rock and sediment cores in the continental crust (Magnabosco et al., 2018; Onstott et al., 2019), the model estimates roughly 3-4 orders of magnitude variation in microbial CH₄ production rates at the same depth (Fig. 6c).

The lowest resolvable microbial CH₄ production values (Kloof) in the results presented here are from ~2.8-3.5 km depth and the highest resolvable microbial CH₄ production values at depths >1 km are at ~2.7 km (Driefontein), ~1.9 km (Masimong), and ~2.0 km (Merriespruit) depths, but there is a significant range in microbial CH₄ production at every site with multiple samples measured that span approximately the range established by the deepest and shallowest endmembers (Fig. 5c). This has previously been attributed to hydrogeological controls induced by faulting that connects groundwater systems residing in different rock units, which have different lithologies and produce different amounts of H₂ (Ward et al., 2004; Sherwood Lollar et al., 2006; Onstott et al., 2006b; Onstott et al., 2006a; Borgonie et al., 2019). Microbial CH₄ production is significantly greater at <1 km depth, as exemplified by Beatrix,

South Africa; Enonkoski, Finland; and Ylivieska, Finland (Fig. 5c). However, there are sites at <1 km depth, such as Juuka and Outokumpu, Finland, where the model estimates little to no microbial CH₄ production.

3.6 Multiple abiotic and microbial isotopic endmembers

The isotopic endmember results which best fit the data for each region are summarized in Table 3. The results from the MCMC application of the biogeochemical model presented here show that multiple microbial and abiotic isotopic endmembers exist in the subsurface of the Precambrian lithosphere (Fig. 4) with different sources reflecting differences in geologic setting. The MCMC outputs suggest that the microbial and abiotic isotopic endmembers for the Canadian Shield and Witwatersrand Basin are generally similar on a gross scale (Fig. 4) and thus the isotopic trend for microbially dominated to abiotically dominated sites is also similar between these regions (Fig. 3). In Finland, however, the isotopic trend of $\delta^2\text{H-CH}_4$ ‰ VSMOW is distinctly different from the trends in South Africa and Canada (Fig. 3), which is supported by the results of the MCMC independently selecting best fit parameter values for abiotic and microbial isotopic endmembers (Fig. 4a, 4c). It is also consistent with the different abiotic isotopic endmembers previously proposed by (Sherwood Lollar et al., 1993b).

4.0 Discussion

4.1 Geochemical and geophysical controls on rates of abiotic and microbial CH₄ production

From the proposed model, abiotic CH₄ production varies considerably between Witwatersrand Basin versus the Canadian and Fennoscandian Shield sample sites. Microbial CH₄

production varies by 3-4 orders of magnitude between different groundwaters sampled at the same depth, even in the same mine. The influence of variations in the lithologies surrounding the sample sites, craton-wide and site-specific hydrogeologic variations, differences in regional thermal histories, and subsurface microbial activity will now be evaluated as controls on abiotic and microbial CH₄ production rates.

4.1.1 Variations in site lithology

It is striking that the Fennoscandian Shield and Canadian Shield sites, which are dominated by similar ultramafic, mafic, granitic, and sedimentary lithologies, are estimated to have very similar abiotic CH₄ production rates, while Witwatersrand Basin, which contains metasedimentary (Upper and Lower Witwatersrand Supergroups) and mafic (Ventersdorp Supergroup) lithologies—lacking any significant ultramafic lithology at the subset of sites sampled for this study—has a two orders of magnitude lower an abiotic CH₄ production rate (Fig. 5a). A lithologic control for variations in abiotic versus microbial CH₄ production rates has been hypothesized by other studies (Ward et al., 2004; Kietäväinen et al., 2017). Generally, the results presented here show that sites within or proximal to ultramafic rock (Kidd Creek, Thompson, Birchtree, Enonkoski, Ylivieska, Outokumpu, Juuka) tend to have higher CH₄ concentrations relative to He concentrations compared to sites dominated primarily by mafic (Kloof and Mponeng) and metasedimentary lithologies (Beatrix, Masimong, Merriespruit, Evander, Driefontein) (Fig. 7). In some cases, this can be principally attributed to microbial CH₄ production (e.g. Enonkoski and Ylivieska, Finland), while in other cases it might relate to some combination of enhanced abiotic CH₄ production (e.g. Kidd Creek) coupled with possibly

enhanced microbial CH₄ production at some point during the residence times of these fluids (e.g. Birchtree).

The dominant country rock lithology impacts the amount of H₂ that is available for consumption to form CH₄ via CO₂ reduction, as well as the availability of catalysts to facilitate FTT reactions. H₂ production in the Precambrian lithosphere has been shown to occur via radiolysis (Lin et al., 2005a; Lin et al., 2005b; Onstott et al., 2006b; Sherwood Lollar et al., 2014; Warr et al., 2019) and water-rock interactions (WRI; Sherwood Lollar et al., 2014; Warr et al., 2019) including serpentinization. Radiolysis and WRI in the Canadian Shield produce roughly similar orders of magnitude of H₂, with WRI/radiolysis production ratios varying between ~0.1-10, and with ultramafic and mafic sites containing more H₂ relative to felsic sites (Warr et al., 2019). Globally, sites within or proximal to ultramafic lithologies (e.g. Kidd Creek, Thompson, Birchtree, Outokumpu, Juuka) typically have higher reconstructed H₂ concentration values relative to He concentrations (Fig. 8). This can be attributed to the greater prevalence of water-rock interactions, including serpentinization, in generating H₂ relative to radiolysis.

Metal catalysts including awaruite (Sleep et al., 2004) and ruthenium (Etiope and Ionescu, 2015; Etiope et al., 2018) facilitate the reduction of CO₂ by H₂ to form CH₄. These catalysts are most abundant in plutonic and subaerial mafic to ultramafic rocks of Archean-Proterozoic-Mesozoic age (Haldar, 2017), which are the lithologies characteristic of the Canadian and Fennoscandian sites with the highest abiotic CH₄ production rate estimates, with the exception of Thompson and Birchtree Mines which are surrounded by pelitic metasediments derived from these lithologies (Section 1.2). The presence of ultramafic rocks may therefore have two distinct, but interconnected, effects with respect to CH₄ production: 1)

increased H₂ production via serpentinization and 2) increased conversion of H₂ to CH₄ via presence of catalysts. While it is already known that Canadian Shield sites with ultramafic and mafic lithologies are associated with higher H₂ production relative to sites with felsic lithologies (Warr et al., 2019), the exact mechanisms by which H₂ is converted to CH₄ in Precambrian Shield settings are not definitively known.

Sample sites in Witwatersrand Basin used in this study are dominated by non-ultramafic lithologies compared to Kidd Creek, Birchtree, Thompson, Outokumpu, and Juuka. These lithologies in Witwatersrand Basin typically have higher radionuclide concentrations than are found in ultramafic rocks (Heard et al., 2018), and thus it is reasonable to expect H₂ production at these sites to be dominated by radiolysis, as was demonstrated by Lin et al., 2005a; Onstott et al., 2006b. This factor explains why Witwatersrand Basin groundwater samples typically have lower CH₄ and reconstructed H₂ concentrations compared to the ultramafic-lithology-hosted Canadian sites, which have higher reconstructed H₂ values than can be explained by radiolysis alone (Fig. 8). Lithology of the country rock surrounding the samples sites therefore affects microbial CH₄ production rates by affecting the availability of H₂ for CO₂ reduction. Lithology of the surrounding country rock also affects the abiotic CH₄ production rates at these sites by both controlling the availability of H₂, and possibly also by controlling the amount of metal catalysts available to facilitate FTT reactions (Sleep et al., 2004; Etiope and Ionescu, 2015; Etiope et al., 2018).

The variations between fluids with predominantly abiotic CH₄ versus microbial CH₄ within Witwatersrand Basin have been attributed to the rock units in which fluids were sampled (Ward et al., 2004). Samples from Beatrix, Merriespruit, Masimong, Driefontein, and Evander

Mines—which are primarily dominated by microbial CH₄— were all collected from the Upper and Lower Witwatersrand Supergroup (Ward et al., 2004). Notably, the sample sites in these mines are all overlain by the organic-matter-bearing Karoo sediments. Samples from Kloof and Mponeng Mines, the most abiotic CH₄ dominated sites in Witwatersrand Basin, were collected in the Ventersdorp Supergroup (Ward et al., 2004). The Karoo sediments do not overlie these mines due to removal by erosion (Johnson et al., 1996). It is notable that the Ventersdorp Supergroup is comprised of mafic lava flows, which would likely contain more metal catalysts to facilitate FTT reactions relative to the metasedimentary lithologies (Haldar, 2017), providing a self-consistent hypothesis where lithology primarily controls variations in the rate of abiotic CH₄ production between different sample sites in Witwatersrand Basin, as well as between Witwatersrand Basin and the Canadian and Fennoscandian Shield sample sites investigated in this study.

4.1.2 Hydrologic variations

There appear to be two separate regimes of hydrologically-enhanced microbial CH₄ production: 1) enhanced microbial CH₄ production at sample sites >1 km depth spurred by ancient, H₂-rich brines mixing with paleometeoric water (Fig. 6c) and 2) enhanced microbial CH₄ production in groundwaters that fall near the Global Meteoric Water Line (GMWL). At all sites >1 km depth with >2 groundwater samples, the samples with the highest microbial/abiotic CH₄ production rate ratio have $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) H₂O isotopes in between the most paleometeoric (closest to the GMWL) and the most evolved (furthest from the GMWL) isotopic endmembers at their individual sites. Sites that show this trend include Kidd Creek, Kloof,

Mponeng, Evander, and Driefontein Mines (Figs 6c, S1-S5). Some groundwaters with high microbial CH₄ production, such as Beatrix, Masimong, and Merriespruit Mines have $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) H₂O isotopes near or on the GMWL.

4.1.2.1 Enhanced microbial CH₄ production after mixing of ancient, H₂-rich brines with paleometeoric water

Driefontein sample DR938 H3 071202 is the single sample with an estimated microbial CH₄ production rate $>2\text{e-}9 \text{ M year}^{-1}$ that also has $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values far from the GMWL. It has the highest estimated microbial CH₄ production rate for depths $>1 \text{ km}$ (Fig. 5c). DR938 H3 071202 has a higher microbial CH₄ production rate than Driefontein samples that fall closer to the GMWL, as well as a Driefontein sample that falls far from the GMWL (Fig. 6b). This implies that enhanced methanogenesis in DR938 H3 071202 is caused by mixing between a deeper saline water source—which is likely H₂-rich due to its long residence time—and paleometeoric water. This same behavior is also apparent at Kidd Creek, Kloof, Mponeng, Evander, and Driefontein Mines, which are all the mines $>1 \text{ km}$ depth with >2 collected groundwater samples (Figs 6c, S1-S5). This behavior is unsurprising given the distribution of redox energy in deep subsurface systems and the tendency of microbial communities to consume available redox energy in groundwaters they inhabit. Kieft et al., (2005) noted that many H₂-rich fluids in Witwatersrand Basin were uninhabited by H₂-utilizing microorganisms despite them being teeming with consumable redox energy. It is thus logical that once methanogens are introduced into these H₂-rich, ancient, saline fluids via mixing with methanogen-hosting paleometeoric water, microbial CH₄ production would be quickly

enhanced as these organisms take advantage of Gibbs Free Energy conditions that are highly favorable for their metabolisms. This behavior was noted in Thompson Mine groundwaters, where measured concentrations of methanogens were highest in mixed paleometeoric and ancient saline fluids (Telling et al., 2018).

Even a small quantity of presumably methanogen-hosting paleometeoric water infiltration into highly evolved H₂-rich brines appears to be sufficient to enhance microbial CH₄ production. Samples in Witwatersrand Basin with the lowest microbial-to-abiotic CH₄ production ratios (Kloof and Mponeng Mines) have either $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values consistent with paleometeoric water or consistent with an evolved saline fluid (Fig. 6c). At these sites, there also appears to be no correlation between the exact mixing ratios of paleometeoric and older groundwater and the ratio of microbial CH₄ versus abiotic CH₄. The Evander, Driefontein, and Kidd Creek Mine samples also lack any significant correlation between $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values and microbial-versus-abiotic CH₄ percentage. Therefore, while young meteoric water infiltration appears to affect microbial CH₄ production rates—in that all but one sample with microbial CH₄ production rates greater than $\sim 2\text{e-}9\text{ M year}^{-1}$ fall along the GMWL—, >1 km depth samples from Witwatersrand Basin do not show a strong correlation between percentage paleometeoric water and percentage microbial CH₄. Rather, mixing of paleometeoric water and older, saline water appears to control microbial CH₄ production in these deeper localities.

4.1.2.2 Enhanced microbial CH₄ production in young paleometeoric water

All but one of the sample sites in Witwatersrand Basin with microbial CH₄ production rates greater than $\sim 2 \times 10^{-9}$ M year⁻¹ (Masimong, Merriespruit, and Beatrix) have $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values that fall near the global meteoric water line (GMWL) (Fig. 6b). Hydrology may impact the abundance of methanogens—and therefore the rate of microbial CH₄ production—in groundwaters, as younger groundwater typically contains more methanogens compared to older groundwater that has not recently been mixed with paleometeoric water (e.g. Ward et al., 2004; Lin et al., 2006a; Lin et al., 2006b; Chivian et al., 2008; Lollar et al., 2019). Proposed correlations between presence of abiotic versus microbial CH₄ and hydrogeology include that microbial CH₄ is primarily associated with paleometeoric water that falls near the GMWL whereas abiotic CH₄ is primarily associated with more ancient and evolved fluids (e.g. Ward et al., 2004). The results presented here show that microbial CH₄ production rates are indeed maximized in fluids with $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values that fall along the GMWL, agreeing with that specific component of the hypothesis presented by Ward et al., (2004). The primary difference in the results reported here is the observation of microbial CH₄ production rate enhancement in mixed evolved H₂-rich brines and paleometeoric water, as described in Section 4.1.2.2.

Beatrix Mine is the shallowest sampled site in Witwatersrand Basin, with the lowest estimated fluid residence times based on dissolved He concentrations (Fig. 9). In groundwaters at this site, microbial CH₄ production rates are enhanced and $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values fall near the GMWL likely due to relatively young groundwater residence times. Because we only possess one characterized groundwater sample from both Merriespruit and Masimong Mines, it is difficult to determine whether enhanced microbial CH₄ production rates at these

sites are caused by a minor amount of H₂-rich evolved brines mixing with paleometeoric water, or due to these fluids being paleometeoric with relatively short mean residence times. The dissolved He concentrations at Merriespruit and Masimong Mines are not remarkably low compared to other sites at similar depths (Fig. 9), meaning these fluids are not particularly young. It is therefore possible that the samples at Merriespruit and Masimong Mines follow the behavior described in Section 4.1.2.1 and represent mixtures of H₂-rich evolved brines and a large quantity of paleometeoric water, pushing the $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values close to the GMWL.

4.1.2.3 Physical parameters controlling hydrogeology in Witwatersrand Basin

Hydrogeologic processes are largely driven by the physical structure of the subsurface including the distribution of fracture networks, faults, and cross-cutting dykes. Determining the major factors influencing the hydrogeology of Witwatersrand Basin is key to understanding the geochemistry of its subsurface groundwater. Stress-induced fracture network expansion, faulting, and the existence of more permeable dykes affect the infiltration depths of meteoric water and its mixing with deeper fluids, which is traced by $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopes in H₂O (Fig. 6). The large and small scale fault networks of host-rock surrounding Kloof, Mponeng, and Driefontein Mines have been seismically mapped (Manzi et al., 2012; Manzi et al., 2013; Manzi et al., 2015) and have been quantitatively correlated with reports of groundwater and CH₄ (Manzi et al., 2012). Faulting in these rock units has been attributed to three distinct tectonic events at ~2.90 Ga, ~2.73 Ga, and ~2.7-2.64 Ga (Manzi et al., 2013) that predate the Vredefort impact at 2.023 ± 0.004 Ga (Reimold and Gibson, 1996). Formation of this ~300 km

diameter impact crater certainly induced a significant amount of fracturing around the impact structure (Reimold and Gibson, 1996; Therriault et al., 1997; Onstott et al., 2006a; Collins, 2014). It is possible that this impact-induced fracturing permitted penetration of meteoric water to greater depths (Fig. 6), possibly even introducing microorganisms into deeper groundwaters. Uplift of the 2.0 Ga Vredefort Dome has also caused deformation of the surrounding rock formations (Coward et al., 1995), inducing fracturing. Kloof, Mponeng, and Driefontein mines are all located in the Carletonville region of Witwatersrand Basin, which is notably influenced by fault zones radiating from the Vredefort impact structure (Onstott et al., 2006a). Whether the paleometeoric water and H₂-rich evolved brine mixing that locally enhances microbial CH₄ production in some groundwater samples within these sites is tied to faulting associated with the Vredefort impact rather than Archean tectonics should be investigated, as this may illuminate some difference in the faulting history of Witwatersrand Basin versus other cratons that do not contain large impact structures.

4.1.2.4 Introduction of methanogens to Witwatersrand Basin

He and chlorinity are positively correlated in Witwatersrand groundwaters (Onstott et al., 2006a), which is consistent with mixing between meteoric water and a 2.0-2.3 Ga highly saline He-rich hydrothermal fluid (Drennan et al., 1999; Frimmel and Hallbauer, 1999) during uplift of the Kaapvaal craton 30-90 Ma (Omar et al., 2003; Onstott et al., 2006a). The 2.0-2.3 Gyr age of this hydrothermal fluid (Drennan et al., 1999; Frimmel and Hallbauer, 1999) notably corresponds to the $\sim 2.023 \pm 0.004$ Ga timing of the Vredefort impact event (Reimold and Gibson, 1996). Large bolide impacts such as Vredefort typically generate impact-induced

hydrothermal systems (e.g. Therriault et al., 1997; Ames et al., 1998; Osinski et al., 2001; Kirsimäe et al., 2002; Turtle et al., 2003; Abramov and Kring, 2004; Osinski et al., 2005; Kirsimäe and Osinski, 2012; Ivarsson et al., 2013; Abramov and Kring, 2018). It is possible that the microbial communities in Witwatersrand Basin were introduced to the fracture networks via this recent mixing of paleometeoric waters with 2.0 Gyr old hydrothermal fluids (Fig. 6) preserved from the Vredefort impact event (Drennan et al., 1999; Frimmel and Hallbauer, 1999; Omar et al., 2003; Onstott et al., 2006a). However, it is unclear if the methanogens responsible for CH₄ production in some of the samples used here were originally residents of the paleometeoric water which entered the system 30-90 Ma or if they predated its incursion. *Firmicutes* have been shown to be primarily associated with these deep, saline fluids encountered in the Witwatersrand Basin (Magnabosco et al., 2016) and similar correlations between fluid origin and microbial inhabitants has been reported in the Fennoscandian Shield (Itävaara et al., 2011b), the Cedars in northern California (Suzuki et al., 2013), the Tablelands Ophiolite (Brazelton et al., 2013), and additional serpentinization systems (Schrenk et al., 2013). It is feasible therefore for future metagenomic approaches and studies to be applied to the sites sampled here to distinguish the provenance of methanogens currently present in these systems.

4.1.2.5 Impact of isostatic rebound on Fennoscandian Shield hydrogeology

The Fennoscandian shield was covered with glaciers 160-140 ka during the Late Saalian glaciation, at 60-50 ka during the Middle Weichselian glacial maximum, and at ~20 ka during the Late Weichselian glacial maximum (Svendsen et al., 2004). It has been free of ice-cover for

~10.5 kyr (Björck, 1995). Seismicity-inducing isostatic rebound is currently occurring in the Fennoscandian shield due to this relatively recent deglaciation (Wahlström, 1993). The fracturing/faulting that induces this seismicity may permit greater meteoric water penetration to depth. However, the $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values for this site do not support this hypothesis, as Enonkoski and Ylivieska—the most microbial CH_4 dominated Fennoscandian sites—fall far from the GMWL (Fig. 6). Outokumpu, one of the two most abiotic CH_4 dominated Fennoscandian sites, falls on the GMWL, but this might be due to it being an open borehole that meteoric water can directly infiltrate (Fig. 6). There is not $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic data available for our sample from Juuka. Overall, the $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values establish no relationship between microbial CH_4 production rates and enhanced infiltration of meteoric water for the Fennoscandian Shield sites used in this study.

4.1.3 Variations in microbial activity

Abiotic and microbial CH_4 production rates are inherently negatively correlated, as both consume the same oxidant and reductant energy sources to produce CH_4 . Abiotic H_2 -consuming reactions limit the amount of available redox energy available for consumption by microbial communities in oceanic hydrothermal mixing zones (McDermott et al., 2020). It is possible that the relatively high prevalence of methanogens in Witwatersrand Basin compared to the sampled groundwaters in the Canadian and Fennoscandian Shields lowers the rate abiotic CH_4 production there. Likewise, if abiotic CH_4 production rates are higher in certain settings due to presence of ultramafic lithologies (e.g. Kidd Creek), the amount of available H_2 for microbial CH_4 production will be lessened. The interplay of these two H_2 -consuming pathways to CH_4

formation, and whether they have a major or minor impact relative to other factors such as lithology and hydrology, should be investigated further.

4.2 Implications for atmosphere of early Earth

Abiotic CH₄ formation in seafloor spreading environments has been invoked as a potential greenhouse atmosphere production mechanism for Archean Earth (Kasting et al., 1983; Pavlov et al., 2000; Kasting, 2005; Emmanuel and Ague, 2007). Based on the previous comparison presented here of abiotic CH₄ production volumes in the subsurface of the Precambrian lithosphere with current estimates for CH₄ production from seafloor spreading centers (Merdith et al., 2020) (0.1-6% of the CH₄ currently produced globally at slow spreading ridges), it is possible that abiotic CH₄ formation in the terrestrial subsurface also contributed greenhouse gases to Early Earth's atmosphere. Abiotic CH₄ production within the crust would also then occur independent of plate tectonics, a planetary process whose time of initiation(s) is poorly constrained (Korenaga, 2013). Upper mantle temperatures during this time would have been ~200 K higher than at present (Abbott et al., 1994), which would lessen the depth range at which low temperature abiotic CH₄ production could occur. Still, abiotic CH₄ formation in the Earth's crust, independent of plate tectonics, might have been an especially important process for forming greenhouse atmospheres during the Archean that match the geologic record of relatively warm conditions (Sagan and Mullen, 1972; Mojzsis et al., 1996; Valley et al., 2002).

4.3 Necessity of diversifying deep subsurface groundwater sample set

The biogeochemical model proposed here incorporates the following data from each locality to quantify the average rates of microbial and abiotic CH₄ production: dissolved He concentration, dissolved CH₄ concentration, $\delta^2\text{H-CH}_4$ ‰ VSMOW, $\delta^{13}\text{C-CH}_4$ ‰ VPDB of each groundwater sample, and radionuclide concentrations of the surrounding rock matrix. Locations at depths >1 km in which all these data have been measured are few, and are primarily restricted to Witwatersrand Basin, the Canadian Shield, and the Fennoscandian Shield (Fig. 1). There exists a considerably larger set of localities where depths >1 km have been accessed in the continental subsurface globally (e.g. Sherwood Lollar et al., 2014 and refs. therein; Zgonnik, 2020 and refs. therein), but dissolved He concentration, dissolved CH₄ concentration, $\delta^2\text{H-CH}_4$ ‰ VSMOW, $\delta^{13}\text{C-CH}_4$ ‰ VPDB of each groundwater sample, and radionuclide concentrations of the surrounding rock matrix have not all been measured at these sites, and therefore there is insufficient data for incorporation into the model presented here. Considering the lateral and vertical heterogeneity of the continental crust (Jagoutz and Kelemen, 2015), particularly the Precambrian crust, the datapoints used here are certainly under-representative of the true diversity of the deep Precambrian crust. Still, this sampling demonstrates a remarkable similarity in H₂ and CH₄ production processes, isolation timescales, and supported microbial communities, but also a notable diversity in the relative rates and timescales at which these processes operate, hinting at underlying lithologic, hydrologic, and biological controls. Expanding the existing datasets to incorporate data from depths >1 km on Earth, from sites with a wider diversity of lithologies, geologic histories, and geographic distributions will further illuminate the individual and integrated effects of lithology, hydrology, and biology on the (bio)geochemical architecture of Earth's subsurface. Understanding the

interplay of these factors will be critical for accurate extrapolation of these processes to other planetary objects, and will be necessary for understanding how they affect planetary evolution in general. As such, diversifying the sample suite of deep groundwaters on Earth, and other planetary objects, should be a prime objective for Earth and planetary science as well as astrobiology in the coming decades.

5.0 Conclusions

The conclusions of this study can be summarized as 5 main findings:

- 1) Abiotic CH₄ production rates vary regionally in the Precambrian lithosphere's deep subsurface, with Witwatersrand Basin having approximately two orders of magnitude lower an abiotic CH₄ production rate compared to the Canadian and Fennoscandian Shields.
- 2) Microbial CH₄ production rates vary considerably site-to-site (Fig. 5c), show no conclusive correlation with depth globally at sites deeper than 1 km, and are significantly enhanced in groundwaters shallower than 1 km. Hydrogeologic factors appear to influence the relative contribution of microbial CH₄ compared to abiotic CH₄. There appear to be two regimes of hydrogeologically enhanced microbial CH₄ production: 1) heightened microbial CH₄ production during mixing of ancient, evolved, and H₂-rich saline brines with paleometeoric water (e.g. Kidd Creek, Kloof, Mponeng, Evander, and Driefontein Mines) and 2) heightened microbial CH₄ production in young paleometeoric water with $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) isotopic values that fall on the GMWL (e.g. Beatrix, Masimong, Merriespruit Mines; Ward et al., 2004). Telling et al., (2018)

note that methanogens are most prevalent in Thompson Mine groundwaters that are mixtures of evolved saline brines and paleometeoric water, which is a manifestation of regime 1.

- 3) The abiotic and microbial $\delta^2\text{H-CH}_4$ ‰ VSMOW and $\delta^{13}\text{C-CH}_4$ ‰ VPDB isotopic endmembers are different in all three cratons. The slope of the isotopic mixing trend is similar for the Witwatersrand Basin and the Canadian Shield sites, but significantly different for the Fennoscandian Shield sites.
- 4) The estimates of abiotic and microbial CH_4 production rates in the Precambrian lithosphere presented here are consistent with estimates of H_2 production rates in the Precambrian lithosphere by two independent methods (Sherwood Lollar et al., 2014; Warr et al., 2019).
- 5) Lithology and hydrology affect the prevalence and rates of abiotic and microbial CH_4 production in the subsurface of the Precambrian lithosphere.

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Figures

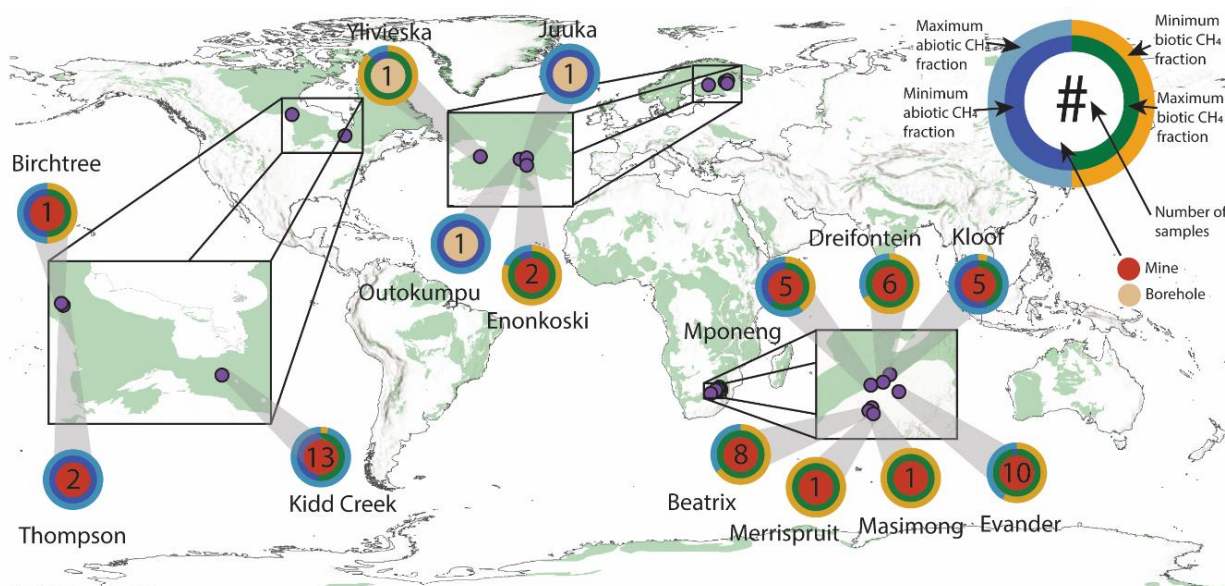


Figure 1 | Deep subsurface sample sites used in this study. Dissolved gases and the isotopic values of CH₄ were measured in 3 mines in Canada, 3 boreholes in Finland, 1 mine in Finland, and 7 mines in South Africa. The purple dots indicate the location of the sampled mine/borehole. Light green color on the map indicates exposed Precambrian lithosphere. The number at the center of the red or tan circle indicates the number of samples acquired at the specified site in which He and CH₄ gas volumes, water flow rates, gas flow rates, $\delta^{13}\text{C-CH}_4$, and $\delta^2\text{H-CH}_4$ were all measured. Inner dots colored red indicate that the sample site was a mine, while tan inner dots indicate the sample site was a borehole. The dark blue/green circle outside of the inner dot indicates the ratio of abiotic versus biotic CH₄ for the water/gas sample with the highest biotic CH₄ fraction (green) and lowest abiotic CH₄ fraction (dark blue) measured at the site. The outermost light blue/yellow circle indicates the ratio of abiotic versus biotic CH₄ for the water/gas sample with the lowest biotic CH₄ fraction (yellow) and highest abiotic CH₄ fraction (light blue) measured at the site.

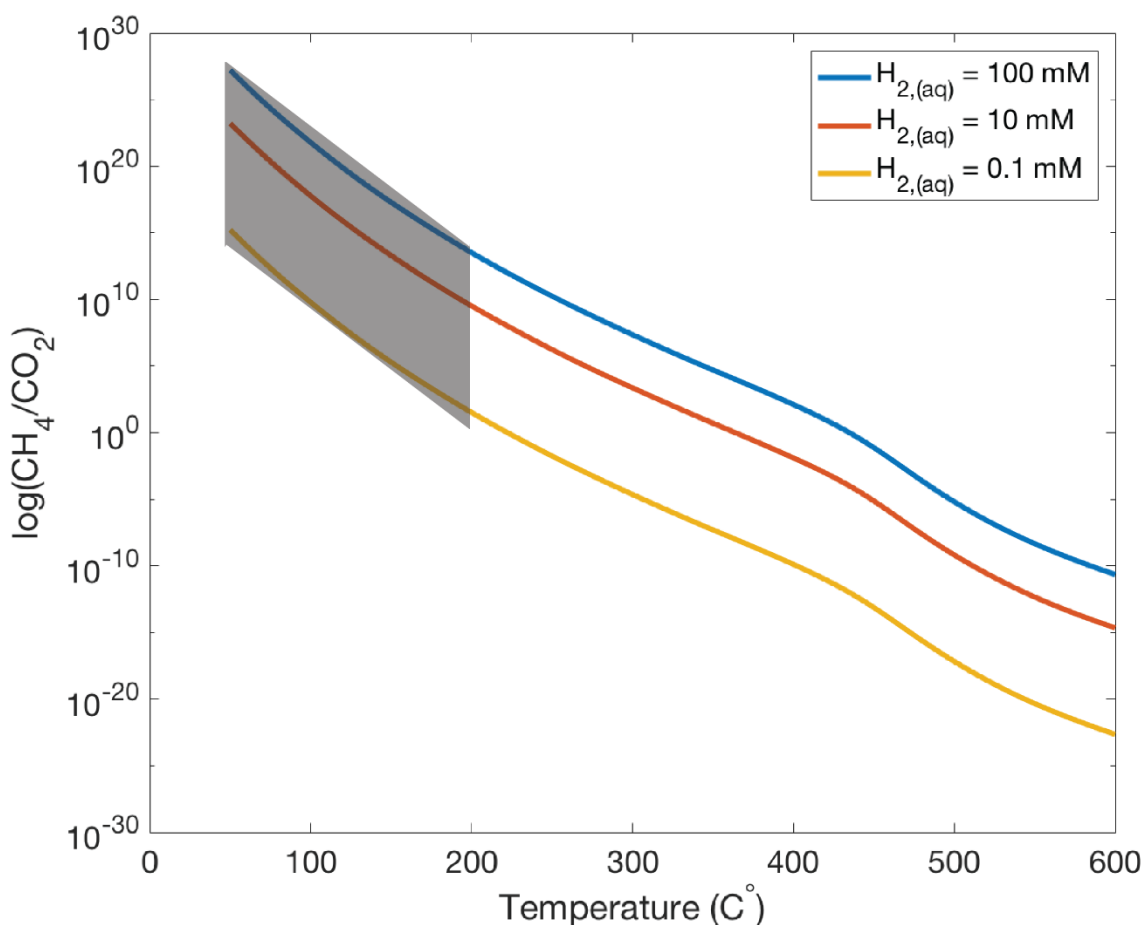


Figure 2 | Equilibrium ratios of CH_4/CO_2 with respect to temperature and different concentrations of H_2 . After McCollom (2013). Pressure = 50 MPa, which is equivalent to the hydrostatic pressure at ~ 2 km depth in Earth's continental crust. Equilibrium ratios were calculated using R implementation of CHNOSZ (Dick, 2008), which uses the SUPCRT92 thermodynamic database (Shock et al., 1989; Johnson et al., 1992). The sample sites used here typically contain $>0.1 \text{ mM}$ H_2 and are at temperatures $<200^{\circ}\text{C}$, thus CH_4 is the thermodynamically stable predominant carbon species under these conditions, as is approximately represented by the shaded region.

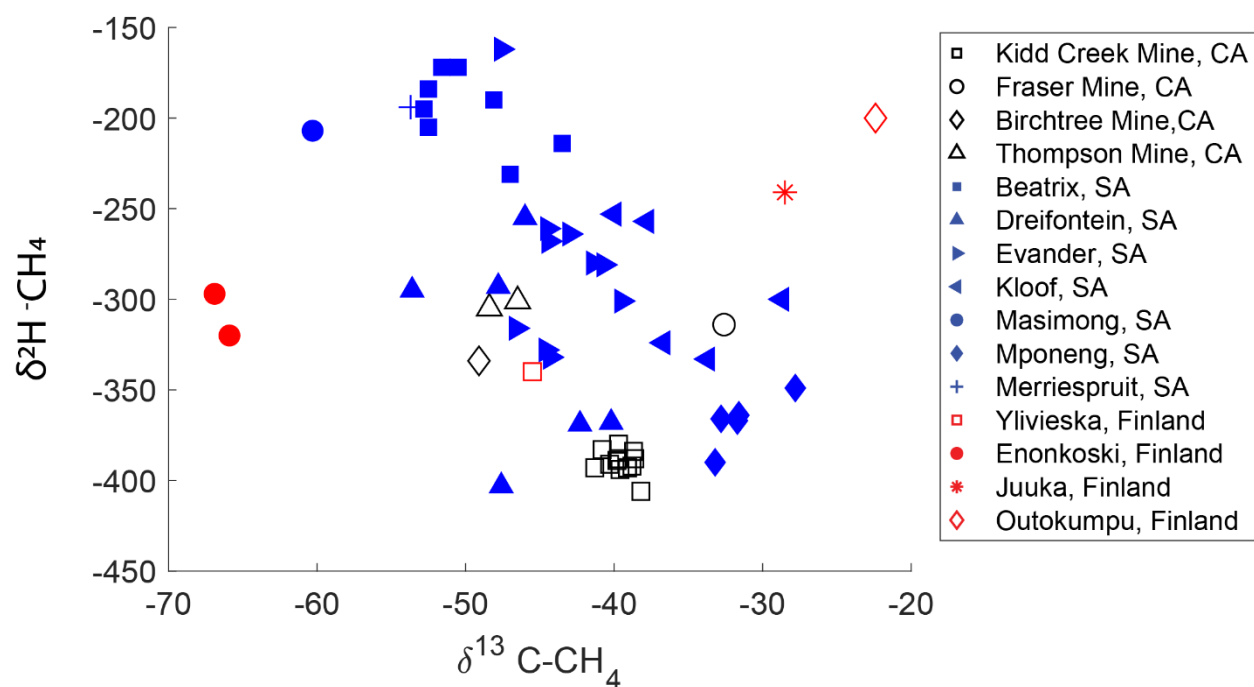


Figure 3 | $\delta^{13}\text{C-CH}_4$ ‰ VPDB versus $\delta^2\text{H-CH}_4$ ‰ VSMOW for CH_4 from each sample at each site. For Canadian and South African sites, more microbial CH_4 typically trends towards more enriched $\delta^2\text{H-CH}_4$ ‰ VSMOW values and more depleted $\delta^{13}\text{C-CH}_4$ ‰ VPDB values, and vice-versa is true for more abiotic CH_4 dominated sites. For the sites in Finland, more microbial CH_4 typically occupies a depleted $\delta^{13}\text{C-CH}_4$ ‰ VPDB and slightly depleted $\delta^2\text{H-CH}_4$ ‰ VSMOW region of the distribution, while abiotic CH_4 dominated sites have very enriched $\delta^2\text{H-CH}_4$ ‰ VSMOW compared to South African and Canadian sites that are considered to be similarly dominated by abiotic CH_4 . There thus appears to be 2 distinct microbial-to-abiotic trends, 1 of which is followed by the Canadian and South African sites, and 1 of which is followed by the Finland sites.

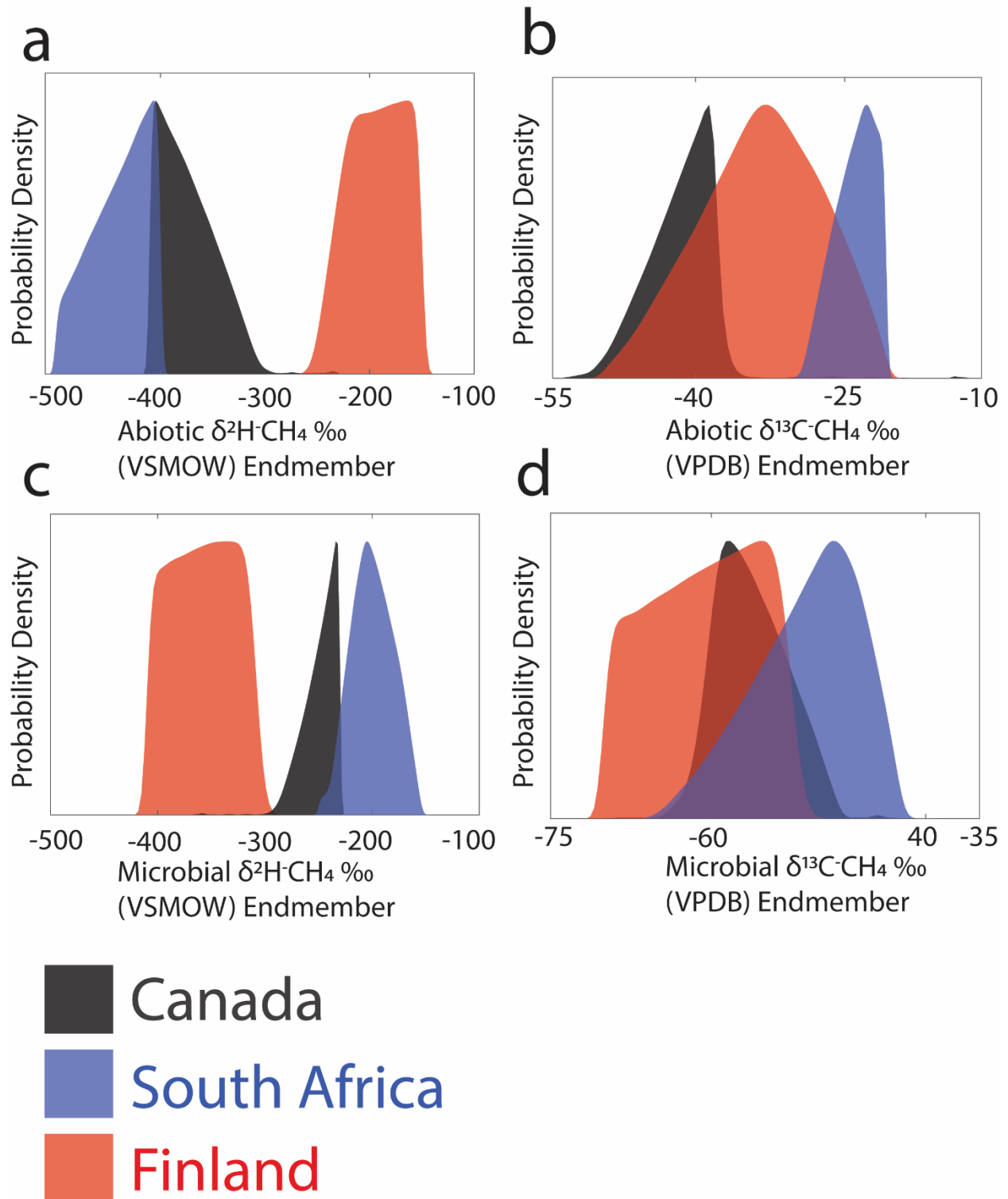


Figure 4 | Isotopic endmembers for Fennoscandian Shield (Finland), Canadian Shield (Canada), and Witwatersrand Basin (South Africa) that achieve best fits to data using forward model application to MCMC. (a) Best fit value distributions for the abiotic $\delta^2\text{H}-\text{CH}_4$ ‰ VSMOW isotopic endmember value. Canadian and South African sites have similar values, while Finland sites show a different isotopic endmember. (b) Best fit value distributions for the abiotic $\delta^{13}\text{C}-$

CH₄ ‰ VPDB isotopic endmember value. (c) Best fit value distributions for the microbial $\delta^2\text{H}$ -CH₄ ‰ VSMOW isotopic endmember value. Canadian and South African sites have similar values, while Finland sites show a different isotopic endmember. (d) Best fit value distributions for the microbial $\delta^{13}\text{C}$ -CH₄ ‰ VPDB isotopic endmember value.

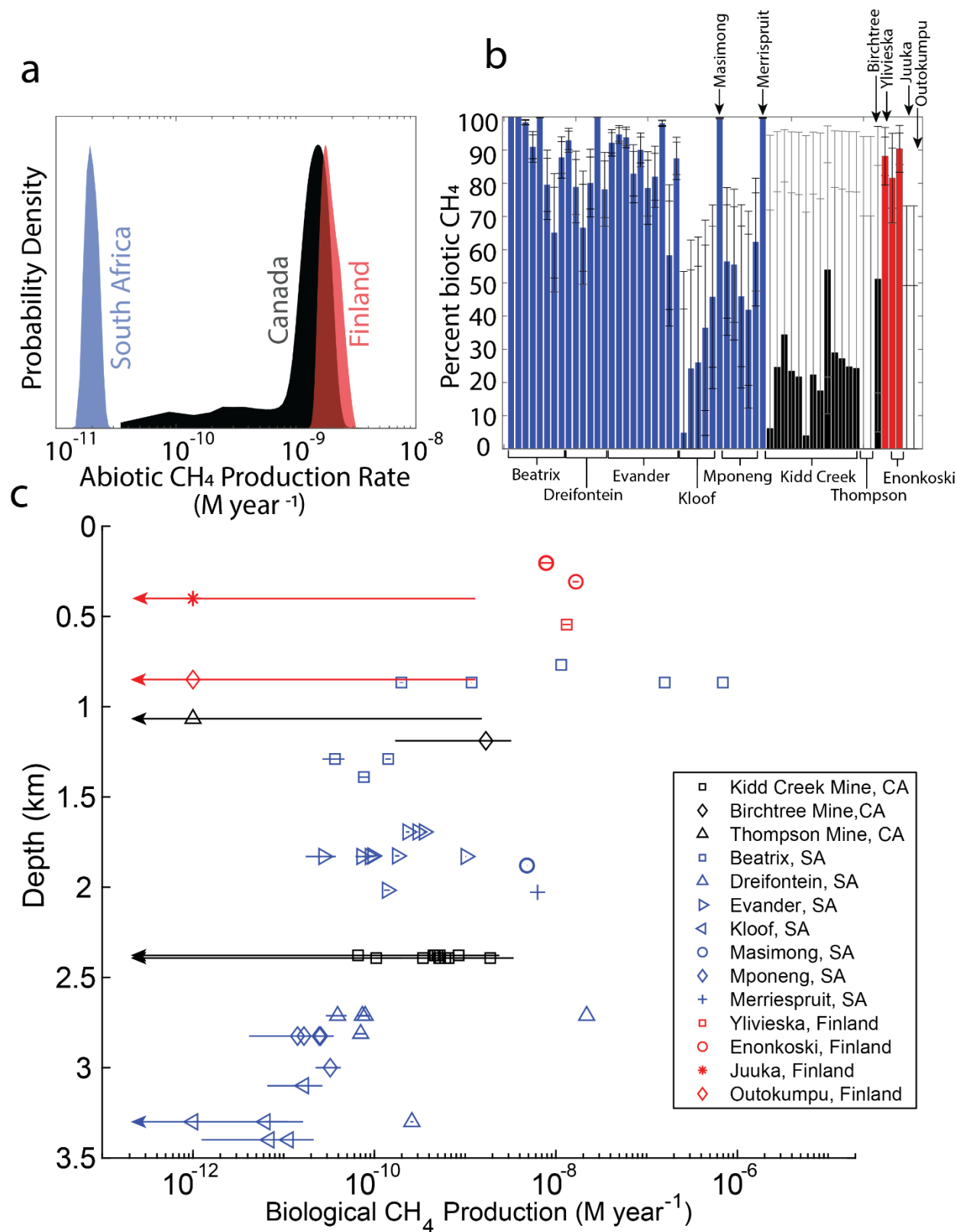


Figure 5 | Abiotic and biotic CH_4 production in Earth's deep subsurface. (a) Abiotic CH_4 production rate estimates from application of Markov Chain Monte Carlo (MCMC) to dissolved

He, CH₄, $\delta^{13}\text{C-CH}_4$, and $\delta^2\text{H-CH}_4$ measurements using the adapted Onstott et al., (2006b) model as a forward model. Abiotic CH₄ production rates vary by ~2 orders of magnitude between the sampled regions, with the lowest production rate in South Africa (blue), the middle production rate in Canada (black), and the highest rate in Finland (red). The probability density distribution of the possible range of abiotic CH₄ production rates is defined by the spread of values for which the forward model achieves the best fit to the data. (b) Percent microbial CH₄ in each measured sample for each sample site. The 1 σ and 2 σ error bars are shown, with 1 σ being the innermost brackets, and 2 σ being the outermost. If bottom brackets are not shown, that is because the 1 σ or 2 σ error values extend to 0%. If no error bars are apparent, it is because they are smaller than the width of a bracket as displayed in this figure. Error bars are particularly large for ancient groundwaters, like Kidd Creek, because variations in abiotic CH₄ production rates propagate linearly with respect to fluid mean residence time. The South African samples (blue) typically have higher microbial CH₄ production than the Canadian samples (black), with the notable exceptions of Kloof and Mponeng groundwaters. Finland sites Enonkoski and Ylivieska both have high microbial CH₄ production, while Juuka and Outokumpu have no microbial CH₄ production. The South African samples (blue) typically have higher microbial CH₄ production than the Canadian samples (black), with the notable exceptions of Kloof and Mponeng groundwaters. Finland sites Enonkoski and Ylivieska both have high microbial CH₄ production, while Juuka and Outokumpu have no microbial CH₄ production. An enlarged version of this figure component is shown in Fig. S6. (c) Microbial CH₄ production versus depth for each measured sample at each sample site. 2 σ error bars are shown as lines going through each individual data point. If no line is visible, the 2 σ error is significantly smaller than the size of the plotted datapoint. Error bars are particularly large for ancient groundwaters, like Kidd Creek, because variations in abiotic CH₄ production rates propagate linearly with respect to fluid mean residence time. There is significant (~2 orders of magnitude) variability in microbial CH₄ production rates at individual sampling sites, and significant outliers to the trend (Masimong, Merriespruit, and 1 Driefontein sample). The results here agree well with studies of microbial versus abiotic CH₄ ratios specific to each of these individual sites.

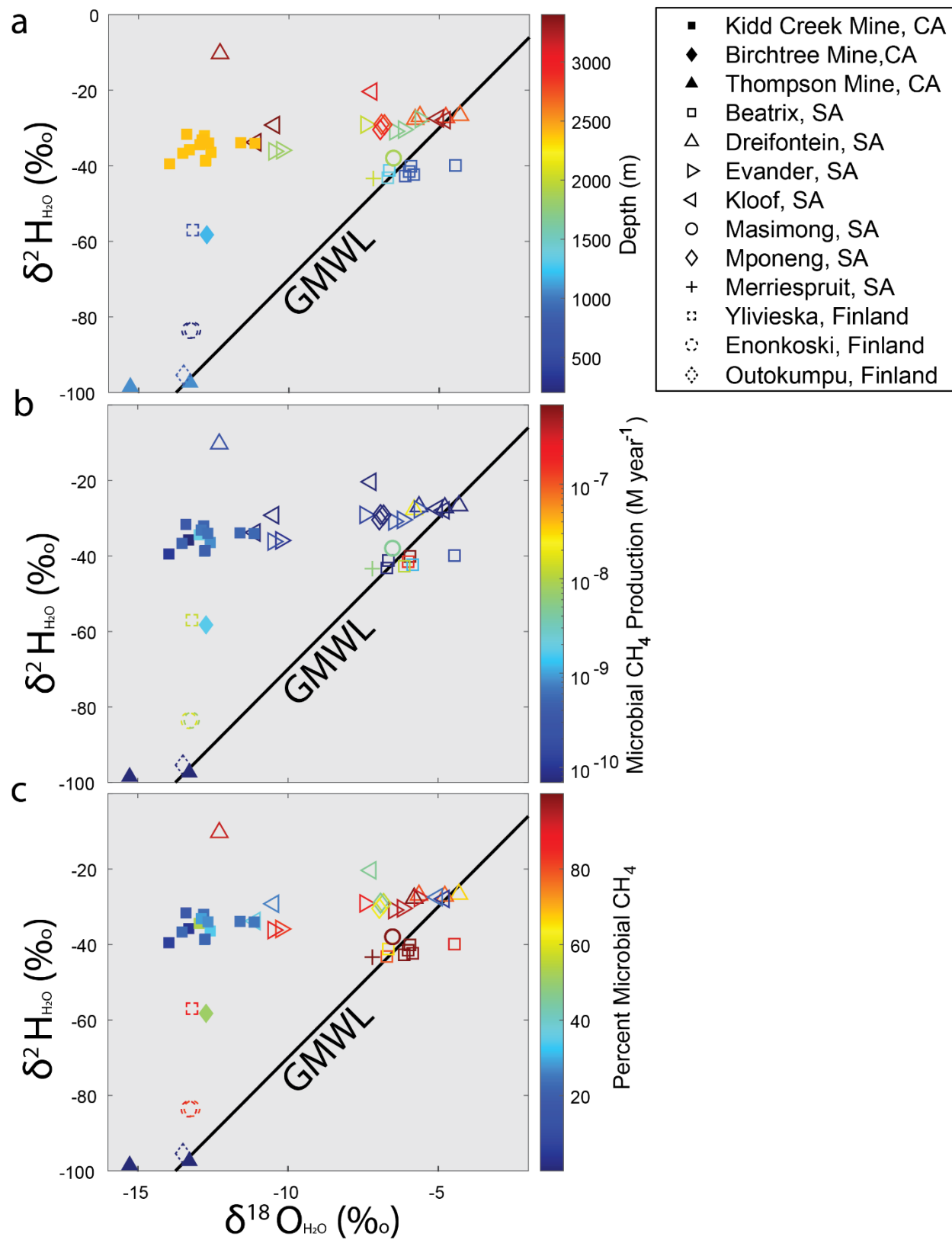


Figure 6 | $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) for water in Canadian Shield, Fennoscandian Shield, and Witwatersrand Basin samples. (a) $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) for Canadian Shield,

Fennoscandian Shield, and Witwatersrand Basin groundwater samples, with datapoints colored by the borehole depth. The black line is the global meteoric water line (GMWL). (b) Isotope data is the same, but the datapoints are colored by the microbial CH_4 production rate calculated by the model used here. (c) Isotope data is the same, but the datapoints are colored by the percent microbial CH_4 calculated by the model used here (Fig. 5b).

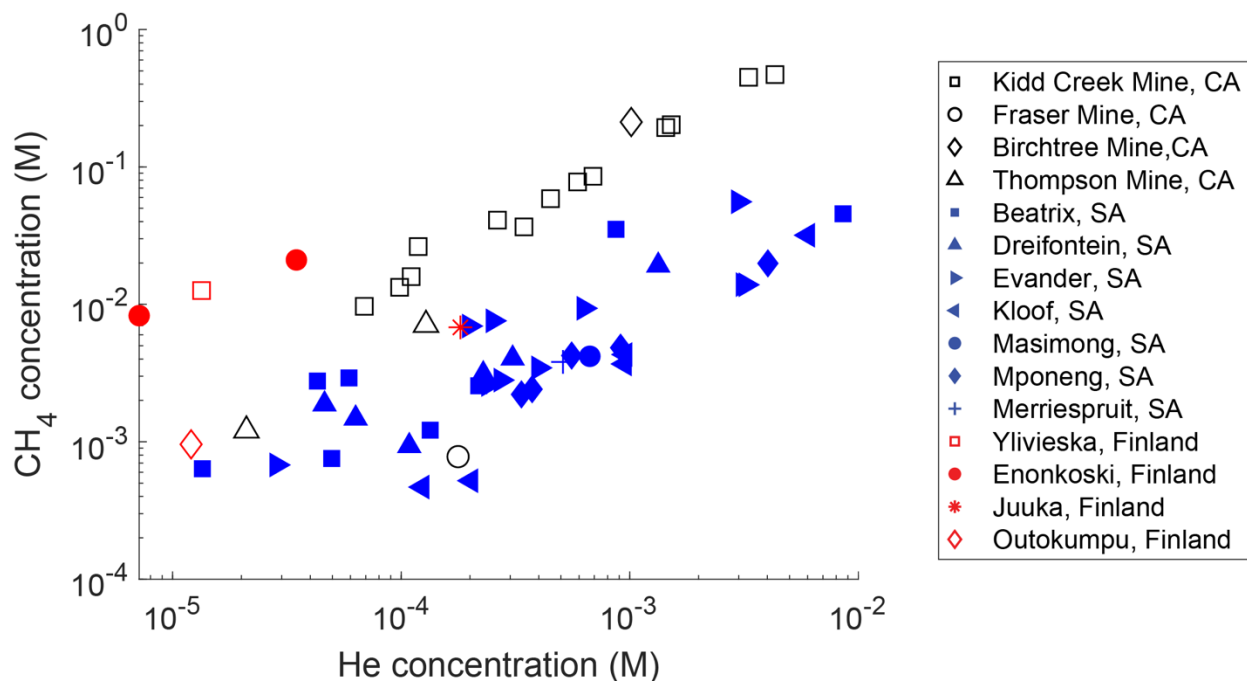


Figure 7 | Dissolved He concentration (M) versus Dissolved CH_4 concentration (M) for each sample at each site. The sample sites in Canada have higher CH_4 concentrations compared to South African sites with similar He concentrations. The reasons for this are likely twofold: 1) South African sites typically have higher radionuclide contents than the Canadian sites, which increases the He production rate. 2) Canadian sites are proximal to more ultramafic lithologies than South African sites, which affects both the availability of H_2 and, perhaps, the amount of substrate available for conditions favorable to CH_4 production via CO_2 reduction by H_2 . The Finland sites show significant spread in their CH_4/He concentrations, but these sites are also all <1 km depth, and Juuka and Outokumpu both fall at the very top of the South Africa trend and near the bottom/middle of the Canadian Shield trend.

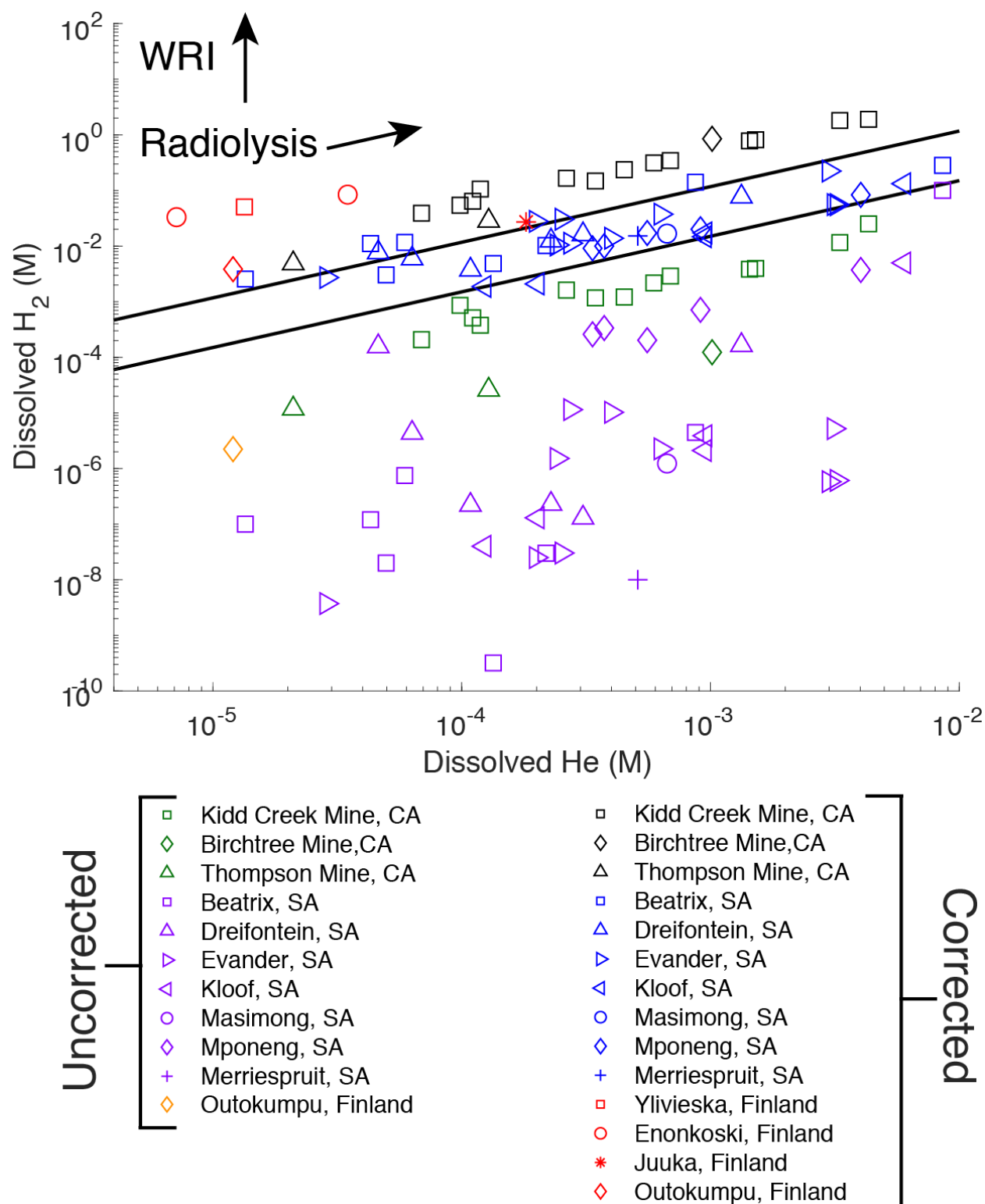


Figure 8 | He concentrations versus reconstructed H_2 concentrations (reconstructed $[H_2] = [H_2] + 4[CH_4]$) for each of the samples used in this study. Black lines show H_2/He ratios from radiolysis of 15 (bottom line) and 117 (top line) which are expected for the Precambrian lithosphere (Sherwood Lollar et al., 2014). H_2 production in South African samples can be

explained purely by radiolysis, while H_2 concentrations in Canadian Shield samples require additional contribution from water rock interactions, as was previously shown by (Warr et al., 2019). There is spread in the Finland samples, but Juuka and Outokumpu fall towards the lower H_2/He part of the Canadian trend, indicating that some water rock interaction is likely necessary to generate these H_2 concentrations.

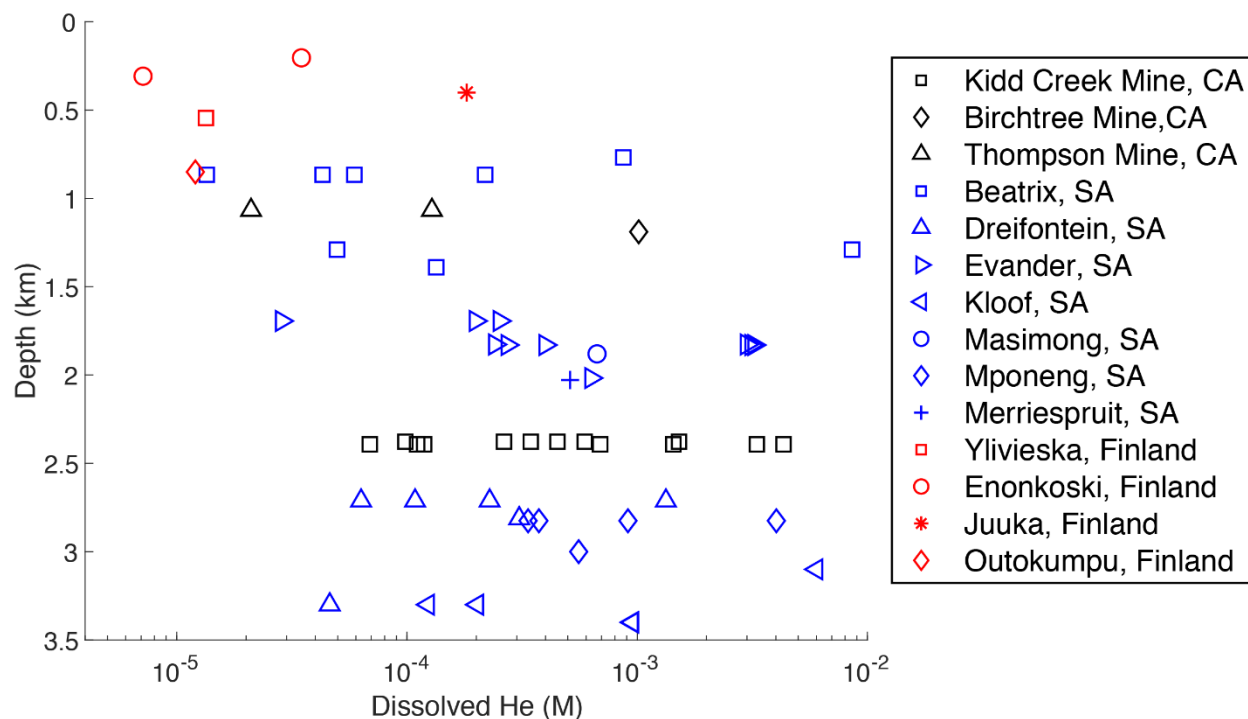


Figure 9 | Dissolved He concentrations versus depth of measurement. There is a general trend of He concentrations increasing with depth, likely due to increased mean residence time with depth, as reported by (Warr et al., 2018). However, there is also significant spread in He concentrations at the same measurement depth, likely due to variations in hydrological connectivity of shallower environments with more meteoric water between the sampled compartmentalized fracture networks.

Tables

Site	U (ppm)	Th (ppm)	K (wt %)	P_{He} mole m ⁻³ year ⁻¹
Upper Witwatersrand Formation	4.7 ^a	10.9 ^a	1.91 ^a	7e-11
Lower Witwatersrand Formation	4.7 ^b	7.3 ^b	1.47 ^b	4e-11
Ventersdorp Supergroup	0.83 ^b	5.2 ^b	1.45 ^b	2.6e-11
Thompson Mine	1.8 ^{c,d}	12.6 ^{c,d}	3.7 ^{c,d}	7e-11
Birchtree Mine	1.8 ^{c,d}	12.6 ^{c,d}	3.7 ^{c,d}	7e-11
Kidd Creek Mine	2 ^{d,e}	9 ^{d,e}	2 ^{d,e}	6e-11
Fennoscandian Shield sites	3 ^{f,g}	9 ^{f,g}	2 ^{f,g}	8e-11

Table 1 | Radionuclide concentrations and calculated He production rates for each site.

^a(Heard et al., 2018), ^b(Lin et al., 2005a), ^c(Zwanzig et al., 2007), ^d(Warr et al., 2019), ^e(Moulton et al., 2011), ^f(Kietäväinen et al., 2014), ^g(Trincherio et al., 2014)

	<i>Estimated H₂ production (moles H₂ per year)</i>	<i>Estimated CH₄ production (moles CH₄ per year)</i>	<i>Reference</i>
<i>Precambrian crust (top 5-km)</i>	$\sim[4-23] \times 10^{10}$	--	Sherwood Lollar et al. (2014)
<i>Precambrian crust (top 10-km)</i>	$[0.4-5.4] \times 10^{10}$	--	Warr et al. (2019)
<i>Precambrian crust abiotic (top 10-km)</i>	--	$\sim[0.08-7.1] \times 10^9$	This study
<i>Precambrian crust microbial (1-10 km depth)</i>	--	$\sim[0.03-4] \times 10^9$	This study
<i>Mid-ocean ridges</i>	$\sim 10^{12}$	--	Worman et al. (2016)
<i>Mid-ocean ridges</i>	$\sim 7 \times 10^{11}$	$\sim[7-12] \times 10^{10}$	Merdith et al. (2020)
<i>Mid-ocean ridges</i>	--	$\sim 1.6 \times 10^{11}$	Emmanuel and Ague, (2007)
<i>Slow-spreading ridges</i>	$\sim 1.67 \times 10^{11}$	$\sim 2.4 \times 10^{11}$	Cannat et al. (2013)
<i>Transform offset faults</i>	$\sim[6.1-10.7] \times 10^{11}$	--	(Rüpke and Hasenclever, 2017)
<i>Oceanic crust</i>	$\sim[0.3-2.0] \times 10^{11}$	--	Canfield et al., (2006); Sleep and Bird, (2007); Kasting and Canfield, (2012)
<i>Oceanic crust</i>	$\sim 4.5 \pm 3.0 \times 10^{11}$	--	Bach & Edwards (2003)

Table 2 | Compilation of H₂ and CH₄ production estimates for settings in the continental and oceanic crusts.

	Canadian Shield	Witwatersrand Basin	Fennoscandian Shield
Abiotic CH ₄ production rate (M year ⁻¹)	$[1.7 \pm 1.1] \times 10^{-9}$	$[1.9 \pm 0.8] \times 10^{-11}$	$[1.8 \pm 0.9] \times 10^{-9}$
$\delta^2 H_{CH_4A}$	-404 ± 53	-407 ± 52	-159 ± 47
$\delta^{13} C_{CH_4A}$	-39 ± 7	-22 ± 5	-33 ± 15
$\delta^2 H_{CH_4B}$	-234 ± 31	-204 ± 40	-324 ± 53
$\delta^{13} C_{CH_4B}$	-58 ± 7	-49 ± 11	-55 ± 9

Table 3 | Results from Markov Chain Monte Carlo application of biogeochemical model to data from each region. Approximate 2σ uncertainties are reported.

Supplementary Tables

Mine	Borehole / Sample Name	H ₂	He	CH ₄	C ₂ H ₆	C ₃ H ₈	$\delta^{13}C_{CH_4}$	$\delta^2H_{CH_4}$	$\delta^{18}O$ (‰)	δ^2H (‰)	Depth (m)	Sources
Beatrix	BE116 FW 031401 IDW	0.1	13.5	637.03	-	-	-48.1	-190	-5.94	-40.13	866	1-4
Beatrix	BE116 GS 031401 EDW	0.75	59.09	2913.51	-	-	-43.5	-214	-6	-41.52	866	1, 2, 3
Beatrix	BE116 H1 031601 GDW	0.12	43	2755.15	5.723	0.306	-51.6	-172	-5.85	-42.33	866	1, 2, 3
Beatrix	BE116 H2 031601 GDW	0.03	218.4	2547.3	2.99	0.388	-52.5	-205	-4.46	-39.91	866	1, 2, 3
Beatrix	BE224 FW 032601C18W 17	4.44	870.31	35165.46	-	-	-47	-231	-6.13	-42.72	768	1-4
Beatrix	BE327 H3 032701 CTS	0.00032	133.94	1211.67	1.172	0.168	-52.8	-195	-6.71	-43.18	1390	2, 3
Beatrix	BE325 GS 032701 CTS	-	8571.83	45420.98	84.263	6.444	-50.5	-172	-6.66	-41.2	1290	2, 3
Beatrix	BE325 H1 032701 CTS	0.02	49.69	751.72	1.821	0.204	-52.5	-184	--	--	1290	2, 3
E. Driefontein	DR548 FW 090901	156.6	46.19	1678.47	88.635	6.263	-47.6	-403	-12.29	-10.3	3300	3-5
W. Driefontein	DR938 CH 091202	0.23	228.58	2911.36	79.066	12.69	-46	-255	--	--	2712	3, 5
W. Driefontein	DR938 H1 082001	0.22	108.45	876.71	23.652	2.706	-53.6	-295	-4.31	-26.67	2712	3, 5
Driefontein	DR938 H3 110701	164.74	1332.22	17492.21	731.687	73.006	-40.2	-368	-5.64	-26.93	2712	3-5
W. Driefontein	DR938 H3 071202	4.36	63.2	1462.01	-	5.845	-42.3	-369	-5.8	-27.71	2712	3-5
W. Driefontein	DR940 FW 092602	0.13	307.32	3740.54	126.821	15.542	-47.8	-293	-4.78	-27.2	2812	3, 5

Evander	EV522 FW 030801HWD	0.0037 3	28.53	654.81	11.628	0.128	-47.6	-162	- 5.63	- 27.6 7	1694	1, 3
Evander	EV522 H1 041801CTS	0.0250 6	198.35	6313.96	278.513	26.273	-43	-264	- 6.48	- 30.8 6	1694	1, 3, 4
Evander	EV522 H2 041801CTS	0.0302 4	251.96	6863.74	317.569	29.835	-44.5	-261	- 6.19	- 30.4 2	1694	1, 3, 4
Evander	EV818 FW 030601 FBH	1.52	240.83	2350.44	117.385	8.906	-40.7	-281	- 10.2 4	- 35.8 9	1827	3, 4
Evander	EV818 FW 051001 FBH	0.58	2983.5 5	50401.3 8	2364.61 3	211.67 8	-41.4	-280	- 10.5	- 36.1 8	1827	3, 6
Evander	EV818 H5 102702	10.25	398.46	3234.11	98.789	6.163	-46.6	-316	--	--	1830	3, 4
Evander	EV818 H5 102502	11.45	272.67	2624.19	87.218	3.554	-44.3	-332	--	--	1830	3, 4
Evander	EV818H6 102702	0.61	3216.4 2	12958.5 1	461.792	-	-44.6	-328	--	--	1830	3, 4
Evander	EV 818 H6 111502	5.21	3126.0 8	12880.6 5	472.094	29.941	-44.4	-268	--	--	1830	3, 6
Evander	EV821 FW 101601	2.26	629.67	7701.03	694.043	90.311	-39.5	-301	- 7.44	- 29.1 2	2017	3, 6
Kloof	KL441 HWDS H2 050201	0.13	202.12	494.56	11.666	0.962	-37.8	-257	-4.8	- 27.9 1	3300	3-5
Kloof	KL441 HWDS H3 111401	0.04	123.63	437.8	14.046	0.772	-40	-253	- 5.03	- 27.4 6	3300	3, 5
Kloof	KL443 HWDN FW 030501	2.11	949.52	3389.2	123.685	15.896	-36.7	-324	- 10.4 8	- 29.2 1	3400	1, 3, 4
Kloof	KL443 HWDN FW 050801	3.89	955.06	3987.58	141.615	14.491	-33.7	-333	- 11.1	- 33.7 8	3400	1, 3, 4
Kloof	KL739 FW 062901	4975.5 1	6011.3	29725.6 9	917.293	91.173	-28.7	-300	- 7.24	- 20.3 5	3100	3-5
Masimon g	MM51870 FW 030402	1.23	669.04	4141.62	22.853	-	-60.3	-207	- 6.52	- 37.9 6	1880	2, 3
Mponeng	MP104 E65XC H1 091602	259	335.74	1851.1	150.153	20.173	-31.6	-364	- 6.82	- 29.1 3	2825	3, 4
Mponeng	MP104 E65XC H1 091902	336	374.05	2012.49	166.512	22.595	-31.7	-367	--	--	2825	3, 4
Mponeng	MP104 E65XC H1 092702	711.7	911.57	4032.13	331.146	47.807	-32.8	-366	- 6.92	- 29.0 5	2825	3-5

Mponeng	MP104 E65XC H1 110902	3714	4020.8 3	16598.6 4	1346.20 7	191.98 7	-33.2	-390	--	--	2825	3, 4
Mponeng	MP109 FW 101701	202.84	556.89	3805.56	179.959	24.792	-27.8	-349	- 6.96	- 30.4 4	3000	3, 5
Merrispruit	MS151 FW 022202	0.01	510.65	3767.77	21.826	-	-53.7	-194	- 7.19	- 43.3 5	2028	2, 3

Supplementary Table 1 | Witwatersrand Basin data.

Measured gas abundances are in μM

$\delta^2H_{CH_4}$ is in ‰VSMOW

$\delta^{13}C_{CH_4}$ is in ‰VPDB

1 is Ward et al. (2004)

2 is (Lin et al., 2006a)

3 is (Onstott et al., 2006a)

4 is (Lin et al., 2005a)

5 is (Sherwood Lollar et al., 2006)

6 means some measurements are unpublished

Mine	Borehole / Sample Name	Water Flow	Gas Flow	H ₂	He	CH ₄	C ₂ H ₆	C ₃ H ₈	$\delta^{13}C_{CH_4}$	$\delta^2H_{CH_4}$	$\delta^{18}O$ (‰)	δ^2H (‰)	Depth (m)	Source
Kidd Creek	10.05.2007_KC7850_Station_12262	0.214	11.1	8.37	2.91	69.1	5.82	0.67	-39.6	-394	-13.97	-39.5	2392.68	1, 2
Kidd Creek	27.08.2007_KC_7800_Station_12287A	0.079	0.11	10.67	2.47	72.17	6.56	0.61	-40.8	-383	-12.78	-38.7	2377.44	1, 2
Kidd Creek	11.02.2008_KC_7800_RR_12299	0.7	3	6.52	2.15	71.98	6.86	0.45	-38.8	-392	-12.59	-36.45	2377.44	1
Kidd Creek	11.02.2008_KC_7800-RR_12261	0.003	0.065	3.16	2.45	72.15	6.05	0.4	-40.3	-391	-12.81	-32.03	2377.44	1
Kidd Creek	19.06.2008_KC_7850_RR_12299	0.4	2.6	3.23	2.42	67.7	6.1	0.79	-38.6	-388	-12.76	-38.55	2377.44	1
Kidd Creek	Mar31.2009_KC_L7850_12299	0.28	1.175	4.82	2.87	64.37	6.61	0.52	-39.8	-389	-13.31	-35.78	2377.44	1, 3
Kidd Creek	12.01.2010_KC_7850_RR_12299	0.172	1.4	4.62	2.54	71.49	6.47	0.85	-38.7	-384	-13.53	-36.68	2377.44	1, 2
Kidd Creek	20.09.2013_KC_7850_BH12299	0.25	2.25	5.55	2.68	70.6	6.64	0.82	-41.3	-393	-13.4	-31.65	2392.68	1
Kidd Creek	02.04.2014_KC_7850_BH12299	0.12	0.3	2.62	1.66	77.64	7.52	0.99	-39.7	-380	-12.96	-34.42	2392.68	1
Kidd Creek	03.04.2014_KC_7850_BH12299	0.18	0.3	5.33	2.32	70.64	6.66	0.93	-39.7	-388	-12.89	-33.14	2392.68	1
Kidd Creek	12.07.2016_KCL7850_BH12299	0.116	0.115	3.63	2.43	71.89	6.97	0.93	-39.1	-393	-12.67	-34	2392.68	1
Kidd Creek	06.06.2017_KCL7850_BH12299	0.1268	5.9375	4.29	2.47	70.73	6.77	0.96	-39.1	-393	-11.13	-34.05	2392.68	1
Kidd Creek	06.06.2017_KCL7850_BH12261	0.1338	2.7285	3.26	2.46	70.94	6.43	0.88	-38.2	-406	-11.6	-33.9	2392.68	1
Thompson	1163630 13.06.06	0.03	0.045	0.3	2.99	36.6	2.9	0.29	-46.5	-301	-13.29	-97.39	1066.8	1, 4
Thompson	1163930 14.06.06	0.03	0.0067	0.92	3.29	43.83	2.72	0.23	-48.4	-305	-15.275	-98.475	1066.8	1, 4
Birchtree	27.03.2008_BT_3950_9167N_BT1	0.045	1.2	0.08	1.33	62.92	4.69	0.24	-49.1	-334	-12.73	-58.26	1066.8	1
Fraser	06.03.2014_FML4700_FR47774	2.83	1.13	0	15.52	18.44	0.1	0	-32.6	-314	--	--	1432.56	1

Supplementary Table 2 | Canadian Shield Data.

Measured gas abundances are in vol %

Water and gas flow rates are in (L/min)

$\delta^2H_{CH_4}$ is in ‰VSMOW

$\delta^{13}C_{CH_4}$ is in ‰VPDB

1 is Warr et al. (2019)

2 is Li et al., (2016)

3 is (Sherwood Lollar et al., 1993b)

4 is Telling et al. (2018)

5 is (Sherwood Lollar et al., 2002)

Site name	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	He	Depth (m)	$\delta^{13}\text{C}_{\text{CH}_4}$ ‰ VPDB	$\delta^2\text{H}_{\text{CH}_4}$ ‰ VSMOW	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Source
Ylivieska	-	206.5	30.1	5.26	0.3	545	-45.5	-340	-13.2	-340	1, 3
Enonkoski	-	416.5	25.5	1.33	0.78	204	-65.9	-320	-13.2	-320	1, 3
Enonkoski	-	142.3	8.69	8.6	0.16	308	-66.9	-297	-13.3	-297	1, 3
Juuka	-	148.33	2.05	-	4.07	401	-28.5	-241	--	-241	2, 3
Outokumpu	0.05	21.24	0.12	-	0.27	850	-22.4	-200	-13.5	-200	2, 3

Supplementary Table 3 | Fennoscandian Shield data.

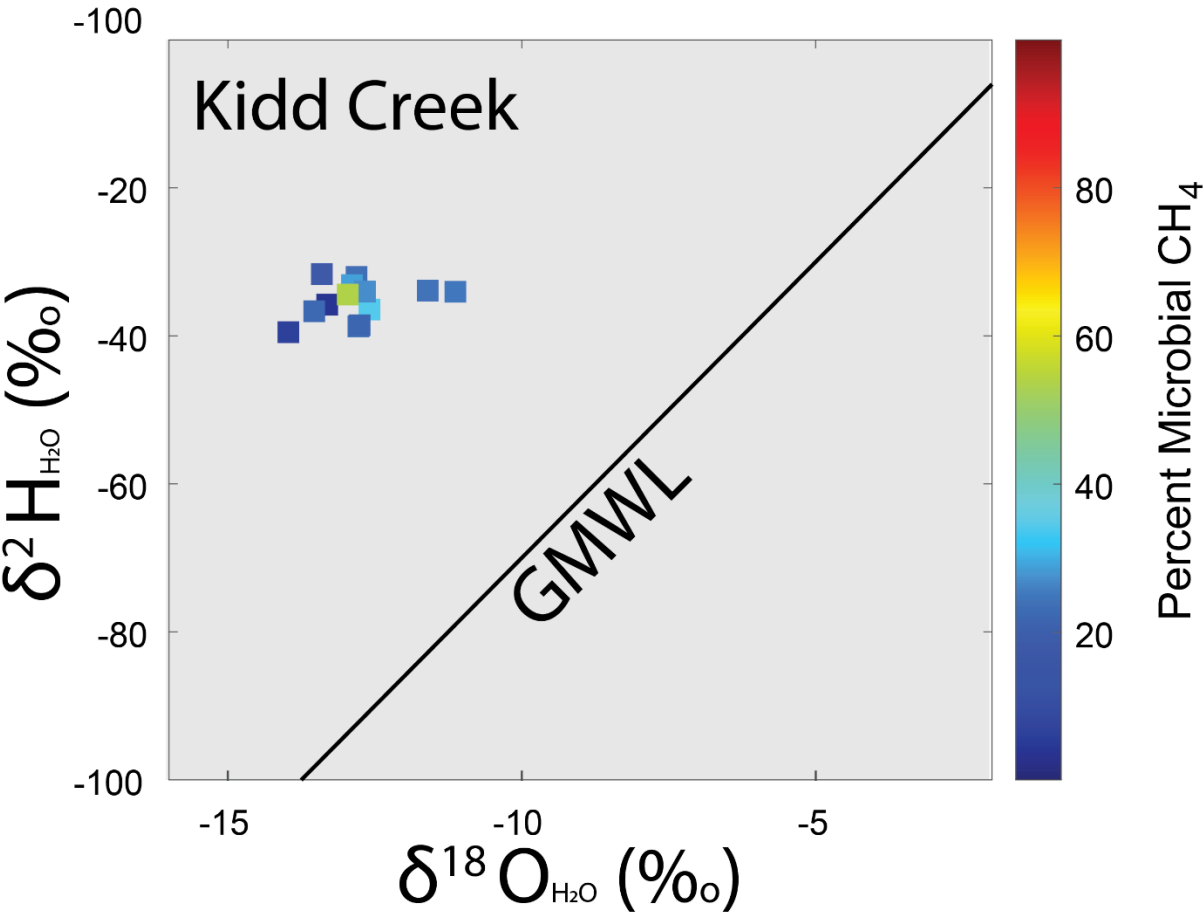
Measured gas concentrations are in (cc(STP)_{gas}/kg_{fluid}).

1 is (Sherwood Lollar et al., 1993a)

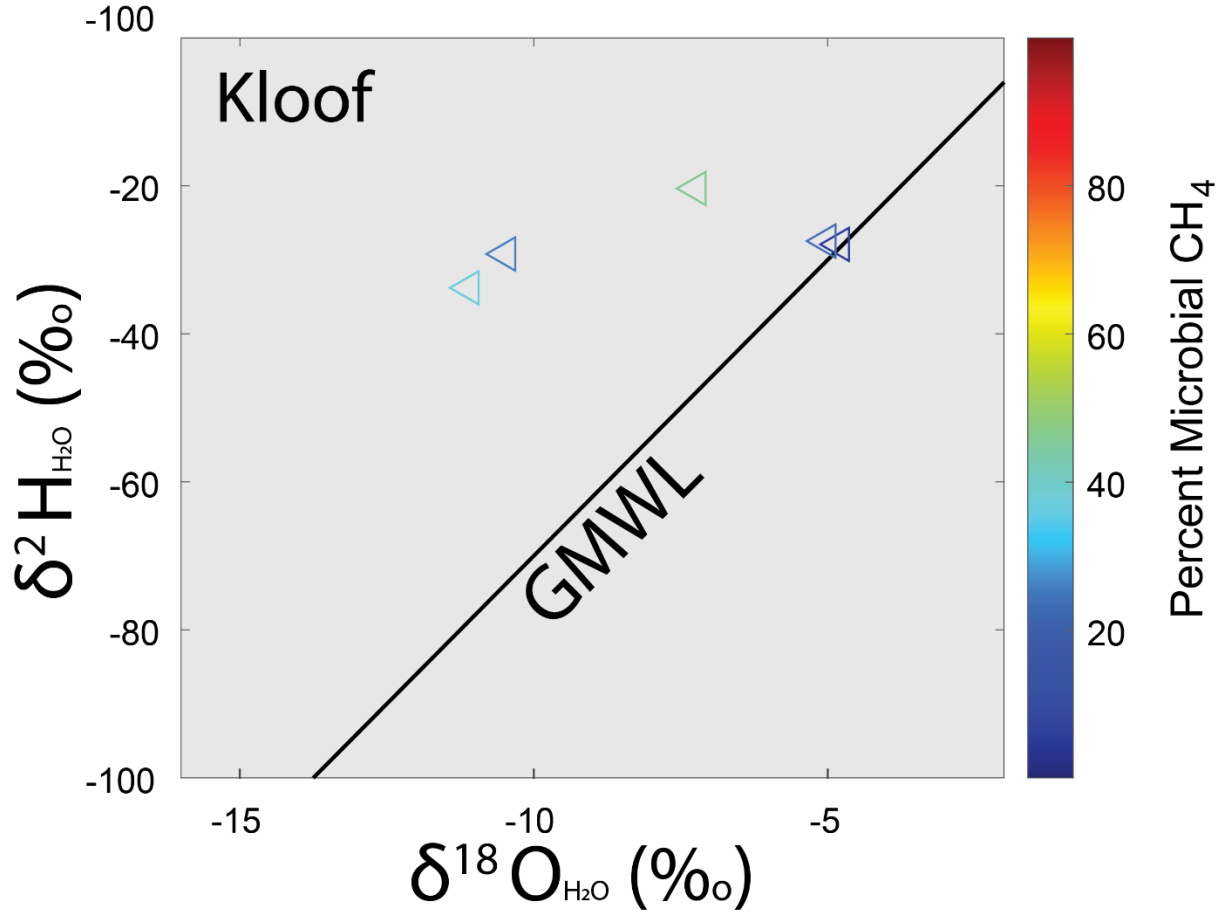
2 is (Sherwood Lollar et al., 1993b)

3 is this study

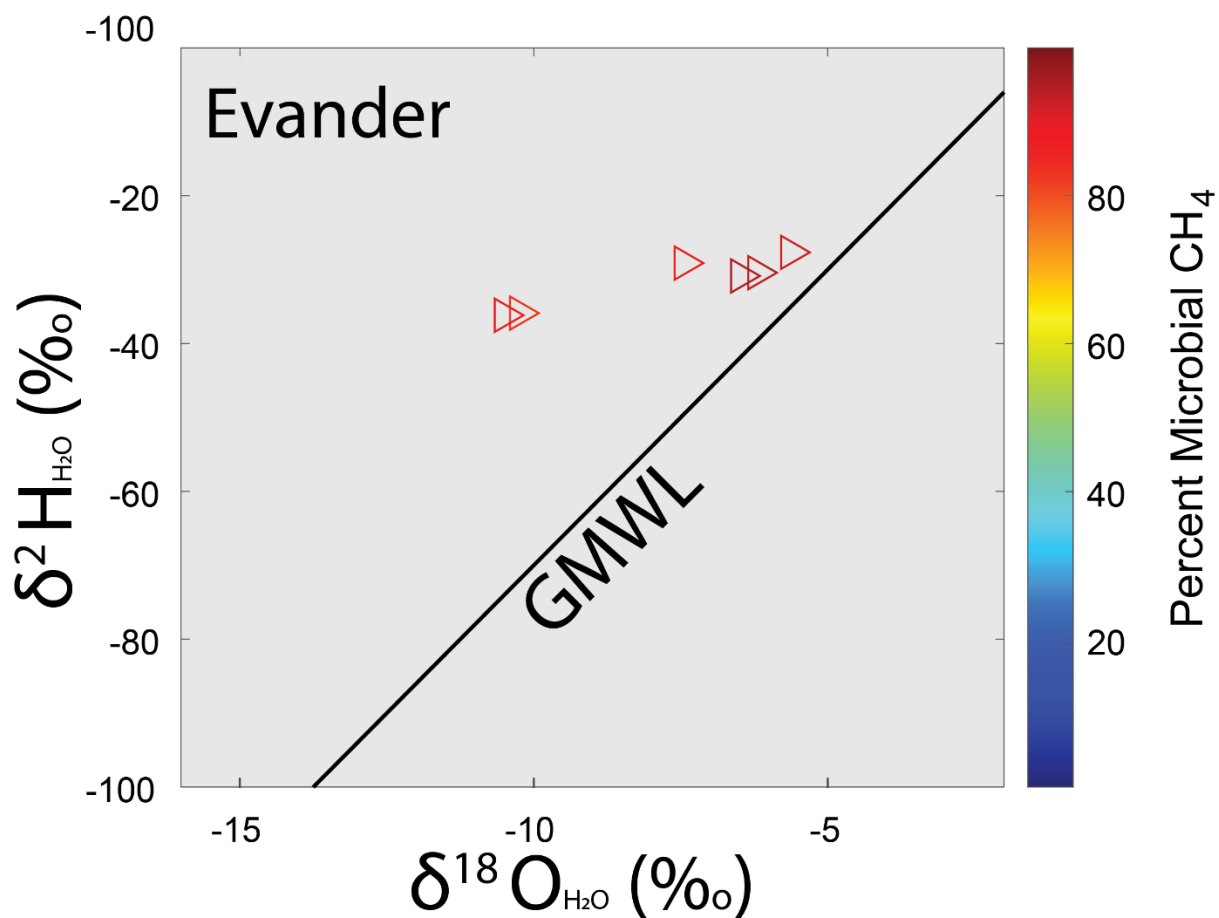
Supplementary figures



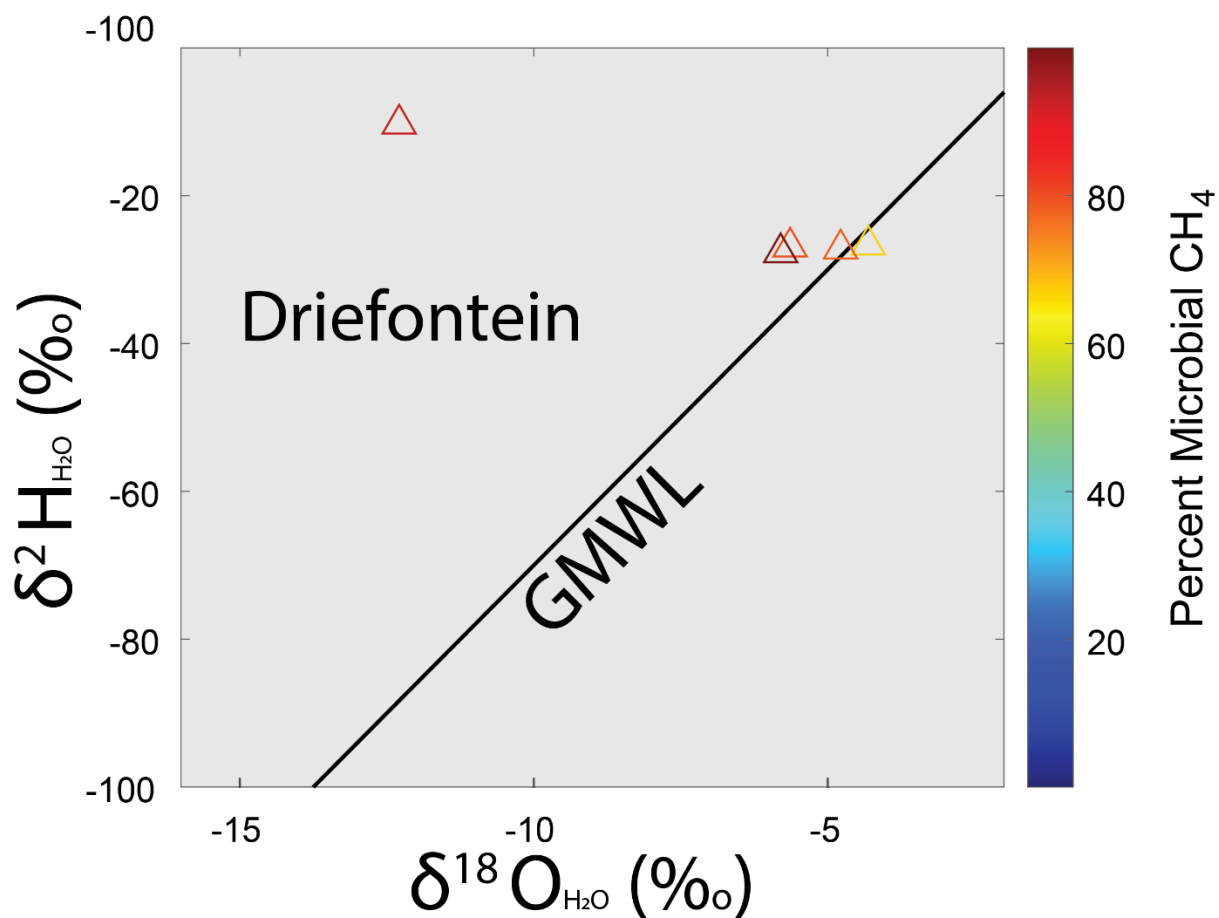
Supplementary Figure 1 | $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) for Kidd Creek Mine groundwater samples. The data point with the highest percent of microbial CH_4 has an intermediate $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) isotopic value between the site's isotopic endmembers closest and furthest from the Global Meteoric Water Line (GMWL).



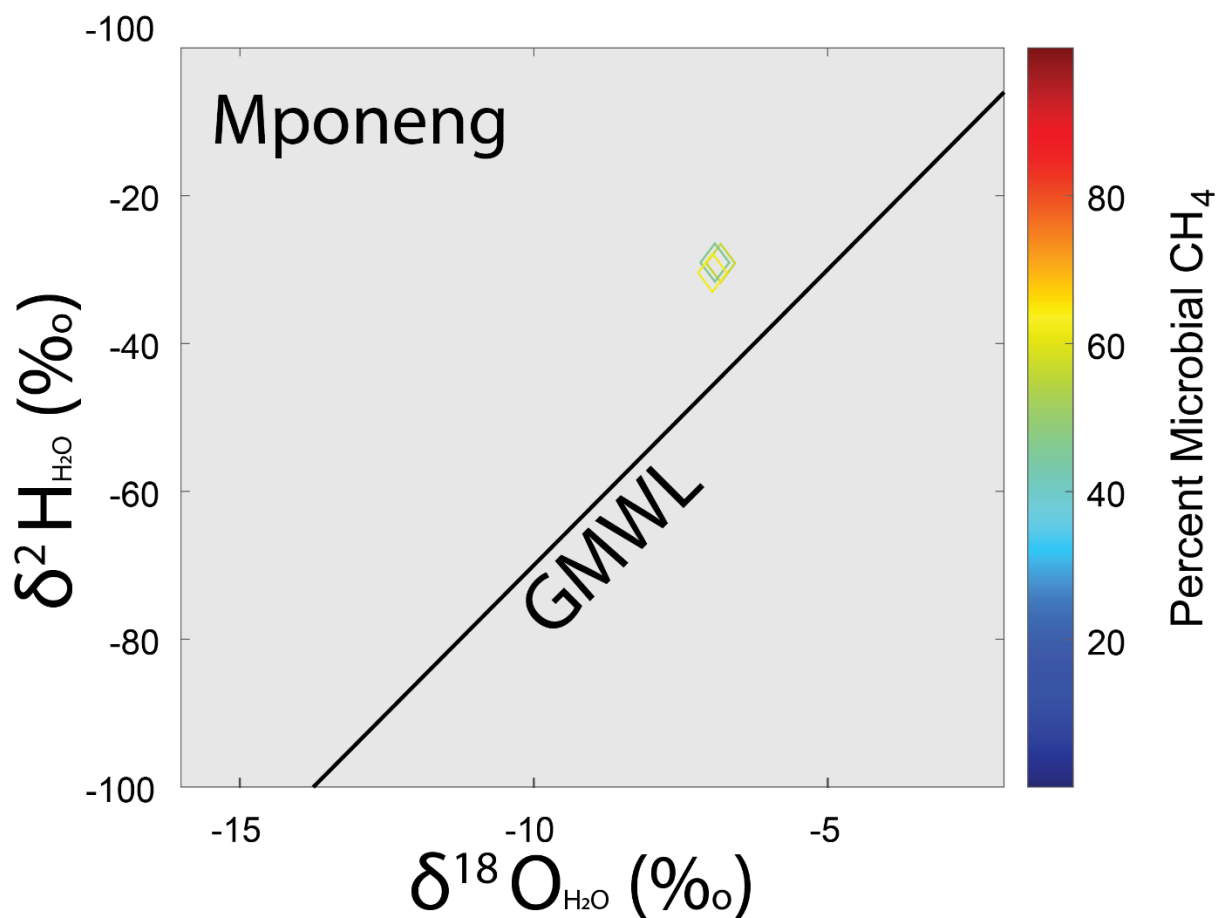
Supplementary Figure 2 | $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) for Kloof Mine groundwater samples. The data point with the highest percent of microbial CH_4 has an intermediate $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) isotopic value between the site's isotopic endmembers closest and furthest from the Global Meteoric Water Line (GMWL).



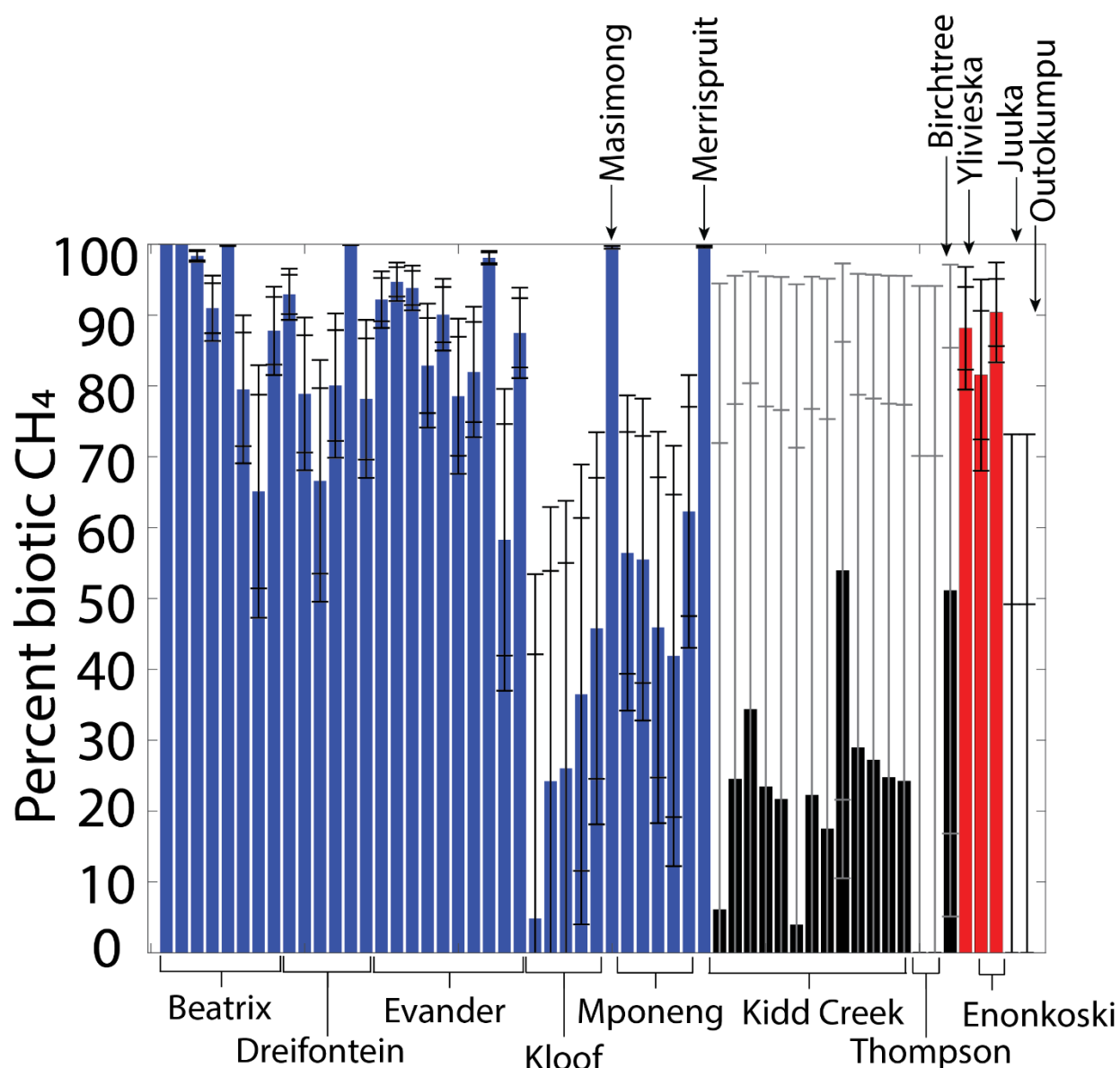
Supplementary Figure 3 | $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) for Evander Mine groundwater samples. The data point with the highest percent of microbial CH_4 has an intermediate $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) isotopic value between the site's isotopic endmembers closest and furthest from the Global Meteoric Water Line (GMWL).



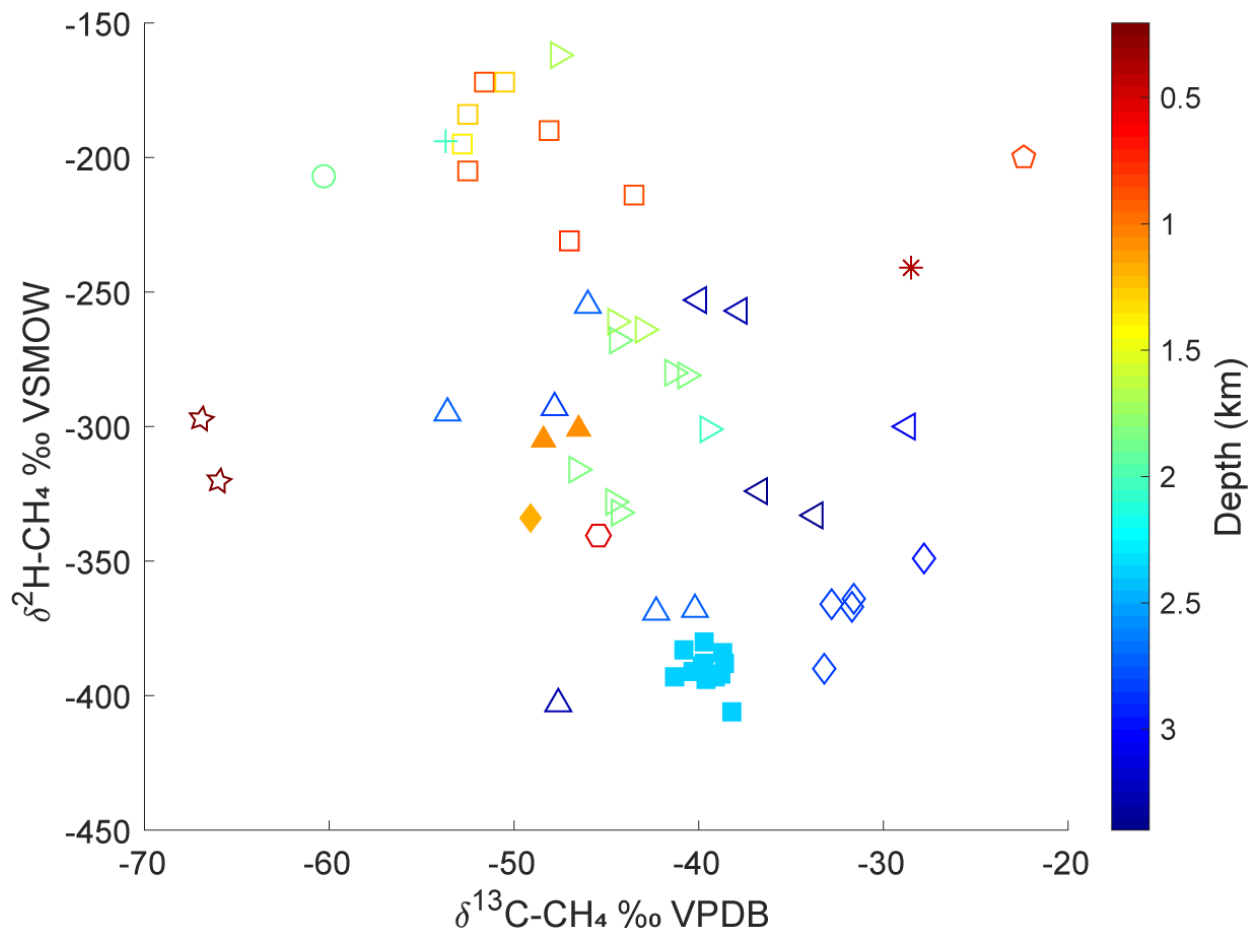
Supplementary Figure 4 | $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) for Driefontein Mine groundwater samples. The data point with the highest percent of microbial CH_4 has an intermediate $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) isotopic value between the site's isotopic endmembers closest and furthest from the Global Meteoric Water Line (GMWL).



Supplementary Figure 5 | $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) for Mponeng Mine groundwater samples. The data point with the highest percent of microbial CH_4 has an intermediate $\delta^{18}\text{O}$ (‰) versus $\delta^2\text{H}$ (‰) isotopic value between the site's isotopic endmembers closest and furthest from the Global Meteoric Water Line (GMWL).



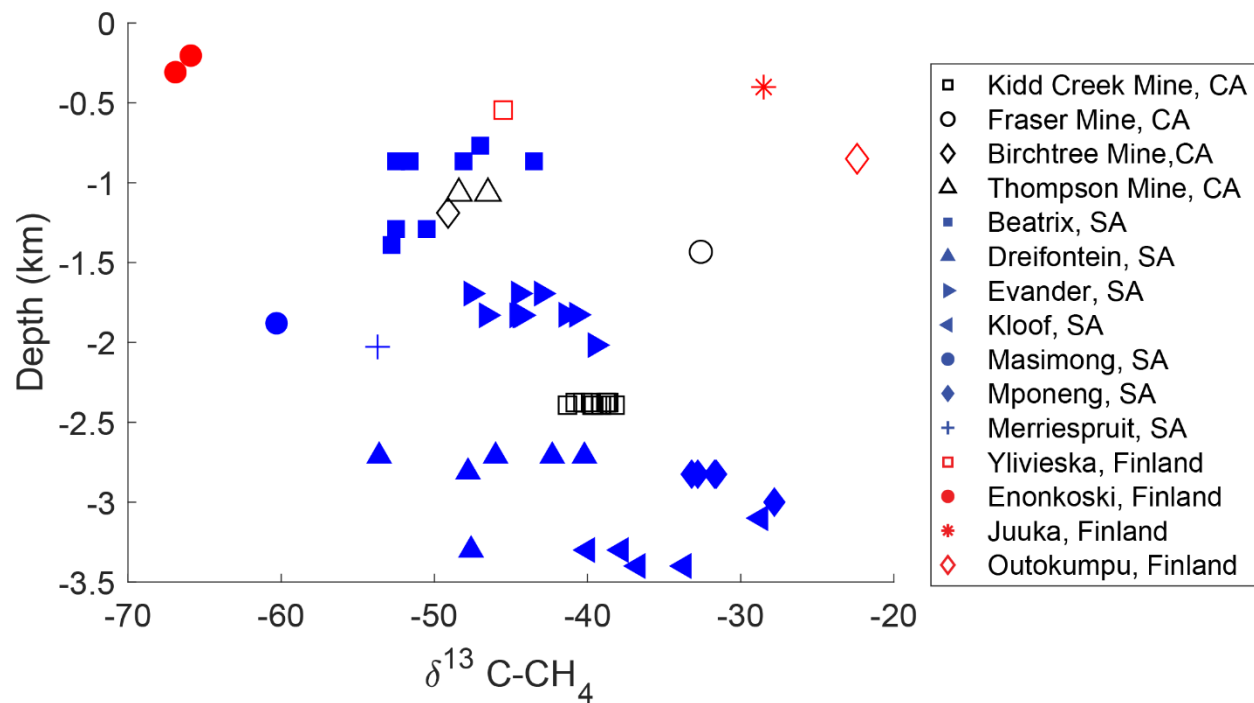
Supplementary Figure 6 | Histogram of percent microbial CH_4 in each groundwater sample, with 1σ and 2σ uncertainties shown (enlarged view of Fig. 5b). The 1σ and 2σ error bars are shown, with 1σ being the innermost brackets, and 2σ being the outermost. If bottom brackets are not shown, that is because the 1σ or 2σ error values extend to 0%. If no error bars are apparent, it is because they are smaller than the width of a bracket as displayed in this figure. Error bars are particularly large for ancient groundwaters, like Kidd Creek, because variations in abiotic CH_4 production rates propagate linearly with respect to fluid mean residence time. The South African samples (blue) typically have higher microbial CH_4 production than the Canadian samples (black), with the notable exceptions of Kloof and Mponeng groundwaters. Finland sites Enonkoski and Ylivieska both have high microbial CH_4 production, while Juuka and Outokumpu have no microbial CH_4 production.



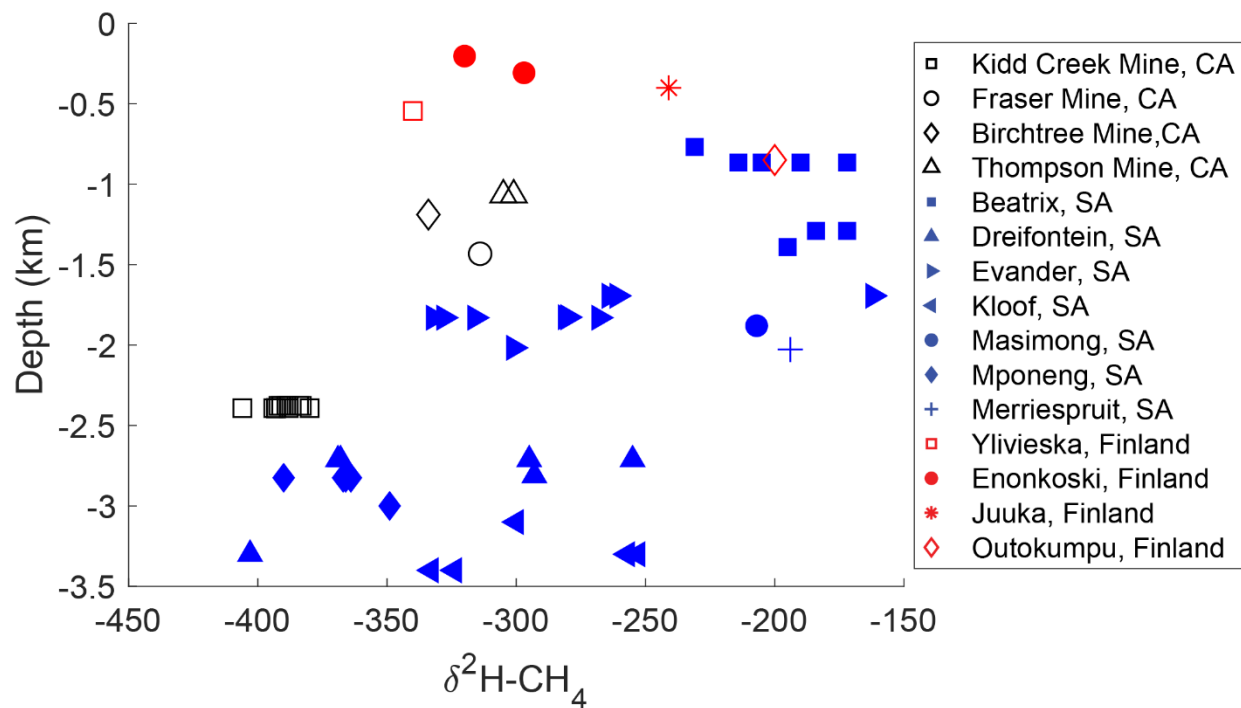
- Kidd Creek Mine, CA
- ◆ Birchtree Mine, CA
- ▲ Thompson Mine, CA
- Beatrix, SA
- ▲ Dreifontein, SA
- Evander, SA
- ◄ Kloof, SA
- Masimong, SA
- ◆ Mponeng, SA
- + Merriespruit, SA
- Ylivieska, Finland
- ★ Enonkoski, Finland
- * Juuka, Finland
- ◆ Outokumpu, Finland

Supplementary Figure 7 | $\delta^{13}\text{C-CH}_4$ ‰ VPDB versus $\delta^2\text{H-CH}_4$ ‰ VSMOW for CH_4 from each sample at each site, with datapoints colored by depth of measurement. There does not

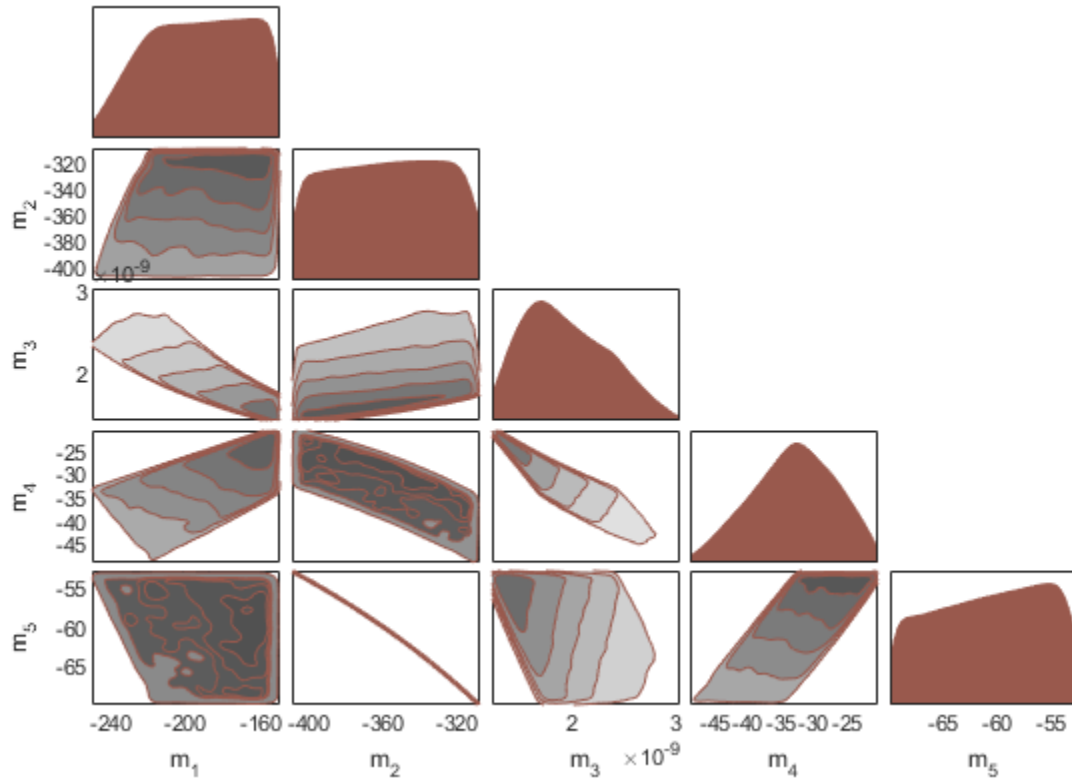
appear to be a clear global trend between stable isotope values of CH₄ and depth of measurement.



Supplementary Figure 8 | $\delta^{13}\text{C-CH}_4$ versus depth for each sample at each site. There is a weak trend between $\delta^{13}\text{C-CH}_4$ and depth.

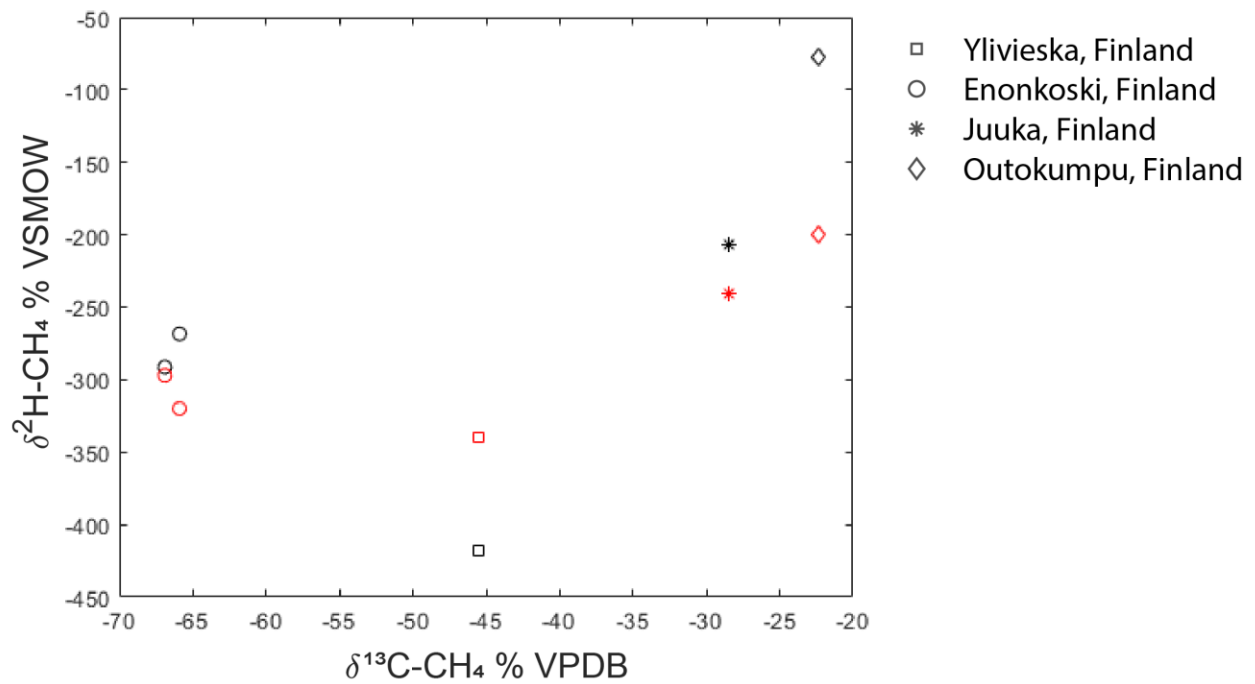


Supplementary Figure 9 | $\delta^2\text{H-CH}_4$ versus depth for each sample at each site. There is no significant trend between $\delta^2\text{H-CH}_4$ and depth.

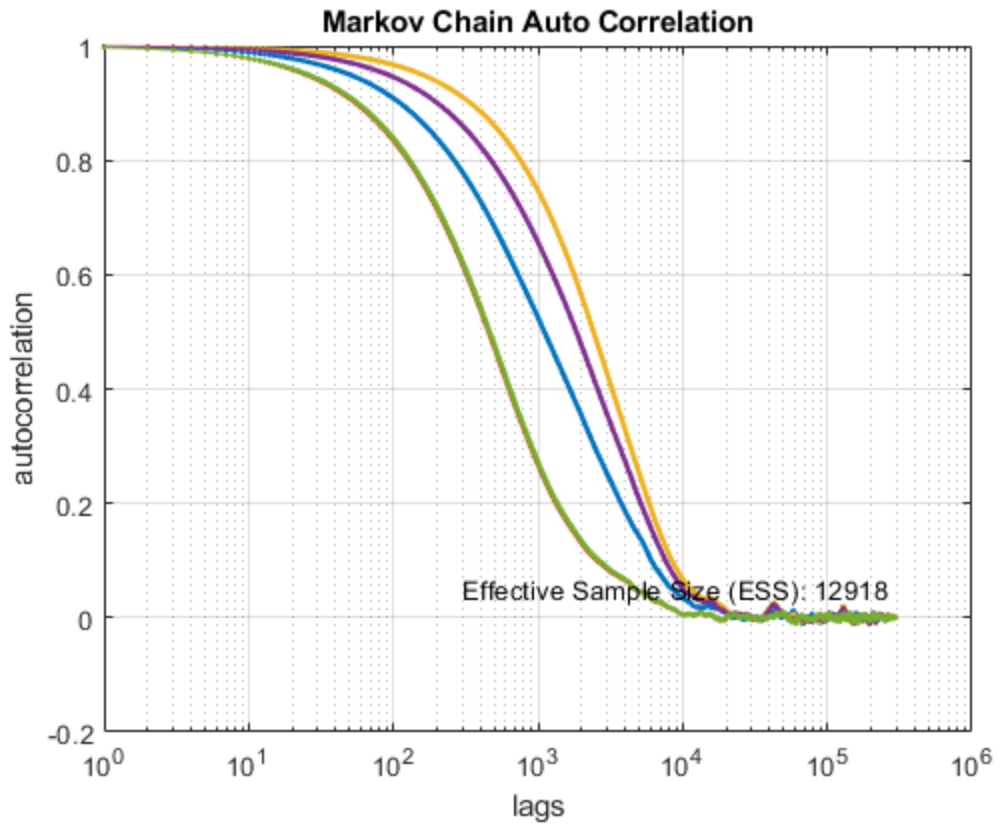


Supplementary Figure 10 | MCMC best fit parameter outputs for Fennoscandian Shield data.

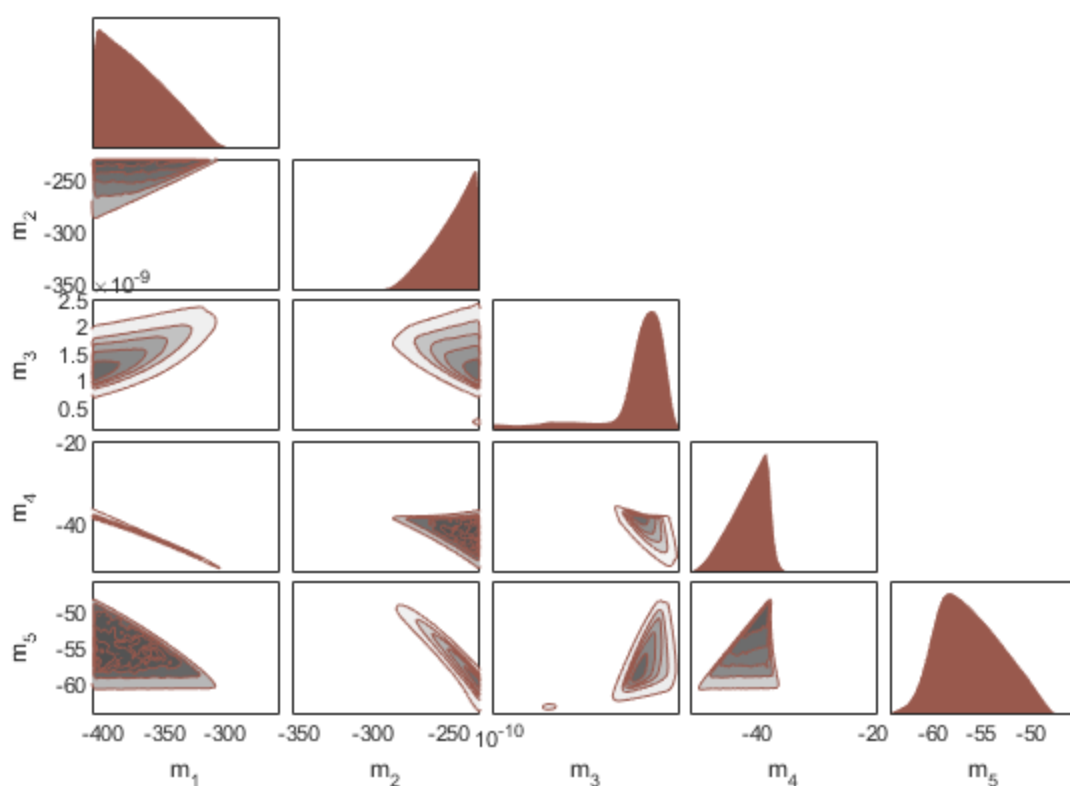
m_1 is abiotic $\delta^2\text{H-CH}_4$ endmember, m_2 is microbial $\delta^2\text{H-CH}_4$ endmember, m_3 is abiotic CH_4 production rate (M year^{-1}), m_4 is abiotic $\delta^{13}\text{C-CH}_4$, and m_5 is microbial $\delta^{13}\text{C-CH}_4$ endmember.



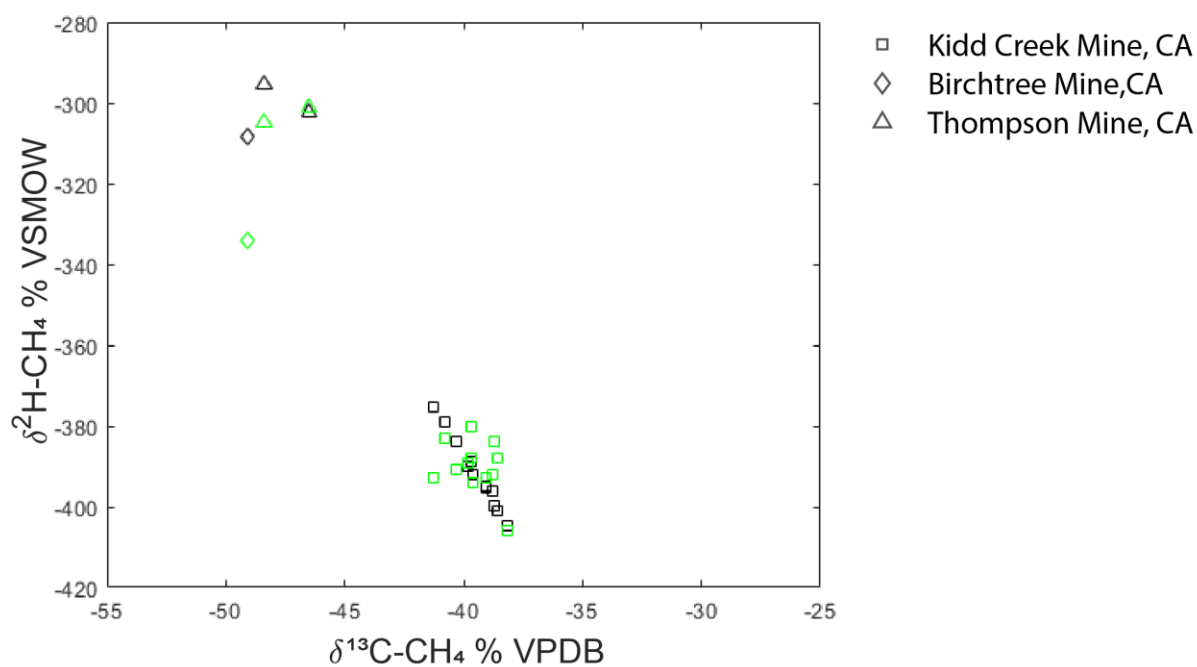
Supplementary Figure 11 | Best fit model to Fennoscandian Shield isotopic data from median values of MCMC best fit parameters. The measured values are plotted in red and modeled values are plotted in black. These black datapoints are generated by inputting the measured He and CH₄ concentrations, P_{He} values, and median parameter values computed by the MCMC for the abiotic $\delta^2\text{H-CH}_4$ endmember, the microbial $\delta^2\text{H-CH}_4$ endmember, the abiotic CH₄ production rate (M year^{-1}), the abiotic $\delta^{13}\text{C-CH}_4$, and the microbial $\delta^{13}\text{C-CH}_4$ endmember into equations 6 and 7.



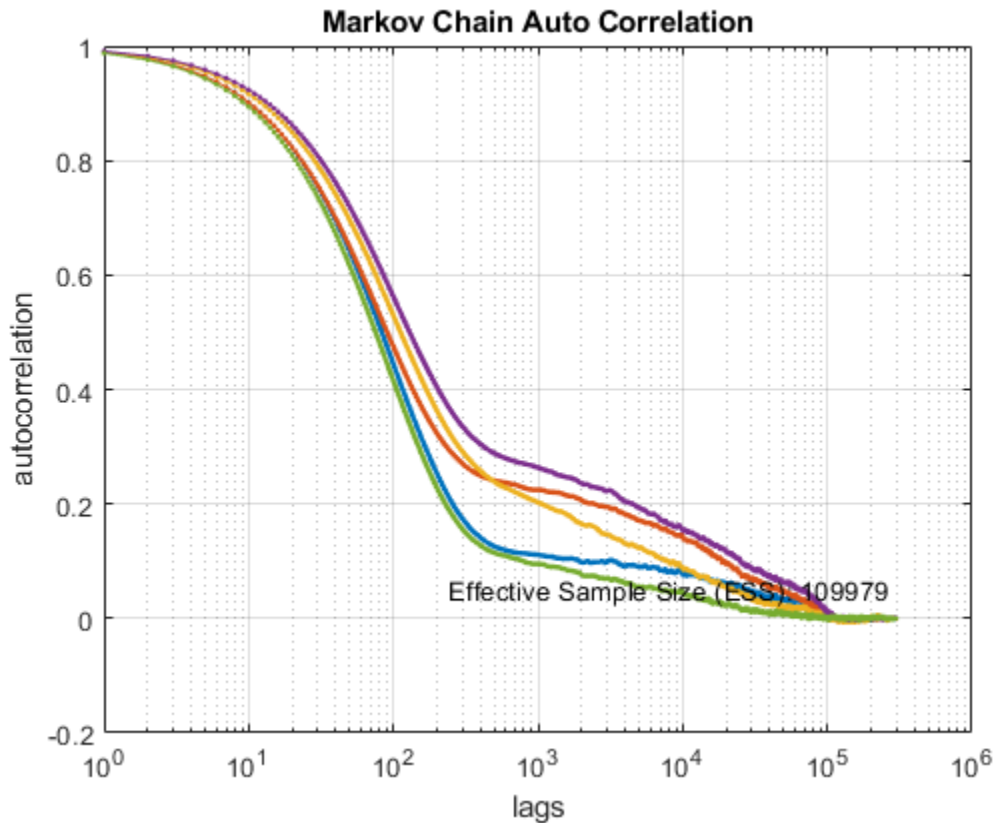
Supplementary Figure 12 | Autocorrelation between MCMC free parameters m_{1-5} with respect to steps progressed by MCMC for the Fennoscandian Shield model. The free parameters show an autocorrelation close to zero by the end of the MCMC run.



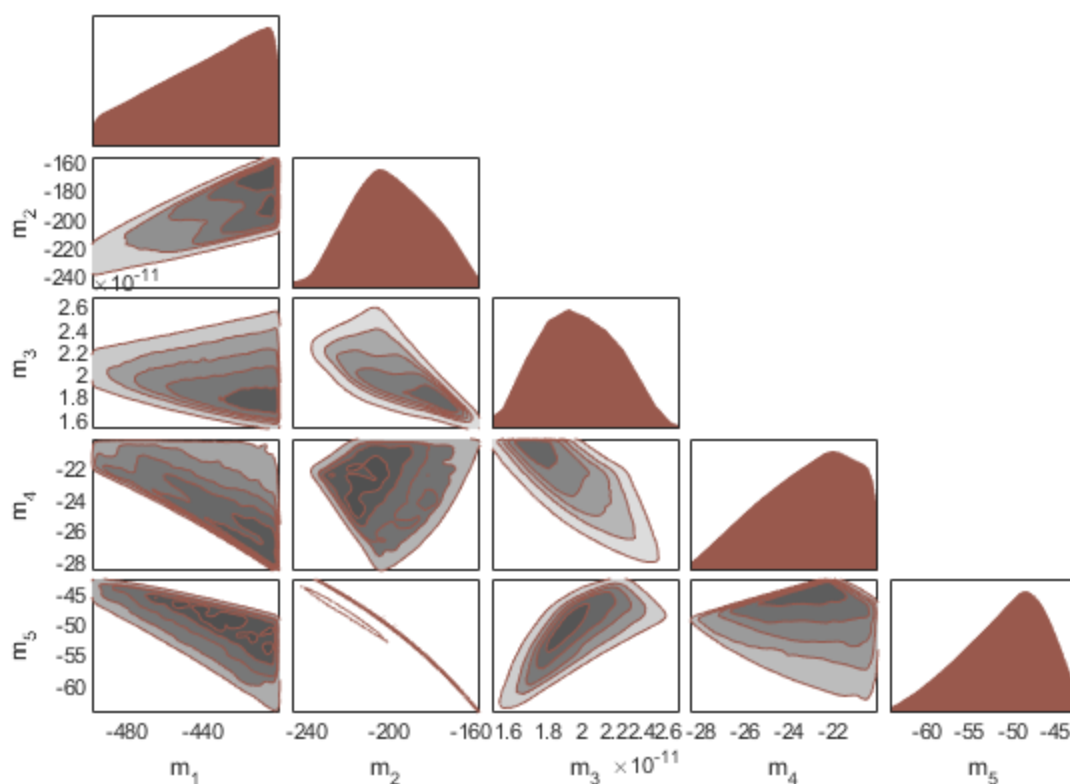
Supplementary Figure 13 | | MCMC best fit parameter outputs for Canadian Shield data. m_1 is abiotic $\delta^2\text{H-CH}_4$ endmember, m_2 is microbial $\delta^2\text{H-CH}_4$ endmember, m_3 is abiotic CH_4 production rate (M year^{-1}), m_4 is abiotic $\delta^{13}\text{C-CH}_4$, and m_5 is microbial $\delta^{13}\text{C-CH}_4$ endmember.



Supplementary Figure 14 | Best fit model to Canadian Shield isotopic data from median values of MCMC best fit parameters. The measured values are plotted in green and modeled values are plotted in black. These black datapoints are generated by inputting the measured He and CH₄ concentrations, P_{He} values, and median parameter values computed by the MCMC for the abiotic $\delta^2\text{H-CH}_4$ endmember, the microbial $\delta^2\text{H-CH}_4$ endmember, the abiotic CH₄ production rate (M year^{-1}), the abiotic $\delta^{13}\text{C-CH}_4$, and the microbial $\delta^{13}\text{C-CH}_4$ endmember into equations 6 and 7.

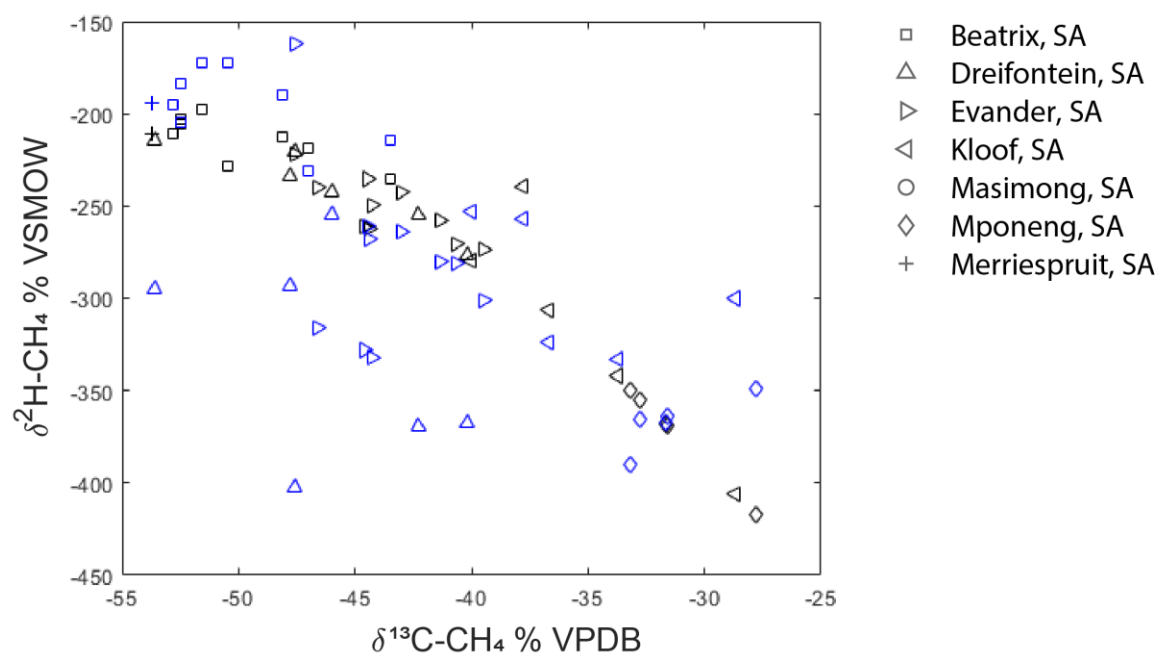


Supplementary Figure 15 | Autocorrelation between MCMC free parameters m_{1-5} with respect to steps progressed by MCMC for the Canadian Shield model. The free parameters show an autocorrelation close to zero by the end of the MCMC run.

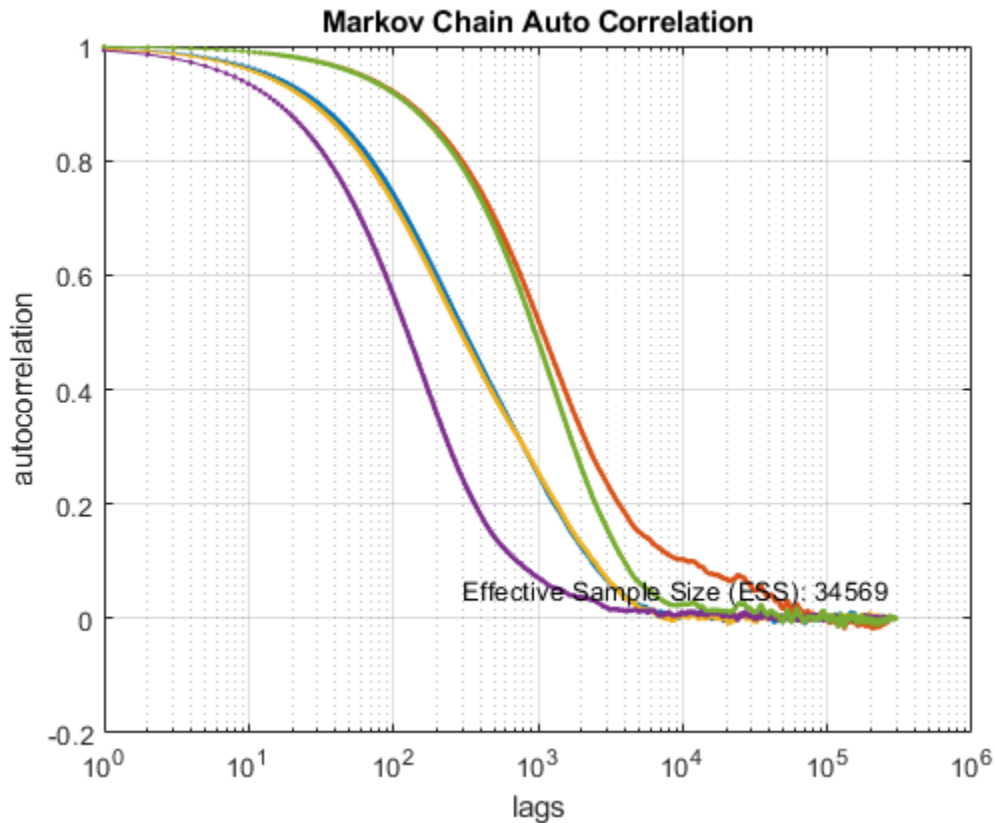


Supplementary Figure 16 | | MCMC best fit parameter outputs for Witwatersrand Basin data.

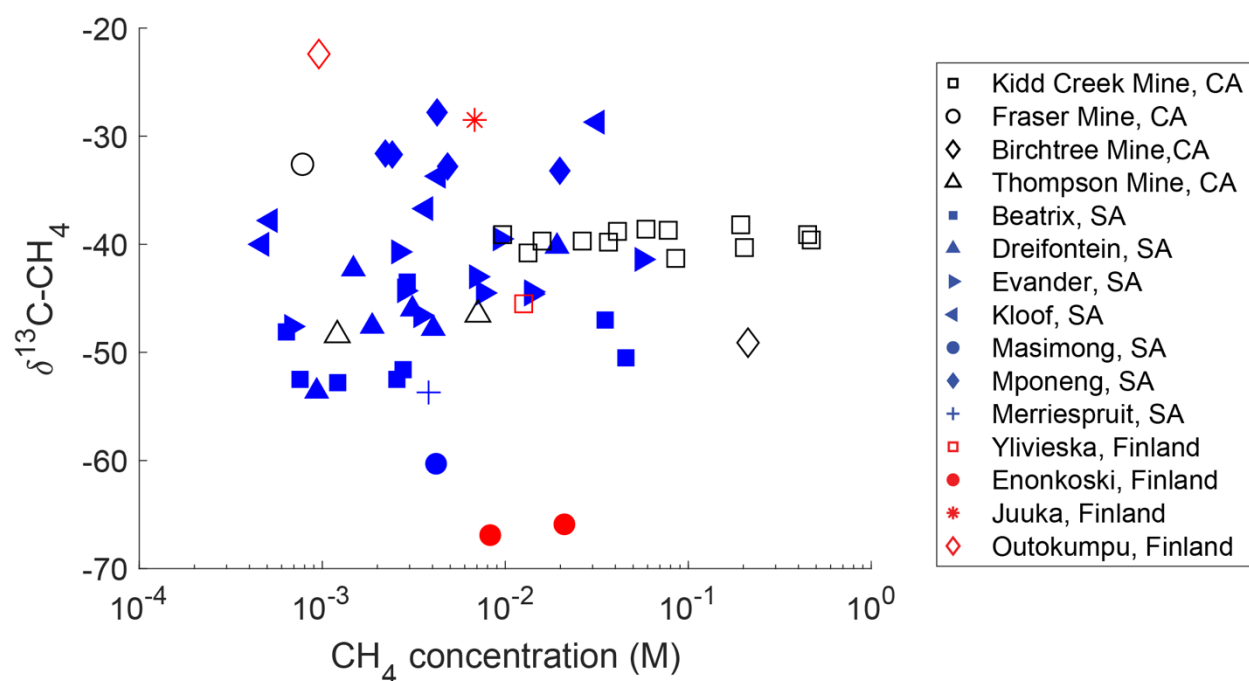
m_1 is abiotic $\delta^2\text{H-CH}_4$ endmember, m_2 is microbial $\delta^2\text{H-CH}_4$ endmember, m_3 is abiotic CH_4 production rate (M year^{-1}), m_4 is abiotic $\delta^{13}\text{C-CH}_4$, and m_5 is microbial $\delta^{13}\text{C-CH}_4$ endmember.



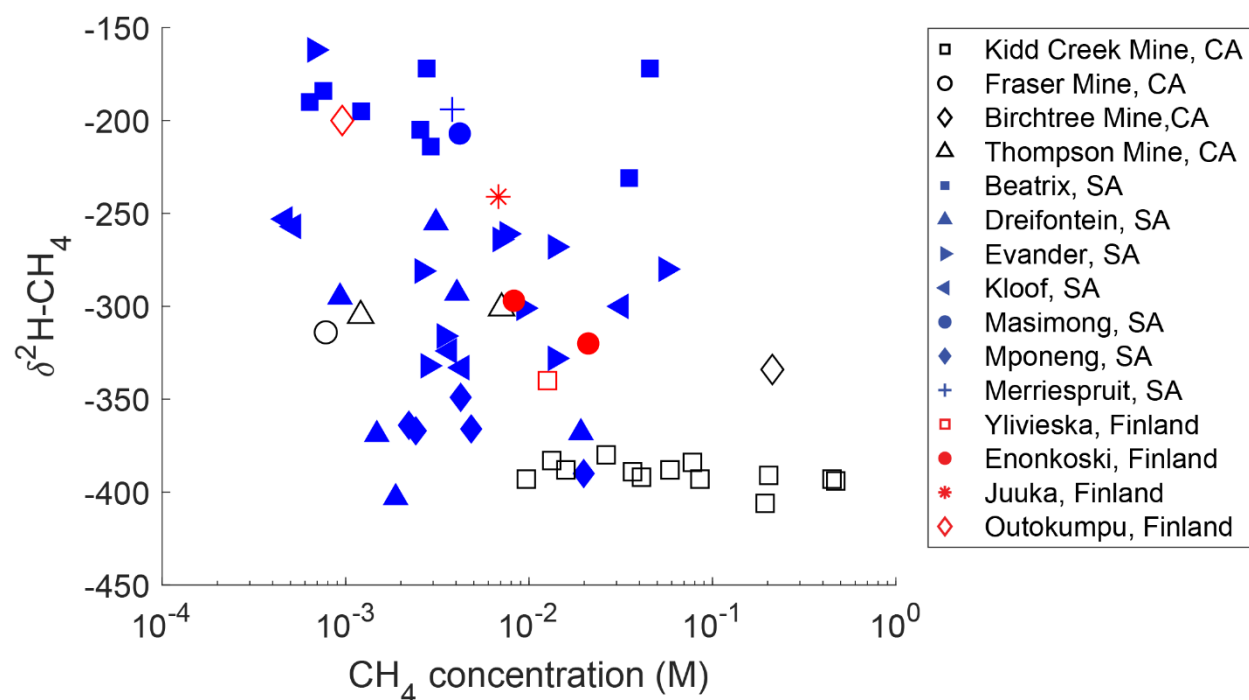
Supplementary Figure 17 | Best fit model to Witwatersrand Basin isotopic data from median values of MCMC best fit parameters. The measured values are plotted in blue and modeled values are plotted in black. These black datapoints are generated by inputting the measured He and CH₄ concentrations, P_{He} values, and median parameter values computed by the MCMC for the abiotic $\delta^2\text{H-CH}_4$ endmember, the microbial $\delta^2\text{H-CH}_4$ endmember, the abiotic CH₄ production rate (M year^{-1}), the abiotic $\delta^{13}\text{C-CH}_4$, and the microbial $\delta^{13}\text{C-CH}_4$ endmember into equations 6 and 7.



Supplementary Figure 18 | Autocorrelation between MCMC free parameters m_{1-5} with respect to steps progressed by MCMC for the Witwatersrand Basin model. The free parameters show an autocorrelation close to zero by the end of the MCMC run.



Supplementary Figure 19 | Dissolved CH_4 concentration (M) versus $\delta^{13}\text{C}-\text{CH}_4$ for each sample at each site. There is no apparent trend between these parameters.



Supplementary Figure 20 | Dissolved CH_4 concentration (M) versus $\delta^2\text{H}-\text{CH}_4$ for each sample at each site. There is no apparent trend between these parameters.

CHAPTER 2: Earth-like habitable environments in the subsurface of Mars

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Abstract

In Earth's deep continental subsurface, where groundwaters are often isolated for $>10^6$ - 10^9 years, energy released by radionuclides within rock produces oxidants and reductants that drive metabolisms of non-photosynthetic microorganisms. Similar processes could support past and present life in the martian subsurface. Sulfate-reducing microorganisms are common in Earth's deep subsurface, often using hydrogen derived directly from radiolysis of pore water and sulfate derived from oxidation of rock-matrix-hosted sulfides by radiolytically-derived oxidants. Radiolysis thus produces redox energy to support a deep biosphere in groundwaters isolated from surface substrate input for millions to billions of years on Earth. Here we demonstrate that radiolysis by itself could produce sufficient redox energy to sustain a habitable environment in the subsurface of present-day Mars, one in which Earth-like microorganisms could survive wherever groundwater exists. We show that the source localities for many martian meteorites are capable of producing sufficient redox nutrients to sustain up to millions of sulfate-reducing microbial cells per kg rock via radiolysis alone, comparable to cell densities observed in many regions of Earth's deep subsurface. Additionally, we calculate variability in supportable sulfate-reducing cell densities between the martian meteorite source regions. Our results demonstrate that martian subsurface groundwaters, where present, would largely be habitable by sulfate-reducing bacteria from a redox energy perspective via radiolysis alone.

1.0 Introduction

The surface of Mars is an extremely hostile environment characterized by freezing temperatures, desiccating conditions, high levels of ionizing radiation, oxidizing chemicals, low pressures, and a lack of liquid water that preclude any Earth-like organisms from surviving without adaptation that is unprecedented on Earth. Though some extremophiles on Earth have evolved to tolerate certain conditions relevant for Mars, any martian life formed in earlier eras would have taken refuge in the subsurface for survival^{1,2}. Within the last three decades, researchers have discovered that fluids preserved within Earth's kilometers deep subsurface contain significant quantities of biomass utilizing a wide diversity of redox reactions to drive their microbial metabolisms³. Similar habitable subsurface environments could potentially have existed on ancient Mars^{3,4}, may still exist on modern Mars⁵, and could exist on other planetary objects including ocean worlds, small bodies like Ceres, and exoplanets, making them an exciting frontier of planetary exploration^{2,6}.

In Earth's subsurface, actively metabolizing microbes can be sustained by fluids that have been isolated from surface substrate input for $>10^6$ - 10^9 years (refs. ⁷⁻¹¹)—similar to groundwater isolation timescales expected on Mars¹²—powered solely by redox energy derived from water-rock reactions including radiolysis and serpentinization^{13,14}. Radiolysis, the breaking of H₂O molecules in pore spaces by α , β , and γ radiation released from decay of radionuclides within host rock, generates both dissolved reductants (e.g. H₂; ref. ^{14,15}) and dissolved oxidants (e.g. H₂O₂; ref. ^{9,16}). The dissolved H₂ generated by radiolysis can be used directly as a reductant by subsurface microbes, while the primary oxidant byproducts of radiolysis can oxidize sulfides within the host rock matrix to form dissolved sulfate (SO₄) (refs. ^{9,16}) that can then be used by

microbes as an oxidant^{7,9,11,15,17}. Sulfate-reducing microorganisms are found kilometers deep on Earth in many groundwaters that have been isolated for $>10^7$ years (refs. ^{7,9,11,15,17}), and a significant component of the H_2 and SO_4 in especially ancient groundwaters is typically derived from radiolysis^{9,14}. Thus, these Earth systems prove that in any subsurface environment containing radionuclides, liquid H_2O , and sulfides, radiolysis alone has the potential to provide sufficient biologically-supportive redox energy to sustain a subsurface biome^{13,18}. There are many alternative potential pathways to generate additional redox couples for life in subsurface martian environments, which will not be considered here. Accordingly, the gas production rates and supportable cell density ranges presented in this work should be considered conservative estimates.

2.0 Geochemical data from Mars meteorites and missions

Meteorites from Mars and robotic missions to Mars provide constraints on available geochemical ingredients that can generate oxidants and reductants during radiolysis. Here, measured radionuclide and sulfide concentrations on Mars are used to estimate H₂ and sulfate production rates. Martian meteorites and remote measurements by the Gamma Ray Spectrometer (GRS) onboard Mars Odyssey¹⁹, which is sensitive to the top ~tens of cm of the martian crust, provide first-order constraints for radionuclide concentrations in the martian subsurface (Fig. 1). Elemental concentrations in martian meteorites range from ~0.01-0.4 wt. % K, ~0.01-2 ppm Th, and ~0.003-0.36 ppm U (ref. ²⁰) (Fig. 1e). Some U enrichment in these samples is possible through desert contamination⁴. K and Th concentrations estimated from GRS measurements range from ~0.07-0.6 wt. % and ~0.015-1.1 ppm (refs. ^{4,19}), respectively (Fig. 1a-b,e).

Martian meteorites also contain sulfides of both magmatic (pyrrhotite)^{21,22} and hydrothermal (pyrite)²³⁻²⁵ origins. Pyrite is much less abundant than pyrrhotite as it was described only in an orthopyroxenite (ALH84001), two chassignites and a few nakhlites (as minor pyrrhotite replacement product), as well as in regolith breccias (as primary hydrothermal precipitate). Sulfide abundances range from <0.01-1.0 wt. % and average grain sizes range from 5-100 µm with occasional outliers up to 400 µm (Fig. 1f; Supplementary Table 1 and refs. therein). Thus, the martian crust contains the radionuclides and sulfides required as prerequisites for a radiolysis-supported subsurface biome, and it is reasonably assumed that liquid water is present somewhere in the subsurface¹². Radionuclide concentrations in the top ~tens of cm in the martian crust vary with latitude and longitude (Fig. 1a-b), and volcanic

shergottite-nakhlite-chassigny (SNC) martian meteorites generally have lower radionuclide contents than regolith breccias (Fig. 1e) that are likely representative of the Noachian crust²⁶ (Fig. 1). Sulfide concentrations are also typically lower in SNC meteorites than in regolith breccias^{21–24}, while sulfide grain sizes are relatively consistent across martian meteorite samples (Fig. 1f). The original report of sulfides in Gale crater via CheMin XRD data is no longer supported after recalibration of the data²⁷, but evolved gas analysis-mass spectroscopy (EGA-MS)²⁸ and sulfur isotope measurements using the Sample Analysis at Mars (SAM) instrument²⁹ support the presence of sulfides in multiple Gale crater samples. Sulfides in Gale crater are diagenetic/epigenetic, likely resulting from thermal reduction of preexisting sulfates²⁹.

The amount of radiolytic hydrogen and sulfate that would be produced in each of the different martian meteorite source regions is calculated based on their individual K, Th, and U concentrations (Fig. 1e, Table S2), sulfide concentrations (Fig. 1f, Table S1), average sulfide grain sizes (Fig. 1f, Table S1), and estimated range of porosity (Fig. 1c, Table S2) before the impact events that ejected these rocks from the martian gravity well. Based on the produced amounts of these redox nutrients, the number of supportable sulfate-reducing cells per kg rock is calculated for each of these meteorite source regions using the range of sulfate-reducing metabolic rates observed in Earth's deep subsurface^{7,17}. Porosity range assumptions are based on density estimates of different martian terrains from orbital gravimetry (Fig. 1c-d)³⁰, a range that is supported by rover gravimetry³¹. The radiolysis model applied here is similar to the one employed in refs. ^{15,9,32,4,14}.

3.0 Habitable redox conditions in martian meteorite source regions

The results presented here show that the shergottite, nakhlite, chassignite, and regolith breccia martian meteorite source localities would all produce sufficient redox energy to support sulfate-reducing life where liquid groundwater exists within these lithologies. In all cases, based on the calculations herein, sulfate is the limiting redox nutrient in comparison with H₂. The regolith breccia source locality could support significantly more sulfate-reducing life than the SNC localities because it has higher concentrations of both radionuclides and sulfides. Of the SNCs, the shergottite and nakhlite source localities could support the highest densities of sulfate-reducing cells. Key findings are illustrated in Fig. 2, displayed in Table 1, and are summarized below as:

- (1) *Regolith breccia source locality*: The sulfate production rates for the regolith breccia source locality vary from $\sim[2 \times 10^{-14}] - [7 \times 10^{-12}]$ moles (kg rock)⁻¹ year⁻¹, while H₂ production rates range from $\sim[1-3] \times 10^{-11}$ moles (kg rock)⁻¹ year⁻¹, which could support $[7 \times 10^2]-[1 \times 10^6]$ sulfate-reducing cells per kg rock. The regolith breccia source locality would generate the most redox energy for sulfate-reducing microorganisms compared to the other martian meteorite source localities.
- (2) *Shergottite source locality*: The sulfate production rates for shergottite source localities vary from $\sim[8 \times 10^{-18}] - [2 \times 10^{-13}]$ moles (kg rock)⁻¹ year⁻¹, while H₂ production rates range from $\sim[4 \times 10^{-14}]-[4 \times 10^{-12}]$ moles (kg rock)⁻¹ year⁻¹, which could support $[2 \times 10^{-1}]-[3 \times 10^4]$ sulfate-reducing cells per kg rock wherever liquid water exists.
- (3) *Nakhlite source locality*: The sulfate production rates for nakhlite source localities vary from $\sim[1 \times 10^{-16}] - [2 \times 10^{-13}]$ moles (kg rock)⁻¹ year⁻¹, while H₂ production rates range

from $\sim[5 \times 10^{-13}]$ - $[6 \times 10^{-12}]$ moles (kg rock) $^{-1}$ year $^{-1}$, which could support $[3]$ - $[3 \times 10^4]$ sulfate-reducing cells per kg rock.

(4) *Chassignite source locality*: The sulfate production rates for chassignite source localities vary from $\sim[1 \times 10^{-17}]$ - $[6 \times 10^{-15}]$ moles (kg rock) $^{-1}$ year $^{-1}$, while H₂ production rates range from $\sim[2 \times 10^{-13}]$ - $[2 \times 10^{-12}]$ moles (kg rock) $^{-1}$ year $^{-1}$, which could support $[4 \times 10^{-1}]$ - $[1 \times 10^3]$ sulfate-reducing cells per kg rock.

The sulfate production rates from these calculations are several orders of magnitude lower than those of ref. ¹⁶ because those authors assumed 5-10 wt. % pyrite in the martian crust, while this study uses lower sulfide concentrations based on measured values from martian meteorites (Fig. 1f, Table S1). Because the model uses the lowest and highest measured sulfate-reducing metabolic rates in Witwatersrand Basin for calculating cell density estimates^{7,17}, there is a difference between the estimated maximum and minimum range for sulfate production rates and the estimated maximum and minimum range for number of supportable sulfate-reducing cells per kg rock. H₂ production estimates, in units of H₂ dissolved in water, range from 0.002-0.165 nM H₂/year. This compares to estimates by ref. ³² of 0.001-1.2 nM H₂/year for proposed Mars landing sites. The differences in the dissolved H₂ estimates between this study and ref. ³² derive from differences in radionuclide concentrations and porosity used for calculations in the two studies.

The number of supportable sulfate-reducing cells per kg rock in the nakhlite, shergottite, and regolith breccia source localities are comparable to those found in Earth's deep subsurface ($\sim 10^4 - 10^6$ cells per kg rock; ref. ³) (Fig. 2). Estimates for the chassignite source locality meanwhile are slightly lower ($\sim 10^1 - 10^3$ cells per kg rock). In all cases, sulfate is the redox

nutrient that limits sustainable cell densities, and as such estimated cell densities are most sensitive to estimated sulfate production rates. The martian regolith breccia NWA 7034 and one of its paired samples, NWA 7533, contain the highest radionuclide and sulfide concentrations of the currently known martian meteorites, and thus their source locality would host sulfate production rates capable of supporting the greatest density of sulfate-reducing microorganisms relative to other known martian meteorites. Regolith breccia meteorites are likely representative of the southern highlands, which is a major fraction of Mars' total crustal volume. The results presented here support growing evidence that the subsurface is potentially the largest, longest-lived, and most consistently habitable environment on Mars^{1,5,3,4} and could serve as a refugia for any life that ever existed on the martian surface^{1,2}. Other viable processes could produce redox nutrients to sustain additional metabolisms in the martian subsurface, including H₂ and CH₄ production via serpentinization and Fischer-Tropsch-type synthesis, respectively (e.g. ¹⁴), atmospheric O₂ dissolution (ref. ³³), atmospheric H₂ and CO dissolution (ref. ³⁴), as well as Fe²⁺ and Fe³⁺ from minerals (e.g. ref. ³). These results provide scientific justification for future missions to search for signs of extant life in the martian subsurface—which is an intriguing next frontier for planetary exploration^{2,6}—and identifies key characteristics of optimal regions for future landing sites.

Even the relatively small sampling of Mars' petrologic diversity via four martian meteorite classes (shergottites, nakhlites, chassignites, regolith breccias) shows a wide range in redox energy production rates from these different rock types/localities (Fig. 2). Some of these localities, such as the source regions for regolith breccias, shergottites, and nakhlites could support comparable concentrations of extant life to those found in Earth's deep

subsurface^{3,35,36}. As is demonstrated by the diversity of radionuclide concentrations, sulfide concentrations, and sulfide grain sizes in martian meteorites, some regions of the martian crust will support higher sulfate-reducing cell densities than others. Because sulfate is likely the limiting nutrient for hydrogenotrophic sulfate-reducing metabolisms in a martian subsurface biosphere rather than H₂, the highest concentrations of sulfate-reducing microorganisms would exist in a water-bearing crustal section with high sulfide abundance, low sulfide grain sizes, and relatively high radionuclide concentrations. Future missions should focus on characterizing where these criteria are met, as these would be prime landing site targets for extant life investigation from a redox energy perspective.

4.0 Potential for higher cell densities elsewhere on Mars

The possibility of relatively high sulfide concentrations on Mars has been recognized for decades due to the presence of ultramafic lithologies there^{37–39}. Concentration of magmatic sulfides are assumed to derive from assimilation of crustal sulfates and/or S-rich regolith in lava flows, as sampled by nakhlites, which likely crystallized from a sulfide-saturated melt after this assimilation^{40,41}. Additional evidence for the existence of concentrated martian sulfides has continued to accrue in the form of sulfides in martian meteorites (Table S1 and refs. therein), in Gale crater^{29,28}, the prevalence of sulfate-hematite assemblages on the martian surface (e.g. ref. ⁴²), which may or may not have formed as weathering products of sulfides (e.g. ref. ⁴³), verifiable orbital detections of serpentine outcrops in Noachian terrains⁴⁴, which are often associated with formation of reduced sulfides and metal alloys on Earth (e.g. refs. ⁴⁵), Cu concentrations in Gale crater that are likely caused by presence of sulfides⁴⁶, and the low oxygen fugacity (ref. ⁴¹ and refs. therein) and high sulfur fugacity of the ancient martian mantle relative to Earth's (refs. ^{41,47} and refs. therein) (see Materials and Methods for more discussion). Pyrrhotite hosts magnetization in multiple classes of martian meteorites (ref. ⁴⁸ and refs. therein) and thus at high enough concentrations its subsurface presence could explain Mars' crustal magnetic field anomalies⁴⁹.

High concentrations of sulfides could form via differentiation of sulfide-saturated lavas that were contaminated by crustal assimilation of sulfates^{37,38} as occurred in nakhlite lava flows^{40,41}, differentiation of impact melt accompanied by crustal sulfur assimilation as occurred in Sudbury, Ontario (e.g. ref. ⁵⁰), later hydrothermal sulfide precipitation with or without serpentinization, as is recorded in regolith breccia martian meteorites²⁴, or differentiated

intrusions (Fig. 3; see Materials and Methods for further discussion). Once formed, fluid fracture networks within such sulfide-rich regions in the subsurface of Mars could support high concentrations of radiolytically-fueled sulfate-reducing microorganisms and would be key locations to investigate the possibility of extant life on Mars.

If Earth-like chemolithotrophic life ever existed on Mars and survived until present, it could potentially be sustained in these subsurface regions by harnessing the same radiolytically-derived energy that drives the metabolisms of microbial ecosystems on Earth sustained in groundwaters $>10^6$ - 10^9 years old (refs. ^{7,11,17}). Furthermore, this subsurface environment has likely remained habitable since the Noachian⁴, making it the longest-lived habitable environment on Mars and the most likely refugia for any life on the planet^{1,2}. The parameters outlined here –radionuclide abundance, sulfide abundance, average sulfide grain size, and porosity—along with characterization of the locations of liquid groundwater, can be used to constrain an optimal landing site for a mission to detect Earth-like extant sulfate-reducing martian life in the subsurface. Additional microbial metabolisms, for which redox energy availability is more difficult to model, could also exist in the martian subsurface, as they do in Earth’s subsurface, potentially increasing the measured biomass in any subsurface region that contains groundwater. This should be considered in the context of future extant life detection missions to Mars.

Figures

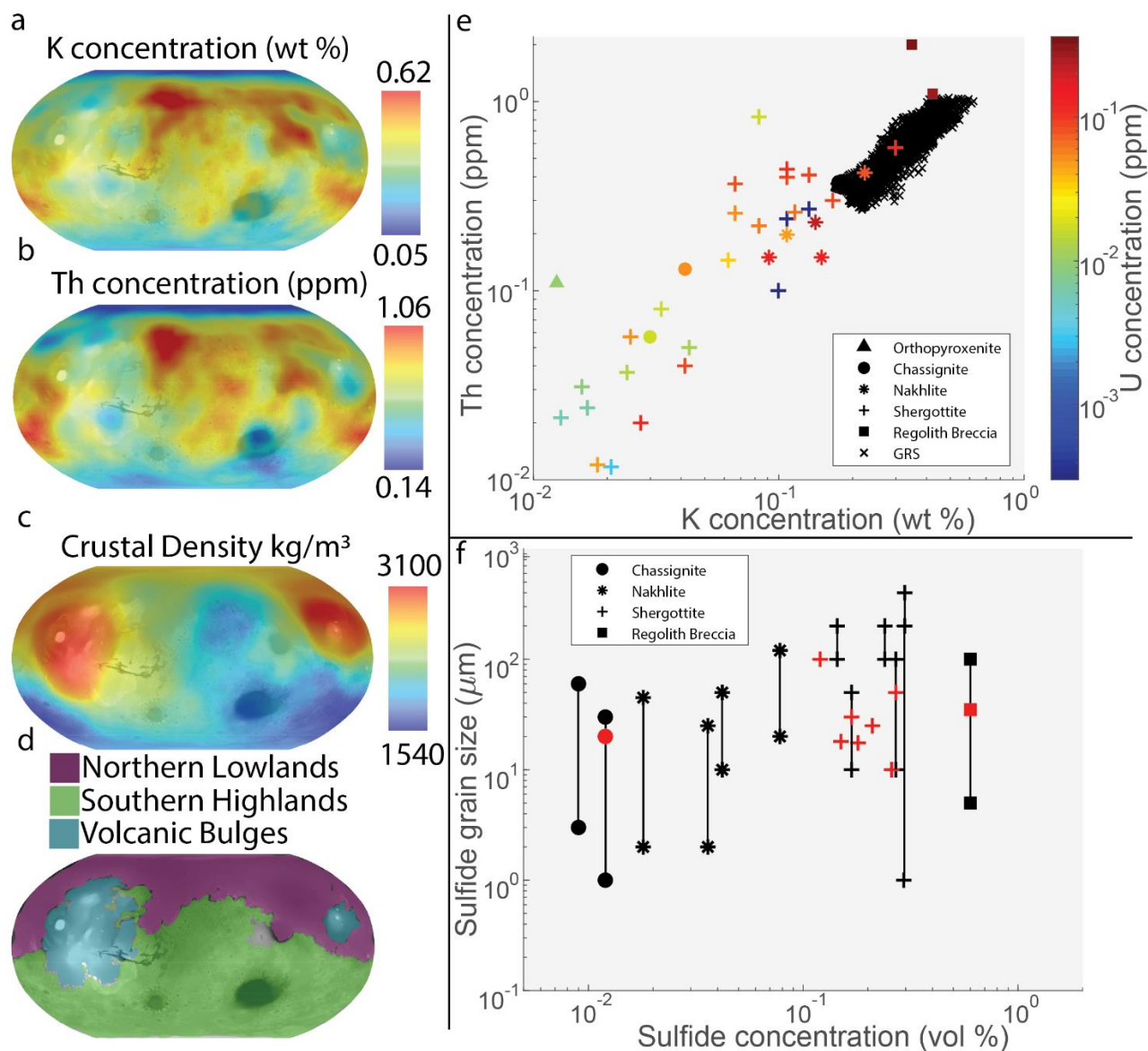


Figure 1 | Model input data. (a) K concentration (wt. %) from GRS data, corrected for contributions Cl, H, and S (refs. ^{4,19}). (b) Th concentration (ppm) from GRS data, corrected for contributions Cl, H, and S (refs. ^{4,19}). (c) Possible crustal density estimates from orbital gravimetry³⁰ that are supported by rover gravimetry³¹. (d) Division of Mars into 3 different regions. (e) Radionuclide abundances in martian meteorites²⁰ and GRS data from 60°S-60°N, where near surface ice does not contaminate measurements (refs. ^{4,19}). The lower spatial resolution of GRS data (100s of km) means the calculated K and Th concentrations are more closely clustered than in the martian meteorites. There are also no U concentration measurements from GRS data, thus the color is black. (f) Sulfide concentrations and grain sizes in martian meteorites are compiled and referenced in Table S1. Black symbols show the

maximum and minimum reported grain sizes, while red symbols show the reported average grain size.

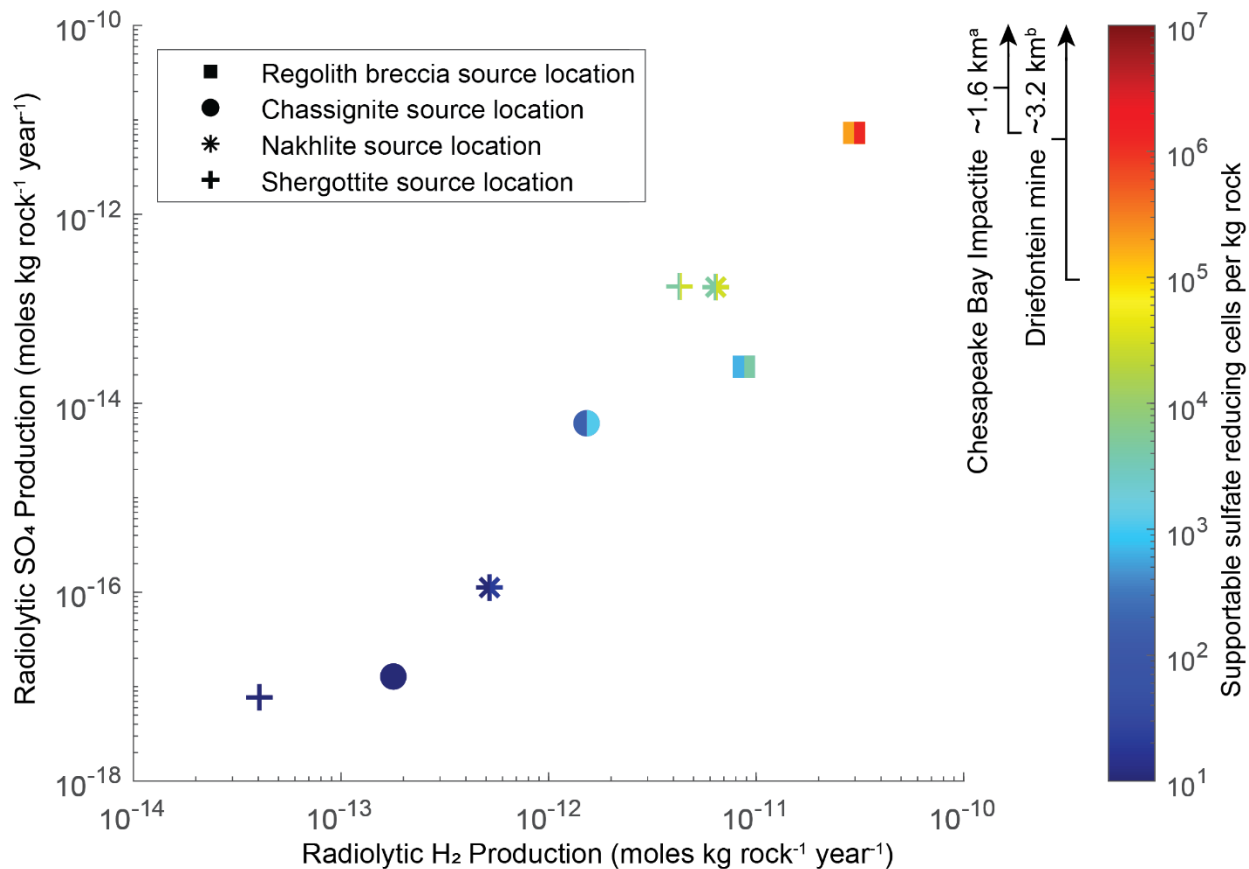


Figure 2 | Radiolytic redox energy production and number of supportable sulfate-reducing cells in Mars meteorite source regions. The datapoints represent the highest and lowest endmembers for each given category, with the assumed values for the calculations presented in Table S2. The different colors of the same datapoints represent the supportable sulfate-reducing cells per kg rock assuming the highest and lowest metabolic rates observed in Earth's deep subsurface ($5.5 \times 10^{-18} - 3.6 \times 10^{-17}$ moles $\text{cell}^{-1} \text{ year}^{-1}$; refs. ^{7,17}). Cell density measurements from Earth's deep subsurface come from ^aref. ³⁶, ^bref. ³⁵.

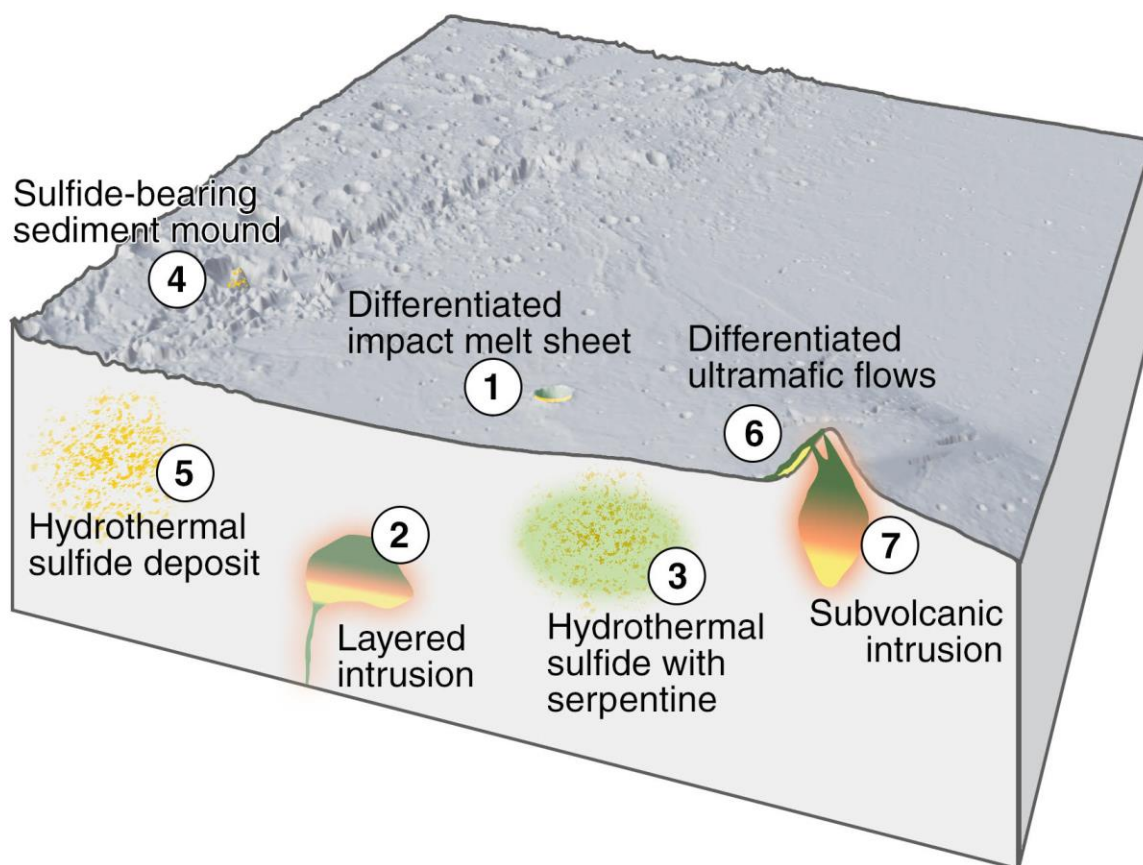


Figure 3 | Possible sulfide concentration settings on Mars in addition to those found in martian meteorites. Topographic cross-section of Mars using data from the Mars Orbital Laser Altimeter (MOLA) from 10°S, 141°E; 29°N, 149°E; 4°S, 104°E; 35°N, 96°E. See Materials and Methods for discussion of possible sulfide concentration settings on Mars, in addition to sulfide concentrations found in martian meteorites that are used for calculations in this study. (1) Differentiated impact melt sheet similar to sulfide concentrations at the Sudbury Impact Structure in Canada⁵⁰. (2) Sulfide concentration in layered intrusion, similar to Bushveld Igneous Complex in South Africa and many other localities on Earth. (3) Sulfide hydrothermally concentrated in serpentinite, similar to many ophiolite localities on Earth. Mg-serpentinite has been detected on Mars⁴⁴. (4) Sulfide concentrations in sediments, such as those in Gale crater^{29,28}. (5) Sulfide hydrothermally concentrated without associated serpentinite minerals, such as those in regolith breccia martian meteorites^{21–24}. (6) Concentrations of sulfides in differentiated ultramafic-to-mafic lava flows, as occurs in many localities on Earth including the Kambalda and Perseverance deposits in Australia. Sulfides are also concentrated in picrites, including the Pechenga deposits in Russia. This is a possible formation setting for nakhlites, which crystallized from sulfide saturated magmas after assimilation of S from the crust/regolith^{40,41}. (7) Concentration of sulfides in ultramafic-to-mafic subvolcanic intrusions beneath volcanic provinces such as Tharsis, Elysium, and Syrtis Major.

Tables

	<i>Radiolytic H₂ production rate in moles (kg rock)⁻¹ year⁻¹</i>	<i>Radiolytic Sulfate production rate in moles (kg rock)⁻¹ year⁻¹</i>	<i>Supportable sulfate-reducing cell density in cells (kg rock)⁻¹</i>
<i>Regolith breccia</i>	$\sim[1-3] \times 10^{-11}$	$\sim[2 \times 10^{-14}] - [7 \times 10^{-12}]$	$[7 \times 10^2]-[1 \times 10^6]$
<i>Shergottite</i>	$\sim[4 \times 10^{-14}]-[4 \times 10^{-12}]$	$\sim[8 \times 10^{-18}] - [2 \times 10^{-13}]$	$[2 \times 10^{-1}]-[3 \times 10^4]$
<i>Nakhlite</i>	$\sim[5 \times 10^{-13}]-[6 \times 10^{-12}]$	$\sim[1 \times 10^{-16}] - [2 \times 10^{-13}]$	$[3]-[3 \times 10^4]$
<i>Chassignite</i>	$\sim[2 \times 10^{-13}]-[2 \times 10^{-12}]$	$\sim[1 \times 10^{-17}]-[6 \times 10^{-15}]$	$[4 \times 10^{-1}]-[1 \times 10^3]$

Table 1 | Estimated H₂ and sulfate production rates for martian meteorite source regions and associated supportable sulfate-reducing cell densities.

S1.0 Materials and methods

S1.1 Summary

The model used to estimate H₂ production rates, sulfate production rates, dissolved H₂ concentrations, dissolved sulfate concentrations, and supportable sulfate-reducing cell densities is similar to models employed in refs. ^{16,9,51}. Porosity, radionuclide concentrations, sulfide concentrations, average sulfide grain sizes, and sulfate-reducing metabolic rates are the key parameters necessary to constrain the model. H₂ production rates are dependent on porosity and radionuclide concentrations, increasing as porosity and radionuclide concentrations increase. Sulfate production rates are dependent on porosity, radionuclide concentrations, sulfide concentrations, and average sulfide grain size. They increase as porosity, radionuclide concentrations, and sulfide concentrations increase and decrease as sulfide grain size increases, as less reactive surface area is exposed when sulfide grains are larger. Dissolved H₂ and sulfate concentrations increase as porosity decreases, as there is less fluid in which to dissolve the H₂ and sulfate that is produced. Supportable sulfate-reducing cell densities in units of cells (kg rock)⁻¹ increase as porosity and sulfate production rates increase, since sulfate is the limiting redox nutrient in all model results presented here. Supportable sulfate-reducing cell densities in units of cells L⁻¹ decrease as porosity increases because there is less fluid per volume rock for the cells to reside in. Supportable sulfate-reducing cell densities are higher when the assumed sulfate-reducing metabolic rate is lower.

Porosity is constrained using density estimates for the martian crust from orbital gravimetry³⁰ that are supported by rover gravimetry³¹. Radionuclide concentrations, sulfide concentrations, and average sulfide grain sizes are constrained by their measured values in

martian meteorites. The maximum and minimum assumed sulfate-reducing metabolic rates are based on the fastest and slowest sulfate-reducing metabolic rates estimated for fracture fluids in the gold mines of the Witwatersrand Basin^{7,17}. The calculated sulfate-reducing cell densities are compared to those found in Earth's deep subsurface^{3,35,36,52} (Fig. 2).

S1.2 Porosity model

The average porosity ranges for the martian meteorite source regions are estimated using density estimates for the different regions of Mars' crust from orbital gravimetry³⁰ that are validated by rover gravimetry in Gale crater that estimates a porosity range of $40 \pm 6\%$ for the top ~300 meters of bedrock³¹. Porosity in this context includes both fracture and pore space within rocks. The orbital gravimetry estimates give average densities of $\sim 1600 \text{ kg m}^{-3}$ for the southern highlands, 2400 kg m^{-3} for the northern lowlands, and $\sim 2800 \text{ kg m}^{-3}$ for the volcanic bulges. It is assumed that the volcanic bulges and northern lowlands are the possible source regions for the SNCs and the southern highlands are the source region for the regolith breccias²⁶. In the estimation, an average solid crust matrix density range of $2000\text{-}3200 \text{ kg m}^{-3}$ is used for the southern highlands crust, consistent with its mineralogy⁵³, and $2600\text{-}3200 \text{ kg m}^{-3}$ is used for the northern lowlands and volcanic bulges, consistent with volcano-specific orbital gravimetry⁵⁴. It is assumed the difference between the gravimetry density measurements and rock matrix density estimates is caused by pore space filled with ice or water. The densities add linearly such that $\rho_{bulk} = \rho_{rock}(1 - \theta) + \rho_{H_2O}(\theta)$ where θ is porosity. This means the composition of the southern highlands rock is assumed to vary, on average, between pure phyllosilicate ($\sim 2000 \text{ kg m}^{-3}$) and dense basalt ($\sim 3200 \text{ kg m}^{-3}$), while the composition of the

northern lowlands and volcanic bulges rocks are assumed to vary between 50-50 phyllosilicate-basalt mixture ($\sim 2600 \text{ kg m}^{-3}$) and dense basalt ($\sim 3200 \text{ kg m}^{-3}$). Given uncertainties in density estimates from orbital gravimetry, to be conservative, estimated porosities were reduced by 10%. This does not model depth dependence of porosity, but rather the average porosity of the source regions for the individual martian meteorites. This gives approximate average porosity ranges of 15-35% for the regolith breccias, 5-15% for the SNCs. The SNC porosity assumptions are supported by images of porous float vesicular basalt rocks in Gusev crater imaged by the Spirit rover^{55,56}.

S1.3 Radiolysis model

The model used here follows the radiolytic H_2 and SO_4 production models presented in refs. 4,9,14,15,57. This calculates radiogenic dose rate as

$$(1) E_{net,i} = \frac{E_i \times W \times S_i}{1 + W \times S_i}$$

where i is α , β , or γ radiation, E_{net} is the net dosage absorbed by pore water ($\text{eV kg}^{-1} \text{ s}^{-1}$), E is the apparent dosage from radioactive element decay ($\text{eV kg}^{-1} \text{ s}^{-1}$), W is the weight ratio of pore water to rock, and S is the stopping power of minerals within the rock matrix with respect to each type of radiation particle/ray, where $S_\alpha = 1.5$, $S_\beta = 1.25$, $S_\gamma = 1.14$ (refs. 4,14,15,57). The stopping power of minerals can be estimated using Bragg's law⁵⁸ and typically varies by <0.5 for silicate minerals⁵⁹.

W , the weight ratio of pore water to rock, primarily depends on the rock porosity with additional minor variations induced by differences in water density in solid ($\sim 900 \text{ kg m}^{-3}$) or liquid ($\sim 1000 \text{ kg m}^{-3}$) phase. Values from ref. 60 are used for E for 1 wt. % K, 1 ppm Th, and 1

ppm U for α , β , and γ radiation, which are $E_{K,\alpha} = 0$ (Gy ka⁻¹), $E_{K,\beta} = 0.782$ (Gy ka⁻¹), $E_{K,\gamma} = 0.243$ (Gy ka⁻¹), $E_{Th,\alpha} = 0.061$ (Gy ka⁻¹), $E_{Th,\beta} = 0.027$ (Gy ka⁻¹), $E_{Th,\gamma} = 0.048$ (Gy ka⁻¹), $E_{U,\alpha} = 0.218$ (Gy ka⁻¹), $E_{U,\beta} = 0.146$ (Gy ka⁻¹), $E_{U,\gamma} = 0.113$ (Gy ka⁻¹). 1 Gy = 6.2415×10^{18} eV kg⁻¹.

H₂ yield is calculated as

$$(2) Y_{H_2} = \sum E_{net,i} \times G_{H_2,i}$$

where Y_{H_2} is the total yield of H₂ molecules (molecules kg⁻¹ s⁻¹) and G_{H_2} is the number of H₂ molecules produced per 100 eV of radiation. The conversion factor between (kg water) and (kg water and rock matrix) is W , the weight ratio of pore water to rock. For H₂O, $G_{H_2,\alpha} = 0.96$ H₂ molecules (100 eV)⁻¹, $G_{H_2,\beta} = 0.6$ H₂ molecules (100 eV)⁻¹, $G_{H_2,\gamma} = 0.4$ H₂ molecules (100 eV)⁻¹ (refs. ^{4,14,15,57}). The value of G_{H_2} changes depending on the liquid or solid substance filling the pore space, and has received extensive study due to its importance in the context of nuclear waste storage. It is typically higher for chloride brines than for pure water^{61,62} due to the reaction of dissolved brine ions (e.g. Cl⁻) with ions formed via radiative destruction of neutral H₂O molecules (e.g. OH[•]). This causes a depletion of ions that would react with H[•] generated by radiolysis, leaving more H[•] in solution, which reacts to form H₂ (2H[•] → H₂) (ref. ⁶³). Hydrated chloride salts, embedded in either pore space or within the rock matrix, will also produce H₂, though at lower production efficiencies relative to pure water, ice, or brine⁶¹. These different production efficiencies are summarized in ref. ⁴ and references therein. Presence of certain minerals, such as zeolites, can significantly increase H₂ and oxidant production efficiency from radiolysis⁶⁴. Zeolites are found in both bedrock⁶⁵ and dust⁶⁶ on Mars, thus this mineral is expected to enhance radiolytic H₂ and oxidant production in some parts of the crust, but this effect is not modeled here in order to focus on the most conservative estimates possible.

SO₄ production is calculated as

$$(3) Y_{SO_4} = \sum E_{net,i} \times G_{SO_4,i}$$

where Y_{SO_4} is the total yield of SO₄ molecules (moles m⁻² sulfide year⁻¹) and G_{SO_4} is the number of SO₄ molecules produced per m² sulfide per Gy radiation. A G_{SO_4} value from ref. ¹⁶ is used that is also used in refs. ^{9,51}, which is 2.1×10^{-9} mol m⁻² Gy⁻¹. However, while the experiments of ref. ¹⁶ were performed under high-energy radiation, they showed that G_{SO_4} increases under low-radiation-dose conditions, which correspond to typical radiation doses in natural systems⁹. Furthermore, these experiments only investigated the oxidation, structural damage, and chemical weathering of sulfides exposed to γ radiation. As ref. ¹⁶ notes, accounting for increased oxidation, structural damage, and chemical weathering of sulfides from α and β radiation—which typically represent >90% of total irradiated energy—would increase the G_{SO_4} value, perhaps significantly. This means once again that the calculated sulfate production rates, and thus supportable sulfate-reducing cell densities herein, are likely conservative estimates.

The concentration of sulfate in fluid from radiolytic production is expressed as

$$(4) C_{SO_4} = Y_{SO_4} \times C_{sulfide} \times S_{sulfide} / W$$

where C_{SO_4} is the production rate of dissolved sulfate (M year⁻¹), $C_{sulfide}$ is the concentration of sulfide in the rock matrix (volume ratio), and $S_{sulfide}$ is the average specific surface area of sulfides in the rock matrix (m⁻² sulfide/kg). $C_{sulfide}$ values used in this study are listed in Table S2, which encompasses the values found in martian meteorites^{21–24,48,67–71}. $S_{sulfide}$ values ranging from 2.26×10^1 m² kg⁻¹ and 1.41×10^3 m² kg⁻¹ are used, which correspond to average sulfide grain sizes of 2–125 μ m. The $S_{sulfide}$ values for each meteorite class are assigned based on the range of sulfide grain sizes measured in those martian meteorites (Fig. 1f;

Supplementary Tables 1 & 2). Finally, following ref. ⁵¹, minimum and maximum sulfate-reducing metabolic rates of $5.5 \times 10^{-18} - 3.6 \times 10^{-17}$ moles cell⁻¹ year⁻¹ are assumed, which correspond to the minimum and maximum sulfate-reducing metabolic rates estimated in deep subsurface fracture fluids of the gold mines from the Witwatersrand Basin^{7,17}.

S1.4 Sulfide concentrations

The assumed sulfide concentration ranges are derived based on sulfide concentrations found in martian meteorites^{21–24,40,47,48,67–74} (Fig. 1f; Supplementary Table 1). Martian meteorites contain variable abundances of sulfides with relatively consistent grain sizes for grains >10 µm. Published abundances for sulfides in martian meteorites, and reported average grain sizes and grain size range, are presented in Supplementary Table 1. Magmatic sulfides (pyrrhotite) and hydrothermal sulfides (pyrite) are typically associated with SNCs and regolith breccias, respectively^{21–24,48,67–71}. Sulfide abundances are typically higher in regolith breccias than in SNCs. The listed sulfide abundances are also minimum abundances, as desert weathering of martian meteorite samples causes oxidation of sulfides and partial S losses^{21–24,48,67–71}.

S1.5 Sulfide grain sizes

A compilation of published measured sulfide average grain sizes and grain size ranges in martian meteorites is presented in Supplementary Table 1 and plotted in Fig. 1f. It is noteworthy that many of these studies do not consider sulfides <10 µm in diameter, thus these results may skew average sulfide grain sizes towards larger-than-true values. Since sulfate

production in the calculations increases as sulfide grain size decreases as a result of greater specific surface area, this ensures the calculations are conservative. Sulfide grain sizes depend on a wide array of parameters, including temperature, supersaturation of fluids, nucleation rates, and fracturing. For each individual martian meteorite class, the range of measured average sulfide grain sizes in those meteorites are used as the basis for the calculations.

<i>Sample</i>	<i>Sulfide abundance (wt. %)</i>	<i>Average grain size (μm)</i>	<i>Grain size min (μm)</i>	<i>Grain size max (μm)</i>	<i>Publications</i>	<i>Type</i>
<i>NWA 998</i>	0.13	-	20	120	⁶⁷	Nakhlite
<i>Nakhla</i>	0.07 (0.08)	-	10	50	^{67, 47}	Nakhlite
<i>Governador Valadares</i>	0.06	-	2	25	⁶⁷	Nakhlite
<i>NWA 817</i>	0.03	-	2	30±15	⁶⁷	Nakhlite
<i>MIL 03346</i>	0.05	-	-	-	⁴⁰	Nakhlite
<i>And paired samples</i>						
<i>Y000593</i>	0.08	-	-	-	⁴⁷	Nakhlite
<i>ALH A77005</i>	0.3 (ref. ²¹ and refs. therein), 0.12 (ref. ⁴⁰), 0.19 (ref. ⁴⁷)	100	-	-	²¹ and refs. therein, ^{40, 47}	Lherzolithic shergottites
<i>LEW 88516</i>	0.3	17.5	-	-	²¹ and refs. therein	Lherzolithic shergottites
<i>Y-293605</i>	0.05	-	-	-	²¹ and refs. therein	Lherzolithic shergottites
<i>Tissint</i>	0.6 (ref. ⁷⁵), 0.35 (ref. ⁴⁰)	-	<1	200	^{40, 75}	Olivine-phyric shergottite
<i>EET A79001-A</i>	0.52 (ref. ⁴⁷), 0.28 (ref. ⁴⁰)	-	-	-	⁴⁰	Olivine-phyric shergottite
<i>DaG 476/489</i>	0.45	50	10	100	²¹ and refs. therein	Olivine-phyric shergottites
<i>SaU 005/094</i>	0.30 (ref. ²¹ and refs. therein), 0.16 (ref. ⁴⁰), 0.38 (ref. ⁴⁷)	30	10	50	²¹ and refs. therein, ^{40, 47}	Olivine-phyric shergottites
<i>Dhofar 019</i>	0.5 (ref. ²¹ and refs. therein), 0.20 (ref. ⁴⁰)	25	-	-	²¹ and refs. therein	Olivine-phyric shergottites
<i>NWA 1068/1110</i>	0.8	-	-	-	²¹ and refs. therein, ⁴⁰	Olivine-phyric shergottites
<i>Y-980459</i>	0.1 (ref. ⁴⁰), 0.4 (ref. ⁴⁷)	30	5	50	²¹ and refs. therein, ^{40, 47, 68}	Olivine-phyric shergottites
<i>Zagami</i>	0.7 (ref. ²¹ and refs. therein), 0.24 (ref. ⁴⁰), 0.35 (ref. ⁴⁷)	<10	100	200	²¹ and refs. therein, ^{40, 47}	Basaltic shergottite
<i>Shergotty</i>	0.4	-	100	200	²¹ and refs. therein	Basaltic shergottite

<i>EET A79001-B</i>	0.12	-	-	-	⁴⁰	Basaltic shergottite
<i>QUE 94201</i>	0.3 (ref. ²¹ and refs. therein), 0.13 (ref. ⁴⁰)	-	-	-	²¹ and refs. therein	Basaltic shergottite
<i>NWA 480</i>	0.24	-	100	200	²¹ and refs. therein	Basaltic shergottite
<i>NWA 856</i>	0.1	-	-	-	²¹ and refs. therein	Basaltic shergottite
<i>Los Angeles</i>	0.67 (ref. ²¹ and refs. therein), 0.32 (ref. ⁴⁰)	-	200	400	²¹ and refs. therein	Basaltic shergottite
<i>Y000097</i>	0.12	-	-	-	⁴⁷	Lherzolithic shergottite
<i>LAR 12011</i>	0.35	-	-	-	⁴⁷	Lherzolithic shergottite
<i>LAR12095</i>	0.5	-	-	-	⁴⁷	Lherzolithic shergottite
<i>Mean of 37 shergottites</i>	0.21±0.18	-	-	-	^{40,72}	Shergottites
<i>NWA 7533</i>	1±0.1	35	-	-	^{23,24}	Regolith breccia
<i>Chassigny</i>	0.02	20	1-5	30	²²	Chassignite
<i>NWA 2737</i>	0.015 ± 0.005	-	3	60	⁷⁶	Chassignite
<i>NWA 8693</i>	<0.01	-	1	20	⁷³	Chassignite

Supplementary Table 1 | Sulfide concentrations and grain sizes in martian meteorites. Assume density

of 5000 kg/m³ for sulfide and 3000 kg/m³ for host rock to convert from vol % to wt %. Franz et al.

(2014, 2019) and Wang and Becker (2017) data are calculated from whole-rock S contents assuming 38 wt.% S for pyrrhotite and 54 wt. % for pyrite. Other sulfide abundances are from image analyses on polished thick sections.

S1.6 Radionuclide concentrations

For calculations of SO₄ and H₂ production in martian meteorites, the measured values for K, Th, and U in each individual meteorite class were used^{18,20}, integrating both the maximum and minimum radionuclide concentration values measured (Fig. 1e; Table S2). The K and Th concentration ranges for SNCs are substantially lower than K and Th concentrations measured in GRS data (Fig. 1e), meaning the majority of the martian crust at depths shallower than ~0.5 m typically has higher radionuclide concentrations than are represented by the SNCs. Following refs. ^{4,77}, the GRS data is normalized to correct for contributions from Cl, H, and S. Compared to the martian meteorite and GRS K concentrations given in the main text, K concentrations measured by Mars rovers range from 0.05 wt. % measured by Spirit to 4.4 wt. % measured by Curiosity (refs. ^{78,79}).

<i>Category</i>	<i>K₂O concentration (wt %)</i>	<i>Th concentration (ppm)</i>	<i>U concentration (ppm)</i>	<i>Sulfide concentration (vol %)</i>	<i>Sulfide grain size (um)</i>	<i>Porosity (%)</i>
<i>Regolith breccia</i>	0.42-0.51 ^{a,b,c}	1.1-2 ^{a,b,c}	0.29-0.36 ^{a,b,c}	0.6±0.1 ^{a,b,c}	2- 100 ^{a,b,c}	15-35
<i>Chassignite</i>	0.036-0.05 ^d	0.057-0.13 ^d	0.018-0.056 ^d	0.006-0.012 ^{e,f}	2-60 ^{e,f}	5-15
<i>Nakhlite</i>	0.11-0.27 ^d	0.15-0.42 ^d	0.052-0.23 ^d	0.018-0.078 ^g	2-50 ^g	5-15
<i>Shergottite</i>	0.0156-0.35 ^d	0.0117-0.57 ^d	0.00303-0.12 ^d	0.03-0.6 ^h	10-200 ^h	5-15

Supplementary Table 2 | Range of values for martian meteorites calculations. ^aAgee et al.

(2013), ^bWittman et al. (2015), ^cLorand et al. (2018a), ^dMeyer et al. (2016), ^eLorand et al.

(2018b), ^fLorand et al. (2012), ^gChevrier et al. (2011), ^hLorand et al. (2005), ⁱLe Deit et al. (2016),

^jBoynton et al. (2007), ^kHahn et al. (2011), ^lTarnas et al. (2018), ^mVaniman et al. (2014). Sulfide grain size excludes the few unusually large sulfide grains reported in each meteorite class.

S1.7 Evidence for concentrated sulfides on Mars

The conclusions from this study do not require concentrated sulfides on Mars, but as described in main text, are based on the large body of data for disseminated sulfides on Mars. As such, the estimates are appropriately conservative and are consistent with the body of lithological and geochemical data available. The presence of concentrated sulfide deposits on Mars can be considered, however, and supporting evidence includes (1) sulfur assimilation and sulfide saturation in nakhlite melts, (2) geologic evidence for high sulfide concentrations elsewhere in the martian crust based on expected mantle oxygen^{80,81} and sulfur⁸² fugacities, (3) surface evidence for sulfide oxidation^{43,83,84}, and (4) orbital detections of past serpentinization^{44,85}, which produces reducing fluids and is often associated with generation of hydrothermal sulfide deposits on Earth (e.g. refs. ^{45,86–90}).

1. Nakhrites likely crystallized from a sulfide saturated melt after S assimilation from the crust/regolith based on $\Delta^{33}\text{S}$, $\delta^{34}\text{S}$, and HSE patterns⁴¹. Some amount of sulfur accumulation from S-rich regolith occurred after the nakhlite lavas were emplaced on or near the martian surface^{40,41}. Nakhrites are the only SNC meteorite class known to likely have crystallized from a sulfide-saturated melt, as shergottites crystallized from sulfide undersaturated parent magmas⁴⁷. Still, 1/3 of volcanic martian meteorite classes exhibiting geochemical characteristics consistent with crystallization from a sulfide saturated melt implies that characteristically similar volcanism could have occurred throughout Mars' history. Sulfates are prevalent across the surface of Mars⁵³, S-rich regolith is effectively ubiquitous across the surface^{91,92}, and elemental sulfur concentrations measured by GRS range from 0.7-3.2 wt. % at GRS spatial resolution⁹³, thus a substantial amount of sulfur for accumulation by lavas commonly exists on the martian surface. Therefore, it is likely that lavas saturated with respect to sulfide after assimilation of S from the crust/regolith—similar to those from which nakhlites crystallized—were common throughout Mars' history, thus resulting in the formation of high sulfide concentration zones.
2. The martian mantle is generally expected to be more reducing than Earth's^{80,81}, with estimates for mantle oxygen fugacity based on basalts measured in Gusev crater varying from iron-wüstite (IW) to IW+1 (ref. ⁸⁰). Oxygen fugacity estimates from shergottites are estimated to be [QFM-4]-[QFM-1] (ref. ⁹⁴), and from nakhlites are ~QFM (ref. ⁴¹). Earth's mantle has an oxygen fugacity range of [QFM-1]-[QFM+1]

(refs. ^{95,96}). Still, on Earth, pyrrhotite is found in volcanic rocks derived from partial melting of a more oxidized mantle relative to Mars [e.g. ^{97,98}], though concentrations are typically higher in silicic magmas than basalt, the latter of which is more common on Mars. Thus, magmatic sulfides are expected in some volcanic rocks derived from the wide variability in melt oxygen fugacities from the martian mantle. Martian mantle sulfur abundance estimates range from ~400-2200 ppm (ref. ⁴⁷), while Earth's mantle sulfur abundance is ~250 ppm (ref. ⁹⁹). Additional sulfur is incorporated into martian melts via crustal assimilation of sulfates and/or S-rich regolith, as occurred in the nakhlite lavas^{40,41}. As such, sulfur activity in martian melts is typically higher than in most melts on Earth, while oxygen fugacity is lower than in most melts on Earth, both of which increase the likelihood of sulfide precipitation.

3. Sulfide oxidation has been invoked to explain multiple mineral assemblages found on the martian surface¹⁰⁰, including the hematite enrichment in Meridiani Planum⁴³, the Burns formation –a sulfate-rich sandstone in Meridiani Planum⁴³, sulfate-carbonate assemblages found using orbital hyperspectral data⁸⁴, akaganeite detections made from orbit¹⁰¹, and acidic fluid diagenetic mineral assemblages detected by the Curiosity rover¹⁰². In its type locality on Earth, akaganeite forms as an alteration product of pyrrhotite¹⁰³. To concentrate the abundances of sulfur needed to form the Burns formation, pre-concentration of sulfur via magmatic or hydrothermal sulfides may be required⁴³. Furthermore, oxidation of sulfides to form the acid-mine-drainage-like mineral assemblages of sulfates and oxides seen on the

martian surface provides a functional hypothesis for generation of these assemblages. Formation of concentrated sulfides could have occurred on Mars via differentiation/crustal assimilation from ultramafic lavas³⁷, the existence of which is supported by possible observations of ultramafic volcanism on the martian surface^{104–106}, ultramafic lithologies in martian meteorites³⁷, and evidence that nakhlites crystallized from sulfide-saturated melts after S assimilation from the crust/regolith^{40,41}.

4. Mg-rich serpentine has been detected on Mars using CRISM hyperspectral images^{44,85}, but most of these detections have been called into question after discovery of a 2.1 μm spectral artifact in CRISM TRR3 data that can resemble the diagnostic absorption feature of Mg-rich serpentine⁴⁴. Still, at least 3 Mg-rich serpentine detections have been validated as unrelated to this artifact⁴⁴, demonstrating that serpentinization has occurred on Mars. The fluids generated via serpentinization are highly reducing, which can cause precipitation of reduced alloys and minerals such as awaruite^{107,108} (NiFe alloy) and sulfides^{45,86–90}. As such, serpentinization would have generated reducing fluids on Mars that could have precipitated and concentrated sulfide minerals, making regions containing serpentine potential ‘hotzones’ for both ancient chemolithotrophic life that consumed H_2 from serpentinization, as well as modern chemolithotrophic life that may consume H_2 and SO_4 from radiolysis in sulfide-rich zones.

S1.8 Possible settings of concentrated sulfides on Mars

1. *Differentiated impact melt sheet*: The Sudbury Impact Structure in Ontario, Canada is one of the three largest discovered impact structures on Earth—the others being Chicxulub and Vredefort—and hosts concentrations of sulfides of high economic value. Sulfides were concentrated via gravitational differentiation from the impact melt sheet¹⁰⁹. Sulfur was likely introduced to the impact melt via assimilation from the surrounding country rock during the depressurization melting that formed the Sudbury Igneous Complex^{110–112}. Because of the prevalence of sulfur on Mars in the form of sulfates and S-rich regolith, and the larger number of preserved impact structures on Mars relative to Earth, Sudbury-type differentiated impact melt sheet sulfide concentrations may be more common on Mars than they are on Earth (ref. ¹¹³) (Fig. 3 Setting 1).
2. *Layered intrusions*: Sulfides are commonly concentrated in ultramafic-to-mafic layered intrusions on Earth, such as the Bushveld Igneous Complex in South Africa¹¹⁴, Voisey's Bay in Canada¹¹⁵, Jinchuan in China¹¹⁶, and the Noril'sk-Talnakh deposits in Siberia¹¹⁷. Sulfides are typically concentrated as residue in restricted conduits/channels, and thus are often concentrated at the base of the layered intrusion, in sills, or in stratiform reef-style deposits¹¹⁸. Such intrusions typically form in intracratonic settings, often via mantle plume activity¹¹⁹. This is similar to settings of non-subvolcanic and subvolcanic intrusions formed on Mars, which is a single-plate planet. There is evidence for ultramafic volcanism on Mars^{104,105} and basaltic volcanism is prevalent across the entire planet¹²⁰. Mantle plumes have caused volcanism on Mars, likely forming the Tharsis and Elysium volcanic bulges^{121–123}. It is

thus plausible that both subvolcanic and non-subvolcanic ultramafic-to-mafic magmatic intrusions exist on Mars, providing structures for potential concentration of sulfides (Fig. 3 Settings 2 & 7).

3. *Hydrothermal sulfides.* Sulfides are concentrated by hydrothermal fluids that are S-rich and reducing. Many hydrothermally-formed sulfide deposits are associated with serpentinites, due to the highly reducing fluids formed during the process of serpentinization^{107,108} causing formation of metal alloys¹⁰⁷ and sulfides^{45,86–90}. Hydrothermal sulfides are found in regolith breccia martian meteorites^{24,25,74,23}. Minerals potentially produced by hydrothermal alteration, including smectites, carbonates, chlorite, hydrated silica, and zeolites⁶⁵, and small amounts of Mg-serpentine^{44,85} are detected on the martian surface from orbit using CRISM. Evidence for past hydrothermal alteration has been seen by every Mars rover. NASA's Opportunity rover observed evidence for multiple diagenetic episodes in the Burns Formation¹²⁴, as well as hydrothermal alteration of bedrock due to meteorite impact at Endeavour crater^{125,126}. NASA's Spirit rover observed carbonate-bearing olivine-rich rocks (Comanche) formed via alteration of ultramafic tuff (Algonquin)^{106,127}, silica deposits¹²⁸ that likely formed in hot spring settings^{129,130}, and hydrothermal alteration of Home Plate resulting in precipitation of silica¹³¹. NASA's Curiosity rover has found evidence for multiple diagenetic episodes in the stratigraphy of Mount Sharp, including cross-cutting Ca-sulfate veins¹³², jarosite veins dated to 2.1 ± 4 Gyr (ref. ¹³³), and evidence for diagenetic episodes that cross-cut multiple stratigraphically distinct units¹³⁴. Sulfides could also be concentrated via

- hydrothermal activity during submarine volcanism –as likely occurred in Eridania Basin¹³⁵. As such, hydrothermal alteration has occurred on Mars in a wide variety of geochemical settings, including some that precipitated pyrite in regolith breccias^{24,25,74,23}, and some that formed serpentinite^{44,85}. It is plausible that higher concentrations of sulfides than those found in NWA 7533 and NWA 7034— which were ejected from Mars by the same impact event²⁵—could form from hydrothermal alteration in other regions of the martian crust (Fig. 3 Settings 3 & 5).
4. *Sulfide-bearing sediments.* Mount Sharp in Gale crater is an example of a sulfide-bearing sediment mound on Mars^{136,29,28} (Fig. 3 Setting 4). These sulfides are diagenetic/epigenetic, likely resulting from thermal reduction of preexisting sulfates. It is possible that a similar sulfate thermal reduction process could occur in other sulfate-bearing martian sediments, which are widespread⁵³, thus generating a higher concentration of sulfides in those localities. Cu-enrichments in Gale crater are potentially due to presence of detrital sulfides⁴⁶. It is therefore plausible that sulfides could be concentrated in martian sediments in detrital form and also via diagenetic processes.
 5. *Differentiated ultramafic-to-mafic lava flows.* Examples of sulfide concentrations in komatiitic lava flows on Earth include the Kambalda and Perseverance deposits in Australia. Sulfides are also concentrated picrites, including the Pechenga deposits in Russia¹¹⁹. Due to the presence of ultramafic lithologies in martian meteorites, the possibility of sulfide concentration in komatiite-type settings has been known for decades³⁷. Since then, further evidence for ultramafic volcanism on Mars has been

presented^{104–106}. The magmas that precipitated the nakhlites assimilated sulfur from the crust, forming a sulfide-saturated melt^{40,41}. Thus, there is already evidence for some degree of sulfide concentration in differentiated ultramafic-to-mafic lava flows on Mars via the martian meteorites (Fig. 3 Setting 6).

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CHAPTER 3: Successes and challenges of factor analysis/target transformation application to visible-to-near-infrared hyperspectral data

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Abstract

We developed a laboratory visible-to-near-infrared (VNIR) hyperspectral experiment to test the effectiveness of factor analysis/target transformation for detecting minerals mixed with Mars Global Simulant-1 (MGS-1). The results demonstrate that factor analysis/target transformation is prone to both false positive and false negative detections, but in certain applications, including Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT), it can be useful for highlighting spectrally interesting areas in hyperspectral images for follow-up investigation. Applications that solely employ factor analysis with no target transformation step—such as guided factor analysis (GFA)—are useful for extracting spectra of endmember variance signal components without ratioing or unmixing. Elimination of the target transformation step significantly lowers the propensity for false positive results. The results presented here demonstrate that applications of factor analysis/target transformation to VNIR hyperspectral datasets should be used to highlight small outcrops and/or weak spectral signals in pixels for follow-up investigation. This emphasizes the need for supporting evidence to be obtained, in addition to factor analysis/target transformation, before interpretations of planetary surface processes should be made. Factor analysis by itself can be used to extract endmember variance components that are recognizable combinations of mineral spectra whose presence can be further supported by construction of band parameter maps, and is therefore overall a more reliable approach compared to factor analysis/target transformation.

1.0 Introduction

Factor analysis (Malinowski, 1991) is the extraction of orthogonal eigenvectors that describe variance in a multivariate dataset. In the present study, the multivariate datasets consist of various VNIR spectra. Ideally, the eigenvectors that describe the signal subspace of input spectra can be distinguished from those associated with noise, though this is rarely the case in practical applications, as nearly all data contain some structured noise. In target transformation, the eigenvectors from factor analysis are combined via unconstrained linear least squares fitting to target spectra (e.g. Glotch and Bandfield, 2006; Thomas and Bandfield, 2017; Amador et al., 2018). If the fit to a target spectrum is considered good via similarity metrics such as Root Mean Square Error (RMSE), spectral angle, or by-eye expert assessment, then that spectrum is considered an endmember component within the dataset, even if it does not exist in spectrally pure form in any specific measurement.

Factor analysis of data from Mars was first used to separate out the infrared spectral components of the martian atmosphere (atmospheric dust, water-ice, and a blackbody component) from surface emissivity as measured by the Thermal Emission Spectrometer (TES) (Bandfield et al., 2000; Smith et al., 2000). It was later applied to separate the spectral shapes of gray hematite, basaltic sand, surface dust, silica-sulfate rich material, and two atmospheric spectral shapes in emissivity observations of Meridiani Planum measured by the Miniature Thermal Emission Spectrometer (Mini-TES) onboard the Opportunity rover (Glotch and Bandfield, 2006). These factor analysis applications used spectra at infrared wavelengths, where spectral mixing of physical components is linear (Ramsey and Christensen, 1998). Spectral mixing at VNIR wavelengths, which are the wavelengths of CRISM, is non-linear (e.g. Hapke and Wells, 1981). Differences in wavelength-dependent mixing regimes, combined with

the high amount of structured noise in CRISM data, makes it unlikely that factor analysis/target transformation (FA/TT) will work as reliably in these data. As such, claiming mineral detections in CRISM data solely using FA/TT should be approached with caution.

FA/TT has recently been applied to CRISM scenes for the purpose of detecting components of mineral mixtures, weak spectral signals broadly distributed across an image, and/or spatially small outcrops of specific spectral signals (Amador et al., 2018; Thomas and Bandfield, 2017). Both of these innovative studies applied FA/TT to uniformly subsampled CRISM data and presented possible mineral detections based on their results. These studies collected spectra from 4% of the pixels in each CRISM image (every 5th row and every 5th column), evenly distributed across sensor space in each image, and used FA/TT to reconstruct spectral endmembers, which are presumed to represent spectra of minerals rather than artifacts, or combinations of minerals and artifacts, or combinations of spatially separate minerals. These studies, which report most of their detections based solely on results from FA/TT, do not constrain where the reported possible mineral detections are physically present within the analyzed CRISM images.

FA/TT techniques show exciting promise in identifying the presence of minerals in data collected from mineralogically complex terrains or in widespread low abundance. However, while factor analysis can sometimes separate signal from random noise, it cannot separate signal from structured noise (e.g. Glotch and Bandfield, 2006). Therefore, in the presence of structured noise, significant false positives are possible. CRISM data are known to contain significant quantities of structured noise (Wiseman et al., 2016), some of which can resemble diagnostic absorption features of minerals (e.g. Leask et al., 2018). Experiments are presented

here to test the sensitivity of FA/TT to structured noise, its ability to detect broadly distributed minerals at low abundance, and its propensity for false positive and false negative detections. They also test the mineral-specific modal abundance thresholds at which FA/TT can detect calcite, gypsum, nontronite, montmorillonite, and kaolinite in intimate mixtures at different grain sizes with Mars Global Simulant-1 (MGS-1; Cannon et al., 2019).

Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT) (Lin et al., 2018; Tarnas et al., 2019; Lin et al., 2020) was developed to leverage the advantages of FA/TT methods applied to CRISM data while preserving information regarding the spatial distribution of detected spectral signals within an image. This is implemented by iteratively performing FA/TT in a ~50 pixel window that moves across a hyperspectral image in sensor space one pixel at a time. The target transformation fits that are within an empirically selected threshold RMSE are classified as positive detections by DAFA/TT. Five different ~50 pixel window shapes are used, and only the pixels with positive detections in all window shapes are considered true detections. This means that while DAFA/TT is susceptible to false positive detections due to structured noise and/or association of absorptions with incorrect minerals, the regions where spectral signals are proposed to exist are highlighted, allowing for vetting via extraction of spectra from those pixels. Factor analysis of spectra (Malinowski, 1991) has been applied to spectral data for characterization of spectrally active components during measurement of chemical evolutionary processes including chromatography and titration (Schostack and Malinowski, 1993; Malinowski, 1996). It is notable that DAFA/TT is similar to some of these earliest applications of factor analysis to spectral datasets (e.g. Schostack and Malinowski, 1993; Malinowski, 1996), where spectra were subset in windows that moved in temporal

space—during evolution of the chemicals of interest—in order to more effectively analyze the data. Spectra that dominate the variance in one subset of the dataset, be it in spatial or temporal dimensions, are present as higher eigenvalue eigenvectors of the variance matrix of that subset compared to their signal power within the entirety of the dataset. This is the fundamental principle that makes subsetting data for factor analysis an effective method for improving performance, no matter the dimension(s) in which subsetting occurs.

DAFA/TT's effectiveness has been demonstrated by its capability to detect spectrally weak and spatially small distributions of minerals such as hydrated silica and Al-phylosilicate in Jezero crater and its watershed rock units (Tarnas et al., 2019), as well as serpentine elsewhere in Nili Fossae (Lin et al., 2020). It is notable that in some cases DAFA/TT did mistake the 2.1 μm artifact, characterized by Leask et al., (2018), for serpentine when it was present within pixels covering a smectite outcrop. However, because the pixels of interest were highlighted, these detections could be vetted following the methodology of Leask et al., (2018) and therefore a true, non-artifact-derived outcrop of serpentine could be verified (Lin et al., 2020).

Statistically-based approaches, including machine learning, are regularly employed in hyperspectral data analysis (e.g. Li et al., 2019). For large-scale geologic applications, these methods are typically verified using hyperspectral images of well-characterized field sites on Earth (e.g. Ni et al., 2020). For smaller-scale geologic applications, such as drill-core analysis, these methods are typically validated using complementary mineral identification techniques such as Mineral Liberation Analysis (Contreras et al., 2018; Contreras Acosta et al., 2019; Laura Tuşa et al., 2020a; Tuşa et al., 2020b). In planetary sciences, validation and verification often relies on detection of spectral signatures in areas where the target signal of interest was

previously identified by more “traditional” techniques (e.g. Bue, 2014; Dundar and Ehlmann, 2016; Allender and Stepinski, 2017; He et al., 2019; Lin et al., 2020). “Traditional” techniques typically include extraction of spectra from a hyperspectral image of a planetary surface, followed by comparison of these spectra with laboratory spectra. Spectra are compared either directly or following application of data processing techniques to enhance weak or noisy diagnostic features of minerals in remotely acquired data, including continuum removal or ratioing target spectra to a spectrally neutral material (e.g. Mustard et al., 2005, 2008). If the position, shape, and strength of absorption features identified in the remotely acquired data conform with the same features in a spectrum acquired of a known material in the laboratory, then the science community concurs that the material—often a mineral—represented by the laboratory spectrum exists at that specific location on the planetary surface.

To date, groundtruthing of remotely acquired mineral detections on Mars has only occurred in the Murray Formation, Bagnold Dunes, Vera Rubin Ridge, and Glen Torridon rock units in Gale crater (Bristow et al., 2019; Buz et al., 2017; Ehlmann et al., 2017; Fraeman et al., 2020, 2013; Jacob et al., 2020; Lapotre et al., 2017; Milliken et al., 2010; Rampe et al., 2020, 2018, 2017; Seelos et al., 2014), the Burns formation and Endeavour crater rim in Meridiani Planum (Arvidson et al., 2015; Fox et al., 2016; Noe Dobrea et al., 2012; Wray et al., 2009), and the Comanche carbonate in Columbia Hills (Carter and Poulet, 2012; Morris et al., 2010). Fraeman et al., (2020) successfully groundtruthed orbital VNIR spectra (CRISM) using VNIR spectra with an overlapping wavelength range acquired from the Curiosity rover (Mastcam) that includes diagnostic features of the mineral of interest, and this was solely for hematite. In other cases, false negative identifications from orbit have been induced by either dust, soil, and

coating covers (e.g. Arvidson et al., 2015) or nonlinear mixing effects (e.g. Jacob et al., 2020). These few regions of Mars—where remote mineral identification groundtruthing has occurred—have rarely been used to date for validation of new hyperspectral analysis methods applied to CRISM data. As such, most mineral detections used for technique validation to date are lacking in groundtruth and have only been investigated from orbit. Testing new hyperspectral analysis methods in a laboratory setting using relevant mineral mixtures for a given planet, in this case Mars, is therefore an important validation step.

Here we test FA/TT, DAFA/TT, and GFA's capabilities for mineral detection using laboratory hyperspectral data of well-characterized mineral mixtures. The mixtures consist of secondary minerals and MGS-1 (Cannon et al., 2019). MGS-1 approximates the integrated chemical, mineralogical, and spectral properties of martian regolith (Cannon et al., 2019). Secondary minerals mixed with the regolith simulant are gypsum, kaolinite, calcite, montmorillonite, and nontronite, which have been directly or indirectly detected on the surface of Mars in remotely sensed data and/or data from landers (Bishop et al., 2008; Cannon et al., 2012; Clark et al., 2007; Langevin et al., 2005; McKeown et al., 2009). This study seeks to assess whether these minerals can be detected via FA/TT techniques when mixed with MGS-1, and to evaluate the abundance thresholds at which detection is no longer possible for these specific intimate mixtures. We also test the propensity of various FA/TT techniques for false positive and false negative detections in VNIR hyperspectral images with realistic amounts of structured noise, which is still less than the amount of structured noise in CRISM TRR3 data. By using laboratory-acquired hyperspectral data with a similar wavelength range as CRISM and OMEGA, we are able to evaluate the strengths, weaknesses, and limits of different FA/TT methods.

2.0 Methodology

2.1 Experimental Setup

Mineral mixtures

We designed a hyperspectral experiment—termed the “Mars tray”—to test different mineral target detection techniques, including various implementations of FA/TT which are the focus of this study. We mixed calcite, kaolinite, nontronite, montmorillonite, and gypsum with MGS-1 at abundances listed in Table S1 and placed these mixtures into individual sections of a tray. Hyperspectral images of the trays were measured using a Headwall hyperspectral camera. These hyperspectral images can be used to test any VNIR hyperspectral image target detection method.

The secondary minerals were first ground with a mortar and pestle and sieved to known particle sizes, which are listed in Table S1. We made two-component mixtures of Mars Global Simulant-1 (Cannon et al., 2019) with 125+ μm gypsum, 45-75 μm gypsum, 125+ μm kaolinite, 45-75 μm calcite, 125+ μm calcite, 125+ μm montmorillonite, and 125+ μm nontronite at 50%, 20%, 10%, 5%, 2.5%, and 1% volumetric abundances of the non-MGS-1 component (Table S1). 125+ μm powders primarily consist of 125-250 μm particles, with a few larger particles included. The mixtures were put into $2.5 \times 2.5 \times 1$ cm trays, which were filled to the top except for in some cases when an insufficient amount of material was available. A straight edge was drawn across the top of each mixture tray in a U-shaped motion, which leveled the surface without preferentially aligning mineral grains. For each experiment, MGS-1 was put into two $5 \times 5 \times 1$ cm trays which were placed such that they subtended every pixel column containing

spectra of the mineral mixtures. The sample trays, composed of Acrylonitrile Butadiene Styrene (ABS) plastic filament, were 3D printed and then painted with Nextel black suede coating 3101 paint, which has a reflectance of 0.03 from 0.3-2.8 μm .

An important caveat to these experiments is that our pixel size ($0.34 \times 0.34 \text{ mm}$) is similar to our mineral mixture grain sizes ($\sim 45\text{-}250 \mu\text{m}$). This is not comparable to pixel size/grain size ratio scales from orbital hyperspectral data, which currently have 10s of meters spatial resolution at best. As such, the types spectral mixing (linear versus nonlinear) may be different in certain pixels of our experiment compared to spectral mixing of airborne or orbital VNIR hyperspectral datasets. Because the methods tested in this study are for target detection and not abundance determination, this should not drastically change our results.

Data acquisition

We used the Brown University Imaging Spectrometer (BUIs) to measure hyperspectral images of the mixture trays. BUIs consists of two Headwall spectrometers, a visible-near infrared (VNIR) spectrometer and a short wavelength infrared spectrometer (SWIR) that are co-boresighted and provide optical observations across the wavelength range 400 – 2600 nm. For this project, we used only the SWIR spectrometer. The SWIR instrument measures the 900 – 2600 nm wavelength region using a HgCdTe detector with 384 spatial pixels and 167 spectral bands. The spectral sampling interval is 8.98 nm and the Full Width Half Maximum is 9 nm. The lens on the SWIR instrument produces an Instantaneous Field Of View (FOV) of 6.748 mrad and an angular FOV of 24° . Both instruments are mounted inside an aluminum frame with a data system running software that controls the operation of both sensors and stores data on a 1 Tb solid state drive (SSD). Light entering the VNIR and SWIR lenses first passes through a dichroic

filter that transmits wavelengths ≥ 1000 nm to the SWIR instrument and reflects wavelengths in the 400 – 1000 nm range to the VNIR instrument. The VNIR and SWIR instruments are boresight aligned. For these measurements, the spectrometer was fixed 25 cm above a translation table, which moved at a speed synced to the spectrometer's frame acquisition and averaging rate, resulting in spatially accurate square pixels. The spatial resolution of the pixels is 0.34 mm. The field of view of the instrument is illuminated with a quartz halogen lamp and there is a fixed Spectralon® strip on one end of the table that subtends all pixel columns.

The Spectralon® target provides the white reference used for calibration of data to apparent reflectance. We acquire dark current digital number (DN) measurements that are also used for calibration. The DN spectra of all pixels covering the Spectralon® target in each individual column are averaged to produce a column-dependent DN white reference spectrum. The dark current DN spectrum is subtracted from the DN spectrum of each pixel as well as the white reference DN spectra. The DN spectrum of each pixel in a column with the dark current DN spectrum subtracted is divided by the white reference DN spectrum for that column, which also has the dark current DN spectrum subtracted. This ratio is then multiplied by the absolute reflectance spectrum of 99% reflectance Spectralon®. This process is summarized by the equation

$$AR = \frac{S - DC}{WR - DC} \times R_{Spec}$$

where AR is apparent reflectance, S is the DN spectrum of each sample, DC is the dark current spectrum, WR is the white reference DN spectrum for the pixel column containing S , and R_{Spec} is the absolute reflectance spectrum of Spectralon® measured in the Reflectance Experiment

Laboratory (RELAB) at Brown University resampled to the wavelengths of the BUIS SWIR spectrometer.

For our full-image FA/TT analysis, where all pixels are used for FA/TT and no spatial information regarding spectral signal distribution is returned, we subset the data such that only the pixels for each individual mixture tray are analyzed via FA/TT. For our DAFA/TT analysis, we apply DAFA/TT to the entire hyperspectral image cube.

2.2 Factor determination

We employ 2 different methods of factor determination in our experiment: R-mode factor analysis and the HySime algorithm (Bioucas-Dias and Nascimento, 2008). In R-mode factor analysis as employed in Bandfield et al., 2000 and Glotch and Bandfield, 2006, the collection of spectra that are mixtures of multiple components can be written as $D = R \cdot C$, where D is an $n \times m$ matrix of measured spectra with n being the number of spectra and m being the number of spectral bands; R is a matrix of endmember spectra, and C is a matrix of endmember concentration values (Bandfield et al., 2000). This assumes that the concentrations of endmembers linearly combine to produce the measured spectra, which is not typically the case for modal abundances of minerals at VNIR wavelengths (Hapke and Wells, 1981). We therefore refer to C as a matrix of endmember spectral contribution ratios, rather than ascribing physical properties to it. There exist several methods for estimating R including the iterative power method, the Jacobi method, singular value decomposition, and nonlinear iterative partial least squares (NIPALS) (Malinowski, 1991), as well as the power method (Press and TSA, 1995) which was employed for the R-mode factor analysis factor determination

method used in this study, as well as in Amador et al., 2018; Bandfield et al., 2000; and Thomas and Bandfield, 2017. The HySime algorithm is described in Bioucas-Dias and Nascimento, 2008.

The presence of structured noise is a common issue in scientific and technical fields reliant on image data. Though its presence was apparent from the development of film, its tendency to skew scientific/medical results was first appreciated in the context of radiology (e.g. Kundel, 1975; Kundel and Revesz, 1976). Structured noise is still present in digital images, and a significant number of studies (e.g. Kanemura et al., 2007) and patented technologies (e.g. Lukac, 2013) have been developed to mitigate it in a variety of contexts, both entertainment and scientific. It is still a known issue in the vast majority of hyperspectral image datasets.

2.3 Target transformation

We follow the target transformation methods described in Amador et al., 2018; Bandfield et al., 2000; Glotch and Bandfield, 2006; Malinowski, 1991; and Thomas and Bandfield, 2017. This implements unconstrained linear least squares fitting of factor analysis-derived signal eigenvectors to library spectra of specific mineral phases. We collect spectra from the RELAB database and have 30-400 individual spectra for each individual mineral phase. We qualitatively determine which library spectrum for each mineral provides the best results in our experiments and display those results in Figs. 4-5, 12-20, and S1-S20. We use Root-Mean-Square-Error (RMSE) as our fitting metric. Target transformation can induce false positive detections via inflating structured noise features in eigenvectors, or combining eigenvectors derived from spatially separate parts of a hyperspectral image, in order to obtain optimal fits to library spectra.

2.4 Full image FA/TT

Previous applications of FA/TT to CRISM data (Amador et al., 2018; Thomas and Bandfield, 2017) have used every 5th pixel in a hyperspectral image (or subset of a hyperspectral image) for a single FA/TT process to fit target minerals. Though this amounts to 4% of the total data per image cube, we refer to it as full-image FA/TT throughout the text, as the pixels used for FA/TT are distributed evenly in sensor space. These studies have implemented R-mode factor analysis. Fits from full-image FA/TT to target minerals are deemed good versus bad based on goodness-of-fit metrics such as RMSE and/or spectral angle, as well as by-eye inspection by expert users. In these previous studies, good fits to target minerals via full-image FA/TT are used as evidence for the presence of those minerals in analyzed CRISM images. We apply full-image R-mode factor analysis to a CRISM image where Amador et al., 2018 find a good fit to serpentine via full-image FA/TT. These authors interpret this fit as evidence for the presence of serpentine within the image, without extracting an I/F spectrum consistent with the presence of serpentine to support this claim.

We also applied full-image FA/TT to the individual mixture trays in our Headwall data, using both R-mode FA and HySime to calculate eigenvectors. This tests the tendencies from full-image FA/TT for true detections, false negative detections, and false positive detections, as well as the performance of HySime versus R-mode factor analysis, in a controlled laboratory setting. We also perform experiments using HySime with a 10 eigenvector threshold and HySime with a 15 eigenvector threshold to test how the number of eigenvectors affects performance. Following Amador et al., 2018, we threshold our full-image R-mode FA/TT to 15 eigenvectors.

For our full-image FA/TT application to CRISM data, we used 54 serpentine library spectra from RELAB. We also tested the propensity of this method for false positives by using spectral libraries of vegetation, artificial construction materials, and chocolate, none of which could possibly be present on the surface of Mars. We used 75 library spectra of vegetation, 23 library spectra of artificial construction materials, and 7 library spectra of chocolate. The vegetation and artificial construction materials spectral libraries were obtained from USGS, and the chocolate library spectra were obtained from the RELAB database.

For full-image FA/TT of Headwall data, we used 70 carbonate, 87 gypsum library spectra, 394 nontronite, 92 kaolinite, and 390 montmorillonite library spectra, all of which were obtained from the RELAB database. To test the performance of full-image FA/TT application to Headwall data, we selected a library spectrum for each mineral type that had good fits to the 100%, 50%, and 20% abundance mixtures. We then inspected the fits—for each mixture tray, each eigenvector calculation method, and each eigenvector thresholding number—by-eye to determine if they were good or bad. We provide descriptions for why fits were deemed good or bad via by-eye inspection. We measured the average spectra of each mixture tray. Situations where full-image FA/TT fits displayed good fits to the diagnostic absorption features of each targeted mineral, and where the average spectrum of the tray showed those same diagnostic absorptions, were classified as true positive detections. Situations where full-image FA/TT fits displayed good fits to the diagnostic absorption features of each targeted mineral, but where the average spectrum of the tray did not show those same diagnostic absorptions, were flagged for further inspection of the pixels. We inspected every pixel within those flagged mixture trays to determine if any of their spectra contained diagnostic spectral features of the targeted

mineral. If one or more single pixel spectra contained the right diagnostic features, we classified them as “spectrum exists in tray”. If no single pixel spectra contained the right diagnostic features, we classified these as false positives. Situations where full-image FA/TT fits displayed mediocre fits to diagnostic absorption features of each targeted mineral, but the average spectrum of the tray did not show those same diagnostic absorptions, were also tested via the aforementioned single-pixel inspection. If one or more single pixel spectra contained the right diagnostic features, we classified them as “spectrum exists in tray”. If no single pixel spectra contained the right diagnostic features, we classified these as borderline false positives. If FA/TT badly fit the diagnostic absorption features and the average spectrum of the mixture tray did not contain diagnostic absorption features, the performance was classified as a true negative detection.

2.5 Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT)

DAFA/TT was applied to both CRISM and Headwall data to test its performance. We applied DAFA/TT to 50 CRISM TRR3 FRT images to test its capability to detect serpentine spectra on Mars that were verifiable via extraction of I/F and radiance-derived I/F ratio spectra following the method of Leask et al., 2018. We used 54 serpentine library spectra obtained from the RELAB database. We used the first 50 images acquired during the CRISM mission for this test.

For DAFA/TT application to Headwall data, we applied DAFA/TT to each image cube without spatially subsetting any of the data. We used HySime with a 15 eigenvector threshold, HySime with a 10 eigenvector threshold, and R-mode factor analysis with a 15 eigenvector

threshold to test how eigenvector calculation methods and the number of eigenvectors affects target detection performance. Other than using different methods for eigenvector calculation, we followed the same method as Lin et al. (2020). Following Lin et al. (2020), we used a RMSE threshold of 1.5×10^{-4} to differentiate good and bad fits.

The fits for DAFA/TT clusters were inspected by-eye for goodness of fit to diagnostic absorption features consistent with each mineral. If the fits to these diagnostic features were good, we deemed this cluster a good detection. Only clusters deemed good detections are displayed in the figures. We then took the average spectrum of each cluster to test for the presence of those diagnostic absorption features. If the diagnostic absorption features existed in the average spectra, we deemed these true positive detections. If the diagnostic absorption features did not exist in the average spectra, single-pixel spectra inspection was performed. If one or more single pixel spectra contained the right diagnostic features, we classified them as “spectrum exists in tray”. If no single pixel spectra contained the right diagnostic features, we classified these as false positives. If DAFA/TT did not detect the presence of a mineral within a tray mixture whose average spectrum demonstrably contains diagnostic spectral features consistent with that mineral, a false negative detection was assigned for those trays. If DAFA/TT clusters only partially covered a tray whose average spectrum contains diagnostic spectral features of that mineral, it was classified as a partial true detection. If DAFA/TT did not detect the presence of a mineral within a mixture tray and the average spectrum of that mixture tray did not contain diagnostic absorption features consistent with that mineral, the performance was classified as a true negative detection.

2.6 Guided factor analysis (GFA)

We present a modified factor analysis application termed guided factor analysis (GFA), which builds on the original factor analysis chromatography applications (Malinowski, 1996; Schostack and Malinowski, 1993), applications to Earth mineralogic analysis (Bandfield et al., 2002), early applications of factor analysis to data from Mars (Bandfield et al., 2000; Glotch and Bandfield, 2006), and finally application of factor analysis to CRISM data (Amador et al., 2018; Thomas and Bandfield, 2017). If prior information can guide the subsetting of data such that the subsets primarily contain data with the same variance-contributing components, these components will appear as higher eigenvalue eigenvectors relative to their appearance in factor analysis of the entire dataset –if they show up at all in full-dataset factor analysis. This principal is demonstrably correct based on many of the aforementioned past studies, in particular Amador et al., 2018; Bandfield et al., 2002; Malinowski, 1996; Schostack and Malinowski, 1993, which showed that the performance of factor analysis is improved via subsetting of data by isolating individual components thought to contain a specific shared variance-contributing spectral signal. Data subsetting allows for analysis of spectral signals that do not generate high amounts of variance across the entire combined dataset, but do generate high amounts of variance within specific, discrete, and/or compartmentalized components of the dataset.

GFA maps the dot product of each eigenvector with each pixel in the subsetted data to determine which pixels contain the strongest signal from each eigenvector. Users practice by-eye selection to determine which eigenvectors resemble true signals and which resemble structured noise, similar to the evaluation methods employed in Bandfield et al., 2002, 2000; Glotch and Bandfield, 2006; Malinowski, 1996; Schostack and Malinowski, 1993. An expert user

can typically determine which eigenvectors resemble true signals from the dataset, and which appear to be structured noise, or combinations of true signals and structured noise. The dot product mapping of eigenvectors can also be used to differentiate signal eigenvectors from structured noise eigenvectors, or eigenvectors that are combinations of signal and structured noise, based on the distribution of the eigenvector's correlation across an image. For example, eigenvectors with correlation that is patterned following individual columns in sensor space are likely structured noise eigenvectors.

We evaluate the effectiveness of GFA application to VNIR hyperspectral data by testing its ability to detect spectra of the individual mineral components comprising MGS-1. We also test its ability to reproduce the results of past CRISM detections of high and low calcium pyroxene in Jezero crater (Horgan et al., 2020). For this test, we use CRISM image HRL000040FF and apply GFA to both CRISM TRR3 data and the same image cube processed by the University of Massachusetts at Amherst (UMass) pipeline (Itoh and Parente, 2021). We use both R-mode FA and HySime to test the consistency of eigenvector shapes between these two methods. We use LCPINDEX2 and HCPINDEX2 (Viviano-Beck et al., 2014) to select which pixel subsets are used for GFA.

CRISM data is often ratioed to 'bland' spectra from the same columns as the target pixels to remove instrumental structured noise in spatial and spectral dimensions. However, many CRISM scenes do not contain 'bland' spectra in every column, making the ratio technique fraught with potential for false positive detections. Factor analysis is an effective way to remove structured noise in CRISM data (Thomas and Bandfield, 2017). Theoretically, GFA can extract eigenvectors that represent spectral variance components of the dataset that do not contain

spatial and spectral structured noise –particularly if they are high eigenvalue eigenvectors. This may therefore provide a more reliable method compared to ratioing for extracting ‘clean’ spectra from hyperspectral images, one that is applicable even where no truly ‘bland’ spectra exist in the same column as the pixels containing the target material.

3.0 Results

3.1 Full-image FA/TT

CRISM image FRT0000AA03

The results of R-mode full-image FA/TT application to CRISM image FRT0000AA03 are displayed in Figs. 1-3. Amador et al., 2018 interpreted good fits to a serpentine library spectrum via 15 eigenvector threshold R-mode full-image FA/TT application to this CRISM image as evidence for the presence of serpentine in it. This study used every 5th pixel of the image for their analysis. We use every pixel in the image for our analysis. We find a good fit to serpentine in this image by using 18 eigenvector threshold R-mode full-image FA/TT, but were unable to reproduce the results of (Amador et al., 2018) using a threshold of 15 eigenvectors, derived using every pixel in the image, for any of our 54 serpentine library spectra. The RMSE for our best fit to serpentine was 3.13e-4. We looked at all the eigenvectors calculated by full-image R-mode FA for this CRISM image (Fig. 2a) and at how target transformation stretched out specific eigenvector features via coefficient multiplication (Fig. 2b-d) in order to assess which eigenvectors contributed to generating a good fit to serpentine for this image. We find that eigenvectors 1, 2, 4, 5, and 9 dominate the target transformed eigenvectors used to achieve a

good fit to the serpentine spectrum. It is unclear if eigenvectors 5 and 9 are signal components of the image or are structured noise, but they contain random noise throughout their structure.

Applying 15 eigenvector threshold R-mode full-image FA/TT to this same CRISM image, fits were found to spectra of gloss paint (RMSE = $1.15\text{e-}4$), a dry tree leaf ($1.87\text{e-}4$), and chocolate ($9.46\text{e-}4$) that were comparable to the fits to serpentine spectra calculated with an 18 eigenvector threshold. The fits to gloss paint and dry tree leaf spectra were quantitatively better than the fit to serpentine. Clearly gloss paint, dried tree leaves, and chocolate do not exist on the surface of Mars, therefore these results constitute obvious false positives. We looked at all the eigenvectors calculated by R-mode FA for this image (Fig. 3a), which are the same eigenvectors used to find good fits to serpentine, and analyze how target transformation stretched out specific eigenvector features via coefficient multiplication (Fig. 3b-d) in order to assess which eigenvectors contributed to generating a good fit to gloss paint for this image. We find that eigenvectors 1, 2, 5, 9, and 10 dominate the target transformed eigenvectors used to achieve a good fit to the gloss paint spectrum. It is unclear if eigenvectors 5, 9, and 10 are signal components of the image or are structured noise. Eigenvectors 5, 9, and 10 all contain some random noise throughout their structure, and eigenvector 10 appears to contain at least some structured noise at $\sim 2.18\text{ }\mu\text{m}$ that is likely an atmospheric residual. This test demonstrates an enormous potential for false positives in full-image FA/TT applications.

Headwall images

The results for our full-image FA/TT experiments on Headwall images are summarized in Table 1. The experimental outputs used to generate Table 1 are described below.

Gypsum 125+ μm

We used gypsum spectrum RELAB ID C2PG03 for this analysis. For 15 eigenvector R-mode FA/TT, fits for the 100%, 50%, 20%, 10%, 5%, and 2.5% trays are good because the shape of the 1.45, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well. Fits to the 1% and 0% trays are borderline because the 1.45, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well (Fig. S2a). For 10 eigenvector HySime FA/TT, fits for the 100%, 50%, 20%, 10%, 5%, and 2.5% trays are good because the shape of the 1.45, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well (Fig. S2b). Fits to the 1% tray are borderline because the 1.45, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well (Fig. S2b). Fits to the 0% tray are bad because the 1.75 and 2.2 μm features do not exist (Fig. S2b). For 15 eigenvector HySime FA/TT, fits for the 100%, 50%, 20%, 10%, 5%, and 2.5% trays are good because the shape of the 1.45, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well (Fig. S2c). Fits to the 1% and 0% trays are borderline because the 1.45, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well (Fig. S2c).

The average spectra for the 100%, 50%, 20%, and 10% trays have 1.45, 1.75, and 2.2 μm absorptions with shapes consistent with gypsum, as well as a 2.4 μm shoulder consistent with gypsum (Fig. S2d-e). The 5% and 2.5% trays have single pixel spectra consistent with gypsum (Fig. 13). For the gypsum 125+ μm Mars tray, there were 5 borderline false positives (Table 1).

Gypsum 45-75 μm

We used gypsum spectrum RELAB ID C2PG03 for this analysis. For 15 eigenvector R-mode FA/TT, fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.45, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well (Fig. S3a). Fits to the 2.5%, 1%, and 0% trays are borderline because the 1.45, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well (Fig. S3a). For 10 eigenvector HySime FA/TT, fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.45, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well (Fig. S3b). Fits to the 2.5%, 1%, and 0% trays are bad because the 1.75 and 2.2 μm features do not exist (Fig. S3b). For 15 eigenvector HySime FA/TT, fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.45, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well (Fig. S3c). Fits to the 2.5%, 1%, and 0% trays are borderline because the 1.45, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well (Fig. S3c).

The average spectra for the 100%, 50%, 20%, and 10% trays have 1.45, 1.75, and 2.2 μm absorptions with shapes consistent with gypsum, as well as a 2.4 μm shoulder consistent with gypsum (Fig. S3d-e). For the gypsum 45-75 μm Mars tray was the best performance in our whole-image FA/TT experiment, there were 6 borderline false positives (Table 1).

Kaolinite 125+ μm

We used kaolinite spectrum RELAB ID CAKA03 for this analysis. For 15 eigenvector R-mode FA/TT, fits to the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 2.2 μm feature is fit well and there is at least some absorption at 1.4 μm in each fit (Fig. 4a). Fits for the 2.5%, 1%, and 0% trays are not good because the 2.2 μm features shape is badly fit and

no 1.4 μm feature exists (Fig. 4a). For 10 eigenvector HySime FA/TT, fits to the 100%, 50%, 20%, 10%, and 5% tray fits are good because the shape of the 2.2 μm feature is fit well and there is at least some absorption at 1.4 μm in each fit (Fig. 4b). The 2.5%, 1%, and 0% tray fits are bad because the 2.2 μm features shape is badly fit and no 1.4 μm feature exists (Fig. 4b). For 15 eigenvector HySime FA/TT, fits to the 100%, 50%, 20%, 10%, and 5% tray are good because the shape of the 2.2 μm feature is fit well and there is at least some absorption at 1.4 μm in each fit (Fig. 4c). Fits to the 2.5%, 1%, and 0% tray fits are bad good because the shape of the 2.2 μm feature is fit well and there is at least some absorption at 1.4 μm in each fit (Fig. 4c).

The average spectra for the 100%, 50%, 20%, 10%, and 5% trays have clear 2.2 μm absorptions with shapes consistent with kaolinite, as well as a 1.4 μm absorption consistent with kaolinite (Fig. 4d-e). The kaolinite 125+ μm Mars tray was the best performance in our whole-image FA/TT experiment. No false positives, borderline false positives, false negatives, or borderline false negatives were detected (Table 1).

Calcite 45-75 μm

We used calcite spectrum RELAB ID C1SH01 for this analysis. For 15 eigenvector R-mode FA/TT, all trays have good fits because the 2.3 μm absorption and partial 2.5 μm absorption are fit well (Fig. S1a). For 10 eigenvector HySime FA/TT, all trays have good fits because the 2.3 μm absorption and partial 2.5 μm absorption are fit well (Fig. S1b). For 15 eigenvector HySime FA/TT, all trays have good fits because the 2.3 μm absorption and partial 2.5 μm absorption are fit well (Fig. S1c).

The average spectra for the 100%, 50%, and 20% trays have clear 2.3 μm absorptions consistent with calcite, as well as a partial 2.5 μm absorption for the 100% and 50% mixtures (Fig. S1d-e). The 10% mixture tray contains at least 2 single pixel spectra consistent with calcite (Fig. S9), therefore we classify these as “spectrum exists in tray” true detections. Our sampled wavelength range only encompasses half of the 2.5 μm feature of calcite. The calcite 45-75 μm Mars tray was the second worst performance in our whole-image FA/TT experiment (Table 1). This is likely due to the existence of structured noise in our data that resembles the diagnostic absorptions for calcite within the measured wavelength range (Figs. 6-7). There are 11 false positive detections.

Calcite 125+ μm

We used calcite spectrum RELAB ID C1SH01 for this analysis. For 15 eigenvector threshold R-mode FA/TT, all trays have good fits because the 2.3 μm absorption and partial 2.5 μm absorption are fit well (Fig. 5a). For 10 eigenvector threshold HySime FA/TT all trays have good fits to the 2.3 μm absorption and partial 2.5 μm absorption except for the 5% tray (Fig. 5b). The fit to the 5% tray is still good enough to be considered a borderline positive detection. For 15 eigenvector threshold HySime FA/TT results, all trays have good fits to the 2.3 μm absorption and partial 2.5 μm absorption (Fig. 5c).

The average spectra for the 100%, 50%, and 20% trays have clear 2.3 μm absorptions consistent with calcite, as well as a partial 2.5 μm absorption for the 100% and 50% mixtures (Fig. 5d-e). Our sampled wavelength range only encompasses half of the 2.5 μm feature of calcite. The calcite 125+ μm Mars tray was the worst performance in our whole-image FA/TT

experiment (Table 1). This is likely due to the existence of structured noise in our data that resembles the diagnostic absorptions for calcite within the measured wavelength range (Figs. 6-7). There are 11 false positives and 1 borderline false positive.

Nontronite 125+ μm

We used nontronite spectrum RELAB ID C1JB791B for this analysis. For 15 eigenvector R-mode FA/TT, fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4 and 2.3 μm are fit well, as is the 2.4 μm feature in some cases (Fig. S4a). Fits to the 2.5%, 1%, and 0% trays are borderline because the 1.4 and 2.3 μm features exist, but the 2.3 μm feature does the library spectrum well (Fig. S4a). For 10 eigenvector HySime FA/TT, fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4 and 2.3 μm are fit well, as is the 2.4 μm feature in some cases (Fig. S4b). Fits to the 2.5%, 1%, and 0% trays are bad because 2.3 μm feature does not exist (Fig. S4b). For 15 eigenvector HySime FA/TT, fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4 and 2.3 μm are fit well, as is the 2.4 μm feature in some cases (Fig. S4c). Fits to the 2.5%, 1%, and 0% trays are borderline because the 1.4 and 2.3 μm features exist, but the 2.3 μm feature does not fit the library spectrum well (Fig. S4c).

The average spectra for the 100%, 50%, 20%, 10%, and 5% trays have clear 1.4 and 2.3 μm absorptions consistent with nontronite (Fig. S4d-e). The nontronite 125+ μm Mars tray results contained 6 borderline false positives (Table 1).

Montmorillonite 125+ μm

We used montmorillonite spectrum RELAB ID C1CY25 for this analysis. For 15 eigenvector R-mode FA/TT, fits for all trays are good because the shape of the 1.4 and 2.2 μm absorptions are fit well (Fig. S5a). For 10 eigenvector HySime FA/TT, fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4 and 2.2 μm are fit well (Fig. S5b). Fits to the 2.5%, 1%, and 0% trays are bad because 2.2 μm feature does not exist (Fig. S5b). For 15 eigenvector HySime FA/TT, fits for all trays are good because the shape of the 1.4 and 2.2 μm absorptions are fit well (Fig. S5c).

The average spectra for the 100%, 50%, 20%, 10%, and 5% trays have clear 1.4 and 2.2 μm absorptions consistent with montmorillonite (Fig. S5d-e). The montmorillonite 125+ μm Mars tray results contained 6 false positives and 1 borderline false positive (Table 1).

3.2 DAFA/TT

CRISM data

DAFA/TT did not detect any verifiable serpentine in 49/50 of the first CRISM FRT images acquired during the mission, but highlighted many regions that after inspection proved not to contain spectral features consistent with serpentine. In FRT00003584, we detected a group of 9 pixels with I/F ratioed spectra consistent with serpentine (Fig. 9). These pixels were detected via 2 overlapping DAFA/TT clusters with good fits to serpentine, where each DAFA/TT cluster was derived using different serpentine library spectra. We looked at the eigenvectors associated with these clusters and how they were stretched and combined via target transformation to obtain good fits to serpentine library spectra (Figs. 10-11). We find that the first 3 eigenvectors dominated the target transformation fitting for serpentine spectrum RELAB

ID C1JB529 (Fig. 10), and the first 4 eigenvectors dominated the target transformation fitting for serpentine spectrum RELAB ID CASR19 (Fig. 11).

Because a 2.1 μm artifact exists in CRISM TRR3 I/F data, a ratioed spectrum generated from radiance data must be acquired to confirm the true presence of a 2.1 μm feature (Leask et al., 2018). We perform this test and find a spectrum that is still consistent with serpentine (Fig. 9f). The serpentine is associated with exposed bedrock proximal to and within a mound/ridge-like positive topographic feature, with dunes surrounding the exposed bedrock (Fig. 9d).

Headwall data

The results from our DAFA/TT experiments using Headwall data are summarized in Table 2. The experimental results used to generate the content of Table 2 are described below.

Gypsum 125+ μm HySime with 10 eigenvector threshold

We find 7 good fits to our gypsum library spectrum (RELAB ID 1101F556) applying 10 eigenvector threshold HySime DAFA/TT to the gypsum 125+ μm tray (Fig. 12b). The entirety of the 100%, 50%, and 20% mixture trays were detected (clusters 1-3). The clusters for the 10%, 5%, and 2.5% mixture trays only cover part of each tray (clusters 4-6). There is another detection cluster on top of the translation table (cluster 7) (Fig. 12a). Clusters 1-4 have average spectra consistent with the presence of gypsum based on the presence of 1.45, 1.75, 2.22 μm absorption features and a 2.4 μm shoulder. Clusters 5, 6, and 7 do not have average spectra consistent with the presence of gypsum, as they lack all the aforementioned absorption features (Fig. 12c-d). However, single-pixel spectra inspection shows that they all contain some

pixels with spectra consistent with gypsum (Fig. 13). Cluster 7 is a detection of 2 gypsum grains that were spilt on the translation table before measurement.

Gypsum 125+ μm HySime with 15 eigenvector threshold

We find 5 good fits to our gypsum library spectrum (RELAB ID 1101F556) applying 15 eigenvector threshold HySime DAFA/TT to the gypsum 125+ μm tray (Fig. 20b). The entirety of the 50%, and 20% mixture trays were detected (clusters 2-3). The clusters for the 100% and 10% mixture trays only cover part of each tray (clusters 1 and 4). There is another detection cluster on top of the translation table (cluster 5) (Fig. 20a). Clusters 1-5 have average spectra consistent with the presence of gypsum based on the presence of 1.45, 1.75, 2.22 μm absorption features and a 2.4 μm shoulder (Fig. 20c-d). Cluster 5 is a detection of gypsum grains that were spilt on the translation table before measurement.

Gypsum 125+ μm R-mode FA with 15 eigenvector threshold

We find 4 good fits to our gypsum library spectrum (RELAB ID 1101F556) applying 15 eigenvector threshold R-mode DAFA/TT to the gypsum 125+ μm tray (Fig. 19b). The clusters for the 100%, 50%, 20%, and 10% mixture trays only cover part of each tray (clusters 1-4) (Fig. 19a). Clusters 1-4 have average spectra consistent with the presence of gypsum based on the presence of 1.45, 1.75, 2.22 μm absorption features and a 2.4 μm shoulder (Fig. 19c-d).

Gypsum 45-75 μm HySime with 10 eigenvector threshold

We find 5 good fits to our gypsum library spectrum (RELAB ID 1101F556) applying 10 eigenvector threshold HySime DAFA/TT to the gypsum 45-75 μm tray (Fig. S6b). The entirety of the 50%, and 20% mixture trays were detected (clusters 1-3). The clusters for the 100% and 5% mixture trays only cover part of each tray (clusters 4-6). There are multiple detection clusters on top of the translation table (cluster 7) (Fig. S6a). Clusters 1-3 have average spectra consistent with the presence of gypsum based on the presence of 1.45, 1.75, 2.22 μm absorption features and a 2.4 μm shoulder (Fig. S6c-d). Clusters 4 and 5 do not have average spectra consistent with the presence of gypsum, as they lack all the aforementioned absorption features (Fig. S6c-d). However, single-pixel spectra inspection shows that they all contain some pixels with spectra consistent with gypsum (Fig. S7).

Gypsum 45-75 μm HySime with 15 eigenvector threshold

We find 5 good fits to our gypsum library spectrum (RELAB ID 1101F556) applying 15 eigenvector threshold HySime DAFA/TT to the gypsum 45-75 μm tray (Fig. S13b). The entirety of the 50% mixture tray was detected (cluster 2) (Fig. S13a). The clusters for the 100% and 20% mixture trays only cover part of each tray (clusters 1 and 3), with the 100% cluster only covering the tray's outline (Fig. S13a). There are multiple detection clusters on top of the translation table (clusters 4 and 5) (Fig. S13a). Clusters 1-3 have average spectra consistent with the presence of gypsum based on the presence of 1.45, 1.75, 2.22 μm absorption features and a 2.4 μm shoulder (Fig. S13c-d). Clusters 4 and 5 do not have average spectra consistent with the presence of gypsum, as they lack all the aforementioned absorption features (Fig. S13c-d).

However, single-pixel spectra inspection shows that they all contain some pixels with spectra consistent with gypsum (Fig. S7).

Gypsum 45-75 μ m R-mode FA with 15 eigenvector threshold

We find 5 good fits to our gypsum library spectrum (RELAB ID 1101F556) applying 15 eigenvector threshold HySime DAFA/TT to the gypsum 45-75 μ m tray (Fig. S18b). The clusters for the 100%, 50%, and 20% mixture trays cover a small portion of each tray (clusters 1-3) (Fig. S18a). There is a detection cluster on top of the translation table (cluster 4) (Fig. S18a). Clusters 1-3 have average spectra consistent with the presence of gypsum based on the presence of 1.45, 1.75, 2.22 μ m absorption features and a 2.4 μ m shoulder. Cluster 4 does not have an average spectrum consistent with the presence of gypsum, as it lacks all the aforementioned absorption features (Fig. S18c-d). However, single-pixel spectra inspection shows that it contains some pixels with spectra consistent with gypsum (Fig. S7).

Kaolinite 125+ μ m HySime with 10 eigenvector threshold

We find 5 good fits to our kaolinite library spectrum (RELAB ID BIR1JB798) applying 10 eigenvector threshold HySime DAFA/TT to the kaolinite 125+ μ m tray (Fig. S12b). The entirety of the 100% and 50% mixture trays were detected (clusters 1 and 2). The clusters for the 20% and 5% mixture trays only cover part of each tray (clusters 3 and 4) (Fig. S12a). Clusters 1-4 have average spectra consistent with the presence of kaolinite based on the presence of a 2.2 μ m absorption doublet that is deeper at 2.21 μ m, as well as a 1.4 μ m absorption (Fig. S12c-d).

Kaolinite 125+ μm HySime with 15 eigenvector threshold

We find 5 good fits to our kaolinite library spectrum (RELAB ID BIR1JB798) applying 15 eigenvector threshold HySime DAFA/TT to the kaolinite 125+ μm tray (Fig. 15b). The entirety of the 100% and 50% mixture trays were detected (clusters 1 and 2). The clusters for the 20% and 5% mixture trays only cover part of each tray (clusters 3 and 4) (Fig. 15a). Clusters 1-4 have average spectra consistent with the presence of kaolinite based on the presence of a 2.2 μm absorption doublet that is deeper at 2.21 μm , as well as a 1.4 μm absorption (Fig. 15c-d).

Kaolinite 125+ μm R-mode FA with 15 eigenvector threshold

We find 5 good fits to our kaolinite library spectrum (RELAB ID BIR1JB798) applying 15 eigenvector threshold R-mode DAFA/TT to the kaolinite 125+ μm tray (Fig. S19b). The clusters for the 100%, 50%, 20%, and 5% mixture trays only cover part of each tray (clusters 1-4) (Fig. S19a). Clusters 1-4 have average spectra consistent with the presence of kaolinite based on the presence of a 2.2 μm absorption doublet that is deeper at 2.21 μm , as well as a 1.4 μm absorption (Fig. S19c-d).

Calcite 125+ μm HySime with 10 eigenvector threshold

We find 7 good fits to our calcite library spectrum (RELAB ID C1SH01) applying 10 eigenvector threshold HySime DAFA/TT to the calcite 125+ μm tray (Fig. 14b). The entirety of the 100%, 50%, and 20% mixture trays were detected (clusters 1-3). The clusters for the 10% and 0% mixture trays only cover part of each tray (clusters 4 and 5) (Fig. 14a). Clusters 1-3 have average spectra consistent with the presence of calcite based on the presence of 2.34 μm

absorption feature and a partial 2.5 μm absorption for the 100% and 50% mixture trays.

Clusters 4 and 5 do not have average spectra consistent with the presence of calcite, as they lack the aforementioned absorption features (Fig. 14c-d). However, the average spectrum of the entire 10% mixture tray shows a small 2.34 μm absorption (Fig. 5e-f). Single-pixel spectra analysis of the 0% mixture tray was performed, and no spectra in that tray are consistent with calcite.

Calcite 125+ μm HySime with 15 eigenvector threshold

We find 7 good fits to our calcite library spectrum (RELAB ID C1SH01) applying 15 eigenvector threshold HySime DAFA/TT to the calcite 125+ μm tray (Fig. S16b). The entirety of the 100%, 50%, and 20% mixture trays were detected and these clusters also spill out onto the empty trays (clusters 1, 6, and 7) (Fig. S16a). The clusters for the 10%, 5%, and 0% mixture trays cover most of each tray and also spill out onto the empty tray (clusters 5 and 9) (Fig. S16a). The clusters for the 2.5% and 1% mixture trays cover a large portion of each tray, and also spill out onto the empty trays (Fig. S16a). There are two clusters on top of empty trays (clusters 2 and 8). Clusters 1 (100%), 6 (50%), and 7 (20%) have average spectra consistent with the presence of calcite based on the presence of 2.34 μm absorption feature and a partial 2.5 μm absorption for the 100% and 50% mixture trays (Fig. S16a). Clusters 3-5 and 7-9 do not have average spectra consistent with the presence of calcite, as they lack the aforementioned absorption features (Fig. S16c-d). Single-pixel spectra analysis of clusters 3-5 and 7-9 tray was performed, and no spectra in these clusters are consistent with calcite.

Calcite 125+ μm R-mode FA with 15 eigenvector threshold

We find 7 good fits to our calcite library spectrum (RELAB ID C1SH01) applying 15 eigenvector threshold R-mode DAFA/TT to the calcite 125+ μm tray (Fig. S17b). The entirety of the 50% mixture tray was detected (clusters 2) (Fig. S17a). The clusters for the 100% and 20% mixture trays only cover part of each tray (clusters 1 and 3) (Fig. S17a). There is a small cluster in the 10% mixture tray (cluster 4) and a small cluster on the painted rim of separating the two 0% trays (cluster 5) (Fig. S17a). Clusters 1-4 have average spectra consistent with the presence of calcite based on the presence of 2.34 μm absorption feature and a partial 2.5 μm absorption for the 100% and 50% mixture trays (Fig. S17c-d). Cluster 5 does not have an average spectrum consistent with the presence of calcite, as it lacks the aforementioned absorption features (Fig. S17c-d). Single-pixel spectra analysis of the cluster 5 was performed, and no spectra in that cluster are consistent with calcite.

Calcite 45-75 μm HySime with 10 eigenvector threshold

We find 5 good fits to our calcite library spectrum (RELAB ID C1SH01) applying 10 eigenvector threshold HySime DAFA/TT to the calcite 45-75 μm tray (Fig. S8b). The entirety of the 100% and 50% mixture trays were detected (clusters 1 and 2) (Fig. S8a). The clusters for the 20%, 10%, and 0% mixture trays only cover part of each tray (clusters 3-5) (Fig. S8a). Clusters 1-3 have average spectra consistent with the presence of calcite based on the presence of 2.34 μm absorption feature and a partial 2.5 μm absorption for the 100% and 50% mixture trays (Fig. S8c-d). Clusters 4 and 5 do not have average spectra consistent with the presence of calcite, as they lack the aforementioned absorption features (Fig. S8c-d). Single-pixel spectra analysis of

the 10% mixture tray cluster (cluster 4) was performed, and there are at least 2 spectra in that tray that are consistent with calcite (Fig. S9). Single-pixel spectra analysis of the 0% mixture tray cluster was performed, and no spectra in that tray are consistent with calcite.

Calcite 45-75 μ m HySime with 15 eigenvector threshold

We find 7 good fits to our calcite library spectrum (RELAB ID C1SH01) applying 15 eigenvector threshold HySime DAFA/TT to the calcite 45-75 μ m tray (Fig. 16b). The entirety of the 100%, 50%, and 20% mixture trays were detected and these clusters also spill out onto the empty trays (clusters 1-3) (Fig. 16a). The clusters for the 10%, 5%, 1%, 2.5%, and 0% mixture trays cover most of each tray and also spill out onto the empty tray (clusters 4-8) (Fig. 16a). There is a cluster on top of an empty tray (clusters 9) (Fig. 16a). Clusters 1-4 have average spectra consistent with the presence of calcite based on the presence of 2.34 μ m absorption feature and a partial 2.5 μ m absorption for the 100% and 50% mixture trays (Fig. 16c-d). Clusters 5-9 do not have average spectra consistent with the presence of calcite, as they lack the aforementioned absorption features (Fig. 16c-d). Single-pixel spectra analysis of clusters 5-9 tray performed, and no spectra in these clusters are consistent with calcite.

Calcite 45-75 μ m R-mode FA with 15 eigenvector threshold

We find 2 good fits to our calcite library spectrum (RELAB ID C1SH01) applying 15 eigenvector threshold R-mode DAFA/TT to the calcite 45-75 μ m tray (Fig. 18b). The cluster for the 100% mixture tray covers most of the tray (cluster 1) (Fig. 18a). The cluster for the 50% mixture tray covers a fraction of the tray's outline (cluster 2) (Fig. 18a). Clusters 1-2 have

average spectra consistent with the presence of calcite based on the presence of 2.34 μm absorption feature and a partial 2.5 μm (Fig. 18c-d).

Nontronite 125+ μm HySime with 10 eigenvector threshold

We find 3 good fits to our nontronite library spectrum (RELAB ID C1JB791B) applying 10 eigenvector threshold HySime DAFA/TT to the nontronite 125+ μm tray (Fig. S10b). The entirety of the 100% and 50% mixture trays were detected (clusters 1 and 2) (Fig. S10a). The cluster for the 20% mixture tray only covers part of the tray (cluster 3) (Fig. S10a). Clusters 1-3 have average spectra consistent with the presence of nontronite based on the presence of 1.4, 2.3, and 2.4 μm absorptions (Fig. S10c-d).

Nontronite 125+ μm HySime with 15 eigenvector threshold

We find 3 good fits to our nontronite library spectrum (RELAB ID C1JB791B) applying 15 eigenvector threshold HySime DAFA/TT to the nontronite 125+ μm tray (Fig. S14b). The entirety of the 100% and 50% mixture trays were detected (clusters 1 and 2) (Fig. S14a). The cluster for the 20% mixture tray only covers part of the tray (cluster 3) (Fig. S14a). Clusters 1-3 have average spectra consistent with the presence of nontronite based on the presence of 1.4, 2.3, and 2.4 μm absorptions (Fig. S14c-d).

Nontronite 125+ μm R-mode FA with 15 eigenvector threshold

We find 3 good fits to our nontronite library spectrum (RELAB ID C1JB791B) applying 15 eigenvector threshold R-mode DAFA/TT to the nontronite 125+ μm tray (Fig. 17b). The entirety

of the 100% and 50% mixture trays were detected (clusters 1 and 2) (Fig. 17a). The cluster for the 20% mixture tray only covers part of the tray (cluster 3) (Fig. 17a). Clusters 1-3 have average spectra consistent with the presence of nontronite based on the presence of 1.4, 2.3, and 2.4 μm absorptions (Fig. 17c-d).

Montmorillonite 125+ μm HySime with 10 eigenvector threshold

We find 4 good fits to our montmorillonite library spectrum (RELAB ID C1CY25) applying 10 eigenvector threshold HySime DAFA/TT to the montmorillonite 125+ μm tray (Fig. S11b). The entirety of the 100% and 50% mixture trays were detected (clusters 1 and 2) (Fig. S11a). The clusters for the 10% and 20% mixture trays only cover parts of the trays (clusters 3 and 4) (Fig. S11a). Clusters 1-4 have average spectra consistent with the presence of montmorillonite based on the presence of 1.4 and 2.2 μm absorptions (Fig. S11c-d).

Montmorillonite 125+ μm HySime with 15 eigenvector threshold

We find 4 good fits to our montmorillonite library spectrum (RELAB ID C1CY25) applying 15 eigenvector threshold HySime DAFA/TT to the montmorillonite 125+ μm tray (Fig. S15b). The entirety of the 100% and 50% mixture trays were detected (clusters 1 and 2) (Fig. S15a). The clusters for the 10% and 20% mixture trays only cover parts of the trays (clusters 3 and 4) (Fig. S15a). Clusters 1-4 have average spectra consistent with the presence of montmorillonite based on the presence of 1.4 and 2.2 μm absorptions (Fig. S15c-d).

Montmorillonite 125+ μm R-mode FA with 15 eigenvector threshold

We find 3 good fits to our montmorillonite library spectrum (RELAB ID C1CY25) applying 10 eigenvector threshold HySime DAFA/TT to the montmorillonite 125+ μm tray (Fig. S20b). The entirety of the 100% tray was detected (cluster 1) (Fig. S20a). The clusters for the 50% and 20% mixture trays only cover parts of the trays (clusters 2 and 3) (Fig. S20a). Clusters 1-3 have average spectra consistent with the presence of montmorillonite based on the presence of 1.4 and 2.2 μm absorptions (Fig. S20c-d).

3.3 Guided factor analysis

MGS-1

Using guided factor analysis, we detect 3 mixtures of MGS-1 components and 2 pure endmember components (Fig. 23). One pure endmember component of MGS-1 is epsomite, and eigenvector 2 from both HySime and R-mode FA are consistent with an epsomite spectrum (Fig. 23b). Eigenvector 3 from both HySime and R-mode FA is consistent with pure endmember component ferrihydrite (Fig. 23c). Though the eigenvector and ASD spectrum are not exact matches, they share the same absorption features. Eigenvector 4 from both HySime and R-mode FA is consistent with a spectral mixture of ferrihydrite and low calcium pyroxene (LCP) (Fig. 23d). This eigenvector has absorptions at 1.4 and 2.4 μm that are consistent with minor absorptions in LCP, including the LCP component used in MGS-1. It also has a broad 2 μm absorption consistent with pyroxene, but this absorption also contains a broad 1.9 μm feature with a position and shape consistent with ferrihydrite. Eigenvector 5 from both HySime and R-mode FA is consistent with a spectral mixture of bassanite and ferrihydrite (Fig. 23e). It possesses a 1.4 μm feature consistent with both spectra, but with a slight doublet nature

consistent with bassanite. Its 1.9 μm feature has a similar width as that of ferrihydrite, but a similar sharpness to bassanite at its absorption minimum. The 2.4 μm shoulder is also consistent with bassanite. Its slight 1.75 μm feature is consistent with both bassanite and ferrihydrite. HySime eigenvector 9 and R-mode FA eigenvector 11 are consistent with a spectral mixture of contaminated plagioclase and bassanite (Fig. 23f). The 1.4, 1.75, and 1.9 μm absorption features are consistent with bassanite. The 2.25 and 2.35 μm features are consistent with contaminated plagioclase. Factor analysis of MGS-1 follows the behavior reported by Bandfield et al., 2002, in that it returns some eigenvectors that are pure endmembers (e.g. Fig. 23b-c), some that are combinations of pure endmember components (e.g. Fig. 23d-f), and some that are combinations of signal and structured noise (e.g. Figs. 6-7), or just structured noise (e.g. Figs. 6-7).

CRISM data

Eigenvector 3 from the HRL000040FF pixels presented in Fig. 24f shows a shape and 2 μm band minimum position consistent with HCP (Fig. 24d). The presence of HCP spectra in these pixels is consistent with the findings of previous studies (Horgan et al., 2020). Eigenvector 3 from the TRR3 and UMass CRISM image cubes are effectively the same, with the primary difference being increased presence of high frequency noise in the TRR3 eigenvector. The eigenvectors from HySime and R-mode FA are exactly the same. The wavelength position of this eigenvector's peak near 1.5 μm , and the shape of the decrease in unitless proxy reflectance towards shorter wavelengths is also consistent with HCP. The unitless proxy reflectance

minimum position of the 2 μm absorption is at 2.1 μm , which is also consistent with HCP. This eigenvector is a spectrally cleaner example of HCP than the MICA HCP spectrum.

Eigenvector 3 from the pixels shown in Fig. 24g shows a shape and 2 μm absorption minimum position consistent with LCP. LCP associated with this mound has been reported in previous studies (Ehlmann et al., 2008; Horgan et al., 2020). Eigenvector 3 from the TRR3 and UMass CRISM image cubes are effectively the same, with the primary difference being increased presence of high frequency noise in the TRR3 eigenvector. The eigenvectors from HySime and R-mode FA are exactly the same. The position and shape of the peak of the eigenvector near 1.3 μm is consistent with LCP. The minimum position of the 2 μm absorption at ~ 1.8 μm is also consistent with LCP. In fact, this eigenvector very closely resembles the MICA LCP spectrum, but appears to have a 2 μm band minimum position at an even shorter wavelength, consistent with a more LCP-dominated spectrum. The eigenvectors resembling LCP from the pixels shown in Fig. 24h-k, which were selected using the LCPINDEX2 (Viviano-Beck et al., 2014) band parameter strength, show similar behavior in their agreement between the TRR3 and UMass image cubes and HySime versus R-mode FA, though we only display the HySime results here due to space considerations. While these eigenvectors are not as spectrally 'clean' as the LCP-bearing-mound eigenvector, they have 2 μm band minimum positions consistent with LCP (Fig. 24l)

Our guided factor analysis application to HRL000040FF confirms the presence of LCP and HCP where they have previously been mapped (Horgan et al., 2020), but uniquely allows for extraction of clean LCP spectra from these areas without ratioing (e.g. Ehlmann et al., 2008; Horgan et al., 2020) (Fig. 24). HCP is typically the spectrally dominant component of pixels that

also contain LCP in this image, with the exception of the pixels shown in Fig. 24g, which comprise the strongest LCP signal in Jezero crater (Ehlmann et al., 2008). Extracting an LCP spectrum from these HCP-spectrally-dominated pixels would therefore require ratioing to a spectrum that also contains an HCP spectral component, thus producing a spectrum of LCP due to removal of the HCP spectral contribution. Guided factor analysis, however, circumvents this step by separating the LCP and HCP components of the pixels into their own eigenvectors.

The eigenvectors from the pixels shown in Fig. 24g-k are consistent with pyroxene compositions that are more Ca-poor than the MICA LCP spectrum. Both the MICA LCP and HCP spectrum are not pure endmembers, which is obvious via comparison to RELAB spectra (Fig. 24d-e), and consistent with geologic expectations whereby pure pyroxene endmembers seldom occupy an 18×18 m distribution, which is the size of a single CRISM pixel. The eigenvector from the pixels shown in Fig. 24f is consistent with approximately the same pyroxene composition as the MICA HCP spectrum.

4.0 Discussion

4.1 FA/TT

We find that full-image FA/TT methods produce both false positive and false negative results when applied to VNIR hyperspectral images that contain some structured noise (Figs. 1-5, S1-S5; Table 1). The propensity of FA/TT for generating false positives is partly dependent on the number of diagnostic absorptions for a specific mineral within the measured wavelength range. For example, FA/TT application to our calcite trays (Figs. 5, S1) resulted in the highest number of false positives, and this mineral has only one strong diagnostic absorption

completely encompassed by our measured wavelength range (2.3 μm), which also overlaps with the wavelength position of similarly shaped structured noise (Figs. 6-7). The results of our full-image FA/TT experiments can be summarized as:

- 1) Full-image FA/TT methods are prone to false positives and false negatives when applied to hyperspectral images to detect the presence of minerals. All claimed detections of spectrally active compounds using FA/TT or DAFA/TT must be backed up by extraction of spectra from a hyperspectral image indicating presence of that mineral. We used full-image FA/TT to find better fits to spectra of a dry tree leaf and gloss paint than to serpentine in CRISM image FRT0000AA03—where full-image FA/TT has previously been used as evidence for the presence of serpentine (Amador et al., 2018)—even though it is impossible for these compounds to exist on the surface of Mars.

When applying full-image FA/TT to an image with $\sim 10^4$ - 10^5 pixels or more, eigenvectors derived from true spectral signals from the surface and structured artifacts from the instrument or data processing can be combined to produce fits to spectra that do not exist within any pixels contained in the scene. Furthermore, true mineral surface signals from different parts of the image can be combined to achieve a good fit to a mineral that does not exist within the pixels, as is exemplified by the spectra of individual components of MGS-1 combining to achieve decent fits to completely different minerals (e.g. Fig. S2 0% gypsum). As such, previous global maps derived solely from full-image FA/TT application to CRISM data (e.g. Amador et al., 2018) are perhaps

simply mapping the most spectrally diverse and highest signal-to-noise CRISM images rather than the actual presence of any specific mineral.

FA/TT applications, including DAFA/TT, are powerful tools for detecting weak and/or spatially small spectral signals (e.g. Fig. 9), but must be employed with extreme caution due to their propensity for false positives. Furthermore, no geologic interpretations should be made based solely on FA/TT methods of any type. If no evidence of a spectrum can be found in the pixels of a hyperspectral image, then that signal likely does not exist in that image, whether or not a good fit is achieved.

The shortcomings of FA/TT techniques are largely introduced during the process of target transformation. While the eigenvectors calculated from HySime, R-mode factor analysis, or any other eigenvector extraction method applied to a hyperspectral image are accurate representations of components of the signal and structured noise subspaces of that image, when they are stretched via coefficient multiplication and combined with other eigenvectors, these combinations can achieve good fits to spectra that cannot be present within the scene (e.g. Figs. 1, 3). Factor analysis by itself can be a powerful method for analyzing hyperspectral data, and one less prone to false positives if an expert user differentiates the signal and structured noise eigenvectors (e.g. Figs. 23-24).

- 2) Minerals with a greater number of coupled diagnostic absorption features within the measured wavelength range are less likely to have false positive detections, provided good fits to all coupled diagnostic absorption features are used as “good fit” criteria

during by-eye target transformation analysis. Coupled diagnostic absorptions are defined as absorptions whose combined presence is indicative of a specific mineral (e.g. 2.3 μm and 2.5 μm absorptions for carbonates; 1.75 μm , 2.21 μm , and 2.4 μm absorptions/inflections for gypsum; 1.4 μm and 2.2 μm centered doublet absorptions for kaolinite; and 1.4 μm and 2.2 μm singlet absorptions for montmorillonite).

- 3) Requiring good fits to weak diagnostic absorption features minimizes false positives, but can result in a high propensity for false negatives (e.g. 2.12 μm absorption in calcite), the severity of which is dictated by the minor diagnostic absorption's strength. For example, the minor 2.12 μm absorption for calcite is not detected even in the 50% calcite-50% MGS-1 mixtures for either calcite grain size (Figs. 5, S1), while the 1.75 μm feature in gypsum is detected at 20% abundance and above (Figs. S2-S3).
- 4) Diagnostic absorption features near spectral wavelengths with significant structured noise (e.g. 2.2-2.5 μm region for the Headwall spectrometer used in this study) can be fit by this structured noise if it is of a shape resembling the absorption (e.g. Figs. 5-7, S1). This is especially important for analysis of orbital hyperspectral data, such as data from CRISM, where structured noise in TRR3 data around 2.1 μm has been shown to resemble a diagnostic absorption feature of serpentine, perchlorate, and other minerals (Leask et al., 2018).

- 5) Use of HySime versus R-mode FA for eigenvector estimation makes a difference during the FA/TT process. The eigenvectors calculated by HySime and R-mode factor analysis methods are sometimes not exactly the same (Figs. 6-7, 23). This can lead to differences in the RMSE of a fit to a library spectrum that can mean the difference between a true detection (e.g. Fig. 20-21) and a false negative (e.g. Fig. 19, 22). Generally, the performance of HySime is better than the performance of R-mode FA (Tables 1-2).
- 6) Using more eigenvectors equates to more false positives, but fewer false negatives. Our 10 eigenvector HySime experiments for both full-image FA/TT and DAFA/TT showed the lowest propensity for false positive detections, but also in many cases displayed a greater propensity for false negative detections (Tables 1 & 2). In the two types of hyperspectral data we analyzed, CRISM and Headwall data, the first ~5 eigenvectors typically contain true signals that are representative of the surface material spectra, and eigenvectors >5 typically contain combinations of structured noise with true surface material spectra, or purely structured noise. Exactly where these transitions occur is not consistent, but generally, the Headwall (Figs. 6-7) and CRISM (Fig. 2-3, 10-11) eigenvectors >10 contain purely structured and random noise. However, it is reasonable to expect this to vary on a case-by-case basis.

Any subset of pixels within a hyperspectral image will likely have different characteristics regarding the number of signal eigenvectors, signal-noise eigenvectors, and pure noise eigenvectors. A different hyperspectral imager, differences in detector temperatures for the same hyperspectral imager, or different methods of processing

hyperspectral images (e.g. Itoh and Parente, 2021), will also produce different eigenvector behavior. Inspecting every eigenvector by-eye is ideal, but unfeasible when applying FA or FA/TT methods to large datasets of hyperspectral images, especially using iterative mapping methods like DAFA/TT. As such, the most robust approach is to use multiple methods of eigenvector estimation (e.g. HySime and R-mode) and multiple thresholds for the maximum number of eigenvectors to determine which results are most consistent with spectra extracted from pixels within the hyperspectral image.

4.2 DAFA/TT

- 1) DAFA/TT is prone to both false positive and false negative detections (Tables 1-2). The DAFA/TT experiments presented here show significantly fewer false positive detections, but more false negative detections, compared to full-image FA/TT (Tables 1-2). Increasing the RMSE threshold for a positive detection would reduce the number of false negative detections but increase the number of false positive detections, and vice-versa. In many cases, DAFA/TT detection clusters only partially covered trays containing strong mineral signals, to varying levels of severity (e.g. Fig. 15a vs. Fig. S18a). R-mode factor analysis showed the worst behavior in this respect (Table 2).

Due to the logistics of presenting experimental results, we only showed results from DAFA/TT analysis of a single library spectrum for each mineral. In practice, using ~50+ library spectra for each mineral, analyzing the fits, and seeing where the positive detection clusters overlap is a more effective method of data analysis. This was the

method employed to detect a spectrum consistent with serpentine in FRT00003584 (Fig. 9). Using multiple library spectra and analyzing regions where their detection clusters overlap may provide an effective way to mitigate false positives and false negatives in DAFA/TT analysis, and one that is feasible to implement when applying the method to large hyperspectral image datasets.

- 2) Each mineral should have its own tailored fitting metric. We used the same fitting metric RMSE, for each mineral in our DAFA/TT experiment. However, this assigns equal weight to wavelengths of the spectrum containing diagnostic features and wavelengths that contain no diagnostic features. It would be valuable to construct tailored fitting metrics for each mineral by assigning weights to diagnostic features that included the shapes of those features (e.g. 2.2 μm feature for kaolinite versus 2.2 μm feature for gypsum or 2.2 μm feature for montmorillonite).
- 3) DAFA/TT is limited by its spectral library. Application of any FA/TT technique requires knowledge of which spectrally active compounds are being searched for, and a spectral library of those compounds. This largely precludes using DAFA/TT to detect any novel compounds that are not already known or hypothesized to exist on a planetary object. However, DAFA/TT could detect spectra of a compound that is spectrally similar to one of the mapped target minerals, if it is similar enough to have a low RMSE consistent with a positive detection. Having a breadth of mineral types, and a number of spectra within

those mineral type categories that are representative of the spectral diversity of that compound, are important prerequisites for DAFA/TT analysis.

4.3 Guided Factor Analysis

- 1) GFA detects component endmembers of pixels in VNIR hyperspectral images that generate variance, but current applications require by-eye interpretation of eigenvectors by a user who is experienced in differentiating between true signals and structured noise.
- 2) GFA is not as prone to false positive results as FA/TT due to the elimination of the target transformation step. While the extracted eigenvectors are the same and comprise true endmember component signal, or combinations of true endmember component signals, or mixed true signal and structured noise, or pure structured noise, an expert user can differentiate between these different shapes and select those most consistent with true signal. A target transformation step would stretch and combine all calculated eigenvectors (to a certain eigenvector number threshold) regardless of whether they are true signal or contain significant structured and/or random noise. Factor analysis, be it guided or otherwise, is far less prone to false positives compared to FA/TT.
- 3) Subsetting VNIR hyperspectral data for factor analysis allows for spectral signals that are dominant in segments of a dataset, but not throughout the entirety of a dataset,

to appear as higher power variance eigenvectors. This decreases the likelihood that these eigenvectors will be combined with structured noise in lower power eigenvectors, producing cleaner spectra.

- 4) GFA appears to be a viable alternative in some cases to extraction of a ratio spectrum, as it can produce clean spectra of components within pixels of interest without the need for a denominator spectrum. This is particularly useful in CRISM scenes with no 'bland' pixels, or when the target material of interest is the most 'bland' material within the image, as is the case for the LCP and HCP-bearing material in HRL000040FF.

- 5) Guided factor analysis allows for extraction of spectra from low-spectral-abundance components without utilization of a denominator spectrum. While epsomite only comprises 4% of MGS-1 (Cannon et al., 2019), it imparts enough variance upon the MGS-1 tray spectral data to comprise the 2nd eigenvector from both HySime and R-mode FA. This is possibly because isolated pixels rich in epsomite grains are spread throughout the data, which is feasible considering that ~50% of the grains in MGS-1 have diameters >0.1 mm. It is also possible that the presence of varying amounts of epsomite across the dataset contributes to variations in the average MGS-1 spectra that are consistent with epsomite absorptions.

- 6) As was demonstrated in previous applications of factor analysis (Bandfield et al., 2002), multiple true endmember components can combine into single eigenvectors.
- 7) The dot product between an eigenvector and each pixel within a subset dataset can be used to map the signal strength of eigenvectors with respect to each pixel. This is another tool that can be used to differentiate between signal eigenvectors and structured noise eigenvectors, as signal eigenvectors will correlate to terrain whereas structured noise eigenvectors will correlate to patterns in sensor space.

4.4 Geologic history of Jezero crater

The results of our guided factor analysis application to HRL000040FF also are consistent with current conceptions of Jezero crater's geologic history. Other than the LCP detection on the mound proximal to the crater rim, which may have been uplifted during the Jezero-crater-forming impact (Ehlmann et al., 2008), all other LCP detections are associated with either the delta (Ehlmann et al., 2008; Horgan et al., 2020) or the underlying area immediately proximal to the delta front. Because the fluvial channels feeding into Jezero crater incise the Nili Fossae basement, which contains spectra consistent with LCP throughout (Mustard et al., 2009; Scheller and Ehlmann, 2020), much of the LCP in the delta is likely detrital basement material (Goudge et al., 2015). The HCP detection associated with the Jezero volcanic floor unit (Horgan et al., 2020) is also consistent with the geologic history of Syrtis Major. Older Syrtis Major lava flows excavated by impacts contain spectra consistent with LCP, while younger overlying Syrtis Major lava flows contain spectra consistent with HCP (Skok et al., 2010). The volcanic floor unit

is presumably younger than the basement unit, which is present in the Jezero delta as detrital sediment (Goudge et al., 2015), therefore its spectral richness in HCP is consistent with the overall progression of LCP to HCP-rich volcanism during the evolution of Syrtis Major.

The most intriguing result from guided factor analysis of Jezero crater is the presence of LCP-bearing material in the volcanic floor unit immediately proximal to the delta front. HiRISE images do not show any detrital material eroding from the delta front (at the spatial resolution of HiRISE) where this volcanic floor LCP is detected. It has previously been noted that the smoothing of the volcanic floor unit proximal to the Jezero delta could be due to the delta stratigraphically overlying the volcanic floor unit, thereby shielding it from cratering as it erodes toward the crater rim via aeolian processes (Ruff, 2017). If a more friable LCP-bearing layer of the volcanic floor unit is also preserved via this same mechanism, it could explain the distribution of the LCP detection immediately proximal to the delta front. However, the notion of the Jezero delta overlying the volcanic floor unit is highly controversial and inconsistent with many past studies of the crater's stratigraphy (Schon et al., 2012; Goudge et al., 2015, 2017; Shahrzad et al., 2019; Mangold et al., 2020). The evidence presented here is far from conclusive, but intriguingly is consistent with the hypothesis of the Jezero delta overlying the volcanic floor unit.

5.0 Conclusions

FA/TT methods are useful for extracting information from spectral datasets that is not obvious via other methods of analysis, such as band parameter mapping. However, they are also fraught with the potential for false positive results, particularly during the target

transformation step. Factor analysis alone, if employed by an expert user who can differentiate spectral shapes of true signals versus known structured noise within the dataset, is much less prone to false positives compared to FA/TT. We have demonstrated that full-image FA/TT is prone to false positive results, DAFA/TT is prone to false negative and some false positive results, and guided factor analysis is a viable method for extracting clean spectra of variance contributing components within a given data subset. Overall, our results demonstrate that detection claims made by full-image FA/TT and/or DAFA/TT analysis must be supported by extraction of I/F spectra, otherwise the potential for these detections to be false positives is very high.

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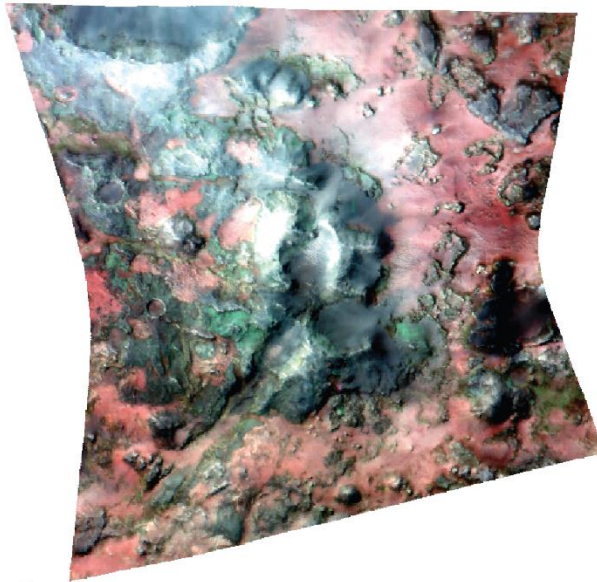
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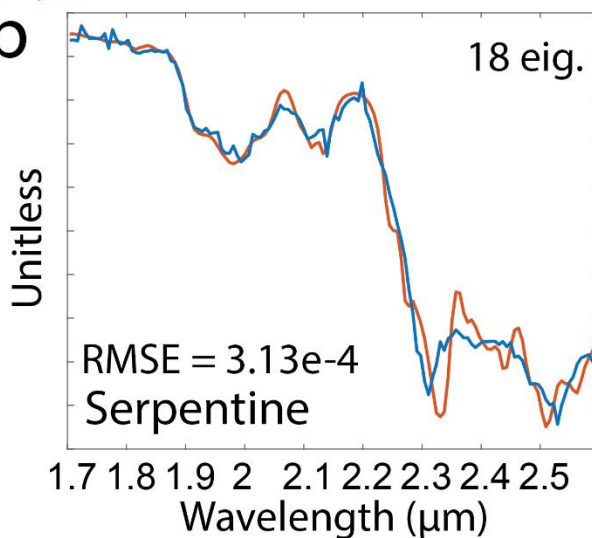
Wray, J.J., Dobrea, E.Z.N., Arvidson, R.E., Wiseman, S.M., Squyres, S.W., McEwen, A.S., Mustard, J.F., Murchie, S.L., 2009. Phyllosilicates and sulfates at Endeavour Crater, Meridiani Planum, Mars. *Geophysical Research Letters* 36. <https://doi.org/10.1029/2009GL040734>

FRT0000AA03 full image R-mode FA/TT Tests

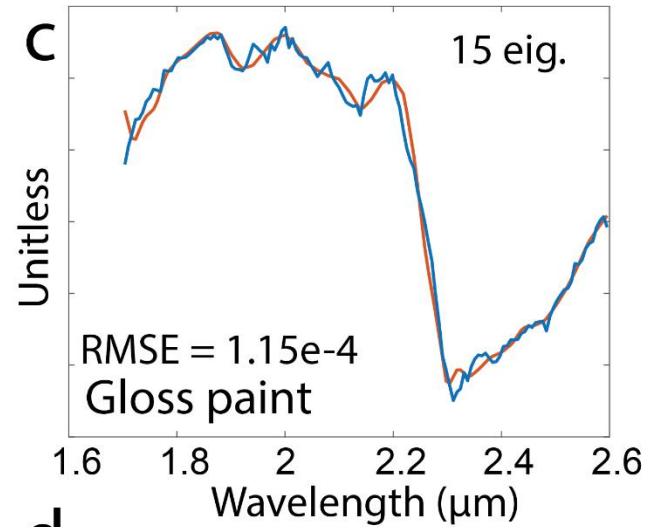
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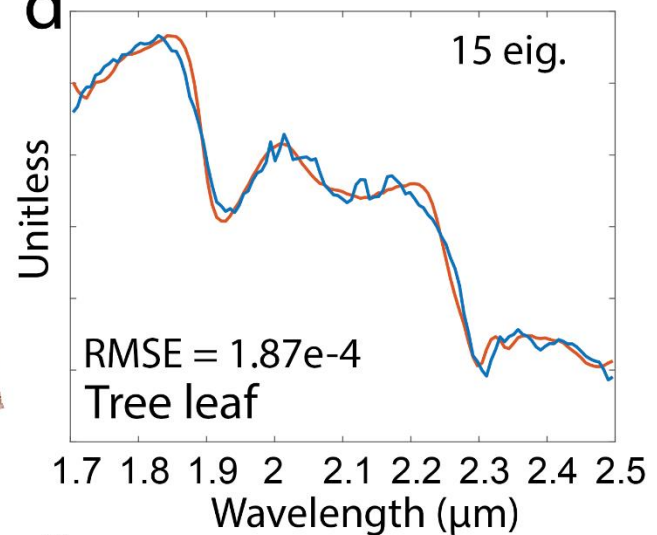
b



c



d



e

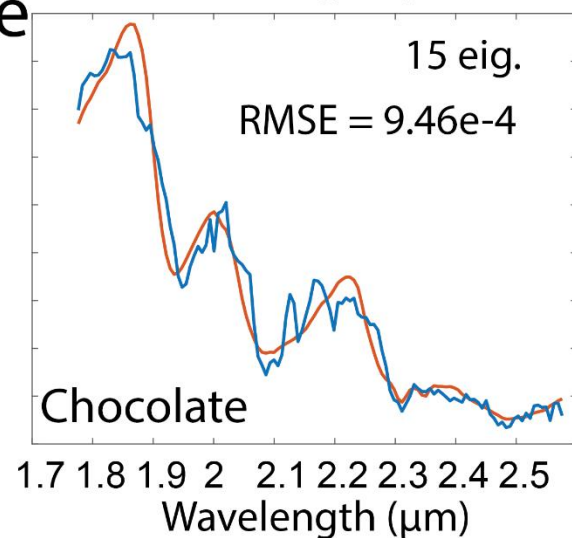


Figure 1 | Fits to various spectra applying full-image R-mode FA/TT to CRISM image FRT0000AA03. (a) CRISM image FRT0000AA03 in the Nili Fossae region. Amador et al. (2018)

used full-image R-mode FA/TT as evidence for serpentine in this image. (b) The fit to serpentine using full-image FA/TT. RELAB ID is C1SP06. (c) The fit to gloss paint using full-image FA/TT. The library spectrum is USGS Spectral Library olivine green gloss paint ID: construction-paint-solid-0385uuu. (d) The fit to a dry tree leaf using full-image FA/TT. The library spectrum is USGS Spectral Library Spectrum CDE031: Bigberry Manzanita (Pericarp). (e) The fit to chocolate using full image FA/TT. The RELAB ID for the library spectrum is C1CH12. The fits to gloss paint, a dry tree leaf, and chocolate are qualitatively comparably as good as the fit to serpentine. The fits to gloss paint and a dry tree leaf are quantitatively better than the fit to serpentine. Because it is impossible for gloss paint, dry tree leaves, or chocolate to exist on the martian surface, this demonstrates the fraught nature of full-image FA/TT without supporting evidence for the presence of minerals via extraction of I/F spectra.

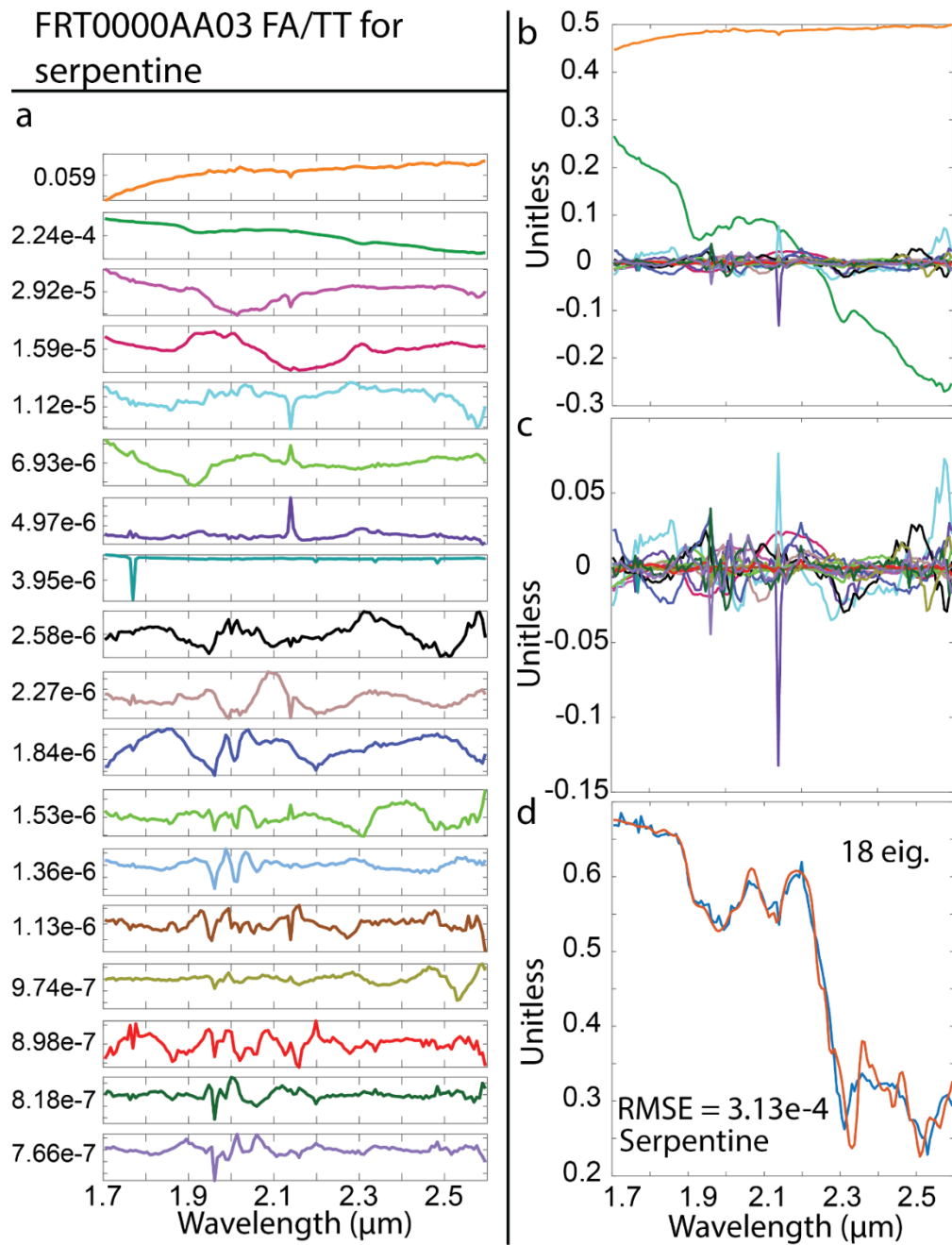


Figure 2 | Breakdown of full-image FA/TT process for serpentine in CRISM image FRT0000AA03. (a) The first 18 eigenvectors from R-mode FA/TT of every pixel in FRT0000AA03, with associated eigenvalues displayed on the left of each plot. (b) The first 18 R-mode FA eigenvectors after being multiplied by the coefficients from target transformation. (c) R-mode FA eigenvectors 3-18 after being multiplied by the target transformation coefficients. (d) The calculated fit to serpentine RELAB ID C1SP06. R-mode eigenvectors 1, 2, 4, 5, and 9 dominate the target transformed eigenvectors used to achieve a good fit to the serpentine spectrum.

FRT0000AA03 FA/TT for gloss paint

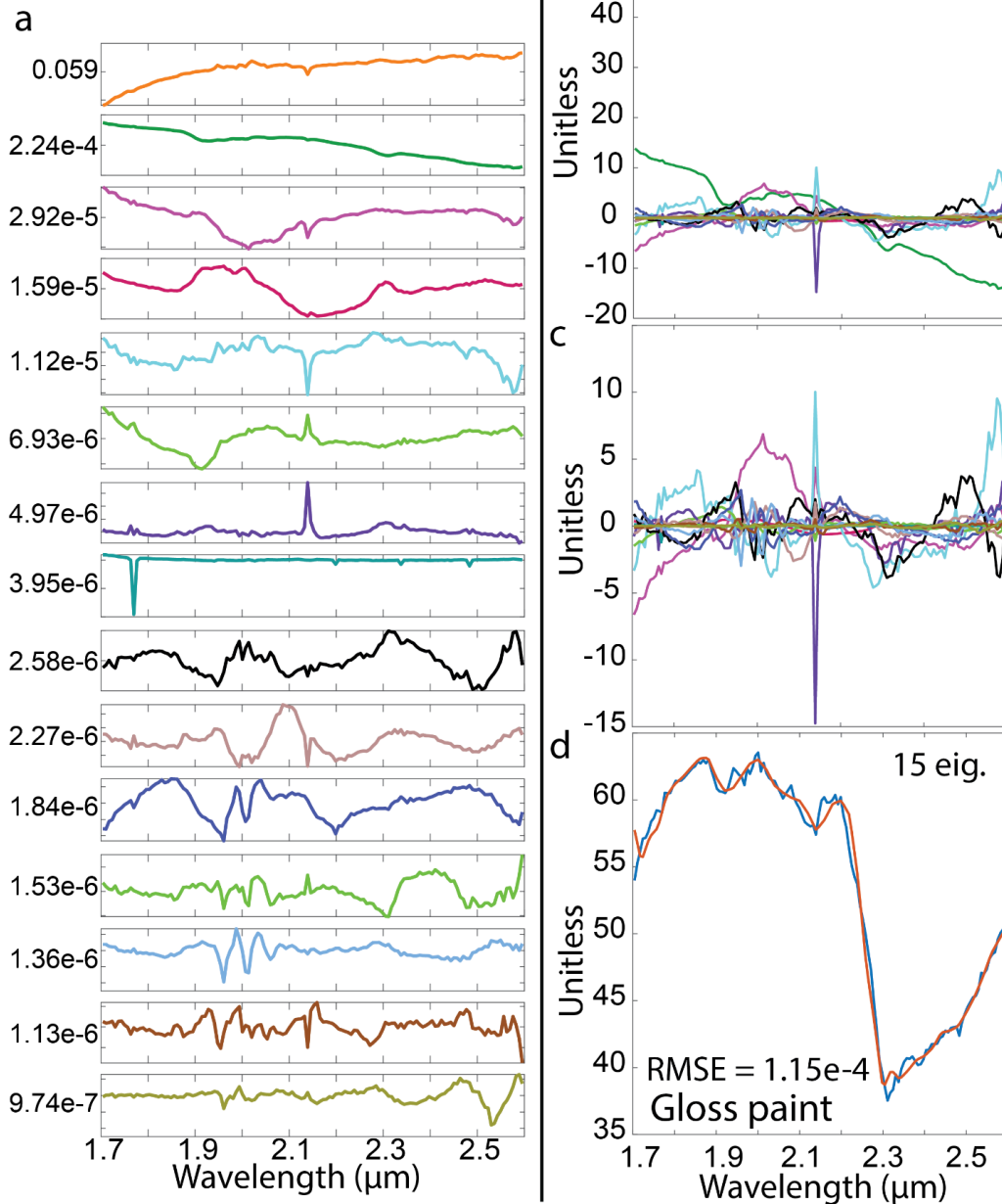


Figure 3 | Breakdown of full-image FA/TT process for gloss paint in CRISM image

FRT0000AA03. (a) The first 18 eigenvectors from R-mode FA/TT of every pixel in FRT0000AA03, with associated eigenvalues displayed on the left of each plot. (b) The first 15 R-mode FA eigenvectors after being multiplied by the coefficients from target transformation. (c) R-mode FA eigenvectors 3-15 after being multiplied by the target transformation coefficients. (d) The calculated fit to gloss paint USGS Spectral Library olivine green gloss paint ID: construction-paint-solid-0385uuu. Gloss paint does not exist on the surface of Mars, indicating that full-image FA/TT without supporting evidence via extraction of I/F spectra can lead to erroneous

results. R-mode eigenvectors 1, 2, 5, 9, and 10 are used to achieve a good fit to the gloss paint spectrum.

Kaolinite (125+ μm) and Mars Global Simulant 1 Mixtures

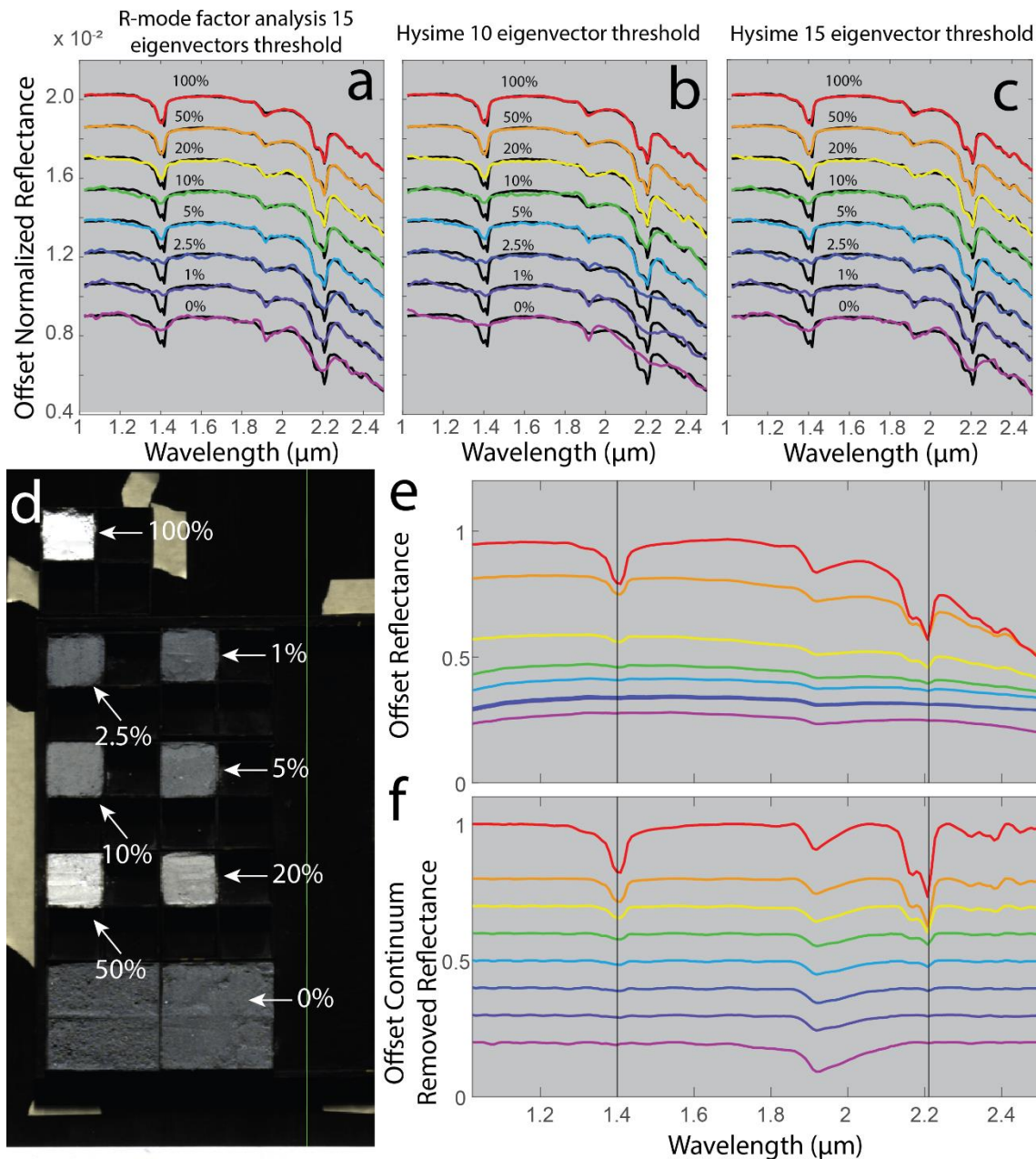


Figure 4 | Results from 15 eigenvector R-mode FA, 15 eigenvector HySime FA, and 10 eigenvector HySime FA to kaolinite Mars tray. (a) 15 eigenvector R-mode FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the

shape of the 2.2 μm feature is fit well and there is at least some absorption at 1.4 μm in each fit. Fits for the 2.5%, 1%, and 0% trays are not good because the 2.2 μm features shape is badly fit and no 1.4 μm feature exists. (b) 10 eigenvector HySime FA/TT results for each individual tray. Using the same criteria as described in (a), the 100%, 50%, 20%, 10%, and 5% tray fits are good and the 2.4%, 1%, and 0% tray fits are bad. (c) 15 eigenvector HySime FA/TT results for each individual tray. Using the same criteria as described in (a), the 100%, 50%, 20%, 10%, and 5% tray fits are good and the 2.4%, 1%, and 0% tray fits are bad. (d) The kaolinite Mars tray, with the percentage kaolinite in each tray labeled. (e) The average spectrum of each individual tray, with the color scheme following that of (a-c). Lines are at 1.4 and 2.21 μm . (f) The continuum removed average spectrum of each individual tray with the same color scheme as (a-c) and same lines as (e). The kaolinite Mars tray provided our best performance in this whole-image FA/TT experiment.

Calcite (125+ μm) and Mars Global Simulant 1 Mixtures

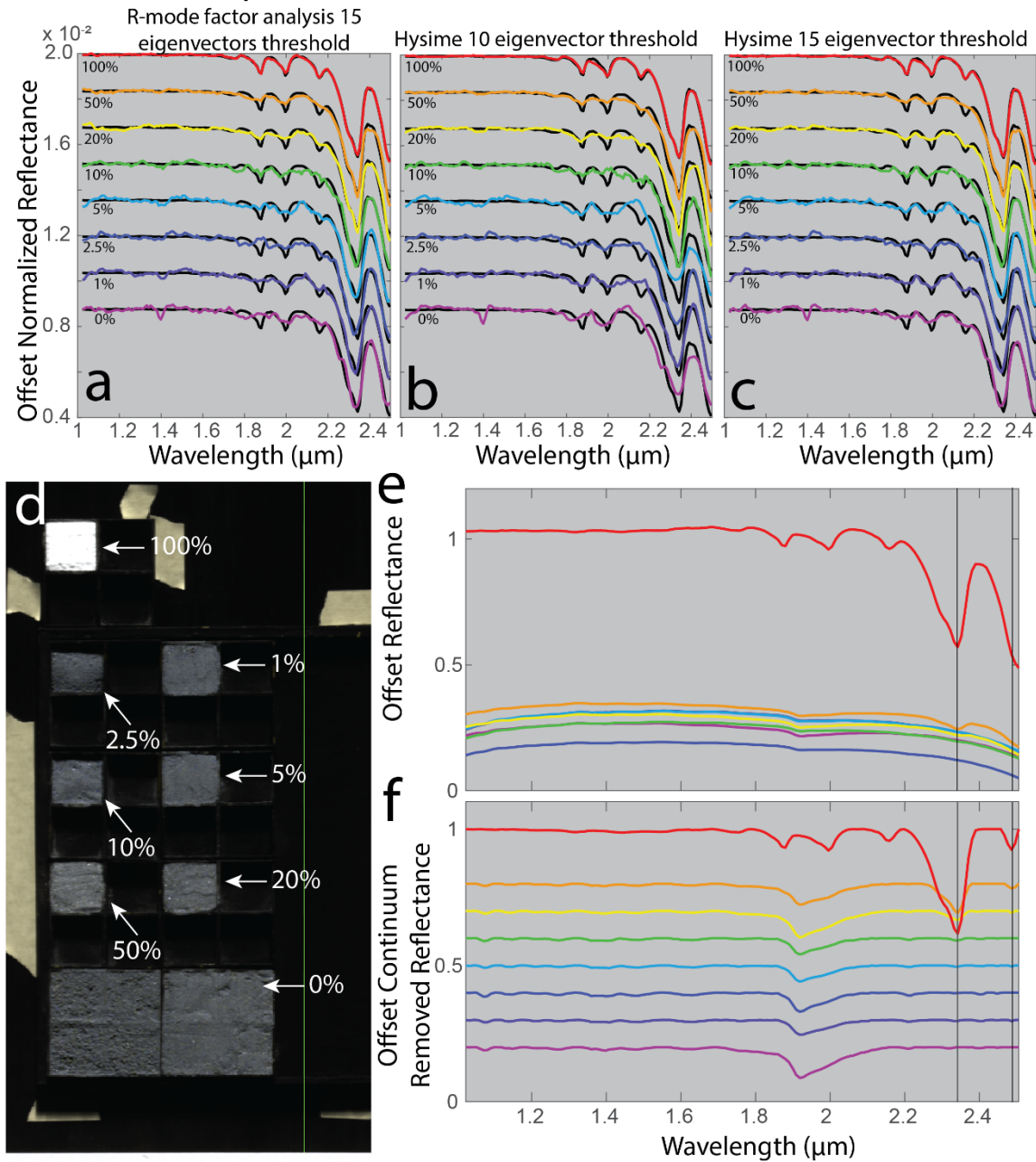


Figure 5 | Results from 15 eigenvector R-mode FA, 15 eigenvector HySime FA, and 10 eigenvector HySime FA to calcite 125+ μm Mars tray. (a) 15 eigenvector R-mode FA/TT results for each individual tray. All trays have good fits because the 2.3 μm absorption and partial 2.5 μm absorption are fit well. (b) 10 eigenvector HySime FA/TT results for each individual tray. Using the same criteria as described in (a), all trays have good fits except for the 5% tray. The 5% tray's fit is still good enough to be considered a borderline false positive. (c) 15 eigenvector HySime FA/TT results for each individual tray. Using the same criteria as described in (a), all trays have good fits. (d) The calcite 125+ μm Mars tray, with the percentage calcite in each tray

labeled. (e) The average spectrum of each individual tray, with the color scheme following that of (a-c). The line is at 2.34 μm . (f) The continuum removed average spectrum of each individual tray with the same color scheme as (a-c) and same lines as (e). The calcite 125+ μm Mars tray provided our worst performance in this whole-image FA/TT experiment. This is likely due to the existence of structured noise in our data that resembles the diagnostic absorptions for calcite within the measured wavelength range.

		Gypsum 125+ μm	Gypsum 45-75 μm	Calcite 125+ μm	Calcite 45-75 μm	Kaolinite 125+ μm	Nontronite 125+ μm	Montmoril. 125+ μm
100%	R-m. 15 eig.	✓	✓	✓	✓	✓	✓	✓
	Hy. 10 eig.	✓	✓	✓	✓	✓	✓	✓
	Hy. 15 eig.	✓	✓	✓	✓	✓	✓	✓
50%	R-m. 15 eig.	✓	✓	✓	✓	✓	✓	✓
	Hy. 10 eig.	✓	✓	✓	✓	✓	✓	✓
	Hy. 15 eig.	✓	✓	✓	✓	✓	✓	✓
20%	R-m. 15 eig.	✓	✓	✓	✓	✓	✓	✓
	Hy. 10 eig.	✓	✓	✓	✓	✓	✓	✓
	Hy. 15 eig.	✓	✓	✓	✓	✓	✓	✓
10%	R-m. 15 eig.	✓	✓	✓	●	✓	✓	✓
	Hy. 10 eig.	✓	✓	✓	●	✓	✓	✓
	Hy. 15 eig.	✓	✓	✓	●	✓	✓	✓
5%	R-m. 15 eig.	●	✓	+	+	✓	✓	✓
	Hy. 10 eig.	●	✓	~+	+	✓	✓	✓
	Hy. 15 eig.	●	✓	+	+	✓	✓	✓
2.5%	R-m. 15 eig.	●	~+	+	+	×	~+	+
	Hy. 10 eig.	●	×	+	×	×	×	~+
	Hy. 15 eig.	●	~+	+	+	×	~+	+
1%	R-m. 15 eig.	~+	~+	+	+	×	~+	+
	Hy. 10 eig.	~+	×	+	+	×	×	×
	Hy. 15 eig.	~+	~+	+	+	×	~+	+
0%	R-m. 15 eig.	~+	~+	+	+	×	~+	+
	Hy. 10 eig.	×	×	+	+	×	×	×
	Hy. 15 eig.	~+	~+	+	+	×	~+	+

✓	= true detection	~+	= borderline false positive detection
×	= true non-detection	+	= false positive detection
●	= spectrum exists in tray		

Table 1 | Results summary for full-image FA/TT experiments for each individual mixing ratio tray. The results used to generate this table are displayed in Figs. 7 and 8, as well as Figs. S1-S5.

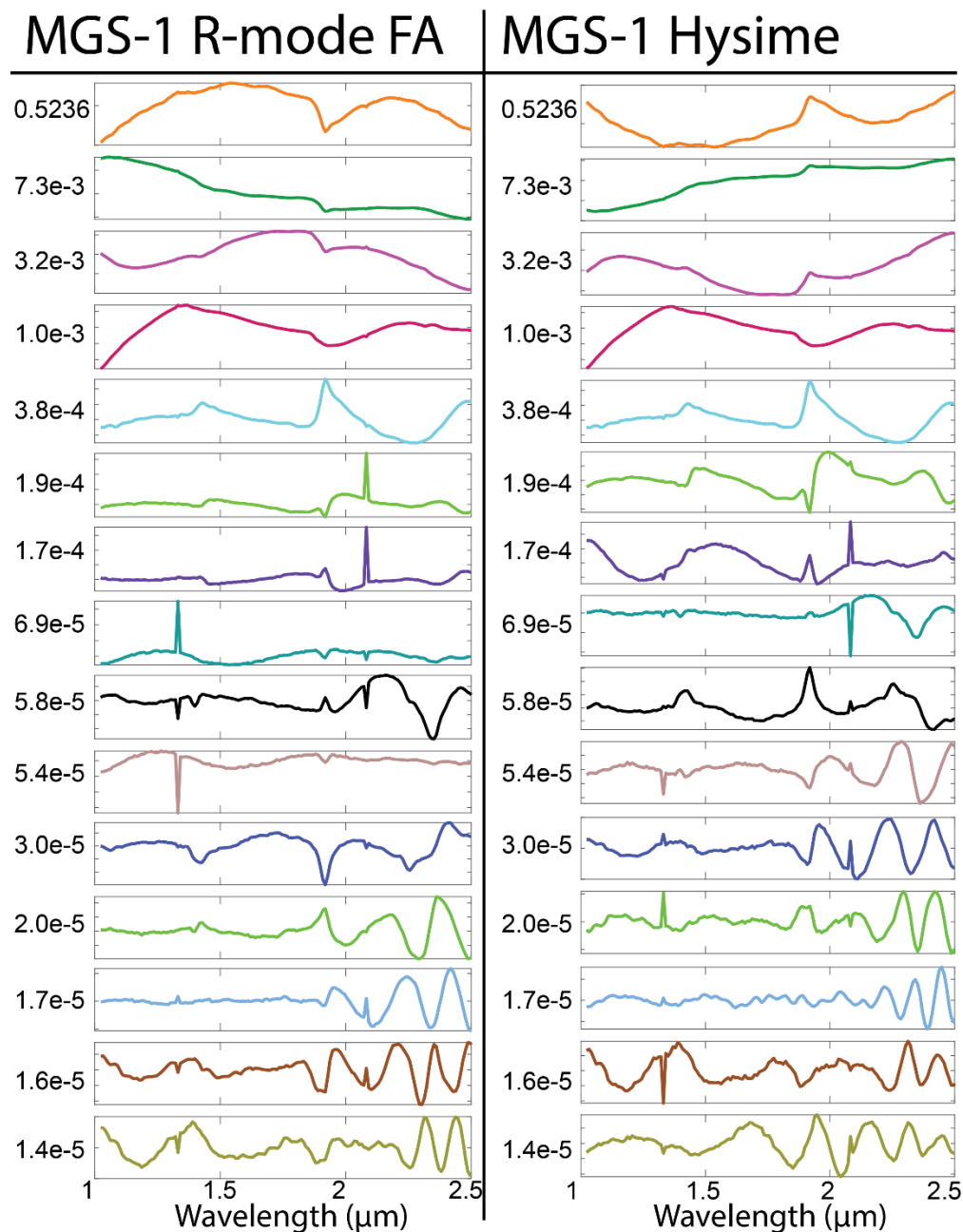


Figure 6 | R-mode and HySime FA results for MGS-1. (a) Eigenvectors for MGS-1 tray calculated via -mode factor analysis, with associated eigenvalues displayed to the left of the plots. Eigenvectors 1-5 and 11 contain spectra of real minerals within the MGS-1, or combinations of those components (Fig. 23). Eigenvectors 6 and 7 appear to contain combinations of image structured noise and real mineral spectra. Eigenvectors 8-10 and 12-15

contain image structured noise. Eigenvectors 12-15 contain features that could be expanded and added via target transformation in order to resemble the diagnostic absorptions of calcite within our measured wavelength range. (b) Eigenvectors for MGS-1 tray calculated via R-mode factor analysis, with associated eigenvalues displayed to the left of the plots. Eigenvectors 1-6 and 9 contain spectra of real minerals within the MGS-1, or combinations of those components (Fig. 23). Eigenvectors 7 and 8 appear to contain combinations of image structured noise and real mineral spectra. Eigenvectors 10-15 contain image structured noise. Eigenvectors 10-15 contain features that could be expanded and added via target transformation in order to resemble the diagnostic absorptions of calcite within our measured wavelength range.

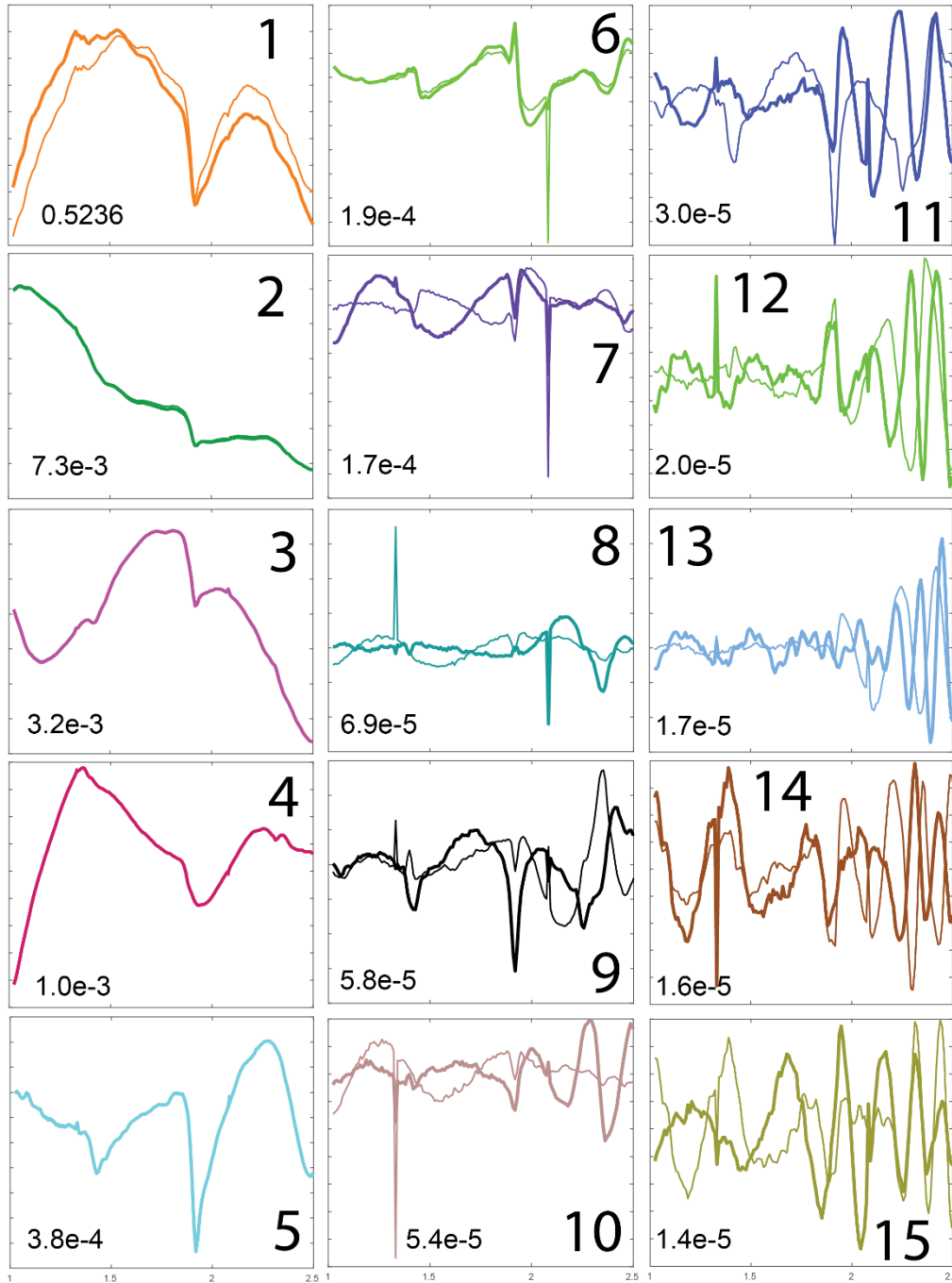


Figure 7 | Differences between eigenvectors calculated via R-mode FA and HySime algorithm. Eigenvectors calculated via R-mode FA are shown as a thinner line and the eigenvectors of the same number calculated via HySime are shown as a thicker line. Eigenvalues are displayed in the lower-left hand corner of the plots and the eigenvector number is displayed as a larger number.

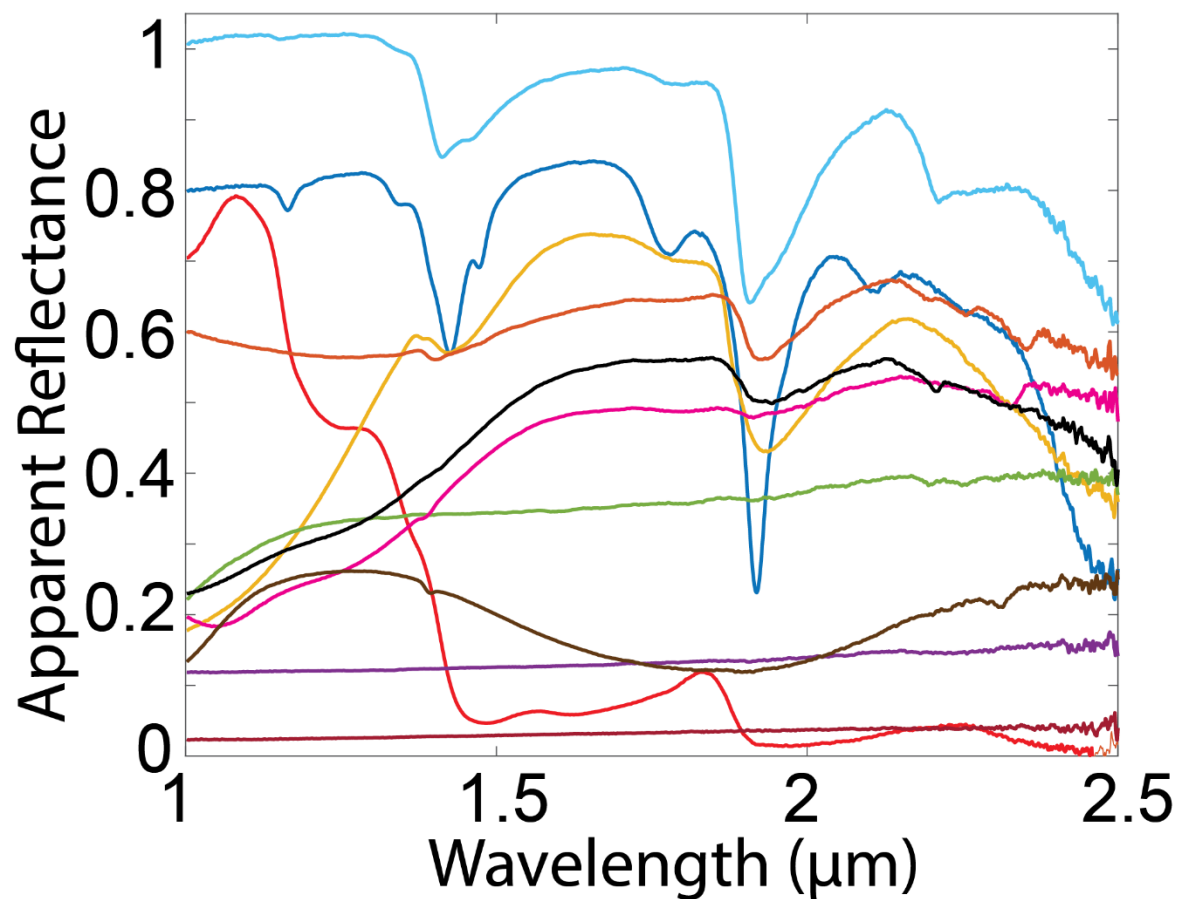


Figure 8 | Point spectra of MGS-1 Components. Each spectrum of the individual MGS-1 components were measured using an ASD point spectrometer. The spectrum colors correspond to the legend colors.

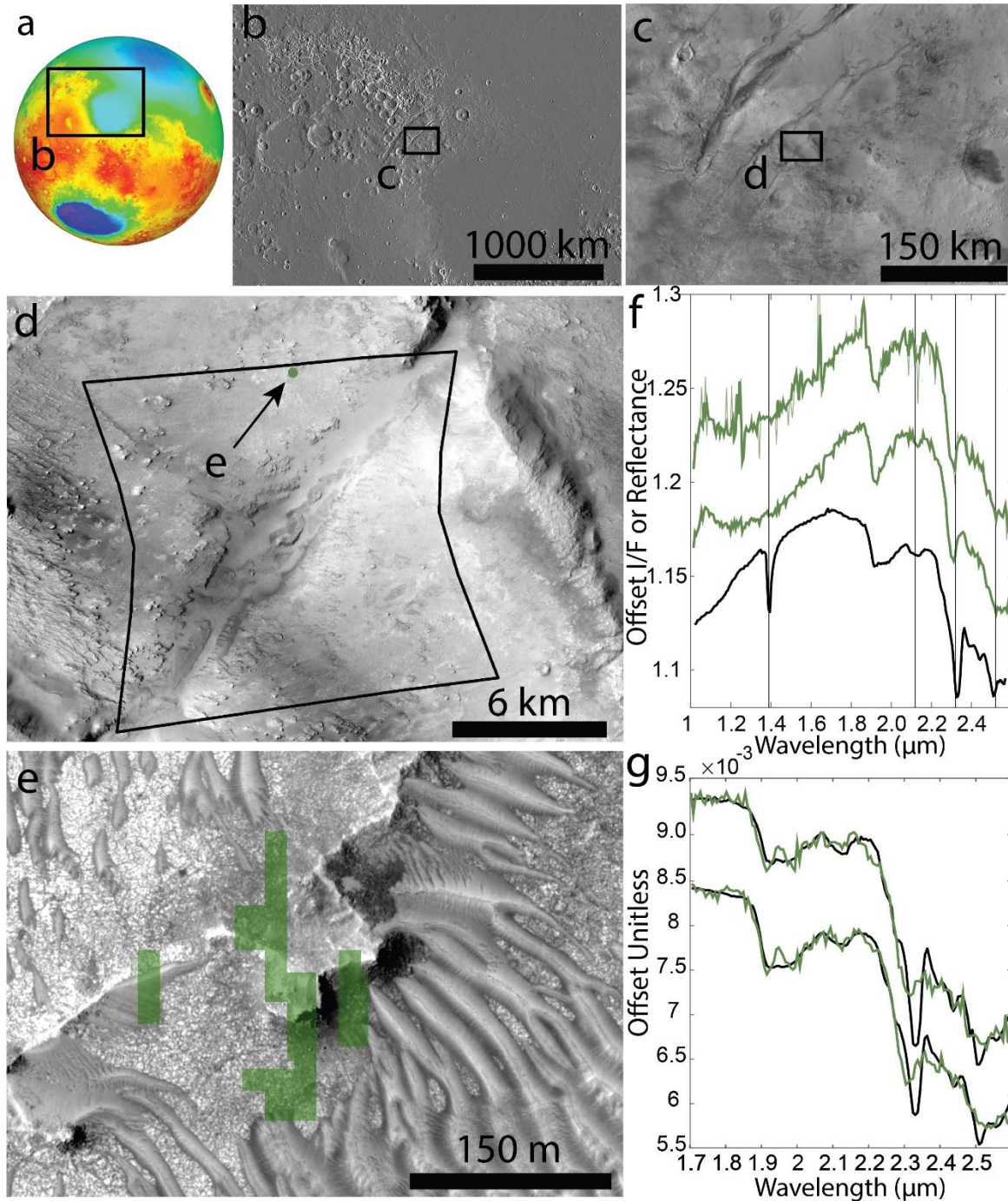


Figure 9 | Detection of I/F spectrum consistent with serpentine using DAFA/TT. (a) Location of Nili Fossae region on Mars globe, with colored topography. (b) MOLA hillshade of Nili Fossae region. (c) CTX mosaic (Dickson et al., 2018) of central Nili Fossae region. (d) Outline of CRISM footprint for FRT00003584 overlain on HiRISE image PSP_001754_2020, with the location of extracted I/F spectrum marked by green dot. (e) CRISM pixels from which I/F spectrum was extracted (green) coregistered and overlain on HiRISE image PSP_001754_2020. (f) (top) ratioed radiance data for spectrum consistent with serpentine, following the method of Leask et al.

(2018); (middle) ratioed I/F data for spectrum consistent with serpentine; (bottom) serpentine library spectrum RELAB ID C1LZ02. (g) DAFA/TT fits to overlapping detection clusters used to locate pixels containing I/F spectrum consistent with serpentine in both radiance and I/F data. RELAB IDs are C1JB529 and CASR19.

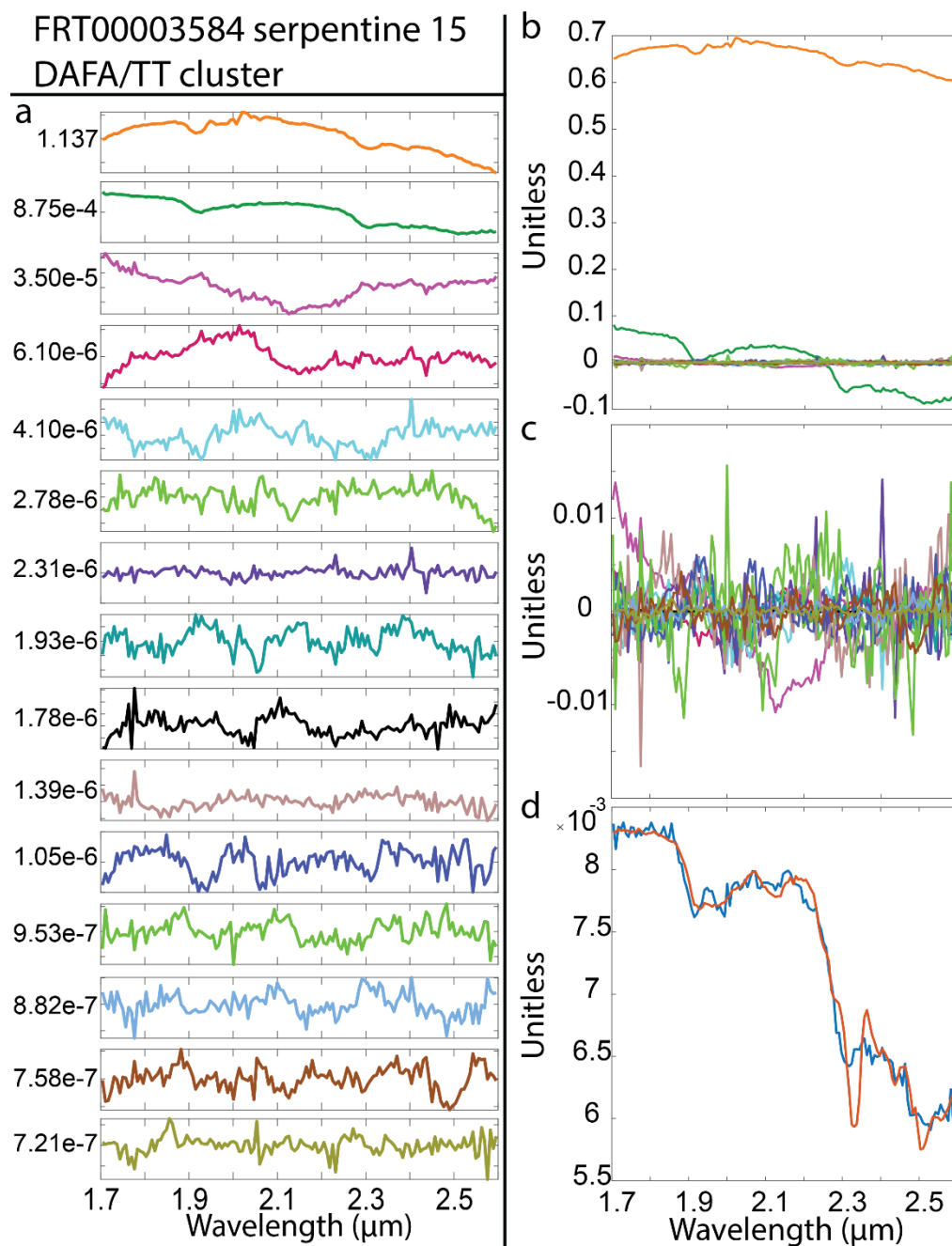


Figure 10 | Breakdown of HySime FA/TT process for DAFA/TT cluster used to locate serpentine spectrum. (a) The first 15 eigenvectors from HySime FA/TT pixels within one DAFA/TT cluster used to locate serpentine spectrum, with associated eigenvalues displayed on

the left of each plot. (b) The first 15 HySime FA eigenvectors after being multiplied by the coefficients from target transformation. (c) HySime FA eigenvectors 3-15 after being multiplied by the target transformation coefficients. (d) The calculated fit to serpentine spectrum RELAB ID C1JB529. HySime eigenvectors 1-3 are used to achieve a good fit in the diagnostic $2.1\text{ }\mu\text{m}$ region.

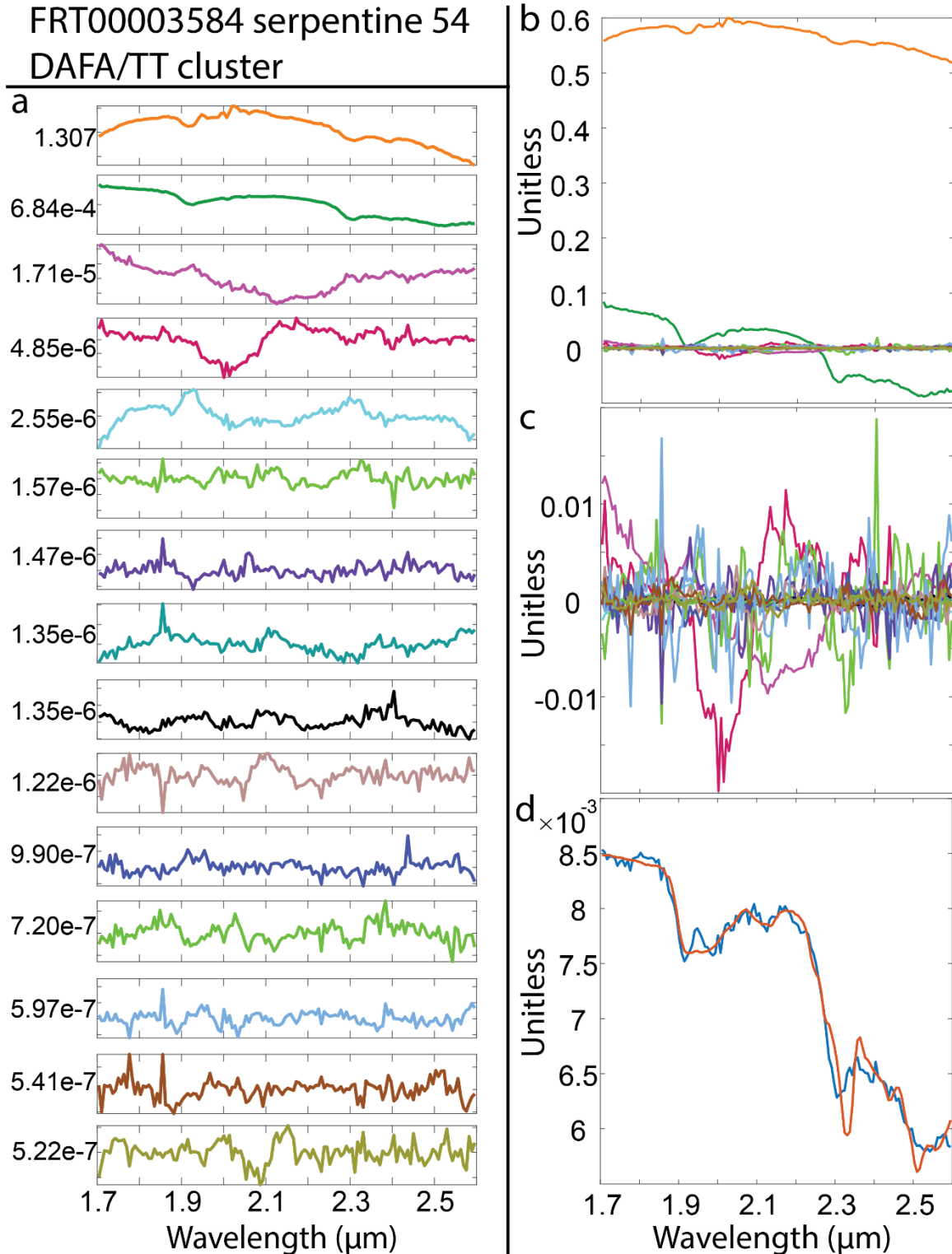


Figure 11 | Breakdown of HySime FA/TT process for DAFA/TT cluster used to locate serpentine spectrum. (a) The first 15 eigenvectors from HySime FA/TT pixels within one DAFA/TT cluster used to locate serpentine spectrum, with associated eigenvalues displayed on the left of each plot. (b) The first 15 HySime FA eigenvectors after being multiplied by the

coefficients from target transformation. (c) HySime FA eigenvectors 3-15 after being multiplied by the target transformation coefficients. (d) The calculated fit to serpentine spectrum RELAB ID CASR19. HySime eigenvectors 1-4 are used to achieve a good fit in the diagnostic 2.1 μm region.

Gypsum 125+ μm 10 eigenvector Hysime DAFA/TT

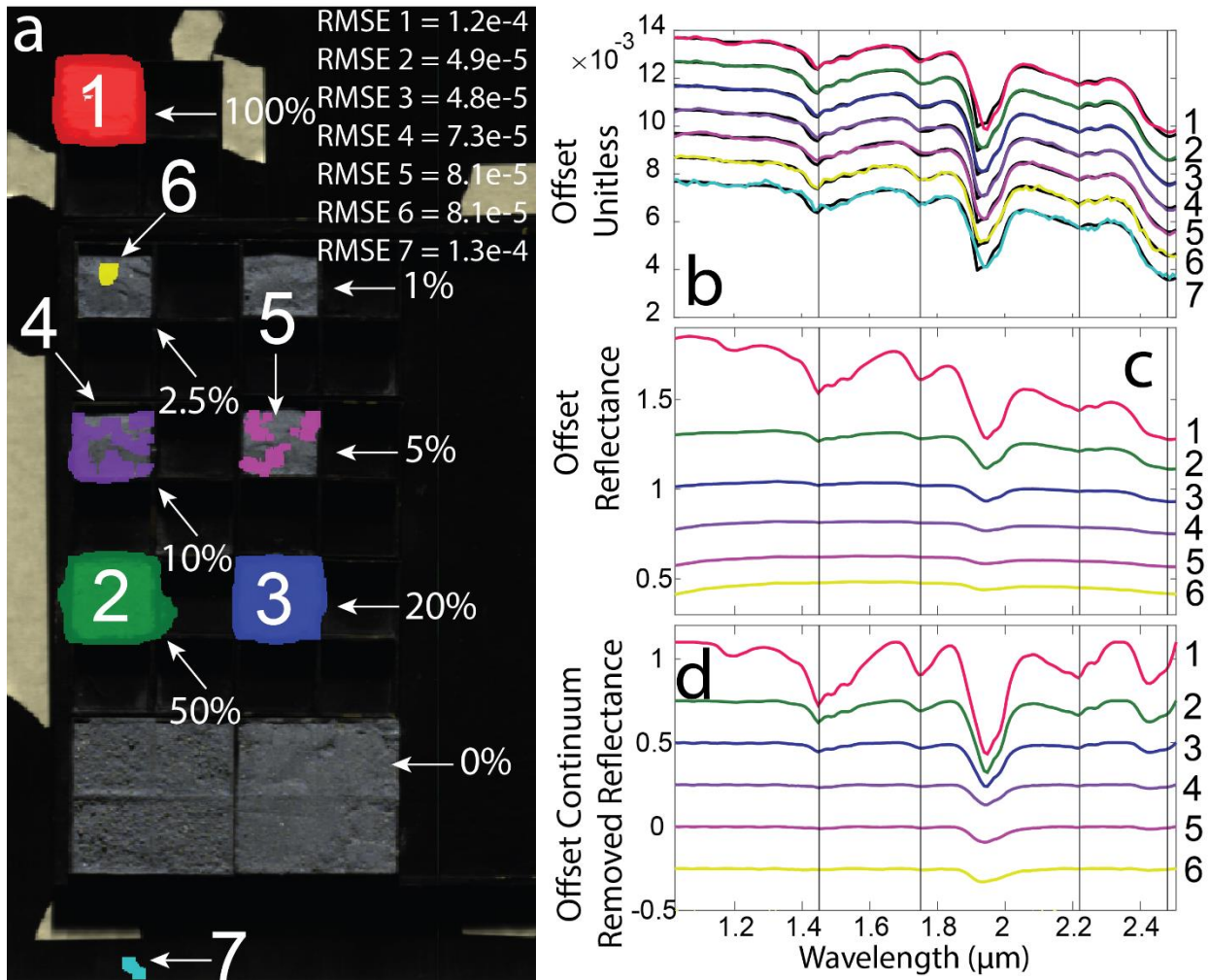


Figure 12 | 10 eigenvector HySime DAFA/TT analysis of gypsum 125+ μm tray. (a) DAFA/TT results for gypsum 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. The spectra from cluster 7 are shown in Fig. 13, and illustrate that a grain of gypsum was dropped on the translation table. Lines are at 1.45, 1.75, 2.22, and 2.42 μm .

Gypsum 125+ μm 10 eigenvector Hysime DAFA/TT false positive determination test

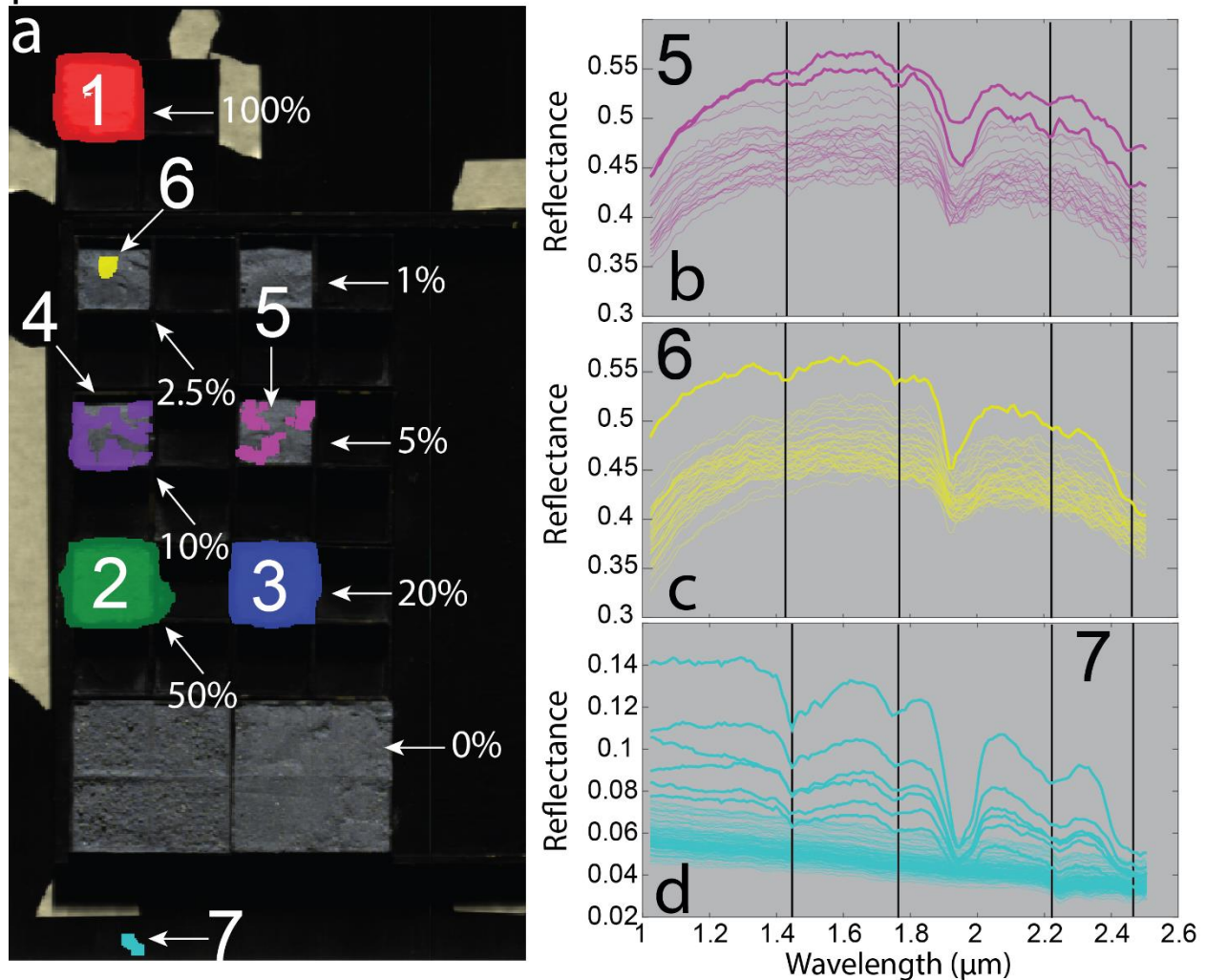


Figure 13 | Analysis of possible false positive detection clusters in gypsum 125+ μm tray detected via 10 eigenvector HySime DAFA/TT analysis. (a) Gypsum 125+ μm tray 10 eigenvector HySime DAFA/TT analysis results. (b) All spectra from cluster 5, with spectra containing diagnostic absorptions consistent with gypsum highlighted as thicker lines. (c) All spectra from cluster 6, with spectra containing diagnostic absorptions consistent with gypsum highlighted as thicker lines. (d) All spectra from cluster 7, with spectra containing diagnostic absorptions consistent with gypsum highlighted as thicker lines. Lines are at 1.45, 1.75, 2.22, and 2.42 μm .

Calcite 125+ μm 10 eigenvector Hysime DAFA/TT

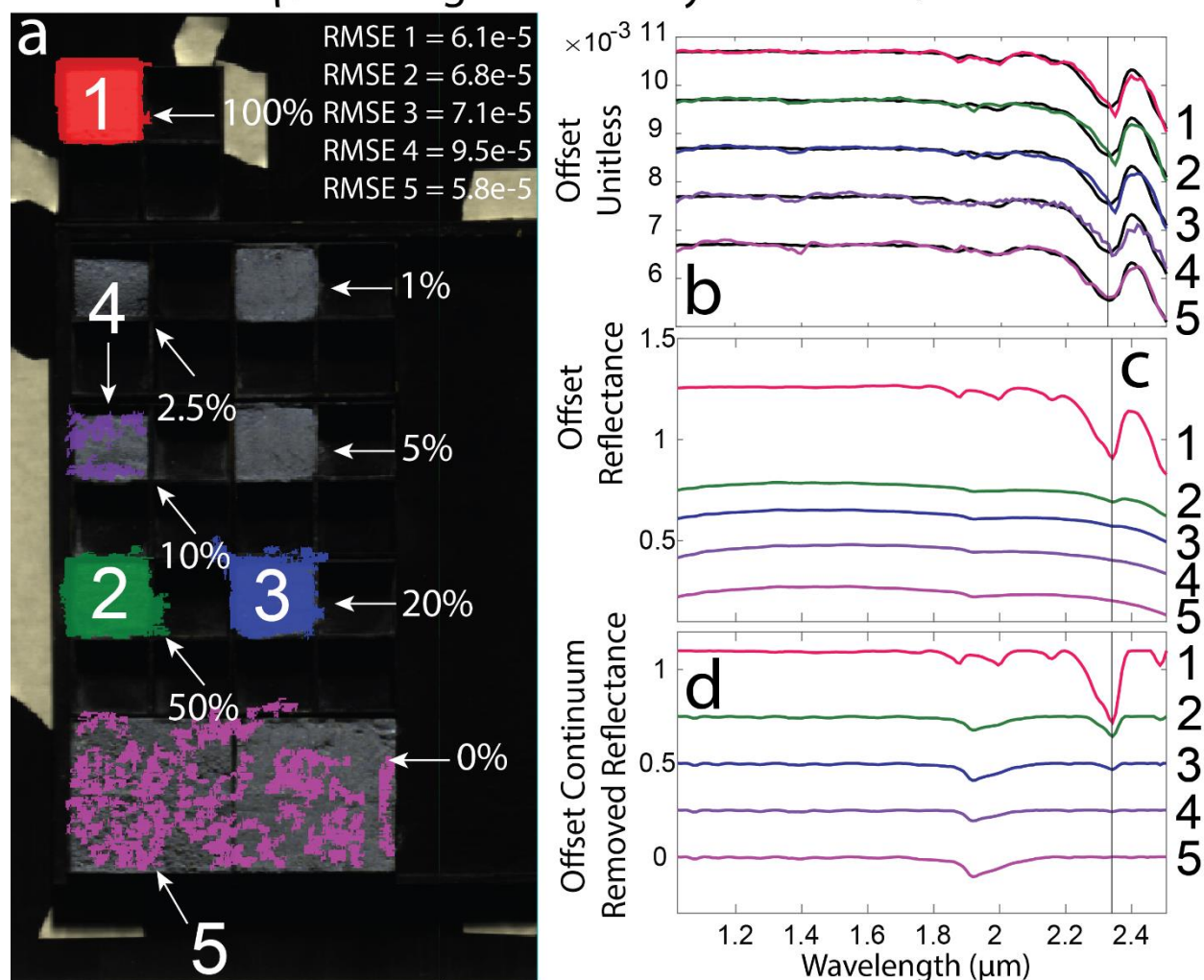


Figure 14 | 10 eigenvector HySime DAFA/TT analysis of calcite 125+ μm tray. (a) DAFA/TT results for calcite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. We applied the same false positive testing as illustrated in Fig. 13 to the false positive clusters here, but do not find any spectra consistent with calcite. The line is at 2.34 μm .

Kaolinite 125+ μm 15 eigenvector Hysime DAFA/TT

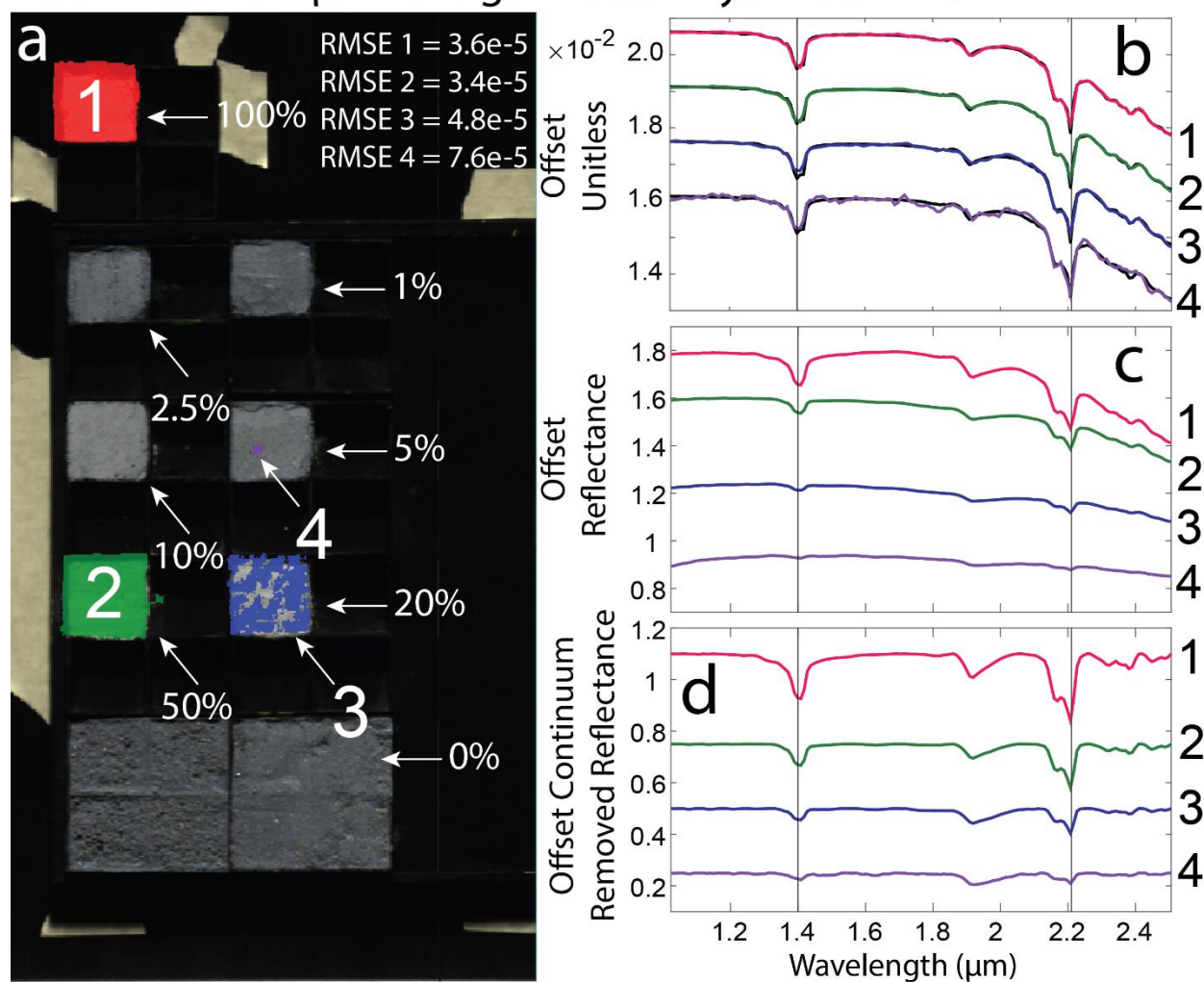


Figure 15 | 15 eigenvector HySime DAFA/TT analysis of kaolinite tray. (a) DAFA/TT results for kaolinite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.4 and 2.21 μm .

Calcite 45-75 μm 15 eigenvector Hysime DAFA/TT

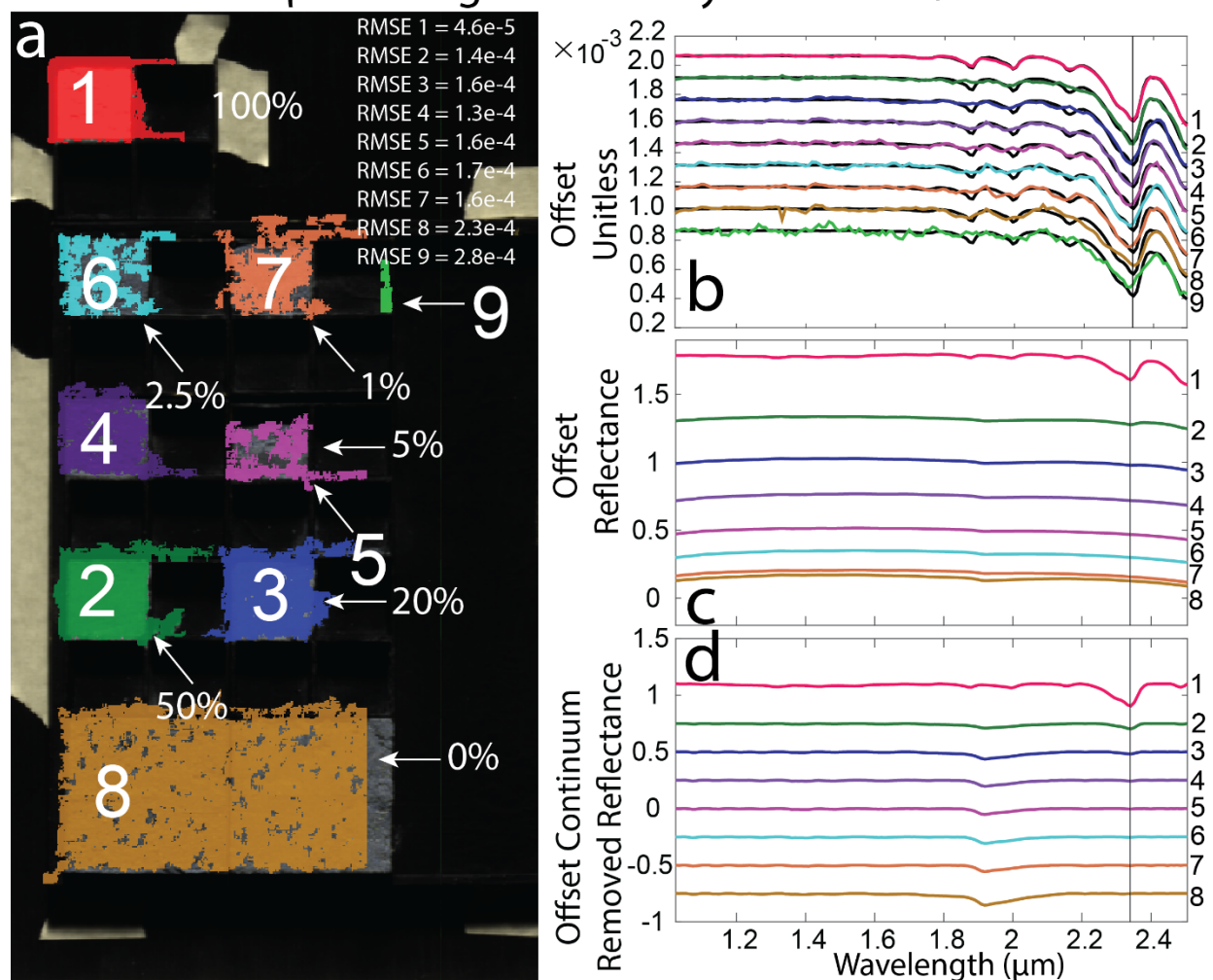


Figure 16 | 15 eigenvector HySime DAFA/TT analysis of calcite 45-75 μm tray. (a) DAFA/TT results for calcite 45-75 μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. The line is at 2.34 μm .

Nontronite 125+ μm 15 eigenvector R-mode DAFA/TT

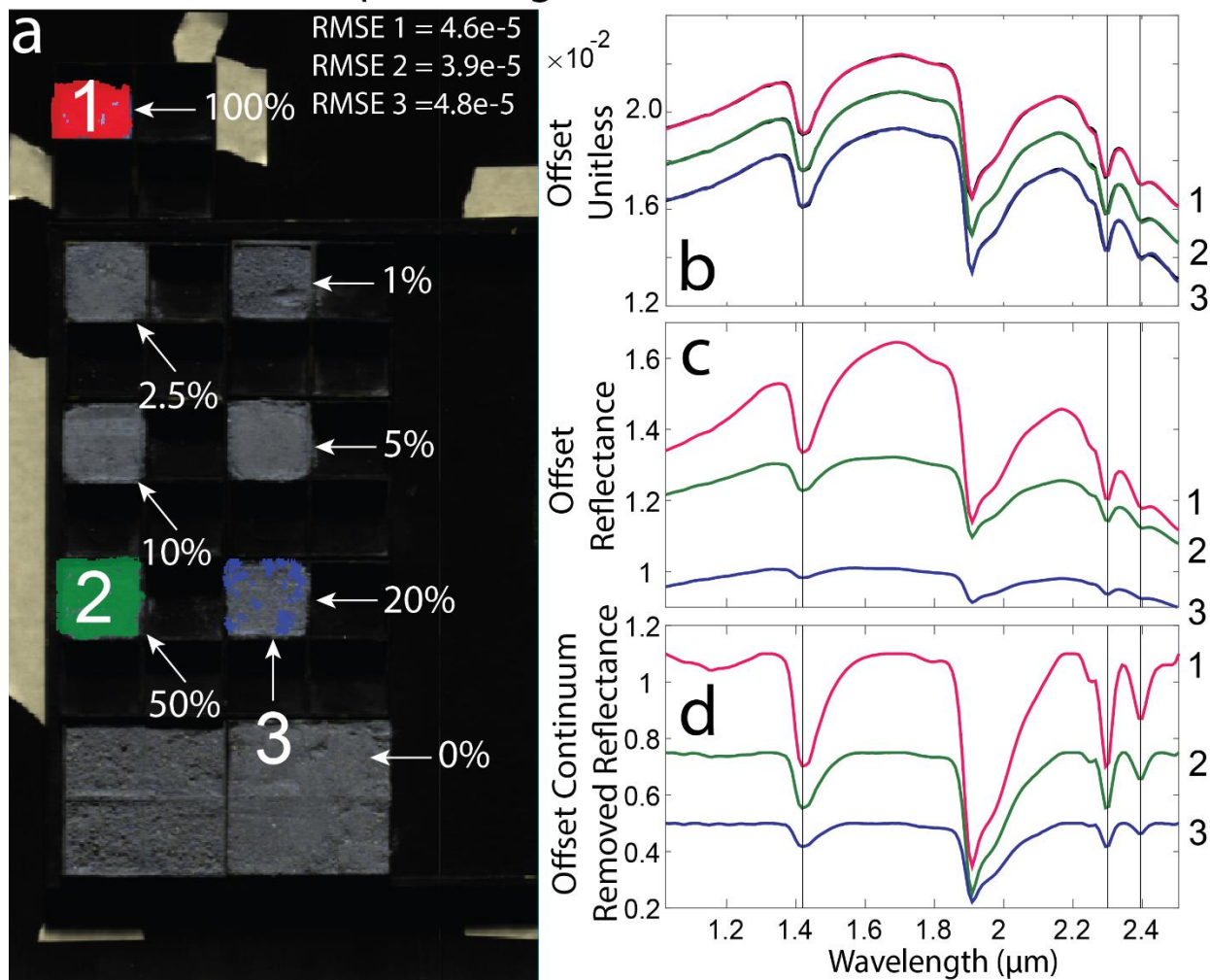


Figure 17 | 15 eigenvector R-mode DAFA/TT analysis of nontronite tray. (a) DAFA/TT results for nontronite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.42, 2.3, and 2.4 μm .

Calcite 45-75 μm 15 eigenvector R-mode DAFA/TT

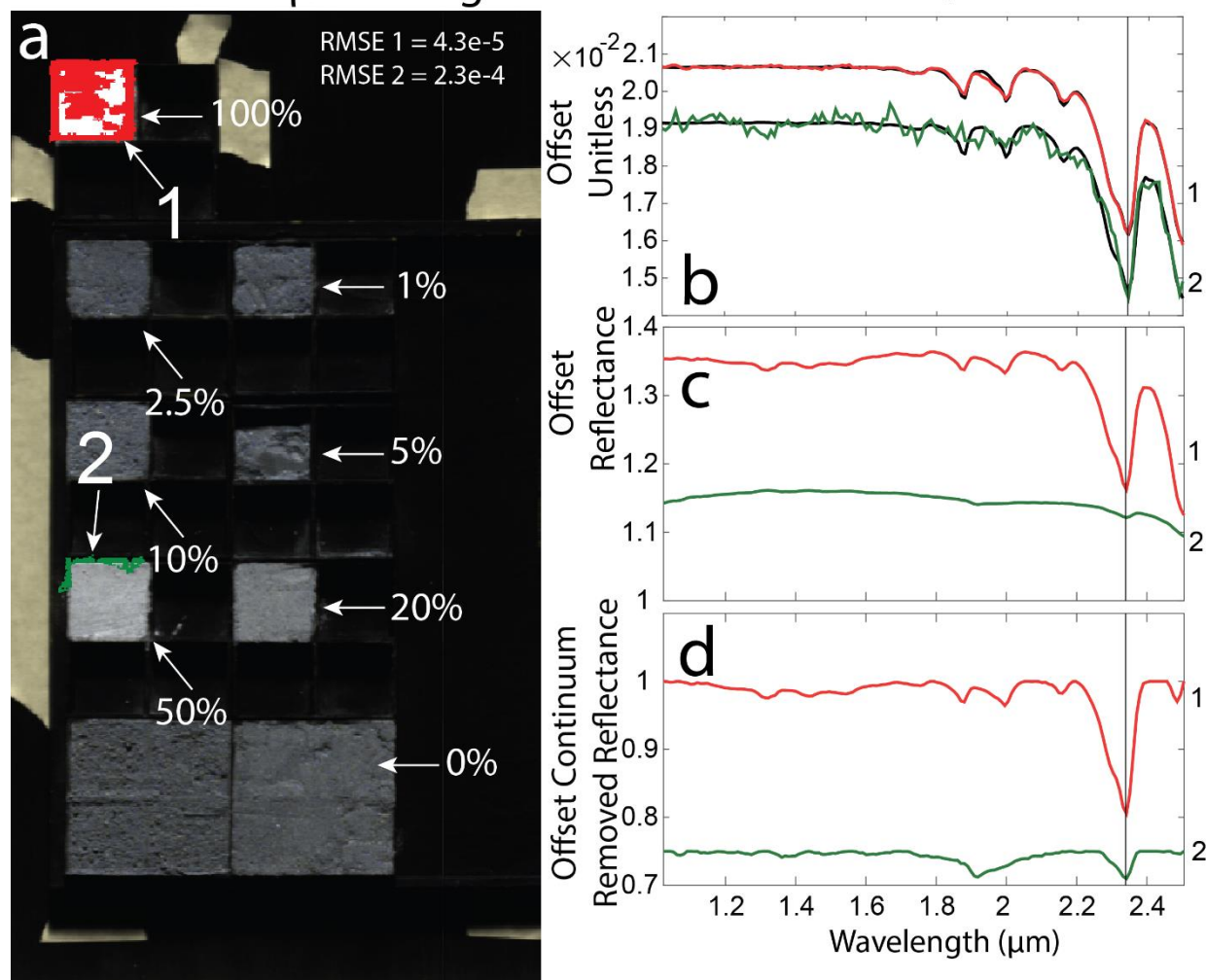


Figure 18 | 15 eigenvector R-mode DAFA/TT analysis of calcite 45-75 μm tray. (a) DAFA/TT results for calcite 45-75 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. The line is at 2.34 μm .

Gypsum 125+ μm 15 eigenvector R-mode DAFA/TT

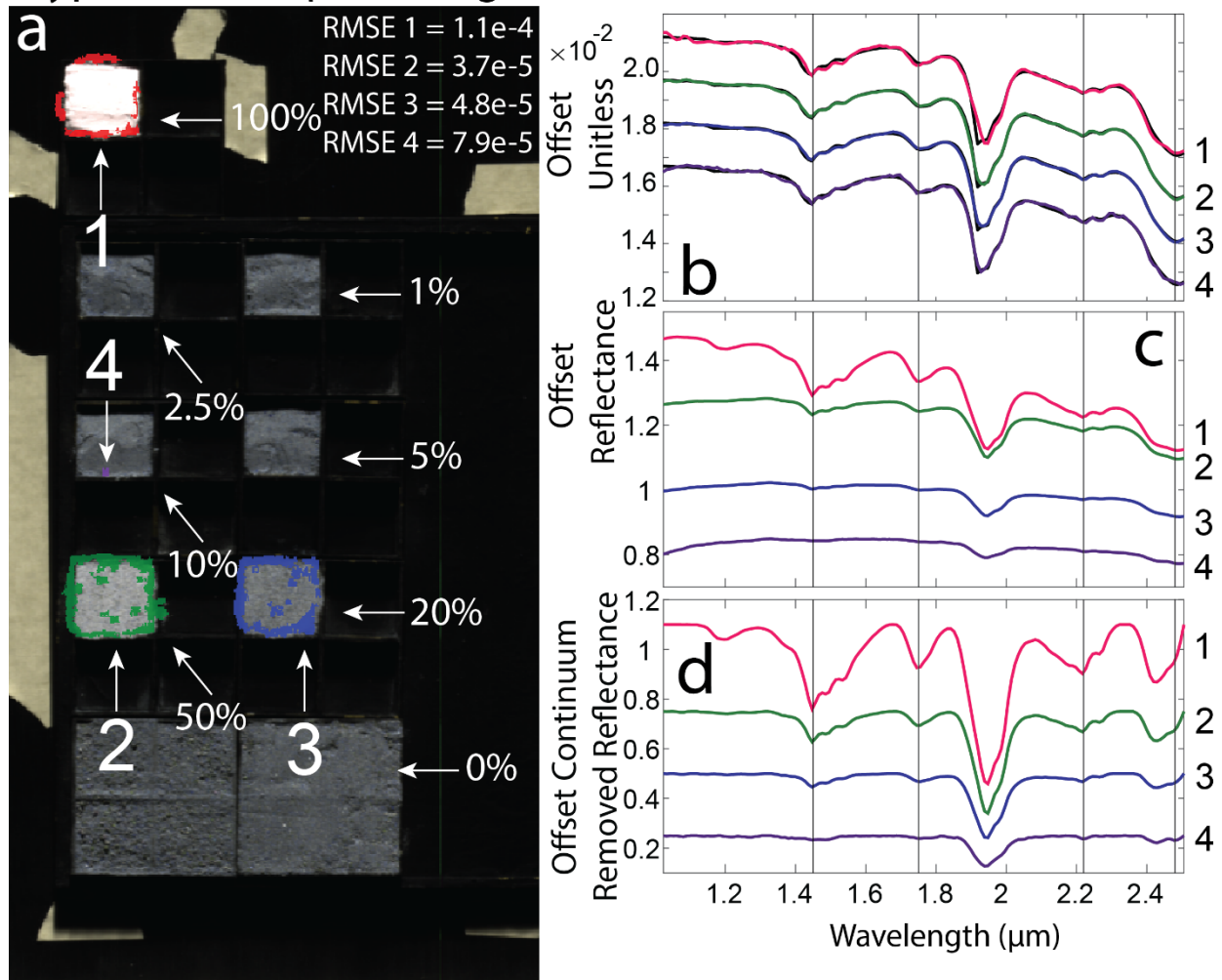


Figure 19 | 15 eigenvector R-mode DAFA/TT analysis of gypsum 125+ μm tray. (a) DAFA/TT results for gypsum 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.45, 1.75, 2.22, and 2.42 μm .

Gypsum 125+ μm 15 eigenvector Hysime DAFA/TT

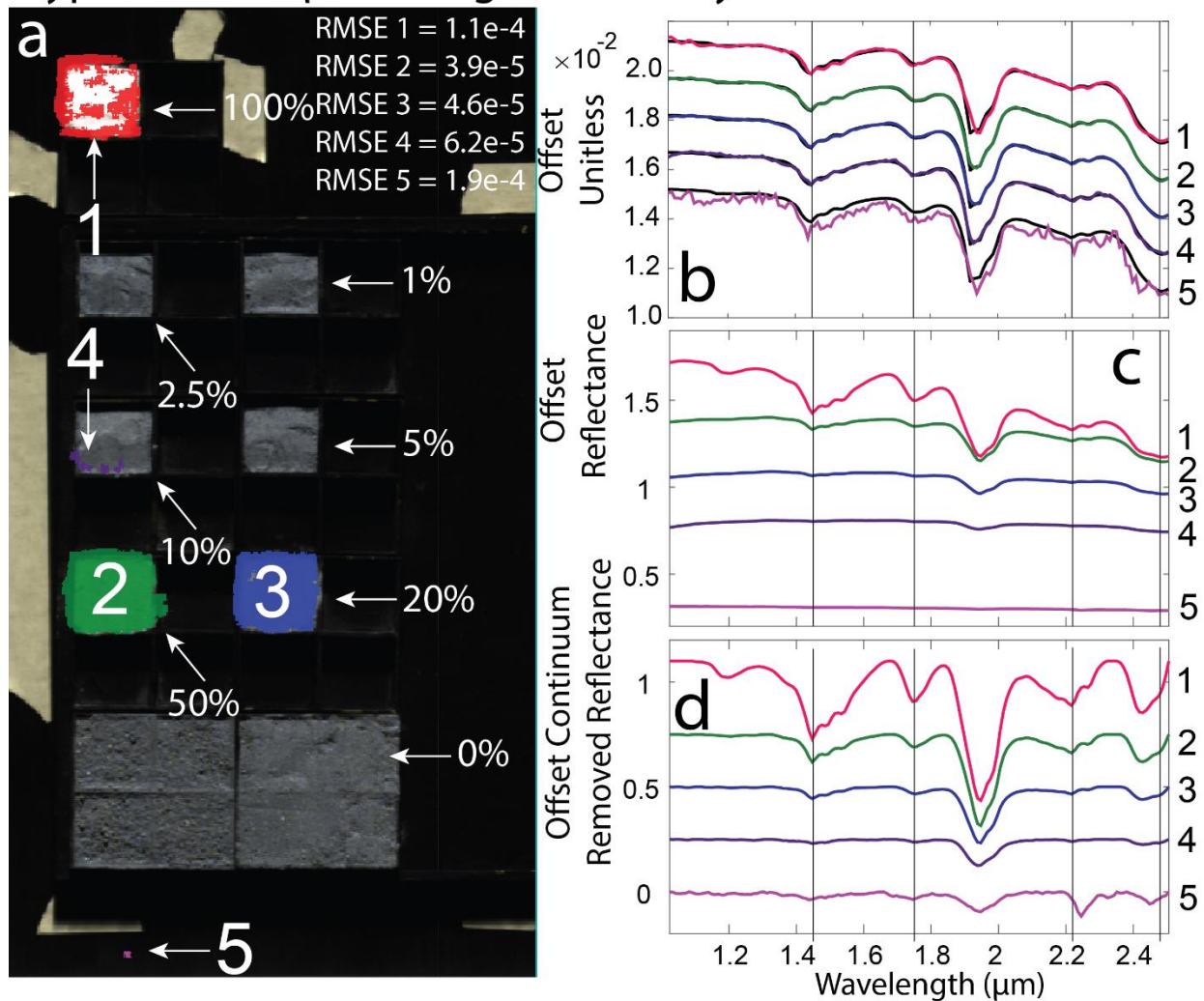


Figure 20 | 15 eigenvector HySime DAFA/TT analysis of gypsum 125+ μm tray. (a) DAFA/TT results for gypsum 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.45, 1.75, 2.22, and 2.42 μm .

Gypsum 125+ μm 50%
mixture 7x7 subset Hysime FA/TT

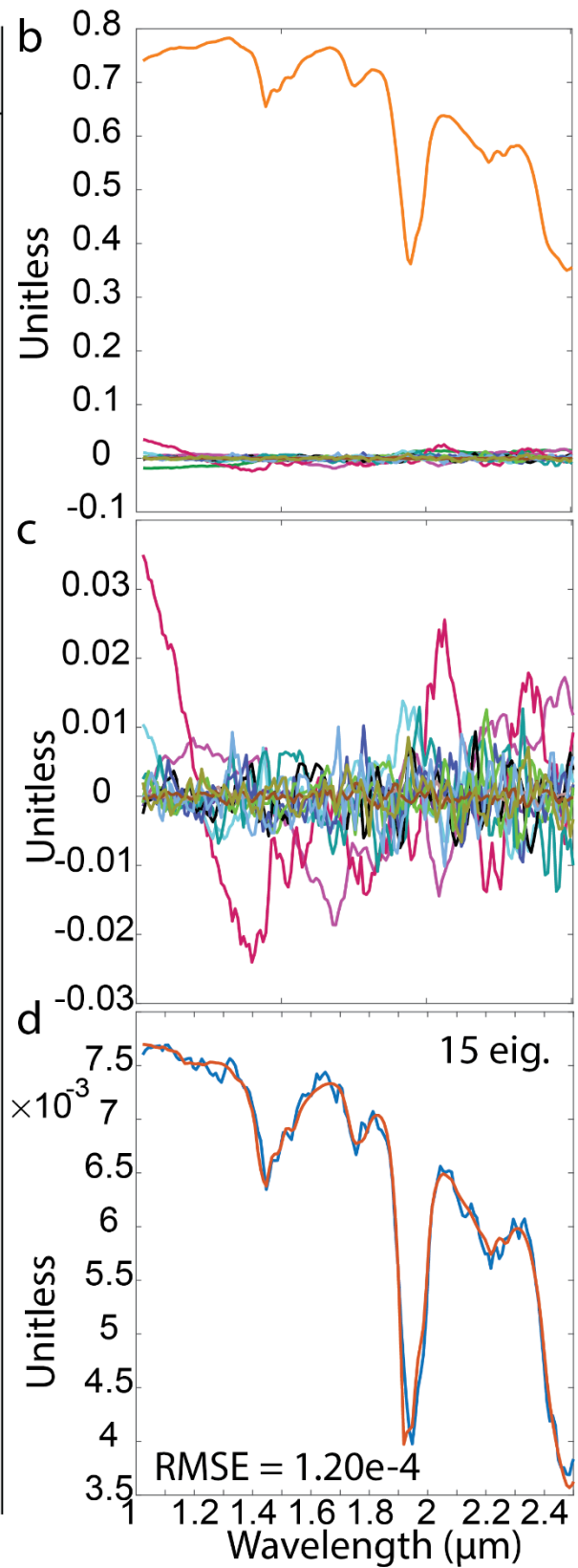
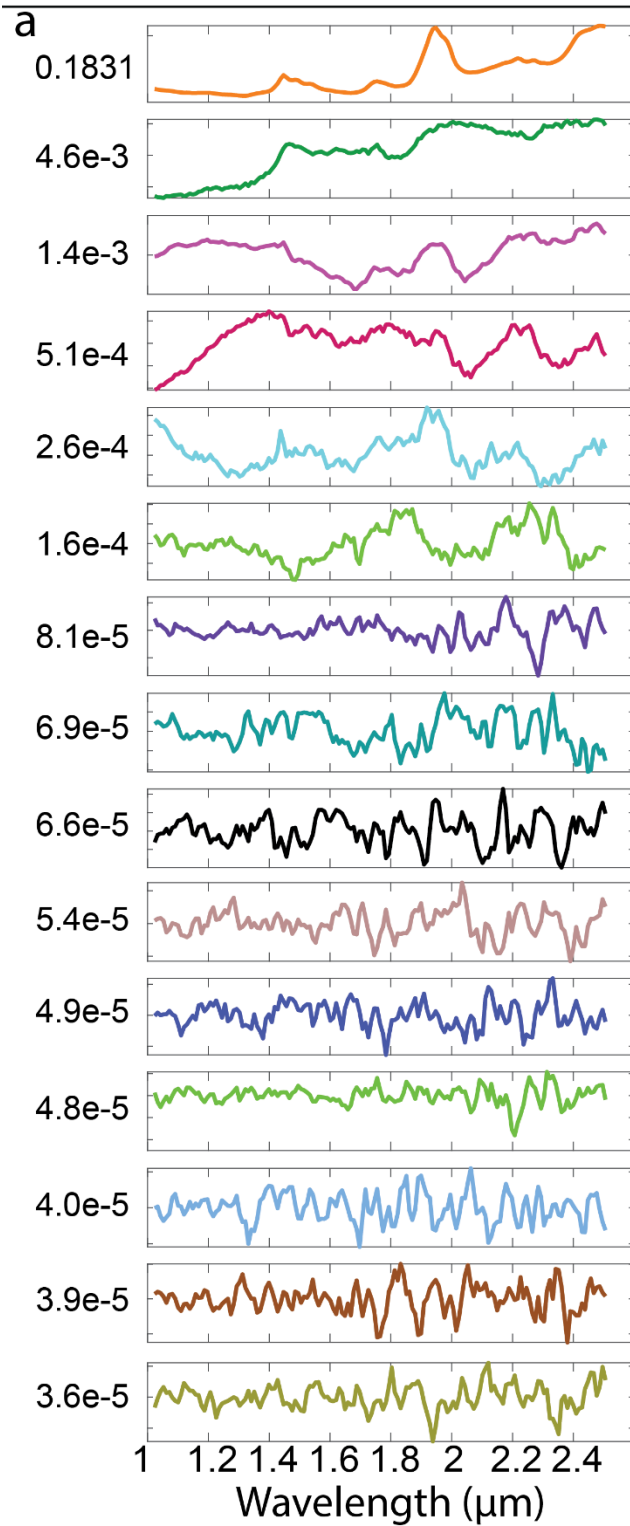


Figure 21 | Breakdown of HySime 15 eigenvector DAFA/TT cluster in 50% gypsum 125+ μm box center. (a) The first 15 eigenvectors from HySime FA/TT pixels within one DAFA/TT cluster used to locate serpentine spectrum, with associated eigenvalues displayed on the left of each plot. (b) The first 15 HySime FA eigenvectors after being multiplied by the coefficients from target transformation. (c) HySime FA eigenvectors 3-15 after being multiplied by the target transformation coefficients. (d) The calculated fit to gypsum RELAB ID 1101S556.

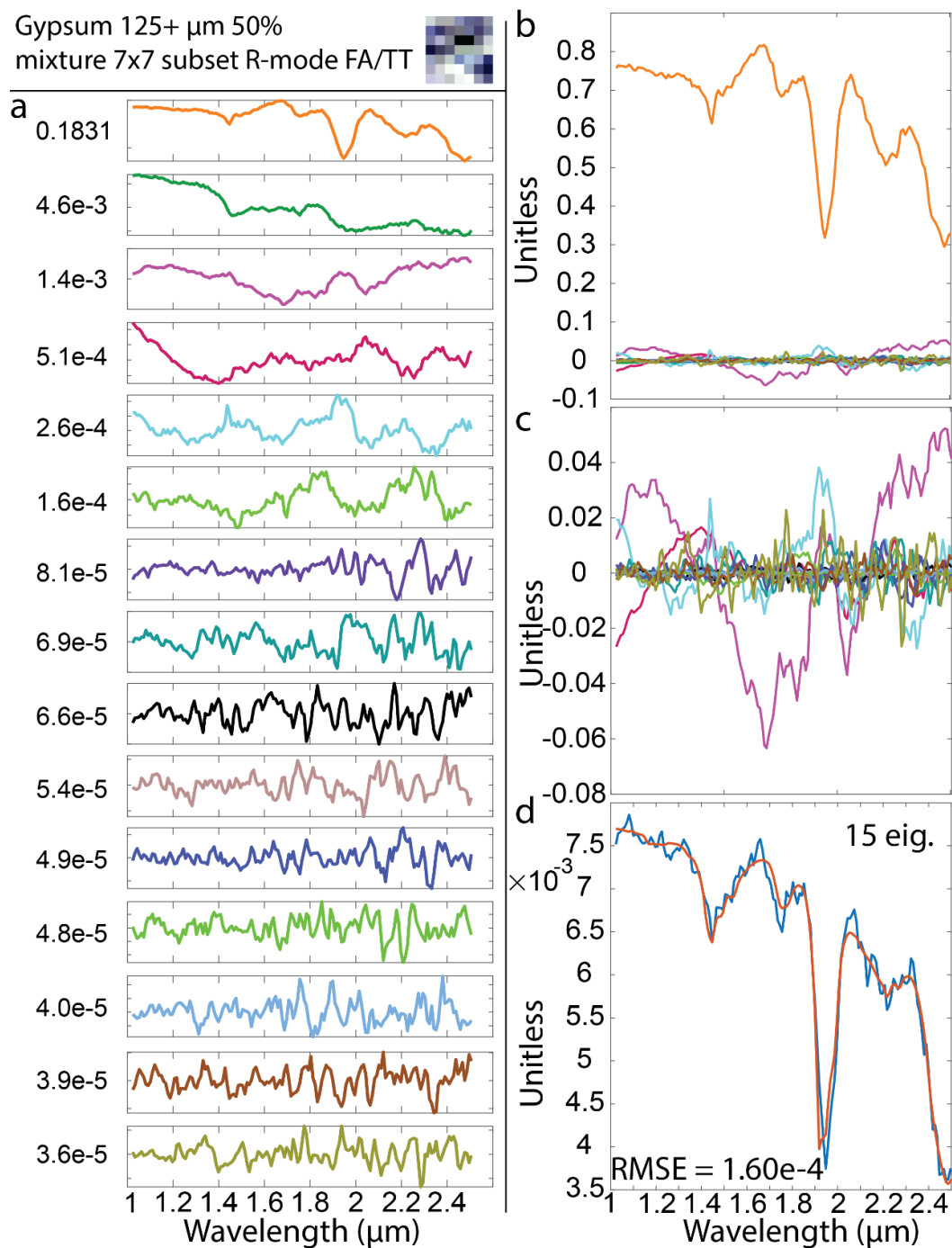


Figure 22 | Breakdown of R-mode 15 eigenvector DAFA/TT cluster in 50% gypsum 125+ μm box center. (a) The first 15 eigenvectors from R-mode FA/TT pixels within one DAFA/TT cluster used to locate serpentine spectrum, with associated eigenvalues displayed on the left of each plot. (b) The first 15 HySime FA eigenvectors after being multiplied by the coefficients from target transformation. (c) HySime FA eigenvectors 3-15 after being multiplied by the target transformation coefficients. (d) The calculated fit to gypsum RELAB ID 1101S556.

		Gypsum 125+ μm	Gypsum 45-75 μm	Calcite 125+ μm	Calcite 45-75 μm	Kaolinite 125+ μm	Nontronite 125+ μm	Montmoril. 125+ μm
100%	R-m. 15 eig.	~√	~√	~√	~√	~√	√	√
	Hy. 10 eig.	√	~√	√	√	√	√	√
	Hy. 15 eig.	~√	~√	√	√	√	√	√
50%	R-m. 15 eig.	~√	~√	√	~√	~√	√	~√
	Hy. 10 eig.	√	√	√	√	√	√	√
	Hy. 15 eig.	√	√	√	√	√	√	√
20%	R-m. 15 eig.	~√	~√	~√	—	~√	~√	~√
	Hy. 10 eig.	√	√	√	~√	~√	~√	~√
	Hy. 15 eig.	√	~√	√	√	~√	~√	~√
10%	R-m. 15 eig.	~√	—	~√	—	—	—	—
	Hy. 10 eig.	√	—	~√	●	—	—	~√
	Hy. 15 eig.	~√	—	√	●	—	—	~√
5%	R-m. 15 eig.	—	—	×	×	~√	—	—
	Hy. 10 eig.	●	●	×	×	~√	—	—
	Hy. 15 eig.	—	—	+	+	~√	—	—
2.5%	R-m. 15 eig.	—	×	×	×	×	×	×
	Hy. 10 eig.	●	×	×	×	×	×	×
	Hy. 15 eig.	—	×	+	+	×	×	×
1%	R-m. 15 eig.	×	×	×	×	×	×	×
	Hy. 10 eig.	×	×	×	×	×	×	×
	Hy. 15 eig.	×	×	+	+	×	×	×
0%	R-m. 15 eig.	×	×	×	×	×	×	×
	Hy. 10 eig.	×	×	+	+	×	×	×
	Hy. 15 eig.	×	×	+	+	×	×	×
Table	R-m. 15 eig.	—	●	+	×	×	×	×
	Hy. 10 eig.	●	●	+	×	×	×	×
	Hy. 15 eig.	●	●	+	+	×	×	×

√	= full true detection	×	= true non-detection
~√	= partial true detection	—	= false negative true detection
●	= spectrum exists in cluster	+	= false positive detection

Table 2 | Results summary for full-image DAFA/TT experiments for each individual mixing ratio tray. The results used to generate this table are displayed in Figs. 12-20, as well as Figs. S6-S20.

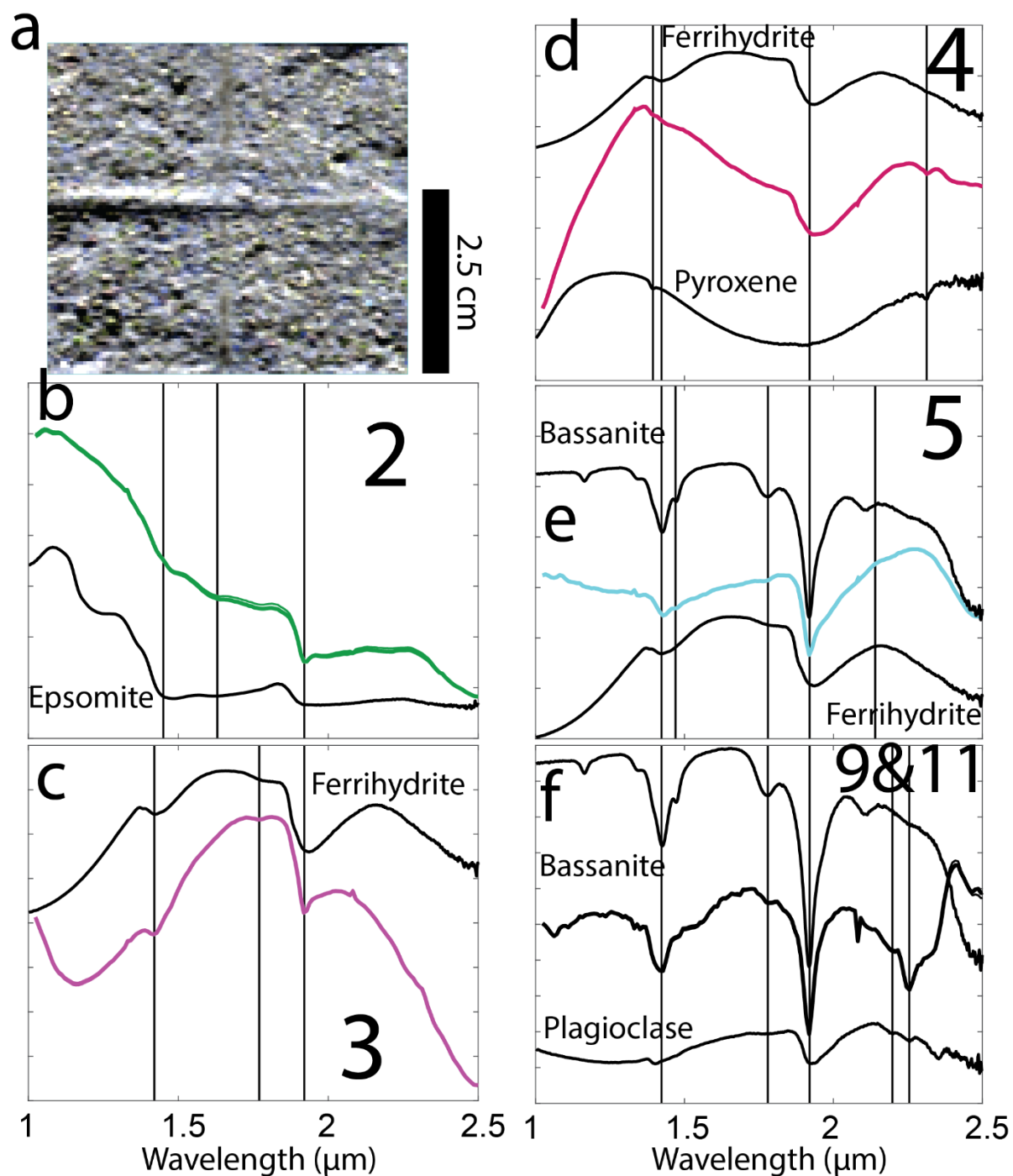


Figure 23 | MGS-1 tray eigenvectors compared to point spectra of individual MGS-1 components. (a) An MGS-1 tray measured during the nontronite Mars tray experiment. (b) Comparison of the 2nd HySime (thick green) and R-mode FA (thin green) eigenvector with a point spectrum of MGS-1 component epsomite. The HySime and R-mode FA eigenvectors are exactly the same. (c) Comparison of the 3rd HySime (thick purple) and R-mode FA (thin purple) eigenvector with a point spectrum of MGS-1 component ferrihydrite. (d) Comparison of the 4th

HySime (thick pink) and R-mode FA (thin pink) eigenvector with a point spectrum of MGS-1 components ferrihydrite and pyroxene. The HySime and R-mode FA eigenvectors are exactly the same. Eigenvector 4 appears to be a combination of pyroxene and ferrihydrite component spectra. (e) Comparison of the 5th HySime (thick cyan) and R-mode FA (thin cyan) eigenvector with a point spectrum of MGS-1 components ferrihydrite and bassanite. The HySime and R-mode FA eigenvectors are exactly the same. Eigenvector 5 appears to be a combination of bassanite and ferrihydrite component spectra. It possesses the a 1.4 μm feature consistent with both spectra, but with a slight doublet nature consistent with bassanite. Its 1.9 μm feature has a similar width as that of ferrihydrite, but a similar sharpness to bassanite at its absorption minimum. The 2.4 μm shoulder is also consistent with bassanite. Its slight 1.75 μm feature is consistent with both bassanite and ferrihydrite. (f) Comparison of the 9th HySime (thick middle black) and 11th R-mode FA (thin middle black) eigenvector with a point spectrum of MGS-1 components ferrihydrite and bassanite. These eigenvectors appear to be a combination of bassanite and contaminated plagioclase component spectra. The 1.4, 1.75, and 1.9 μm absorption features are consistent with bassanite. The 2.25 and 2.35 μm features are consistent with contaminated plagioclase.

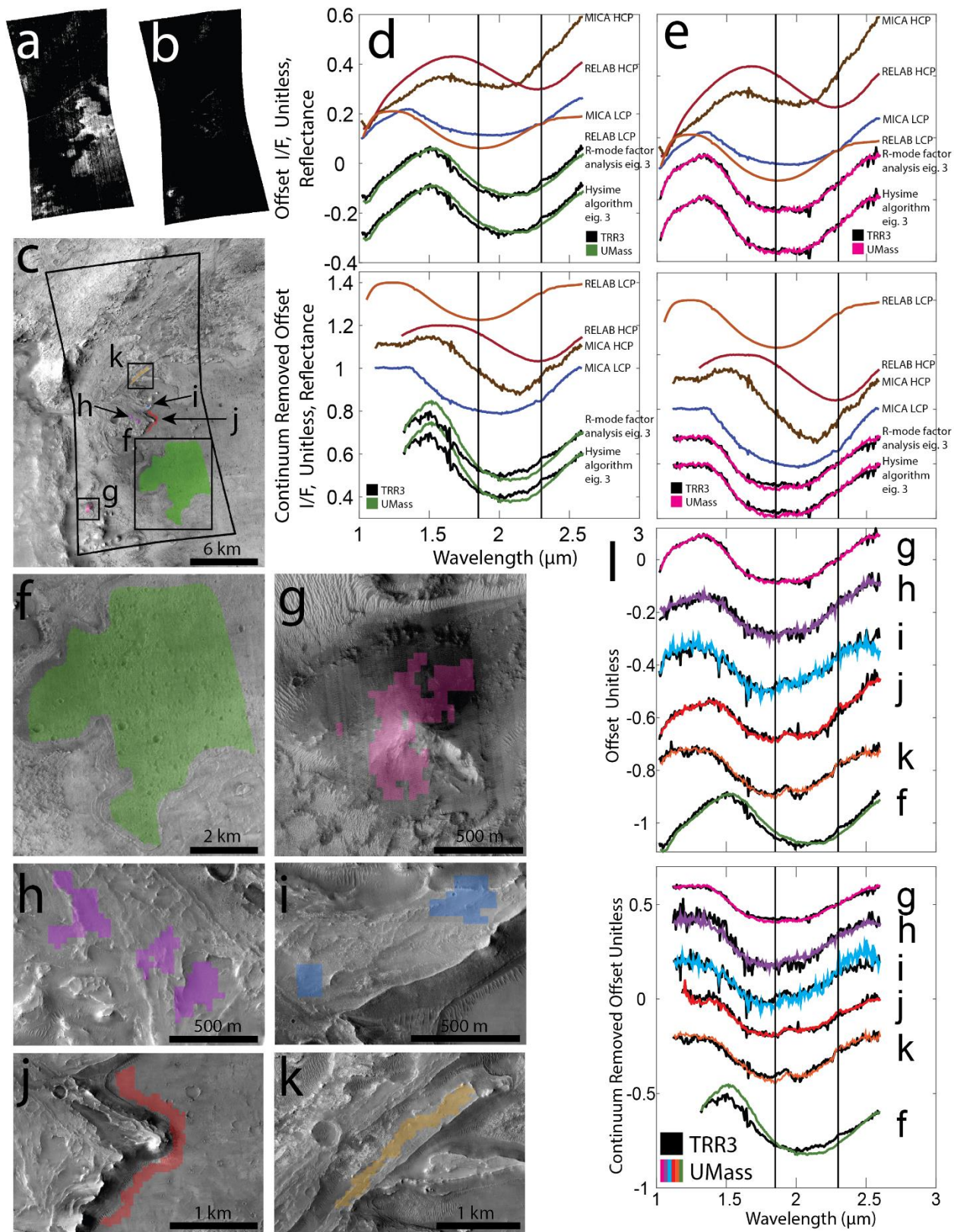


Figure 24 | Guided factor analysis results for high calcium and low calcium pyroxenes in Jezero crater, Mars. Parts (c & f) use the CTX mosaic from (Dickson et al., 2018) and parts (f-k) use the HiRISE mosaic by these same authors. (a) HCPINDEX2 (Viviano-Beck et al., 2014) band parameter map for CRISM image HRL000040FF thresholded to minimum: -0.0146, maximum: 0.0200. This was used to guide construction of the green ROI shown in part (f). (b) LCPINDEX2 (Viviano-Beck et al., 2014) band parameter map for CRISM image HRL000040FF thresholded to minimum: -0.0144; maximum: 0.0100. This was used to guide construction of the ROIs shown in parts (g-k). (c) Overview map of site showing outline of CRISM image HRL000040FF and each individual ROI. (d) Top panel shows non-continuum removed spectra, while the bottom panel shows continuum removed spectra. Eigenvector 3 of green pixels shown in (f) from both HySime and R-mode FA, applied to both CRISM TRR3 data and CRISM data processed by the University of Massachusetts at Amherst empirical atmospheric correction and denoising pipeline (Itoh and Parente, 2021). The MICA LCP and HCP spectra, as well as their paired RELAB spectra in Viviano-Beck et al. (2014), are displayed for comparison. This eigenvector appears to resemble HCP based on its shape and the $\sim 2.1 \mu\text{m}$ wavelength position of the $2 \mu\text{m}$ absorption minimum. (e) Top panel shows non-continuum removed spectra, bottom panel shows continuum removed spectra. Eigenvector 3 of pink pixels shown in (g) from both HySime and R-mode FA, applied to both CRISM TRR3 data and CRISM data processed by the University of Massachusetts at Amherst empirical atmospheric correction and denoising pipeline (Itoh and Parente, 2021). The same MICA and RELAB spectra as shown in part (d) are displayed. This eigenvector appears to resemble LCP based on its shape and the $\sim 1.8 \mu\text{m}$ wavelength position of the $2 \mu\text{m}$ absorption minimum. (f) Pixels used in guided factor analysis shown in parts (d and l) are shown in green. (g) Pixels used in guided factor analysis shown in parts (e and l) are shown in pink. (h) Pixels used in guided factor analysis shown in part (l) are shown in purple. (i) Pixels used in guided factor analysis shown in part (l) are shown in blue. (j) Pixels used in guided factor analysis shown in part (l) are shown in red. (k) Pixels used in guided factor analysis shown in part (l) are shown in orange. (l) Top panel shows non-continuum removed eigenvectors while the bottom panel shows continuum removed eigenvectors. The eigenvectors from the CRISM pixels shown in parts (f-k) that are consistent with pyroxene are displayed, with colors corresponding the colors in parts (f-k). Pixels shown in parts (h-k) have pyroxene eigenvectors consistent with LCP, agreeing with the results of (Horgan et al., 2020). Pixels shown in part (f) have a pyroxene eigenvector consistent with HCP, agreeing with the results of (Horgan et al., 2020).

Supplementary Figures

Calcite (45-75 μm) and Mars Global Simulant 1 Mixtures

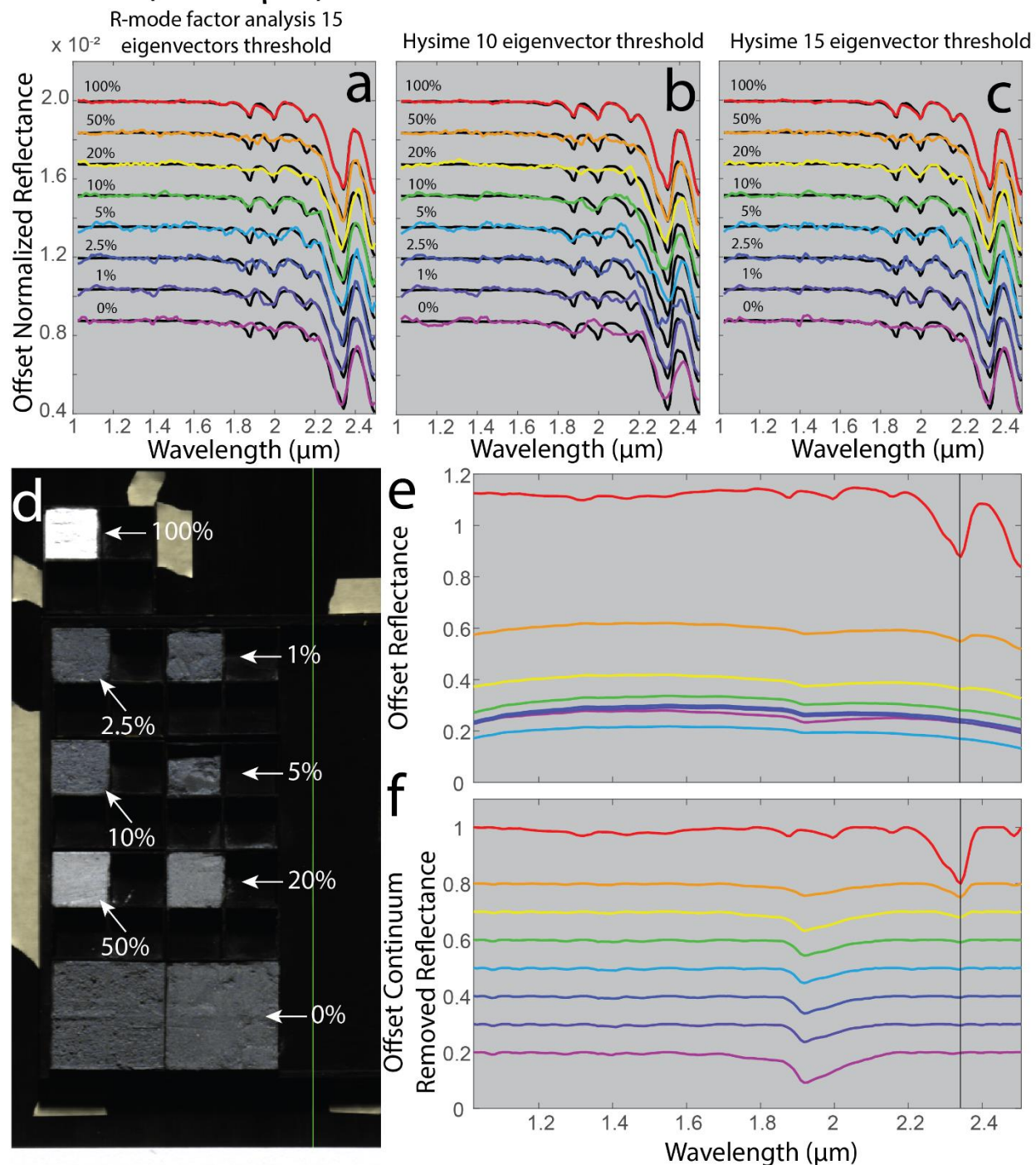


Figure S1 | Results from 15 eigenvector R-mode FA, 15 eigenvector HySime FA, and 10 eigenvector HySime FA to calcite 45-75 μm Mars tray. (a) 15 eigenvector R-mode FA/TT results for each individual tray. All trays have good fits because the 2.3 μm absorption and partial 2.5 μm absorption are fit well. (b) 10 eigenvector HySime FA/TT results for each individual tray.

Using the same criteria as described in (a), all trays have good fits except for the 5% tray. The 5% tray's fit is still good enough to be considered a borderline false positive. (c) 15 eigenvector HySime FA/TT results for each individual tray. Using the same criteria as described in (a), all trays have good fits. (d) The calcite 45-75 μm Mars tray, with the percentage calcite in each tray labeled. (e) The average spectrum of each individual tray, with the color scheme following that of (a-c). The line is at 2.34 μm . (f) The continuum removed average spectrum of each individual tray with the same color scheme as (a-c) and same lines as (e). The calcite 45-75 μm Mars tray provided our second worst performance in this whole-image FA/TT experiment. This is likely due to the existence of structured noise in our data that resembles the diagnostic absorptions for calcite within the measured wavelength range.

Gypsum (125+ μm) and Mars Global Simulant 1 Mixtures

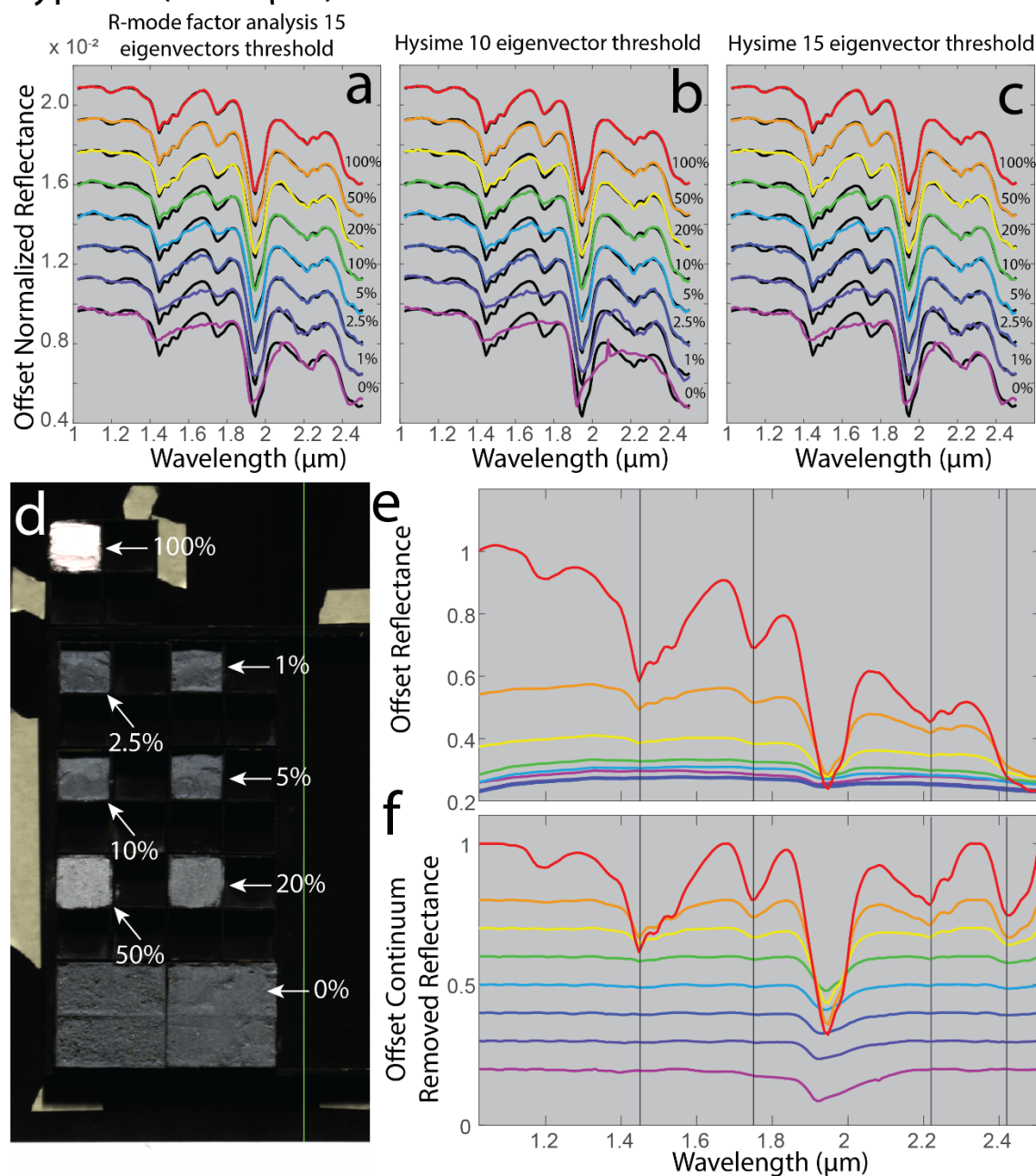


Figure S2 | Results from 15 eigenvector R-mode FA, 15 eigenvector HySime FA, and 10 eigenvector HySime FA to gypsum 125+ μm Mars tray. (a) 15 eigenvector R-mode FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, 5%, and 2.5% trays are good because the shape of the 1.4, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well. Fits to the 1% and 0% trays are borderline because the 1.4, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well. (b) 10 eigenvector HySime FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, 5%, and 2.5% trays are good because the shape of the 1.4, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well. Fits to the 1% tray are borderline

because the 1.4, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well. Fits to the 0% tray are bad because the 1.75 and 2.2 μm features do not exist (c) 15 eigenvector HySime FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, 5%, and 2.5% trays are good because the shape of the 1.4, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well. Fits to the 1% and 0% trays are borderline because the 1.4, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well. (d) The gypsum 125+ μm Mars tray, with the percentage gypsum in each tray labeled. (e) The average spectrum of each individual tray, with the color scheme following that of (a-c). Lines are at 1.45, 1.75, 2.22, and 2.42 μm . (f) The continuum removed average spectrum of each individual tray with the same color scheme as (a-c) and same lines as (e).

Gypsum (45-75 μm) and Mars Global Simulant 1 Mixtures

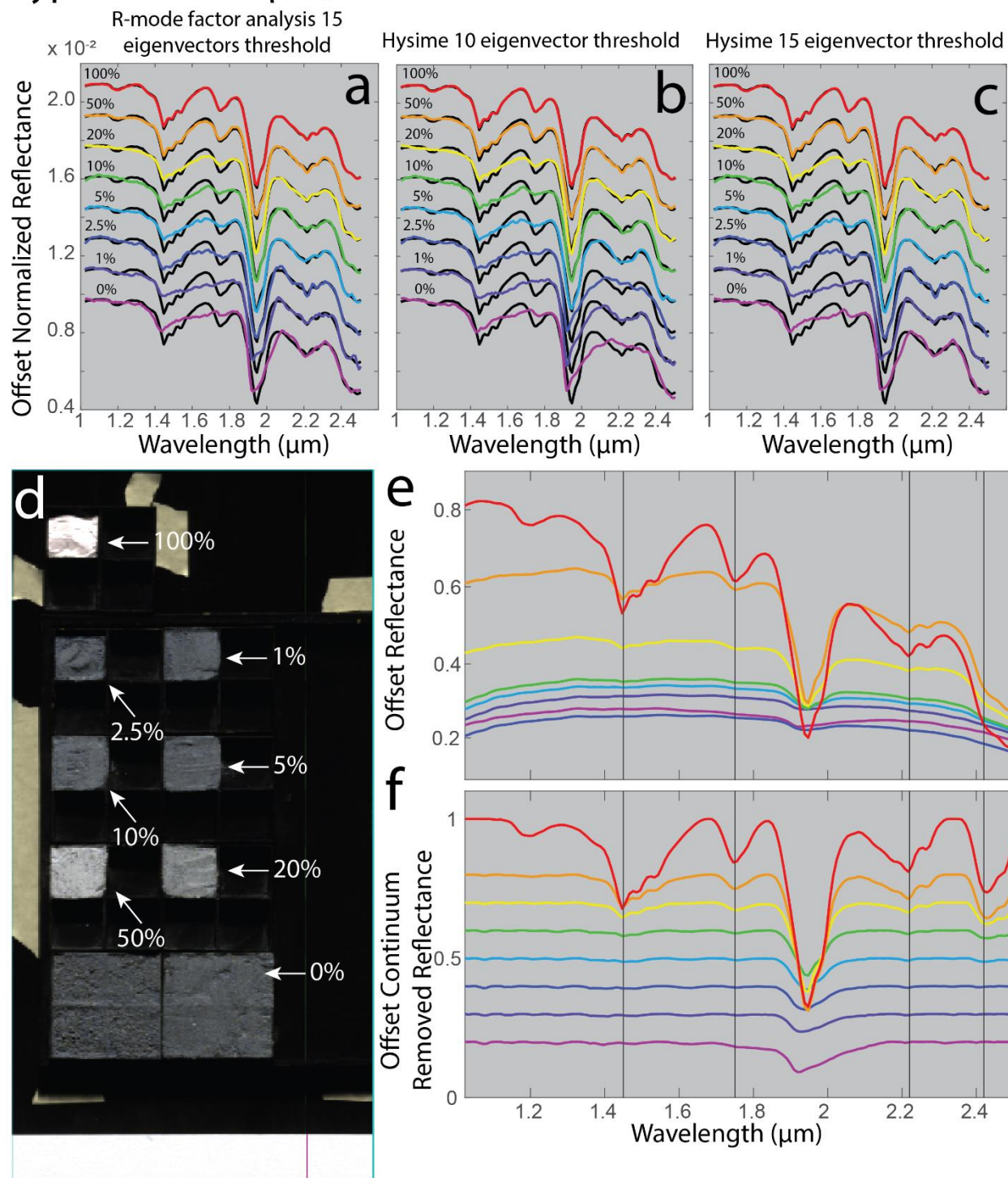


Figure S3 | Results from 15 eigenvector R-mode FA, 15 eigenvector HySime FA, and 10 eigenvector HySime FA to gypsum 45-75 μm Mars tray. (a) 15 eigenvector R-mode FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well. Fits to

the 2.5%, 1%, and 0% trays are borderline because the 1.4, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well. (b) 10 eigenvector HySime FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well. Fits to the 2.5%, 1%, and 0% trays are bad because the 1.75 and 2.2 μm features do not exist (c) 15 eigenvector HySime FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4, 1.75, and 2.2 μm features and 2.4 μm shoulder are fit well. Fits to the 2.5%, 1%, and 0% trays are borderline because the 1.4, 1.75, and 2.2 μm features exist, but do not fit the library spectrum well. (d) The gypsum 45-75 μm Mars tray, with the percentage gypsum in each tray labeled. (e) The average spectrum of each individual tray, with the color scheme following that of (a-c). Lines are at 1.45, 1.75, 2.22, and 2.42 μm . (f) The continuum removed average spectrum of each individual tray with the same color scheme as (a-c) and same lines as (e).

Nontronite (125+ μm) and Mars Global Simulant 1 Mixtures

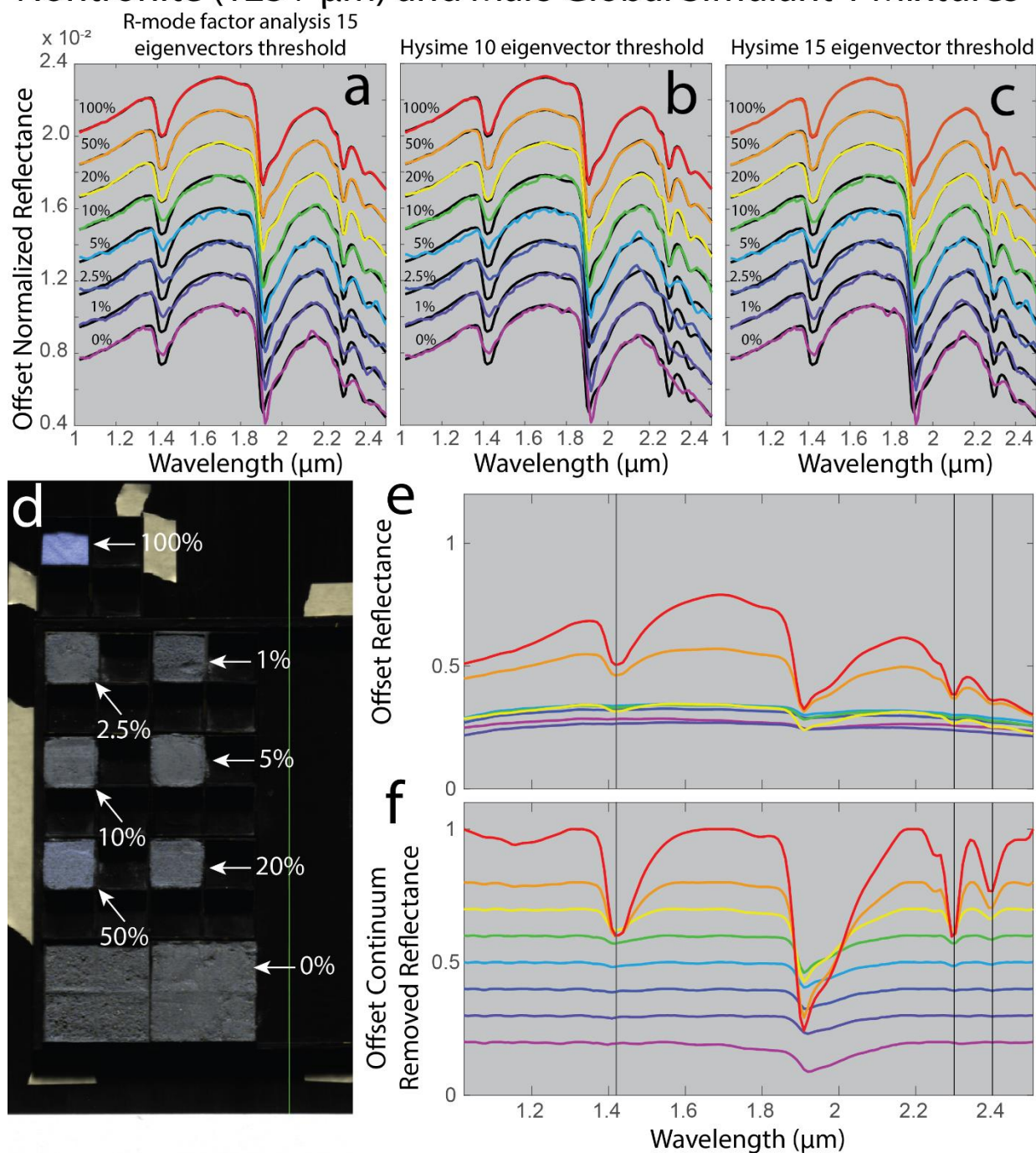


Figure S4 | Results from 15 eigenvector R-mode FA, 15 eigenvector HySime FA, and 10 eigenvector HySime FA to nontronite 125+ μm Mars tray. (a) 15 eigenvector R-mode FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4 and 2.3 μm are fit well, as is the 2.4 μm feature in some cases. Fits to the 2.5%, 1%, and 0% trays are borderline because the 1.4 and 2.3 μm features exist, but the 2.3 μm feature does the library spectrum well. (b) 10 eigenvector HySime FA/TT results for each

individual tray. Fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4 and 2.3 μm are fit well, as is the 2.4 μm feature in some cases. Fits to the 2.5%, 1%, and 0% trays are bad because 2.3 μm feature does not exist. (c) 15 eigenvector HySime FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4 and 2.3 μm are fit well, as is the 2.4 μm feature in some cases. Fits to the 2.5%, 1%, and 0% trays are borderline because the 1.4 and 2.3 μm features exist, but the 2.3 μm feature does the library spectrum well. (d) The nontronite Mars tray, with the percentage nontronite in each tray labeled. (e) The average spectrum of each individual tray, with the color scheme following that of (a-c). Lines are at 1.42, 2.3, and 2.4 μm . (f) The continuum removed average spectrum of each individual tray with the same color scheme as (a-c) and same lines as (e).

Montmorillonite (125+ μm) and Mars Global Simulant 1 Mixtures

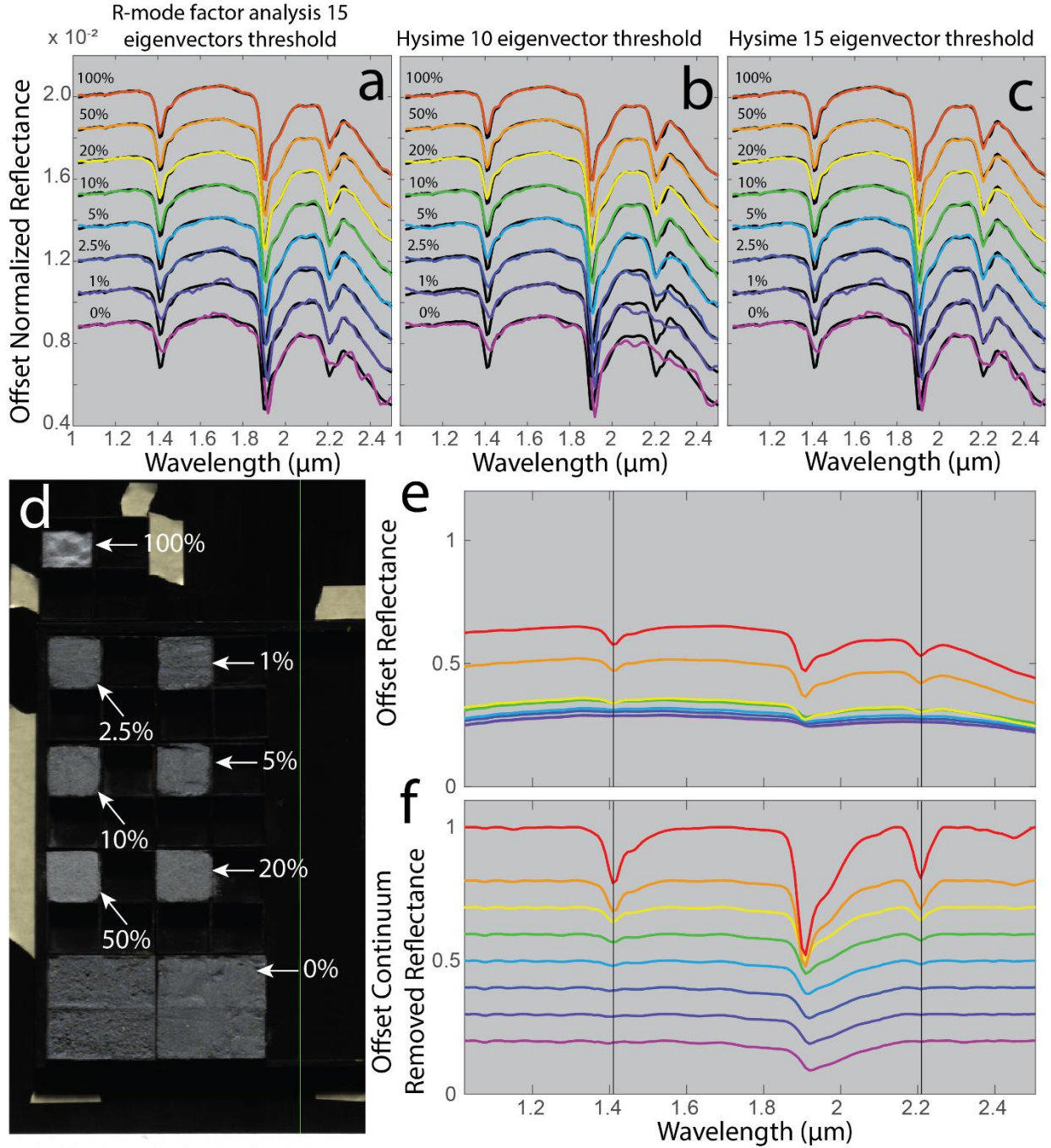


Figure S5 | Results from 15 eigenvector R-mode FA, 15 eigenvector HySime FA, and 10 eigenvector HySime FA to montmorillonite 125+ μm Mars tray. (a) 15 eigenvector R-mode FA/TT results for each individual tray. Fits for all trays are good because the shape of the 1.4 and 2.2 μm absorptions are fit well. (b) 10 eigenvector HySime FA/TT results for each individual tray. Fits for the 100%, 50%, 20%, 10%, and 5% trays are good because the shape of the 1.4 and 2.3 μm are fit well, as is the 2.4 μm feature in some cases. Fits to the 2.5%, 1%, and 0% trays are

bad because 2.2 μm feature does not exist. (c) 15 eigenvector HySime FA/TT results for each individual tray. Fits for all trays are good because the shape of the 1.4 and 2.2 μm absorptions are fit well. (d) The montmorillonite Mars tray, with the percentage montmorillonite in each tray labeled. (e) The average spectrum of each individual tray, with the color scheme following that of (a-c). Lines are at 1.41 and 2.21 μm . (f) The continuum removed average spectrum of each individual tray with the same color scheme as (a-c) and same lines as (e).

Gypsum 45-75 μm 10 eigenvector Hysime DAFA/TT

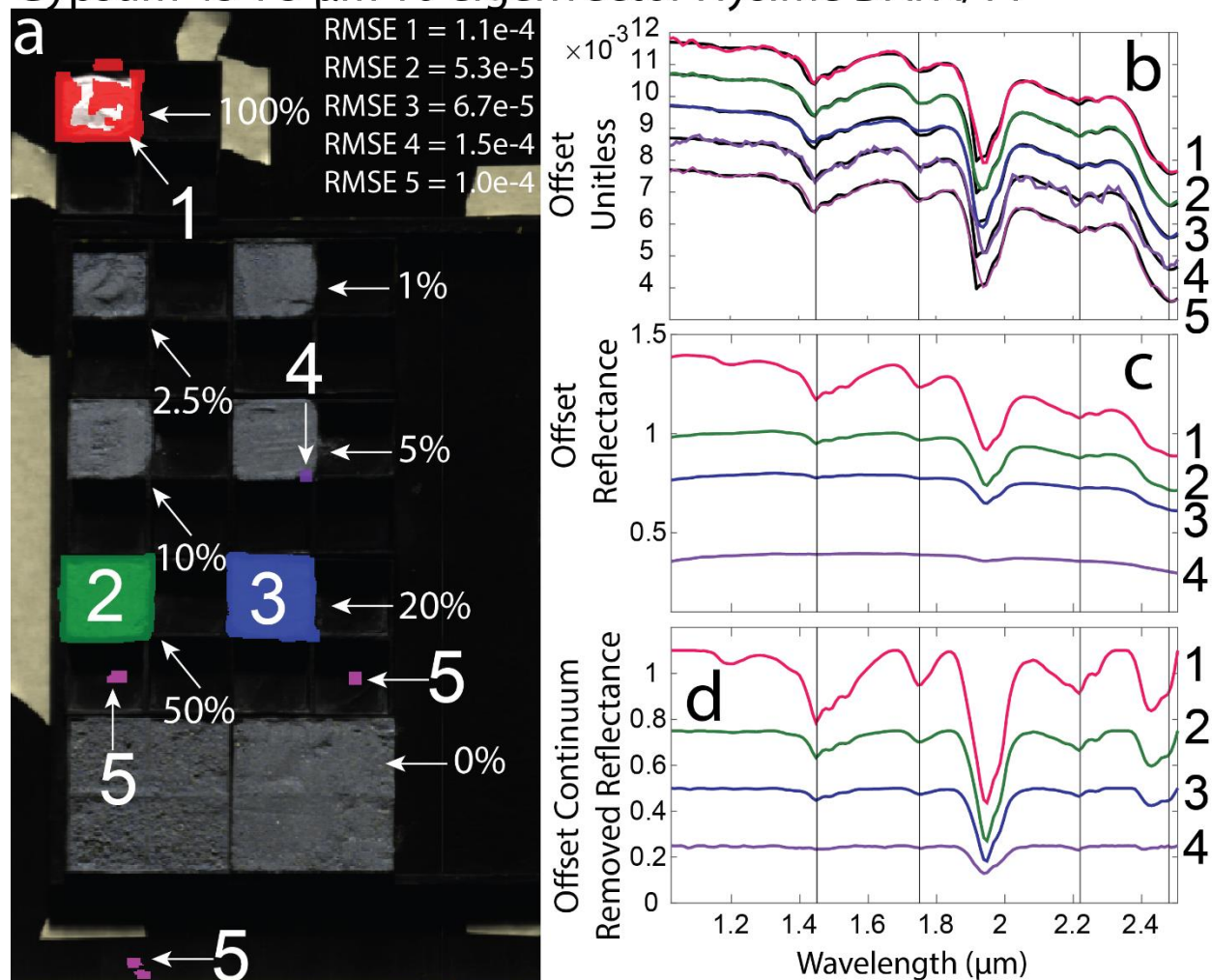


Figure S6 | 10 eigenvector HySime DAFA/TT analysis of gypsum 45-75 μm tray. (a) DAFA/TT results for gypsum 45-75 μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. The spectra from cluster 5

are shown in Fig. S7, and illustrate that a grain of gypsum was dropped on the translation table and empty tray sections.

Gypsum 45-75 μm 10
eigenvector Hysime
DAFA/TT false positive
determination test

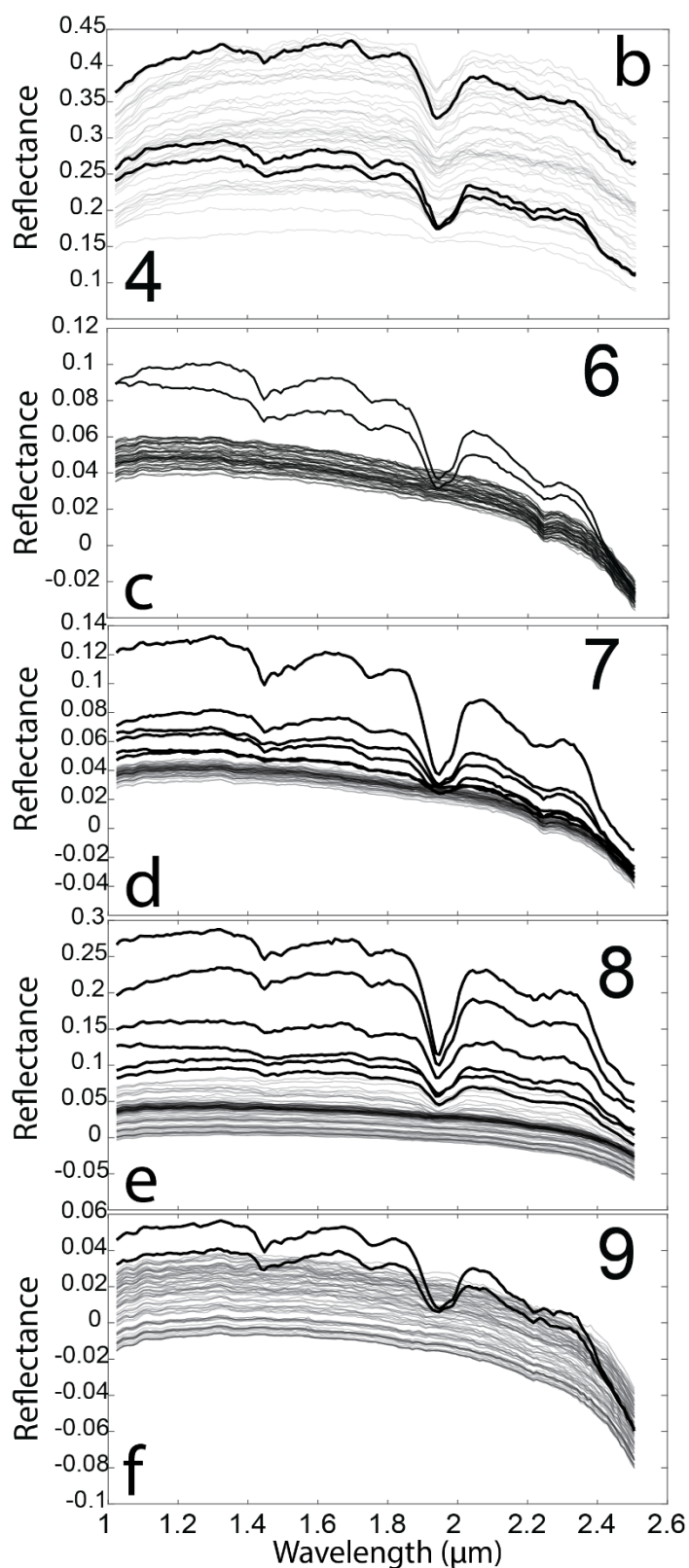
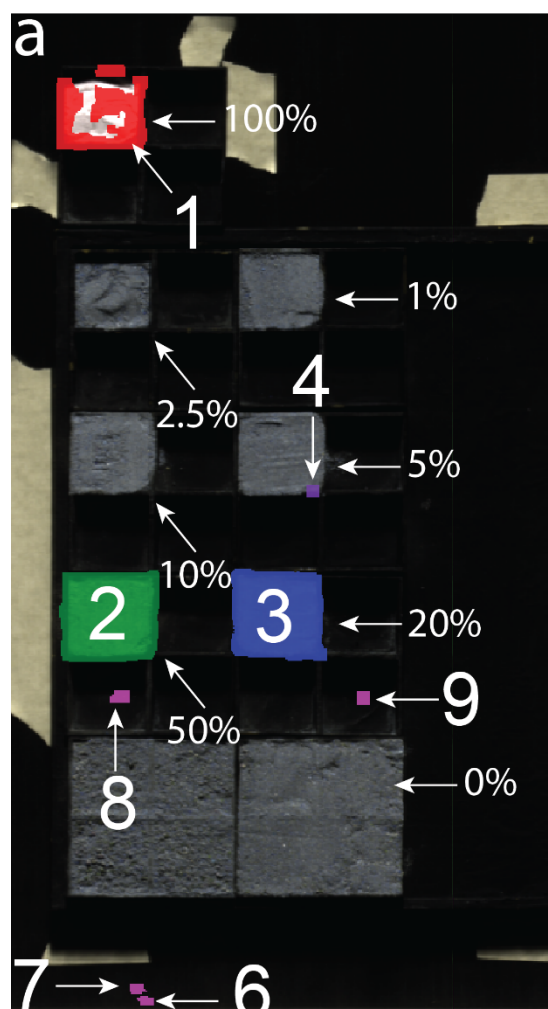


Figure S7 | Analysis of possible false positive detection clusters in gypsum 45-75 μm tray detected via 10 eigenvector HySime DAFA/TT analysis. (a) Gypsum 45-75 μm tray 10 eigenvector HySime DAFA/TT analysis results. (b) All spectra from cluster 4, with spectra containing diagnostic absorptions consistent with gypsum highlighted as thicker lines. (c) All spectra from cluster 6, with spectra containing diagnostic absorptions consistent with gypsum highlighted as thicker lines. (d) All spectra from cluster 7, with spectra containing diagnostic absorptions consistent with gypsum highlighted as thicker lines. (e) All spectra from cluster 8, with spectra containing diagnostic absorptions consistent with gypsum highlighted as thicker lines. (f) All spectra from cluster 9, with spectra containing diagnostic absorptions consistent with gypsum highlighted as thicker lines.

Calcite 45-75 μm 10 eigenvector Hysime DAFA/TT

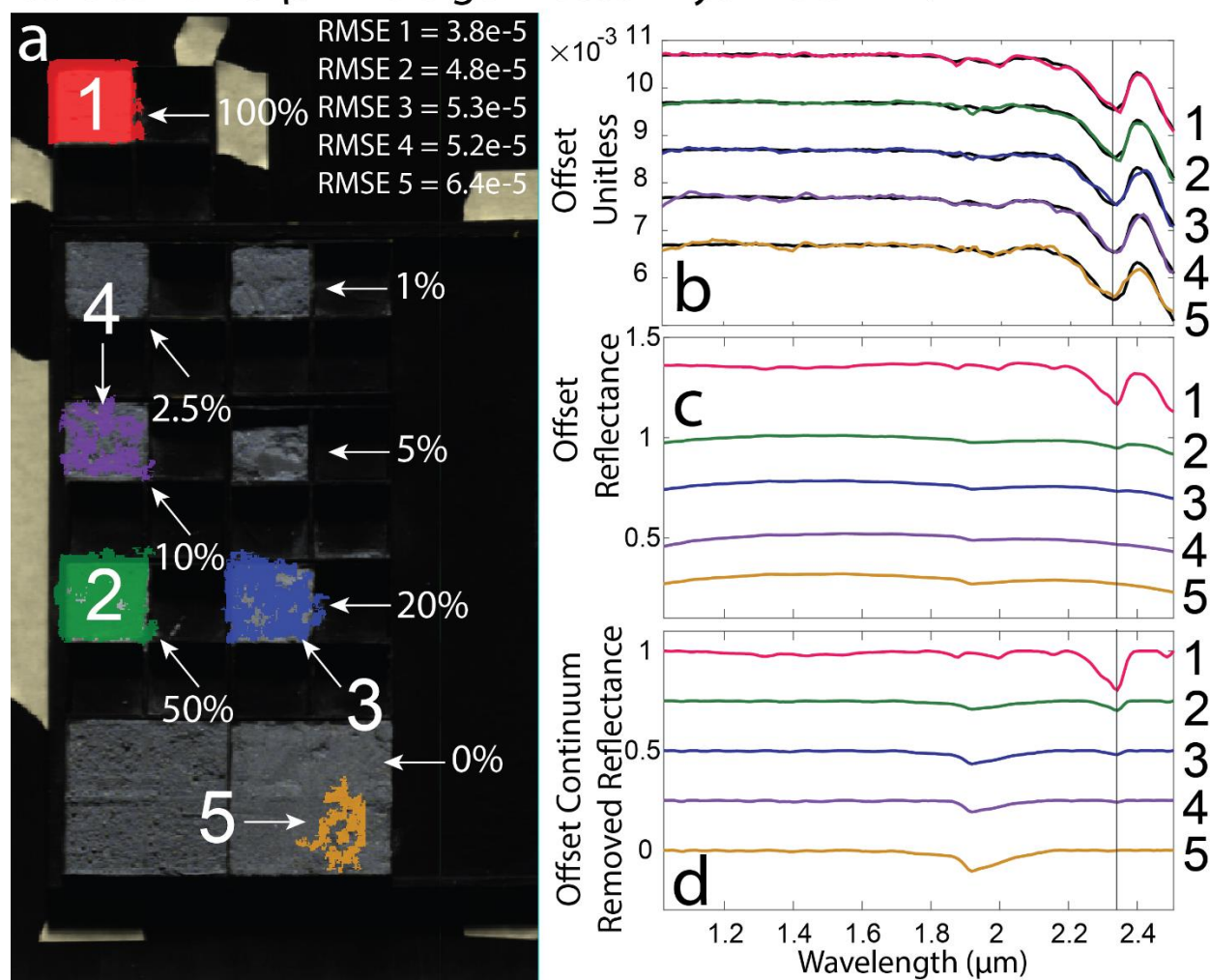


Figure S8 | 10 eigenvector HySime DAFA/TT analysis of calcite 45-75 μm tray. (a) DAFA/TT results for calcite 45-75 μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits

for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. The spectra from cluster 4 are shown in Fig. S9, and illustrate that individual pixel spectra of calcite exist within cluster 4. The line is at $2.34\ \mu\text{m}$.

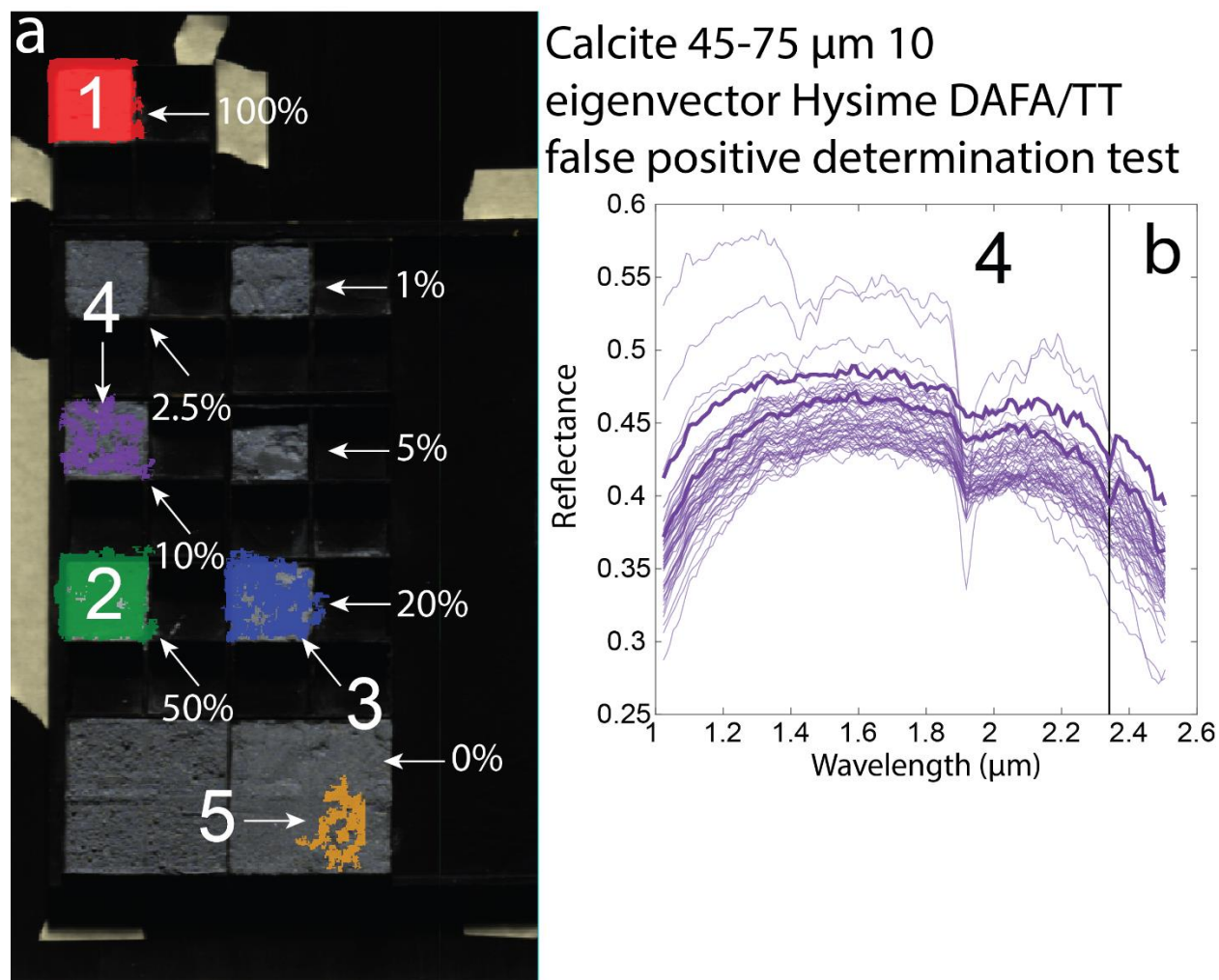


Figure S9 | Analysis of possible false positive detection clusters in calcite 45-75 μm tray detected via 10 eigenvector HySime DAFA/TT analysis. (a) Calcite 45-75 μm tray 10 eigenvector HySime DAFA/TT analysis results. (b) All spectra from cluster 4, with spectra containing diagnostic absorptions consistent with calcite highlighted as thicker lines. The line is at $2.34\ \mu\text{m}$.

Nontronite 125+ μm 10 eigenvector Hysime DAFA/TT

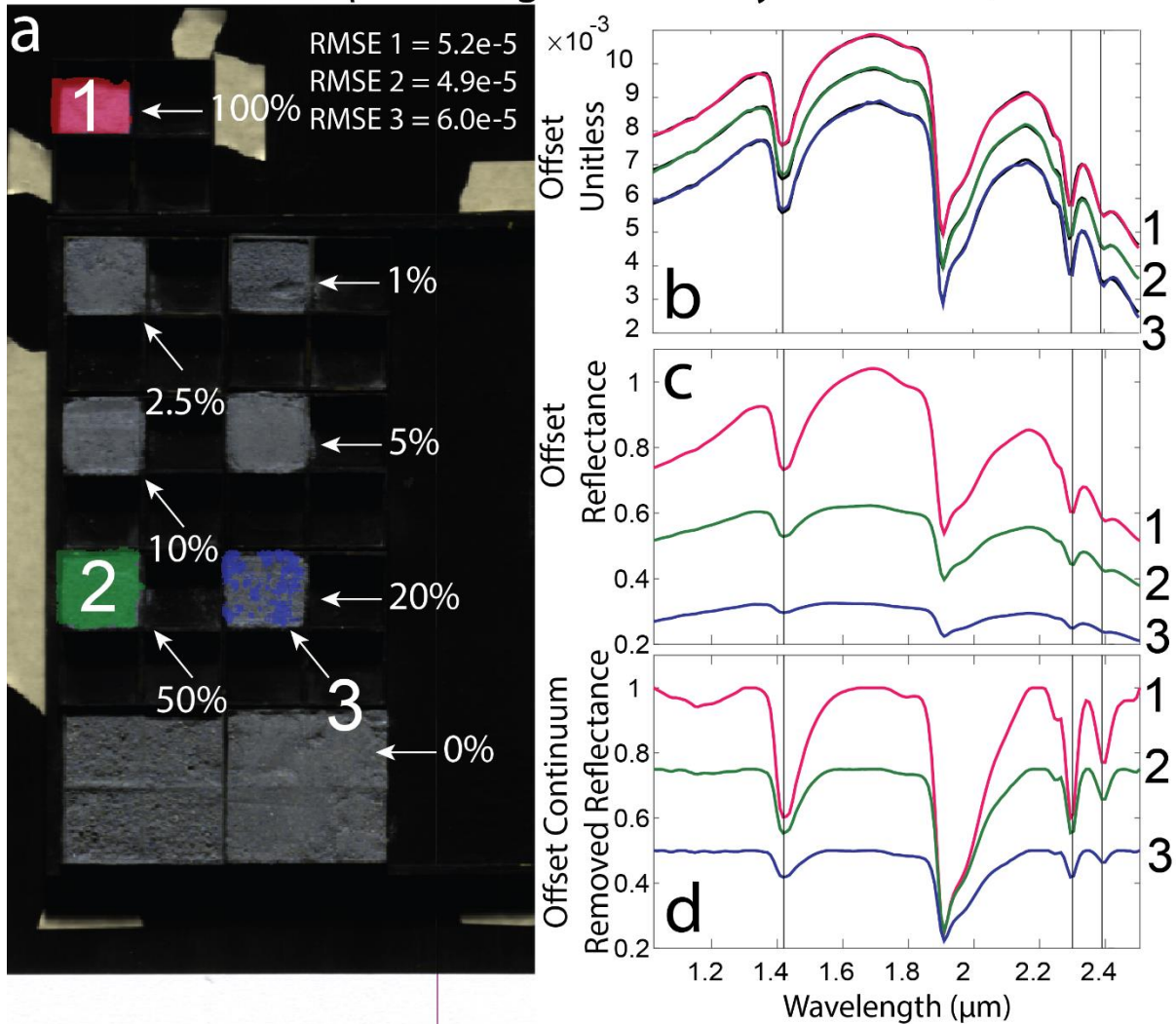


Figure S10 | 10 eigenvector HySime DAFA/TT analysis of nontronite 125+ μm tray. (a) DAFA/TT results for nontronite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.42, 2.3, and 2.4 μm .

Montmorillonite 125+ μm 10 eigenvector Hysime DAFA/TT

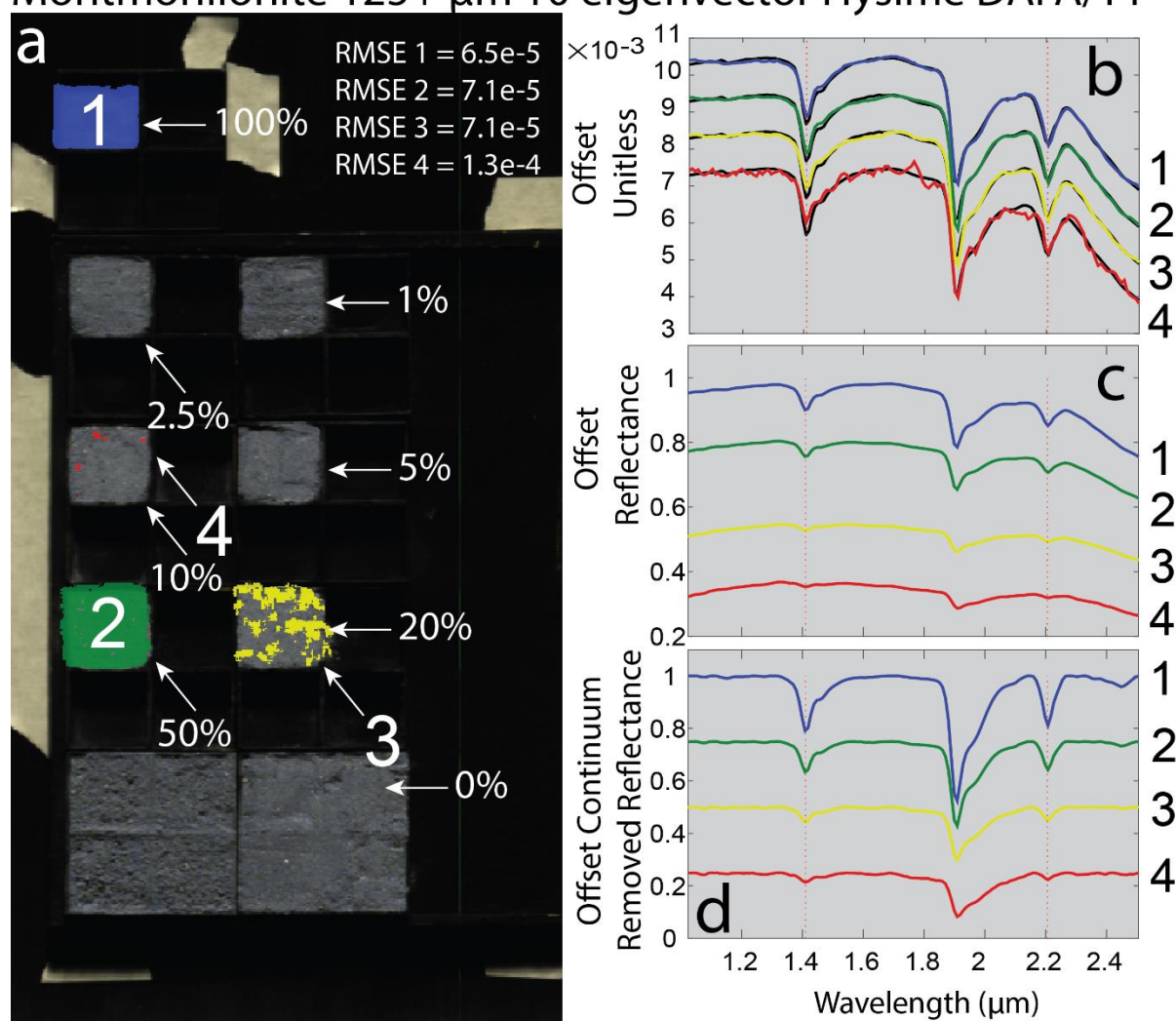


Figure S11 | 10 eigenvector HySime DAFA/TT analysis of montmorillonite 125+ μm tray. (a) DAFA/TT results for montmorillonite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.41 and 2.21 μm .

Kaolinite 125+ μm 10 eigenvector Hysime DAFA/TT

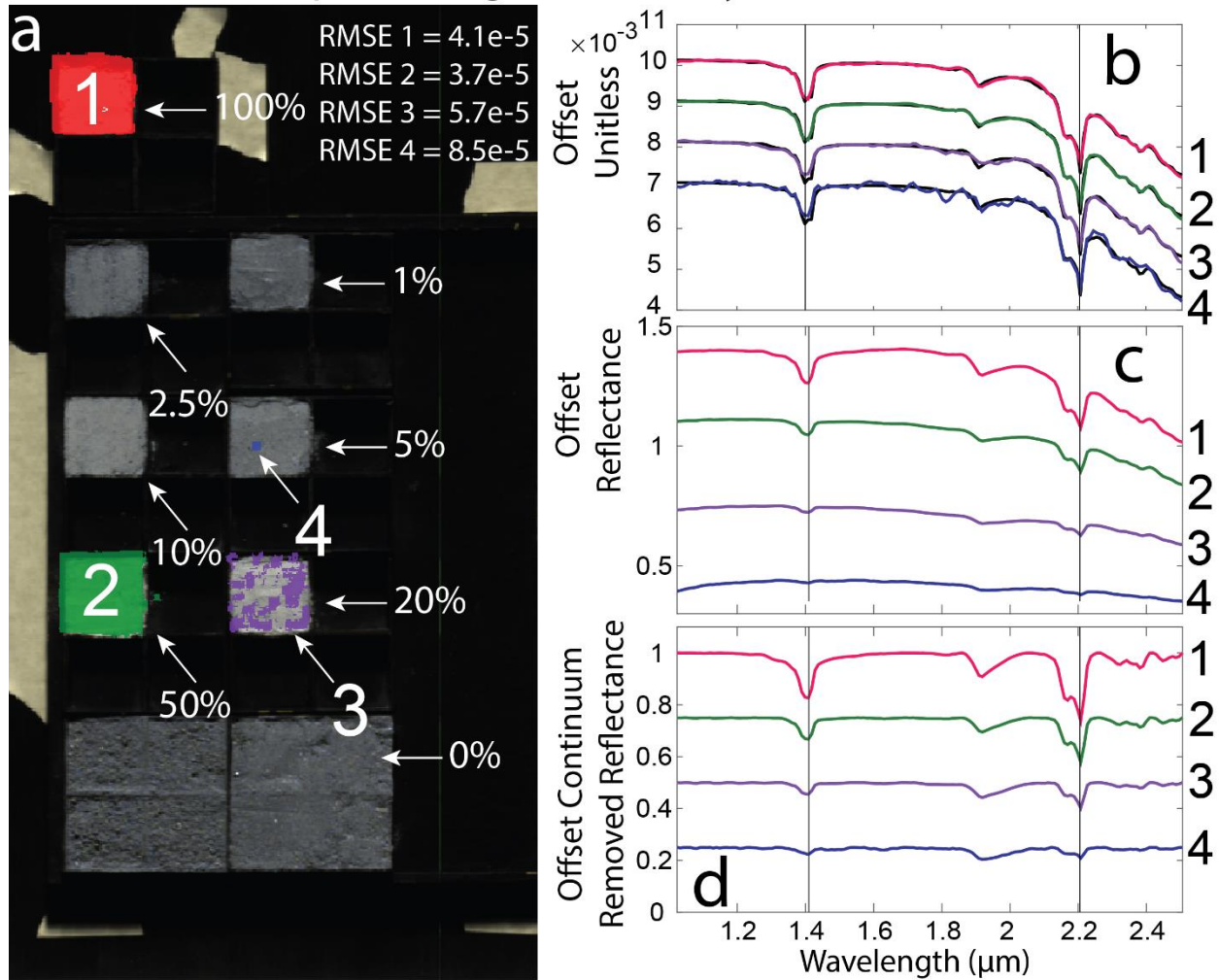


Figure S12 | 10 eigenvector HySime DAFA/TT analysis of kaolinite 125+ μm tray. (a) DAFA/TT results for kaolinite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.4 and 2.21 μm .

Gypsum 45-75 μm 15 eigenvector Hysime DAFA/TT

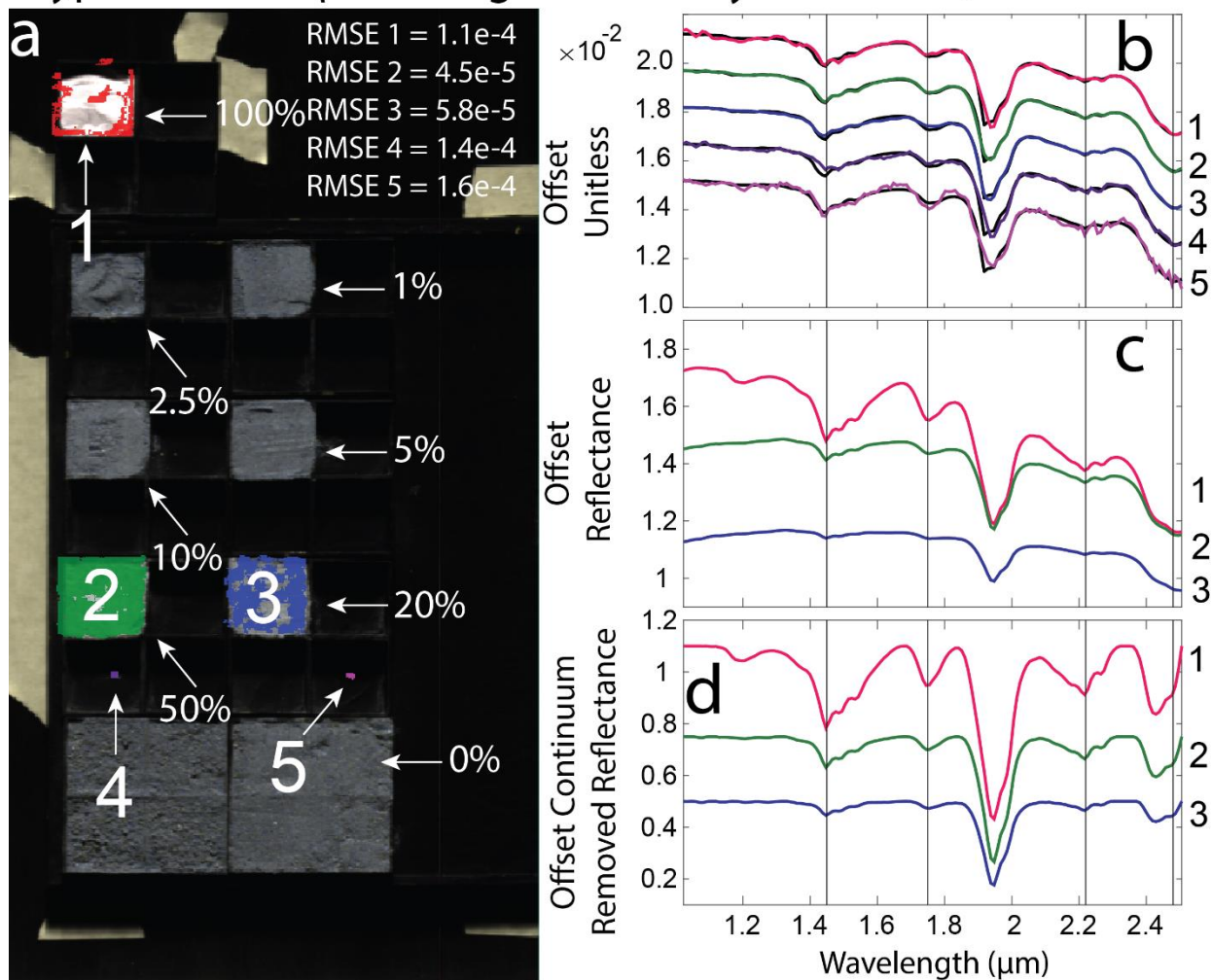


Figure S13 | 15 eigenvector HySime DAFA/TT analysis of gypsum 45-75 μm tray. (a) DAFA/TT results for gypsum 45-75 μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure.

Nontronite 125+ μm 15 eigenvector Hysime DAFA/TT

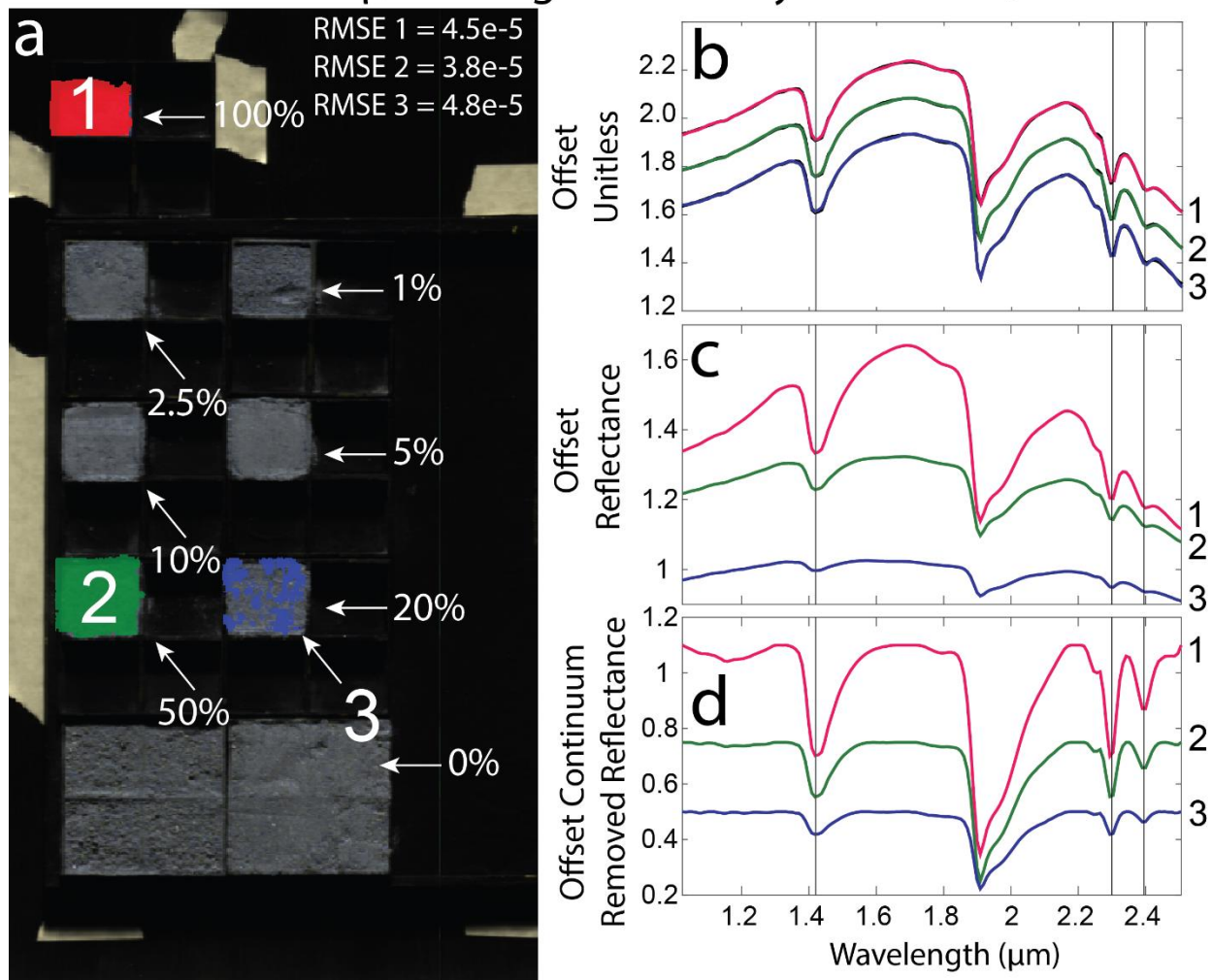


Figure S14 | 15 eigenvector HySime DAFA/TT analysis of nontronite 125+ μm tray. (a) DAFA/TT results for nontronite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.42, 2.3, and 2.4 μm .

Montmorillonite 125+ μm 15 eigenvector Hysime DAFA/TT

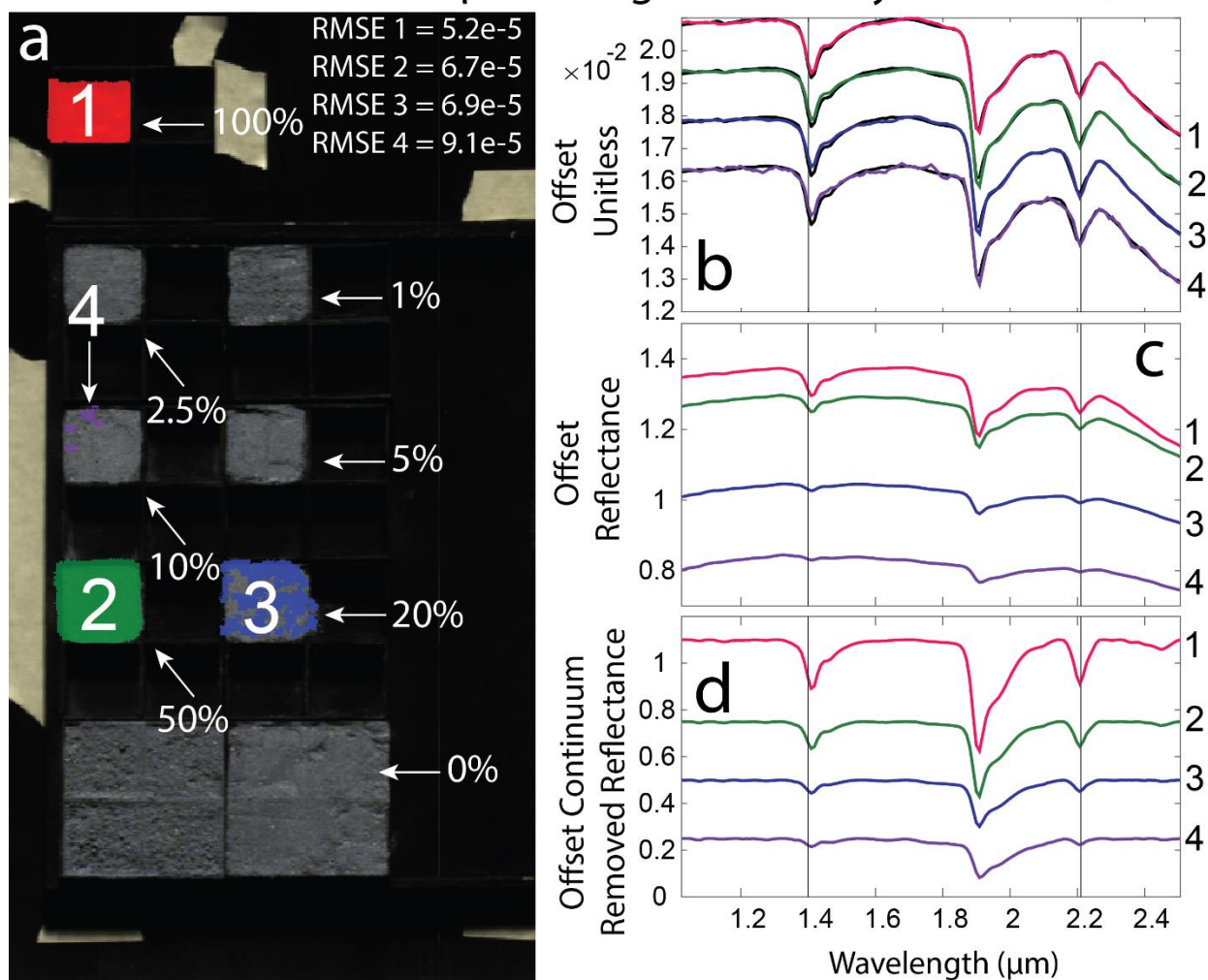


Figure S15 | 15 eigenvector HySime DAFA/TT analysis of montmorillonite 125+ μm tray. (a) DAFA/TT results for montmorillonite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.41 and 2.21 μm .

Calcite 125+ μm 15 eigenvector Hysime DAFA/TT

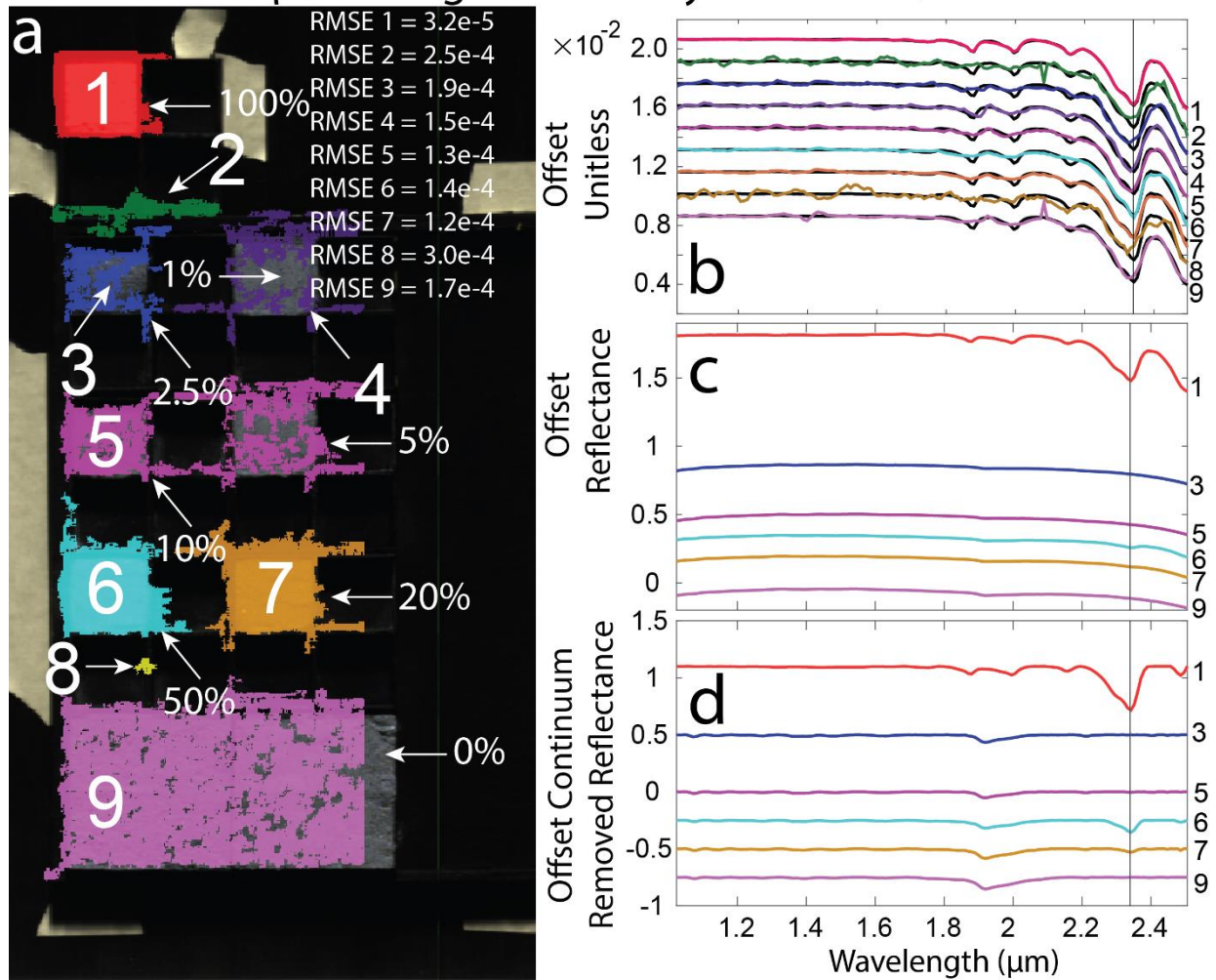


Figure S16 | 15 eigenvector HySime DAFA/TT analysis of calcite 125+ μm tray. (a) DAFA/TT results for calcite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. The line is at 2.34 μm .

Calcite 125+ μm 15 eigenvector R-mode DAFA/TT

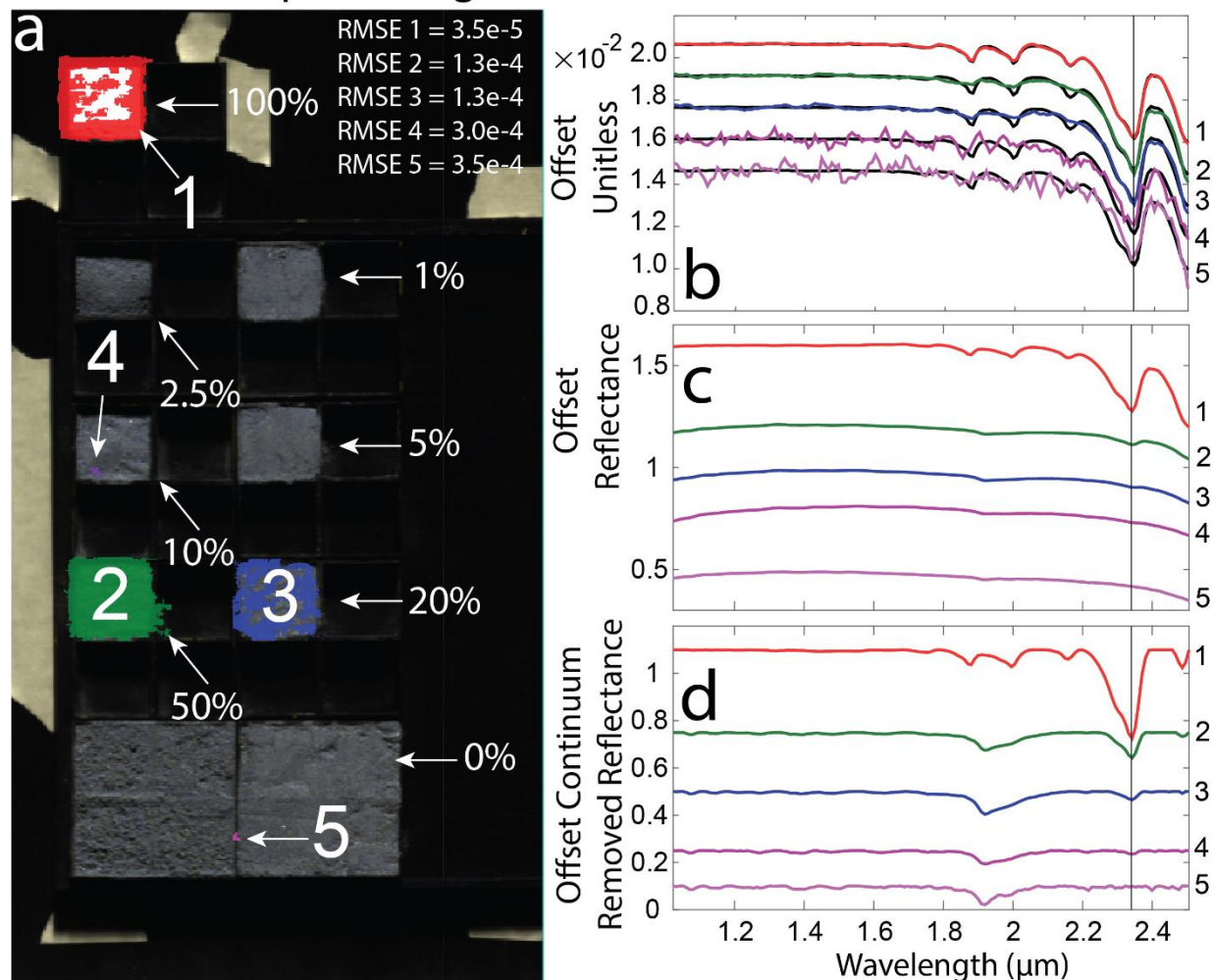


Figure S17 | 15 eigenvector R-mode DAFA/TT analysis of calcite 125+ μm tray. (a) DAFA/TT results for calcite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. The line is at 2.34 μm .

Gypsum 45-75 μm 15 eigenvector R-mode DAFA/TT

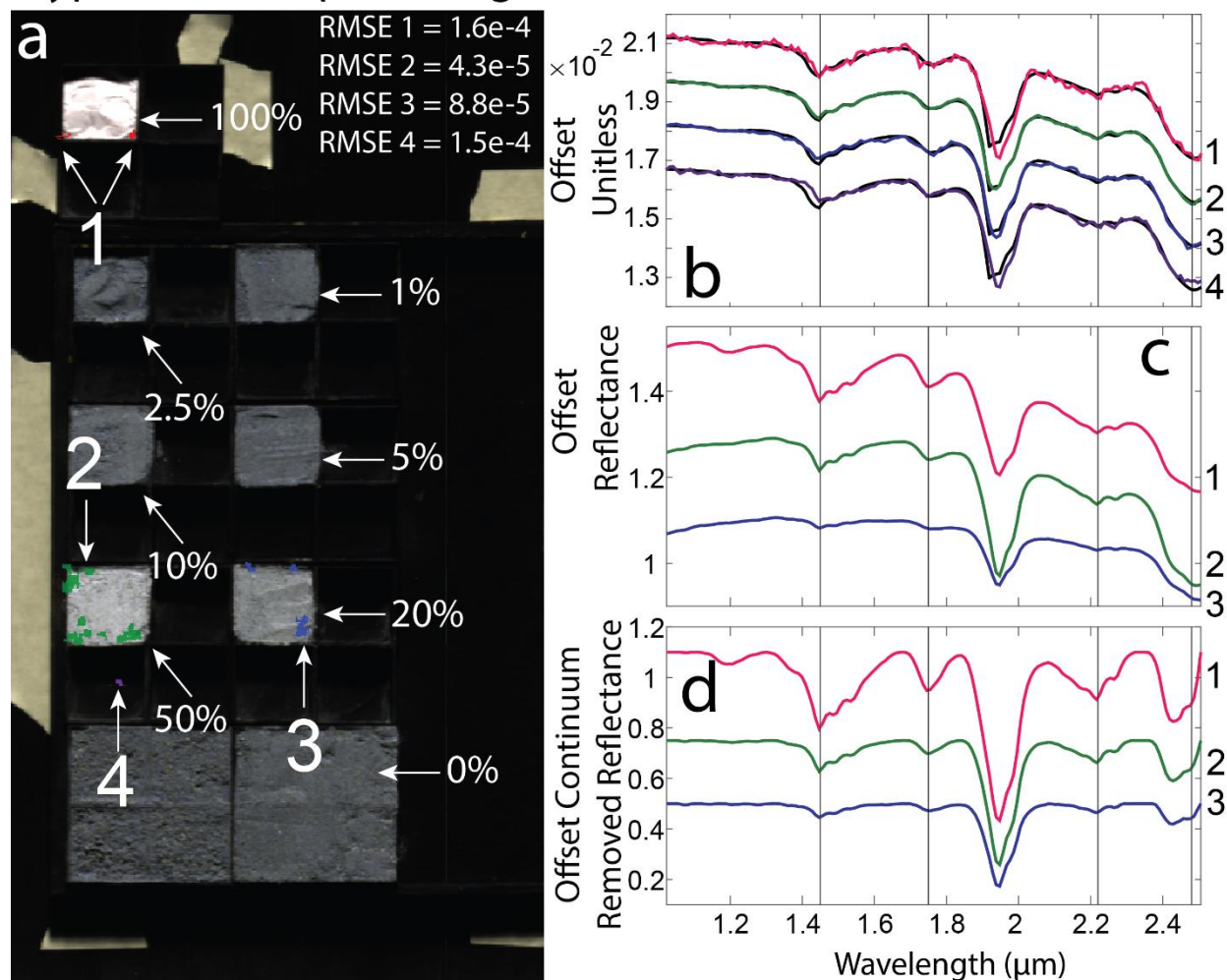


Figure S18 | 15 eigenvector R-mode DAFA/TT analysis of gypsum 45-75 μm tray. (a) DAFA/TT results for gypsum 45-75 μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure.

Kaolinite 125+ μm 15 eigenvector R-mode DAFA/TT

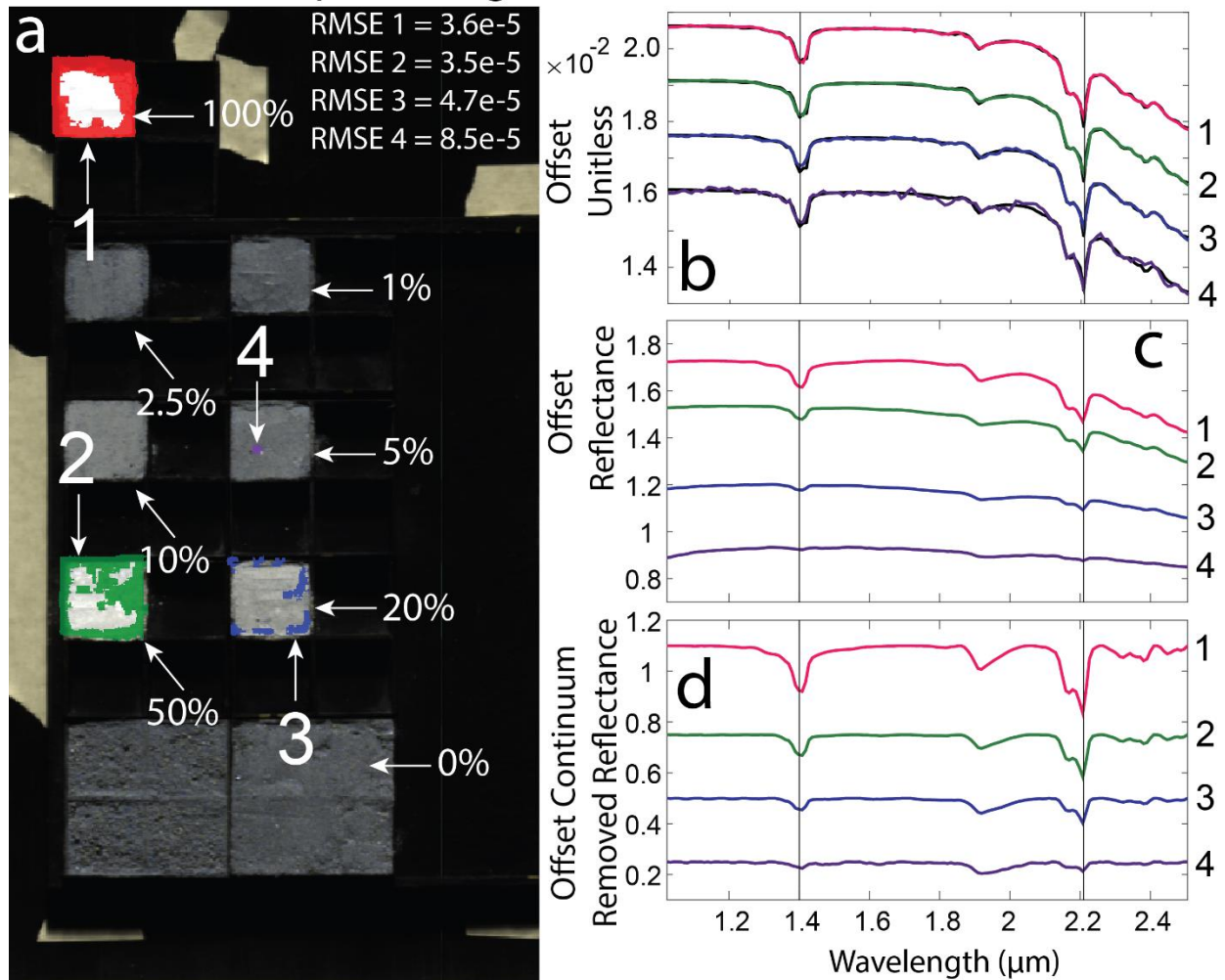


Figure S19 | 15 eigenvector R-mode DAFA/TT analysis of kaolinite 125+ μm tray. (a) DAFA/TT results for kaolinite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.4 and 2.21 μm .

Montmorillonite 125+ μm 15 eigenvector R-mode DAFA/TT

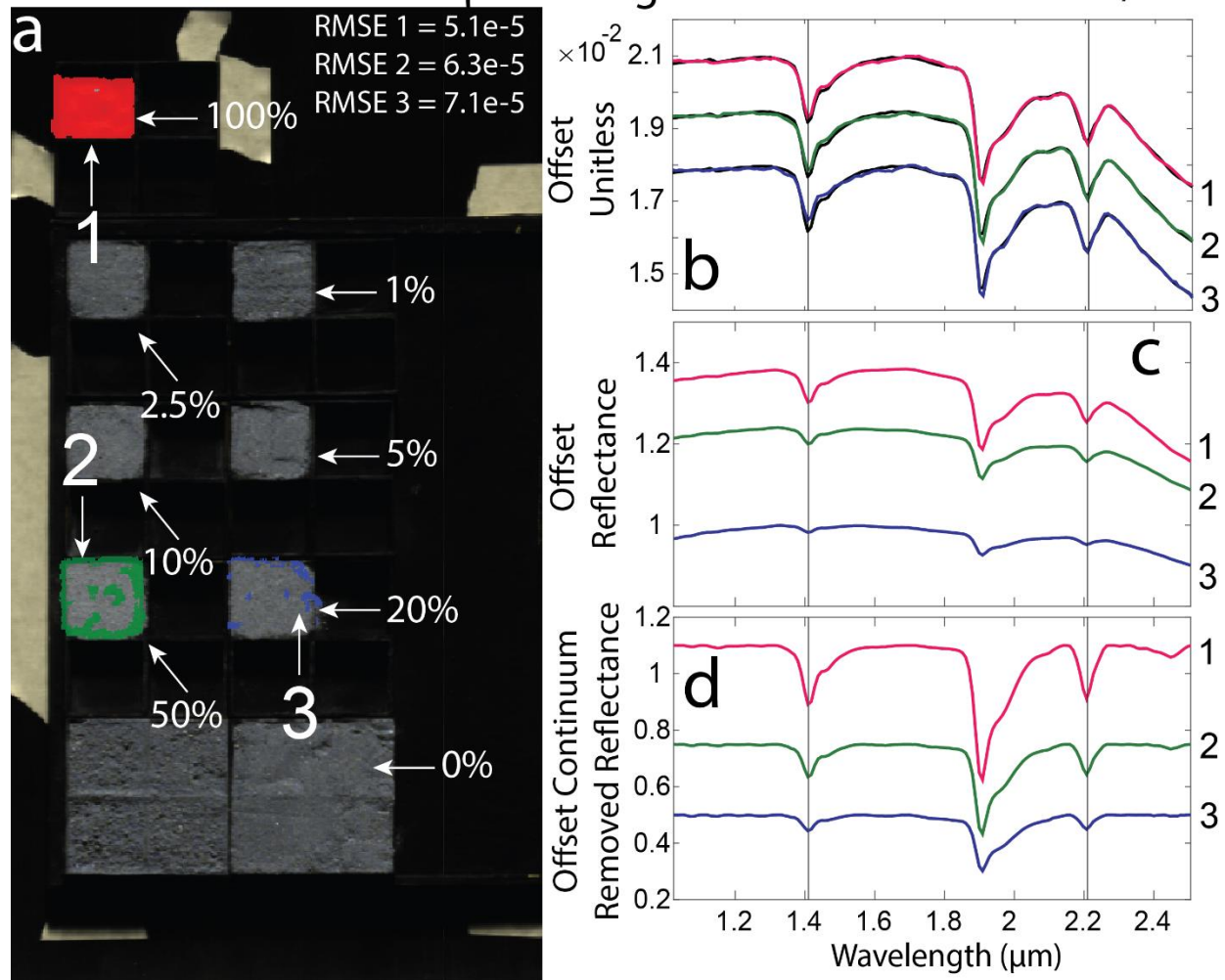


Figure S20 | 15 eigenvector R-mode DAFA/TT analysis of montmorillonite 125+ μm tray. (a) DAFA/TT results for montmorillonite 125+ μm Mars tray, where the colors are individual DAFA/TT clusters. (b) Fits for each individual DAFA/TT cluster shown in (a). (c) Average spectra of each individual DAFA/TT cluster. (d) Continuum removed average spectra of each individual DAFA/TT cluster. The colors and labelling numbers correspond throughout the figure. Lines are at 1.41 and 2.21 μm .

Supplementary Tables

	Gypsum		Calcite		Nontronite	Montmorillonite	Kaolinite
Grain size range	>125 μm	45-75 μm	>125 μm	45-75 μm	>125 μm	>125 μm	>125 μm
Mixture 1 volume abundance	50.0%	50.0%	50.0%	50.0%	50.0%	50.0%	50.0%
Mixture 2 volume abundance	20.0%	20.0%	20.0%	20.0%	20.0%	20.0%	20.0%
Mixture 3 volume abundance	10.0%	10.0%	10.0%	10.0%	10.0%	10.0%	10.0%
Mixture 4 volume abundance	5.0%	5.0%	5.0%	5.0%	5.0%	5.0%	5.0%
Mixture 5 volume abundance	2.5%	2.5%	2.5%	2.5%	2.5%	2.5%	2.5%
Mixture 6 volume abundance	1.0%	1.0%	1.0%	1.0%	1.0%	1.0%	1.0%

Supplementary Table 1 | Volume abundances and grain sizes of secondary minerals mixed

with MGS-1. The remainder of the mixtures was composed of MGS-1. The imaged tray also contained pure secondary mineral and MGS-1 endmembers.

CHAPTER 4: Orbital identification of hydrated silica in Jezero crater, Mars

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Abstract

Silica has the highest demonstrated potential of any phase to preserve microfossils on Earth and therefore may host potential biosignatures on Mars. We detected hydrated silica in Jezero crater, the landing site of NASA's Mars 2020 rover mission, by applying Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT) to images from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM). Hydrated silica detections with DAFA/TT were verified using commonly accepted CRISM analysis methods. The morphology of geologic units associated with silica were characterized with high resolution imaging. Several hypotheses are presented for the formation environment of hydrated silica. All are testable via *in-situ* investigation. We assess the likelihood of silica to preserve biosignatures in these different scenarios based on habitability considerations and biosignature preservation in Earth analog environments and materials. Also reported are possible detections of hydrated silica in the Nili Fossae basement and olivine-rich units, as well as Al-phyllsilicate within Jezero crater.

1.0 Introduction

Opaline silica (amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$) was first detected on Mars using the Miniature-Thermal Emission Spectrometer (Mini-TES; Christensen et al., 2003) onboard both Mars Exploration Rovers (MERs) in Meridiani Planum (Glotch et al., 2006) and Columbia Hills (Squyres et al., 2008). These detections confirmed theoretical geochemical arguments that sedimentary silica would be a common alteration product where water-rock interaction had occurred in Mars' dominantly basaltic primary crust (McLennan, 2003). More widespread outcrops of hydrated silica were identified in a variety of ancient aqueous environments using

hyperspectral visible and shortwave-infrared images from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM; Murchie et al., 2007) (Bishop et al., 2008; Ehlmann et al., 2009; Fraeman et al., 2016; Milliken et al., 2008; Murchie et al., 2007; Mustard et al., 2008; Skok et al., 2010; Smith & Bandfield, 2012; Sun & Milliken, 2015, 2018). High silica occurrences were identified with thermal infrared emissivity spectra from the Thermal Emission Spectrometer (TES; Christensen et al., 2001) and the Thermal Emission Imaging System (THEMIS; Christensen et al., 2004) (Bandfield, 2008; Bandfield et al., 2013). Both detrital and authigenic cementing silica (Morris et al., 2016) as well as silica enrichments formed by later infiltration of both alkaline and acidic fluids (Yen et al., 2017) have also been detected in Gale crater by the Mars Science Laboratory (MSL).

Formation hypotheses for silica detected on Mars include sedimentary deposition (detrital), direct precipitation (authigenic), and leaching of basaltic protolith (cation removal) (Squyres et al., 2008; Bishop et al., 2008; Milliken et al., 2008; Ruff et al., 2011; Skok et al., 2010; Yen et al., 2017). On Earth, silica forms in a wide range of settings including hot springs in both neutral-alkaline and acidic hydrothermal systems (e.g. Campbell et al., 2015), volcano-fumarolic settings (e.g. Seelos et al., 2010), marine environments (e.g. Bohrmann et al., 1994), and lacustrine settings (e.g. Eugster, 1969; Peterson & Borch, 1965). Secondary silica initially precipitates as opal-A—an amorphous phase—and becomes more crystalline upon further water-rock interaction (e.g. Kastner & Gieskes, 1983). Sun & Milliken (2018) showed that opal-A on Mars tends to be associated with bedrock while more crystalline silica exists primarily in unconsolidated sediments. The prevalence of opal-A on Mars has been interpreted to imply limited water-rock interaction throughout the planet's history (Tosca & Knoll, 2009).

Siliceous sinter (deposit of silica surrounding a hot spring or geyser) and chert (sedimentary microcrystalline silica) all have high potential to preserve biosignatures relative to other mineral phases on Earth. This is because silicification of organic matter is caused by the bonding of silicic acid to organic cell walls and/or envelopes, causing both organic matter and morphologic biosignatures to be preserved (e.g. Knoll et al., 1985; McMahon et al., 2018). The silicification process is insensitive to variations in cell type, substrate type, pH, and salinity (McMahon et al., 2018; Orange et al., 2009, 2013, 2014). Permineralized cells, organic carbon (which may or may not appear morphologically similar to cells), molecular fossils (e.g. lipids), and microbially induced sedimentary structures are preserved exceptionally well in these mineral phases (Farmer & Des Marais, 1999; McMahon et al., 2018). Silica's rigidity, impermeability, and resistance to chemical weathering allows preserved microfossils and other biosignatures to remain relatively unaffected by external environmental conditions (McMahon et al., 2018). Determining where silica exists on the Martian surface, as well as the habitability of its various formation environments, is thus key to maximizing chances of detecting Martian biosignatures.

The Nili Fossae region is one of the most mineralogically diverse regions of Mars (Mustard et al., 2008; Ehlmann et al., 2009) and hosts a well-defined stratigraphy, including—in order from bottom to top—a Fe/Mg-phyllosilicate and Al-phyllosilicate-bearing Noachian brecciated basement unit, an olivine-enriched unit variably altered to carbonate, an olivine-poor mafic capping unit, and a locally-exposed, layered sulfate-bearing unit (Ehlmann & Mustard, 2012). Jezero crater, located within the Nili Fossae region, contains some of the best preserved deltaic outcrops on Mars (Fassett & Head, 2005; Goudge et al., 2017) and once

hosted an open basin lake fed by two inlet valleys from the north and west and drained through an outlet valley to the east (Goudge et al., 2015) (Fig. 1c). Two deltas exist within the crater, one at each inlet channel entrance (Fassett & Head, 2005). Fassett & Head (2008) derived an age of 3.8 ± 0.1 Gyr for the Jezero valley system using buffered crater counting and the Neukum isochron system (Neukum & Hiller, 1981). This implies that fluvial activity around Jezero likely occurred during the main phase of Martian valley network formation. As Jezero crater is the landing site of NASA's Mars 2020 rover mission, its imminent *in situ* investigation will enable characterization of the physical and chemical processes that occurred during the main phase of Martian valley network formation in the Noachian.

Goudge et al., (2015, 2017) generated a geomorphic map of Jezero crater and its watershed and further constrained the location of carbonate- and smectite-bearing rock units in the crater. The regionally widespread olivine-rich unit also exists within Jezero crater (Goudge et al., 2015; Kremer et al., 2019) and is no older than the ~ 3.96 Ga Isidis impact (Werner, 2008) and no younger than the Syrtis Major lavas that stratigraphically overlie it, which have been dated to ~ 3.6 Ga (Hiesinger & Head, 2004). Sedimentological evidence demonstrates the existence of an ancient lacustrine environment in Jezero crater (Fassett & Head, 2005; Schon et al., 2012; Goudge et al., 2017). The presence of carbonate in the Jezero deltas and surrounding Nili Fossae region may indicate neutral- to alkaline-pH water-rock interactions in the Jezero-hosted paleolake, the lake's watershed, and possibly the pre-paleolake crater environment, favoring the existence of potentially habitable environments in all of these settings (Ehlmann et al., 2008, 2009; Goudge et al., 2015). Ehlmann et al. (2008) assessed the biosignature preservation potential of deltaic smectite clays in Jezero crater, but

no study has rigorously evaluated CRISM data for the presence or absence of silica in Jezero crater or assessed its potential to host biosignatures.

2.0 Methods

Hydrated silica has near-infrared (NIR) and shortwave-IR (SWIR) absorption features at 1.37-1.46 μm (OH stretching overtones from Si-OH and H₂O), 1.91-1.96 μm (H₂O combination bending and stretching mode), and 2.21-2.26 μm (OH stretching-Si-OH bending combination mode) (Burneau et al., 1990; Sun & Milliken, 2018) (Figs. S3-S6). Most hydrated minerals have absorptions around 1.4 μm and 1.9 μm , but unique to hydrated silica is the presence, and broad shape of, the 2.21-2.26 μm absorption feature (e.g. Rice et al., 2013). An Al-OH vibrational absorption also exists near 2.2 μm but can be differentiated from the Si-OH absorption based on its shape, where the Al-OH absorption is significantly narrower than the Si-OH absorption (Fig. 1e) (Stolper, 1982; Milliken et al., 2008). Sun & Milliken (2018) showed that the band minimum position of the 1.4 μm feature shifts to shorter wavelengths in more amorphous silica (1.37-1.42 μm) and shifts to longer wavelengths in more crystalline silica (1.41-1.44 μm). We use the presence of a 2.2 μm absorption feature with a broad shoulder towards longer wavelengths, accompanied by 1.4 μm and 1.9 μm absorptions, as evidence for the presence of Si-OH bonds in CRISM data, thus indicating the presence of hydrated silica where these spectral features exist.

We analyzed CRISM TRR3 (version 3 of CRISM processing pipeline) images over Jezero crater and the surrounding Nili Fossae region that are reduced and calibrated to I/F (radiance observed by CRISM/solar radiance at Mars) using two different data processing methods. The

first processing method uses the CRISM Analysis Toolkit (CAT) v7.4 (Murchie et al., 2007) and applies standard volcano-scan atmospheric, photometric, and denoising corrections (McGuire et al., 2009). The second method applies scene-dependent atmospheric correction and denoising (Itoh & Parente, 2019). We analyzed the 1.0-2.6 μm spectral range of CRISM images FRT00005C5E, HRL000040FF, FRT000047A3, FRT00016A73, and FRT00003E12.

We used Dynamic Aperture Factor Analysis/Target Transformation (DAFA/TT) (Lin et al. 2018) to detect potential hydrated silica outcrops that were then validated using commonly applied CRISM data analysis methods of band parameter mapping and extraction of ratioed and unratioed I/F spectra. DAFA/TT, similar to previous applications of factor analysis and target transformation to CRISM data (Thomas & Bandfield, 2017; Amador et al., 2018), is capable of detecting phases present in low abundance and in complex convolutions. By spatially subsetting the CRISM data in an iterative manner, DAFA/TT is also capable of characterizing the spatial distribution of modeled minerals within a given image. Factor analysis was performed via the Hysime algorithm (Bioucas-Dias & Nascimento, 2008), which extracts the spectral endmembers that describe the signal subspace within a given set of pixels. It then performs target transformation via linear-least squares fitting of extracted signal subspace endmembers to a suite of library spectra for a variety of specific minerals (Malinowski, 1991; Bandfield et al., 2000; Glotch & Bandfield, 2006; Thomas & Bandfield, 2017; Amador et al., 2018). We perform target transformation for spectra in the 1.7-2.6 μm range in order to avoid the 1.6 μm region of CRISM, which is particularly noisy. If the target transformation fit falls below an empirically determined Root Mean Square Error (RMSE) threshold of 1.5×10^{-4} , we consider it a positive

detection. RMSE is defined as $\sqrt{\frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{n}}$ where n is the number of bands analyzed, $\hat{y}_i$ is the

normalized I/F of the library spectrum at band i , and y_i is the normalized I/F of the target transformation fit at band i . Normalization is performed by dividing the I/F value at each wavelength by the sum of I/F in all wavelengths from 1.7-2.6 μm , which mitigates spectral variability caused by albedo differences in CRISM images. We perform this RMSE calculation for spectra from 1.7-2.6 μm . We applied this process to clusters of ~ 50 CRISM pixels with different geometries that move across the scene, shifting the center of the cluster one pixel at a time, and then only accepted pixels with detections in all cluster geometries as true detections (Lin et al. 2018). We used ~ 50 hydrated silica library spectra acquired from the Keck/NASA Reflectance Experiment Laboratory (RELAB) database as the target spectra in our CRISM image analysis, as a way to represent the significant spectral variability of this phase. The number of eigenvectors used to generate each DAFA/TT fit to library spectra is usually ≤ 15 . The results of DAFA/TT analysis are maps used to highlight targets for subsequent investigation by commonly accepted spectral analysis methods, including band parameter mapping (e.g. Fig. S6) and manual inspection of individual I/F spectra. If unratioed and ratioed spectra from those DAFA/TT highlighted pixels show a 2.2 μm absorption with a broad shape towards longer wavelengths, as well as 1.4 and 1.9 μm absorptions, we deem this a robust detection.

We determined the geologic context for the positive detections of hydrated silica and associated minerals using images from the High Resolution Imaging Science Experiment (HiRISE; McEwen et al., 2007) with a spatial resolution of ~ 0.25 m/pixel. Atop the HiRISE images, we used manually generated tiepoints to coregister mineral detections from the CRISM DAFA/TT analysis. These mineral maps have a spatial resolution of ~ 18 m/pixel (Full-resolution Targeted; FRT) or ~ 32 m/pixel (Half-resolution Long; HRL). We also analyzed the topographic setting of

hydrated silica using HiRISE and Context Camera (CTX) (Malin et al., 2007) digital elevation maps (DEMs) produced using the Ames Stereo Pipeline (Shean et al., 2016; Beyer et al., 2018). Most HiRISE image mosaics and DEMs used in this study were generated by the Bruce Murray Lab for Planetary Visualization at the California Institute of Technology (Dickson et al. 2018).

We constrained the possible formation mechanisms for detected hydrated silica deposits by assessing their stratigraphic context and the morphological characteristics of associated rock units apparent in HiRISE images. We also used the minerals detected in association with hydrated silica to infer the geochemistry of alteration conditions that formed these silica deposits, provided that they were a product of water-rock interaction rather than primary volcanism. We base geochemical interpretations on laboratory and field studies of silica assemblage formation on Earth (e.g. Fialips et al., 2000; Streit et al., 2012; Falk & Kelemen, 2015). We also searched for exposures of hydrated silica in the olivine-rich and basement units in the greater Nili Fossae region to ascertain whether this assemblage is prevalent throughout this region of Mars.

3.0 Results

Both the DAFA/TT analysis (Fig. 1h) and inspection of individual I/F spectra (Figs. 1e, 2d, 2i, S2-S5) indicate the presence of hydrated silica near the western and northern Jezero deltas. These detections were also reported by Dundar et al. (2019) and Parente et al. (2019). The I/F spectra for both hydrated silica detections have broad 2.2 μm absorption features, as well as a weak 1.4 μm absorption feature and stronger 1.9 μm absorption feature with band minima positions consistent with hydrated silica (Sun & Milliken, 2018) (Figs. 1e, 2d, 2i, S2-S5). Both

detections of hydrated silica are likely associated with olivine and Fe/Mg-smectite based on the presence of accompanying broad 1 μm and narrow 2.3 μm absorption features (Figs. 1e, 2d, 2i, S3-S6) in both hydrated silica spectra. We also detected possible hydrated silica in the olivine-rich unit elsewhere in the Nili Fossae region, where it is associated with olivine, magnesite, and Fe/Mg-smectite (Fig. 3e-3g). This is based on the presence of a 2.2 μm shoulder accompanied by broad 1 μm , narrow 2.3 μm , narrow 2.39 μm , and narrow 2.5 μm absorption features (Fig. 3g). Additionally, hydrated silica is detected in the basement unit, the oldest unit in the exposed Nili Fossae stratigraphy (Bramble et al., 2017), based on the presence of a broad 2.2 μm absorption feature accompanied by 1.4 and 1.9 μm absorption features. This hydrated silica is associated with Al-phylosilicate (Fig. 3d) based on the presence of a narrow absorption feature centered at 2.2 μm and accompanied by 1.4 and 1.9 μm absorption features. Because we have detected hydrated silica in the basement unit and possible hydrated silica in the olivine-rich unit, which are the units incised by the fluvial channels in Jezero's watershed (Goudge et al. 2015), we refer to these as possible hydrated silica detections in the Jezero watershed *rock units*.

Both detections of hydrated silica in Jezero crater are associated with dark-toned material that covers the olivine-rich unit. The olivine-rich unit can be seen protruding through the smooth dark-toned material in some areas. The dark-toned material appears smooth at the scale of HiRISE and is covered in some areas by aeolian bedforms (Fig. 2e, 2j). Delta remnants surround the hydrated silica detections on the north and south sides (Fig. 2a-2c, 2f-2h). There is no geomorphic evidence for the existence of the volcanic floor unit in this area, which stratigraphically overlies the delta remnants (Goudge et al. 2015), and indeed the observed

silica-bearing smooth dark-toned material does not contain the large fractures and numerous small impact craters typically found in the volcanic floor unit as defined by Goudge et al (2015) (Fig. 2e, 2j). The olivine-rich unit is exposed from beneath the smooth dark-toned material cover ~200 meters southeast of the hydrated silica detection near the western delta and ~300 meters northeast of the hydrated silica detection near the northern delta.

Al-phylosilicate is detected with DAFA/TT near a mound south of the western Jezero delta (Fig. S1) and its presence is verified via extraction of spectra that exhibit a narrow 2.2 μm absorption feature accompanied by 1.4 μm and 1.9 μm absorption features. There is also a 2.3 μm absorption feature associated with the Al-phylosilicate, indicating that it is mixed with Fe/Mg-smectite. Magnesite and Fe/Mg-smectite are associated with both the delta and the olivine-rich unit in Jezero crater (Ehlmann et al., 2009; Goudge et al., 2015, 2017), in contrast to hydrated silica which is primarily associated with dark-toned material that covers the olivine-rich unit and is smooth at the scale of HiRISE spatial resolution. These new detections of hydrated silica and Al-phylosilicate increase the mineral diversity observed within Jezero crater that similarly resembles that observed in the greater Nili Fossae region (Ehlmann et al., 2009), which includes the watershed for the Jezero deltas.

4.0 Discussion

We cannot discern whether the hydrated silica in Jezero crater is opal-A or opal-CT via the method of Sun & Milliken (2018), which uses the band minimum position of the 1.4 μm feature to estimate crystallinity of silica. The 1.4 μm features in our spectra are quite weak, making it difficult to interpret the crystallinity of these samples. Laboratory studies show that

the weakness of the 1.4 μm absorption feature in some hydrated silica spectra can be attributed to the dehydration of silica through either heating or exposure to a Mars analog atmosphere, as has been witnessed in other hydrated silica spectra on Mars (Skok et al. 2010). The hydrated silica detection near the northern delta has a 1.4 μm feature with a band minimum at 1.41 μm (Figs. S3 & S4), which can be attributed to either opal-A or opal-CT via the method of Sun & Milliken (2018). The ratioed spectrum for the hydrated silica near the western delta has a 1.4 μm feature centered near 1.42 μm , which indicates that it is closer in crystallinity to opal-CT than opal-A based on the findings of Sun & Milliken (2018), but is not uniquely diagnostic of either opal-A or opal-CT. As such, the crystallinity of this silica cannot be used to constrain the amount of water-rock interaction experienced by this phase, in contrast to hydrated silica detected elsewhere on Mars (Morris et al., 2016; Sun & Milliken, 2018).

Hydrated silica detected by rovers on Mars likely formed in a variety of geochemical conditions, which varied widely in their degrees of habitability. The Spirit rover discovered opaline silica that likely formed as a hot spring sinter deposit (Ruff & Farmer, 2016), while the Curiosity rover discovered detrital silica, silica formed as a cement (Morris et al., 2016), as well as silica enrichments formed via infiltration of alkaline fluids that transitioned to acidic fluids (Yen et al., 2017). Fine-grained and/or amorphous silica formed by water-rock interaction is an exceptional material for preserving biosignatures on Earth and therefore has high biosignature preservation *potential*. Constraining the types of geochemical environments in which hydrated silica in Jezero crater could have formed is key to assessing these environments' habitability and thus the likelihood of this silica to host biosignatures.

The geochemical origin and provenance of the dark-toned material associated with hydrated silica—which covers the olivine-rich unit and appears smooth at HiRISE spatial resolution—is ambiguous. The silica-bearing smooth dark-toned material appears to occur exclusively in close proximity to the delta remnants (Figs. 1f, 1g, 2a, 2f). It may represent the stratigraphically lowest component of the deltaic unit, as the olivine-rich unit protrudes through it and directly underlies it at multiple contacts visible in HiRISE images (Figs. 2c, 2e, 2h). Alternatively, it may be colluvial material that has been sourced from the breakdown of the adjacent deltaic outcrops. It is unlikely that the spectral signature for hydrated silica comes primarily from the aeolian bedforms overlying the smooth dark-toned material, as these bedforms cover a minor proportion of the CRISM pixels used to generate the hydrated silica spectra from near the northern and western deltas (Figs. 2a, 2c, 2e, 2f, 2h, 2j) relative to the smooth dark-toned material. The aeolian bedforms cover an especially small area in the CRISM pixels used to generate the hydrated silica spectrum near the western delta (Fig. 2e). Therefore, we hypothesize that the silica is most likely associated with the smooth dark-toned material rather than the overlying aeolian bedforms.

If the smooth dark-toned material associated with hydrated silica is the stratigraphically lowest component of the deltaic unit, then deltaic hydrated silica is present in Jezero crater. If this potential deltaic hydrated silica is an alteration product, it could have formed authigenically in three possible scenarios: (1) via precipitation during formation of the western and northern deltas (silica is cement), (2) precipitation in the lake water column (silica is in fine sediment grains within the cementing matrix), which may have also occurred in Gale crater (Morris et al. 2016), or (3) later diagenesis via fluid infiltration, as seen in Gale crater (Yen et al. 2017).

Alternatively, it could be detrital material that formed in the Jezero watershed in either a neutral-pH hydrothermal system (detrital hypothesis 1) or an acidic hydrothermal system (detrital hypothesis 2), such as those hypothesized to exist based on the mineral assemblages detected in the Jezero watershed rock units (Fig. 3d-3g). If this silica is hydrated volcanic glass, it could have been deposited within the Jezero watershed and would have remained undissolved during fluvial transport, which is theoretically possible in cold, acidic, silica-saturated solutions. Alternatively, it could be hydrated volcanic glass-bearing material transported to its current location via aeolian processes. All formation hypotheses for detected silica are presented in Table S1.

Possible hydrated silica in the Jezero watershed rock units is present in association with magnesite and Fe/Mg-smectite in the olivine-rich unit (Fig. 3e-g)—favoring formation in neutral-pH hydrothermal conditions (e.g. Falk & Kelemen, 2015; Streit et al., 2012)—as well as in association with Al-phylosilicate in the Noachian basement unit (Fig. 3d), favoring formation in highly acidic hydrothermal conditions (Fialips et al., 2000). As such, none of the detrital origin hypotheses can be ruled out for the hydrated silica in Jezero crater. Similarly, none of the authigenic hypotheses, nor the primary volcanic hypotheses for hydrated silica's origin can be ruled out either. *In situ* investigation is therefore necessary to distinguish between these possible formation scenarios. We evaluated some of the *in situ* observations that would be consistent with each origin hypothesis in Table S1.

The various geochemical conditions implied by the proposed formation hypotheses for hydrated silica in Jezero crater span from uninhabitable with no chance for biosignature preservation, to habitable with high likelihood to preserve biosignatures (Table S1), if life

existed in Jezero crater's lake, in an ancient hydrothermal system in Jezero crater, or elsewhere in the Jezero watershed. Earth analog environments and materials can be used to assess where biosignatures in silica would likely be found for each different origin hypothesis that involves habitable geochemical conditions. Authigenic silica cements preserve 3.4 Gyr old microfossils in the Strelley Pool Formation in Western Australia (Wacey et al., 2011). Such silica cements are the types of materials where biosignatures could be hosted in possible deltaic secondary silica in Jezero crater, if this material formed via authigenic hypotheses 1 or 2. Detrital silica sediments preserve Proterozoic-age microfossils in bedded cherts found in the Buxa Formation in Northeast India (Schopf et al., 2008). This scenario, where microfossils are preserved in detrital silica sediment grains rather than the cementing matrix, is analogous to where biosignatures from detrital silica could be located in possible deltaic hydrated silica in Jezero crater or in silica that formed in a habitable environment and was transported to Jezero crater via aeolian processes.

Hydrated silica formed via alteration of preexisting units in Jezero crater during a later diagenetic event (authigenic hypothesis 3) has the potential to preserve biosignatures, given that it could have formed in water-rock alteration systems with a wide range of possible temperatures and pHs. Earth analogs in which ancient microfossils are preserved in silica also exist for this scenario. For example, silica precipitated in subsurface hydrothermal systems (not in surficial hot springs) preserves 3.5 Gyr old kerogen biosignatures in the North Pole area, Western Australia (Ueno et al., 2004). Silica associated with smooth dark-toned material in Jezero crater may be associated with smectite, but this assemblage is not indicative of any particular pH during silica formation. Overall, hydrated silica detected in Jezero crater are an

excellent target for *in situ* astrobiological investigation, if it is secondary rather than volcanic in origin. However, the possibility of a volcanic origin for this silica cannot be ruled out from orbit, thus *in situ* investigation is required to fully constrain the likelihood of this material to host biosignatures.

5.0 Conclusions

We have detected occurrences of hydrated silica in Jezero crater associated with dark-toned material that covers the olivine-rich unit and appears morphologically smooth at HiRISE spatial resolution. From orbit, we cannot definitively determine whether this silica is hydrated volcanic glass or a secondary alteration product. Possible hydrated silica was detected in the Jezero watershed rock units, in both the olivine-rich unit and the basement unit (Fig. 3d-g). In the olivine-rich unit, possible hydrated silica is associated with magnesite and smectite, whereas in the basement unit it is associated with Al-phylosilicate. We interpret the former mineral assemblage to be indicative of neutral- to alkaline-pH alteration conditions and interpret the latter mineral assemblage to be indicative of acidic alteration conditions (Fialips et al., 2000; Streit et al., 2012; Falk & Kelemen, 2015).

The likelihood of detected silica to host biosignatures is highly dependent on the geochemical conditions of its formation environment. We have proposed 9 hypotheses for the origin of hydrated silica in Jezero crater, including primary volcanism, diagenesis via fluid infiltration of the olivine-rich or deltaic units, authigenic formation in a lacustrine environment, detrital transport of material formed authigenically in the Jezero watershed, or transport to Jezero crater via aeolian processes. We are limited in our ability to further constrain these

formation hypotheses from orbit, but with imminent *in situ* exploration of this area by NASA's Mars 2020 rover mission, we will soon be able to more accurately constrain the origin of this detected silica and thus can assess its likelihood to preserve biosignatures with greater confidence, precision, and accuracy.

Data Availability

The datasets used in this study are available on Harvard Dataverse.

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Author contributions

J.D.T. and H.L. developed DAFA/TT with primary advisement from J.F.M., advisement from X.Z., and feedback from E.S.A. that improved the method. J.D.T. used DAFA/TT to detect

hydrated silica and used traditional CRISM data analysis to verify the detection, and wrote the manuscript. T.A.G. provided input regarding the geologic units associated with silica and geomorphological interpretations. C.H.K. and M.S.B. helped significantly with geomorphologic interpretations and figure development. Y.I. and M.P. processed CRISM images through their pipeline to cross-verify detections and generate more easily-interpretable data. All authors contributed to the interpretation and final version of the manuscript.

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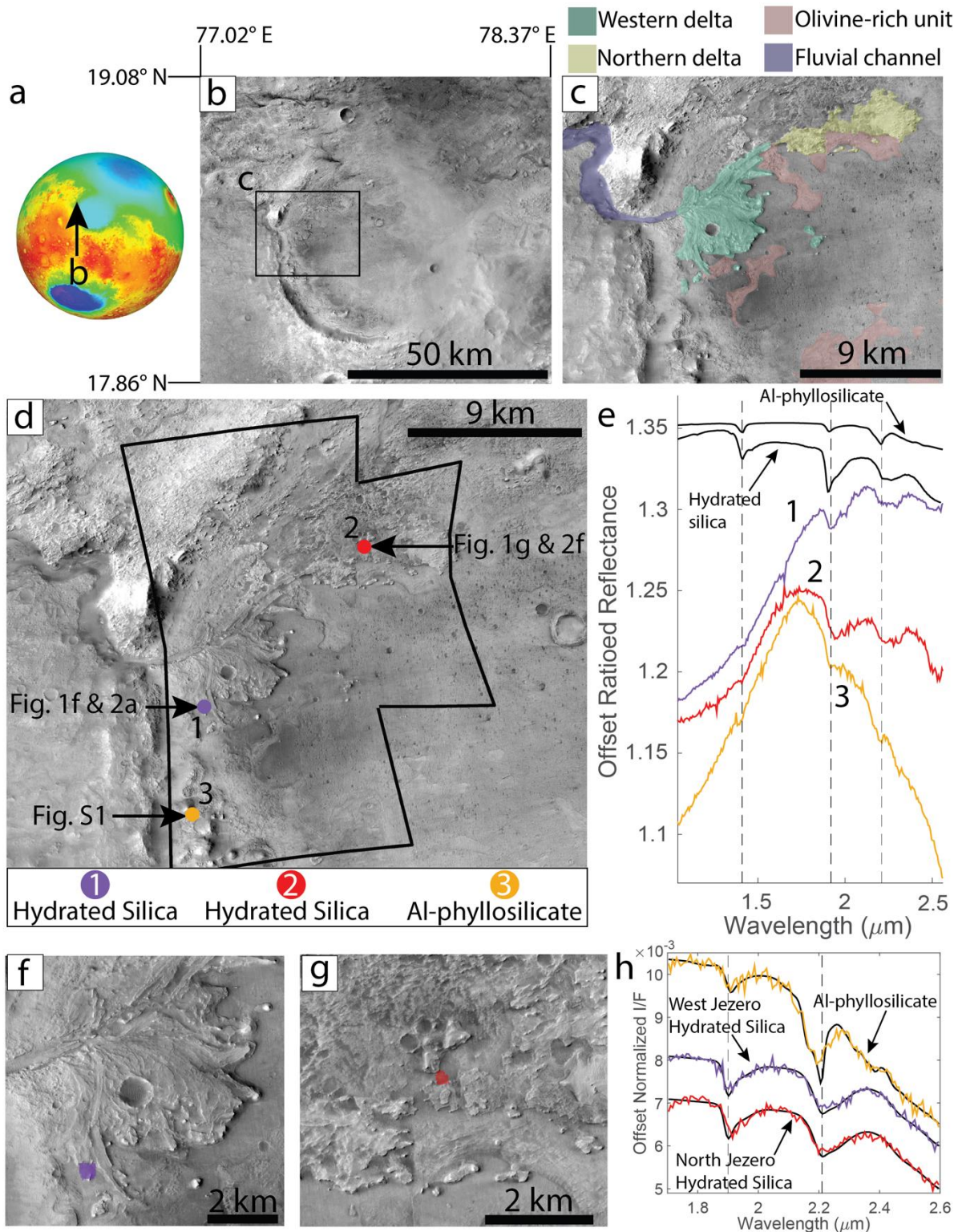


Figure 1 | Overview map of Jezero crater mineralogy. (a) Location of Jezero crater on Mars globe colored with Mars Orbital Laser Altimeter (MOLA) topography. (b) Overview image of Jezero crater. (c) Enlarged view of western Jezero crater, with geomorphic maps from Goudge et al. (2015) of both deltas, fluvial channels, and the olivine-rich unit overlain. (d) Hydrated

silica detections and an Al-phyllsilicate detection in Jezero crater generated via DAFA/TT analysis of CRISM images FRT000047A3 and HRL000040FF, with CRISM image boundaries shown in black. Detections 1 and 2 (hydrated silica) were discovered via DAFA/TT analysis and verified by extraction of ratioed spectra. Detection 3 (Al-phyllsilicate) was discovered via DAFA/TT analysis and verified by extraction of an unratioed spectrum (Fig. S1). I/F spectra of each detection are shown in (e). (e) Spectra from dot locations indicated in (d), where dot colors correspond to spectra colors. Detections 1 and 2 have 2.2 μm absorptions that broaden towards longer wavelengths, as well as 1.9 μm and 1.4 μm absorptions (Figs. S2-S5). These features indicate the presence of hydrated silica. Detection 3 is Al-phyllsilicate, based on the presence of a narrow 2.2 μm absorption accompanied by a 1.9 μm absorption (extracted from Itoh & Parente 2019 processed CRISM image) (Fig. S1). The black spectra are library spectra for hydrated silica (RELAB Spectral ID C1OP09, Sample ID OP-MCG-009) and Al-phyllsilicate (RELAB Spectral ID BIR1JB799, Sample ID JB-JLB-799), (f) Overview of hydrated silica DAFA/TT detection near the western Jezero delta (purple). (g) Overview of hydrated silica DAFA/TT detection near the northern Jezero delta (red). (h) DAFA/TT fits to library spectra for Al-phyllsilicate, hydrated silica near the western delta, and hydrated silica near the northern delta. These minerals were initially discovered via DAFA/TT analysis and then verified via extraction of I/F spectra shown in (e). The hydrated silica library spectrum for both detections is RELAB Spectral ID BKR1OP007, Sample ID OP-MCG-007. The Al-phyllsilicate library spectrum is RELAB Spectral ID BIR1JB799, Sample ID JB-JLB-799. North is up in all images.

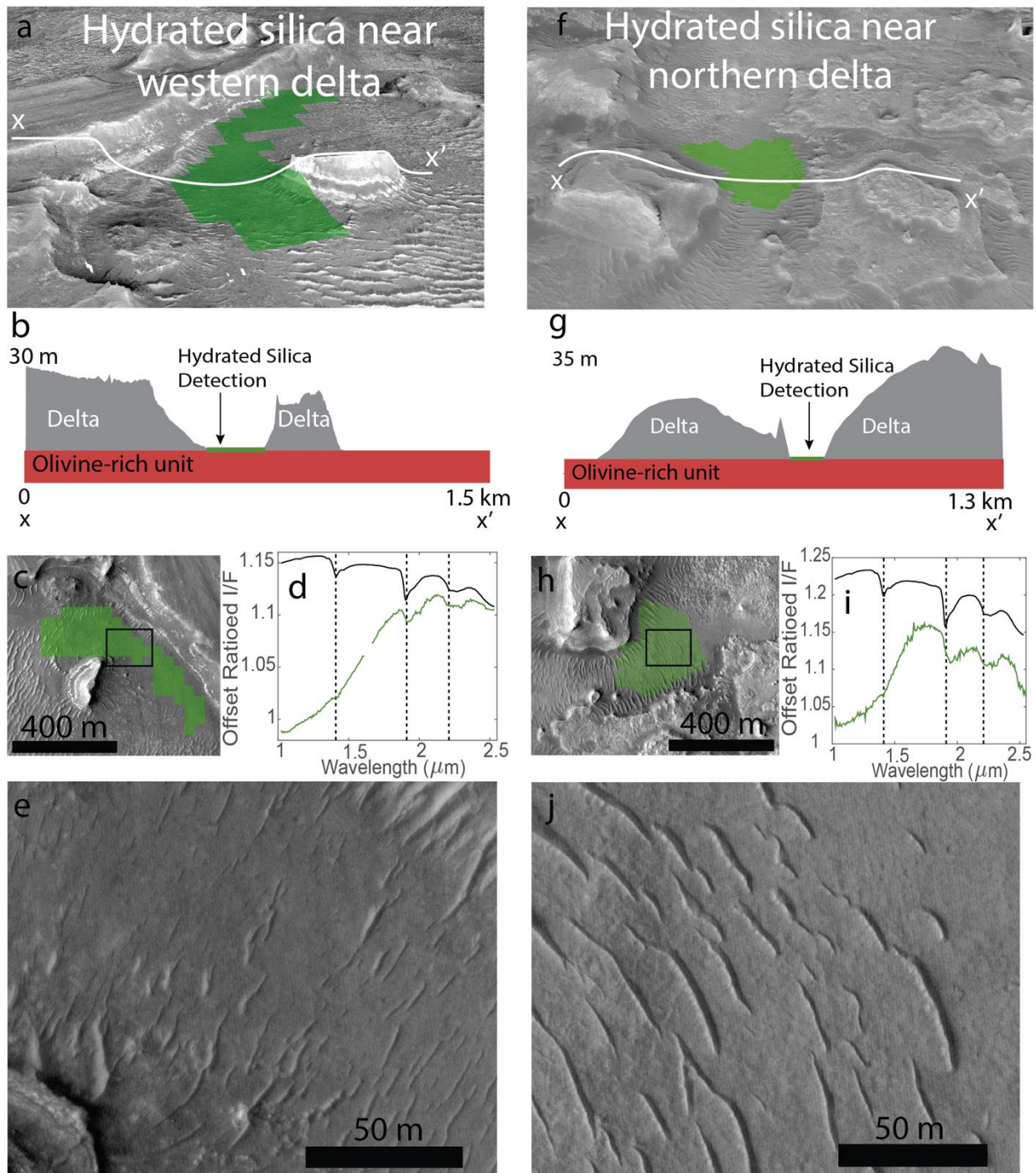


Figure 2 | Hydrated silica detections in Jezero crater. (a) Hydrated silica detection (green) near the western delta overlain on HiRISE DEM and images. The white line denotes the elevation profile cross-section shown in (b). (b) Elevation profile from cross-section shown in (a) illustrating the relationship between the elevation profile, silica detection, olivine-rich unit, and deltaic unit. (c) Location of hydrated silica detected near western Jezero delta (green). The rectangle shows the area that is enlarged in part (e). (d) (black) Library spectrum of hydrated silica (RELAB Spectral ID C1OP09, Sample ID OP-MCG-009). (green) Ratio spectrum of hydrated silica near western delta from green pixels in (a) and (c). The dotted lines are at 1.41 μm , 1.93

μm , and $2.21 \mu\text{m}$. (e) Enlarged view of hydrated silica detection near the western delta. The linear features are aeolian bedforms. The underlying smooth dark-toned material bears the hydrated silica spectral signal. (f) Hydrated silica detection (green) near the northern delta overlain on CTX DEM and HiRISE images. The white line denotes the elevation profile cross-section shown in (g). (g) Elevation profile from cross-section shown in (f) illustrating the relationship between the elevation profile, silica detection, olivine-rich unit, and deltaic unit. (h) Location of hydrated silica detected near northern delta (green). The rectangle shows the area that is enlarged in part (j). (i) (black) Library spectrum of hydrated silica (RELAB Spectral ID C1OP09, Sample ID OP-MCG-009). (green) Ratioed spectrum of hydrated silica near northern delta from green pixels in (f) and (h). The dotted lines are at $1.41 \mu\text{m}$, $1.93 \mu\text{m}$, and $2.21 \mu\text{m}$. (j) Enlarged view of hydrated silica detection near the northern delta. The linear features are aeolian bedforms. The underlying smooth dark-toned material bears the hydrated silica spectral signal. North is up in parts b-e and g-j. North is to the left in parts a and f.

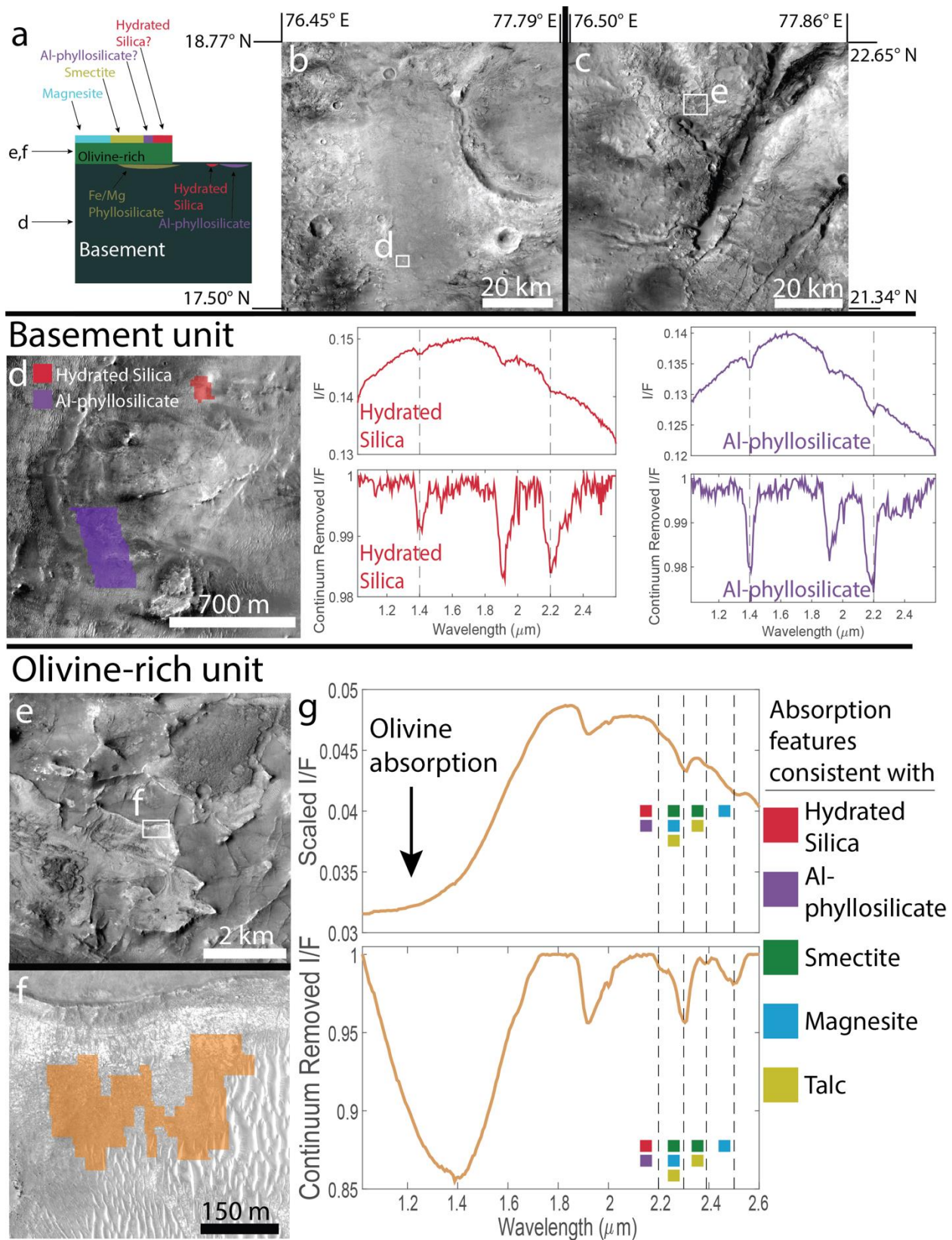


Figure 3 | Hydrated silica and associated minerals detected in Jezero watershed rock units. (a) Conceptual stratigraphic cross-section showing relationship between Nili Fossae basement unit

and overlying olivine-rich unit, with detected alteration minerals shown. (b) Overview of circum-Jezero region. (c) Overview of other location in Nili Fossae where hydrated silica is detected in the olivine-rich unit. (d) Detection of Al-phyllosilicate (purple) and hydrated silica (red) in the basement unit. The purple spectrum is from the purple pixels, the red spectrum is from the red pixels. The presence of hydrated silica is indicated by the presence of 1.4 μm , 1.9 μm , and 2.2 μm absorptions, where the 2.2 μm absorption broadens towards longer wavelengths. The presence of Al-phyllosilicate is indicated by the presence of 1.4 μm , 1.9 μm , and 2.2 μm absorptions, where the 2.2 μm absorption is significantly narrower than that of hydrated silica. Spectra are shown in standard I/F and in continuum removed I/F. Presence of this mineral assemblage is possibly indicative of acidic hydrothermal alteration. (e) Overview of area where hydrated silica is detected in the olivine-rich unit. (f) Enlarged view of olivine-rich unit with its characteristic fractured texture. The orange pixels contain the spectral signal shown in (g). (g) Hydrated silica or Al-phyllosilicate detected in assemblage with magnesite and smectite or talc. The orange spectrum is from the orange pixels in (f). The spectrum is shown in standard I/F and in continuum removed I/F. the broad absorption feature centered at 1 μm is indicative of olivine. It appears to be centered at 1.4 μm in the continuum removed spectrum because the continuum starts at 1.03 μm due to the wavelength range of the CRISM long wavelength detector (1.03-3.92 μm). Boxes near dotted lines going through absorptions at 2.2 μm , 2.3 μm , 2.39 μm , and 2.5 μm indicate the minerals with which these absorption features are consistent. The 2.3 μm and 2.39 μm features are also present in talc, so hydrated silica/Al-phyllosilicate may be associated with magnesite and talc rather than magnesite and smectite. North is up in all images. All spectra shown in this figure were extracted from CRISM TRR3 images processed through the pipeline described in Itoh & Parente (2019).

Supplementary Figures

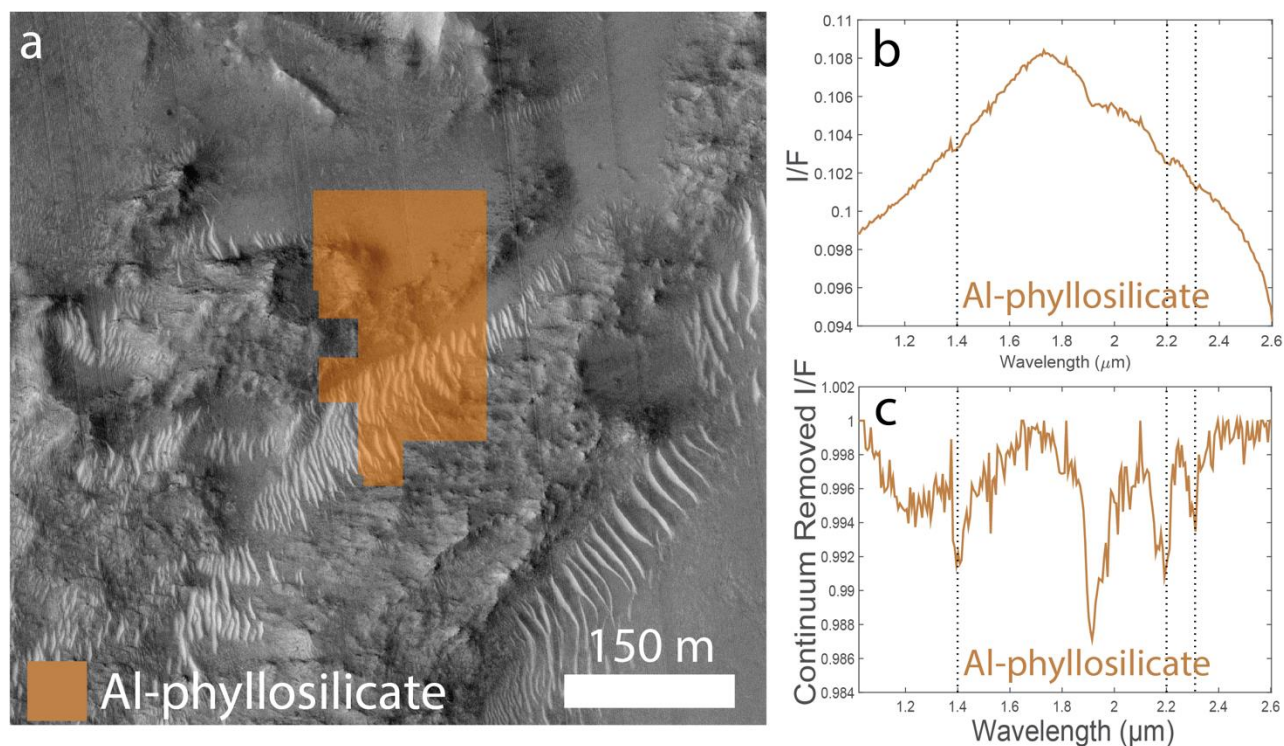


Figure S1. | **Al-phyllsilicate detection in Jezero crater.** (a) Enlarged view of the Al-phyllsilicate detection in Jezero crater shown in Fig. 1. It is associated with either light-toned unconsolidated material or dark-toned bedrock. (b) I/F spectrum of Al-phyllsilicate from area covered by orange pixels in (a). Vertical lines are through 1.4, 2.2, and 2.3 μm . (c) Continuum removed I/F spectrum of (b) with vertical lines through the same wavelengths. All spectra shown in this figure were extracted from CRISM TRR₃ images processed through the pipeline described in Itoh & Parente (2019).

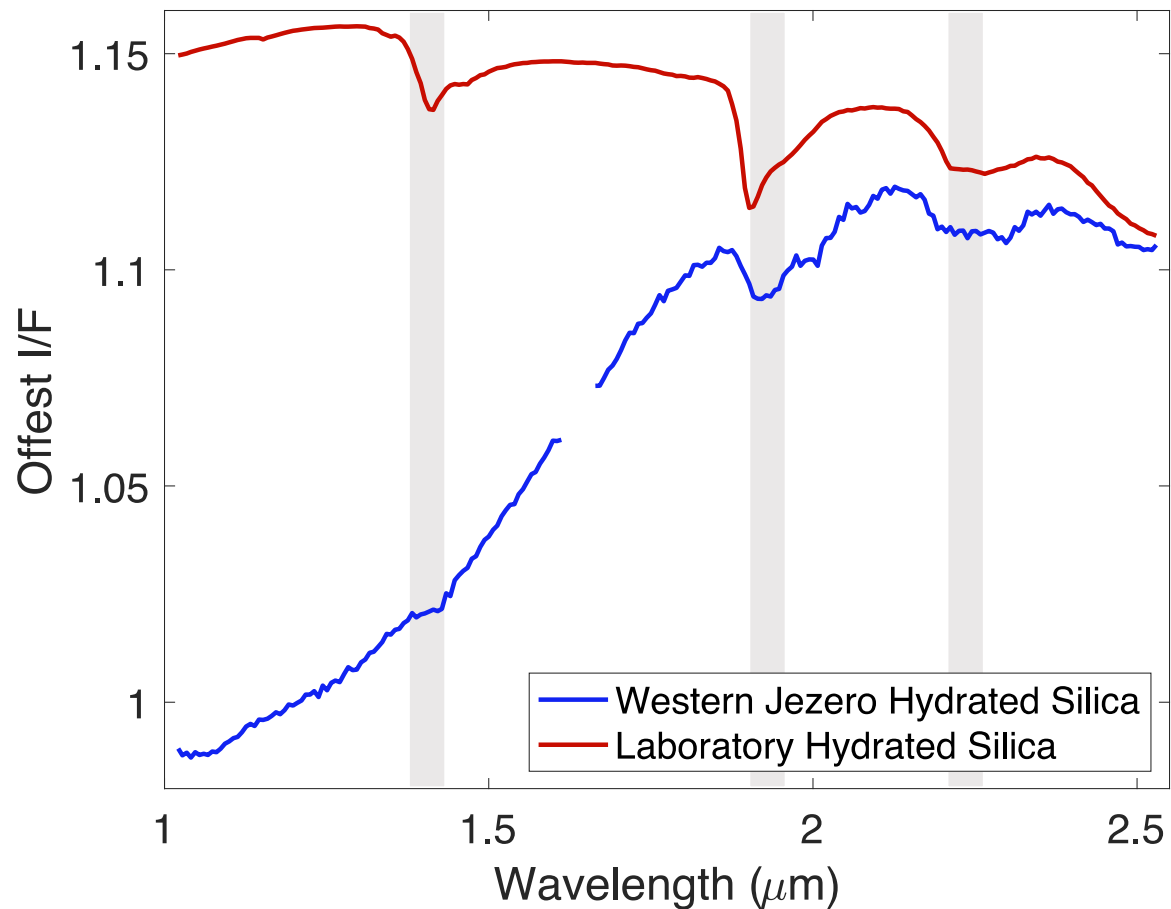


Figure S2 | **Enlarged ratioed spectrum of hydrated silica detection associated with smooth dark-toned material near the western Jezero delta.** The spectra shown here show 1.4, 1.9, and 2.2 μm absorptions, with the 2.2 μm absorption having distinctly broad shoulders towards longer wavelengths, which is diagnostic of hydrated silica. The laboratory spectrum is RELAB Spectral ID C1OP09, Sample ID OP-MCG-009. The grey shading indicates the band minima position ranges of the 1.4, 1.9, and 2.2 μm features from Sun & Milliken (2018), which are 1.375-1.435 μm , 1.90-1.96 μm , and 2.21-2.26 μm , respectively. The silica appears to be mixed with smectite, as is indicated by the increased absorption depth around 2.3 μm . It also appears to be mixed with olivine based on the presence of a broad absorption feature centered around 1 μm . The 1.4 μm feature in the western Jezero hydrated silica spectrum (blue) is centered around 1.42 μm , which is not uniquely diagnostic of either opal-A or opal-CT following the method of Sun & Milliken (2018), but falls more towards the opal-CT field. However, the 1.4 μm absorption minimum position may be influenced by mixing with smectite, thus we advise caution in this interpretation. The zone where the blue spectrum has been clipped is a region of noise caused by a detector contact.

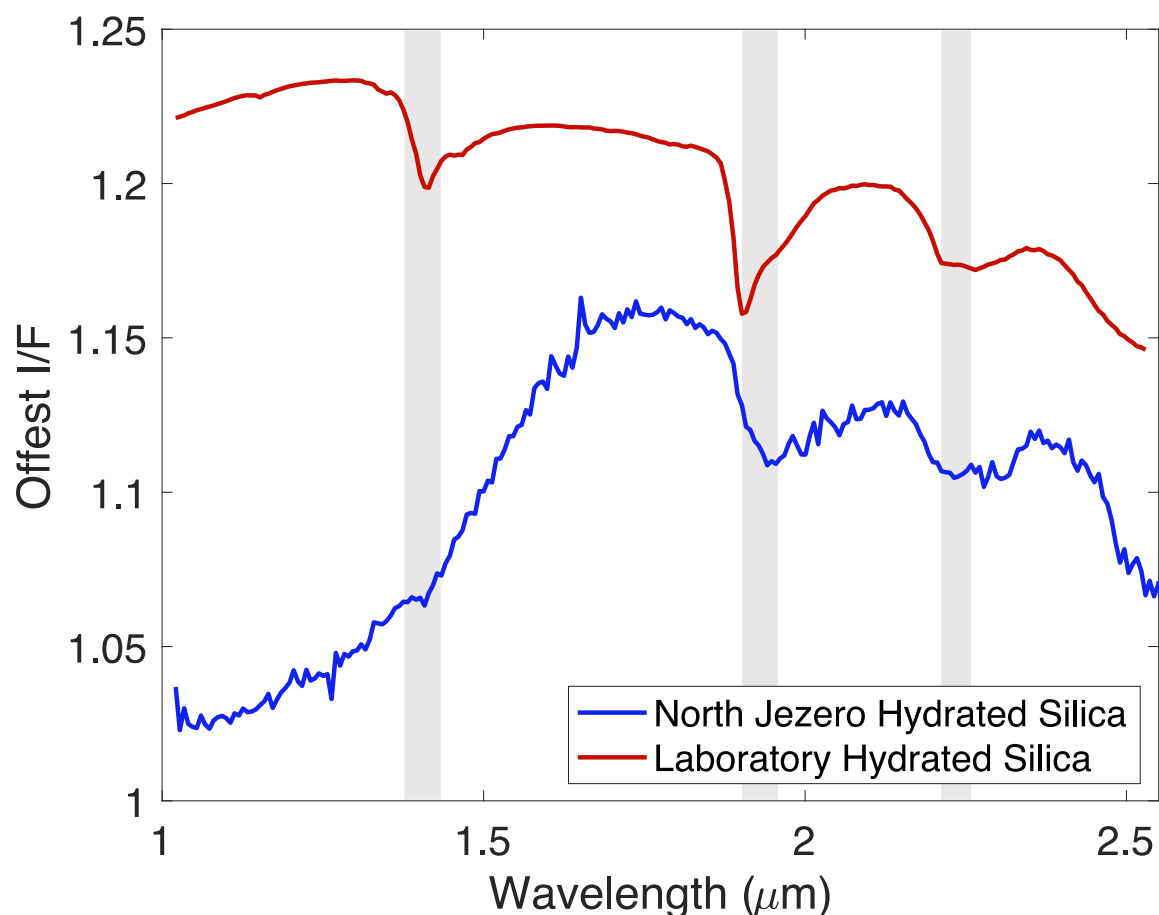


Figure S3 | **Enlarged ratioed spectrum of hydrated silica detection associated with smooth dark-toned material near the northern Jezero delta.** The spectra shown here show 1.4, 1.9, and 2.2 μm absorptions, with the 2.2 μm absorption having distinctly broad shoulders towards longer wavelengths, which is diagnostic of hydrated silica. The laboratory spectrum is RELAB Spectral ID C1OP09, Sample ID OP-MCG-009. The grey shading indicates the band minima position ranges of the 1.4, 1.9, and 2.2 μm features from Sun & Milliken (2018), which are 1.375-1.435 μm , 1.90-1.96 μm , and 2.21-2.26 μm , respectively. The silica appears to be mixed with smectite, as is indicated by the increased absorption depth around 2.3 μm . Mixture with smectite may also contribute to the shift in the 1.9 μm band minimum position. It also appears to be mixed with olivine based on the presence of a broad absorption feature centered around 1 μm . The 1.4 μm feature in the northern Jezero hydrated silica spectrum (blue) is centered around 1.41 μm , which can be attributed to either opal-A or opal-CT following the method of Sun & Milliken (2018). However, the 1.4 μm absorption minimum position may be influenced by mixing with smectite, thus we advise caution in this interpretation.

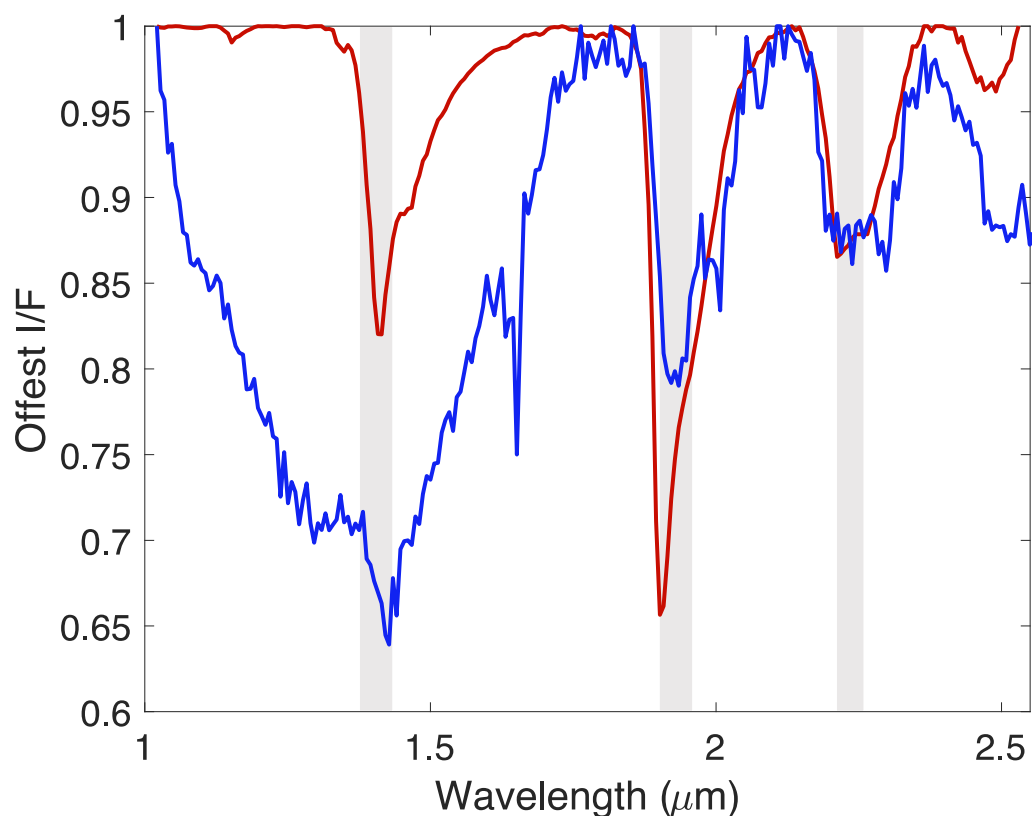


Figure S4 | Enlarged continuum-removed ratioed spectrum of hydrated silica detection associated with smooth dark-toned material near the western Jezero delta. The continuum-removed spectra shown here show 1.4, 1.9, and 2.2 μm absorptions, with the 2.2 μm absorption having distinctly broad shoulders towards longer wavelengths, which is diagnostic of hydrated silica. The laboratory spectrum is RELAB Spectral ID C1OP09, Sample ID OP-MCG-009. The grey shading indicates the band minima position ranges of the 1.4, 1.9, and 2.2 μm features from Sun & Milliken (2018), which are 1.375-1.435 μm , 1.90-1.96 μm , and 2.21-2.26 μm , respectively. The silica appears to be mixed with smectite, as is indicated by the increased absorption depth around 2.3 μm . It also appears to be mixed with olivine based on the presence of a broad absorption feature centered around 1 μm , though in the continuum-removed spectrum it appears to be centered around 1.4 μm since the continuum fit starts at 1.03 μm , as this is the shortest wavelength of the CRISM long wavelength detector. The 1.4 μm feature in the western Jezero hydrated silica spectrum (blue) is centered around 1.42 μm , which is not uniquely diagnostic of either opal-A or opal-CT following the method of Sun & Milliken (2018), but falls more towards the opal-CT field. However, the 1.4 μm absorption minimum position may be influenced by mixing with smectite, thus we advise caution in this interpretation.

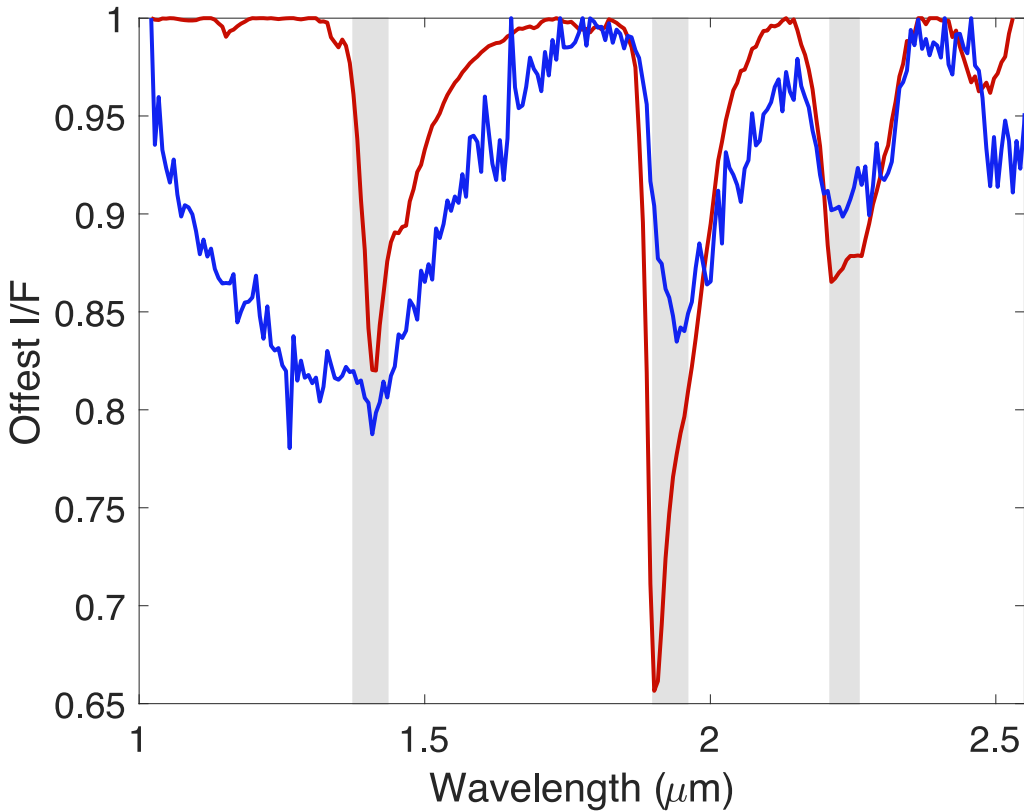


Figure S5 | Enlarged continuum-removed ratioed spectrum of hydrated silica detection associated with smooth dark-toned material near the northern Jezero delta. The continuum-removed spectra shown here show 1.4, 1.9, and 2.2 μm absorptions, with the 2.2 μm absorption having distinctly broad shoulders towards longer wavelengths, which is diagnostic of hydrated silica. The laboratory spectrum is RELAB Spectral ID C1OP09, Sample ID OP-MCG-009. The grey shading indicates the band minima position ranges of the 1.4, 1.9, and 2.2 μm features from Sun & Milliken (2018), which are 1.375-1.435 μm , 1.90-1.96 μm , and 2.21-2.26 μm , respectively. The silica appears to be mixed with smectite, as is indicated by the increased absorption depth around 2.3 μm . Mixture with smectite may also contribute to the shift in the 1.9 μm band minimum position. It also appears to be mixed with olivine based on the presence of a broad absorption feature centered around 1 μm , though in the continuum-removed spectrum it appears to be centered around 1.4 μm since the continuum fit starts at 1.03 μm , as this is the shortest wavelength of the CRISM long wavelength detector. The 1.4 μm feature in the northern Jezero hydrated silica spectrum (blue) is centered around 1.41 μm , which can be attributed to either opal-A or opal-CT following the method of Sun & Milliken (2018).). However, the 1.4 μm absorption minimum position may be influenced by mixing with smectite, thus we advise caution in this interpretation.

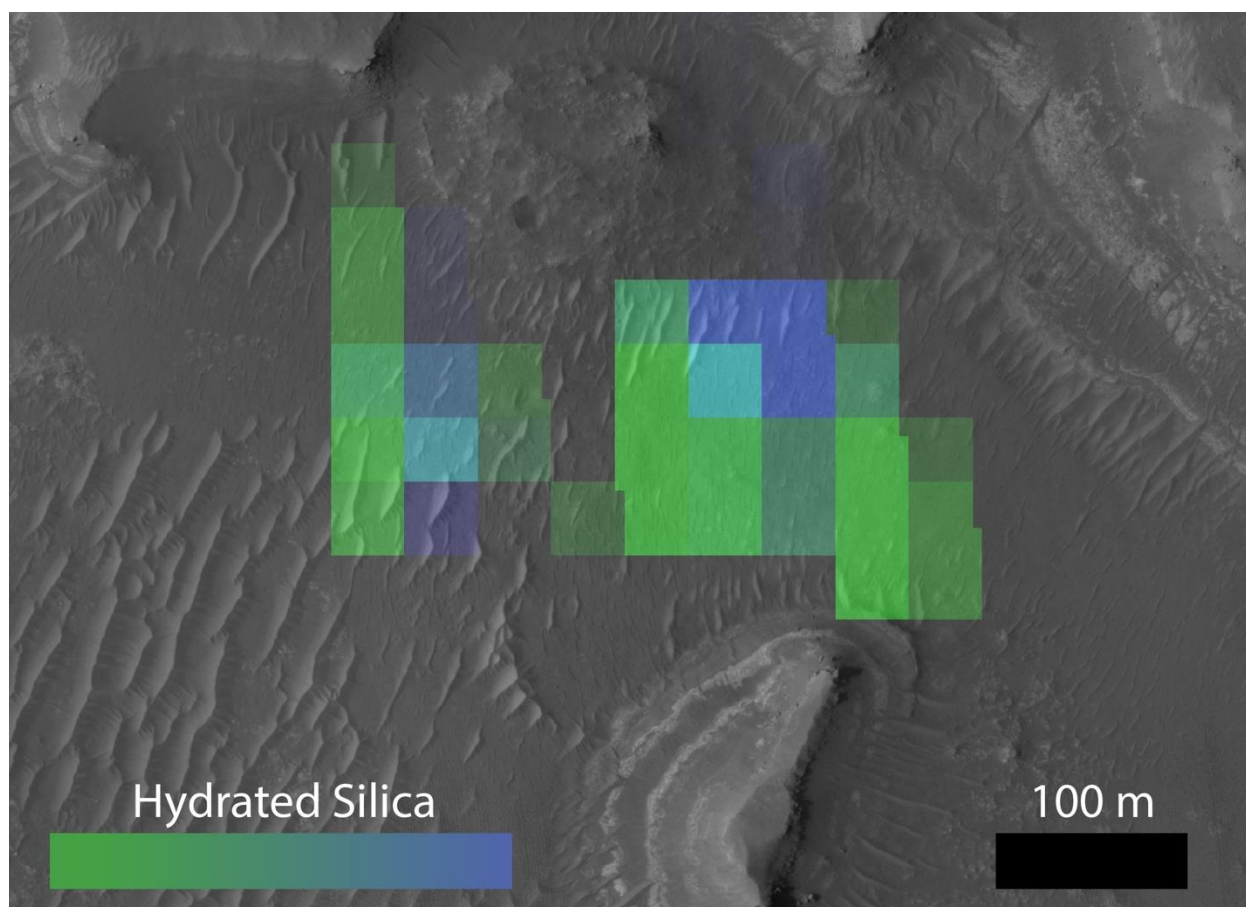


Figure S6 | **Band parameters consistent with presence of silica.** Blue colors in this figure are for CRISM band parameter D2200 (dropoff at 2.2 μm) and green colors are for CRISM band parameter BD2210_2 (band depth at 2.21 μm) (Viviano-Beck et al. 2014). Blue and green colors, or a mixture of the two, are consistent with the presence of silica.

<i>Associated unit</i>	<i>Formation process type</i>	<i>Formation environment</i>	<i>Habitability of formation environment</i>	<i>Biosignature preservation in Earth-analogs</i>	<i>Observational characteristics in situ</i>
<i>Smooth dark-toned material</i>	Authigenic	Acidic-to-neutral pH hydrothermal system.	Possibly habitable hydrothermal environment.	Poorly studied and poorly characterized.	Olivine-rich unit altered to silica in veins or massive clumps. No morphological evidence for hot spring deposits.
<i>Smooth dark-toned material</i>	Authigenic	Hot spring.	Habitable hot spring environment similar to those observed on volcanos on Earth.	High.	Sinter deposits morphologically and mineralogically similar to those observed by Spirit in Columbia Hills (Ruff et al., 2011) or hot springs on Earth.
<i>Smooth dark-toned material</i>	Volcanic	Quenching of melt during deposition of ash-fall material.	Uninhabitable.	No biosignatures preserved	Silica-rich unaltered glass component in ultramafic ash-fall
<i>Deltaic</i>	Authigenic	Precipitation during formation of the western and northern Jezero deltas (authigenic hypothesis 1).	Habitable lacustrine environment.	High.	Silica as cement matrix binding together sediment grains.
<i>Deltaic</i>	Authigenic	Precipitation in the lake water column (authigenic hypothesis 2).	Habitable lacustrine environment.	High.	Silica exists as fine sediment grains within the cementing matrix.
<i>Deltaic or smooth dark-toned material</i>	Authigenic	Later diagenesis via fluid infiltration, as seen in Gale crater (authigenic hypothesis 3).	Acidic-to-neutral pH fluids. Formation timescale poorly constrained. Habitability poorly constrained.	No known examples.	Silica exists as veins, or is enriched in rock surrounding alteration veins due to cation leaching by fluids, or is enriched in rock in diagenetic veins that are too small to be resolved in imagery.
<i>Deltaic</i>	Detrital	Formed in Jezero watershed rock units in neutral-pH hydrothermal fluids. Transported during period of high fluvial activity and deposited in Jezero delta (detrital hypothesis 1).	Habitable neutral-pH hydrothermal environment.	High.	Silica-rich sediment grains in Jezero delta cemented by other mineral(s). Possibly associated with carbonate or other neutral-pH indicating minerals.
<i>Deltaic</i>	Detrital	Formed in Jezero watershed rock units in acidic hydrothermal fluids. Transported during period of high fluvial activity and deposited in Jezero delta (detrital hypothesis 2).	Habitable acidic-pH hydrothermal environment.	High.	Silica-rich sediment grains in Jezero delta cemented by other mineral(s). Possibly associated with jarosite or other acidic-pH indicating minerals.

<i>Smooth dark-toned material</i>	Detrital	Dark-toned material is transported via aeolian processes after hydrated silica formation elsewhere.	Cannot be constrained by current observations.	Ranges from no biosignatures preserved (volcanic glass) to high biosignature preservation (detrital chert).	Dark-toned material is silica-rich and unconsolidated
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Table S1. | **Formation hypotheses for hydrated silica in Jezero crater.** This table presents the 9 formation hypotheses for hydrated silica detected in Jezero crater in this study. Column 1 shows the unit of association for each hypothesis, column 2 specifies the proposed process by which the material was created/transported to Jezero crater, column 3 presents the formation environment for each formation hypothesis, column 4 presents the degree of habitability of each formation environment, column 5 presents the biosignature preservation potential of each formation environment based on characterized Earth-analogs, and column 6 presents *in situ* observations that would favor each specific formation hypothesis.

References

- Viviano-Beck, C., et al. (2014) Revised CRISM spectral parameters and summary products based on the currently detected mineral diversity on Mars, *JGR Planets* 119: 1403-1431.
- Itoh, Y. & Parente, M. (2019) A new simultaneous atmospheric correction and de-noising of CRISM data, *50th LPSC*, 2025.

CHAPTER 5: Synthesis and future directions –the search for extinct and extant extraterrestrial life in the Solar System

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1.0 Summary of major contributions

Chapter 1 quantifies the rate of microbial and abiotic CH₄ production in Earth's deep continental subsurface by applying a Bayesian analysis approach to a biogeochemical model that uses measurements of dissolved CH₄ concentration, dissolved He concentration, $\delta^{13}\text{C-CH}_4$, $\delta^2\text{H-CH}_4$, and rock matrix radionuclide concentrations to constrain its estimates. The average rate of abiotic CH₄ production is roughly 2 orders of magnitude higher in the Canadian and Fennoscandian Shield sample sites compared to sites sampled in Witwatersrand basin. This is likely controlled by lithology of the surrounding rock units, whereby ultramafic units produce more H₂ for abiotic CH₄ formation and contain more metal catalysts to promote abiotic CH₄ formation relative to mafic or sedimentary lithologies. Microbial CH₄ production is particularly enhanced at depths shallower than 1 km, but varies widely even among boreholes within the same mine. We find that the percentage of microbial CH₄ relative to abiotic CH₄ in groundwater is enhanced by mixing between H₂-rich ancient groundwaters and paleometeoric water containing methanogens, which then consume the abundant dissolved H₂ to produce CH₄.

Chapter 2 demonstrates that the source regions for the martian meteorites could support sulfate-reducing bacteria—commonly found in Earth's deep subsurface— wherever groundwater is present via the same radiolytic chemical processes that produce H₂ and SO₄ in deep subsurface settings on Earth. Radiolysis of pore/fracture water in the presence of rock-matrix hosted sulfides produces complimentary H₂ (directly via pore water radiolysis) and SO₄ (via oxidation of sulfides by H₂O₂ produced directly via pore water radiolysis) (Lefticariu et al., 2010; Li et al., 2016). A biogeochemical model has been developed and validated on Earth to estimate H₂ and SO₄ production rates, as well as the cell densities that could be supported by

estimated concentrations of these redox compounds (Li et al., 2016; Altair et al., 2018). Radionuclide concentrations, sulfide concentration, average sulfide grain size, porosity, and sulfate-reducing bacterial metabolic rates are the relevant parameters for this model. The martian meteorites have radionuclide concentrations, sulfide concentrations, and sulfide grain sizes characterized to high precision (Baumgartner et al., 2017; Chevrier et al., 2011; Franz et al., 2019, 2014; Greenwood et al., 2000a, 2000b; Hewins et al., 2020, 2017; Jean-Pierre Lorand et al., 2018; J. -P. Lorand et al., 2018; Lorand et al., 2015, 2005; Rochette et al., 2005, 2001; Wang and Becker, 2017), while porosity of different martian terrains associated with these meteorites can be estimated via orbital gravimetry (Goossens et al., 2017; Broquet and Wieczorek, 2019) that is supported by rover gravimetry (Lewis et al., 2019). Sulfate-reducing metabolic rate range estimates are derived from values measured in Earth's deep subsurface. Through this constrained model, we demonstrate that the regolith breccia source lithology could support the highest sulfate-reducing cell densities of any currently known martian meteorite lithology, though nakhlite and shergottite source lithologies could also sustain sulfate-reducing cell densities measurable by current instrumentation and comparable to those found in Earth's subsurface (Onstott et al., 2003; Cockell et al., 2012).

Chapter 3 tests the propensity of factor analysis/target transformation methods (Amador et al., 2018; Thomas and Bandfield, 2017) to produce accurate target detection results, false positive results, and false negative results when applied to laboratory and orbital VNIR hyperspectral images. Results of factor analysis/target transformation techniques can be interpreted erroneously when they cannot be validated via additional methods such as extraction of spectra or ratio spectra. However, they can also be useful for analyzing

hyperspectral images to find spatially small and/or spectrally weak phases that can be validated (e.g. DAFA/TT; Lin et al., 2018; Tarnas et al., 2019), for denoising data (Thomas and Bandfield, 2017), and/or for unmixing the individual spectral components contributing variance to a set of spectra. In this study, we introduce guided factor analysis, which is a slight modification of previous factor analysis techniques (e.g. Bandfield et al., 2000, 2002; Glotch and Bandfield, 2006) and similar to some of the original factor analysis applications to chromatography data (Schostack and Malinowski, 1993; Malinowski, 1996), whereby band parameter and/or morphological mapping is used to select the pixels from which a set of spectra are derived for factor analysis. This subsetting allows for detection of spectra that contribute significant variance to a subset of data, but little variance to the entirety of the dataset.

Chapter 4 implements DAFA/TT to detect outcrops of hydrated silica and Al-phylosilicate in Jezero crater, Mars. Hydrated silica has high biosignature preservation potential on Earth –preserving fossils in a variety of geologic settings with ages >3 Gyr. We also report detections of Al-phylosilicate and hydrated silica in the Nili Fossae basement unit, as well as possible hydrated silica mixed with carbonate and phyllosilicate phases in the olivine-rich unit. Because both of these units are incised by the fluvial channels that flow into Jezero crater, it is possible that the detected hydrated silica is detrital, though an authigenic origin cannot be ruled out. Hydrated silica in Jezero crater may have formed in a habitable environment. Therefore, it is an excellent target for biosignature investigation by NASA’s Perseverance rover. Smaller outcrops of this hydrated silica may exist elsewhere in Jezero crater at spatial scales below the resolution of CRISM.

2.0 Future directions

2.1 Current strategy for extinct extraterrestrial life detection

NASA's Mars Exploration Program constitutes its first mission series focused on detecting extinct extraterrestrial life. Originally spurred by a claimed biosignature detection in ALH84001 (Friedmann et al., 2001; McKay et al., 1996; Taylor et al., 2001; Thomas-Keprta et al., 2002, 2001, 2000) that later was demonstrated to be inconclusive (Golden et al., 2004, 2001; Treiman, 2003), NASA's Mars Exploration Program has to date been focused on detecting previously habitable environments, culminating in NASA's Curiosity rover finding evidence for the existence of a habitable paleolake in Gale crater (Grotzinger et al., 2014). Another Mars Exploration Program astrobiological highlight is the Spirit rover's detection of potential hot spring sinter deposits in Columbia Hills (Ruff et al., 2011; Ruff and Farmer, 2016; Ruff et al., 2019), which often host biosignatures on Earth (Djokic et al., 2017; Guido et al., 2019; Teece et al., 2020). NASA's Perseverance rover will now go to another paleolake, Jezero crater (Fassett and Head, 2008; Goudge et al., 2012; Schon et al., 2012; Goudge et al., 2017), and look for biosignatures in rocks there that will be cached for return to Earth via the Mars Sample Return mission (Mustard et al., 2013; Williford et al., 2018; Beaty et al., 2019). In this way, NASA's Mars Exploration Program has come full circle –starting with a claimed biosignature detection in a Mars rock that made its way to Earth, and culminating in the collection of more Mars rocks for return to Earth, but this time from the environment deemed most likely to be previously habitable, to host lithologies conducive to biosignature preservation, and to be accessible via current reasonably-priced robotic spacecraft.

The delta in western Jezero crater contains detrital material from two aqueously altered rock units that are part of a distinct stratigraphy in the Nili Fossae region (Ehlmann et al., 2008; Goudge et al., 2015), termed the basement unit and olivine-rich unit, which overlies the basement unit (Ehlmann and Mustard, 2012). The delta therefore has concentrated this material within a relatively small spatial extent, and NASA's Perseverance rover instruments are capable of analyzing material for biosignatures at sediment grain scales (Allwood et al., 2015; Beegle et al., 2015). Thus, while paleolakes are only one of many possible habitable paleoenvironments on Mars—including geothermally-driven hydrothermal systems (Ehlmann et al., 2009), hot springs (Ruff et al., 2019, 2011; Ruff and Farmer, 2016), or the deep subsurface (Michalski et al., 2018, 2013; Onstott et al., 2019; Tarnas et al., 2018)—the delta deposit will theoretically contain detrital material from any possible previously habitable environments preserved in the basement and olivine-rich rock units (Goudge et al., 2015). Therefore, it is a reasonably good target for maximizing chances of biosignature detection via collection of samples from a single site. If biosignatures are detected and unambiguously confirmed, then NASA's Mars Exploration Program will have accomplished a major scientific objective of space exploration. If biosignatures are not detected, or if the evidence is ambiguous, then the true outcome of NASA's Mars Exploration Program's astrobiological component will be in question. Some may claim that this outcome is effectively proof that life never existed on Mars, as the landing site deemed most likely to host biosignatures was devoid of any. A more accurate description of such an outcome is that life was not preserved in rocks from Jezero crater's paleolake, or in the basement and olivine-rich rock units, but could be fossilized in other rocks on Mars. In either scenario, NASA's Perseverance rover and Mars Sample Return missions, as

well as ESA's ExoMars rover, will be the only space missions with a reasonable chance of finding extinct life in the next decade based on the current search strategy.

2.2 Current strategy for extant extraterrestrial life detection

The Viking landers hosted the only extraterrestrial extant life detection instrumentation ever to be flown on spacecraft. Europa Clipper and Europa Lander are the only active missions that could reasonably be portrayed as focused on characterizing the possibility of extant extraterrestrial life. The Mars Reconnaissance Orbiter's Shallow Radar (SHARAD) and Mars Odyssey's Mars Advanced Radar for Subsurface and Ionosphere Sounding (MARSIS) cannot penetrate deep enough into Mars' subsurface to have a reasonable chance at detecting liquid water (Fois et al., 2007), though a controversial detection of a perchlorate-rich subsurface brine pocket ~1.5 km beneath the South Polar Cap has been claimed (Orosei et al., 2018). The High Resolution Imaging Science Experiment (HiRISE), Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), and Context Camera (CTX) primarily serve the function of characterizing ancient habitable environments from orbit. The Trace Gas Orbiter (TGO) on ExoMars could possibly be portrayed as having applicability to extant life, as it could detect metabolic gas byproducts from subsurface microorganisms, but the Curiosity rover has actually detected more gases of biosignature relevance (Webster et al., 2018; Trainer et al., 2019).

Europa Clipper and Europa Lander are effectively NASA's ocean world version of the Mars Reconnaissance Orbiter and Perseverance rover sequential mission approach. Europa Clipper will characterize surface morphology and mineralogy from global to fine scales, search the subsurface for brine pockets, and assess the physical and chemical processes operating in

the subsurface ocean (equivalent to a global groundwater table on Mars) (Phillips and Pappalardo, 2014; Bayer et al., 2018). Europa Lander would theoretically explore an accessible location deemed most likely to host biosignatures (Pappalardo et al., 2013; Hand, 2017), which could be preserved at >1 cm depth in mid-to-high latitudes, or >10-20 cm depth within radiation lenses on Europa's leading and trailing hemispheres (Nordheim et al., 2018). Because of the young age of Europa's ice shell (Zahnle et al., 2006; Pappalardo et al., 2017), any detected biosignatures of extinct life would present reasonably strong evidence for extant life in the subsurface. The same could be said for detection of extinct life in mineralized hydrothermal veins from a young (~10s Myr) impact on Mars (Carrier et al., 2020). While such a result is perhaps a satisfactory extant life detection for geologists and planetary scientists, it stops short of the potentially most interesting part of extraterrestrial extant life detection: characterizing extraterrestrial biological and chemical systems/mechanisms and comparing them to Earth-based life. For this reason, any extant life detection effort will eventually need to include subsurface drilling and liquid water collection. Whether the biological systems are investigated via instruments onboard spacecraft (more likely due to cost limitations) or are returned alive to Earth for laboratory analysis, determining their similarities and differences to Earth life is key to maximizing the scientific return of extant life discovery. This is true for extant life detection mission strategies to any extraterrestrial planetary object.

3.0 Optimizing the search strategy for extinct extraterrestrial life

3.1 Target selection criteria

Given finite budgets for space exploration, selection of optimal targets to investigate for extinct life is key to maximizing the likelihood of a positive detection. Jezero crater has been deemed the best target for extinct life detection on Mars, which is reasonable since it hosts detrital material from two aqueously altered Noachian rock units as well as possible authigenic material precipitated in Jezero crater's paleolake. However, if biosignatures are not detected in Jezero crater, this does not mean that life never arose on Mars, it would simply imply that no confirmable biosignatures were preserved in the basement and olivine-rich units of Nili Fossae, nor the Jezero crater paleolake. Because the largest, longest-lived, and most consistently habitable environment on Mars may be the deep subsurface (Michalski et al., 2013, 2018; Tarnas et al., 2018; Onstott et al., 2019), investigation of the diverse megabreccia blocks within the Nili Fossae basement unit (Scheller and Ehlmann, 2020) is potentially key to maximizing chances of biosignature detection by NASA's Perseverance rover. Including a sample of megabreccia within the collection would diversify the potentially habitable environments that are sampled. While there may be pieces of megabreccia within the sediment on the Jezero delta, it will be difficult to unambiguously determine the ultimate provenance of individual sets of sediment grains. In situ sampling of paleosubsurface martian material would greatly enhance the chances of positive extinct life detection.

Human searches for extinct life include a perhaps inevitable bias towards surface life due to the highly photosynthetic nature of modern day Earth (Michalski et al., 2018). Searching for extinct life on Mars, where photosynthesis may never have arisen, would perhaps be better suited to exploration of ancient habitable environments such as hot springs or other hydrothermal systems (including impact-generated hydrothermal systems), where redox

energy can be derived from water-rock interactions at a variety of temperatures (Michalski et al., 2018). Such systems are known to have existed on Mars under a variety of pH conditions – from highly acidic hydrothermal systems (e.g. the Ca-sulfate and jarosite vein precipitation episodes at Gale crater; Martin et al., 2017; Yen et al., 2017) to olivine weathering to carbonate under potentially alkaline conditions (e.g. formation of Comanche carbonate from alteration of Algonquin olivine; Morris et al., 2010; Ruff et al., 2014). Magmatically/geothermally/impact heated fluids with redox nutrients introduced by water-rock reactions are perhaps better targets for extinct life detection on Mars, though material from such systems could be concentrated in deltaic deposits if incised by fluvial channels.

4.0 Optimizing the search strategy for extant extraterrestrial life

4.1 Target selection criteria

The subsurfaces of planetary objects typically have higher habitability potential for Earth-like life compared to their respective surface environments. While transient habitable environments may have existed on Mars in the past (e.g. Grotzinger et al., 2014; Ruff and Farmer, 2016; Ruff et al., 2019), Earth-like life could not survive on the surface of Mars today without adaptation to multiple stressors (temperature, pressure, desiccation, oxidation, radiation) that is unprecedented on Earth (Carrier et al., 2020). Earth-like life can typically adapt to one or two environmental stressors. For example, *Deinococcus radiodurans* is resistant to radiative and oxidative stresses (Cox and Battista, 2005; Slade and Radman, 2011); hypothermophiles are resistant to low temperature stresses (Rivkina et al., 2000); and halophiles are resistant to low water activity stresses (Antón et al., 2000). However, adaption to

at least five major environmental stressors, each of which is harsher on the surface of Mars than in its most extreme manifestation on Earth, would be unprecedented by life on Earth (Carrier et al., 2020). This is also the case for the surfaces of every other object in the Solar System, excluding Earth, where conditions are some combination of colder, lower pressure, more desiccating, and/or more irradiated compared to Mars' surface. The lower cloud layer on Venus is a notable exception, as temperatures and pressures there are relatively moderate (~0-60 °C, 0.4-2 atm), redox species including sulfur compounds, iron compounds, and CO₂ exist, as well as likely liquid water aerosols (Carleton et al., 1997; Limaye et al., 2018; McGouldrick et al., 2011; Schulze-Makuch et al., 2004). As such, subsurface exploration represents the only feasible chance for extant life detection outside of Earth and perhaps the clouds of Venus. To optimize chances of extant life detection and maximization of scientific output from NASA's limited budget, extant life search strategies should follow a 3-pronged approach: 1) identify redox compound availability, 2) detect liquid water, and then 3) drill towards or into the liquid water.

Exploration of subsurface environments that are largely isolated from an atmosphere or the vacuum of space—a key factor for enabling habitability on a planet with an uninhabitable atmosphere or no atmosphere—is logistically difficult, even on Earth. This logistical difficulty is most often overcome by large budgets associated with either resource extraction or nuclear waste storage, though programs including the Integrated Ocean Drilling Program (IODP) and the International Continental Scientific Drilling Program (ICDP) notably access subsurface environments primarily for scientific purposes. Exploring the subsurface of another planet will therefore also present logistical challenges, but given sufficient funding, the technology to drill

~100 meters or more into an extraterrestrial subsurface environment could be flown in the next decade (Stamenkovic et al., 2020). Technology to detect brine pockets in the ice shell of Europa is currently being built for the Europa Clipper mission (Phillips and Pappalardo, 2014; Bayer et al., 2018), and transient electromagnetic sounding technology (Stamenkovic et al., 2020) for detection of deep groundwater reservoirs on Mars is at TRL 4. The optimal strategy for implementing subsurface liquid water detection/drilling to detect extant extraterrestrial life is an interplay between site characterization, landing/drilling operations logistics, and planetary protection. Physically drilling into a subsurface liquid water pocket, which may contain extant life, is currently a violation of NASA's Planetary Protection Office protocols (Office of Safety and Mission Assurance, 2011). As such, there are four different possible approaches to future extant life detection missions: 1) adjust NASA's Planetary Protection protocols to allow robotic spacecraft to contact liquid water; 2) improve sterilization to the point where no microbes exist on any liquid-water-contacting components of spacecraft; 3) develop mission architectures that can detect biosignatures of extant life without physically contacting liquid water; 4) detect extinct life in geologically young material and infer that life still exists within that planetary object. The advantages and drawbacks of each approach are outlined below.

1. Adjust NASA's Planetary Protection protocols to allow robotic spacecraft to contact liquid water. Planetary protection is an important component of NASA's exploration program, as it reduces risk of planetary objects being contaminated by Earth life, which could have unforeseen consequences including false positive extraterrestrial biosignature detection and/or interference with a native extraterrestrial biosphere (Office of Safety and Mission Assurance, 2011). Planetary protection is an interplay

between prioritization of scientific discovery versus contamination risk mitigation, as well as an exercise in calculation of risk tolerance. NASA's Planetary Protection office does not mandate that a spacecraft be completely sterilized before being sent to Mars, but rather that a maximum of 300 spores per m² be present on a spacecraft's exposed external and internal surfaces (Office of Safety and Mission Assurance, 2011). This inherently introduces a subjective risk tolerance threshold that derives from a combination of the limits of modern sterilization/microbial characterization technology, as well as an understanding that a relatively small number of Earth spores will have a difficult time propagating in the harsh conditions of Mars' surface. This implies that there may be a threshold of sterilization that is eventually deemed sufficient for a spacecraft to drill into liquid water reservoirs, though there is currently a "zero tolerance" policy for introducing Earth microorganisms into extraterrestrial waters (Office of Safety and Mission Assurance, 2011). Such a development in planetary protection policy would significantly simplify extraterrestrial extant life detection missions from a policy perspective. However, without complete, perfect, and absolute sterilization of the components of a spacecraft that contact liquid water, there will always be a substantial risk of contaminating an extraterrestrial biosphere. As human and robotic space exploration becomes more widespread, this contamination might eventually be inevitable in some locations if Planetary Protection enforcement is toothless.

2. Improve sterilization to the point where no microbes exist on any liquid-water-contacting components of extant life detection spacecraft. The ideal path forward for

detecting extant life is to improve sterilization technology to the point where an entire spacecraft, or at least the liquid-water-contacting components of a spacecraft, are completely sterilized. This is also the most logistically difficult path. Bacterial spores can survive for at least several years in the vacuum of space (Horneck et al., 1993; 1994), with exposure to UV radiation being the most effective sterilization component of the space environment. Exposing spacecraft to intense UV radiation on Earth will not guarantee that spores will not inhabit the spacecraft during integration with its cruise stage and launch vehicle, as well as during the launch process itself. Extant life detection spacecraft may need to be sterilized with UV radiation at a station in low Earth orbit via concentration of solar UV radiation using concave mirrors. While such a facility may have little practical use outside of sterilization, it is potentially the most effective way to guarantee full spacecraft sterilization, or sterilization of the liquid-water-contacting spacecraft components. However, even after nearly six years of exposure to unprotected space vacuum and solar UV radiation, 10^4 viable spores were recovered from the NASA Long Duration Exposure Facility (1-2% of the original number of spores; Horneck et al., 1994). It is therefore possible that concentration of solar UV radiation in low Earth orbit is insufficient to guarantee complete sterilization, and additional technologies/procedures must be developed before robotic spacecraft can safely contact extraterrestrial liquid water.

Humans will need to find a perfectly effective sterilization method that can be performed in low Earth orbit. Otherwise, we will either i) contaminate extraterrestrial liquid water by contacting it or ii) never access extraterrestrial liquid water and

therefore likely never directly sample extant extraterrestrial life. Scenario (ii) is unlikely to be perpetual if Solar System colonization occurs, as some entity will likely tap liquid water reservoirs eventually, whether or not sterilization technology has been perfected. It is interesting to consider whether sterilization technology might be the rate-limiting factor that prevents humans from directly sampling extraterrestrial extant life before much of it is contaminated, if it exists in the first place.

3. Develop mission architectures that can detect biosignatures of extant life without physically contacting liquid water. If a liquid water reservoir is characterized, but cannot be directly drilled into due to planetary protection or technology limitations, more creative methods for extant life detection must be implemented, such as characterizing gas gradients with depth, measuring organic molecules with complexities ranging from ethane to lipids, and measuring clumped isotopologues of gases such as CH₄. Measuring gas and organic molecule gradients with depth allows for extrapolation regarding the size and depth of the subsurface reservoir producing these compounds (Stamenkovic et al., 2020). This is the current framework for the Volatiles And Life: KeY Reconnaissance & In-situ Exploration (VALKYRIE) mission concept, which seeks to evaluate the habitability of the martian subsurface and search for evidence of extant life there without actually drilling into liquid water (Stamenkovic et al., 2020) that is expected in large reservoirs only at deeper depths on Mars than is feasible to drill to (Plesa, A.-C., 2020). This implementation of indirect biosignature detection—never physically sampling microorganisms, only their metabolic byproducts and former pieces of their cellular structures—requires multiple lines of reasonably strong evidence indicative of

extant life in order to claim discovery. An example suite of measurements that would constitute a “remote” Earth-like extant life detection includes CH₄ isotopologue measurements that are similar to those of microbially-derived CH₄ on Earth (Young, 2019; Young et al., 2017), sampling of complex molecule fluxes such as volatile lipids or amino acids, and gas gradient measurements that constrain the source locality for gas to the same depth locations that transient electromagnetic sounding or radar detects liquid water. If one or more of these measurements is lacking, and no additional evidence of extant life is found, it will be difficult to unambiguously identify an extant life biosignature. Furthermore, extraterrestrial extant organisms could not be directly sampled by this approach, which would make it difficult to evaluate the similarities and differences in their biochemical systems relative to those of Earth life.

4. Detect extinct life in geologically young material and infer that life still exists within that planetary object. This extant life detection strategy has recently been proposed for Mars (Carrier et al., 2020). Detecting recently extinct life may seem as impactful as extant life detection from a geologic perspective, but would not enhance our understanding of the variability in biological mechanisms and compounds possibly employed by life outside of Earth. Even a “remote” extant life biosignature detection would allow for analysis of metabolic byproducts and cellular molecular building blocks of extraterrestrial life. It is possible that relic, nonsilicified organic matter could exist in relatively young (<1 Gyr) extraterrestrial fossils, which could be analyzed for differences with Earth life, but the potential for alteration during the entombment process required to preserve fossils could alter the chemical characteristics of the analyzed biomaterial. As such, this search

strategy is the least satisfactory approach to extant life detection, though it is likely the simplest from an engineering and logistics perspective.

5.0 Final thoughts

Detection of extinct and/or extant life would be interesting from a planetary evolution perspective, specifically with respect to biological processes enhancing kinetic progression of geochemical systems towards thermodynamic equilibrium. While NASA's extinct life detection program is culminating in the Perseverance rover and Mars Sample Return missions, either a positive or negative biosignature detection outcome should not represent the end of astrobiological exploration of the Solar System. If biosignatures are detected, more intensified questions including comparison of origin of life settings for organisms on Earth, Mars, Europa, and/or other planetary objects should be undertaken. Testing of hypotheses regarding life as a fundamental phenomenon of information organization and transfer, rather than fundamentally a biochemical phenomenon, (Kim et al., 2019; Marshall et al., 2017; Walker, 2014; Walker et al., 2017, 2016; Walker and Davies, 2013) could also be evaluated through further sampling of potentially habitable worlds.

Jezero crater was selected as the landing site for NASA's Perseverance rover based on remote sensing observations of site morphology and mineralogy, which are inherently limited in their potential to definitively indicate the habitability of a given environment. There are many conditions in which carbonates and clays can form, some of which are habitable, some of which are not. If Earth were to lose its water and organic matter and be oxidized for billions of years, it would be difficult to discern/rank the habitability of regions containing hydrated

minerals via morphological and compositional remote sensing. If NASA's Perseverance rover does not detect life in Jezero crater, the possibility of it having existed in a variety of other settings on Mars including the deep subsurface, impact generated hydrothermal systems, or hot springs is still plausible. However, purely extinct life detection missions to Mars are unlikely to be funded after NASA's Perseverance rover and Mars Sample Return, thus future Mars missions will likely focus on deep subsurface exploration and couple extinct life exploration with extant life exploration. Extinct life exploration in every possible habitable environment on Mars will be a natural consequence of human colonization, which could plausibly occur in the next two decades. Perhaps we will be surprised by what we find on Mars during the course of human settlement.

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