

**Diffusion, Dissolution and Defects: The Application of Non-
Equilibrium Thermodynamics to Geological Materials**

Katherine D. Burgess

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in Geological Sciences at Brown University

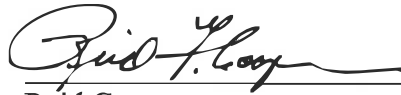
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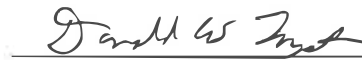
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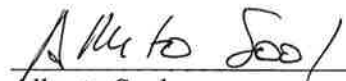
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- basaltic glass, *Geochemistry Geophysics Geosystems*, 11, Q10007, doi:10.1029/2010GC003248.
- Bowles, J., J. S. Gee, **K. Burgess**, and R. F. Cooper (2011), Timing of magnetite formation in submarine basaltic glass: a comparison of natural and synthetic samples with implications for geomagnetic paleointensity studies, *Geochemistry Geophysics Geosystems*, doi:10.1029/2010GC003404.
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- Burgess, Katherine**, Alberto E. Saal, Alison M. Koleszar, Eric H. Hauri, Yan Liang, Reid F. Cooper (2009). Melt Inclusions from the Galápagos Plume: Clues to the Origin of ‘Ghost Plagioclase.’ *AGU 2009 Fall Meeting*. San Francisco, CA, United States. (Oral presentation)
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CHAPTER 1

Introduction: An application of WHAT!?

“It is precisely through irreversible processes associated with the arrow of time that nature achieves its most delicate and complex structures.”

—Ilya Prigogine, Nobel Laureate [*The End of Certainty*, 1996, p 26]

The science chapters of this thesis, while covering a wide range of topics and systems, from oxidation of and diffusion in basaltic glass to dissolution of plagioclase in reaction with magma to formation and stability of extended defects in olivine, all explore the role of non-equilibrium thermodynamics in determining the textures, compositions and physical properties of minerals and rocks. This introductory chapter seeks to outline the common threads amongst the separate projects and explore the application of these ideas in igneous petrogenesis.

1. When Equilibrium Thermodynamics Fails

1.1. The Basic Idea

Understanding of thermodynamics begins with the First and Second Laws, which state, respectively, that energy is conserved, and there is a preferred direction for reactions that leads to the increase in entropy in the universe (or more pithily put, there is no such thing as a free lunch, and the house always wins). From these first principles, we can determine the equilibrium state of a system and derive the equations that lead to the Law of Mass Action, the Phase Rule, and Clapeyron's Equation, among others. Phase diagrams are a direct consequence of calculations based on these laws and equations—the number of phases, the variance, and the slope of phase boundaries in pressure-temperature (P - T) space are clear results. We can use the change in Gibbs free energy, $\Delta_r G$, of a reaction to determine whether or not the reaction will occur spontaneously (irreversibly), and partition coefficients predict equilibrium concentrations even for trace elements. Phase diagrams are used to represent systems where all components are at equilibrium—i.e., having the same P , T , chemical potential μ , and magnetic field B , among other thermodynamic potentials. However, phase diagrams, and equilibrium

thermodynamic calculations in general, are not used to inform us about the path taken to reach equilibrium, nor is there any information about texture (e.g., grain size, crystal morphology, phase spatial relationships) or how quickly reactions can take place. To understand what these characteristics tell us about a system, we need to think about the thermodynamics of irreversible processes and what happens when systems are held far from equilibrium by persistent forces.

When a system is near equilibrium, even though it is changing, we can estimate the final result of those changes by assuming the system equilibrates completely at infinitely small steps along a potential gradient. Large changes can take place where the overall process, such as cooling of a pluton, clearly results in an irreversible change in the energy of the system, but if the driving forces or gradients remain small, equilibrium thermodynamics is well suited to inform us of the phases present, their modal abundances, and their compositions. Even zoning in crystals, which occurs when crystal growth is so rapid that diffusive exchange between the crystal and melt cannot keep up and the core of the crystal is no longer in chemical equilibrium with the fractionating melt, is easily reconciled to the equilibrium phase diagram.

This approach, however, does not capture the complexity present in real systems, where driving potentials often exceed the conditions under which near-equilibrium processes can be maintained. All of thermodynamics is concerned with the minimization of free energy, but where equilibrium thermodynamics shows us what a system looks like in its lowest free-energy state, non-equilibrium thermodynamics allows us to study which fluxes (e.g., heat, mass, current) or reactions can dissipate state differences in energy (i.e., thermochemical driving potentials) most rapidly. It is through nature “selecting” (that is,

through atomic-level sampling by random thermal vibration) the steepest $\Delta_r G/dt$ —regardless of the final free-energy state—that various textures arise and can be understood. Many important features present in earth materials commonly studied are metastable at best, and often have little resemblance to the equilibrium state of the system. Important geological processes include many examples of large driving potentials, from thermal and chemical potential gradients during eruptions, melt-wall rock reaction, magma mixing, and weathering to almost instantaneous post-seismic stress relaxation.

1.2. An Example



Figure 1.1: A typical pahoehoe lava flow, showing a top lava lobe covering an earlier emplaced bottom lobe, from Kilauea. From *Burkhard* [2003].

When a subaerial, basaltic volcanic eruption occurs, as in Hawai'i, very hot ($\sim 1200^\circ\text{C}$), relatively reduced (approximately the quartz-fayalite-magnetite—QFM—buffer for oxygen) lava comes abruptly into contact with the ambient atmosphere ($\sim 22^\circ\text{C}$, humid, highly oxidizing). A glassy quench rind rapidly forms at the surface of a lava flow, while the degree of crystallization and size of crystals increases with depth from the air interface. Repeated flows in the same place cause reheating of the original lobe and

slower cooling as more material is emplaced above [Burkhard, 2003; Fig. 1.1]. The resulting lobe-interface and lobe surface texture bears little resemblance to the interior of the flow or intrusive rocks of the same initial composition.

Notably, the interface between two lava lobes has been observed to have a reddish-brown surface film indicative of Fe-(hydr)oxides [Burkhard and Muller-Sigmund, 2007]. The precise composition of the film, which is generally enriched in Fe and also Mg and Ca, depends not only on the initial composition of the material, but also the temperature to which it was reheated and the length of time an elevated temperature was maintained. The formation of such a film has no straightforward explanation if approached from an equilibrium thermodynamics perspective. However, eruptions of basaltic lava are among the clearest examples of extreme, abrupt changes in thermodynamic potentials affecting geologic materials, and all processes occurring during and after eruption, including glass formation, nucleation, and grain growth, are impacted by resulting potential gradients and play a role in the processes leading to the cation-enriched film being produced.

Experiments on synthetic Fe^{2+} -bearing silicate glasses and melt, as well as natural basalt, have recreated the conditions of oxidation that occur upon eruption and help to elucidate the processes occurring in the creation of the film [Cooper *et al.*, 1996a,b; Cook and Cooper, 2000; Smith and Cooper, 2000; Burkhard, 2003; Burkhard and Muller-Sigmund, 2007; Ch. 2 of this dissertation]. Although it might be expected that a gradient in oxygen chemical potential would lead to the diffusion of oxygen, either molecular or ionic, into the glass or melt, observations show clearly that this cannot be the dominant reaction; cation depletion of the sample at depth, the source for the enriched layer at the

surface, serves to increase the oxygen to cation ratio in the oxidized region. Thus, the reaction that has the largest $\Delta_r G/dt$, and therefore dissipates the energy most rapidly, must be cation migration. But why does the film composition change with time and temperature, and what can the process tell us about cation mobility and glass or melt (molecular) structure? In the following sections, I will introduce the basic concepts in non-equilibrium thermodynamics (NET) then return to examine the problem of dynamic oxidation of basalt in more detail.

2. Introducing Non-Equilibrium Thermodynamics

2.1. Starting from the Phase Diagram

While the ability of a T - X equilibrium phase diagram to predict the way a system will behave becomes more limited in systems responding to large driving forces, G - X phase diagrams help illustrate how the large magnitude of change in free energy with, e.g., a large degree of undercooling can allow for metastable states. As the simple example below shows, many different reactions can take place in addition to the equilibrium one represented in the T - X diagram. These diagrams alone, although instructive, do not contain the information necessary to determine which reactions take place. We must combine this knowledge of the thermodynamics with the phenomenology in order to make a full, correct interpretation of the processes leading to the observed compositions and textures.

Here we examine the Pb-Sn binary phase diagram using both the equilibrium T - X diagram and G - X diagrams at two different temperatures (Fig. 1.2). When the system—assume the homogeneous liquid alloy of the eutectic composition, $X_{\text{Sn}} = 0.735$ —is brought slowly from high T to just slightly below the eutectic temperature T^{eu} , the driving

force for solidification, $\Delta_r G$, remains small and only one reaction state is accessible to the system, specifically that of the α - β eutectic with each solid having its equilibrium composition (Fig. 1.2b; ΔG^M is the integral Gibbs free energy of mixing). (The texture of the system depends on interfacial energy amongst the two crystalline and liquid phases, the liquid-solution entropy and the rates of diffusion of the different components—here Pb and Sn—in the liquid [e.g., *Hunt and Jackson*, 1966; *Crocker et al.*, 1973].) If instead the degree of undercooling is large, the final product may contain phases created through reactions other than the equilibrium eutectic reaction (Fig. 1.2c). Both Reaction A, which creates a single α phase with the bulk composition (dashed tangent), and Reaction B, a two-phase assemblage with both phases having the β structure (dotted tangent), are accessible reactions. A homogenous glass is also possible. These are metastable states, all of which *can* occur because they lower the free energy of the system. The key to understanding which of the possible reactions do happen lies in the rate of energy dissipation Θ .

Figure 1.2: T - X phase diagram and associated ΔG^M - X diagrams at different T for the binary Pb-Sn system at ambient pressure, constructed using computer program WinPhaD (CompuTherm LLC). (b) For the eutectic-composition liquid, denoted by the star, at the eutectic temperature, T^{eu} , only one reaction—equilibrium eutectic solidification of the liquid solution to the α and β solid-solution alloys—is possible. (c) As undercooling increases—here an example of an undercooling of $\sim 123\text{K}$ below T^{eu} —other reactions become possible for solidification of the liquid of eutectic composition, e.g., a single α phase with the bulk composition (Reaction A; dashed tangent), or a two-phase assemblage both with the β structure (Reaction B; dotted tangent) or even a homogeneous glass. (The equilibrium reaction (dot-dot-dash line) is possible, too, of course.) The metastable states are made “available” by a large $\Delta_r G$. All of these states *can* occur—each lowers the free energy; which one(s) do(es) occur is a function of the energy dissipation rate Θ .

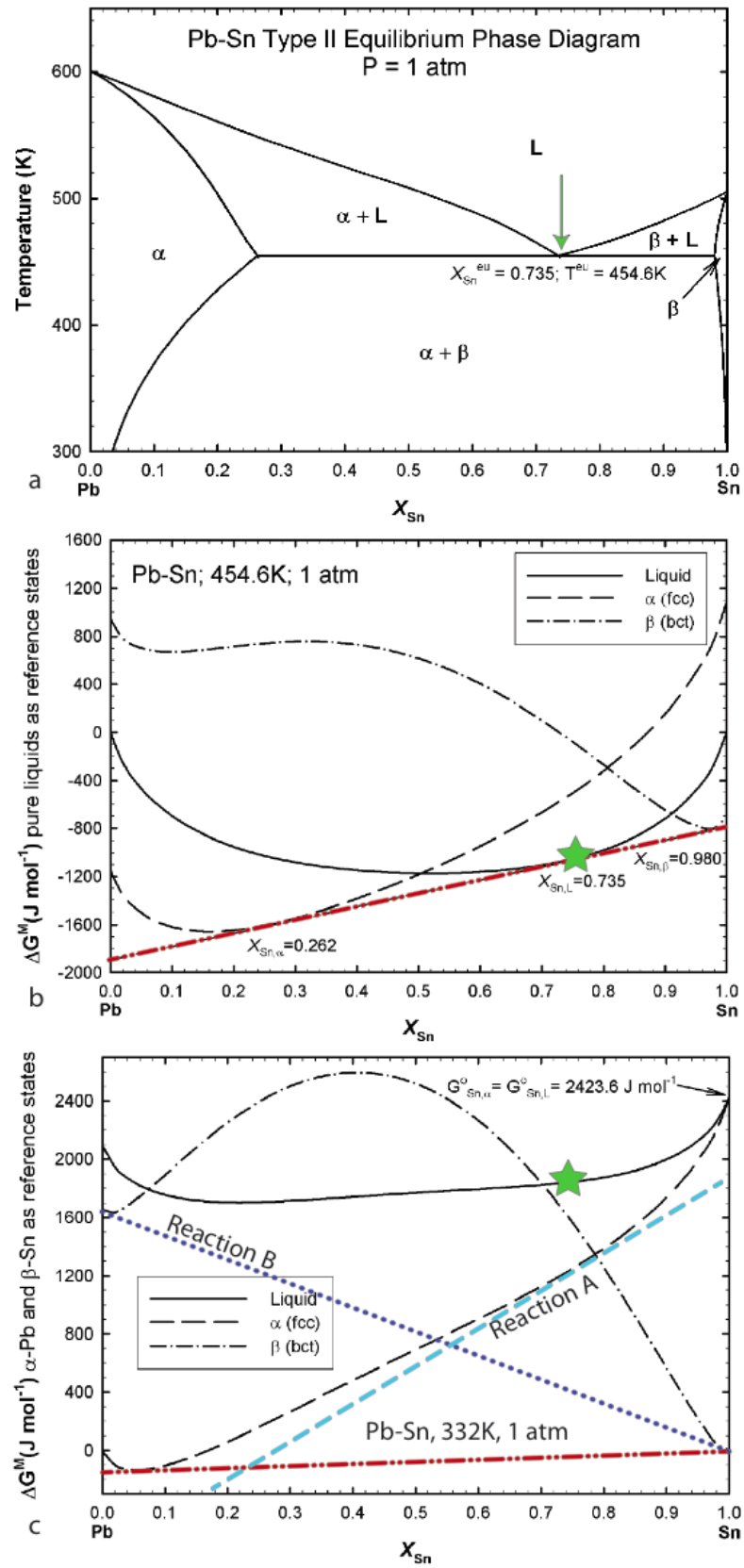


Figure 1.2

2.2. Energy Dissipation

When two otherwise identical blocks at different T are placed next to each other in an isolated system, they will both change T until the system is uniform. The amount of heat being transferred to the low- T block is equal to the heat being lost from the high- T block (1st Law). The change in entropy by volume for the system over the time increment dt is the change in heat dq per volume V multiplied by $1/T_1 - 1/T_2$ (with $T_2 > T_1$); we know $dS_{system} > 0$ (2nd Law). Because the temperature difference between the two blocks is greatest at $t = 0$, so too is the volumetric rate of entropy production, dS_{system}/Vdt . Alternatively, starting from Fourier's Law, we can show that the entropy-production rate is a function of the temperature gradient dT/dx . Recognizing that the total dissipated energy is calculated by multiplying entropy by temperature (cf. $\Delta G = \Delta H - T\Delta S$), we get the volumetric energy dissipation rate

$$\Theta = T\sigma = -\frac{Q}{T} \frac{dT}{dx} \quad \left(\text{units } \frac{\text{J}}{\text{m}^3 \text{s}} = \frac{\text{W}}{\text{m}^3} \right), \quad (1)$$

where σ is the volumetric entropy production rate ($\text{J}/(\text{m}^3 \text{Ks})$) and Q is heat flux ($\text{J}/(\text{m}^2 \text{s})$). Θ is thus revealed to be a function of the thermodynamic driving force, which in this case is the (negative, because heat flows toward lower temperature) temperature gradient normalized by T , times the flow rate, here heat flux. The same relationship amongst equations holds for those irreversible processes (e.g., diffusion, electronic conduction) described by a flux (e.g., matter, current) and a force or gradient in an intensive thermodynamic variable (e.g., chemical potential – $d\mu/dx$, electrical potential – $d\phi/dx$) [Devereux, 1983, ch. 13; Schmalzried, 1995, ch. 4; Zhang, 2008, p562]. “Fluxless” reactions, such as attachment-limited crystal growth, also dissipate energy, but

dimensional analysis highlights different quantities. The total energy dissipation rate is a sum of all processes, and at equilibrium, it is zero. When the driving force is small, the energy dissipation rate is small also, to the point of approximating equilibrium at the macroscopic scale.

2.3. Activation Energy

An important parameter in determining how likely and how rapidly a process can occur, and thus its ability to dissipate excess energy, is the activation energy E_a . (A related parameter, the activation volume, becomes important for processes occurring at high pressures; this can be important in geologic processes occurring at depth, but V_a is not dealt with further here.) A specific amount of energy input is required in many cases for a reaction to occur; for instance, bonds in a molecule must be broken before new bonds can be formed to create a new molecule. Processes such as these occur at rates proportional to the exponential of T , allowing the logarithm of the rate constant to be plotted as a linear function of $1/T$ (i.e., on an Arrhenius plot). The rate constant, and thus the slope of such a line, is a function of E_a , that is, the amount of energy required for a system to reach a state from which it can again lower the energy. E_a can therefore be determined by running a set of experiments at various temperatures. Fig. 1.3 illustrates schematically the effect of E_a when there is a driving force present (here, $\Delta_r G/\lambda$), such as a chemical potential gradient driving diffusion through a crystal lattice.

Figure 1.3: There is an activation energy E_a associated with processes such as chemical diffusion, as illustrated schematically here. The bias, or driving force, which here represents a chemical potential gradient (i.e., $\nabla G = \Delta_r G/\lambda$ where λ is the spacing between equivalent ion sites), gives a $\Delta_r G$ for the total reaction or diffusion step, while E_a represents the energy needed for an ion to move out of a potential energy well or minima associated with a specific lattice site.

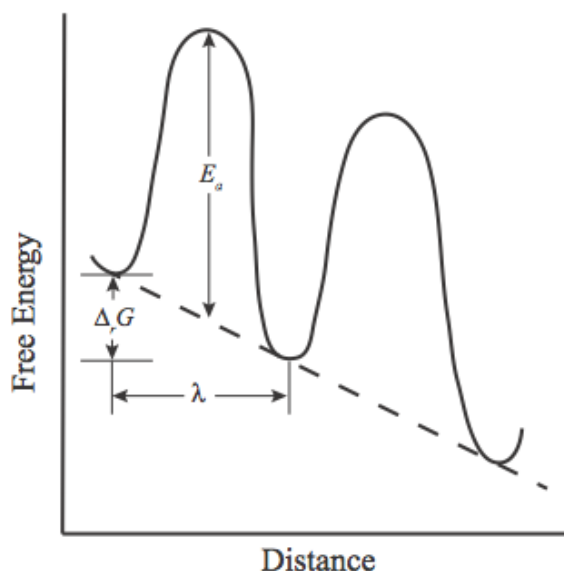


Figure 1.3

Statistical mechanics provides a link between micro-scale, molecular-level processes and macro-scale thermodynamic properties such as heat, work, free energy and entropy. For a large number of particles in thermal equilibrium, there is an average energy associated with those particles, and individual particles can have an energy either smaller or larger than that average energy; Boltzmann statistics provides a description of how those individual particles are distributed amongst different energy levels [McQuarrie and Simon, 1997, p711]. The quantity $k_B T$, where k_B is Boltzmann's constant and is equal to the gas constant R divided by Avogadro's number N , has units of energy per molecule and is on the order of that average energy; it is close to the available thermal energy associated with a motional degree of freedom [Schmalzried, 1995, p95]. Thus if the energy required for a particle to change states (e.g., location in the chemical diffusion schematic of Fig. 1.3), that is, the activation energy, is much larger than $k_B T$ (or RT if the measurements involve molar quantities) the likelihood of the process occurring is low. The form of $\exp(-E_a/RT)$ can be thought of as proportional to the probability of a certain process happening, and as T increases, so does the likelihood of the reaction. It is the

required positive activation energy that can prevent even spontaneous reactions (i.e., $\Delta_r G < 0$) from running away or going to completion. Without the activation energy necessary for processes such as oxidation and combustion of many organic molecules, spontaneous human combustion would be more than a conspiracy theory. (Luckily for us, the activation energy for such processes is actually quite high.)

If the Gibbs energy change of each elementary step of a single atomic particle or molecule is much less than the average thermal energy per particle (i.e., $\Delta_r G \ll RT$ for molar quantities) [Schmalzried, 1995, p5], local equilibrium is maintained. Within the confines of local equilibrium, the linearity of the phenomenological laws discussed below holds and reactions are reproducible even given large driving forces.

2.4. Phenomenological Laws

Although the physical direction of, for example, electric current through a conductor, and the energy dissipated by the process are determined based on the electrical potential gradient, the phenomenological law that describes electrical fluxes (i.e., Ohm's Law) cannot be derived directly from the first and second laws of thermodynamics. In the general form of such "laws," the flux is defined by the thermodynamic driving force multiplied by a transport coefficient L ; other examples include Fourier's Law for heat flow and Fick's First Law for mass diffusion. When n irreversible processes are occurring, the flux of each process is a function of all forces, combined in an $n \times n$, symmetrical matrix $\mathbf{L}$. Thus, in general, the rate of energy dissipation is

$$\Theta = T\sigma = \sum_i J_i X_i = \sum_i \sum_j L_{ij} X_i X_j \quad (2)$$

where J_i is the flux and X_i is the driving force of process i [Devereux, 1983, ch. 13]. Near equilibrium, the cross-terms can often be neglected, but when persistent forcings are

present, they can be significant and either positive or negative; the diagonal terms are inherently positive. An example of large cross-terms is the Soret effect, which is created by the effect of a temperature gradient on diffusion of matter; in a simple system, like a solid Cu bar, vacancies are created at the hot end, leading to a concentration, and thus chemical potential, gradient. The vacancies will therefore diffuse toward the cold end while the flux of Cu will be toward the hot end. Thermocouples work based on a thermal gradient creating a voltage as electrons diffuse from the hot end to the cold end in wires of two different compositions. Even when the only process being examined is diffusion of matter, the interactions between components in a multi-component system can lead to “uphill” diffusion as the chemical potential of one component can strongly affect others [Zhang, 2008, p221]. A notable result from Eq. 2 is that Θ is proportional to the *square* of the driving force times the transport coefficient. Thus, the harder a system is pushed, the more the entropy production rate is accelerated.

2.5. The Transport Coefficient

Diffusion of matter is an important processes acting in geologic materials and is fundamental in determining the textures and compositions discussed in all of the chapters of this thesis. The process can be difficult to understand and analyze, because the driving force is not a negative gradient in concentration (the classical description of Fick), which is relatively simple to measure, but rather a negative gradient in (electro-)chemical potential (the contribution to the study of classical physics by Einstein). Minerals of very different composition, and thus having different concentrations of each component, can still be in chemical equilibrium.

Because Fick's First Law is defined in terms of concentration, the diffusion coefficient D_i is not the transport coefficient as used in Eq. 2. Using the relationship between concentration c_i , activity a_i and chemical potential μ_i of a component i , we can determine the transport coefficient for diffusion, sometimes called the Onsager coefficient, and defined

$$L_i = \frac{c_i D_i}{RT}. \quad (3)$$

This coefficient provides the link between the chemical potential gradient and the flux. The diffusion coefficient normalized by RT (i.e., D_i/RT) is the (Einstein) mobility. Importantly, comparing Eqs. 2 and 3, one sees that the energy dissipation rate for reactions rate-limited by chemical diffusion is linearly related to the concentration of the mobile species. One can concentrate an analysis either on the motion of atoms/ions or on the motions of point defects.

Ion mobility within a crystal lattice is proportional to the concentration point defects, their jump frequency, and the associated activation energy; point defects are present in all crystals above absolute zero. For vacancy diffusion, which occurs in the absence of a driving force (i.e., random walk)

$$D_{\text{Fe}^{2+}} = \frac{1}{6} \lambda^2 \Gamma [V_{\text{Fe}}^{\prime\prime}], \quad (4)$$

where λ is the nearest-equivalent-site atomic spacing (e.g., for diffusion in wüstite from one VI site to an adjacent one), $[V_{\text{Fe}}^{\prime\prime}]$ is the concentration of vacancies (i.e., the probability that the nearest-equivalent-site is filled by a vacancy), the factor of $1/6$ is used for 3-dimensional, isotropic diffusion, and Γ is the jump frequency

$$\Gamma = \Gamma_0 \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where Γ_0 is the frequency of lattice vibrations (approximated well by $k_B T/h$, where h is Planck's constant; the value is $\sim 10^{13} \text{ s}^{-1}$ at 300K) and E_a is the activation energy for the jump between equivalent lattice sites [Kingery *et al.*, 1976, ch. 6]. The dependence of mobility, and thus the transport coefficient, on the concentration of vacancies in a crystal illustrates the importance of all thermodynamic potentials in determining the energy dissipation rate, even when only one process is being scrutinized. In ferromagnesian olivine, for example, [V] for all of the component species, i.e., vacancies on the $\text{Si}_{\text{IV}}^{4+}$, $(\text{Mg,Fe})_{\text{VI}}^{2+}$ and O^{2-} sites, are dependant on T and oxygen fugacity f_{O_2} (as well as on a_{SiO_2}) [Hirsch and Shankland, 1993]; thus if olivine is exposed to more or less oxidizing conditions, the mobility of all species will be changed in most cases of lattice diffusion.

3. NET Application

The question in non-equilibrium thermodynamics is less “what is happening?” (although that is important), and more “what is happening *most*?” As noted for the dynamic oxidation of basaltic glass presented above, we cannot understand the texture based on what might be the expected reaction knowing that a change in oxygen chemical potential creates the driving force. In fact, not only are many oxidation reactions accessible, at least three separate modes of oxidation are actively occurring. Knowing this tells us very little about a system, and only with additional information, for example, about the chemistry and/or phases constituting the cation-enriched surface film, can we determine what mechanism allows for the greatest energy dissipation rate. Using the concepts from NET, we can now discuss the above example in much more detail.

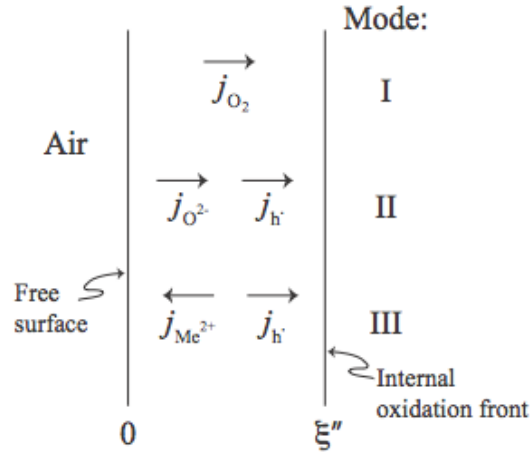


Figure 1.4: Schematic illustrating the modes of oxidation of $\text{Fe}^{2+,3+}$ -bearing glass. Oxidation occurs in the region between the free surface ($\xi = 0$) and the internal oxidation front ($\xi = \xi''$), where Fe^{2+} is changing to Fe^{3+} and the structure of the glass is altered, through several modes. One mode will dominate the reaction, depending on thermodynamic ($T, \Delta\mu_{\text{O}_2}, X_{\text{FeO}}$) conditions. In nepheline- or leucite-normative and/or high-T melts, the transport coefficient for alkalis can match or exceed that of holes, so that they diffuse inward to charge balance divalent cations and act as the “agents” of flux decoupling [Pommier *et al.*, 2010; Pommier *et al.*, 2008].

The key driving force in the formation of the cation-enriched layer is the extreme oxygen chemical potential gradient: at eruption, there is a difference in the f_{O_2} of close to seven orders of magnitude between the lava and air. Several different responses are possible to reduce this driving force and oxidize the basalt, as noted in Chapter 2 of this dissertation and other work by the Cooper lab, and illustrated schematically in Fig. 1.4. Oxidation of Fe^{2+} -bearing glass or melt can occur through three diffusion mechanisms or “Modes”: I) molecular oxygen diffuses into the material; II) ionic oxygen diffuses into the material, charge balanced by inward flux of electron holes ($\text{h}^\bullet$; that is, charge transfer from Fe^{3+} to Fe^{2+} that occurs in the valence band of the nonmetallic, amorphous material); III) network-modifying cations diffuse toward the free surface, charge balanced by inward flux of $\text{h}^\bullet$. The high mobility and high concentration of $\text{h}^\bullet$ leads to the “semiconductor condition,” where an electrochemical potential gradient for the

electronic species cannot be established, and the ionic fluxes are decoupled from each other electrically. When heterovalent cations are not present in the starting material or their concentration is too low, Modes II and III cannot function.

For basaltic glass and melt (and synthetic analogues), the dominant mechanism for oxidation is Mode III, or diffusion of network-modifying cations to the surface compensated by electron-hole migration [Cooper *et al.*, 1996a,b; Smith and Cooper, 2000; Cook and Cooper, 2000; Burkhard and Muller-Sigmund, 2007; Ch. 2 of this dissertation], as illustrated clearly by the cation-enriched film found on basalt lobes as described above. Rather than oxidizing the interior of the basalt lobe or experimental sample through addition of oxygen, the material up to the internal oxidation front instead is depleted in cations by their migration to the free surface while Fe at depth changes from ferrous to ferric through the inward motion of electron holes. Complexity is added by changes in cation diffusivity with temperature and devitrification of glassy material altering cation availability [Cooper *et al.*, 1996a; Cook and Cooper, 2000; Burkhard, 2001; Ch. 2 of this dissertation].

Understanding the response of a basaltic melt or glass to a chemical potential gradient for oxygen requires examination of the transport coefficients for each chemical component. For general Mode III oxidation, $[c_h \cdot D_{h\cdot}] \gg [c_{M^{2+}} D_{M^{2+}}] \gg [c_{O_2} D_{O_2}]$ and $[c_{O^{2-}} D_{O^{2-}}]$, that is, the large transport coefficient of $h\cdot$ leads to the semiconductor condition and divalent cation migration controls the reaction rate and texture. Although aforementioned experiments show the same basic texture and surface reaction (i.e., Mode III oxidation and cation-enriched film formation), the differences between specimens illustrate the power of NET to link phenomenology with thermodynamic parameters.

The applied thermodynamic driving force is the same regardless of the components, thus it is the flux of each component—and their relative dependence or independence—that determines which dominates the system, i.e., which dissipates the energy most rapidly. Because the activation energy for diffusion varies amongst species, so does the overall response with changes in temperature. Additionally, the effect of concentration on the response is important, as noted in the analysis of the transport coefficient above. For example, at very high alkali concentration the transport coefficient of Na^+ can match or exceed that of holes (i.e., $[c_{\text{Na}^+} D_{\text{Na}^+}] \gg [c_{\text{h}} \cdot D_{\text{h}} \cdot]$), so that the cation rather than the electron hole acts as the “agent” of flux decoupling [Pommier *et al.*, 2008; 2010]. Even for Mode III oxidation, it is not necessarily the most rapidly diffusing cation that controls the reaction; a more slowly diffusing cation may make fewer “steps” within a certain amount of time, but if the energy dissipated per step is much larger, the dissipation *rate* Θ for that mechanism may also be larger [e.g., Cooper *et al.*, 2010]. It is only through the lens of non-equilibrium thermodynamics that we can effectively analyze the forces and fluxes and how they contribute to energy dissipation in the system.

4. Introduction to Science Chapters

As has become apparent throughout this introduction, the process that dissipates the energy most rapidly dominates the reacting system and creates the macro-scale texture that we are able to see and analyze for reaction dynamics. Each chapter in this thesis focuses on a different dynamic, non-equilibrium process taking place in geological materials and attempts to improve our understanding of not only the *how* but also the *why* of each texture.

4.1. Dynamic Oxidation of Basaltic Glass

Chapter 2 presents experiments on the oxidation of basaltic glass and demonstrates the formation of a cation-enriched film on the surface of specimens as well as metastable spinodal decomposition of the glass at a very fine scale. Basaltic glasses are often used in paleomagnetic studies, as they host titanomagnetite grains in the size range of 10s to 100s of nanometers, which are in turn able to record the ambient magnetic field at the time of their quench. However, because of the non-equilibrium composition of the titanomagnetite grains and the tendency of glass to devitrify over geologic time scales, there is ongoing debate about how the nanometer-scale grains form and how old are the oldest glasses that reliably record accurate paleomagnetic signatures. The experiments were designed to assess the role of dynamic oxidation in creating or changing the magnetic signature of submarine basaltic glass, as the process can lead to internal nucleation of ferrites [Smith and Cooper, 2000]. The open-system dynamics and the application of NET have been discussed in detail above, and a schematic of the reaction is presented in Fig. 1.5.

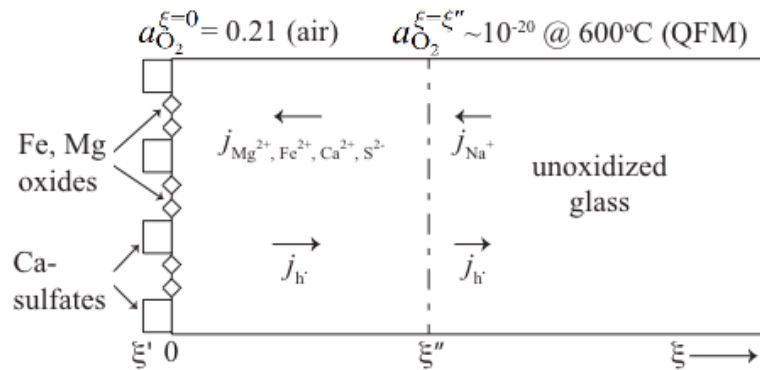


Figure 1.5: This schematic illustrates the dynamics of oxidation seen in basaltic glass and reported in Chapter 2. Mode III oxidation leads to formation of an oxide and sulfate film at the free surface ($\xi = \xi'$) as cations migrate from the oxidized region of the glass in response to the oxygen chemical potential gradient. A structural change in the glass occurs at the internal oxidation front ($\xi = \xi''$), where Fe^{2+} is changed to Fe^{3+} . Na^+ migrates from deeper in the glass and prevents internal nucleation of ferrites.

In addition to formation of a cation-enriched film, as noted in the analysis above, the open-system oxidation involves an accompanying increase in Fe^{3+} within the oxidized region that raises the Fe_2O_3 activity and can effect the internal nucleation of ferrites [Smith and Cooper, 2000], a reaction that would alter the magnetic signature of the material. In the samples described here, however, Na^+ is seen to migrate from depth to the oxidized region, which alters the glass structure and, thus, decreases the Fe_2O_3 activity such that internal nucleation of crystalline ferrite does not take place. As such, the oxidation of the glass at low temperature had no effect on the magnetic signature. However, the closed-system dynamics demonstrate the metastability of the glass phase; the energy input of an electron beam provides enough energy for metastable, amorphous-phase spinodal decomposition to proceed and the texture to coarsen. Ti^{4+} , Fe^{2+} and Fe^{3+} partitioning between the decomposed glass phases contribute to a range in ferrite compositions that would not be at equilibrium. This is consistent with observations of natural submarine glasses from, e.g., pillows [Zhou *et al.*, 1997; Zhou *et al.*, 2000].

4.2. Changing Melt Composition Through Non-Equilibrium Reactions

Dynamic diffusion-dissolution-precipitation processes occurring within lower-crustal mush zone are the focus of Chapter 3. The timescale over which interaction between a primitive melt and an evolved cumulate mush zone takes place is important in determining the erupted lava composition, and many variations in composition are theoretically possible. Starting from conditions far from equilibrium, made possible by the injection of hot, compositionally different magma into the system, crystal growth and dissolution, as well as diffusion in the melt and diffusion in the solid all contribute to the dissipation of energy and thus the final composition, texture, and microstructure of the

phases present. Fig. 1.6 [from *Liang, 2003*] shows the increase then decrease in melt fraction possible due to slow diffusion in the solid relative to the liquid. The significant solid solution of many geologically important minerals, including plagioclase (anorthite and albite), creates a situation where the solid can be “over-dissolved” by the melt and the melt fraction and composition can go through large variations before settling on the equilibrium state.

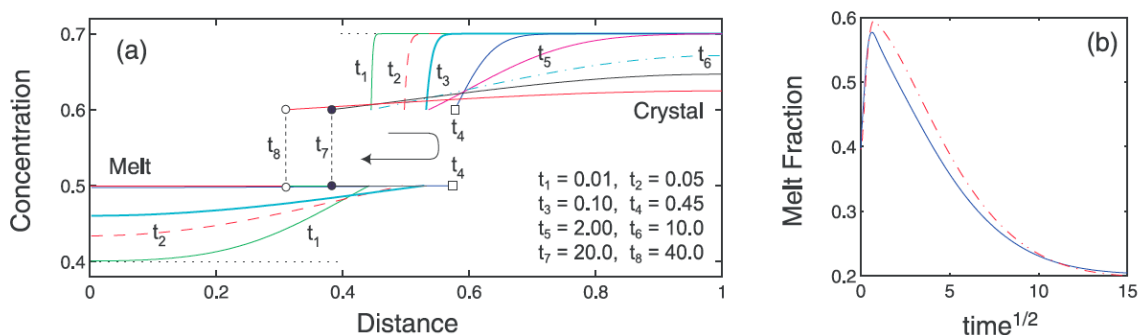


Figure 1.6: (a) Model composition of a crystal and melt in a binary system with solid solution illustrating the effect of diffusion in the melt and solid and the change in interface location due to first, over dissolution of the crystal, then reprecipitation of the equilibrium crystal. (b) The melt fraction through time for the system in (a), showing the increase then decrease in melt fraction. The starting melt fraction is 40% and the equilibrium melt fraction is 20%. From *Liang [2003]*.

A decoupling between major and trace elements has been noted in several ocean island basalts, where among a set of samples that have similar major element compositions, the trace element compositions instead indicate varying levels of interaction with a plagioclase-bearing cumulate, specifically through the presence of a large Sr anomaly. This ‘ghost plagioclase’ signature has been attributed to the presence of eclogite in the source mantle where the melt is far from plagioclase saturation [*Sobolev et al., 2000*]. Other authors have suggested that grain-scale reactions with lower-crustal cumulates, including diffusion and dissolution as well as precipitation of an aluminous phase such as spinel, could create the observed anomalies [*Gurenko and Chaussidon,*

1995; *Danyushevsky et al.*, 2003, 2004; *Gurenko and Sobolev*, 2006; *Saal et al.*, 2007].

The model presented in Chapter 3 demonstrates the creation of a positive Sr anomaly and ‘ghost plagioclase’ signature in melt as it interacts with evolved, enriched plagioclase-bearing cumulates and reprecipitates more primitive plagioclase.

4.3. Extended Defects Formed Due to Extreme Chemical Potential Gradients

Chapter 4 describes the formation of extended planar defects in olivine, driven by very large gradients in chemical potentials between a TiO₂-doped basaltic melt and an olivine grain lacking sufficient Ti⁴⁺ to be in equilibrium with that melt. Because the difference in initial a_{TiO_2} between the two materials in the diffusion couple is so large (several orders of magnitude), the driving force for the insertion of Ti⁴⁺ into the olivine lattice allows initial formation of an ordered-defect superstructure instead of free (i.e., unassociated) point defects. The extended planar defects that form the superstructure, identifiable in high-resolution transmission electron microscope (HRTEM) images, are transient and dissolve into the regular olivine lattice as the chemical potential gradient decreases, both with Ti⁴⁺ incorporation distance into the crystal and with time.

The extended defects can effect rapid diffusion into the olivine at rates much higher than expected for lattice diffusion, as, within the planar defect, both the concentration and mobility of Ti⁴⁺ are enhanced. The experiments recreate the driving forces present in a recent study of rare earth element (REE) diffusion in olivine [*Spandler and O'Neill*, 2010]; the measured diffusivities in the experiments by Spandler and others [2007; 2010] were 3-4 orders of magnitude faster than both in other experiments also purporting to measure REE diffusivity in the olivine lattice [*Cherniak*, 2010] and in previous theoretical work [*Qin et al.*, 1992; *Cottrell et al.*, 2002]. Chapter 4 presents

evidence of titanomagnetite nucleating in the interior of olivine grains at conditions (specifically oxygen activity) where olivine should be stable; the titanium present increases the activity of the spinel phase and allows for the nucleation to proceed. The rapid diffusion of highly charged cations including Ti^{4+} (on the order of Fe-Mg interdiffusion, similar to that measured by *Spandler and O'Neil* [2010]) related to the formation of Ti-rich extended defects in olivine has strong implications for problems such as assessing the fidelity of melt inclusions. Phenocrystic olivines that host melt inclusions can be subjected to large changes in surrounding melt composition and thus intense chemical potential differences (and, thus, gradients); whether or not ordered defect superstructures form would change how rapidly the inclusion re-equilibrates.

5. Beyond This Dissertation

Perfect equilibrium is a pretty boring state—nothing obvious happens at a macroscopic level. Fortunately for us (as scientists and as living beings), equilibrium is a rare state indeed. Gradients in thermodynamic potentials (e.g., in T or in μ) are present that lead to flow of heat or material, and just as a river looks very different raging down a mountain versus flowing over a plain, the magnitude of a thermodynamic potential gradient controls how a system will change. A lot of information is lost if we do not take into account how energy dissipation rate Θ and the driving forces that influence it affect reaction mechanisms and final textures. While application of non-equilibrium thermodynamics is clearly necessary to interpret and understand correctly the processes occurring in the dynamic systems described in this chapter and in more detail in the science chapters of this dissertation, which involve chemical-potential-difference driving forces at nominally isobaric, isothermal conditions, these are far from the only processes

important in igneous petrogenesis. In most processes, heat flux and the rate of temperature change or degree of undercooling is the primary driving force determining the texture and internal compositional variation of a rock; obsidian, rhyolite and granite appear nothing alike, but vary only in cooling rate. By comparing thermal diffusivity to chemical diffusivity and reaction rates, we can estimate from grain size and mineral zoning in a dike, for instance, how long the dike took to cool and what the temperature of the host rock must have been at the time of injection. Cooling rate can have very large effects on mineral presence, growth, and texture [e.g., *Hammer*, 2006], zoning and partitioning of elements between phases [e.g., *Zhou et al.*, 2000] and thermoremanent magnetization [e.g., *Bowles et al.*, 2005].

The role of rates, time and “time’s arrow” (i.e., entropy) in geologic processes is difficult to overlook. When the timescales under discussion can range from billions of years (10^{17} s) back to the formation of the solar system down to picoseconds (10^{-12} s) and the frequency of atomic vibrations that lead to diffusion, understanding the processes by which a system approaches equilibrium and the rates at which it does so is both very important and highly complex. The Earth is a dynamic system, and the importance of the large-scale processes that occur far from equilibrium—for example, plate tectonics driven by the thermal gradient between the core and the surface, and weather patterns driven by energy input from the sun—makes it clear that no analysis of physiochemical processes is complete without investigating the significance of non-equilibrium thermodynamics.

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CHAPTER 2

Effects of Open- and Closed-System Oxidation on Texture and Magnetic Response of Remelted Basaltic Glass

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Abstract

As part of an experimental and observational study of the magnetic response of submarine basaltic glass (SBG), we have examined, using ion backscattering spectrometry (RBS), transmission and scanning electron microscopy, energy dispersive X-ray spectrometry, and surface X-ray diffraction, the textures wrought by the controlled, open and closed system oxidation of glasses prepared by the controlled environment remelting and quenching of natural SBG. Initial compositions with ~9 wt % FeO^{T} were melted at 1430°C with the oxygen fugacity buffered at fayalite-magnetite-quartz; melts were cooled at a rate of 200°C min⁻¹ near the glass transition ($T_g = 680^\circ\text{C}$). In open system experiments, where chemical exchange is allowed to occur with the surrounding atmosphere, polished pieces of glass were reheated to temperatures both below and above T_g for times 1–5000 h; undercooled melts were oxidized at 900°C and 1200°C for 18 and 20 h, respectively. RBS demonstrates unequivocally that the dynamics of open system oxidation involves the outward motion of network-modifying cations. Oxidation results in formation of a Fe-, Ca-, and Mg-enriched surface layer that consists in part of Ti-free nanometer-scale ferrites; a divalent cation-depleted layer is observed at depths >1 μm . Specimens annealed/oxidized above T_g have magnetizations elevated by 1–2 orders of magnitude relative to the as-quenched material; this does not appear to be related to the surface oxidation. Quenched glass (closed system, i.e., no chemical exchange between sample and atmosphere) exhibits very fine scale chemical heterogeneities that coarsen with time under an electron beam; this metastable amorphous immiscibility is the potential source for the nucleation of ferrites with a wide range of Ti contents, ferrites not anticipated from an equilibrium analysis of the bulk basalt composition.

1. Introduction

Submarine basaltic glass (SBG) has been identified as particularly useful in paleointensity studies [*Pick and Tauxe*, 1993, 1994; *Tauxe*, 2006, and references therein] due to its ideal behavior in Thellier-type experiments. The dominant (paleo) magnetic carrier in SBG is submicrometer, low-Ti, single domain (SD) titanomagnetite [*Pick and Tauxe*, 1994]; in addition a strong superparamagnetic (SP) component is evident in hysteresis data [e.g., *Pick and Tauxe*, 1993; *Bowles et al.*, 2005]. Debate about the origin and timing of formation of the nanometer-scale phase, due to its nonequilibrium composition, is ongoing [e.g., *Heller et al.*, 2002], and we have prepared samples for an experimental and observational study in an attempt to understand both open and closed system processes occurring in the creation and evolution of basaltic glass.

In order for the paleointensity experiments to accurately reproduce the intensity of the ambient field, the magnetic carrier must be a liquidus phase and/or form at high temperatures during cooling, thus carrying a thermal remanent magnetization (TRM). Later formation or growth of the phase at constant temperatures below the Curie temperature (T_c) would result in a chemical remanence (CRM), or a thermochemical remanence (TCRM) if acquired under the combined influence of chemical change and temperature decrease. A (T)CRM may be either weaker or stronger than a total TRM, depending on the temperature and mode of the chemical change [*McClelland*, 1996; *Draeger et al.*, 2006; *Yamamoto*, 2006; *Fabian*, 2009]. The low intensity recovered from glass samples relative to whole rock studies for the same time periods has led some to speculate that the remanence may not be a TRM [*Heller et al.*, 2002] though a variety of other sources for this difference are possible [*Leonhardt et al.*, 2006; *Tauxe*, 2006].

Two populations of titanomagnetite have been identified in pillow basalts and glassy margins, labeled groups A and B by *Zhou et al.* [2000]. Group A grains are interpreted to crystallize in (meta)stable equilibrium from the unfractionated melt and increase in maximum size with depth from the quenched margin from $\sim 1\text{ }\mu\text{m}$ up to tens of micrometers at a depth of several centimeters. By contrast, group B grains are found in P- and S-rich immiscible globules embedded in interstitial glass, having formed from a highly differentiated melt. They compose a very narrow size range throughout the pillow, never exceeding one micrometer along the longest axis. Tiny (tens of nm) titanomagnetite crystals found within 0.3 cm of the pillow rim and within the glassy margin are thought to be genetically related to the group A grains. In the interior of the pillow, the Ti content of the group A titanomagnetite grains is tightly grouped near the equilibrium value TM_{60} ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$, where $x = 0.6$, or 60 mol %) for the composition and conditions of cooling; the Ti content variation near the surface is much larger, ranging to almost pure magnetite, which is not an equilibrium phase in basalts containing Ti near the fayalite-magnetite-quartz buffer [*Buddington and Lindsley*, 1964]. *Zhou et al.* [2000] find a wide compositional spread in group B grains similar to that of the near-surface group A grains. Most paleointensity studies which use SBG focus on the small grains in the glassy margin, where cooling rates near the glass transition (T_g) range from ~ 10 to $\sim 330^\circ\text{C min}^{-1}$ [*Bowles et al.*, 2005]. The transition is a kinetic one, and its temperature within a single composition depends on cooling rate [*Dingwell and Webb*, 1989, 1990], but the variation in T_g over the range in cooling rates found to produce glass suitable for paleointensity experiments is limited [*Wilding et al.*, 2000].

Previous work with Fe-bearing silicate melts and glasses has shown the formation of nanometer scale ferrites at and near the surface of the sample during dynamic oxidation [Cooper *et al.*, 1996a, 1996b; Smith and Cooper, 2000]. We explore the possibility that a similar open system process occurring in MORB during underwater eruption and cooling could lead to the formation of the titanomagnetites observed in SBG. The small titanomagnetites found by Zhou *et al.* [2000] very close to the pillow rim could be genetically unrelated to both group A and group B, instead forming through open system dynamic oxidation processes.

When melt or glass equilibrated at relatively low f_{O_2} is brought into contact with more oxidizing conditions, there are three kinetic responses (modes) to such a driving force: mode I, molecular oxygen diffuses into the material; mode II, ionic oxygen diffuses in, charge balanced by inward diffusion of electron holes, $h^\bullet$; and mode III, network-modifying cations diffuse out of the material to the free surface, charge balanced by an inward flux of $h^\bullet$. The process that dissipates the energy of the redox potential most quickly dominates the reaction dynamics. Mode III, (divalent) modifier cation diffusion-limited, is the dominant mode of oxidation in Fe-bearing basaltic and basalt-like glasses at temperatures near T_g [Cooper *et al.*, 1996a, 1996b; Cook and Cooper, 2000]. This case corresponds to $(c_h \cdot D_h) \gg (c_{Me^{2+}} D_{Me^{2+}}) \gg [(c_{O_2} D_{O_2}) \text{ or } (c_{O^{2-}} D_{O^{2-}})]$, where c_i is the concentration and D_i is the mobility of species i (this product, when normalized by RT , where R is the universal gas constant and T is temperature, is the transport coefficient of species i). The electron hole, structurally present as network-modifying Fe^{3+} , serves to decouple electrically the diffusion of cations from each other; thus the internal anion-

cation ratio is increased through removal of cations, with incorporation of new oxygen to the system in the form of oxides at the surface.

Substantial structural changes in the melt/glass are expected as a result of dynamic oxidation: the structural distortion created by the ferric iron “replacing” ferrous iron and the removal of divalent cations leads to a reaction in the glass at depth and nucleation of ferrites [Cooper *et al.*, 1996b; Smith and Cooper, 2000]. However, the presence of alkali cations can instead stabilize the Fe^{3+} cations as tetrahedral network formers [e.g., Mysen and Richet, 2005, p. 341], preventing the precipitation of the ferrite phase. In temperature range above T_g but below the liquidus, crystallization can change cation availability, but the dominant response to oxidation (i.e., cation migration) remains the same [Burkhard and Müller-Sigmund, 2007]. The open system oxidation of FeO-CaO-MgO-Al₂O₃-SiO₂ glass at temperatures slightly below T_g shows the formation of surface (Mg,Fe)₃O₄ and CaO oxide layers and interior nucleation of (magnesio)ferrites [Smith and Cooper, 2000], consistent with this model. By contrast, in nepheline normative tholeiitic basaltic glass oxidized near T_g , the texture included the surface oxide layer, but no ferrites were observed internally; rather a Na⁺-stabilized Fe^{3+} -bearing glass was formed [Cooper *et al.*, 1996a]. The presence of alkalis in SBG, then, although in relatively low concentrations, may affect the oxidation texture and dynamics of the material.

At very low temperatures, we expect alkalis to be the most mobile cation species (that is, have the greatest transport coefficient) responding to an oxidation potential, due primarily to the low activation energy for diffusion for alkalis relative to alkaline earths and other non-alkali network modifiers in silicate melts [Lowry *et al.*, 1982; Henderson *et*

al., 1985; *Chakraborty*, 1995]. Extrapolation of diffusivities in melts to below T_g is difficult because of the very different time scale of relaxation [*Dingwell*, 1990], but there is evidence nevertheless that an Arrhenius relationship is maintained at low temperatures for some glass compositions [*Roselieb and Jambon*, 2002]. This change in dynamics relative to higher temperatures would create an area in the interior of the glass depleted in alkalis, increasing the likelihood of ferrite nucleation. At these very low temperatures, however, the kinetic barriers to diffusion and crystalline nucleation and growth may be too large for characterization in laboratory experiments.

Ti^{4+} fills a complicated structural role in basaltic melts and glasses that varies with composition and temperature [*Dingwell*, 1992; *Mysen and Neuville*, 1995]. There is, however, no evidence that Ti^{4+} is mobilized during redox reactions in basaltic glass [*Cooper et al.*, 1996a]. Thus, it will not move (to first order) with the monovalent and divalent cations affected by dynamic oxidation, including Fe^{2+} , and will instead remain at a constant Ti/Si ratio at all levels of the glass, leading to low Ti/Fe in the surface and (perhaps) near surface region(s) as oxidation progresses. Subsequent crystallization in this region would have a much lower Ti/Fe ratio than expected for the bulk rock.

At the time of eruption mid-ocean ridge basalts have an f_{O_2} slightly below the fayalite-magnetite-quartz (FMQ) buffer [*Christie et al.*, 1986]. The change in conditions, both temperature and oxygen fugacity, during emplacement of the submarine basalts is extreme and immediate. The incredible driving forces for both oxidation and crystallization created by this change in conditions could have large effects on the material, with the extreme disequilibrium leading to the presence of crystalline phases not generated by either equilibrium solidification or fractional solidification of the initial

melt, as normally contemplated. Diffusion of cations under these conditions and at temperatures above the glass transition is fast enough to have measurable effects on concentration to depths of micrometers over tens of hours [Burkhard and Müller-Sigmund, 2007].

Additionally, closed system processes could lead to metastable immiscibility in the glass, leading to the formation of submicrometer titanomagnetite of broadly differing chemistry in the glassy margin in a process potentially similar to that envisioned by Zhou *et al.* [2000] for the formation of group B grains within the interstitial glass. Spinodal decomposition has been noted in quenched basaltic glass [Minitti *et al.*, 2002] and in basaltic melts [Veksler *et al.*, 2007]; clustering of Fe ions, or the segregation of Fe^{3+} from $\text{Fe}^{2+}+\text{Ti}^{4+}$ [e.g., Naslund, 1983], by immiscibility during quench could lead to nonequilibrium phases and so affect magnetic characteristics.

We have prepared samples of quenched and heat-treated/oxidized basaltic glasses in order to elucidate the timing and conditions of ferrite formation in the glass. We have also extended the protocol to characterize oxidized, undercooled melts. Analytical techniques employed for textural analysis include ion (Rutherford) backscattering spectrometry (RBS), transmission and scanning electron microscopy (TEM; SEM), energy dispersive X-ray spectrometry (EDS) and surface X-ray diffraction (XRD). Magnetic analyses included measurement of anhysteretic remanent magnetization (ARM) and thermal demagnetization (typically of saturation isothermal remanence) to determine unblocking temperatures.

2. Experimental Approach

Our starting material N1 (Table 1) was a natural basalt dredged from the Pacific-Antarctic Ridge (courtesy of Pat Castillo). The ambient pressure liquidus temperature for N1, as determined by the thermochemical model MELTS [*Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998*], is $\sim 1220^{\circ}\text{C}$. The material was placed in an alumina crucible (5–6 mL capacity) and remelted in a controlled atmosphere, vertical muffle tube Deltech furnace (MoSi_2 resistance elements) at 1430°C for 3 h; the apparatus, described by *Cook and Cooper [1999]*, includes an elevator system, instrumented with a thermocouple that contacts the melting crucible, that allows precise control of the location of the crucible within the furnace. The oxygen fugacity was buffered at FMQ by a reactive CO-CO_2 gas mixture ($\text{CO:CO}_2 = 1:10$; flow rate of $44 \text{ cm}^3 \text{ min}^{-1}$ [*Myers and Eugster, 1983*]). These melts were either (1) quenched to a glass and then subsequently analyzed and/or received an oxidation annealing treatment prior to analysis or (2) cooled to an undercooled liquid state where they were provided an oxidation anneal prior to further cooling/quenching. Continuing, we describe first approach 1 and follow with approach 2.

To quench, the sample (crucible plus melt) was lowered out of the hot zone of the furnace, but still within the controlled atmosphere of the muffle, where it reached $\sim 800^{\circ}\text{C}$ before the muffle was opened and the sample lowered into the ambient environment. In this way the melt was quenched rapidly to a glass within its crucible: the cooling rate through the glass transition (the endotherm in differential thermal analysis (DTA: argon, $10^{\circ}\text{C min}^{-1}$) determined the glass transition temperature of N1 to be $T_g = 680^{\circ}\text{C}$) was estimated to be $200^{\circ}\text{C min}^{-1}$. Wavelength dispersive X-ray spectroscopy (WDS) analysis, performed on a Cameca SX100 electron microprobe, from the center of the glass sample

gave the starting composition reported in Table 2.1; the values there represent an ~0.8 wt % increase in Al_2O_3 content over the original glass composition due to reaction with the alumina crucible during remelting.

Table 2.1 – Starting material composition (N1) and surface (Slab 1) and near-surface (Slab 2) compositions discerned for oxidized glass specimens (RBS spectral simulation)

	N1 ^a		Slab 1	Slab 2
Oxide	Wt%	Mol%	Wt%	Wt%
SiO_2	50.28	52.32	26.43	50.16
TiO_2	1.48	1.16	0.73	1.37
Al_2O_3	16.49	10.11	8.41	15.81
FeO^b	9.15	7.96	13.17	8.06
MgO	8.33	12.92	11.82	7.69
MnO	0.16	0.14	0.10	0.10
CaO	11.84	13.20	32.89	8.83
Na_2O	2.07	2.09	1.14	7.84
K_2O	0.06	0.04	0.03	0.04
P_2O_5	0.15	0.06	0.05	0.10
SO_3	tr.	tr.	5.23	tr.
T_g	680°C			
Density ^c	2.83 g cm ⁻³			
NBO/T ^d	0.711			

^a Wavelength-dispersive X-ray spectroscopy (WDS; electron microprobe) of remelted and quenched submarine basaltic glass N1

^b Total iron as FeO

^c Following the models of *Lange and Carmichael* [1987] and of *Hormadaly* [1986].

^d Non-bridging oxygen over tetrahedrally-coordinated cations, a glass/melt polymerization index [*Mysen and Richet*, 2005, p.111].

The crucible was cut away from the glass using a slow speed saw. The glass within 1 mm of the crucible wall was also removed to avoid quench crystals and areas of extreme alumina contamination. TEM specimens of as-quenched glass were prepared by crushing (in alcohol) bulk glass from the center of the crucible. Glass particles were allowed to settle for several minutes, then any micrometer-scale shards still suspended at

the liquid surface were scooped onto a carbon grid. TEM was done on a JEOL 2010 microscope operating at 200 kV.

For open system oxidation of reheated glass, the sample was cut into pieces about 1 mm thick by several millimeters on a side, suitable for RBS analysis. One surface of each piece was polished using alumina grit to 0.3 μm . Prepared specimens were then oxidized in a horizontal muffle tube Deltech furnace in bottled air (flow rate = 25 $\text{cm}^3\text{min}^{-1}$) for a range of times (1–100 h) and temperatures (600–1095°C; Table 2.2). One other sample was placed in a lab oven at low temperature (150°C) and allowed to react with the ambient atmosphere for seven months (5000 h). Experimental oxidation specimens are identified uniquely by oxidation temperature (in °C) and time (in h; e.g., N1-730-5.5 for the remelted/quenched natural glass subsequently oxidized at 730°C for 5.5 h).

Table 2.2 – Experimental oxidation conditions for reheated glasses and undercooled melts

Specimen	Temperature (°C)	Time (h)
N1-150-5000	150	5000
N1-600-5.5	600	5.5
N1-600-14.5	600	14.5
N1-600-56	600	56
N1-600-100	600	100
N1-730-5.5	730	5.5
N1-730-14.5	730	14.5
N1-730-24	730	24
N1-730-100	730	100
N1-915-4	915	4
N1-1095-1	1095	1
N1-900-18u	900	18
N1-1200-20u	1200	20

Analysis of the oxidized glass specimens was done using reflected optical microscopy, secondary electron imaging (SEI), backscattered electron imaging (BSI) and EDS in SEM, TEM, surface XRD and RBS. XRD was done on several samples within minutes of their removal from the furnace to avoid transformation of the surface nucleated crystals into amorphous hydroxides via their reaction with ambient, humid air. Oxidized samples were mounted on a conventional diffractometer (Cu-K α radiation) such that the free surface of the sample was aligned with the source and detector optics. Specimens were scanned from $2\theta = 10^\circ$ to 90° , and scan times of 2.5 s per 0.02° were used. Spectra were smoothed slightly using the Savitzky-Golay algorithm. SEM/SEI and BEI were used for micrographs of cross-sectional and surface morphology. TEM cross sections preserving the oxidized surface of N1-600-100 and N1-730-100 were prepared; these were thinned to electron transparency in an ion mill (Ar $^+$, 15 kV).

Surface imaging and analysis was complemented by compositional depth profiling with RBS, a nondestructive, chemical profiling technique that measures the energy loss of accelerated α -particles (helium nuclei, He $^{++}$) impinging on, and backscattering from component-ion nuclei of a specimen; at depth in the specimen, the α -particles, too, interact with inner shell electrons. At issue are the ion-backscattering and ion-stopping cross-sections (functions of both specimen composition and the kinetic energy of the α -particles): each component element directly and characteristically affects the momentum loss of α -particles that scatter off its nuclei while bonding between ions has no effect, thus allowing direct correlation between energy of the rebounding α -particle and composition of the specimen [Chu *et al.*, 1978]. Compositional profiling can

be done to a depth of several micrometers (with resolution ~ 10 nm), limited by the inelastic interactions between the α -particles and electrons. Lateral spatial resolution is limited by beam size, which is ~ 1 mm; spectra average over this area. In analysis of our oxidized specimens, initial α -particle kinetic energies of 2.0 MeV and 3.5 MeV were used. RBS spectra were collected using the accelerator at the Ion Beam Laboratory of SUNY-Albany.

RBS spectral analyses utilize a simulation approach: we employed the commercial analysis software RUMP (CGS, Inc., Ithaca, NY). Spectral simulations use known ion-stopping and ion backscattering cross sections to generate a synthetic spectrum from a stipulated spatial distribution of atoms [Doolittle, 1985]; the synthetic spectrum can be evaluated statistically relative to the actual spectrum (Appendix A). Modeling was done by specifying a series of discrete slabs of constant composition parallel to the specimen surface. Thickness of model layers is measured in 10^{15} atoms cm^{-2} , and density calculations for the glass after simulating compositional changes are necessary to calculate depth in the sample in standard units.

Pursuing approach 2, several samples were not quenched but rather were quickly lowered to 900°C or 1200°C and held to isothermally oxidize and crystallize for 18 and 20 h, respectively. The atmosphere was switched to bottled air immediately after lowering the sample temperature. Flow rate calculations show the furnace tube would have recycled its contents once every 1.5 min. These samples were cut and polished for microprobe analysis. Undercooled melt oxidation samples are denoted by “u” in the sample name (e.g., N1-900-18u). WDS analysis was done on polished cross sections of the specimens; RBS spectra were obtained for the free surface of N1-900-18u.

Magnetic experiments were done on unoxidized samples and representative oxidized samples. Natural remanent magnetization (NRM) was measured in a 2G cryogenic magnetometer, either at the University of Hawaii Paleomagnetic Lab or the Scripps Paleomagnetic Lab. The magnetic moment of many of the glass samples was at or below the noise level of the instrument ($<10^{-10} \text{ Am}^2$); however, we were able to measure the NRM of a few of the more strongly magnetized specimens. If the NRM of the samples was primarily thermal in origin, it was acquired as the samples cooled in the presence of the ambient field in the Brown laboratory. The magnitude of this field is unknown and likely variable in both time and space. Therefore, in order to more directly compare the magnetic capacity of each sample, the samples were given an anhysteretic remanent magnetization (ARM). While not a naturally occurring remanence, the ARM is generally considered to be of a similar magnitude to a thermal remanence [*Dunlop and Özdemir, 1997*]. Prior to ARM acquisition, samples were demagnetized along all three axes in a 100 mT alternating field (AF) in the Scripps Lab. The ARM was then acquired in a 100 mT alternating field with a 100 μT bias field. To place constraints on the composition of the magnetic phase(s) in the bulk glass, a saturation isothermal remanent magnetization (IRM) acquired in a 1 T field was stepwise thermally demagnetized in air at the Institute for Rock Magnetism at the University of Minnesota. Magnetization versus applied field (magnetic hysteresis) was measured up to 1.4 T on a vibrating sample magnetometer at the Institute for Rock Magnetism.

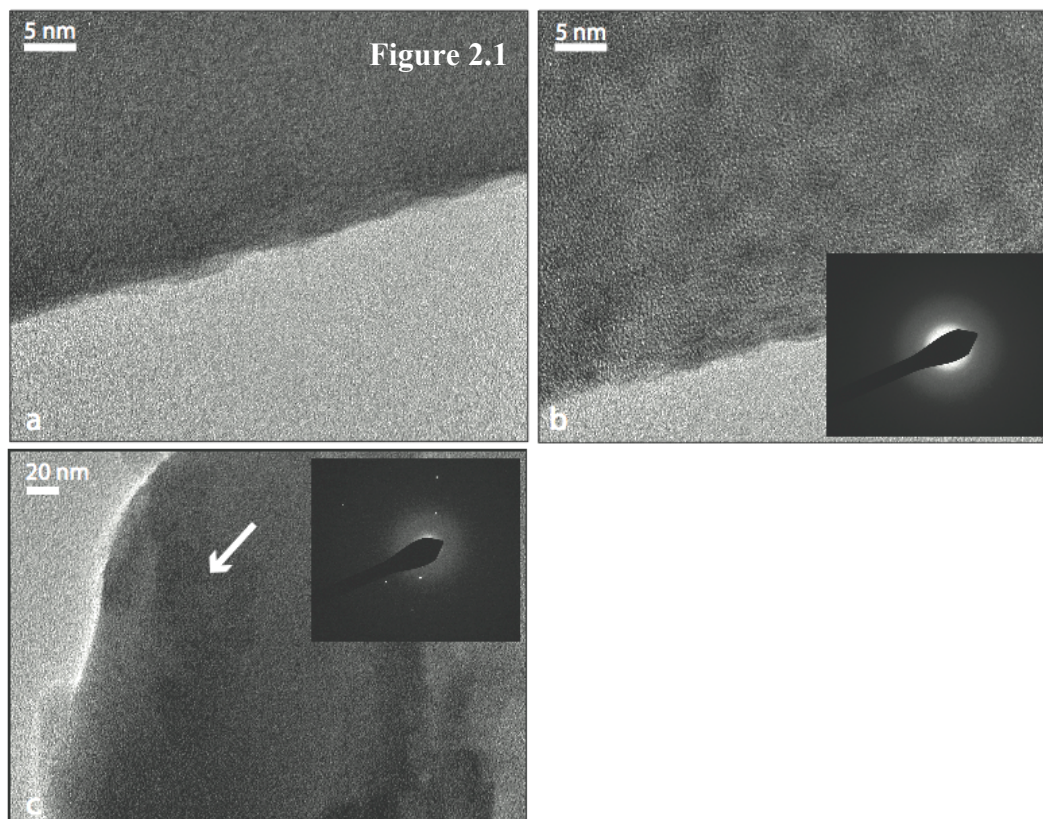
3. Experimental Results

3.1. As-Quenched Glass: TEM Analysis

At a resolution of ~ 30 nm in low-magnification TEM, the as-quenched glass is homogeneous. In high-magnification TEM, however, uniform amorphous immiscibility is evident, as well as the presence of nanocrystals, although these are very sparsely distributed (Fig. 2.1). Modest energy input, i.e., from the electron beam, coarsens the emulsion. On first viewing, i.e., directly after moving the sample area into the electron beam, most of the glass appears uniform, although in some areas light and dark contrast, due to density differences, is evident at the ~ 1 nm scale (Fig. 2.1a). After several minutes' exposure to the beam, there is recognizable coarsening, throughout the imaged area, which continues with time (Fig. 2.1b); the dynamic response and the resultant texture is evidence of spinodal decomposition of the glass [Andreev *et al.*, 1984]. Electron diffraction confirms the material is entirely amorphous in these two-phase regions (Fig. 2.1b, inset).

In broadly scattered locations, diffraction patterns show the presence of nanocrystalline material (Fig. 2.1c). In places, the pattern indicates the presence of several crystals in close proximity contributing to the pattern, but other areas have single crystal diffraction patterns. The diffraction patterns are not straightforwardly indexed, but nevertheless do indicate the presence of a phase with cubic symmetry, e.g., a ferrite.

Figure 2.1: TEM micrographs of as-quenched basaltic glass. (a) There is a transmission density difference ~ 1 nm scale evident in the glass immediately after exposure to the electron beam, evidence of incipient phase separation. (b) Same area as in (a) after nine minutes exposure to the electron beam: the glass is clearly no longer homogeneous, instead exhibiting a texture associated with spinodal decomposition. Inset shows amorphous selected area diffraction (SAD) pattern. (c) Quenched glass with ~ 40 nm cubic grain present (arrow). Inset shows a SAD pattern for a cubic crystal.



3.2. Oxidized Glasses and Undercooled/Crystallizing Melts

3.2.1. Visual Inspection and Microscopy of Oxidized Glasses and Undercooled Melts

When removed from the oxidation furnace, samples oxidized at temperatures above T_g developed a lustrous/iridescent finish ranging from purple to bluish-green, while samples oxidized at lower temperatures did not. Optical microscopy and SEM revealed small individual crystals present on the surface of the lower-temperature samples, with spacing between crystals changing with oxidation annealing time, while the high-temperature samples annealed for more than 5.5 h had $\sim 5\text{-}\mu\text{m}$ -scale surface roughness (undulation) that included a uniform coverage of a $\sim 100\text{-nm}$ -scale phase(s), a complete change from the original polished surface.

At least two populations of crystals are present on the surface of glasses oxidized at 600°C for all anneal times, one phase rich in Fe and Mg with diameters on the order of

0.1 μm and having a cubic habit, one phase rich in Ca and S and ~ 2 μm across. (Chemical concentrations are discerned using EDS.) The larger crystals are euhedral to subhedral. In some cases, the larger crystals appear to be breaking down, possibly becoming amorphous with exposure to the humid, ambient environment (Fig. 2.2a). By annealing times of 100 h, crystals cover the entire surface of the glass, and the two size range populations have grown over and into one another.

In glasses oxidized at 730°C for any length of time, the surface has been entirely covered in new crystalline material. At least two different types of crystals are again recognizable, although the spacing between individuals is much closer than in the lower temperature anneal, and the surface has an undulating texture (Fig. 2.2b). SEM images from cross sections of sample N1-730-100 show some devitrification in the center of the sample, starting at a depth of ~ 100 μm from the surface. Oxidation appears to have affected the specimen to a depth of 6–8 μm , and clusters of spherulitic microcrystals, likely pyroxene, have formed in this region close to the surface (Fig. 2.2c).

Glass samples N1-915-4 and N1-1095-1 exhibit even higher degrees of devitrification in their interiors, as well as layers at the surface, more than 2 μm thick, that are very enriched in iron, although the exact depth of cation enrichment is difficult to determine from EDS due to the high degree of crystallization. N1-1095-1 is dark purple under visual inspection, and SEM imaging shows the entire surface to be covered in “rosettes” of euhedral crystals, preliminarily identified as hematite based on tabular hexagonal habit. N1-915-4 is also highly crystalline on its surface, with two distinct crystal populations, closely resembling the surface texture of N1-730-24 (Fig. 2.2b).

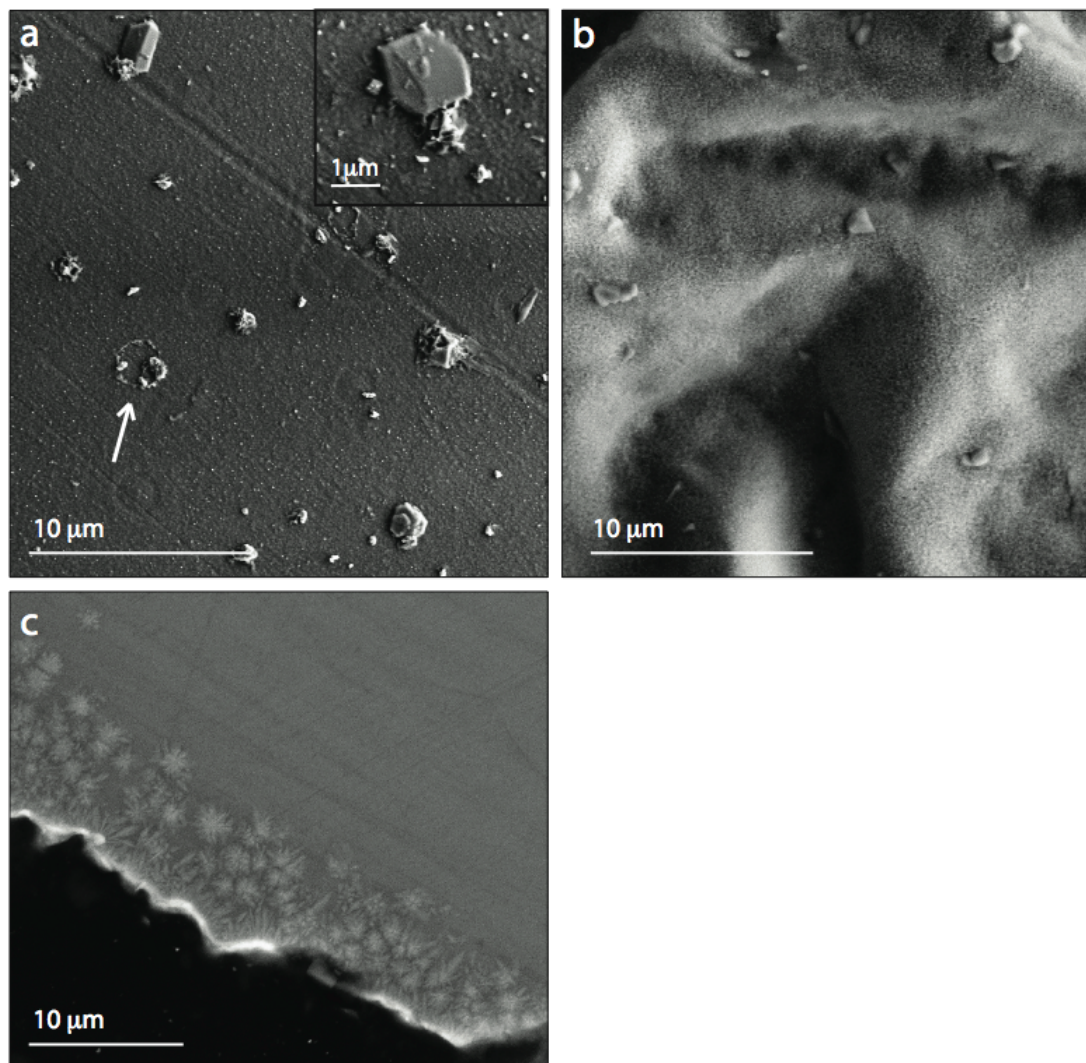


Figure 2.2: SEM/SEI micrographs of the oxidized, free (originally polished) surfaces of (a) N1-600-56 and (b) N1-730-24. The large, μm -scale crystals in both images are S- and Ca-rich; the small (~ 100 nm) crystals are Mg- and Fe-rich. Much more crystallization has taken place on the high-temperature sample, but the scales of the phases are similar. The arrow in (a) points to a crystal reacting with the humid ambient environment; the inset is higher magnification of a euhedral crystal, also showing cubic ferrites. (c) A cross-section of sample N1-730-100. The bright edge indicates the Fe and other heavy cation enrichment at the specimen free surface as a result of oxidation. Fe-rich crystalline spherules have grown in the glass up to $10\ \mu\text{m}$ from the surface; this “coarse, near-surface” devitrification causes the $\sim 5\text{-}\mu\text{m}$ -scale surface undulations evident in (b). The spherulitic growth, probably of pyroxene, is indicative of but sparse internal nucleation of ferrite due to the oxidation treatment [cf. *Beall and Rittler*, 1976; *Cooper et al.*, 1996a].

No ferrites were seen in TEM cross sections of the surface and near-surface region of N1-600-100. Some crystalline material, likely pyroxene, was present in N1-730-100, but there was no evidence of the densely ubiquitous, internally nucleated ferrites like those seen by *Smith and Cooper* [2000] for synthetic glasses of similar polymerization to, and $\text{Fe}^{2+,3+}$ content of, basaltic glass but containing no alkali cations.

Samples isothermally oxidized and crystallized from undercooled melts (i.e., those not first quenched to a glass and then reannealed) have large pyroxenes and plagioclase crystals, in addition to spinels, both Fe- and Al-rich. Some are titanomagnetite, with Ti content approaching the equilibrium value for the composition, TM_{60} , as determined by WDS. Irregular quench textures are present in the glassy region of N1-900-18u; crystalline textures closely resemble those seen by *Hammer* [2006] in experiments done at oxidizing conditions for various degrees of undercooling.

3.2.2. Surface XRD of Oxidized Glass Specimens

In XRD spectra of polished but unoxidized glass, the sole diffraction signal is a hump associated with amorphous silicate from $2\theta = 15^\circ$ to 35° . In N1-600-56, the hump remains dominant, but is overlain by several diffraction peaks associated with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and possibly with brucite or portlandite ($\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, respectively), while N1-730-24 shows, too, clear diffraction peaks associated with an iron oxide phase, between magnetite (Fe_3O_4) and magnesioferrite (MgFe_2O_4) in composition, in addition to peaks identified as gypsum (Fig. 2.3). These data support the EDS observations of the coarser precipitates, which show sulfur present on the surface spatially related specifically to Ca, as well as observations of the fine-particle film, enriched in Fe. When the N1-730-24 specimen was analyzed in XRD again, after being

stored at room temperature in a passive desiccator for several days, the primary peak associated with gypsum decreased in intensity, consistent with its being transformed to the amorphous state, while those for the Fe oxide peaks did not.

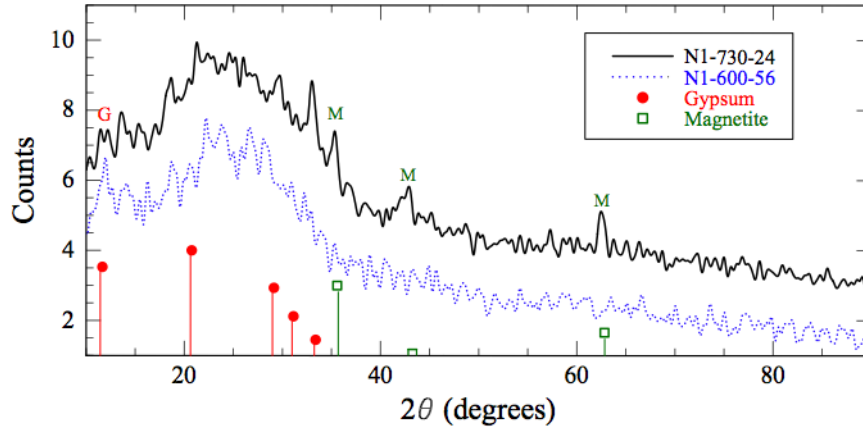


Figure 2.3: XRD ($\text{Cu-K}\alpha$) spectra from originally polished and then oxidized surfaces for glass specimens N1-730-24 (black, solid) and N1-600-56 (blue, dotted; offset for clarity). An amorphous hump is present between $2\theta = 15^\circ$ and 35° . The peak at $2\theta = 11.8^\circ$ is associated with gypsum (G; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Magnesioferrite to magnetite (M; MgFe_2O_4 - Fe_3O_4) peaks are at 33.2° , 35.6° , 43° , and 62.3° .

3.3. RBS

RBS spectra obtained for glasses oxidized at 600°C are presented in Fig. 2.4a. Qualitatively, the effects of oxidation are quite striking. In comparison to unoxidized glass, there are notable increases in Fe and Ca at the free surface. The Fe peak does not grow in height with time, but the thickness of the Fe-enriched material does increase, as seen in the growth in width of the peak. Ca behaves similarly, but its peak is much larger. Sections of the spectrum behind the Fe and Ca peaks are lower than that for unoxidized glass, indicating depletion of Fe and Ca from a finite thickness of original glass now immediately below the enriched layer.

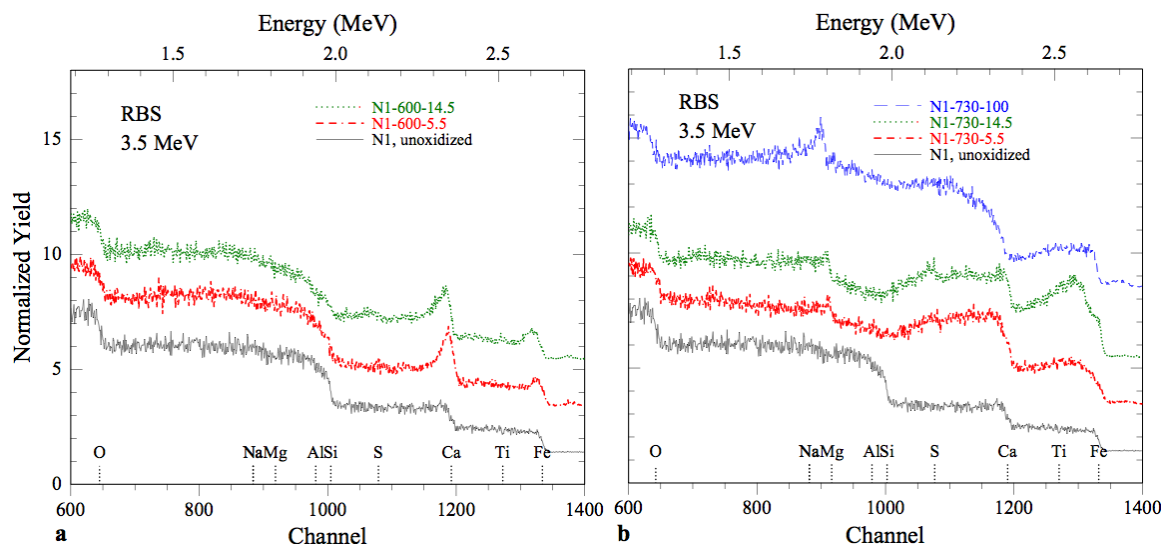


Figure 2.4: RBS spectra acquired at 3.5 MeV for (a) N1 samples oxidized at 600°C and (b) N1 samples oxidized at 730°C for various anneal times; in each figure, the spectrum for unoxidized glass is shown for comparison. The spectra are offset for clarity. For the 600°C oxidation (a), note the peaks at the Fe (2.65 MeV) and Ca (2.35 MeV) edges and their change in width with oxidation time; note too that the Si edge (2.0 MeV) is tilted, indicating there is some Si present at the oxidized surface, but much has been buried by phases rich in Ca, Fe and O. For the 730°C oxidation (b), one sees the enhanced mobilization of Fe and Mg to the surface compared to Ca, the clear evidence of S mobilization to the surface and the Si edge essentially buried by the Ca-, Fe-, Mg-, O- and S-bearing phases. The RUMP simulations for selected spectra are presented in Appendix A.

The most effective spectral simulations were done by keeping the Al/Si, Ti/Si, Mn/Si, K/Si and P/Si ratios fairly constant, which itself is an indication of the most mobile ionic species responding to the gradient in oxygen chemical potential, i.e., the divalent network-modifier species Ca, Mg and Fe and the monovalent modifier Na. Spectral simulations indicate that troughs in both Ca and Fe content occur at the same depth (Fig. A4). There is no shift of the Si edge, indicating the continued presence of Si on the free surface even after oxidation, that is, the crystalline material formed on the surface forms an incomplete layer. The surface material is enriched in S; a factor of four increase in Na concentration at a slight depth within the sample, specifically where Fe and Ca are depleted, is suggested by the increased counts relative to the unoxidized

sample between 1.4 and 1.8 MeV in the 3.5 MeV spectrum. The depth of Na depletion is beyond the resolved depth of the RBS analysis for the acceleration energies used (~ 2 μm). There is also an increase in Mg at the surface, although there is no pronounced peak in the spectra. No peak is seen for Ti. The simplest, statistically sound fits for the 600°C anneal temperature employed three constant composition “slabs” (layers), slab 1 defining the composition of the free surface, slab 2 characterizing the divalent cation-depleted but Na-enriched region and slab 3 being infinitely thick and having the composition of the original glass (Fig. A4). This approach suggests two reaction “fronts” characterize the oxidation, one front external to the (formerly) free surface and one front internal, i.e., within, the glass [cf. *Cooper et al.*, 1996a]; see section 4.2. The compositions of these slabs are presented in Table 1; the thicknesses of the slabs, in atoms cm^{-2} and converted to length following the density models of *Lange and Carmichael* [1987] and of *Hormadaly* [1986], are presented in Table 2.3. The thickness of slab 2 increases in a parabolic fashion with time (Fig. 2.5 and Table 2.3).

Table 2.3 – Thickness of surface/near-surface compositional slabs for N1 glass oxidized at 600°C

	Thickness— 10^{15} atoms cm^{-2} (nm) ^a	
Anneal Time (h)	Slab 1 (very surface)	Slab 2 (Me^{2+} -depleted)
5.5	500 (56)	4800 (619)
14.5	750 (83)	7300 (941)
56	1200 (133)	14000 (1804)
100	1700 (189)	18500 (2385)

^a Converted using magnetite density (Slab 1) and melt/glass density extrapolated to room temperature (Slab 2) (following the models of *Lange and Carmichael* [1987] and of *Hormadaly* [1986]).

In spectra for glasses oxidized at 730°C (Fig. 2.4b), large surface/near-surface enrichments are seen in Fe, Ca and Mg. The Ca edge, although present, is much less

pronounced than for lower temperatures, while the Mg edge, which was not seen at all at 600°C, now has a large peak. The Si edge has been completely hidden (buried) by the other species being mobilized to the free surface from different depths. Areas of depletion of single ions are convoluted in the spectra with the enrichments and depth effects of other ions, but can be modeled for the short anneal times. RBS using α -particles is unable to give information about composition of the samples to the depths affected by the oxidation after only a few hours of annealing at this temperature.

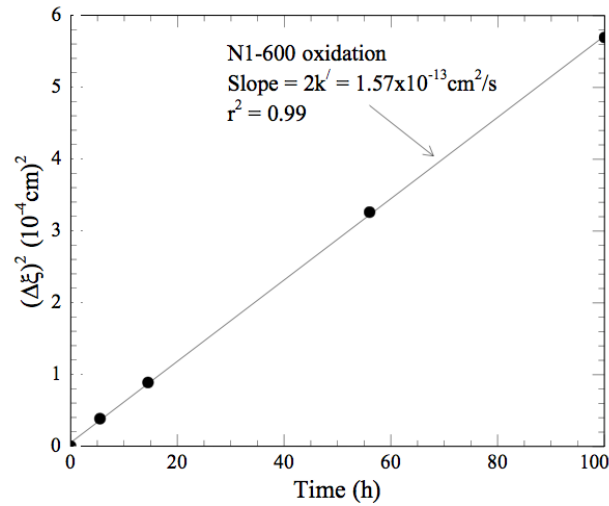


Figure 2.5: Thickness-squared of cation-depleted region (Slab 2; Table 3) versus reaction time for glass samples oxidized at 600°C. The slope of the line is equal to $2k'$, where k' is the parabolic reaction-rate constant. The linear trend indicates that the oxidation reaction is rate-limited by chemical diffusion; the absolute value of k' indicates that the rate-limiting species are divalent network-modifying cations. Substitution of k' into Eq. (1) yields $\bar{D}_{Me^{2+} 600^\circ C} = 2.41 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$.

When comparing the two anneal temperatures, one sees that Fe has moved to the surface much more at higher temperatures than at the lower temperatures, and that even for the same anneal time, the depth affected by the oxidation is much larger at temperatures above T_g .

For oxidation at 150°C, even after several months annealing, the RBS spectrum shows very little change relative to the unoxidized glass. It is possible that Na ($\pm$ K) could be enriched by up to a factor of three (i.e., up to several weight percent Na) without significant change to the spectrum in the region between 1.6 and 1.8 MeV, making analysis inconclusive for these cations. No other elements show significant enrichment at the free surface or depletion elsewhere.

RBS spectra were obtained, too, from the oxidized undercooled melt specimens. For N1-900-18u there is a huge surface Fe peak, and an increase in Ca close to, but not at, the very surface; a significant amount of Mg is also present at the surface.

3.4. Magnetics

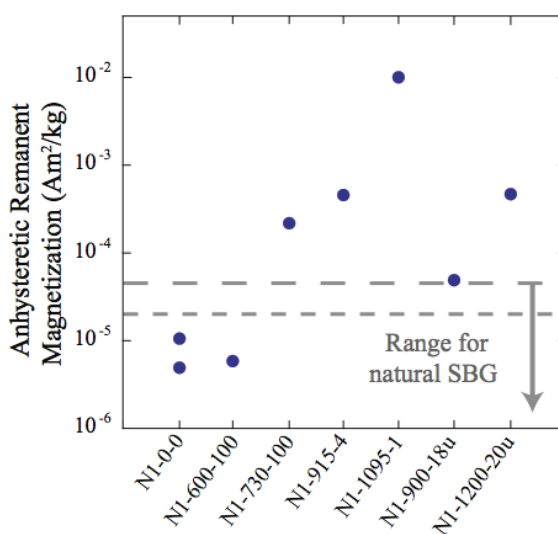


Figure 2.6: ARM acquired by oxidized glass and undercooled melt specimens in a 100 mT alternating field with a 100 μ T bias field. Samples quenched from melt to glass (N1-0-0) have remanences comparable to those of natural SBG. Specimens oxidized below the glass transition temperature, e.g., N1-150-5000 and N1-600-100, have remanence indistinguishable from that of samples that were not reheated or reacted. Specimens that were held in air at higher temperature or allowed to crystallize in air show magnetizations elevated by one-to-three orders of magnitude. The lower dashed line shows the upper limit for 75% of NRM data reported for natural SBG in *Bowles et al.* [2006]; the upper dashed line shows the upper limit for 90% of those data ($n = 459$ samples).

The magnetization (ARM) acquired by the unoxidized samples is roughly in the range of the NRM of natural SBG [Bowles *et al.*, 2006]. Of the oxidized samples, only those oxidized above the glass transition show an observable increase in magnetization, while the samples oxidized at 600°C are characterized by a magnetization indistinguishable from that of samples that were not reheated (Fig. 2.6). The increase in remanence magnitude is seen in all samples that spent time above the glass transition, whether or not they were first quenched to a glass.

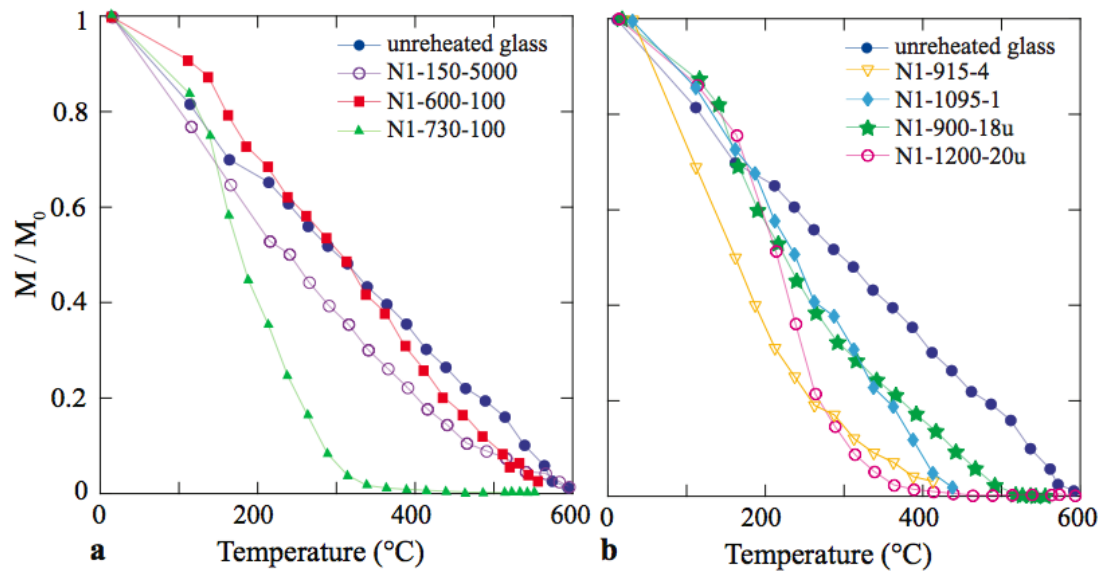


Figure 2.7: Thermal demagnetization of a saturation isothermal remanence (IRM). As-quenched samples display continuous unblocking up to 580°C, which, if all magnetization is attributed to crystalline ferrite, is consistent with a wide range of Ti contents, up to pure magnetite. (a) The same response occurs for glasses annealed/oxidized at temperatures up to 600°C (T_g). Glass and undercooled melts oxidized at temperatures $>T_g$ show evidence for development of a phase that unblocks by $\sim 300^\circ\text{C}$, consistent with the presence of ferrites having a moderate Ti content ($>TM_{45}$). (b) The metastable extension of the immiscibility gap likely falling between samples N1-915-4 and N1-1095-1 could lead to the differences between these samples and also to the differences between the two undercooled melts, such that N1-915-4 and N1-900-18u would have undergone amorphous phase separation while N1-1095-1 would have undergone some equilibration above the metastable solvus and N1-1200-20u would not have phase separated at any point [Visser and Koster van Groos, 1979].

During thermal demagnetization of the IRM, the unoxidized glass, N1-150-5000 and N1-600-100 display continuous unblocking up to 580°C (Fig. 2.7). In contrast, the high-T oxidized samples N1-730-100, N1-915-4 and N1-1200-20u reveal a response consistent with the development of a phase with low unblocking temperatures (<300°C), possibly high-Ti magnetite (or a ferrite incorporating some other non-Fe cation). The unblocking trends of N1-900-18u and N1-1095-1 show intermediate behavior. All samples have coercivity distributions derived from magnetic hysteresis measurements of < 0.3 T, consistent with magnetite or titanomagnetite. N1-900-4 also has an additional harder phase with coercivities > 0.5 T that is completely unblocked by 400°C and may be associated with titanohematite; a titanohematite surface coating on other samples is not untenable, as internal titanomagnetite could easily swamp the hematite signal.

4. Discussion

Zhou et al. [2000] conclude that the variation in titanomagnetite composition with depth in a MORB pillow is consistent with the changes in cooling rate from rim to interior. The Ti/Fe ratio approaches the equilibrium value in slow cooling regions where thermodynamic equilibrium is possible; slow diffusion in more rapidly cooled regions limits compositions to more closely resemble the melt Ti/Fe ratio. Our data presented here show a range of textures that allow us to further elucidate the effects of cooling and chemistry on magnetic response in basaltic glass.

4.1. As-Quenched Glass: Closed System Dynamics

It is clear from Fig. 2.1 that the glass goes through (metastable) amorphous phase separation via spinodal decomposition upon quenching, with further coarsening of the texture with the input of energy from the electron beam; similar processes have been

noted in industrial research glasses [Seward *et al.*, 1968; Chiang and Kingery, 1983]. Phase separation is known from glass-ceramic research to be key in controlling nucleation and composition of the nucleated phase [McMillan, 1979, p. 71]. As such, we suggest that the phase separation seen here and in other tholeiitic basalts [e.g., Philpotts, 1982] could affect the nucleation and chemistry of titanomagnetite found in SBG and lead to ferrites with the broad range of Fe/Ti ratios evidenced by the magnetic response.

Average MORB compositions do not fall within the stable miscibility gap for mafic liquids [Roedder, 1978; Philpotts, 1982], but the shape of the metastable solvus extends below the liquidus to our composition [Visser and Koster van Groos, 1979; Philpotts 2008]. Liquid phase immiscibility segregates Ti^{4+} into the iron-rich liquid [Watson, 1976; Visser and Koster van Groos, 1979]; some amount of Fe will remain in the silica-rich liquid. The ferric/ferrous ratio will be higher in the silica-rich liquid because of the high proportion of alkalis that partition into this liquid and their charge balancing effect on tetrahedrally coordinated Fe^{3+} [Mysen and Richet, 2005, p. 341], increasing the ease of ferrite nucleation in the low-Ti liquid [Beall and Rittler, 1976]. Oxidation of the melt prior to or, particularly, during quenching would expand compositionally the Fe^{3+} -affected miscibility gap and, thus, the likelihood of metastable liquid phase separation [Nashund, 1983; Thompson *et al.*, 2007]. The amount of ferric iron can be increased solely by quenching through redox couple reactions with other heterovalent ions present in the melt, specifically $\text{Ti}^{3+,4+}$, $\pm\text{S}^{2-,4+,6+}$ [Paul, 1990; cf. Cooper *et al.*, 2010]. Analysis of the relative changes in the activity coefficients of the ions with temperature change shows that the relative driving force for the oxidation of

Fe^{2+} versus Ti^{3+} would increase at lower temperature, leading to the oxidation to Fe^{3+} at the expense of Ti^{4+} , again facilitating the nucleation of low-Ti ferrites.

The amorphous phase separation we see and the concentrating of Fe ions could have a large effect on the magnetic response of the material. In a study by *O'Horo and O'Neill* [1976], antiferromagnetically coupled Fe ions are present in quenched calcium aluminum borosilicate glass. Amorphous phase separation, evidenced in TEM imaging of the glass, is very fine scaled (< 10 nm) with a morphology recognized as spinodal decomposition. They note that the separation of the glass into Fe-rich and depleted regions would enhance the possibility of clustering of the Fe ions, although the SP blocking temperature ($T_B < 4.2$ K) indicates clusters less than 3 nm in diameter. Similar low-T ($\sim 2\text{--}4$ K) unblocking was measured in our quenched glass specimens and in natural SBG samples. *Hayashi et al.* [1999] attribute the superparamagnetism of their iron-bearing calcium silicate glass to “microcrystalline” clusters of ~ 5 nm and note areas visible in TEM that indicate iron is not homogeneously distributed in the material. There is a significant stable miscibility gap within the $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ system [*Muan*, 1957; *Phillips and Muan*, 1959], suggesting that metastable immiscibility is possible upon quenching and contributes to the formation of the high-density clusters with varying $\text{Fe}^{3+}/\text{Fe}^{2+}$.

It is possible that the spinodal decomposition in our glass, as noted in Fig. 2.1, could lead to clustering of Fe^{3+} ions and enhanced likelihood of ferrite nucleation throughout the glass at temperatures above T_g [*O'Horo and O'Neill*, 1976], leading to the formation of the group A grains seen in the near surface region by *Zhou et al.* [2000]. A range of Ti contents would be easily obtained due to kinetic fractionation and the

segregation of some iron into the silica-rich liquid, analogous to that seen in the formation of the group B grains within immiscible globules in interstitial glass.

4.2. Open System Oxidation Dynamics: Kinetics and Textural Response

When basaltic glass is placed in an oxygen chemical potential gradient, the dominant mechanism of dynamic oxidation is unequivocally mode III: the high concentrations of divalent cations at and near the surface of the glass show the efficiency of this response in dissipating the energy of the driving force relative to diffusion of molecular and ionic oxygen. The observed reaction morphology of Ca-, Mg- and Fe-rich crystals grown on the surface of all samples can only occur when the diffusion of divalent cations dominates and rate limits the kinetic response to oxidation. Heat treatment alone below the glass transition, with no gradient in oxygen chemical potential, will not affect the surface and near-surface chemistry of the glass [Cooper *et al.*, 1996a].

The kinetic nature of the glass transition means that over time, the molecular structure of a glass annealed at temperatures near T_g will relax, effecting a subtly different molecular structure, that is, one with a different T_g . At chemical equilibrium, this annealing-effected evolution can be characterized as a function of time and rate (i.e., dT/dt), using, e.g., differential scanning calorimetry [e.g., Potuzak *et al.*, 2008]. Open system, isothermal oxidation as pursued here, however, sees the composition of the material in the near-surface region change simultaneously with thermal relaxation, making the characterization particularly complicated. For example, evolving the chemistry of the glass from its original composition to that represented by slab 2 (Table 2.1), realizing that by oxidation the iron in this region is now almost entirely ferric and stabilized in a network-former role by the presence of Na^+ [Cooper *et al.*, 1996a], the

glass polymerization is increased, diminishing the kinetics of mechanical/structural relaxation. Thus, the evolution of T_g of our annealed, oxidizing samples has not been quantified. Monitoring the reaction, which demonstrates parabolic kinetics, i.e., $(\Delta\xi)^2 = 2k't$, where $\Delta\xi$ is the thickness of a monitored reaction layer, t is time and k' is the parabolic reaction-rate constant (Fig. 2.5), demonstrates that the oxidation in air is rate limited by the diffusion process. We follow the model articulated by *Cooper et al.* [1996a] to determine the rate of chemical diffusion of divalent network modifiers in the glass in response to the oxidation potential. The Fick-Einstein equation is applied to analyze the fluxes of the divalent cations and electron holes as a function of the negative gradient in their electrochemical potentials, i.e., $-\nabla\eta_{Me^{2+}}$ and $-\nabla\eta_{h^\bullet}$, respectively. An electrochemical potential gradient for $h^\bullet$ cannot be sustained, however, because of their very high mobility, orders of magnitude greater than that of the cations (the “semiconductor condition”); thus, the driving force for cation diffusion is reduced to the negative chemical potential gradient for the neutral metal species, i.e., $-\nabla\mu_{Me}$. μ_{Me} in the glass/melt is related to the μ_{O_2} through the equilibrium $Me + \frac{1}{2}O_2 = MeO$, and since ionic diffusion across the oxidized glass internal layer (slab 2) occurs at concentration differences $X_{Me^{2+}} < 10^{-3}$, there is essentially no gradient in the μ_{MeO} across the region of oxidation; as such, $-\nabla\mu_{Me} \approx +\frac{1}{2}\nabla\mu_{O_2}$ [Cook and Cooper, 2000]. Thus, in transition metal oxide-bearing glasses, a chemical potential gradient in oxygen can generate a cation flux as the dominant kinetic response to oxidation (or reduction), with little or no movement of an oxygen species.

An average diffusion coefficient for the divalent modifiers, $\bar{D}_{Me^{2+}}$, can be calculated for the oxidized glass, that is, for regions of the glass from which network-modifying cations were removed to form the oxide phases on the free surface, from k' , which is a convolution of the ionic mobility and the (normalized, to RT) driving force [cf. *Schmalzried*, 1983]:

$$k' = X_{Me^{2+}} \bar{D}_{Me^{2+}} \ln \left(\frac{a_{O_2}^{\xi=0}}{a_{O_2}^{\xi=\xi''}} \right) \quad (1)$$

where $X_{Me^{2+}}$ is the atomic fraction of divalent cations in the divalent cation-depleted layer (slab 2 in Table 2.1), a_{O_2} is oxygen activity (with the superscript indicating a specific location), ξ'' is the location of the oxidation front within the glass (the boundary between Slabs 2 and 3) and $\xi=0$ is the original surface of the glass (the boundary between Slabs 1 and 2; thus, $\Delta\xi = \xi''-0$ and diffusion through Slab 1 is treated as a short circuit in the dynamics). For $2k' = 1.57 \times 10^{-13} \text{ cm}^2\text{s}^{-1}$ (Fig. 5), $X_{Me^{2+}} = 0.097$, $a_{O_2}^{\xi=0} = 0.21$ (air) and $a_{O_2}^{\xi=\xi''}$ at 600°C equal to the fayalite-magnetite-quartz (FMQ) buffer ($\sim 10^{-20}$ [*Myers and Eugster*, 1983]), we calculate $\bar{D}_{Me^{2+} 600^\circ\text{C}} = 1.8 \times 10^{-14} \text{ cm}^2\text{s}^{-1}$. Our result is similar to that found by *Cooper et al.* [1996a] for the same temperature ($\bar{D}_{Me^{2+} 600^\circ\text{C}} = 2.4 \times 10^{-14} \text{ cm}^2\text{s}^{-1}$). The rapid growth of the slabs in the 730°C treatment in N1 to thicknesses greater than that seen by RBS prohibits estimation of the average diffusion coefficient with this method.

In this study we see movement of alkali cations to the oxidized region of the sample at low temperatures, as was seen by *Cooper et al.* [1996a] in nepheline normative

basaltic glass. The increased presence of Na^+ in the near surface region of the glass would inhibit precipitation of ferrites from the matrix. This behavior is supported by the fact that no ferrites were seen in TEM cross sections of the oxidized glass surface in the 600°C samples, in contrast to those seen by *Smith and Cooper* [2000] in oxidized glasses of similar polymerization to basalt but containing no alkali oxides. The enrichment of Na^+ in the oxidized region (slab 2) of the basaltic glass, which is otherwise depleted in network-modifying cations, and the region of Na depletion being at depths greater than that measured in RBS, is an indication of its high diffusivity within the glass, as confirmed by other workers [e.g., *Pommier et al.*, 2010]. Alkali diffusion, therefore, does not rate limit the oxidation reaction: while Na^+ participates in the dynamics, its motion is a serial kinetic step in the process overall and, too, is a short circuit compared to the motion of the divalent network modifiers; as such, chemical diffusion of Na^+ is essentially “invisible” in the kinetics.

From the perspective of oxidation dynamics, sulfur is a very potent cation, having a high charge and very rapid diffusion in basalt [*Freda et al.*, 2005]. Its small size allows it to diffuse very quickly, contributing to the surface layer chemistry with extreme elevation in S concentration relative to the starting material. On the surface of oxidized glass samples, sulfur is included in (metastable) calcium silicates, as suggested by EDS chemical analyses of the large surface precipitates on the surfaces of glasses oxidized at 600 and 730°C (Figs. 2.2a and 2.2b), which rapidly react to form gypsum in atmospheric conditions (Fig. 2.3). At our experimental conditions, sulfide, sulfite and sulfate could all be present in the glass [*Métrich et al.*, 2002]. Reaction of one mole of S^{6+} at the surface of the glass is able to release more electron holes than any other cation present into the

interior, contributing to the oxidation of the glass. We did not measure the concentrations of other volatiles (H_2O , CO_2) in the samples either before or after the experiments. Carbon is dissolved in basaltic glasses as carbonate complexes [e.g., *Nowak et al.*, 2003], and so would already be in an oxidized state, while hydrogen, although diffusing very rapidly, has low potency in terms of charge. While the presence of volatiles and their speciation could be important in oxidation dynamics of some natural rocks, we expect the concentrations to be very low in our samples prepared at ambient pressure and anhydrous conditions.

4.3. Magnetic Response

Consistent with *Pick and Tauxe* [1994], we found no change in magnetic signature up to 600°C , where they saw the Cretaceous age sample begin to produce more magnetite as it was heated in magnetic experiments and a slight increase in magnetization in the Holocene glasses they measured. The magnetic phase was clearly present in the glass immediately after quench, a point strongly supported by experiments reported in a companion paper by *Bowles et al.* [2011]. It is clear that dynamic (open system) oxidation of the basalt glasses alone does not lead to the presence of low-Ti magnetites as found in natural SBG; while diffusion may have segregated Fe from Ti, no significant nucleation of magnetic ferrites took place during low-temperature annealing and oxidation, as evidenced by the lack of difference in magnetic response between the as-quenched glass and N1-600-100. Although magnesioferrites are clearly present on the surface of the glass, the signature of the bulk, unreacted glass continues to dominate the signal. For SBG older than a few million years, reheating during Thellier experiments could affect the magnetic response, due to devitrification of the glass over time [*Smirnov*

and Tarduno, 2003]. Our experimental results show that very young glasses will not be strongly affected by such reheating until they are at temperatures above T_g .

The glasses oxidized at temperatures above the glass transition acquire an ARM at least an order of magnitude larger than natural glasses. The distinct change in unblocking behavior in N1-730-100 is consistent with growth of a phase rich in Ti, compared to the linear unblocking trend in as-quenched glass, which indicates that a range of titanomagnetites compositions including very low Ti magnetite is present. The presence of the near-surface pyroxene spherules evident in Fig. 2.2c is indicative of sparse internal nucleation of ferrite in this region of the glass [Beall and Rittler, 1976; Cooper *et al.*, 1996a]; thus any nucleation and growth of titanomagnetite is not due to the oxidation treatment but to devitrification in the bulk glass at high temperature.

It is possible to relate the magnetic responses of the undercooled melts N1-900-18u and N1-1200-20u and the high-T reheated glasses N1-915-4 and N1-1095-1 to the closed system dynamics discussed earlier. While N1-915-4 and N1-1200-20u have both increased ARM relative to natural SBG and lower unblocking temperatures, indicating a moderate to high titanium content in the dominant ferrites, N1-1095-1 and N1-900-18u have thermal unblocking spectra that fall between as-quenched glass and N1-1200-20u (Fig. 2.7). The stable miscibility gap in basaltic melts exists to $\sim 1110^\circ\text{C}$ [Visser and Koster van Groos, 1979]; the metastable extension of the solvus would be well below 1200°C , making it likely that N1-1200-20u never phase separated before nucleating and growing titanomagnetites. Undercooling to below the metastable solvus allowed N1-900-18u and the quenched samples to phase separate; when brought back up to high temperature, the two amorphous phases would have coarsened, and subsequent

nucleation and growth would have taken place in regions with very different Fe/Ti and alkali contents. There is increased likelihood of developing ferrites with lower Fe/Ti in the high-Fe²⁺ phase because alkalis in the low-Ti phase could inhibit ferrite nucleation. It is possible N1-730-100 went through similar phase development during annealing. Because 1095°C is likely to be above the metastable extension, any spinodal decomposition that had taken place upon quench could have reequilibrated to a single phase, leading to growth of moderately high Ti magnetite.

5. Conclusions

The dynamic oxidation of basaltic glass at temperatures below and around the glass transition is due to migration of network modifying cations toward the surface of the glass in response to the oxidation potential gradient.

The magnetic signature of quenched natural material is similar to that of natural SBG. Oxidation and annealing below T_g have no significant effect on the strength or nature of the magnetic response. Both results indicate that the remanence seen in SBG and our quenched experimental glass is a TRM and unrelated to open system processes. Oxidation/ annealing above T_g , however, causes new phase(s) to develop, increasing ARM by several orders of magnitude, but also having a much lower blocking temperatures, indicating the predominance of a high-Ti phase, unlike that found in SBG used in magnetic experiments.

Amorphous metastable phase separation and concomitant segregation of Ti into a single liquid, while Fe would be present in both undercooled liquids, could lead to the nucleation of ferrites with a broad range of Fe/Ti; the presence of such grains in experimental as-quenched glass, low-T oxidized glass and natural SBG lends weight to

the idea that such phase separation is the mechanism by which the compositional range is produced.

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CHAPTER 3

The Origin of ‘Ghost Plagioclase’: Evidence from the Galápagos Plume

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Abstract

We present new trace element data from olivine-hosted melt inclusions from Santiago and Fernandina Islands, Galápagos Archipelago, and use these data to explore possible origins of the ghost plagioclase signature in basaltic samples. The major and trace element compositions of Santiago melt inclusions show an irrefutable signature of plagioclase assimilation. By contrast, Fernandina melt inclusions show strong trace element evidence of interaction between basaltic melt and plagioclase-rich cumulate but do not show major-element compositions consistent with plagioclase assimilation, i.e., a “ghost plagioclase” signature. To explain the observed decoupling between major and trace elements contents in Fernandina inclusions we developed a quantitative model to that considers dissolution-reprecipitation and diffusive interaction between a primitive magma migrating by porous flow through a pre-existing crystal mush (plagioclase-rich cumulate) in a magmatic plumbing system. Dissolution of a sodic plagioclase (An_{65}) in a primitive (high MgO) basaltic melt with simultaneous precipitation of a more calcic plagioclase (An_{80}), concomitant with trace element melt-plagioclase diffusive re-equilibration will produce a strong signature of plagioclase assimilation in the trace element composition of the melt, while buffering the major elements. By invoking variable extents of melt-plagioclase interaction and mixing between melt migrating by porous flow with melt moving in unreacted channelized flow within the crystal mush zone, we are able to recreate the trace element variation with minimal change to the major elements observed in the Fernandina melt inclusions. The good match between the model and the Galápagos data demonstrates that it is not necessary to call upon ancient recycled crust to explain the “ghost plagioclase” signature in ocean island basalts near plagioclase saturation.

1. Introduction

The “ghost plagioclase” signature in primitive mantle-derived basalts and olivine-hosted melt inclusions (small pockets of melt trapped inside a crystal) is characterized by primitive mantle normalized $(\text{Sr}/\text{Nd})_{\text{PM}}$, $(\text{Ba}/\text{Th})_{\text{PM}}$ and $(\text{Eu}/\text{Gd})_{\text{PM}}$ ratios greater than one, suggesting the role of plagioclase in the fractionation of the trace elements, but lacking the petrographic or major element evidence to support such a process (e.g., no plagioclase phenocrysts or xenocrysts, no elevation of Al_2O_3 in the melt). When recognized in basalt samples that are far from saturation with plagioclase, such as some Hawaiian lavas, these observations have been interpreted as a sign of the presence of an ancient recycled oceanic gabbro (rich in plagioclase) within the mantle source that has been transformed into a high-pressure eclogite during the subduction process [e.g. *Hofmann and Jochum*, 1996; *Chauvel and Hémond*, 2000; *Sobolev et al.*, 2000]. In this scenario, the melting of the eclogite within the mantle will produce a melt where the trace element signature of the original plagioclase is present only as a “ghost” signature because the major element composition of the melt will be controlled by the presence of garnet and pyroxene rather than plagioclase in the eclogitic source.

Other researchers have provided an alternative interpretation of the “ghost plagioclase” signature invoking a grain-scale reaction (involving dissolution and crystallization of a different phase, incongruent melting and kinetic interaction) between the melt and the plagioclase-rich cumulate within the magmatic plumbing system, where the hotter primitive magma (high MgO) is in contact with cooler wall rocks and/or pre-existing partially solidified crystal mush zones [e.g. *Yang et al.*, 1998; *Danyushevsky et al.*, 2003; 2004; *Gurenko and Sobolev*, 2006; *Saal et al.*, 2007]. *Danyushevsky et al.*

[2003; 2004] proposed a qualitative model of dissolution of plagioclase into a primitive plagioclase-undersaturated melt with concomitant precipitation of aluminous spinel to explain the decoupling of major and trace element contents in the percolating melt. It is important to note that this model assumes a simple compositional system CAMS; there was no consideration on the effect of Na_2O . However, increasing the Na_2O content of the melt destabilizes spinel [Yoder and Tilley, 1962], and in systems with large amounts of evolved (Na rich) plagioclase present, spinel may never precipitate. Nevertheless, their work recognizes that the assimilation of plagioclase into basaltic melt is not a straightforward binary mixing problem [e.g. Bédard, 1993; Danyushevsky *et al.*, 2003; 2004; Morgan *et al.*, 2006], but can instead lead to melt and mineral assemblages not necessarily expected from simple mixing models. Saal *et al.* [2007] presented a quantitative trace element diffusive interaction model between the percolating Galapagos basalt and lithospheric plagioclase-rich cumulate. However, this model takes the simplistic assumption that the melt is in major element equilibrium but trace element disequilibrium with the plagioclase. Gurenko and Sobolev [2006] applied the IRIDIUM program [Boudreau, 2003] to model the reaction of Icelandic basaltic melt during interaction with plagioclase cumulate. This model considers a chromatographic process where the melt as it percolates reaches complete equilibration at the given pressure, temperature and bulk composition with the crystal assemblage. Although the authors were able to reproduce the trace element patterns of the basalts, they did not reproduce the major elements contents and no consideration of kinetic processes were considered in this research.

We present new melt inclusion trace element data from two islands (Fernandina and Santiago) in the Galápagos Archipelago (Appendix Fig. B1) that show anomalously high $(\text{Sr}/\text{Nd})_{\text{PM}}$, $(\text{Ba}/\text{Th})_{\text{PM}}$ and $(\text{Eu}/\text{Gd})_{\text{PM}}$ ratios, indicative of melt-plagioclase interaction. The Archipelago has been divided into two distinct regions, west and east of the 91°W fracture zone, based mainly on decreasing lithosphere thickness, volcanic and seismic activity, eruptive styles and petrologic as well as geochemical information of whole rock basalts [for a synthesis see *Saal et al.*, 2007]. Among the most significant geochemical differences between lavas from both regions is the increase in the $(\text{Sr}/\text{Nd})_{\text{PM}}$, $(\text{Ba}/\text{Th})_{\text{PM}}$, $(\text{Eu}/\text{Gd})_{\text{PM}}$, $(\text{K}/\text{La})_{\text{PM}}$, and $(\text{Pb}/\text{Ce})_{\text{PM}}$ ratios associated with a general decrease in incompatible trace element contents from west to east. *Saal et al.* [2007] interpreted this spatial geochemical variation as an increase in the interaction (either assimilation or diffusive interaction) of basalts with plagioclase-rich cumulates in lithospheric “mush zones” with decreasing magmatic flux. These authors did not find evidence of such a process in the whole rock compositions of lavas from the western region. Our new results on melt inclusions indicate that while both trace and major element data show varying levels of plagioclase interaction in the melt inclusions from Santiago (eastern region), the Fernandina melt inclusions show a “ghost plagioclase” signature in the western section of the Archipelago.

To evaluate the impact of melt-rock interaction in creating the “ghost plagioclase” signature in systems near plagioclase saturation, we developed a quantitative model that considers dissolution-precipitation and kinetic interaction between a primitive magma and a pre-existing crystal mush with which it is in contact within the magmatic plumbing system. We assume that pre-existing sodic plagioclase is dissolved into a more primitive

melt while calcic plagioclase is being reprecipitated and diffusive trace element exchange is taking place. This is consistent with plagioclase dissolution experiments of *Tsuchiyama* [1985b] and theoretical analysis of dissolution of solid solution-forming minerals in partially molten silicates [*Liang*, 2003a]. In this situation, $(\text{Sr}/\text{Nd})_{\text{PM}}$, $(\text{Ba}/\text{Th})_{\text{PM}}$, $(\text{Eu}/\text{Gd})_{\text{PM}}$, $(\text{K}/\text{La})_{\text{PM}}$, and $(\text{Pb}/\text{Ce})_{\text{PM}}$ ratios would become higher than one in the melt due to the effect of the enrichment of incompatible trace elements in the evolved crystals, high compatibility of Sr, Ba, Eu^{+2} , K and Pb in plagioclase, the difference in trace element partitioning based on plagioclase major element composition [*Bédard*, 2006], and the high diffusivity of Sr, Ba, Eu^{+2} , K and Pb in plagioclase relative to Nd, Th, Gd, La, and Ce, respectively [*Cherniak*, 2010]. Major elements such as Al_2O_3 and CaO, which are often used as measures of plagioclase interaction, would be less affected because the precipitating plagioclase would reverse most dissolution effects.

In this study, we test our quantitative model on the Galápagos melt inclusions, and place constraints on the amount of dissolution-reprecipitation and diffusive interaction needed to reach the enrichment level of $(\text{Sr}/\text{Nd})_{\text{PM}}$, $(\text{Ba}/\text{Th})_{\text{PM}}$ and $(\text{Eu}/\text{Gd})_{\text{PM}}$ ratios without modifying significantly the major element composition seen in the natural samples. Furthermore, in a plumbing system that has large, interconnected mush zones at the base of the crust [*Sinton and Detrick*, 1992], variably evolved mineral phases and melts will coexist, and primitive melt entering the system will interact with phases with which it is not in equilibrium as it cools and fractionates. Both reactive porous flow and channelized flow of melt are thought to take place in regions of high melt flux in the mantle and lower crust, as well as magma chambers [e.g. *Jaupart and Tait*, 1995; *Kelemen et al.*, 1995], with mixing taking place between the variously reacted melts.

Mixing of melts from reactive porous flow and unreacted channel flow can also alter final melt composition to replicate the characteristics of the natural melt.

2. Analytical Methods

The samples analyzed in this study are from the islands of Fernandina, in the western zone of the Galápagos archipelago, and Santiago, in the eastern region (Appendix Fig. B1). All analyzed melt inclusions are completely glassy with no associated crystalline inclusions (Appendix Fig. B2). The major element compositions for the melt inclusions, host olivines and glasses were presented in *Koleszar et al.* [2009]; analyses were done using the Cameca XS-100 electron microprobe at the Department of Geological Sciences, Brown University, as described in that work. Analytical errors (2σ) were <5% for SiO₂, CaO, Al₂O₃, MgO, TiO₂, and FeO and <9% for Na₂O for the glasses and <2% for SiO₂, MgO, and FeO in olivines.

Trace elements in melt inclusions were measured on the Cameca 6F Ion Probe at the Department of Terrestrial Magnetism, Carnegie Institution of Washington using techniques and standards as described by *Hauri et al.* [2002]. Errors for trace elements, determined from replicate analyses of matrix glasses and large melt inclusions, were typically <5% (2σ). Further details about samples and analytical techniques are included in Appendix B.

3. Analytical Results

3.1. Santiago

The olivine phenocrysts in Santiago that host the inclusions have Mg# of 85-87, with one exception having Mg# 82. The Mg# of the olivines are higher than that required for olivine-matrix equilibrium (Mg# 82) indicating FeO-MgO disequilibrium between the

host glasses and phenocrysts. Corrections for host mineral crystallization from the melt inclusion are described in *Koleszar et al.* [2009]; the amount of host olivine added back into the inclusion to reach equilibrium was always less than 15% and usually below 10%. Such corrections have a small effect on major element concentrations and have no effect on incompatible trace elements relative to each other (and changes are close to within error of the original data). Corrected major and trace element data are presented in Appendix Table B1.

The melt inclusion data from Santiago show clear evidence of interaction with plagioclase in both the major and trace elements, as indicated by the increasing Al_2O_3 with decreasing FeO and MgO content and by the large, positive Sr anomalies (Fig. 3.1 and Appendix Fig. B3), very similar to the whole rock Santiago basalt data for the area compiled by *Saal et al.* [2007]. Most of the data fall within a limited range of $(\text{Sr}/\text{Nd})_{\text{PM}}$ ratios between 1.2 and 1.9, with tightly grouped absolute Sr content, and the ratios are correlated positively with Al_2O_3 and negatively with FeO (Fig. 3.2); two inclusions fall off these trends, with $(\text{Sr}/\text{Nd})_{\text{PM}}$ ratios of 3.6 and 0.66 corresponding to the unusual trace element depleted and enriched samples, respectively (Fig. 3.1), described in *Koleszar et al.* [2009]. The inclusion with low $(\text{Sr}/\text{Nd})_{\text{PM}}$ is also notable for its low $\text{Mg}^\#$, Al_2O_3 and CaO and high FeO content, indicating possible plagioclase fractionation. The sample with anomalously high $(\text{Sr}/\text{Nd})_{\text{PM}}$ also has large positive U and Pb anomalies and no K negative anomaly while being depleted in other trace elements in a primitive mantle normalized diagram (dotted line in Fig. 3.1). Positive $(\text{Ba}/\text{Th})_{\text{PM}}$ ratios are also seen in most of the inclusions, but $(\text{Eu}/\text{Gd})_{\text{PM}}$ ratios are generally very close to one.

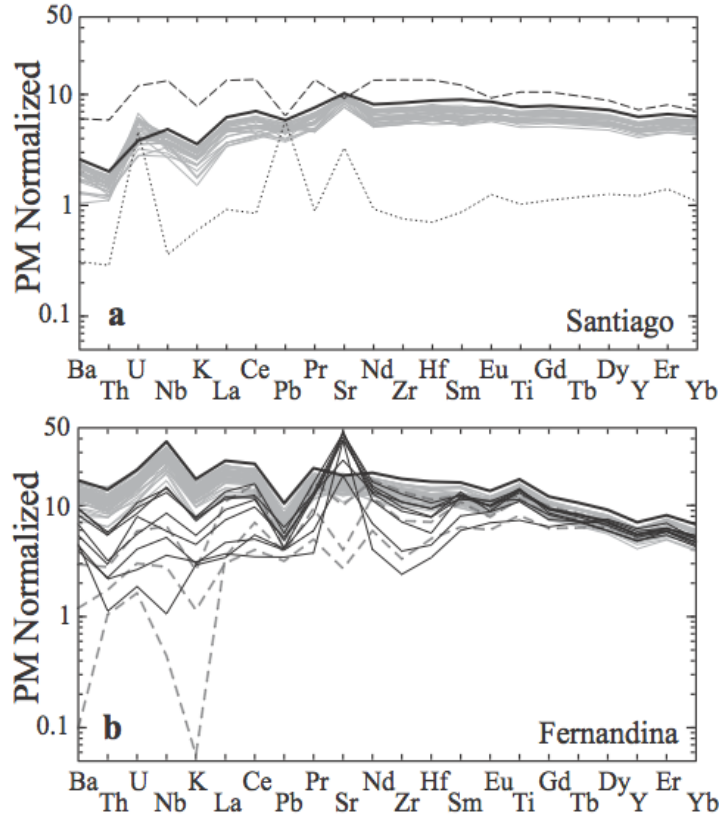


Figure 3.1: Primitive mantle normalized trace element plot for (a) Santiago and (b) Fernandina melt inclusions. The thick, dark line represents the average matrix glass composition from the compilation, which is slightly more evolved than the “normal” inclusions (thin gray lines). (a) The small positive Sr anomaly in the “normal” inclusions from Santiago indicates clearly the influence of plagioclase assimilation on the compositions, consistent with the major element data [Koleszar *et al.*, 2009; and Appendix Fig. B3]. Two inclusions do not follow this trend, one more enriched in all trace elements and the other more depleted but with large positive U, Pb and Sr anomalies. (b) The “normal” inclusions from Fernandina show general enrichment of the incompatible trace elements similar to the host matrix glass. Eight of the 56 inclusions show slightly more depleted incompatible trace elements relative to the normal inclusions and have large, positive Sr anomalies, which are not associated with any differences in major element composition [Koleszar *et al.*, 2009; and Appendix Fig. B4] and therefore represent a “ghost plagioclase” signature. Three other inclusions are also depleted but do not show Sr enrichment. Primitive mantle values are from McDonough and Sun [1995].

Figure 3.2: Plots of $(\text{Sr}/\text{Nd})_{\text{PM}}$ versus (a) Sr, (b) Al_2O_3 and (c) FeO content of the melt inclusions. (a) There is a large increase in Sr content of the Fernandina inclusions as the anomaly increases, although the inclusion with the largest anomaly does not continue the trend; the Santiago inclusions all fall within a small range of Sr content. (b,c) There is a clear correlation between major and trace element plagioclase signatures in the normal Santiago inclusions, as highlighted by the arrow in the insets. Fernandina melt inclusions show no relationship between the large Sr anomalies and enrichment in Al_2O_3 or depletion in FeO.

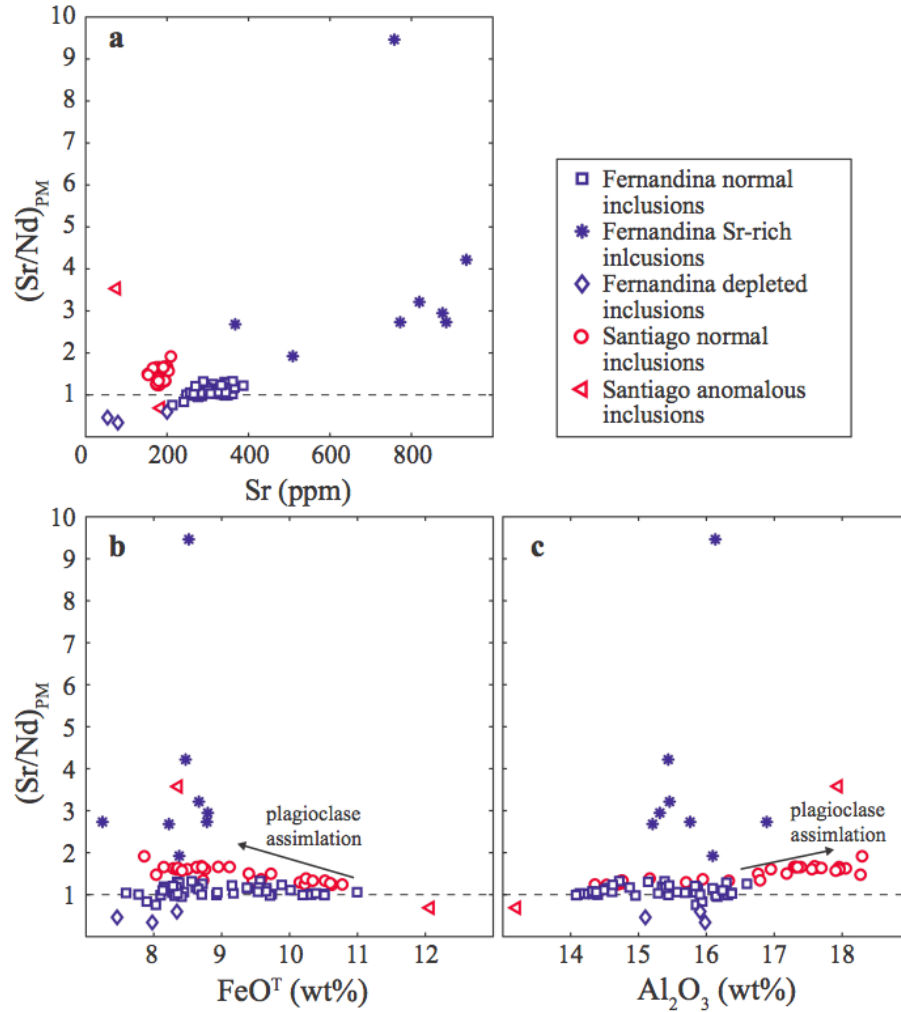


Figure 3.2

3.2. Fernandina

The olivine phenocrysts in Fernandina that host the inclusions have Mg# ranging from 82 to 87. The olivines again are too Mg-rich relative to the matrix glasses (in equilibrium with Mg# 78 olivine) and demonstrate melt-crystal disequilibrium, and corrections for melt inclusion-olivine equilibrium were performed in the same fashion as to the Santiago data [Koleszar *et al.*, 2009]. Plagioclase calculated using MELTS [Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995] to be in equilibrium with the most primitive melt inclusions has An₈₀ (molar, $100 \cdot \text{CaO}/[\text{CaO} + \text{NaO}_{0.5}]$), while that in equilibrium with the Fernandina basalts and submarine glasses [Geist *et al.*, 2006; Saal *et*

al., 2007] is An₆₀-An₇₅. Whole rock samples from the same dredge (AHA D25) consist of 27% plagioclase, 17% olivine, and 1.2% clinopyroxene (cpx) phenocrysts with little to no spinel [D. Geist, personal communication, 2011].

In contrast to the Santiago lavas, no submarine glasses [Geist *et al.*, 2006] or sub-aerial lavas from Fernandina [Saal *et al.*, 2007] show geochemical evidence of plagioclase assimilation (i.e., high (Sr/Nd)_{PM}, increasing Al₂O₃ and CaO with decreasing MgO; Appendix Fig. B4). While the major element data from the melt inclusions do not show evidence interaction with plagioclase, eight of the 56 measured melt inclusions have anomalous positive (Sr/Nd)_{PM} ratios, ranging from 1.9 to 9.5, along with positive (Ba/Th)_{PM} ratios (Fig. 3.1 and 3.2), thus showing a “ghost plagioclase” signature. In most of the anomalous inclusions, the absolute Sr concentration is also elevated to levels above that seen in inclusions with no positive anomaly (Fig. 3.2a). Generally, the inclusions with the largest Sr anomalies also have smaller negative K and Pb anomalies in a primitive mantle normalized diagram (Fig. 3.1), but there is no clear correlation between anomalies. There is no correlation between FeO or Al₂O₃ contents and the degree of Sr enrichment in the inclusions (Fig. 3.2b,c). The inclusion with the largest (Sr/Nd)_{PM} of 9.5 is an outlier in terms of major elements also, and has the lowest MgO content of all measured inclusions (Appendix Fig. B4). Three inclusions from Fernandina show a depleted trace element signature, with the highly and moderately incompatible elements being low relative to the “normal” inclusions. Many, although not all, of the Sr-rich inclusions also show this relative trace element depletion, which is too large to be created by dilution through plagioclase assimilation. The remaining, so-called “normal” inclusions have characteristic enrichment, with the LREE being slightly higher than the

HREE on a primitive mantle normalized plot, similar to the matrix glass and other Fernandina whole rock lavas. Negative K and Pb anomalies are present in all of the normal inclusions, common to most oceanic basalt. Several Fernandina inclusions that are normal in major, volatile, and trace element contents show large positive P anomalies that are not correlated with any other geochemical feature but could be related to melt inclusion interaction with P zoning in the host olivine during migration of the inclusion within the olivine, possibly under a thermal gradient as suggested by the experimental work of *Schiano et al.* [2006]. Fernandina major and trace element data are present in Appendix Table B2.

4. Description of Model

To determine if it is possible to create the “ghost plagioclase” signature through diffusive interaction concomitant with dissolution-reprecipitation processes, we consider a simple mush column in which primitive melt enters the mush from below and interacts with mineral previously crystallized from evolving basaltic melt. We start with a plagioclase-olivine-melt mush. The plagioclase is in equilibrium with an evolved melt (sample M65, Table 3.1) with trace and major elements matching an evolved submarine basalt from Fernandina that crystallized plagioclase An_{65} [*Geist et al.*, 2006]. The primitive melt (sample M80, Table 3.1) that we take as our initial composition interacting with the mush has major elements in the mid-range of the Fernandina inclusion data in equilibrium with plagioclase An_{80} [*Koleszar et al.*, 2009]. Although olivine +/- cpx is likely present in the “mush column,” for simplicity neither mineral is included in the current model reaction. We assume that sodic plagioclase (An_{65} , crystallized from M65) will be partially dissolved by the primitive melt and a more calcic plagioclase (An_{80} , in

equilibrium with M80) will reprecipitate, possibly as rims on the original plagioclase. In some cases, we assume that the reacted melt after interaction with the plagioclase-rich cumulate will be mixed with melt that has traveled through the mush zone without any chemical interaction and thus is the same as the primitive melt composition (M80, Table 3.1). Such melt may pass through the mush zone through crystal-free or plagioclase-free channels or dikes. Details of the mass conservation equations used in the model are presented in Appendix C.

Both diffusive exchange between the melt and the solid phases and dissolution of the solids are important processes occurring in a mush zone. The non-dimensional diffusive exchange parameter (i.e., Damköhler number) $\mathcal{D}_a^i$ is defined as the timescale for melt-solid exchange of the element of interest relative to the timescale over which diffusion can occur in the mineral of interest (i.e., the percolation rate),

$$\mathcal{D}_a^i = \frac{\mathfrak{R}_{plag}^i L}{V_f}, \quad (1)$$

where L is the characteristic length scale, V_f is the velocity of the melt, and $\mathfrak{R}_{plag}^i$ is the exchange rate between the melt and solid and incorporates grain size and geometry, porosity, and the diffusion coefficient for an element. The non-dimensional dissolution/precipitation reaction term for each phase, Θ_{plag}^i , measures reactive mass transfer and is the dissolution rate normalized by the percolation rate, i.e.,

$$\Theta_{plag}^i = \frac{\Gamma_{plag}^i L}{\rho_f \phi_f V_f}, \quad (2)$$

where ρ_f and ϕ_f are the density of the fluid and porosity, respectively, and Γ_{plag}^i is the dissolution rate. (The superscript is used to differentiate between the dissolving An₈₀ and

precipitating An₆₅ plagioclases.) Ion diffusion in the liquid is much faster than in the solid and is not considered in the model. Assuming disequilibrium (i.e., dissolution and diffusion are both occurring), the parameters $\mathcal{D}_a^i$ and Θ_{plag}^i are coupled through the physical properties of which they are both functions (e.g., velocity, length scale, porosity). Thus, for conditions where dissolution is limited, diffusive exchange is also limited, and where dissolution is large, diffusive exchange is too.

The model equations are broadly similar to the mass conservation equations used for Sr evolution during carbonate diagenesis and disequilibrium mantle melting that involve dissolution-reprecipitation in a crystal-melt two phase aggregate [e.g. *Liang*, 2003b; *Richter and DePaolo*, 1987]. The trace elements partition coefficients between plagioclase and melt k_{plag}^i are from *Bédard* [2006] and they are greater for An₆₅ than for An₈₀ (Table 3.2).

To simplify the model, we assume that the diffusion of major elements in the solid is too slow to have a significant effect on the concentrations in the melt and therefore can be neglected (Appendix C). Although tracer diffusion of Ca and Na in labradorite is relatively rapid [e.g., $D_{Ca} = \sim 8 \times 10^{-17} \text{ m}^2/\text{s}$ at 1200°C; *Cherniak*, 2010], the coupled CaAl-NaSi interdiffusion necessary to maintain charge balance is 3-4 orders of magnitude slower [*Cherniak*, 2010] and has a very limited effect on the final melt composition. Thus, the melt major element composition depends on the relative amounts of melt and reacting crystals and how rapidly growth and dissolution take place relative to the residence time of the melt packet.

Table 3.1 — Composition of initial evolved (M65), primitive (M80) and model melts.

Oxide (wt%)	Evolved melt (M65) ^a	Primitive melt (M80) ^b	Model 1 ^c	Model 1 50-50 mix ^d	Model 2 ^e	Model 2 50-50 mix ^d
SiO ₂	47.67	48.48	50.37	49.24	49.46	48.78
TiO ₂	4.16	2.29	2.32	2.43	2.41	2.48
Al ₂ O ₃	15.53	16.32	16.50	15.93	16.08	15.71
FeO	12.89	8.10	6.94	7.54	7.41	7.78
MgO	4.51	8.24	7.61	8.21	8.15	8.48
CaO	8.22	12.34	10.89	11.51	11.35	11.74
Na ₂ O	3.95	2.17	3.39	2.86	2.97	2.65
K ₂ O	1.77	0.21	0.52	0.44	0.48	0.42
Mg#	41	64	64	64	64	64
ppm						
Ba	271	52.28	92.4	87.31	78.08	80.15
Th	2.88	0.62	0.65	0.74	0.65	0.74
U	0.98	0.24	0.22	0.27	0.23	0.27
Nb	47.9	12.64	12.23	15.19	12.47	15.31
K	14693.6	1776.1	3335.6	3169.0	2915.2	2958.8
La	35.14	8.48	10.28	11.19	9.65	10.88
Ce	79.68	21.94	23.78	26.35	23.2	26.06
Pb	2.48	0.73	2.04	1.89	1.77	1.76
Pr	10.8	3.3	2.11	2.24	2.06	2.22
Sr	561	257.73	716.58	513.63	599.21	454.94
Nd	44.96	16.13	16.45	17.25	16.39	17.22
Zr	350	111.87	98.02	115.45	103.98	118.43
Hf	7.55	2.93	2.62	2.99	2.75	3.06
Sm	10.27	4.23	4.03	4.39	4.12	4.44
Eu	3.19	1.31	1.72	1.63	1.59	1.56
Ti	24932.9	13722.5	12657.3	14200.9	13089.7	14417.1
Gd	9.65	4.43	3.96	4.43	4.15	4.53
Tb	1.43	0.72	0.66	0.72	0.68	0.73
Dy	7.78	4.3	3.81	4.21	4.01	4.31
Y	3.16	21.34	19.12	21.06	20.03	21.52
Er	1.5	2.64	2.3	2.51	2.44	2.58
Yb	0.53	2.1	1.83	2.01	1.94	2.07
(Sr/Nd) _{PM}		0.98	2.08	1.64	1.85	1.52

^a Evolved melt used in model: AHA-D31A^b Primitive melt used in model: AHA-2-34^c Model 1 parameters $\Theta_{plag}^{An_{80}} = 0.7$, $\Theta_{plag}^{An_{65}} = 0.525$, $\mathcal{D}_{plag}^{An_{65}, Sr} = 10^{-4}$ ^d Mixture is between melt produced by the model and primitive melt M80.^e Model 2 parameters $\Theta_{plag}^{An_{80}} = 0.4$, $\Theta_{plag}^{An_{65}} = 0.3$, $\mathcal{D}_{plag}^{An_{65}, Sr} = 10^{-4}$

Table 3.2 — Partition and diffusion coefficients used in model.

Element	Partition Coefficient ^a		Log(Diffusion Coefficient) 1200°C (m ² /s) ^b	
	An65	An80	Labradorite	Anorthite
CaAl-NaSi			-20.00	-18.00
Ba	0.408	0.230	-18.06	-19.06
Th	0.083	0.050	-20.48	-21.30
U	0.053	0.024	-20.48	-21.30
Nb	0.066	0.030	-20.48	-21.30
K	0.217	0.171	-15.33	-16.33
La	0.194	0.106	-18.36	-19.30
Ce	0.141	0.081	-18.36	-19.30
Pb	0.606	0.511	-16.60	-16.98
Pr	0.160	0.104	-18.48	-19.30
Sr	2.543	1.813	-16.39	-17.68
Nd	0.139	0.084	-18.48	-19.30
Zr	0.015	0.004	-20.48	-21.30
Hf	0.036	0.015	-20.48	-21.30
Sm	0.096	0.056	-18.48	-19.30
Eu	0.534	0.534	-17.63	-18.82
Ti	0.099	0.076	-20.48	-21.30
Gd	0.045	0.017	-18.44	-19.30
Tb	0.079	0.038	-18.44	-19.30
Dy	0.048	0.019	-18.44	-19.30
Y	0.055	0.023	-18.48	-19.30
Er	0.030	0.012	-18.44	-19.30
Yb	0.035	0.015	-18.48	-19.30

^a *Bedard, 2006*^b *Cherniak, 2010*

We use experimental and observational data from the Galápagos and other ocean island basalt (OIB) regions to estimate possible melt velocities, length scales of the mush zone, grain sizes, diffusivities and dissolution rates in order to constrain $\mathcal{D}_a^i$ and Θ_{plag}^i ; the range of values possible for these parameters is presented in Table 3.3. To illustrate how the variables can combine to give the non-dimensional parameters, we can show that to obtain $\mathcal{D}_a^{An_{80}, REE} = 6 \times 10^{-6}$, we could have spherical grains ($\beta = 15$) with a radius of 5 mm, $\phi = 0.02$, $D_{REE} = 3 \times 10^{-19}$ m²/s at 1200°C in An₈₀ (labradorite) [*Cherniak, 2010*], and an average length scale of 10 km and melt velocity of $\sim 10^{-3}$ m/s [$\sim 10^5$ m/yr; *Koleszar et*

al., 2009]. $\mathcal{D}_a^{An_{80},Sr}$ is approximately two orders of magnitude higher due to its higher diffusivity of Sr in plagioclase, and $\mathcal{D}_a^i$ for all elements is about an order of magnitude lower in An₆₅ relative to An₈₀ due to the slower diffusivity in calcic plagioclase. Diffusion coefficients for each element in the model are presented in Table 3.2. The dissolution rate used for this set of parameters is 10^{-8} cm/s, within the range of dissolution rates measured by *Tsuchiyama* [1985b], *Donaldson* [1985] and *Morgan et al.* [2006]. Due to the coupling of the reaction parameters, $\Theta_{plag}^{An_{65}}$ would be on the order of 3×10^{-1} when $\mathcal{D}_a^{An_{65},Sr} = 6 \times 10^{-4}$. However, different melt compositions could change the dissolution rate significantly.

Table 3.3 — Definitions and values of parameters used in the model.

Parameter	Definition	Units	Range
$\bar{C}_n^i$	concentration in phase n	wt %, ppm	
$\bar{C}_f^{in}$	initial concentration in the fluid	wt %, ppm	
k_n^i	partition coefficient		Table 3.2
ϕ_n	porosity or volume fraction melt		0.01-0.1
w_n^i	weight fraction phase n		0-1
$M_{s/f}$	ratio of solid mass to liquid mass		
$\mathcal{D}_a^i$	diffusive exchange parameter		10^{-12} - 10^{-4}
Θ_{plag}^i	dissolution/precipitation reaction factor		10^{-2} -10
V_f	velocity of inflowing melt	m s ⁻¹	10^{-5} - 10^{-2} ^a
L	length scale	km	1-20
ρ	density	kg m ⁻³	2.7-3.0
Γ_{plag}^i	normalized dissolution/precipitation parameter	kg s ⁻¹	10^{-8} - 10^{-4} ^b
$\mathfrak{R}_n^i$	diffusive exchange rate	s ⁻¹	
β	geometrical factor		10-15
r	radius of grain	m	0.001-0.01
D_n	diffusion coefficient in the solid	m ² s ⁻¹	Table 3.2
M65	evolved Galápagos melt		Table 3.1
M80	primitive Galápagos melt		Table 3.1

^a *Koleszar et al.*, 2009

^b *Donaldson*, 1985; *Tsuchiyama*, 1985

5. Model Results

5.1. Range in Damköhler Number and Reaction Coefficient

Any combination of parameters (length, melt velocity, grain size, porosity, reaction rate) in $\mathcal{D}_a^i$ or Θ_{plag}^i that give the same end value will have the same effect on melt and solid compositions, even though physical values associated with the parameters can vary widely. Increasing melt velocity, or decreasing the characteristic length scale of melt migration will lower both $\mathcal{D}_a^i$ and Θ_{plag}^i , making the effect of dissolution-reprecipitation and diffusion less important over the same time scale. When these parameters are small (e.g., high melt velocity, slow diffusion, large grain size), there is limited exchange between the solid and melt; large $\mathcal{D}_a^i$ and Θ_{plag}^i (e.g., low melt velocity, fast diffusion, long migration distance, small grain size) indicate extensive exchange.

$\Theta_{plag}^{An_{65}}$ and $\Theta_{plag}^{An_{80}}$ are not necessarily the same, as the amount of plagioclase that is dissolved and the amount precipitated do not need to be equal. Using known and estimated values for the physical parameters of the mush zone, $\Theta_{plag}^{An_{65}}$ and $\Theta_{plag}^{An_{80}}$ will likely both be in the range 10^{-1} - 10^2 . Given the relationship between the parameters present in both $\mathcal{D}_a^i$ and Θ_{plag}^i , when $\Theta_{plag}^{An_{80}}$ is 10^{-1} - 10^2 , $\mathcal{D}_a^{An_{65},Sr}$ is between 10^{-7} and 10^{-4} and $\mathcal{D}_a^{An_{65},REE}$ is two orders of magnitude slower, with most elements falling in between and only $\mathcal{D}_a^{An_{65},K}$ being higher.

5.2. Porosity

Porosity is a parameter in Θ_{plag}^i and $\mathcal{D}_a^i$. The effect of increasing the porosity is to decrease both terms and thus dilute the effect of both dissolution and diffusion. A larger amount of melt means that a larger amount of solid must be involved in the

dissolution-reprecipitation reaction to have the same impact on the composition. Seismic data constrain the porosity beneath mid-ocean ridges in the mantle-crust transition zone to no more than a couple of percent [Dunn *et al.*, 2000; 2001]. However, Villagomez *et al.* [2007] suggest that a shallow low-velocity anomaly between 20 and 40 km depth located beneath Fernandina is caused by melt accumulation. The presence of both, a region of limited porosity with melt migrating by porous, reactive flow, and another with high-porosity crystal-free or plagioclase-free channels [Jaupart and Tait, 1995] where no melt-rock reactions take place but magma mixing does occur, would account for the range of compositions seen in the trapped melt inclusions.

5.3. Change in Melt Composition Due Only to Diffusion

When no dissolution or precipitation takes place (i.e., composition of the dissolving plagioclase is changed to be stable in M80) but the cumulate is relatively enriched in trace elements, diffusion of trace elements from a previously crystallized plagioclase into M80 can create a positive anomaly in Sr and Ba while decreasing the negative anomalies initially present for K and Pb. When diffusive exchange between the cumulate and the melt is large (i.e., $\mathcal{D}_a^{An_{65},Sr} > 10^{-4}$), M80 begins to diffusively equilibrate with the evolved plagioclase already present and Sr and K quickly increase in the melt (Fig. 3.3); the much slower diffusivities of most other trace elements means their concentrations in the melt do not change noticeably at these conditions and significant Sr and K anomalies can form. However, Sr concentration in the reacting melt will not exceed the concentration in the melt that formed An₆₅, and therefore the maximum (Sr/Nd)_{PM} cannot increase to levels above the ratio defined by the Sr_{PM} in the melt that crystallized the evolved plagioclase to Nd_{PM} in the percolating melt. This simple

diffusion model produces enrichment in the percolating melt not only in Sr, Ba, and Eu, but also in K and Pb for a given set of conditions. Thus, the modeled compositions end up with large enrichment of K and Pb not seen in the inclusions. The mixing of porous flow melt with unmodified primitive melt migrating by channelized flow mitigates this effect, but with enough mixing the enrichment of Sr will not be large enough to reproduce the melt inclusions composition.

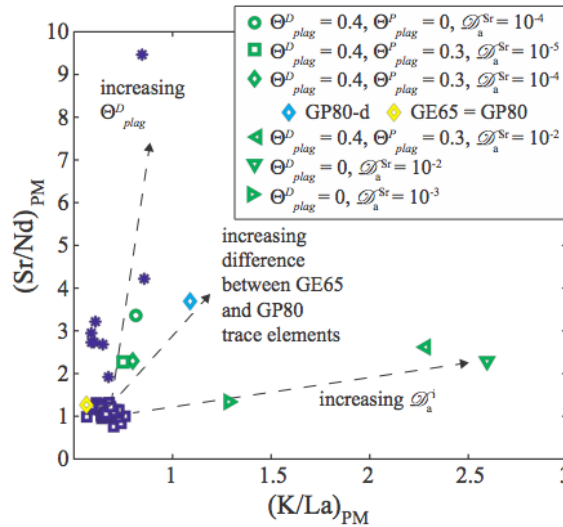


Figure 3.3: Plot of $(\text{Sr/Nd})_{\text{PM}}$ versus $(\text{K/La})_{\text{PM}}$ showing the effect of varying $\mathcal{D}_a^{\text{An}_{65},\text{Sr}}$, $\Theta_{\text{plag}}^{\text{An}_{65}}$, $\Theta_{\text{plag}}^{\text{An}_{80}}$ and melt composition on trace element anomalies. For diffusive interaction only between a “normal” primitive melt (M80) and trace element enriched plagioclase, if $\mathcal{D}_a^{\text{An}_{65},\text{Sr}} \geq 10^{-3}$, $(\text{K/La})_{\text{PM}}$ is much larger than natural samples (green triangles); even when some dissolution/reprecipitation takes place, the anomaly in $(\text{K/La})_{\text{PM}}$ dominates the trace element signal when $\mathcal{D}_a^{\text{An}_{65},\text{Sr}}$ is this large (left pointing triangle). $\mathcal{D}_a^{\text{An}_{65},\text{REE}}$ is about three orders of magnitude smaller than $\mathcal{D}_a^{\text{An}_{65},\text{Sr}}$ due to its lower diffusivity, while $\mathcal{D}_{\text{plag}}^{\text{An}_{65},\text{Sr}}$ is an order of magnitude larger than that of Sr. Dissolution of evolved, enriched plagioclase creates a positive anomaly in Sr, but K only increases slightly when $\mathcal{D}_a^{\text{An}_{65},\text{Sr}}$ is low ($< 10^{-4}$; green circle, square). When the concentration of trace elements is very different between M65 and M80 (e.g., the primitive melt is highly depleted in trace elements), the change in both $(\text{Sr/Nd})_{\text{PM}}$ and $(\text{K/La})_{\text{PM}}$ will be large (blue diamond) for otherwise similar parameters. The diamonds all use same $\Theta_{\text{plag}}^{\text{An}_{65}}$, $\Theta_{\text{plag}}^{\text{An}_{80}}$, and $\mathcal{D}_a^{\text{An}_{65},\text{Sr}}$. A very small positive Sr anomaly is created during dissolution of sodic and reprecipitation of calcic plagioclase in equilibrium with melts having the same trace element concentrations due to the differences amongst $k_{\text{plag}}^{\text{An}_{80},\text{Sr}}$ and $k_{\text{plag}}^{\text{An}_{65},\text{Sr}}$ (yellow diamond). Model 2 parameters match the green diamond. Natural inclusions are as in Fig. 3.2.

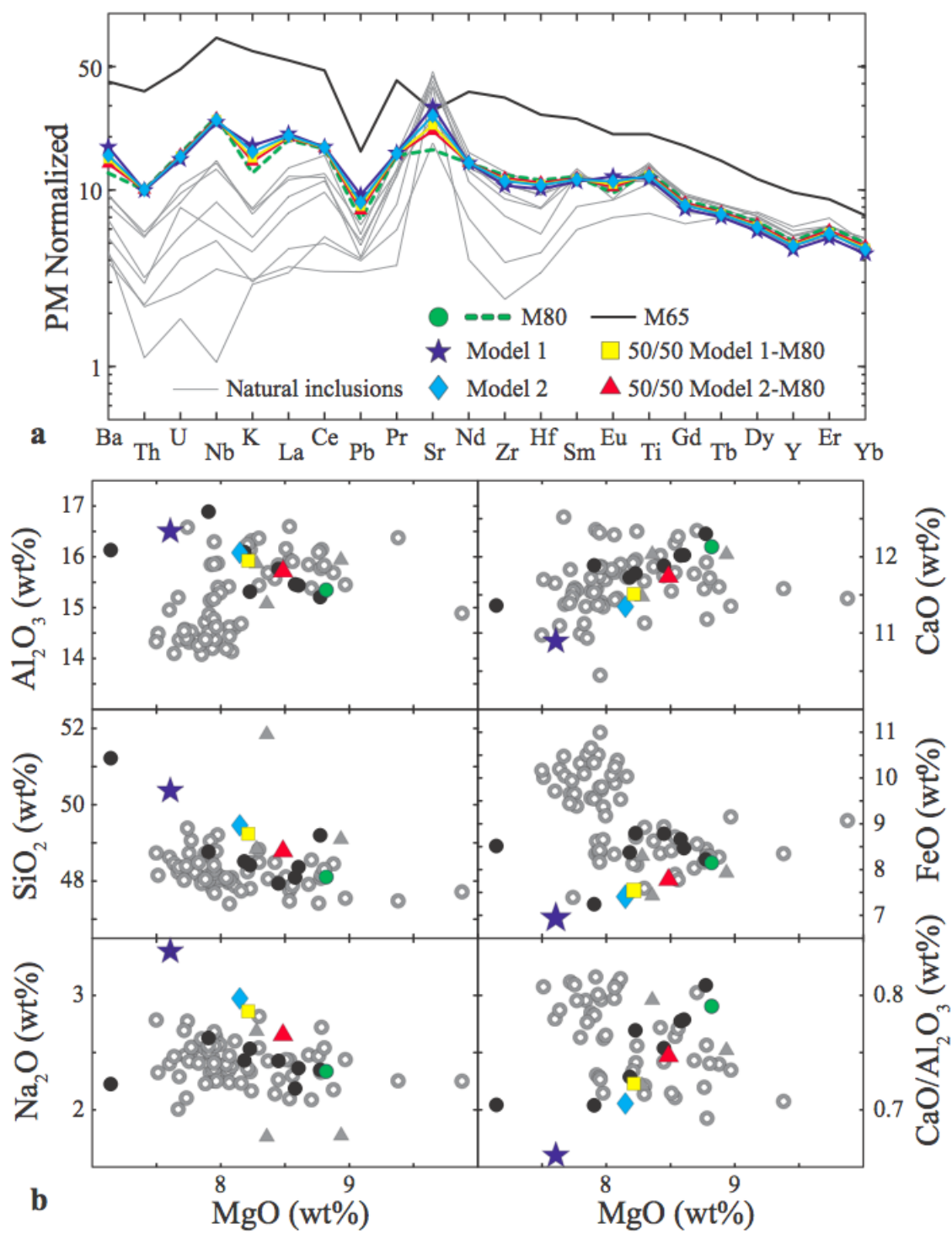


Figure 3.4

Figure 3.4: Plot of (a) trace element and (b) major element chemistry in the interacting melt during dissolution of D-plag and precipitation of P-plag in various amounts and with some mixing with unreacted “normal” channel melts M80. The initial melt composition (green dashed line) in (a) is M80, a normal inclusion. The evolved plagioclase cumulate is in equilibrium with a melt composition equivalent to M65 (solid black line). Natural Sr-rich inclusions are shown for comparison (gray lines). The largest Sr anomaly created by the model is associated with the most change in major elements (blue star; Model 1). When the difference between the amount of plagioclase dissolved and the amount precipitated is large, even if the total amount of dissolution is also small, the change in major element composition of the melt is outside of the range measured in the Fernandina inclusions, mostly due to the decrease in MgO content. By mixing the reacted melt with the “normal” melt M80 (black dotted line; green dot), the match between the model and the natural inclusions is improved for major elements and anomalies in both K and Pb (yellow square). The blue diamond and red triangle show the compositions of Model 2 and the associated 50/50 mixture, respectively. All compositions illustrate the effectiveness of dissolution-precipitation in creating the “ghost plagioclase” signature. Other symbols show major element data from Koleszar et al. (2009): large open circle – average matrix glass; ○ – “normal” inclusions; ● – Sr-enriched inclusions; ▲ – depleted inclusions; + - glasses from a compilation. The small crosses represent 2 sigma error bars. Primitive mantle values are from *McDonough and Sun* [1995].

5.4. Melt Composition Change for Dissolution-Reprecipitation and Diffusion

To increase the model Sr concentration and $(\text{Sr/Nd})_{\text{PM}}$ to the levels measured in the anomalous Fernandina inclusions, and to do so while not creating large anomalies in other rapidly diffusing elements, dissolution of plagioclase into the melt must take place (Fig. 3.3), with or without limited diffusion. Retention of the “ghost plagioclase” signature (i.e., no change in major element) during dissolution, however, requires that some amount of plagioclase also be precipitated and/or that a large amount of mixing between porous flow melt and channelized melt take place prior to inclusion trapping. If the amount of plagioclase dissolved is different from that precipitated, MgO will not remain constant. Dissolution of evolved plagioclase will increase Al_2O_3 and Na_2O content of the melt while lowering MgO. Concurrent crystallization of calcic plagioclase will cause decrease in the Al_2O_3 and CaO and increase of MgO contents, but will not lower the Na_2O content of the melt. It is this balance that allows us to place constraints

on the amount of plagioclase that can react with the melt, and the amount of mixing with unreacted channel melt that is required to reproduce the composition of the Fernandina inclusions before inclusion trapping.

In the process of dissolving the evolved (An_{65}) plagioclase and precipitating a more calcic plagioclase (An_{80}) in equilibrium with the primitive melt, we see an increase in Sr in the melt for two reasons: the high Sr concentration in the dissolving plagioclase due to it having crystallized from a trace element enriched melt, and the higher partitioning of trace elements into sodic plagioclase relative to more calcic plagioclase [Table 3.2; *Bédard, 2006*]. The degree of enrichment also depends on the relative proportion of plagioclase dissolved to that precipitated. For the plagioclase and melt compositions used in the model, the difference in trace element concentrations between the enriched and primitive melts is much more important in creating the positive Sr anomalies than is the difference in partition coefficients between the melt and plagioclases of different major element composition.

Because of the wide range in possible scenarios presented by the model, it is difficult to place more than broad constraints on the values of any individual parameter. As an example, Figure 3.4 shows the effect of $\Theta_{plag}^{An_{65}} = 0.7$ (Model 1; Table 3.1) and 0.4 (Model 2; Table 3.1), with lower $\Theta_{plag}^{An_{80}}$ ($0.75 * \Theta_{plag}^{An_{65}}$), as well as mixing equal portions of the reacted melt and channelized melt (M80). The $(Sr/Nd)_{PM}$ of the new melt compositions and of 50/50 mixtures (in parentheses) are 2.1 (1.6) and 1.8 (1.5), respectively, clearly replicating the anomalous peaks as seen in the natural data (Fig. 3.4a). If major element composition is to remain within the range of the natural inclusions, a large degree of dissolution of plagioclase into the melt, such as for Model 1,

can occur only if mixing with unreacted channelized melt (M80) also takes place before inclusion trapping (Fig. 3.4c). However, as the reacted melt becomes more and more diluted, the degree of Sr enrichment also decreases. Diffusion is limited ($\mathcal{D}_a^{An_{65},Sr} = 10^{-4}$), but a small effect can be seen in the relative increase in K, which decreases the negative anomaly.

The reaction described here shows the creation of a positive (Ba/Th)_{PM} anomaly on the order of what is seen in the Sr-rich inclusions. Small Eu anomalies are also created in the model while the negative K and Pb anomalies become less negative or even positive depending on the degree of the reaction, due to their significant partitioning into plagioclase. When diffusive reaction is large in addition to dissolution, the positive K, Pb and Eu anomalies quickly become more pronounced, while little change takes place in Sr due to its concentration having reached a maximum relative to the diffusive equilibrium.

5.5. Effect of Melt and Cumulate Compositions

The major and trace element compositions used in the model results presented here (Table 3.1) were chosen to resemble those found in samples from the Galápagos [Geist *et al.*, 2006; Koleszar *et al.*, 2009]. We have used “normal” Fernandina melt inclusion compositions for both the channel and porous flow melts in the current model, but a small number of highly depleted inclusions have also been measured. We do not know the origin of these depleted melts, but it is possible that the signature comes from melt-rock reactions, and a small volume of melt in porous flow is depleted. Our model shows that (Sr/Nd)_{PM} is larger when the primitive melt is more depleted (Appendix B). For the same degree of reaction, the Sr anomaly in a percolating initial melt with highly depleted trace elements will be as much as 1.6 times the anomaly in “normal” M80; the

difference in the strength of the anomaly decreases with increasing degree of mixing with the channelized melt. The change in Ba, K, Pb and Eu in the percolating melt is also much less for reactions with initial “normal” melt than for those involving initial depleted melt. On the other hand, if the Sr concentration of M65 and M80 are the same, the ratio of Sr partition coefficients $k_{plag}^{An_{65},Sr} / k_{plag}^{An_{80},Sr}$ is ~ 1.3 [Bédard, 2006], enough to allow for only slight enrichment of the melt through dissolution-reprecipitation (Fig. 3.3); a more evolved (i.e., more sodic) cumulate composition would lead an even larger ratio between the partition coefficients, although with more change in the major elements.

In the case where the major element composition of the dissolving plagioclase is more similar to the precipitating plagioclase (e.g., An_{75} instead of An_{80}), the amount of dissolution and reprecipitation that can take place without changing the major elements is increased relative to the model results shown here (Fig. 3.3). Provided the dissolving plagioclase shows relative enrichment in trace elements, this increases the $(Sr/Nd)_{PM}$ of the model melt. However, if the trace element pattern of the enriched melt that formed the cumulate is different from measured inclusions (e.g., lacks a significant negative K anomaly), a large amount of dissolution will begin to have too large an effect on the overall trace element pattern of the reacted melt. If, on the other hand, the plagioclase cumulates are produced by crystallization from melts more evolved than lavas currently being erupted on Fernandina, and thus having an even more sodic composition, the possible amount of reaction that could happen before measurable change in major elements would be decreased.

5.6. Santiago

In contrast to the model for the Fernandina inclusions, a limited amount of dissolution (i.e., $\Theta_{plag}^{An_{65}} = 0.1$), with no precipitation, is able to match $(\text{Sr/Nd})_{\text{PM}} = 1.9$ for Santiago using the same enriched composition as in the Fernandina model and starting from a relatively primitive Santiago “normal” inclusion composition; the modeled major element composition falls directly on the trend defined by the Santiago melt inclusions, showing the effect of plagioclase assimilation on major element concentrations in the inclusions.

6. Discussion

In our model, we assume that primitive melt is continuously percolating through the mush zone and thus interacting with crystals that grew in more evolved or fractionated melts. Magma chambers beneath some mid-ocean ridges experience recharge, for example, creating changes in melt and phenocryst compositions not predicted by strict fractionation or melting processes [*O'Hara, 1977*] but that require, in addition, some amount of wall rock assimilation [*DePaolo, 1981*]. Complex plumbing systems involving a series of evolving mush zones like those suggested here have been hypothesized for many regions [*Sinton and Detrick, 1992; Marsh, 1996; 1998*], along with regions where both reactive porous flow and unreactive channel flow are taking place [e.g. *Kelemen, 1990*]. Evidence of dissolution and reprecipitation reactions have been seen in other natural inclusions and lavas [*Bédard and Hebert, 1998; Danyushevsky et al., 2003; Danyushevsky et al., 2004*] as well as in laboratory melt-rock reaction experiments and numerical simulations [*Tsuchiyama, 1985b; Liang, 2003a; Morgan et al., 2006; Lo Cascio et al., 2008*]. MgO contents buffered by steady-state magma

chambers have been suggested for Fernandina and other islands in the Galápagos Archipelago [*Geist et al.*, 1999; *Geist et al.*, 2006]; such recharge and buffering would lead to interaction of primitive magmas with an evolved melt and crystal mush, creating a dynamic system of concurrent dissolution and reprecipitation. The lower magmatic flux rates at Santiago compared to Fernandina leads to variability in the amount of reaction that can take place [*Saal et al.*, 2007; *Koleszar et al.*, 2009; *Collier and Kelemen*, 2010].

Experiments by *Tsuchiyama* [1985a] have shown that a melt in equilibrium with calcic plagioclase will dissolve a more sodic plagioclase while precipitating a rim of calcic plagioclase onto the crystal. The presence of resorbed textures in plagioclase, such as dusty, sieve-like or fingerprint-like, found as phenocrysts or in xenoliths, would be evidence of some amount of dissolution occurring in the system. Complexly zoned plagioclases are seen in Fernandina basalts [*Allan and Simkin*, 2000; *Geist et al.*, 2006], and plagioclase phenocrysts in basaltic samples, including some from the same dredge as ours, exhibit a wide range of compositions (An_{49} - An_{96}) and major changes in composition ($>10\%$ An) over ~ 10 microns, indicating that the phenocrysts were alternatingly in contact with more and less evolved melts and could have undergone multiple cycles of dissolution and reprecipitation before being erupted.

6.1. Energetic and Kinetic Considerations

Thus far we have discussed only the chemical changes that take place due to the dissolution-reprecipitation and diffusive reaction, but it is important to consider also whether such reactions would take place within a lower crustal mush zone. The basic energy balance of the process modeled here has been described in detail many times [e.g. *Spera and Bohrsen*, 2001, and references therein]: the addition of a hot melt to a cooling

crystal mush zone will cause dissolution of crystals formed by previous episodes of melt injection; the heat of fusion from crystallization as the melt cools supplies more energy to the system. The details of how much wall rock can be assimilated and the amount of cumulates formed depends on the degree of overheating of the primitive melt, the temperature of the wall rock, and the phases that are being assimilated and fractionated.

Our model results show that, when the level of trace element enrichment in the cumulate is similar to cumulates in equilibrium with the most enriched lavas found on Fernandina, creation of an Sr anomaly matching the highest value found in the natural data requires a larger mass of evolved plagioclase to be dissolved than primitive plagioclase crystallized. Given the thermodynamic quantities used by *Finnila et al.* [1994], if the melt and wall rock are at the same temperature, 1.12 kg An₆₀ can dissolve for every 1 kg An₈₀ crystallized; this assumes all temperatures are constant and heat is not being lost to the surroundings. A small amount of olivine fractionation will be taking place concurrently, increasing the amount of heat available for dissolution, although the assimilated material may include evolved olivine in addition to plagioclase. Conductive heat loss would necessarily mean that less assimilation can take place for the same amount of crystallization, but the relatively high temperature in the mush zone means the effects of heat loss would be limited, and similar reactions in mafic systems at high temperature can be modeled as isenthalpic [*Kelemen*, 1990]. The rate of dissolution of plagioclase can be much faster than crystallization [*Donaldson*, 1985], also, indicating that the equilibrium thermodynamic parameters are not the only consideration, and the amount of material dissolved into the melt could exceed that expected from balancing heats of fusion alone.

The rate of dissolution depends on the degree of overheating of the plagioclase, which in effect reduces the saturation level of the mineral in the melt. More evolved (i.e., sodic) plagioclase will dissolve more rapidly than calcic plagioclase when in contact with a melt at the same temperature [Marvin and Walker, 1985; Tsuchiyama, 1985b]. Although the dissolution rate of plagioclase in basaltic melt is determined by diffusion of cations through the concentration boundary layer in the melt, both compaction and convection serve to keep this boundary layer at a constant thickness such that the dissolution rate can be assumed to be constant [Donaldson, 1985; Marvin and Walker, 1985].

6.2. Isotopic Evidence of Melt-Rock Interaction

Pb isotope systematics are closely related to the age of the plagioclase into which the Pb has partitioned. In ancient, recycled eclogitized plagioclase-rich cumulate, the Pb signature would reflect the age of the ancient subducted oceanic plate, having low Pb isotopes due to the low U/Pb ratio in plagioclase. By contrast, a Pb isotope signature acquired through melt interaction with young oceanic crust/lithosphere would be similar to that of the present day oceanic lithosphere beneath the Galápagos Archipelago. The Pb isotopes of the Sr-enriched melt inclusions are within errors of those measured in the “normal” Fernandina inclusions and within the Pb isotopes range of whole rock basalts from Fernandina [Peterson *et al.*, in prep.]. This observation is a confirmation that recycled crust is inconsistent with the “ghost plagioclase” signature measured in the Fernandina inclusions. The Santiago basalts that show positive Sr anomalies in primitive mantle normalized diagram are also known to have Pb isotopes consistent with modern lithosphere values [Saal *et al.*, 2007].

6.3. Other Phases Present in the Mush Zone

The best fits for the model (Table 3.1) are constrained by the differing effects that dissolution of sodic plagioclase and precipitation of calcic plagioclase have on major and trace element concentrations, but fractional crystallization of olivine (+/- cpx) likely creates the broad trend in the natural data and may explain the difference between the trend of our data and that of the natural Sr-rich inclusions for FeO (Fig. 3.4). The melt inclusions with Sr anomalies lie within the range of normal major element melt inclusion compositions, which means that the effect of fractionation of olivine is similar for both inclusion types. Dissolving plagioclase and fractionating olivine have opposing effects on the MgO content of the melt, but the magnitude of MgO change due to Fo-rich olivine is much greater than that of plagioclase. Thus, even a very limited amount of olivine fractionation has the largest control on MgO content of the melt. Olivine fractionation has no effect on the, incompatible trace element ratios of the melt (i.e., $(\text{Sr}/\text{Nd})_{\text{PM}}$) and we feel that consideration of olivine fractionation by the model is unnecessary because we choose a starting melt composition already fractionated with MgO content in the mid-range of the natural inclusions. Unlike crystallization of olivine, assimilation of evolved olivine from the cumulate ($\sim\text{Fo}_{65}$) will dilute the major elements in the melt most affected by plagioclase dissolution, making it so more overall dissolution can occur before the major element composition is altered to the same degree. Our model does not include the effects of possible pyroxene interaction, which would change the CaO content, in addition to affecting MgO and FeO. We have attempted to keep our model simple in order to constrain the controlling factors; including more phases in the mush zone creates many more possible variations in the amount of any single phase that could be

precipitated or dissolved while maintaining similar major element compositions. Plagioclase is by far the dominant control on Sr content of the melt, which is the noted anomaly in our inclusions that leads to the ‘ghost plagioclase’ signature.

The melt inclusions from Fernandina are close to saturation with plagioclase. However, in areas where the melt composition is further from plagioclase saturation, it is possible that the dissolution reaction would cause the melt to become saturated in aluminous spinel and precipitate that phase in place of plagioclase [*Bédard and Hebert, 1998; Danyushevsky et al., 2004; Morgan et al., 2006*]. However, very little if any aluminous spinel is seen in the Fernandina sample, and thus we have not considered this in the present model. Furthermore, increasing the Na₂O content of the melt destabilizes spinel [*Yoder and Tilley, 1962*], and in systems with large amounts of evolved plagioclase present, spinel may never precipitate.

Melt inclusions with “ghost plagioclase” signature could represent small volume melts from mantle heterogeneities that have not yet been mixed, or melt produced in local reactions between the melt and wall rock in the crystal mush zone of the upper mantle and lower crust. While the compositions used here are specific to lavas and inclusions found in the Galápagos, other ocean islands and ridges are known to have inclusions with a ghost plagioclase signature in addition to more “normal” inclusion compositions. We can easily imagine a similar dissolution-reprecipitation-diffusion reaction taking place wherever primitive melt is able to interact with evolved cumulates in mush zones or magma chambers. The “ghost plagioclase” signature alone does not indicate the presence of ancient recycled crust in the source region.

7. Conclusions

New trace element data from Galápagos show the presence of melt interaction with plagioclase in both whole-rocks and in melt inclusion data from the island of Santiago in the eastern region of the Archipelago, while in Fernandina only the trace element composition of melt inclusion show evidence of such interaction. No evidence of plagioclase interaction has been seen in whole rock data from Fernandina [Koleszar *et al.*, 2009; Saal *et al.*, 2007] or in major element data from the melt inclusions; thus the melt inclusions chemistry shows the influence of a “ghost plagioclase signature”. A small number of inclusions from Fernandina, also with major element compositions indistinguishable from “normal” inclusions, have depleted trace element signatures but lack Sr anomalies.

The presence of a crystal mush and recharging magma chambers beneath the Galápagos Archipelago could lead to interaction between evolved, fractionated crystals and a primitive melt. Diffusive reequilibration associated with dissolution of relatively sodic plagioclase concomitant with the precipitation of more calcic plagioclase will allow for the creation of “ghost plagioclase” signature in the melt. Mixing of this reacted melt with channel melt in varying proportion leads to the range of compositions seen in the natural inclusions. It is not necessary to call on large, whole mantle processes such as crustal recycling to explain the variations and “ghost plagioclase” signature in oceanic basalts with plagioclase as a near-liquidus phase.

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CHAPTER 4

Extended Planar Defects and the Rapid incorporation of Ti^{4+} into Olivine

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Petrologists and geochemists evaluate the minerals ($\pm$ glass) present in rocks, their spatial distribution and shapes, and the within-phase compositional gradients to discern the kinetics of thermal, chemical, and mechanical processes that characterize the evolution of Earth. The simple continuum physics models used to aid in textural interpretation of experimental and natural specimens require assumptions, particularly about the kinetic mechanism. Experiments emphasizing chemical kinetics in solids often involve placing in intimate contact two reactants not initially at equilibrium and then monitoring the rate of the approach to equilibrium and the texture of the reaction to discern the physical mechanism, which is frequently assumed to be chemical diffusion on the crystalline lattice due to uncorrelated motion of lattice point defects. Two recent experimental studies claiming characterization of the lattice diffusion (transport) coefficient of rare-earth-element (REE) cations in ferromagnesian olivine produce results that differ by greater than 10^3 [Cherniak, 2010; Spandler and O'Neill, 2010]. The faster of these studies reacted olivine with a synthetic silicate melt that was heavily doped with trace elements, including significant TiO_2 [Spandler and O'Neill, 2010]. Here we present high-resolution transmission electron microscopy (HRTEM) and electron-energy imaging from experiments replicating the TiO_2 -doped basalt-olivine reaction and demonstrate that the diffusion dynamics involve the nucleation and growth of planar extended defects along $(101)_{\text{ol}}$ that facilitate Ti^{4+} diffusion into olivine at a rate similar to Mg^{2+} – Fe^{2+} interdiffusion on the olivine lattice. The initial extreme driving force for inclusion of Ti^{4+} into olivine leads to the creation of the planar defects; the diminishment of the chemical potential gradient accompanying the reaction results in their dissolution. The presence of extended defects, and their likely association with natural reacting systems experiencing

large chemical potential gradients, requires reevaluation of the dominant kinetic diffusion mechanism and has implications for understanding the robustness of the chemical signature(s) of primitive basaltic melt carried by olivine-hosted melt inclusions.

Our reaction experiments involved sintering/reacting of very-fine-grained olivine-basalt partial melts [Cooper and Kohlstedt, 1984]. The olivine is pulverized peridot from San Carlos, AZ, with composition $\sim\text{Fo}_{90}$. The synthetic basaltic melt mimics that associated with a mid-ocean ridge (MORB) and was designed to be close to equilibrium with the olivine at experimental conditions, with the exception of a notably high, hyper-natural TiO_2 content, $\sim 5\text{wt}\%$, but matching that of Spandler and O'Neill [2010] (Table D1). The activity of TiO_2 in the initial melt is $a_{\text{TiO}_2} = 0.1$; the initial a_{TiO_2} of the olivine is $\sim 10^2$ times lower [Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998]. Experiments were run for 48-50 h at 1310° or 1410°C and buffered at an oxygen fugacity f_{O_2} either one or two log units above or two log units below the quartz-fayalite-magnetite (QFM) buffer (Table D2), well within the stability field of Fo_{90} olivine having a low TiO_2 content.

Figure 4.1: (a) SEM/BEI of specimen M2 (1310°C , QFM+2). Bright titanomagnetite grains are visible in the glass within triple junctions and melt pockets. (b) Bright-field TEM image of M1 (1310°C , QFM+1) showing a glass pocket amongst several olivine grains. Ilmenite, pyroxene (pyx), and olivine are present in the glass and attached to the larger olivine grains. High-contrast, defect-rich regions are visible in the olivine near olivine-glass interfaces, as indicated by the circled areas. (c) Bright-field TEM image of specimen M1 showing an obliquely oriented glass-olivine interface that adjoins olivine intercalated with high-contrast defect-rich regions (Fig. D1). The alternating stripes of darker and lighter regions indicate changes in the relative thickness of the olivine and glass.

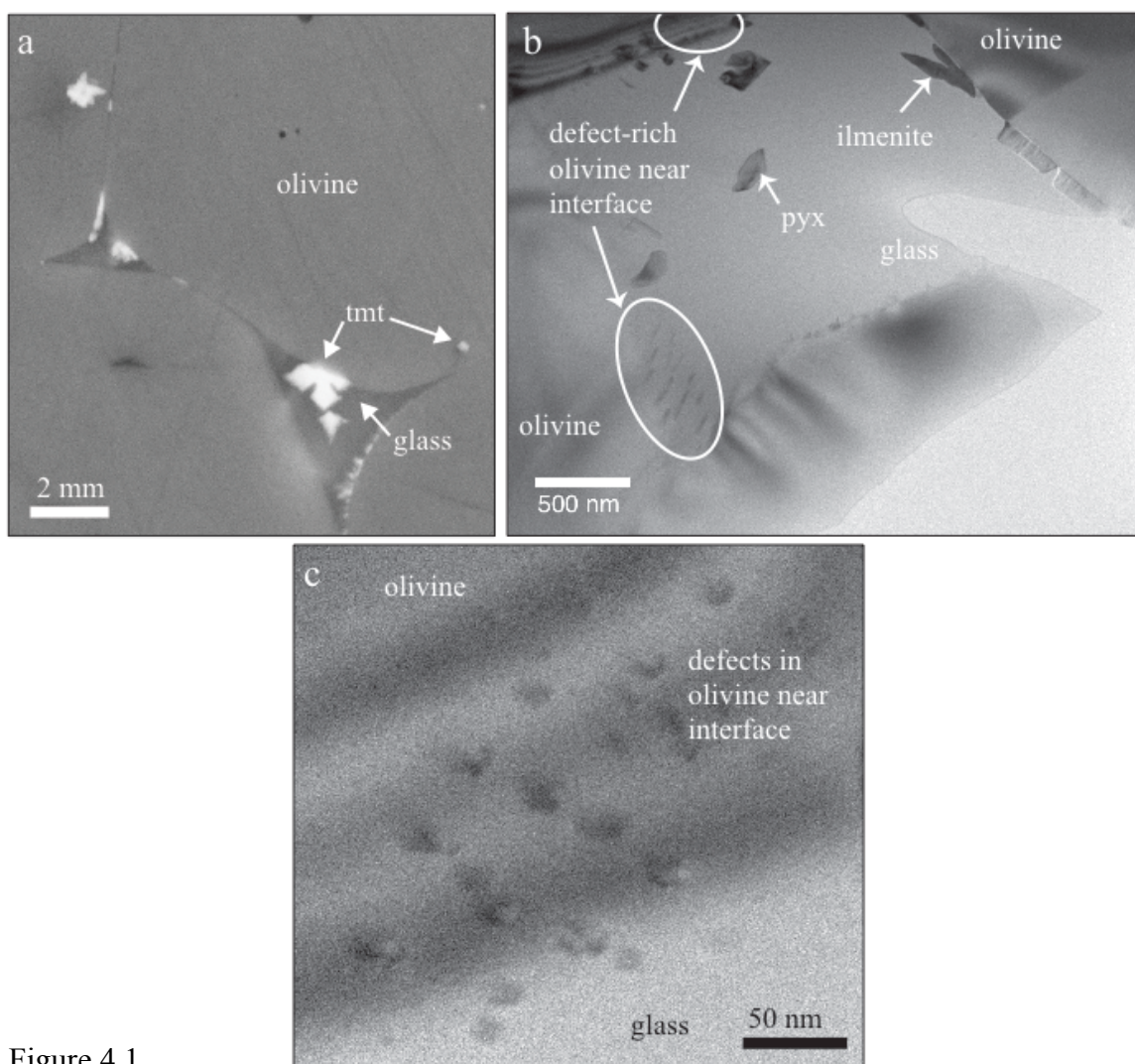


Figure 4.1.

Scanning electron microscope (SEM)/backscattered electron images (BEI) of reacted specimens show well-formed melt (glass)-filled triple junctions and larger melt pockets in all annealed samples; the melt pockets contain quench crystals of titanium oxides that include titanomagnetite at high f_{O_2} (Fig. 4.1a) and ilmenite at all f_{O_2} . TEM images of samples annealed above QFM show ubiquitous titanomagnetite and ilmenite grains in the glass near the olivine interfaces; quench crystals of olivine and pyroxene are also found both surrounded by glass and attached to the olivine surface (Figs. 4.1b). Ilmenite and olivine only are found in the specimen treated at QFM-2. In the vicinity of

many olivine-melt boundaries, small (tens of nm) regions of high-contrast, which indicate changes in density, composition and/or crystal structure, intersect the interface and extend into the olivine (Fig. 4.1c); the image contrast indicates that these regions are thin and extend obliquely through the TEM foil (Fig. D1). A correlation of the defects with Ti enrichment is confirmed by energy-filtered imaging (Fig. 4.2a,b), while Fe is depleted in the same locations (Fig. 4.2c), suggesting Ti^{4+} for (2) Fe^{2+} substitution on the octahedral cation site.

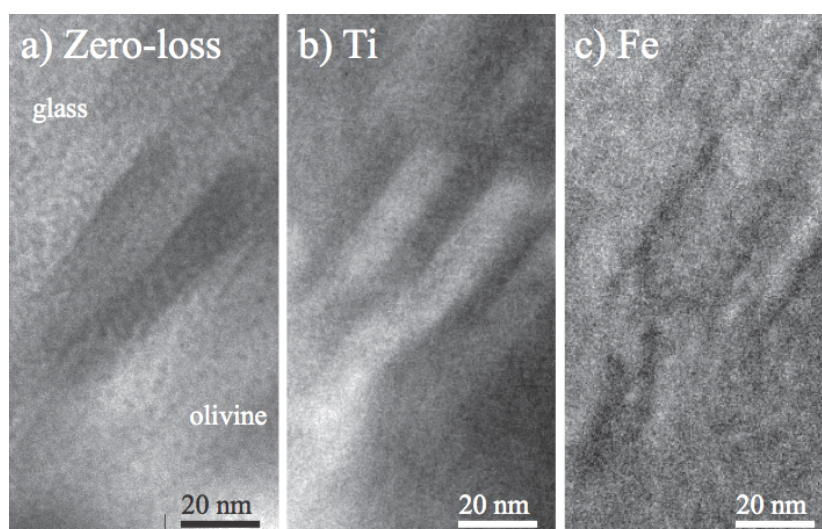


Figure 4.2: (a) Zero-loss energy-filtered bright-field image of an obliquely oriented glass-olivine interface in specimen M1 (1310°C, QFM+1). The central part of the image contains both glass and olivine, with defect-rich structures evident in the olivine. (b,c) Select EELS element maps of the same region showing the enrichment in Ti (25 eV) and depletion of Fe (54 eV) within the defect-rich olivine.

HRTEM imaging of the high-contrast features in all olivine-basalt samples shows the presence of a superstructure in the lattice fringes, indicative of localized changes in the crystal structure of the olivine (Fig. 4.3). We identify these features as ‘extended defects’ in the olivine [though cf. *Maier*, 2004, p208]; in that the defects are associated with specific lattice planes, we refer to them as planar defects. The spacing of the lattice fringes, and thus the dimensions of the unit cell, can be measured using a Fast Fourier

Transform (FFT) of the image—an analog of the electron diffraction pattern; the extended defects are too small to affect significantly the actual selected-area diffraction patterns. The insets in Fig. 4.3 show the FFTs for the defects highlighted in the figure. The “extra” spots, and therefore the planar intercalations they represent, are along $(101)_{ol}$. The tripling of diffraction spots in this plane indicates a defect superstructure involving three unit cells of the olivine; the spots representing the superstructure in the olivine are slightly fuzzy due to the repeat distance of the structure not being perfectly regular. Additionally, there is never a well-defined interface between the olivine and defect on all edges of the defect, with the defect superstructures transitioning smoothly to defect-free olivine.

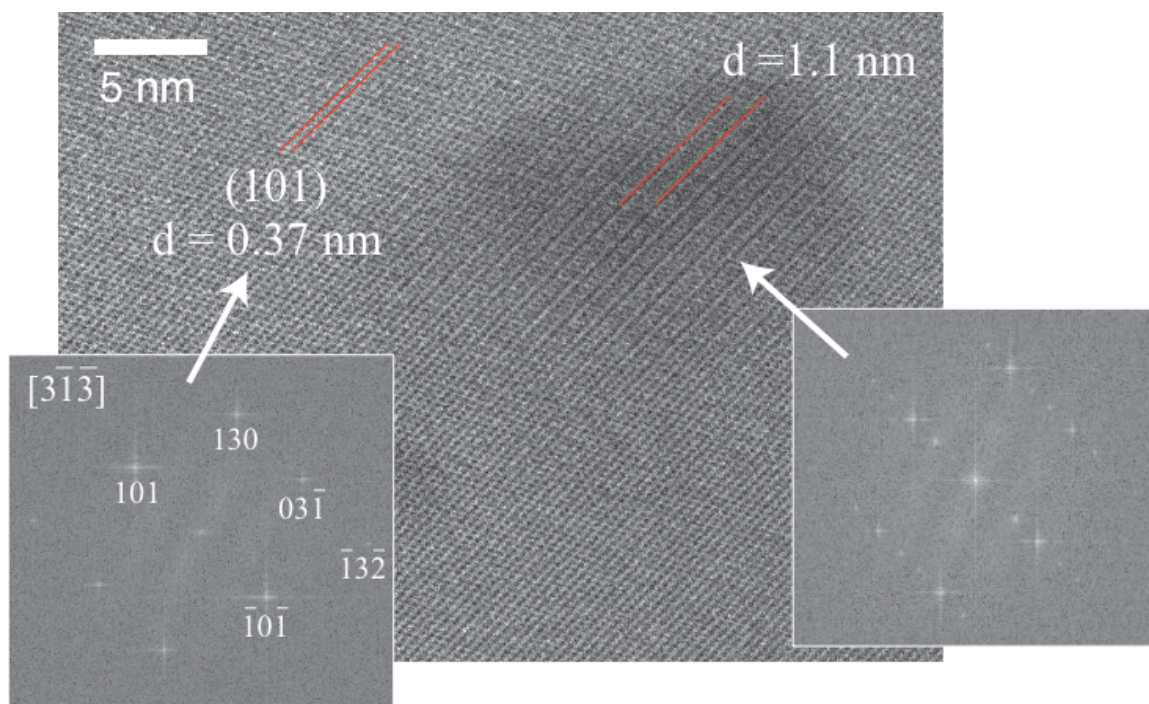


Figure 4.3: HRTEM image from specimen M3 (1410°C, QFM+2) showing planar-defect-rich olivine. The insets show the FFTs for the olivine-only region (lower left) and the olivine with defect-controlled lattice superstructure (upper right). The repeated spots for the defect-rich region are in (101) and show a superstructure involving three unit cells of olivine (i.e., a tripling of the olivine diffraction spots). The olivine zone axis is $[3\bar{1}\bar{3}]$.

As the TEM foil is tilted away from this zone axis, the aspect ratio of the extended defects also changes, such that one dimension remains unchanged while the other becomes longer, indicating that the defects extend some distance into the olivine. The longest observed defects were ~ 160 nm, and all extended defects in the same general location or being intercalated from the same olivine-glass interface have their long axis in the same direction, confirming the importance of the relationship with the olivine lattice. Thus, the observations are uniquely consistent with the defect regions as prolate spheroids (“cigar shaped”) where the long axis extends into the olivine parallel to (101); we were unable to determine if a single direction on (101) is more common for the long axis.

These extended defects are notably absent in basalt-olivine samples with MORB-like TiO_2 (~ 1.5 wt%) prepared at oxidizing (QFM) conditions, which have been viewed in detail by us and by a host of other investigators over the past 25 years [e.g., *Cooper and Kohlstedt*, 1982; *Vaughan and Kohlstedt*, 1982; *Hiraga et al.*, 2004]. The general microstructure of such samples is otherwise similar to those presented here, except that ilmenite and (titano)magnetite are additionally not present as quench crystals in melt at triple junctions.

Both samples annealed at QFM+2 have small titanomagnetite crystals within olivine that can be seen in BEI (Fig. 4.4a). Titanomagnetite + amorphous silica is ubiquitous in the sample reacted at 1410°C , and TEM imaging shows the titanomagnetite grains are 10s to 100s of nanometers across and grow topotactically in the olivine with $(111)_{\text{tmt}}$ parallel to $(100)_{\text{ol}}$ (Fig. 4.4b,c). Comparison of electron-energy-loss spectrometry (EELS) from a titanomagnetite grain and from surrounding olivine reveals

that Ti is present in the grains that nucleated in the interior of the olivine grains (Fig. E7). Magnetite plus silica in the microstructure described in our samples is known in oxidized olivine, but our samples are below the f_{O_2} required for this reaction to take place in Fo₉₀ olivine ($\sim 10^{-4}$ atm at 1300°C, versus 5×10^{-7} atm in our high f_{O_2} sample, M2). However, titanomagnetite was able to nucleate in our samples as the increase in a_{TiO_2} allowed for a decreased dependence on f_{O_2} in the reaction. If Ti is able to diffuse to the center of the ~ 20 μm olivine grains in 50 hours at 1310°C, we calculate $D_{Ti} \sim 10^{-15}$ m²/s, which is on the order of Fe-Mg lattice interdiffusion in olivine [Chakraborty, 2010] and is consistent with Ti^{4+} diffusivity measurements claimed by Spandler and O'Neill [2010], but interpreted by them as straightforward lattice diffusion.

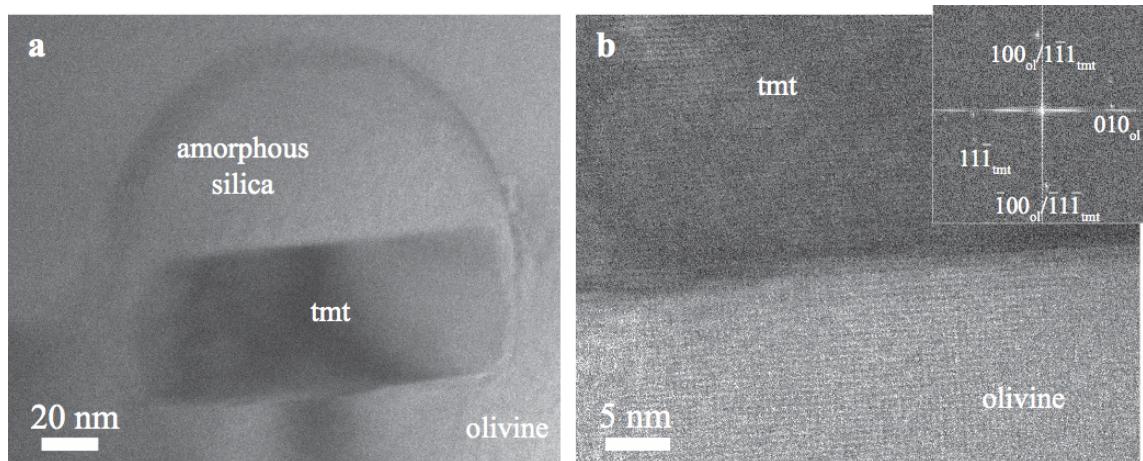


Figure 4.4: (a) Bright-field TEM image from specimen M3 (1410°C, QFM+2) showing a titanomagnetite grain and amorphous silica-rich region within an olivine grain, removed several microns from the nearest olivine-melt interface. (b) HRTEM image showing the relationship of the titanomagnetite and olivine. The FFT in the inset shows $(100)_{ol}$ is parallel to $(111)_{tmt}$. The olivine zone axis is $[001]$.

Condensed planar defects have previously been characterized for extrinsic ferromagnesian olivine: examples include laihunite layers—planar ordering of substitutional Fe^{3+} and charged vacancies on the Mg^{2+} octahedral sites—in oxidized olivine [e.g., Kondoh *et al.*, 1985; Banfield *et al.*, 1990; Khisina *et al.*, 1995] and

intercalation of humite-type layers—ordering of substitutional $(\text{OH})^-$ (or F^-) and Mg^{2+} vacancies [e.g., *Risold et al.*, 2001; *Wirth et al.*, 2001; *Hermann et al.*, 2007] at high activity of H_2O ($\pm \text{F}$). Dramatically, the condensation of point defects in olivine into planar intercalations is the foundation of olivine-structure lithium iron phosphate, LiFePO_4 , which has found utility as a positive electrode in Li-ion batteries [e.g., *Padhi et al.*, 1997]. Li^+ diffuses most rapidly along [001] and its removal leaves planes of (sub-unit-cell) FePO_4 -like layers (ordering of Li^+ vacancies and Fe^{3+} substitutionals) that act essentially as a second phase; this fixes the electrochemical potential of oxygen (required of an effective electrode in this case) while the offset along the planar defect rate-enhances diffusion of Li^+ [*Padhi et al.*, 1997; *Chen et al.*, 2006], i.e., compared to straightforward lattice diffusion, which is critical to the practical power function of the cathode. The formation of the planar defects and lattice superstructure apparent in HRTEM in our specimens and in these other examples is due to association and ordering of the point defects. Because point defects in minerals, such as interstitial or substitutional ions and vacancies, affect locally the electronic structure of the mineral and can strain the lattice, they begin to interact—electrostatically and/or elastically—as their concentration is increased.

The orientation of the extended planar defects seen here in all of the high-Ti basalt-olivine samples (parallel to $(101)_{\text{ol}}$) has not been reported before. Both laihunite and humite-type defect intercalations are parallel to $(001)_{\text{ol}}$ or possibly $(021)_{\text{ol}}$ with rare examples of other orientations [e.g., *Banfield et al.*, 1990; *Banfield et al.*, 1992; *Iishi et al.*, 1997; *Risold et al.*, 2001; *Wirth et al.*, 2001]. The spacing of the defect planes in a regular manner creates the superstructure, which is most often three-layer (Fig. 4.3), but a

two-layer superstructure was also observed. Laihunitite is also known to often have a two- or three-layer structure that in TEM resembles what is seen in our samples [*Kondoh et al.*, 1985; *Banfield et al.*, 1990; *Janney and Banfield*, 1998].

Formation of the planar defects does not require a precipitation reaction associated with, e.g., a temperature decrease: locally, at the melt-olivine interface, the initial TiO_2 chemical potential difference $\Delta\mu_{\text{TiO}_2}$ and gradient $\nabla\mu_{\text{TiO}_2}$ is large enough that nucleation of the condensed defects is an allowed, local-equilibrium response (Fig. D2). The defect-ordering reactions are exothermic [*Schmalzried*, 1981, pp50-51], and any extrinsic (chemical-activity-effected) process that increases the concentration of point defects, such as an increase in f_{O_2} at constant temperature and pressure, or as here, the addition of impurity ions at non-equilibrium conditions, will increase the likelihood of defect complex and planar or three-dimensional structure formation. With sufficient $\nabla\mu_{\text{TiO}_2}$ (in the present case), there is no requirement that a bulk solubility limit must be reached before the ordered defect superstructure can be nucleated. (Chemically-induced grain boundary migration (CIGM), as a parallel example of a high-driving-force reaction, see the recrystallized region behind the moving boundary as often undersaturated in the solute ion [*Hay and Evans*, 1987].) Both the concentration of Ti^{4+} and its mobility (a function of vacancy concentration: each Ti^{4+} replacement for (2) Fe^{2+} creates an octahedral-site vacancy) are enhanced within the extended defect, thus increasing the transport coefficient for Ti^{4+} diffusion within the planar defects relative to that in the unaffected lattice. The defect superstructures are analogous, then, to the initial stages of reactive melt fingers in harzburgite [e.g., *Kelemen et al.*, 1995], both in their transience as individual instabilities and in their ability to enhance transport. At the interior end of the

condensed defects, there is no abrupt interface and the transition to nominally defect-free olivine lattice is smooth (Fig. D2). The $\nabla\mu_{\text{TiO}_2}$ and point defect concentration at this distance from the glass is too small to maintain the defect associations, and they dissolve. Thus, the planar condensed defects are transient; the rapidly quenched specimens allow us to capture these transient features.

Olivine phenocrysts that host melt inclusions are exposed to many conditions under which the chemical potential gradients for many elements meet or exceed that tested here, including during magma mixing or metasomatism. Recognition and identification of the transient defect-rich structures created by such large driving forces requires detailed analysis of natural and experimental specimens.

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APPENDIX A

Modeling of Compositional Layers Using RBS Data and RUMP Software

RBS is a nondestructive, chemical profiling technique that measures the energy loss of accelerated α -particles (helium nuclei, He^{++}) impinging on, and backscattering from component-ion nuclei of a specimen. Each component element directly and characteristically affects the momentum loss of α -particles that scatter off its nuclei while bonding between ions has no effect, thus allowing direct correlation between energy of the rebounding α -particle and composition of the specimen [Chu *et al.*, 1978]. At depth in the specimen, the α -particles interact with inner shell electrons and lose energy depending on the ion-backscattering and ion-stopping cross-sections (functions of both specimen composition and the kinetic energy of the α -particles); knowledge of sample composition and density allows for modeling of the depth at which elastic scattering occurred. Compositional profiling can be done to a depth of several micrometers (with resolution ~ 10 nm), limited by the inelastic interactions between the α -particles and electrons. Lateral spatial resolution is limited by beam size, which is ~ 1 mm; spectra average over this area. In analysis of our oxidized specimens, initial α -particle kinetic energies of 2.0 MeV and 3.5 MeV were used. RBS spectra were collected using the accelerator at the Ion Beam Laboratory of SUNY-Albany.

The RBS analyses presented here and in Chapter 2 of this dissertation employ the commercial analysis software RUMP (CGS, Inc., Ithaca, NY) for simulating spectra. Spectral simulations use known ion-stopping and ion backscattering cross sections to generate a synthetic spectrum from a stipulated spatial distribution of atoms [Doolittle, 1985]; the synthetic spectrum can be evaluated statistically relative to the actual spectrum. Modeling was done by specifying a series of discrete slabs of constant

composition parallel to the specimen surface. Thickness of model layers is measured in 10^{15} atoms cm^{-2} , and density calculations for the glass after simulating compositional changes are necessary to calculate depth in the sample in standard units.

The algorithm developed by *Doolittle* [1985] to simulate RBS spectra sums the energy loss due to each nuclide used in the input model. The energy loss as the ion beam traverses the sample is

$$\frac{dE}{da} = -\varepsilon(E), \quad (1)$$

where a is the path length into the material, measured in areal density units. The sample is broken into sublayers of limited thickness and each sublayer is calculated separately, then summed. The energy of the beam at each depth $E(a)$ is approximated by means of a Taylor series, allowing for rapid, accurate calculation of $E(Nt \sec \theta)$, the energy of the beam after passing through a single sublayer of thickness Nt at angle θ to the sample normal, given an initial beam energy $E(0)$.

In RUMP simulations the final spectrum is a sum of the calculated yields y at each interface

$$t_i = \sum_A y^c \quad (2)$$

where the yield for each nuclide is

$$y^A = \frac{x_A \sigma(E_i)}{[\varepsilon(E_i)]_A \cos \theta} \prod_{\text{layers}} \frac{\varepsilon(E_m)}{\varepsilon(E_{out})}. \quad (3)$$

A is the nuclide, x is the atomic fraction of the nuclide, θ is the angle between the detector and the surface normal and the stopping cross section factor for component A is

$$[\varepsilon(E)]_A = K_A \varepsilon(E) + \varepsilon(K_A E). \quad (4)$$

K is the scattering cross section (i.e., kinematic factor)

$$K = \left[\frac{(1 - x^2 \sin^2 \phi)^{1/2} + x \cos \phi}{1 + x} \right]^2, \quad (5)$$

where x is the ratio of projectile mass to target nuclide mass, and ϕ is the scattering angle.

Because inelastic energy loss becomes extreme with depth in the sample, RBS is limited to the first few micrometers of a material. Modeling of the spectrum is not possible at low energies due to this non-linear increase in energy loss with depth, and also because of non-Rutherford scattering in light elements when α -particle energy is high. In the data for Chapter 2, two acceleration energies are used to get spectra for each sample, 2.0 MeV and 3.5 MeV. The region where models can be well fit and minimize the low energy inelastic effects is shown for a spectrum acquired at 2.0 MeV (Fig. A1).

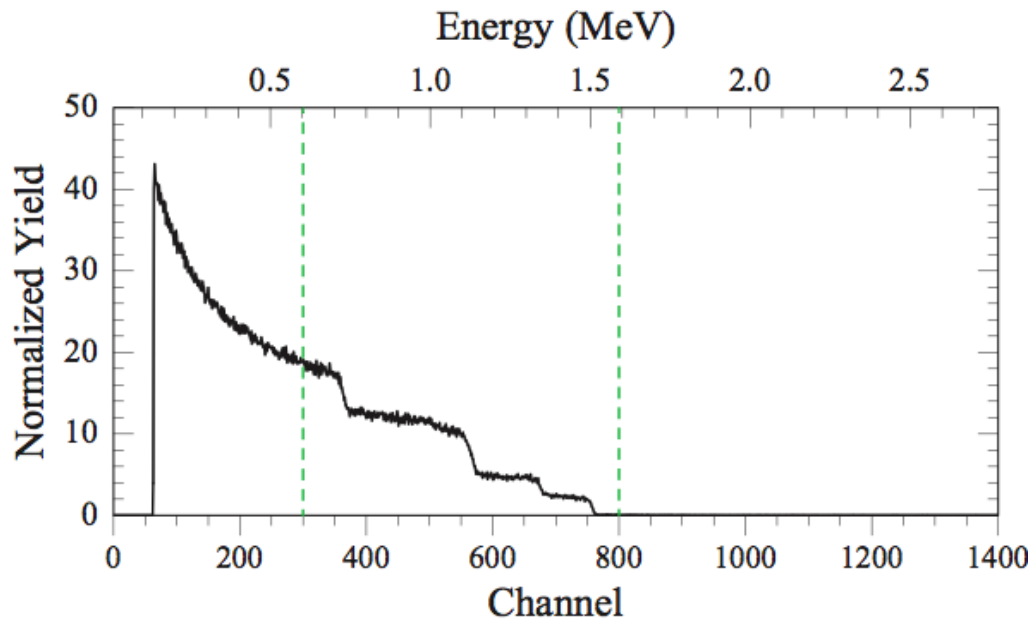


Figure A1: A limited range of the collected spectrum was used for the simulation and modeling, as denoted by the green dashed lines overlying this 2.0 MeV spectrum of an unoxidized sample.

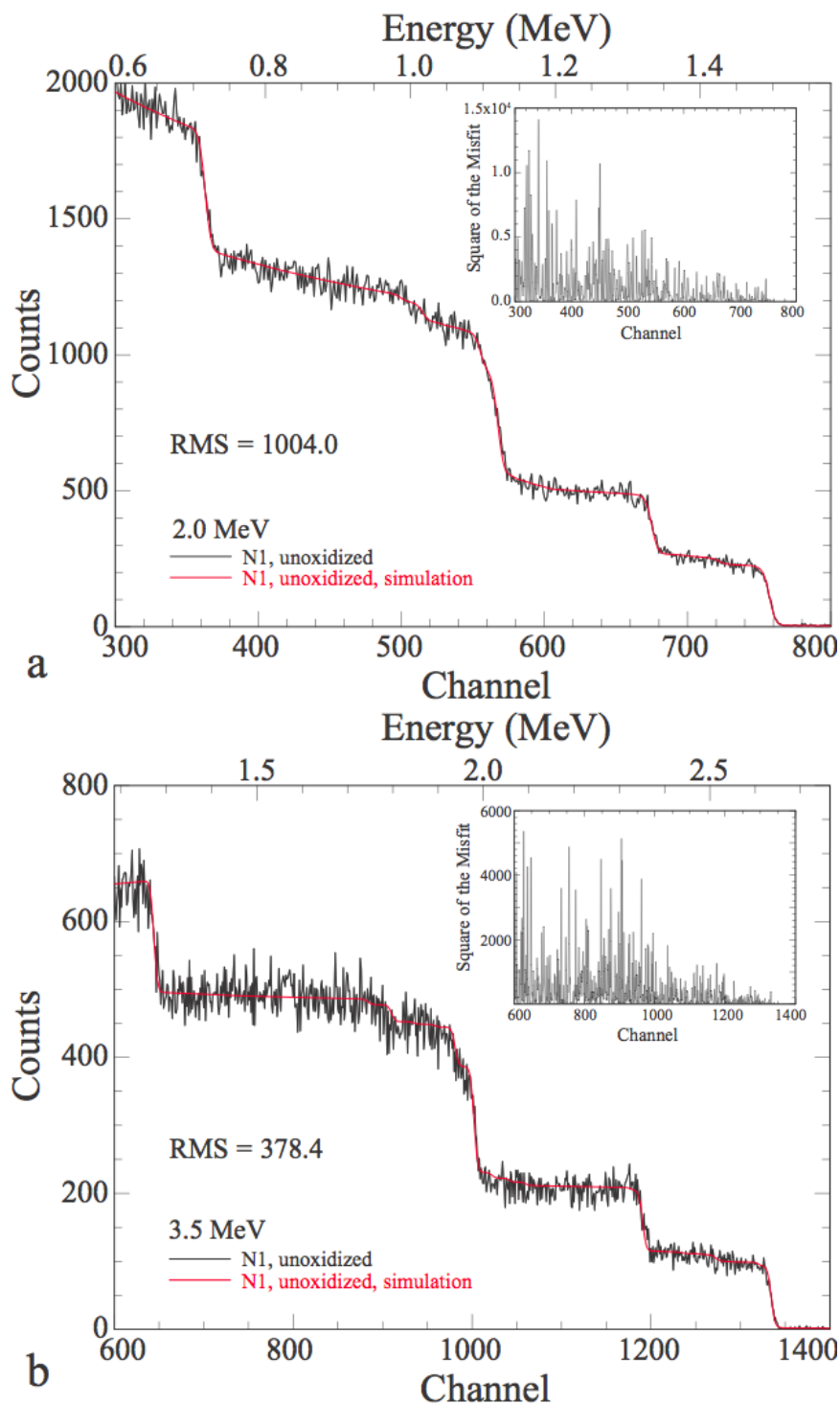


Figure A2: Spectra of the unoxidized sample showing the best-fit RUMP simulation for a homogenous glass. The same composition is used to model the spectrum at both (a) 2.0 MeV and (b) 3.5 MeV. The square of the misfit has been calculated (insets), and when normalized by channel, shows a normal distribution meaning the noise is random. The root mean square of the error (RMS) cannot be compared between energies due to the large difference in total yield.

Qualitatively good fits can be done by examination of peaks and steps in the spectrum relative to the energy for an element at the surface of the sample, and the match between simulations using the composition of the homogeneous glass determined using WDS and the acquired spectra is good. For more quantitative analysis of the goodness of fit, RUMP includes a subprogram PERT, which uses a standard nonlinear least squares technique to maximize the Poisson likelihood function χ^2 between the experimental spectrum and the simulation over a selected region [Doolittle, 1986]. Parameters for the fit are selected by the user, and include concentration of any element in the material, thickness of layers with differing concentrations, and the conversion between detector channel and energy. Iterations are done to find the lowest χ^2 and may require new inputs for parameter values if the starting model was not close enough. The convergence criterion is for $\chi^2(x_j) < \chi_o^2 + 2\delta$ for all x_j . The δ is fixed at unity, but in principle depends on size of the confidence interval of interest. In practice, this has little effect.

For a material that is homogeneous with depth, as in the unoxidized sample, the parameters varied are the concentration of the different (major) elements in a natural basalt, a total of 11 possible parameters. The total concentration is always 100%, so changing any one parameter changes all the others. The fit of the simulation to the spectrum is made better by including the eight most abundant elements, but beyond that fit is no longer improved, as the other elements are not present at high enough concentrations. The same composition model needs to fit two spectra of the same sample, taken at different acceleration energies. The magnitude of the noise is negatively correlated with the channel number in non-normalized spectra.

The RMS value of the misfit in each case allowed for comparison of different spectra, and thus allowed me to compare fits done using all the same parameters, but for the two different energies. In the best fitting model, the RMS value should be at its lowest for both energy levels. Several models have been created that fit the data better than the “known” composition, although the known composition fits within the confidence interval and thus is not meaningfully different. To determine the confidence interval, I used the t-test, $m \pm t_{(1-\alpha)} \sigma$ (Fig. A3). The standard deviation is given by PERT, and for each model fit is the same for all elements as a percentage of their total concentration in the material. The starting concentrations of the elements used in the model affect the end concentrations, since the model is nonlinear and the parameters are not independent.

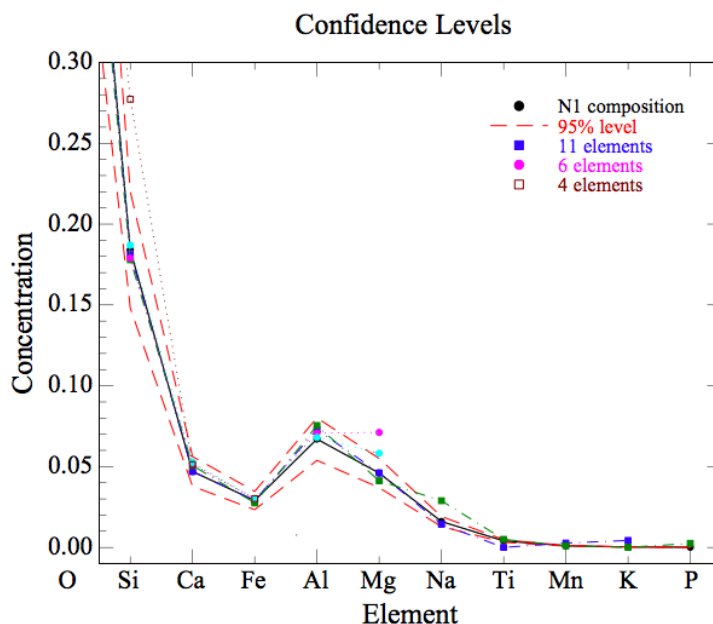


Figure A3: Confidence levels calculated for the simulations of the unoxidized sample using the t-test, $m \pm t_{(1-\alpha)} \sigma$. When fewer parameters are used, the fit tends to be worse, although it is not until elements with atomic concentrations more than 0.01 in the sample are discarded that the fit is statistically worse. Fits with more than seven parameters end up all within the 95% confidence level of the nominal sample, assuming sigma ~10% of the concentration, which is the average sigma for model runs with eight or more parameters.

I selectively decided on which parameters to not include when fewer than 11 were included in the model. Qualitative examination of the spectra gives information on which will be most abundant, and thus have the largest effect upon the model and real spectra.

To examine the residual, I looked at if this error was normally distributed about a mean. In the original data, the misfit does not have a normal distribution. When the misfit is normalized by the channel number, however, the fit to a normal cumulative distribution curve is much better and I can say with some confidence that the error is normal.

When thin films of differing concentration are seen, the physics of RBS are no different, but modeling becomes more complicated. It is theoretically possible to use PERT to simulate diffusion profiles, but this was not done for the data presented in Chapter 2. However, basic confidence levels for certain elements could be determined by adjusting a single element such as Na and calculating RMS for limited channels near the Na energy. In this way it was determined that Na could be increased up to four times, although no sharp peak is present.

Fig. A4 shows the simulations for spectra from the samples oxidized at 600°C. For each time, the basic composition of the slabs did not change significantly but the thickness increased parabolically. The fit for sample N1-600-5.5 is shown for both RBS energies used (Fig. A4a,b); the lack of fit at low energies in Fig. A4b likely indicates that Na diffusion from depth in the sample has not been accounted for fully.

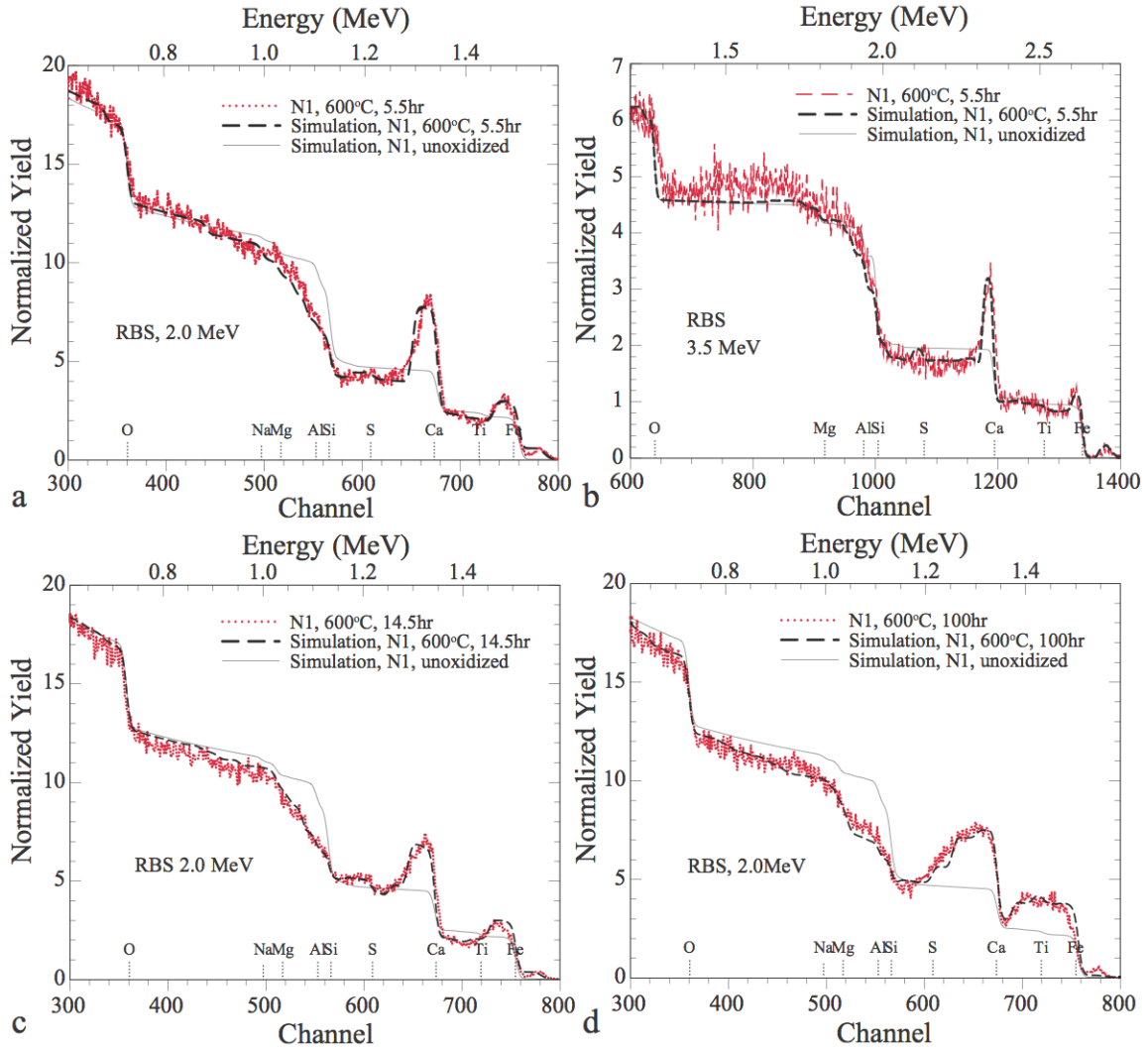


Figure A4: A series of RBS spectra for the sample oxidized at 600°C showing the fit of the simulated model presented in Chapter 2. (a) and (b) show spectra for the same sample, N1-600-5.5, for the two different accelerating energies used. The same layer compositions and thicknesses are used in the simulation and fit the RBS spectra for both energies. (c) N1-600-14.5 and (d) N1-600-100 show the evolution of the peak height and size and were modeled by changing the oxidized and depleted layer thicknesses while not changing the composition of the layers significantly. The simulation of the unoxidized sample shown above is the thin line in each figure.

In these spectra, when complimentary error functions are attempted in PERT simulations with diffusion coefficients of the same order to literature data of diffusion in Fe-bearing glasses, qualitatively the fit is very good for the first peak in Fe. The difficulty lies in creating equations that take into account more than one element, which have

different diffusion rates and concentrations, and different dynamics at different depths and times. Because in these spectra we know that the oxidation gradient drives the diffusion, we know that high concentrations at the surface mean there are depletions at depth. These depletions are more difficult to fit using basic equations and will need more work. The simulations developed for the oxidized materials include only compositional data, not the physics of the process creating the concentration changes.

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APPENDIX B

Major and Minor Element Data for Santiago and Fernandina Melt Inclusions

Analytical Techniques

The compositions of the inclusion and matrix glasses, as well as the forsterite content of the host olivines, are presented in Tables B1 and B2. Major elements of the MI, matrix glasses and olivine phenocrysts were typically analyzed in triplicate using the Cameca XS-100 electron microprobe at the Department of Geological Sciences, Brown University. Analyses were performed using 15 kV accelerating voltage, 10 nA beam intensity for the glasses, and 20 keV, 25 nA for the olivines with a focused beam, and PAP correction procedures [Devine, 1995; Pouchou and Pichoir, 1991]. Synthetic and natural standards were used for calibration. Smithsonian basaltic glasses VG-A99B (USNM 113498) and VG-2B (USNM 111240), and olivines San Carlos (USNM 111312) and Springwater (USNM 2566) were used as monitor samples 24 in routine measurements. Analytical errors (2σ) were <5% for SiO₂, CaO, Al₂O₃, MgO, TiO₂, and FeO, and <9% for Na₂O for the glasses and <2% for SiO₂, MgO, and FeO in olivines. Trace elements (K, Ti, P, Nb, and REE) and volatile analyses (H₂O, CO₂, F, S, and Cl) were performed on the Cameca 6F Ion Probe at the Department of Terrestrial Magnetism, Carnegie Institution of Washington using techniques and standards previously described [Hauri, 2002]. Errors, determined from replicate analyses of matrix glasses and large MI, for trace elements were typically < 5% (2σ).

Sample Details

All MI from Fernandina were selected from a single submarine lava with one of the highest ³He/⁴He ratios measured for the Galápagos islands (Fig. B1) [Kurz *et al.*, 2009], dredged from a depth between 2600-2900 m below sea level [AHA D25C from the AHA Nemo Cruise, 2000]. MI from Santiago were collected from a glassy subaerial

hornito STG06-29. Olivine grains containing MI were hand picked from crushed fractions of both samples, they were carefully polished until the inclusions were exposed, mounted into indium metal, and then polished using diamond pastes down to 0.25 μm . The MI analyzed are between 50 to 250 μm in diameter, with Santiago's inclusions being in average smaller ($\sim 60 \mu\text{m}$) than those from Fernandina ($\sim 125 \mu\text{m}$). The MI are naturally quenched to a homogeneous glass, and have shapes that indicate a primary origin [Sobolev, 1996], as illustrated by images from representative samples (Fig. B2).

Caption, Tables B1 and B2: Major (wt%) and trace (ppm) element compositions of (B1) Santiago and (B2) Fernandina olivine hosted-MI corrected for host olivine crystallization. Correction assumes that Fe_2O_3 is 10% of the total FeO. Total Fe reported as FeO^* . $\text{Mg\#}$ = molar, $100 \cdot \text{MgO} / [\text{MgO} + \text{FeO}]$ of the melt, Fo = molar, $100 \cdot \text{MgO} / [\text{MgO} + \text{FeO}]$ of the host olivine, and % ol indicate the amount of olivine added during the correction. Inclusion numbers with a subscript “D” and “E” indicate the incompatible trace element (ITE) depleted and ITE-enriched compositions respectively; “P” indicates a “ghost plagioclase” signature (i.e., primitive mantle normalized positive Sr anomaly). *Koleszar et al.* [2009] report average and standard deviation (2σ) data for secondary standards VG-2 (major elements) and ALV 159-4-1 (for trace and volatile elements) obtained during the acquisition of the Galápagos geochemical data. Unpublished data are in bold.

Table B1. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Santiago Island.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Host Mg#	Fo	% ol	Rb	Ba	Th	U
Santiago (sample STG06-29) (S 0 19' 5.2", W 90 35' 1.7", subaerial)																		
STG06-29-02A	47.4	1.16	18.3	8.89	0.132	8.91	12.5	2.51	0.050	0.048	100.0	66.4	86.9	5.6	*	*	*	*
STG06-29-02B	46.8	1.32	14.8	11.33	0.205	11.45	11.3	2.39	0.104	0.090	99.9	66.4	86.9	10.4	2.23	15.27	0.12	0.08
STG06-29-03	47.1	1.21	18.1	9.17	0.136	9.00	12.6	2.42	0.076	0.084	99.9	65.9	86.7	3.5	0.95	12.64	0.12	0.07
STG06-29-04	47.2	1.18	18.0	9.00	0.147	9.07	12.7	2.36	0.061	0.087	99.9	66.5	86.9	5.2	0.58	8.73	0.10	0.07
STG06-29-06	46.5	1.34	14.4	11.77	0.197	11.86	11.5	2.14	0.076	0.070	99.9	66.2	86.8	11.9	2.04	15.08	0.13	0.08
STG06-29-07	46.9	1.21	17.6	9.52	0.204	9.28	12.6	2.33	0.071	0.057	99.9	65.7	86.5	6.1	1.00	12.69	0.11	0.08
STG06-29-08	47.4	1.34	17.9	8.77	0.150	8.80	12.7	2.63	0.067	0.095	99.9	66.2	86.8	7.3	*	*	*	*
STG06-29-09	47.1	1.30	17.9	9.05	0.146	8.92	12.7	2.61	0.069	0.092	99.9	66.0	86.7	2.6	*	*	*	*
STG06-29-10 _E	47.2	2.37	13.2	13.28	0.219	9.49	10.9	2.71	0.214	0.240	99.9	58.3	82.4	6.5	4.97	40.08	0.47	0.24
STG06-29-11A	46.8	1.27	16.4	10.38	0.170	10.30	11.8	2.39	0.082	0.091	99.9	66.0	86.7	7.8	*	*	*	*
STG06-29-11B	46.9	1.31	15.2	11.23	0.172	11.17	11.4	2.47	0.094	0.059	100.0	66.0	86.7	10.4	*	*	*	*
STG06-29-12	47.0	1.22	17.6	9.45	0.166	9.41	12.4	2.35	0.076	0.078	99.9	66.2	86.8	6.3	*	*	*	*
STG06-29-13	46.8	1.36	14.7	11.53	0.178	11.35	11.3	2.35	0.091	0.089	99.9	65.8	86.6	11.0	2.01	15.05	0.14	0.08
STG06-29-14	47.8	1.13	18.3	8.71	0.106	8.46	12.5	2.59	0.069	0.100	99.9	65.8	86.6	3.0	0.67	10.81	0.11	0.06
STG06-29-15	46.8	1.22	17.3	9.72	0.167	9.69	12.4	2.33	0.078	0.099	99.9	66.2	86.8	7.3	*	*	*	*
STG06-29-16A	46.9	1.37	15.4	11.26	0.192	10.12	11.9	2.46	0.097	0.089	99.9	63.7	85.5	11.1	*	*	*	*
STG06-29-16B	47.0	1.38	15.7	11.10	0.205	9.97	11.8	2.43	0.069	0.135	99.9	63.6	85.5	10.7	2.04	14.52	0.15	0.12
STG06-29-16C	47.5	1.34	16.3	10.43	0.199	9.30	12.0	2.54	0.090	0.111	99.9	63.7	85.5	8.3	1.93	15.90	0.13	0.09
STG06-29-16D	47.2	1.24	18.2	9.33	0.165	8.33	12.7	2.50	0.074	0.100	99.9	63.7	85.5	6.8	*	*	*	*
STG06-29-17	46.7	1.18	17.3	9.87	0.182	9.79	12.3	2.32	0.063	0.066	99.9	66.1	86.8	5.1	1.03	11.54	0.11	0.06
STG06-29-19 _b	47.8	0.66	17.9	9.11	0.141	9.10	12.4	2.65	0.048	0.041	99.9	66.2	86.8	5.4	1.23	2.05	0.02	0.09
STG06-29-20	47.1	1.23	17.6	9.63	0.179	8.87	12.6	2.41	0.089	0.059	99.9	64.5	85.9	2.8	1.30	13.06	0.12	0.07
STG06-29-21	47.3	1.24	18.0	9.20	0.139	8.44	12.9	2.43	0.069	0.079	99.9	64.3	85.8	5.7	1.01	12.41	0.12	0.14
STG06-29-23A	46.9	1.31	15.3	11.06	0.210	11.08	11.2	2.50	0.094	0.106	99.9	66.2	86.8	9.8	*	*	*	*
STG06-29-23B	46.7	1.38	15.0	11.17	0.129	11.32	11.4	2.56	0.116	0.103	99.9	66.2	86.8	14.7	*	*	*	*
STG06-29-24	47.2	1.21	17.6	9.40	0.153	9.44	12.1	2.60	0.078	0.055	99.9	66.5	86.9	3.9	1.40	13.40	0.12	0.08
STG06-29-25A	47.0	1.41	14.5	11.65	0.171	11.03	11.4	2.40	0.091	0.079	99.9	64.9	86.2	9.6	2.41	15.34	0.14	0.10
STG06-29-25B	46.4	1.39	14.2	12.18	0.205	11.61	11.4	2.26	0.091	0.095	100.0	65.0	86.2	11.6	*	*	*	*

Table B1. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Santiago Island.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Host Mg#	Fo	% ol	Rb	Ba	Th	U
Santiago (sample STG06-29)																		
STG06-29-27	46.7	1.42	14.7	11.20	0.199	11.11	11.8	2.38	0.082	0.114	99.9	66.0	86.7	9.6	2.05	15.19	0.15	0.12
STG06-29-29	46.9	1.29	17.4	9.53	0.142	9.36	12.7	2.30	0.053	0.100	99.9	65.9	86.7	3.3	1.03	11.15	0.13	0.12
STG06-29-32	46.7	1.36	14.8	11.61	0.198	11.25	11.4	2.35	0.094	0.088	99.9	65.4	86.4	11.5	2.51	14.64	0.14	0.12
STG06-29-34A	47.1	1.27	17.0	9.61	0.179	9.57	12.5	2.47	0.064	0.105	99.9	66.1	86.7	7.6	1.25	13.06	0.13	0.11
STG06-29-34B	46.4	1.31	16.8	9.98	0.140	9.97	12.6	2.37	0.083	0.103	99.9	66.1	86.7	7.6	*	*	*	*
STG06-29-35A	47.0	1.31	17.2	10.37	0.190	8.65	12.4	2.55	0.054	0.062	99.9	62.1	84.6	6.0	1.72	8.53	0.09	0.08
STG06-29-35B	46.8	1.29	16.8	10.73	0.190	8.95	12.4	2.53	0.058	0.081	99.9	62.1	84.6	5.1	2.22	8.35	0.10	0.10
STG06-29-37A	47.2	1.22	17.7	9.23	0.167	9.14	12.6	2.37	0.067	0.097	99.9	66.1	86.7	6.1	*	*	*	*
STG06-29-37B	47.2	1.25	17.7	9.15	0.137	9.11	12.8	2.43	0.069	0.086	100.0	66.1	86.7	6.6	1.61	10.97	0.12	0.12
STG06-29-39	47.1	1.26	17.9	9.32	0.159	8.76	12.6	2.57	0.084	0.091	99.9	65.0	86.2	4.2	1.33	14.05	0.13	0.12
STG06-29-40	46.8	1.24	17.3	10.04	0.176	9.35	12.3	2.36	0.072	0.086	99.9	64.6	86.0	8.0	1.61	12.68	0.10	0.11
STG06-29-42A	46.8	1.27	17.3	9.71	0.158	9.51	12.4	2.51	0.090	0.062	99.9	65.8	86.6	7.9	*	*	*	*
STG06-29-42B	47.2	1.22	17.8	8.90	0.169	8.68	13.2	2.54	0.077	0.098	99.9	65.8	86.6	2.9	*	*	*	*
STG06-29-43	46.8	1.23	17.3	9.63	0.169	9.28	12.8	2.39	0.071	0.109	99.9	65.5	86.4	3.1	1.25	13.34	0.13	0.09
STG06-29-44	47.1	1.36	15.9	10.54	0.163	10.29	11.8	2.46	0.098	0.079	99.9	65.7	86.5	8.0	1.69	15.48	0.15	0.10
STG06-29-47	47.6	1.42	16.8	9.65	0.160	9.28	12.1	2.65	0.097	0.090	99.9	65.5	86.4	5.7	1.41	16.16	0.14	0.09
Host Glasses																		
STG host glass	48.5	1.55	16.7	11.29	0.220	7.92	12.7	2.75	0.087	0.120	101.9	58.2	82.0	N/A	*	*	*	*

Table B1. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Santiago Island.

	Nb	K	La	Ce	Pr	Pb	Sr	Nd	P	Zr	Hf	Sm	Eu	Ti	Gd	Tb	Dy	Ho	Er
Santiago (sample STG06-29) (S 0 19' 5.2" , W 90 35' 1.7" , subaerial)																			
STG06-29-02A	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-02B	2.69	737.2	3.31	9.78	1.60	0.81	178.97	8.45	416.31	76.02	2.04	2.92	1.09	7981.8	3.71	0.65	4.19	0.87	2.37
STG06-29-03	2.38	665.1	2.98	8.80	1.44	0.69	197.75	7.64	388.23	68.54	1.93	2.58	0.94	7270.4	3.27	0.56	3.63	0.79	2.28
STG06-29-04	1.93	491.1	2.37	7.26	1.25	0.56	180.93	6.86	357.31	62.59	1.84	2.34	0.93	6866.1	3.21	0.55	3.58	0.75	2.09
STG06-29-06	2.69	725.3	3.39	10.07	1.67	0.82	176.42	8.92	398.19	73.30	2.09	2.95	1.11	7780.9	3.62	0.63	4.15	0.91	2.62
STG06-29-07	2.34	648.0	2.96	8.45	1.40	0.67	195.68	7.47	361.69	65.55	1.74	2.57	0.91	7136.9	3.16	0.55	3.61	0.79	2.29
STG06-29-08	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-09	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-10 _E	8.75	1880.9	8.68	22.87	3.44	0.96	183.90	16.82	918.77	142.26	3.82	4.92	1.44	12687.2	5.72	0.96	5.94	1.26	3.53
STG06-29-11A	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-11B	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-12	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-13	2.88	748.1	3.53	10.20	1.63	0.67	179.39	8.46	424.80	76.89	2.22	2.79	1.13	8162.0	3.92	0.67	4.28	0.92	2.64
STG06-29-14	1.81	555.4	2.36	7.03	1.23	0.75	209.19	6.86	352.85	59.74	1.75	2.41	0.98	6773.5	3.22	0.57	3.80	0.80	2.25
STG06-29-15	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-16A	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-16B	2.74	717.0	3.53	10.35	1.71	0.71	186.76	9.07	408.24	75.94	2.24	3.23	1.12	8001.4	3.70	0.65	4.21	0.91	2.64
STG06-29-16C	2.84	762.1	3.60	10.55	1.74	0.69	195.31	9.22	431.72	78.21	2.31	3.01	1.20	8241.1	3.89	0.66	4.18	0.92	2.70
STG06-29-16D	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-17	2.20	622.7	2.68	8.22	1.36	0.68	191.79	7.25	356.22	62.98	1.75	2.32	1.06	6840.1	3.24	0.56	3.58	0.75	2.08
STG06-29-19 _b	0.24	142.6	0.59	1.42	0.23	0.87	65.64	1.16	48.11	7.92	0.20	0.35	0.19	1232.7	0.61	0.12	0.85	0.20	0.61
STG06-29-20	2.49	663.5	3.06	8.90	1.44	0.67	200.01	7.50	394.43	68.86	1.96	2.60	0.98	7451.2	3.43	0.59	3.75	0.81	2.32
STG06-29-21	2.32	616.3	3.19	8.75	1.45	0.67	196.52	7.71	369.59	65.85	1.95	2.41	0.99	6961.9	3.19	0.56	3.66	0.81	2.36
STG06-29-23A	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-23B	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
STG06-29-24	2.51	698.2	3.05	8.87	1.46	0.66	197.98	7.74	387.37	67.78	1.92	2.53	0.92	7330.7	3.29	0.56	3.62	0.79	2.31
STG06-29-25A	2.93	787.8	3.69	10.65	1.74	0.83	180.99	9.21	434.32	80.28	2.18	3.10	1.16	8404.9	4.00	0.69	4.42	0.94	2.64
STG06-29-25B	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*

Table B1. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Santiago Island.

	Tm	Yb	Y	Sc	Cr (Sr/Nd) _{PM}	(Ba/Th) _{PM}	(Eu/Gd) _{PM}
Santiago (sample STG06-29) (S 0 19' 5.2" , W 90 35' 1.7" , subaerial)							
STG06-29-02A	*	*	*	*	*	*	*
STG06-29-02B	0.38	2.54	23.29	38.52	220.5	1.330	1.568
STG06-29-03	0.34	2.15	20.46	30.64	120.2	1.625	1.254
STG06-29-04	0.32	2.01	20.20	26.95	121.5	1.657	1.105
STG06-29-06	0.40	2.51	22.21	36.59	221.6	1.242	1.397
STG06-29-07	0.34	2.05	19.78	30.70	128.4	1.646	1.381
STG06-29-08	*	*	*	*	*	*	*
STG06-29-09	*	*	*	*	*	*	*
STG06-29-10 _E	0.52	3.15	31.29	37.75	158.5	0.687	1.037
STG06-29-11A	*	*	*	*	*	*	*
STG06-29-11B	*	*	*	*	*	*	*
STG06-29-12	*	*	*	*	*	*	*
STG06-29-13	0.39	2.45	23.27	38.48	227.1	1.332	1.322
STG06-29-14	0.34	2.14	20.62	31.16	130.6	1.915	1.239
STG06-29-15	*	*	*	*	*	*	*
STG06-29-16A	*	*	*	*	*	*	*
STG06-29-16B	0.41	2.59	23.45	37.53	218.7	1.293	1.178
STG06-29-16C	0.40	2.49	23.56	37.60	199.5	1.330	1.454
STG06-29-16D	*	*	*	*	*	*	*
STG06-29-17	0.32	2.11	19.83	30.97	133.3	1.661	1.308
STG06-29-19 _b	0.08	0.48	5.24	16.32	210.9	3.557	1.078
STG06-29-20	0.35	2.17	21.16	34.28	150.1	1.676	1.272
STG06-29-21	0.34	2.06	19.84	26.89	127.4	1.601	1.294
STG06-29-23A	*	*	*	*	*	*	*
STG06-29-23B	*	*	*	*	*	*	*
STG06-29-24	0.35	2.20	20.63	33.89	147.0	1.606	1.308
STG06-29-25A	0.40	2.57	24.32	39.74	224.6	1.234	1.274
STG06-29-25B	*	*	*	*	*	*	*

Table B1. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Santiago Island.

	Tm	Yb	Y	Sc	Cr (Sr/Nd) _{PM}	(Ba/Th) _{PM}	(Eu/Gd) _{PM}
Santiago (sample STG06-29)							
STG06-29-27	0.38	2.40	22.78	37.00	211.8	1.247	1.234
STG06-29-29	0.30	1.91	18.49	30.14	154.8	1.656	1.041
STG06-29-32	0.37	2.34	22.61	38.30	233.7	1.271	1.221
STG06-29-34A	0.32	2.07	19.60	29.53	149.7	1.605	1.236
STG06-29-34B	*	*	*	*	*	*	*
STG06-29-35A	0.36	2.25	22.53	37.12	130.2	1.503	1.133
STG06-29-35B	0.37	2.34	22.26	38.35	149.5	1.497	1.021
STG06-29-37A	*	*	*	*	*	*	*
STG06-29-37B	0.30	1.90	17.62	29.08	173.0	1.636	1.137
STG06-29-39	0.35	2.11	21.22	32.97	145.3	1.571	1.270
STG06-29-40	0.32	1.97	19.16	31.30	168.9	1.658	1.548
STG06-29-42A	*	*	*	*	*	*	*
STG06-29-42B	*	*	*	*	*	*	*
STG06-29-43	0.33	2.10	19.82	32.11	142.0	1.655	1.280
STG06-29-44	0.39	2.50	22.57	34.99	180.0	1.364	1.273
STG06-29-47	0.38	2.44	23.65	37.09	197.8	1.340	1.401
Host Glasses							
STG host glass	*	*	*	*	*	*	*

Table B2. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Fernandina Island.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Host Mg#	Fo	% ol	Rb	Ba	Th	U
Fernandina (sample AHA D25C) (S 0 27' 7.99", W 91 44' 23.9", Depth 4750 m)																		
D25C-2-02	48.5	2.21	16.3	8.91	0.201	8.24	12.3	2.17	0.202	0.116	99.3	64.5	85.9	7.2	3.04	52.28	0.62	0.24
D25C-2-06	48.5	2.44	15.4	9.80	0.103	8.30	11.1	2.82	0.385	0.255	99.3	62.4	84.8	6.6	5.63	83.91	0.89	0.33
D25C-2-09	48.1	2.94	14.3	11.35	0.163	7.84	11.3	2.48	0.419	0.299	99.3	57.6	82.0	6.0	7.26	100.44	0.99	0.38
D25C-2-12	48.2	1.64	15.2	11.54	0.154	7.67	12.5	2.00	0.159	0.149	99.4	56.6	81.4	6.1	*	*	*	*
D25C-2-16A	48.4	2.99	14.4	11.08	0.218	7.68	11.4	2.29	0.399	0.312	99.2	57.7	82.0	4.7	*	*	*	*
D25C-2-16B	48.0	3.09	14.5	11.38	0.167	7.90	11.5	2.56	0.414	0.293	100.0	57.7	82.0	4.6	*	*	*	*
D25C-2-19A	47.9	2.62	15.8	8.82	0.139	8.68	11.8	2.48	0.437	0.501	99.3	65.8	86.6	7.8	7.10	102.11	1.17	0.42
D25C-2-19B	47.8	2.62	15.9	8.68	0.136	8.54	12.2	2.43	0.397	0.548	99.3	65.8	86.6	7.7	6.59	92.99	1.08	0.42
D25C-2-21A	48.2	2.63	14.8	10.76	0.152	7.95	11.7	2.35	0.302	0.233	99.2	59.1	82.9	6.7	*	*	*	*
D25C-2-21B	47.7	2.77	14.7	11.05	0.145	8.16	11.7	2.23	0.393	0.288	99.3	59.2	82.9	6.4	*	*	*	*
D25C-2-21C	48.8	2.57	14.6	10.77	0.164	7.96	11.9	2.25	0.349	0.278	99.7	59.1	82.9	7.3	*	*	*	*
D25C-2-24 _b	51.9	1.62	15.1	8.18	0.155	8.36	12.0	1.78	0.056	0.034	99.3	66.6	87.0	7.5	0.05	7.88	0.14	0.06
D25C-2-25A	47.5	2.21	16.6	9.58	0.142	8.53	11.8	2.10	0.320	0.344	99.2	63.6	85.4	7.3	4.46	80.20	0.79	0.33
D25C-2-26	48.1	2.59	15.7	9.44	0.156	8.37	11.9	2.43	0.289	0.274	99.3	63.4	85.3	8.2	*	*	*	*
D25C-2-27	48.2	2.93	14.3	10.72	0.169	7.96	11.4	2.64	0.420	0.311	99.2	59.3	83.0	6.2	6.94	94.19	0.95	0.37
D25C-2-29 _p	51.2	1.45	16.1	9.39	0.170	7.14	11.4	2.22	0.082	0.040	99.3	59.9	83.3	3.5	1.01	28.72	0.17	0.05
D25C-2-30	48.7	2.87	14.3	11.21	0.136	7.50	11.0	2.78	0.382	0.278	99.3	56.8	81.5	5.0	6.73	99.23	0.95	0.36
D25C-2-34	48.1	2.46	15.3	8.96	0.153	8.82	12.1	2.34	0.325	0.387	99.1	65.9	86.6	7.1	4.86	82.23	0.80	0.33
D25C-2-35 _p	47.9	2.72	15.8	9.52	0.131	8.45	11.9	2.43	0.226	0.143	99.3	63.2	85.2	13.5	2.37	61.10	0.46	0.19
D25C-2-37	48.1	2.23	15.8	9.26	0.157	8.78	11.9	2.33	0.291	0.346	99.3	65.0	86.1	6.8	4.68	73.44	0.79	0.33
D25C-2-38B	48.3	2.74	14.6	10.65	0.177	7.72	11.8	2.47	0.331	0.263	99.2	58.8	82.7	4.4	6.13	82.36	0.87	0.36
D25C-2-38C	48.1	2.77	14.2	11.05	0.178	8.04	11.8	2.40	0.314	0.238	99.2	58.8	82.7	5.8	*	*	*	*
D25C-2-39A _b	49.2	1.43	17.8	7.96	0.147	7.27	13.2	1.90	0.178	0.113	99.3	64.3	85.8	2.7	*	*	*	*
D25C-2-39B	48.5	2.52	15.6	9.19	0.124	8.42	12.0	2.14	0.410	0.263	99.2	64.3	85.8	5.4	5.52	83.12	0.87	0.32
D25C-2-40A	48.6	2.44	15.8	9.50	0.173	7.92	11.6	2.61	0.270	0.214	99.3	62.1	84.6	4.5	4.18	63.13	0.67	0.22
D25C-2-40B	49.2	2.47	15.9	9.45	0.145	7.98	11.3	2.30	0.266	0.245	99.4	62.2	84.6	8.3	3.85	57.37	0.62	0.27
D25C-2-44 _p	49.2	2.16	15.2	8.91	0.128	8.77	12.3	2.35	0.088	0.113	99.3	65.5	86.4	13.6	0.69	25.67	0.18	0.08
D25C-2-46 _p	48.4	2.84	15.4	9.19	0.125	8.60	12.0	2.36	0.079	0.147	99.3	64.4	85.9	12.4	0.63	29.69	0.09	0.04

Table B2. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Fernandina Island.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Host Mg#	Fo	% ol	Rb	Ba	Th	U
Fernandina (sample AHA D25C)																		
D25C-2-48	48.4	3.05	14.4	10.96	0.163	7.73	11.5	2.10	0.413	0.317	99.1	58.1	82.3	3.3	*	*	*	*
D25C-2-51	49.4	2.27	16.6	7.96	0.145	7.74	11.5	2.78	0.404	0.447	99.3	65.1	86.2	15.1	*	*	*	*
D25C-2-52A	48.8	2.44	16.4	8.35	0.081	8.30	11.7	2.54	0.322	0.284	99.3	66.1	86.7	6.4	4.47	75.51	0.81	0.30
D25C-2-52B _p	48.8	2.76	16.9	7.98	0.113	7.90	11.9	2.63	0.113	0.120	99.2	66.1	86.7	5.5	0.79	35.43	0.23	0.16
D25C-2-53A	48.0	2.30	15.8	9.82	0.138	8.45	11.8	2.26	0.308	0.207	99.1	62.8	85.0	6.6	5.31	78.50	0.77	0.35
D25C-2-53B	47.8	2.36	16.1	9.58	0.164	8.23	12.0	2.33	0.299	0.270	99.2	62.8	85.0	5.4	5.21	69.05	0.71	0.32
D25C-2-54	47.5	2.58	15.5	10.04	0.138	8.97	11.4	2.44	0.428	0.262	99.3	63.6	85.4	7.5	6.75	105.99	1.01	0.41
D25C-2-55	49.0	2.44	15.1	9.19	0.164	7.92	12.4	2.32	0.299	0.253	99.2	62.8	85.0	5.2	4.76	71.77	0.70	0.25
D25C-2-56	48.6	2.27	15.4	9.37	0.130	8.71	12.3	2.09	0.185	0.206	99.3	64.5	85.9	8.8	2.78	48.35	0.51	0.20
D25C-2-57 _b	49.2	2.33	16.0	8.67	0.147	8.94	12.0	1.78	0.005	0.094	99.2	66.6	87.0	11.3	0.00	0.65	0.08	0.03
D25C-2-58	48.4	2.50	15.7	9.07	0.139	8.88	11.6	2.18	0.398	0.326	99.3	65.7	86.5	7.8	5.64	91.64	0.92	0.36
D25C-2-59	48.6	2.33	15.0	10.71	0.191	7.60	11.7	2.40	0.393	0.259	99.2	58.2	82.4	4.3	6.26	92.29	0.93	0.34
D25C-2-62	48.2	3.03	14.4	11.36	0.157	7.80	11.0	2.55	0.379	0.283	99.3	57.4	81.8	5.8	7.41	99.48	0.96	0.37
D25C-3-02	48.5	3.14	14.1	11.24	0.144	7.64	11.1	2.47	0.411	0.310	99.1	57.2	81.7	4.9	7.10	96.11	0.88	0.35
D25C-3-07	48.0	2.59	16.3	9.23	0.085	7.95	11.9	2.25	0.327	0.279	99.0	62.9	85.0	5.0	4.11	70.41	0.72	0.28
D25C-3-08	48.5	2.96	14.3	11.11	0.161	7.83	11.1	2.41	0.422	0.330	99.2	58.0	82.2	6.6	*	*	*	*
D25C-3-10	48.0	2.83	14.6	10.88	0.138	8.07	11.8	2.24	0.269	0.238	99.2	59.3	83.0	6.6	4.61	62.04	0.62	0.29
D25C-3-12	48.1	2.40	16.2	9.24	0.128	8.51	11.6	2.44	0.362	0.283	99.3	64.3	85.8	7.5	5.22	84.43	0.85	0.33
D25C-3-14	47.7	2.98	14.4	12.10	0.166	7.95	10.4	2.56	0.410	0.325	99.1	56.3	81.2	7.2	7.27	93.94	0.87	0.34
D25C-3-18	48.2	2.48	16.1	9.12	0.128	8.78	11.2	2.72	0.328	0.219	99.4	65.3	86.4	9.0	4.56	77.17	0.71	0.29
D25C-3-20	47.9	2.63	15.9	8.56	0.146	8.56	12.3	2.30	0.274	0.613	99.2	66.2	86.8	5.7	3.57	72.53	0.67	0.27
D25C-3-21 _p	48.4	2.66	15.3	9.68	0.163	8.23	11.8	2.53	0.148	0.229	99.2	62.5	84.8	6.2	1.86	44.70	0.25	0.11
D25C-3-23 _b	48.9	2.50	15.9	9.02	0.103	8.28	11.5	2.71	0.080	0.141	99.2	63.9	85.6	13.9	1.26	19.48	0.22	0.12
D25C-3-28	48.7	2.81	14.3	10.63	0.170	7.75	11.6	2.42	0.384	0.283	99.2	58.9	82.8	6.0	6.46	92.35	0.80	0.30
D25C-3-29	47.4	3.00	14.4	11.27	0.158	8.07	11.4	2.47	0.390	0.321	99.1	58.4	82.5	6.4	*	*	*	*
D25C-3-30	48.0	3.01	15.4	9.19	0.175	8.06	12.3	2.34	0.377	0.278	99.2	63.3	85.3	5.8	5.55	86.86	0.89	0.35
D25C-3-31	48.7	2.44	14.7	10.54	0.145	7.88	11.5	2.53	0.375	0.273	99.3	59.5	83.1	5.5	5.76	87.62	0.85	0.33
D25C-3-33	47.8	2.90	14.2	11.56	0.159	7.94	11.4	2.46	0.404	0.259	99.2	57.4	81.8	7.0	6.48	92.77	0.93	0.35

Table B2. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Fernandina Island.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Host Mg#	Fo	% ol	Rb	Ba	Th	U
Fernandina (sample AHA D25C)																		
D25C-3-34 _p	48.1	2.92	15.5	9.44	0.137	8.58	12.0	2.19	0.221	0.165	99.3	63.8	85.5	11.3	2.56	62.18	0.44	0.17
D25C-3-35	48.3	2.38	15.9	9.27	0.165	7.95	11.9	2.68	0.417	0.263	99.2	62.7	84.9	5.8	*	*	*	*
D25C-3-37	48.1	2.88	14.1	11.40	0.097	8.09	11.5	2.38	0.342	0.268	99.3	58.1	82.3	8.0	6.72	88.63	0.85	0.30
D25C-3-38	47.4	2.95	16.1	8.96	0.140	8.76	11.6	2.47	0.442	0.334	99.2	65.7	86.5	7.2	6.80	107.69	1.00	0.36
D25C-3-41A	49.1	2.69	14.5	10.33	0.156	7.77	11.6	2.55	0.308	0.233	99.3	59.6	83.2	5.4	5.24	78.56	0.71	0.29
D25C-3-41B	48.2	2.85	14.9	10.52	0.173	7.91	11.6	2.51	0.336	0.196	99.3	59.6	83.2	5.6	5.85	78.95	0.74	0.36
D25C-3-42	48.0	2.42	15.4	10.32	0.152	7.98	11.7	2.39	0.355	0.384	99.3	60.3	83.6	6.1	5.90	87.54	0.93	0.35
D25C-3-43	47.5	2.29	16.4	9.16	0.123	9.38	11.6	2.25	0.329	0.257	99.3	66.7	87.1	8.6	4.51	76.54	0.75	0.30
D25C-3-44	48.0	3.38	14.5	10.41	0.188	7.71	11.4	2.69	0.440	0.311	99.2	59.3	83.0	5.2	*	*	*	*
D25C-3-46	47.9	3.16	14.1	11.58	0.169	7.85	10.9	2.62	0.437	0.303	99.2	57.1	81.7	6.2	7.33	99.93	0.92	0.37
D25C-3-47 _n	50.3	3.18	16.1	7.92	0.104	8.10	10.7	2.38	0.104	0.087	99.0	66.6	87.0	7.8	*	*	*	*
D25C-3-48	48.1	2.95	14.5	11.03	0.184	7.51	11.7	2.32	0.393	0.259	99.1	57.2	81.8	4.2	6.00	84.46	0.80	0.35
D25C-3-49	48.3	2.39	15.8	9.09	0.116	8.80	11.7	2.54	0.217	0.184	99.3	65.5	86.4	7.5	3.42	51.97	0.51	0.22
D25C-3-50	48.0	2.29	14.4	11.72	0.164	7.88	11.7	2.23	0.308	0.258	99.1	56.9	81.5	6.7	*	*	*	*
D25C-3-52	48.2	2.57	16.2	8.95	0.119	8.21	11.9	2.36	0.351	0.243	99.3	64.3	85.8	6.3	4.76	81.47	0.84	0.32
D25C-3-55 _p	48.5	2.28	16.1	9.21	0.103	8.18	11.7	2.43	0.220	0.179	99.0	63.5	85.4	6.5	2.47	54.14	0.43	0.21
D25C-3-56	47.9	2.75	14.6	10.49	0.173	8.11	11.9	2.60	0.317	0.292	99.2	60.3	83.5	6.8	5.72	81.97	0.73	0.32
D25C-3-58	48.1	2.64	15.3	10.11	0.113	8.00	11.7	2.57	0.382	0.278	99.3	60.8	83.9	5.8	5.69	85.35	0.80	0.30
D25C-3-62	48.4	2.86	15.2	8.99	0.172	7.95	12.3	2.41	0.416	0.356	99.1	63.4	85.4	5.9	*	*	*	*
D25C-3-63	47.7	2.42	14.9	9.81	0.118	9.88	11.5	2.25	0.292	0.355	99.3	66.0	86.7	16.0	*	*	*	*
Host Glasses																		
D25C host glass	48.7	3.31	14.6	11.81	0.172	6.18	11.3	2.60	0.438	0.350	99.6	50.9	78.0	N/A	*	*	*	*

Table B2. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Fernandina Island.

	Nb	K	La	Ce	Pr	Pb	Sr	Nd	P	Zr	Hf	Sm	Eu	Ti	Gd	Tb	Dy	Ho	Er
Fernandina (sample AHA D25C) (S 0 27' 7.99", W 91 44' 23.9", Depth 4750 m)																			
D25C-2-02	12.64	1776.1	8.48	21.94	3.30	0.73	253.01	16.13	888.27	111.87	2.93	4.23	1.31	13722.5	4.43	0.72	4.30	0.92	2.64
D25C-2-06	18.20	3108.4	12.13	29.05	4.04	0.94	285.76	18.12	1265.77	129.53	3.39	5.09	1.71	14854.0	4.94	0.77	4.39	0.92	2.53
D25C-2-09	21.72	3630.8	14.75	35.74	4.96	1.28	360.60	22.18	1350.67	161.70	4.14	6.04	1.86	18150.3	5.83	0.93	5.50	1.17	3.32
D25C-2-12	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-16A	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-16B	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-19A	24.24	3932.9	15.13	32.03	4.23	1.01	212.88	17.70	2015.14	133.32	3.33	4.63	1.56	16003.3	4.83	0.78	4.60	0.96	2.66
D25C-2-19B	21.59	3513.9	12.84	29.13	4.05	0.97	241.06	18.14	2336.76	126.77	3.25	4.67	1.49	15778.0	4.95	0.80	4.70	1.01	2.86
D25C-2-21A	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-21B	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-21C	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-24 _p	1.84	275.4	1.97	6.68	1.26	0.47	53.89	7.40	174.52	34.69	1.42	2.60	0.93	9842.4	3.39	0.62	4.31	0.92	2.63
D25C-2-25A	17.07	2746.4	11.40	26.89	3.63	1.10	312.61	15.61	1438.30	118.93	3.14	3.83	1.25	13527.6	4.10	0.65	3.74	0.78	2.15
D25C-2-26	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-27	20.63	3448.2	13.55	32.64	4.57	1.20	332.28	20.60	1344.70	149.94	3.83	5.19	1.83	17963.2	5.61	0.91	5.48	1.14	3.11
D25C-2-29 _p	2.34	745.8	2.38	5.79	0.95	0.51	758.17	5.03	219.11	25.23	0.96	2.42	1.08	8875.4	3.50	0.69	5.06	1.07	3.03
D25C-2-30	20.70	3432.9	14.06	33.59	4.67	1.15	355.92	20.86	1305.23	150.34	4.00	5.39	1.88	17592.9	5.49	0.88	5.20	1.09	3.03
D25C-2-34	17.04	2997.1	12.45	28.68	3.98	1.02	336.01	17.75	1932.45	127.38	3.22	4.83	1.48	15237.3	4.76	0.76	4.46	0.95	2.69
D25C-2-35 _p	8.62	1886.5	8.64	26.26	4.06	0.84	885.59	20.37	628.78	132.93	2.99	5.01	1.52	16501.7	5.18	0.82	4.78	0.99	2.70
D25C-2-37	15.89	2760.9	10.91	26.04	3.59	1.11	268.34	15.89	1426.55	113.82	2.83	4.15	1.43	13430.2	4.45	0.72	4.27	0.91	2.57
D25C-2-38B	19.24	2959.0	12.70	30.78	4.33	1.08	361.68	19.67	1236.83	143.50	3.53	4.85	1.73	17091.0	5.53	0.89	5.33	1.12	3.12
D25C-2-38C	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-39A _b	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-39B	17.97	3075.6	12.45	29.27	4.12	0.95	316.21	18.74	1208.99	135.30	3.43	4.42	1.50	15338.9	4.88	0.76	4.37	0.90	2.44
D25C-2-40A	14.88	2354.3	9.28	23.13	3.38	0.95	297.57	15.99	1060.09	115.94	2.98	4.47	1.39	14676.2	4.92	0.79	4.69	0.98	2.71
D25C-2-40B	13.77	2304.9	8.59	21.30	3.16	0.99	273.37	15.16	958.95	108.27	2.65	4.28	1.31	13618.6	4.29	0.70	4.27	0.90	2.52
D25C-2-44 _p	3.39	720.7	3.01	8.34	1.51	0.60	367.47	8.61	603.40	40.76	1.25	3.27	1.35	13098.7	4.06	0.71	4.66	0.96	2.60
D25C-2-46 _p	0.70	699.9	2.21	9.09	2.10	0.61	934.92	13.92	551.62	74.71	1.59	4.95	1.68	16689.2	5.02	0.82	4.95	1.01	2.73

Table B2. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Fernandina Island.

	Nb	K	La	Ce	Pr	Pb	Sr	Nd	P	Zr	Hf	Sm	Eu	Ti	Gd	Tb	Dy	Ho	Er
Fernandina (sample AHA D25C)																			
D25C-2-48	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-51	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-2-52A	17.39	2874.9	11.31	27.72	3.86	0.96	286.62	17.34	1237.91	127.68	3.31	4.59	1.56	15104.0	4.74	0.78	4.80	1.01	2.82
D25C-2-52B_p	3.87	1071.4	4.81	16.25	3.04	0.78	772.43	17.76	615.81	101.23	2.24	5.36	1.37	16444.3	5.05	0.81	4.79	0.99	2.73
D25C-2-53A	17.17	2958.2	11.23	25.13	3.46	1.04	256.82	15.33	1263.70	108.62	2.87	4.09	1.39	14220.8	4.19	0.67	3.93	0.88	2.62
D25C-2-53B	14.42	2602.3	9.26	22.56	3.29	0.89	247.70	15.55	1236.39	110.19	2.78	4.21	1.40	13828.3	4.18	0.68	4.07	0.86	2.38
D25C-2-54	22.24	3674.4	14.45	34.07	4.61	1.21	386.99	19.93	1360.74	140.53	3.38	4.99	1.51	15609.5	4.92	0.78	4.49	0.94	2.62
D25C-2-55	15.34	2582.1	10.35	25.53	3.61	1.05	341.43	16.43	1034.44	117.73	3.27	4.35	1.43	15046.1	4.34	0.71	4.27	0.91	2.59
D25C-2-56	11.00	1727.1	7.59	19.47	2.88	0.80	288.80	13.77	931.87	98.44	2.93	4.01	1.30	13613.6	4.25	0.68	4.05	0.85	2.34
D25C-2-57_n	0.29	13.6	2.26	11.74	2.39	0.57	79.39	14.74	438.42	76.61	2.01	4.35	1.21	13756.6	4.53	0.74	4.46	0.94	2.63
D25C-2-58	19.23	3349.6	13.20	30.58	4.17	1.02	303.25	18.25	1396.33	136.18	3.42	4.96	1.61	15571.6	5.11	0.81	4.65	0.99	2.79
D25C-2-59	19.44	3461.0	12.84	29.67	4.04	1.23	274.05	17.58	1405.07	130.82	3.43	4.64	1.60	14000.4	4.66	0.75	4.43	0.94	2.65
D25C-2-62	22.28	3707.7	14.67	35.52	4.93	1.53	349.29	22.01	1446.90	162.08	4.07	5.81	1.75	18743.2	5.69	0.92	5.52	1.17	3.28
D25C-3-02	21.34	3520.3	14.34	35.00	4.85	1.38	341.62	21.66	1419.73	161.63	3.96	5.81	1.65	18745.3	5.79	0.91	5.24	1.09	3.03
D25C-3-07	16.69	2577.6	11.24	27.19	3.78	0.86	346.38	16.95	1146.63	127.97	3.13	4.36	1.41	15164.2	4.65	0.74	4.30	0.91	2.54
D25C-3-08	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-3-10	17.22	2323.0	10.65	26.79	3.76	0.97	332.93	16.97	1204.13	133.04	3.45	4.95	1.44	16925.0	5.16	0.84	5.02	1.09	3.13
D25C-3-12	19.15	3031.0	12.75	30.14	4.14	0.85	276.01	18.21	1261.27	137.85	3.41	4.29	1.48	14447.6	4.65	0.74	4.25	0.91	2.56
D25C-3-14	20.49	3304.0	13.45	32.67	4.56	1.29	344.00	20.46	1423.88	151.89	3.59	5.18	1.76	18218.3	5.55	0.90	5.35	1.13	3.14
D25C-3-18	16.43	2729.2	11.35	28.34	4.02	0.86	284.39	18.41	1109.77	131.76	3.37	4.94	1.46	15195.7	4.95	0.79	4.62	0.97	2.71
D25C-3-20	13.81	2495.3	10.25	25.96	3.75	0.78	279.88	17.50	2748.60	125.04	3.06	4.78	1.43	15412.7	4.79	0.75	4.33	0.91	2.53
D25C-3-21_p	5.62	1293.3	5.94	18.86	3.33	0.73	876.36	18.68	1152.90	112.90	2.65	5.11	1.51	15671.6	5.01	0.78	4.46	0.93	2.55
D25C-3-23_n	4.31	629.8	7.08	26.01	4.12	0.60	199.83	21.14	642.36	140.03	3.19	5.01	1.45	15043.1	5.36	0.84	4.75	0.97	2.60
D25C-3-28	19.12	3500.8	13.21	31.45	4.36	1.16	334.13	19.46	1250.56	141.47	3.50	5.23	1.61	17107.5	5.13	0.82	4.74	0.99	2.74
D25C-3-29	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
D25C-3-30	20.45	3320.7	13.71	32.66	4.46	1.10	365.63	19.55	1346.22	148.88	3.60	4.90	1.62	17795.5	5.08	0.80	4.58	0.94	2.53
D25C-3-31	18.56	3217.2	12.80	30.18	4.03	1.09	361.11	17.15	1376.75	138.48	3.55	4.26	1.46	14581.3	4.70	0.77	4.72	1.01	2.86
D25C-3-33	21.09	3374.7	14.20	33.94	4.70	1.15	339.38	20.96	1358.40	156.55	3.92	5.33	1.71	18014.2	5.74	0.90	5.15	1.13	3.27

Table B2. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Fernandina Island.

	Tm	Yb	Y	Sc	Cr (Sr/Nd) _{PM}	(Ba/Th) _{PM}	(Eu/Gd) _{PM}
Fernandina (sample AHA D25C) (S 0 27' 7.99", W 91 44' 23.9", Depth 4750 m)							
D25C-2-02	0.37	2.10	21.34	31.19	115.2	0.985	1.008
D25C-2-06	0.35	1.99	20.46	34.37	130.8	0.991	1.134
D25C-2-09	0.47	2.69	27.02	35.71	147.5	1.021	1.221
D25C-2-12	*	*	*	*	*	*	*
D25C-2-16A	*	*	*	*	*	*	*
D25C-2-16B	*	*	*	*	*	*	*
D25C-2-19A	0.37	2.15	22.55	31.17	119.6	0.756	1.053
D25C-2-19B	0.40	2.31	23.26	31.15	142.0	0.834	1.037
D25C-2-21A	*	*	*	*	*	*	*
D25C-2-21B	*	*	*	*	*	*	*
D25C-2-21C	*	*	*	*	*	*	*
D25C-2-24_p	0.37	2.16	23.11	29.70	159.4	0.457	0.687
D25C-2-25A	0.30	1.72	17.50	25.12	160.3	1.258	1.218
D25C-2-26	*	*	*	*	*	*	*
D25C-2-27	0.43	2.47	26.56	35.09	176.0	1.013	1.190
D25C-2-29_p	0.41	2.20	26.61	32.46	109.5	9.464	1.998
D25C-2-30	0.41	2.32	25.87	35.04	144.6	1.072	1.254
D25C-2-34	0.38	2.20	22.10	31.58	150.2	1.189	1.244
D25C-2-35_p	0.39	2.35	23.53	30.63	190.1	2.731	1.608
D25C-2-37	0.35	1.95	20.51	29.42	189.1	1.061	1.116
D25C-2-38B	0.45	2.65	26.26	36.16	134.9	1.155	1.139
D25C-2-38C	*	*	*	*	*	*	*
D25C-2-39A_b	*	*	*	*	*	*	*
D25C-2-39B	0.35	2.02	20.95	32.72	146.5	1.060	1.147
D25C-2-40A	0.38	2.22	22.98	30.36	149.5	1.169	1.143
D25C-2-40B	0.34	1.89	21.45	28.02	151.7	1.133	1.118
D25C-2-44_p	0.36	2.05	23.56	30.82	168.5	2.681	1.736
D25C-2-46_p	0.39	2.33	25.29	29.90	143.5	4.218	4.018

Table B2. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Fernandina Island.

	Tm	Yb	Y	Sc	Cr (Sr/Nd) _{PM}	(Ba/Th) _{PM}	(Eu/Gd) _{PM}
Fernandina (sample AHA D25C)							
D25C-2-48	*	*	*	*	*	*	*
D25C-2-51	*	*	*	*	*	*	*
D25C-2-52A	0.39	2.22	23.38	29.00	114.5	1.038	1.118
D25C-2-52B_p	0.38	2.20	23.84	29.07	129.7	2.732	1.820
D25C-2-53A	0.36	2.00	20.63	29.93	125.7	1.052	1.226
D25C-2-53B	0.34	1.95	20.50	29.14	213.2	1.000	1.175
D25C-2-54	0.37	2.17	22.82	30.77	134.4	1.220	1.267
D25C-2-55	0.35	1.92	21.27	36.69	205.7	1.305	1.241
D25C-2-56	0.33	1.96	20.45	31.53	221.2	1.318	1.137
D25C-2-57_b	0.38	2.30	21.81	31.88	132.2	0.338	0.095
D25C-2-58	0.38	2.15	23.53	30.43	137.7	1.044	1.194
D25C-2-59	0.38	2.20	21.48	33.89	127.9	0.979	1.192
D25C-2-62	0.46	2.60	26.73	33.96	92.5	0.997	1.247
D25C-3-02	0.43	2.53	26.85	35.46	120.6	0.991	1.321
D25C-3-07	0.34	1.91	21.46	30.72	111.1	1.283	1.180
D25C-3-08	*	*	*	*	*	*	*
D25C-3-10	0.43	2.41	25.01	35.68	159.7	1.232	1.202
D25C-3-12	0.36	2.03	21.53	30.76	178.6	0.952	1.192
D25C-3-14	0.44	2.56	26.85	31.95	44.5	1.056	1.308
D25C-3-18	0.38	2.19	23.47	30.95	190.1	0.970	1.308
D25C-3-20	0.36	2.12	22.71	31.83	131.8	1.005	1.310
D25C-3-21_p	0.36	2.07	22.47	34.83	136.9	2.947	2.128
D25C-3-23_b	0.36	2.09	23.39	29.59	154.7	0.594	1.056
D25C-3-28	0.38	2.21	23.66	35.04	150.2	1.078	1.396
D25C-3-29	*	*	*	*	*	*	*
D25C-3-30	0.35	2.04	22.21	36.19	202.2	1.175	1.180
D25C-3-31	0.40	2.31	24.31	35.02	133.0	1.323	1.249
D25C-3-33	0.44	2.44	26.44	34.62	128.7	1.017	1.197

Table B2. Major (wt%) and trace (ppm) element concentrations in melt inclusions from Fernandina Island.

	Tm	Yb	Y	Sc	Cr	(Sr/Nd) _{PM}	(Ba/Th) _{PM}	(Eu/Gd) _{PM}
Fernandina (sample AHA D25C)								
D25C-3-34 _p	0.35	1.94	20.54	31.64	162.2	3.213	1.714	1.171
D25C-3-35	*	*	*	*	*	*	*	*
D25C-3-37	0.40	2.37	24.79	35.08	165.7	1.030	1.261	1.086
D25C-3-38	0.39	2.24	24.26	31.20	119.8	1.151	1.293	1.180
D25C-3-41A	0.40	2.29	24.49	35.35	163.4	1.150	1.340	1.097
D25C-3-41B	0.38	2.23	23.92	33.91	176.5	1.169	1.284	1.077
D25C-3-42	0.37	2.18	22.74	32.10	176.8	1.163	1.134	1.178
D25C-3-43	0.34	2.07	19.95	31.34	103.9	1.027	1.234	1.118
D25C-3-44	*	*	*	*	*	*	*	*
D25C-3-46	0.45	2.60	27.20	35.60	111.4	0.988	1.308	1.093
D25C-3-47 _b	*	*	*	*	*	*	*	*
D25C-3-48	0.37	2.11	22.73	32.66	160.6	1.109	1.270	1.130
D25C-3-49	0.31	1.78	19.08	31.23	199.9	1.206	1.234	1.037
D25C-3-50	*	*	*	*	*	*	*	*
D25C-3-52	0.36	2.20	21.61	31.89	180.3	1.100	1.173	1.095
D25C-3-55 _p	0.33	1.88	20.80	29.76	165.1	1.921	1.525	1.334
D25C-3-56	0.37	2.26	22.93	35.50	134.8	1.068	1.347	1.085
D25C-3-58	0.37	2.13	23.33	35.48	189.1	1.031	1.281	1.054
D25C-3-62	*	*	*	*	*	*	*	*
D25C-3-63	*	*	*	*	*	*	*	*
Host Glasses								
D25C host glass	*	*	*	*	*	*	*	*

Table B3 — Composition of model melts created using M80-d.

ppm	Evolved melt (M65) ^a	Primitive melt (M80-d) ^b	Model 1-d ^c	Model 1-d 50-50 mix	Model 2-d ^d	Model 2-d 50-50 mix
Ba	271	52.28	58.19	33.03	40.21	24.05
Th	2.88	0.62	0.246	0.193	0.211	0.175
U	0.98	0.24	0.078	0.069	0.073	0.067
Nb	47.9	12.64	3.185	2.512	2.771	2.305
K	14693.6	1776.1	2176.1	1225.8	1646.9	961.1
La	35.14	8.48	4.995	3.481	3.918	2.942
Ce	79.68	21.94	11.278	8.979	9.684	8.182
Pb	2.48	0.73	1.746	1.274	1.431	1.117
Pr	10.8	3.3	1.128	0.936	0.994	0.869
Sr	561	257.73	457.9	255.9	354.9	204.4
Nd	44.96	16.13	9.309	8.357	8.665	8.035
Zr	350	111.87	32.62	33.65	34.17	34.43
Hf	7.55	2.93	1.345	1.382	1.388	1.404
Sm	10.27	4.23	2.677	2.637	2.664	2.631
Eu	3.19	1.31	1.461	1.194	1.285	1.106
Ti	24932.9	13722.5	9471.0	9656.7	9646.6	9744.5
Gd	9.65	4.43	3.081	3.234	3.215	3.301
Tb	1.43	0.72	0.581	0.603	0.600	0.612
Dy	7.78	4.3	3.820	4.064	4.018	4.163
Y	3.16	21.34	20.607	21.861	21.623	22.368
Er	1.5	2.64	2.282	2.454	2.418	2.522
Yb	0.53	2.1	1.882	2.021	1.992	2.076
(Sr/Nd) _{PM}		0.98	58.19	33.03	40.21	24.05

^a Evolved melt used in model: AHA-D31A^b Primitive melt used in model: AHA-2-24^c Model 1 parameters $\Theta_{plag}^D = 0.7$, $\Theta_{plag}^P = 0.525$, $\mathcal{D}_a^{An_{80},Sr} = 10^{-4}$ ^d Mixture is between melt produced by the model and primitive melt M80.^e Model 2 parameters $\Theta_{plag}^D = 0.4$, $\Theta_{plag}^P = 0.3$, $\mathcal{D}_a^{An_{80},Sr} = 10^{-4}$

Figure B1

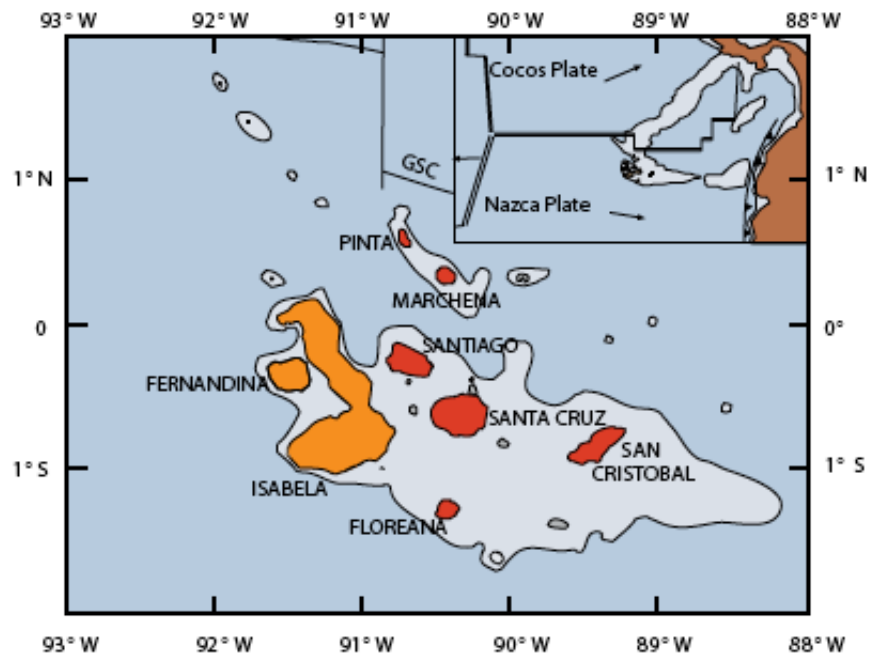


Figure B1: Map of the Galápagos islands, in the Pacific Ocean south of the Galápagos Spreading Center. Fernandina and Santiago are in the western (orange) and eastern (red) groups of islands, respectively. The plume is beneath Fernandina.

Figure B2

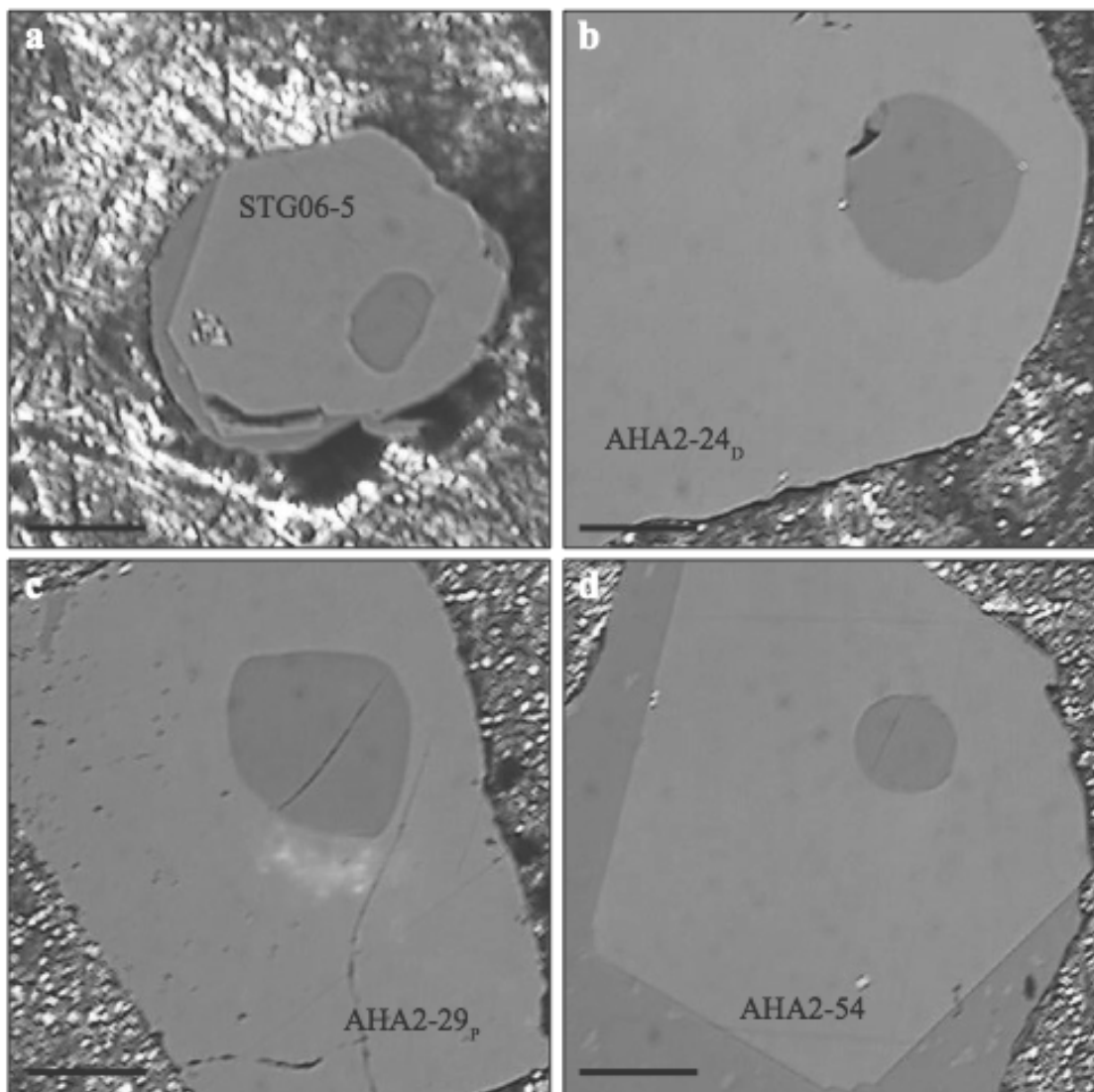


Figure B2: Reflected light images of olivines and melt inclusions from representative samples. (a) Sample STG06-29-5 is a “normal” Santiago inclusion. (b) Sample AHA2-24_D is a depleted Fernandina inclusion. (c) Sample AHA2-29_P is a Fernandina inclusion with a “ghost plagioclase” signature. (d) Sample AHA2-54 is a “normal” Fernandina inclusion. The scale bars are 200 μ m.

Figure B3

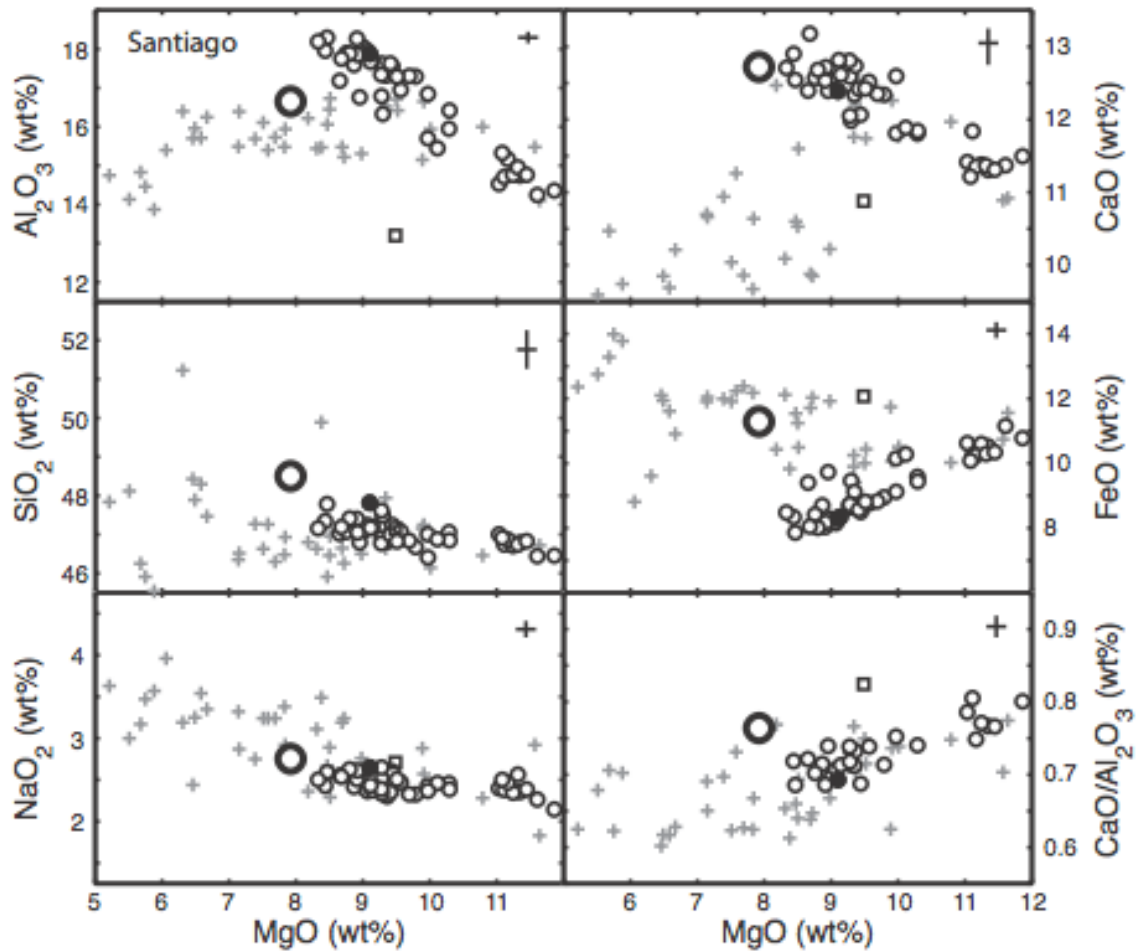


Figure B3: Plots of major elements versus MgO for Santiago melt inclusions, after *Koleszar et al.* [2009]. The different symbols are determined by trace elements as shown in Chapter 3, Fig. 1: $\circ$ – “normal” inclusions; $\square$ – enriched inclusion; $\bullet$ – depleted inclusion; $+$ - glasses from a compilation, as in *Koleszar et al.* [2009]. The thick, dark line and large open circle represent the average matrix glass composition from the compilation. The inclusions from Santiago include a range of primitive to slightly more evolved MgO contents, and a trend is present that indicates clearly the influence of plagioclase assimilation on the compositions, which is also seen in the small positive Sr anomaly in the “normal” inclusions. The small crosses represent 2 sigma error bars.

Figure B4

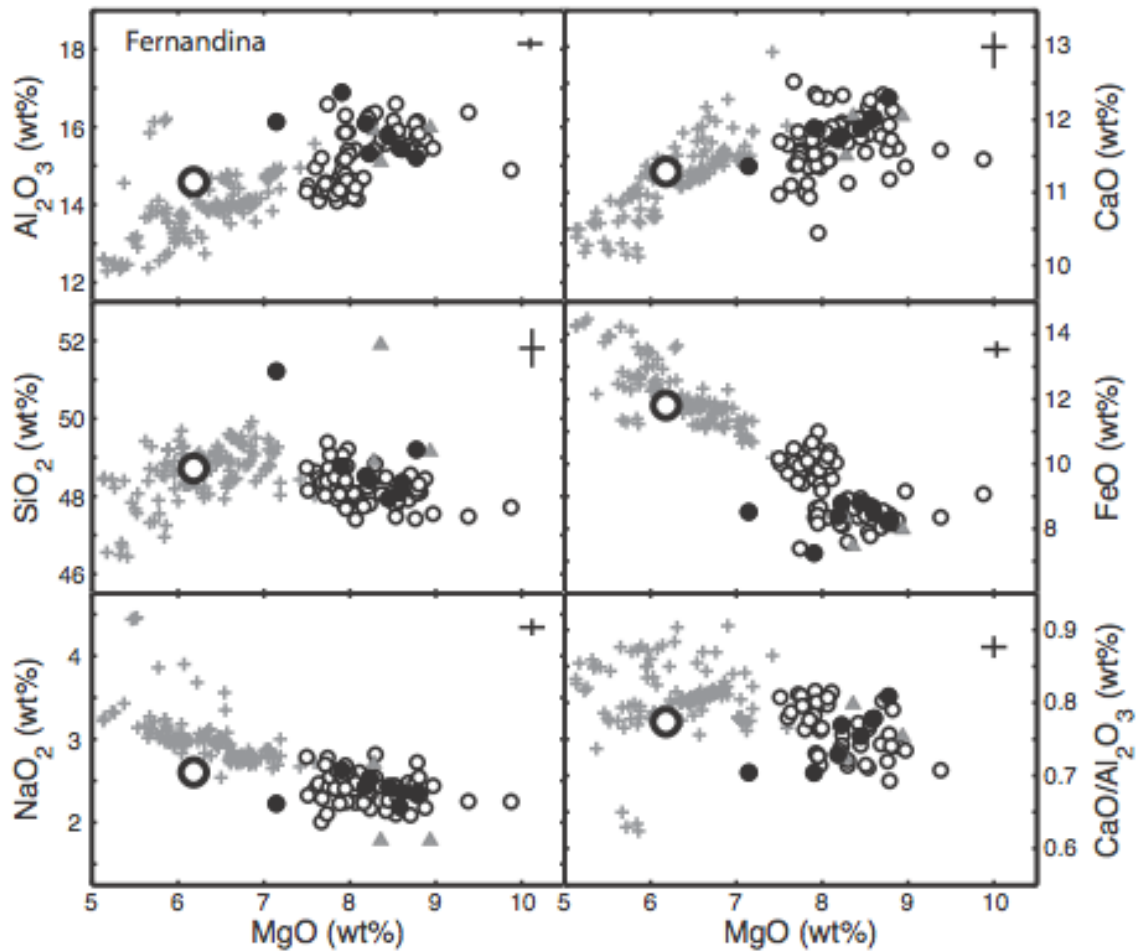


Figure B4: Plots of major elements versus MgO for Fernandina melt inclusions, after Koleszar *et al.* [2009]. The different symbols are determined by trace elements as shown in Chapter 3, Fig. 1: $\circ$ – “normal” inclusion; $\bullet$ – Sr-enriched inclusions; $\blacktriangle$ – depleted; $+$ – glasses from Geist *et al.* [2006]. The large open circle represents the average matrix glass composition from Geist *et al.* [2006], which included samples from the same dredge that supplied these samples. The inclusions from Fernandina, regardless of trace element differences, group within a small range of MgO contents and do not show trends indicative of interaction with plagioclase. Eight of the 56 inclusions, however, show large Sr anomalies, a “ghost plagioclase” signature. The small crosses represent 2 sigma error bars.

Figure B5

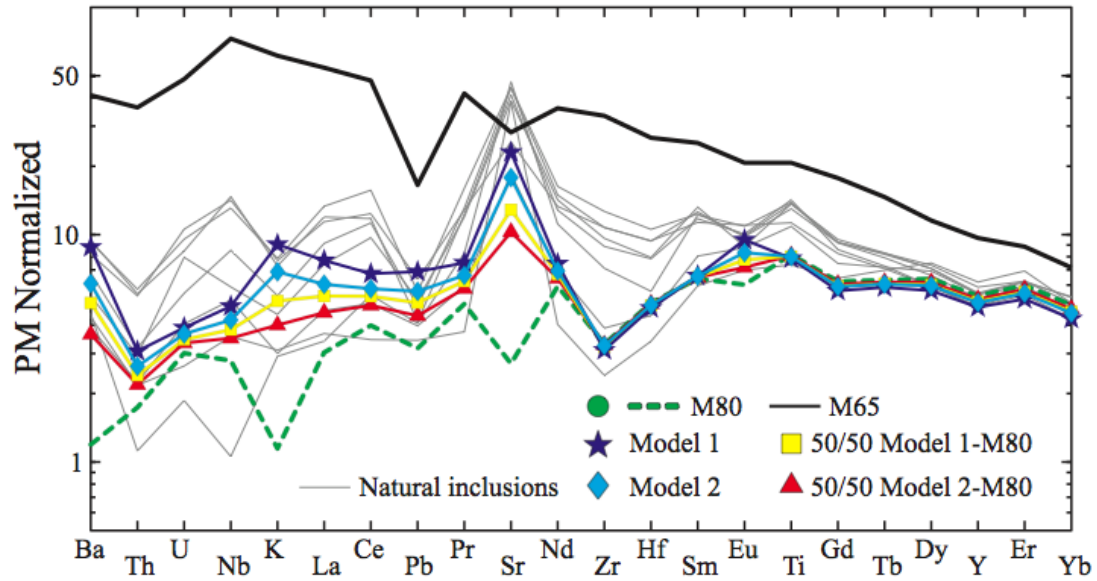


Figure B5. Trace element composition for Models 1 and 2 when using a depleted starting melt. Even with an initial negative anomaly in Sr in the percolating melt M80 (green dashed line), when the trace element concentration difference between M80 and the plagioclase in equilibrium with M65 (black line) is large, as shown here, the dissolution of plagioclase quickly increases the Sr in the melt and creates a positive anomaly. Reprecipitation is required to buffer the major elements, and mixing between the model melts and M80 also increases the goodness of match with the major elements while not eliminating the Sr peak. K is affected largely by diffusion, and thus $\mathcal{D}_a^{D,Sr}$ needs to be small ($\leq 10^{-4}$). The gray lines are the natural Sr-rich inclusions. Primitive mantle values are from *McDonough and Sun* [1995].

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APPENDIX C

Mass Conservation Equations for a Trace Element in a Crystal-Melt Mush

Here we consider a case in which the original plagioclase in the mush (D plag) partially dissolves and reprecipitates as a more anorthite-rich plagioclase (P plag). In the formulation below, we use two mass conservation equations to explicitly track the two kinds of plagioclase. Olivine (+/- cpx) is assumed to be present in the mush but is not included in the reaction for simplicity. Mass conservation equations for the melt and two plagioclases in the porous matrix, accounting for chemical disequilibrium, can be written as

$$\frac{\partial(\rho_f \phi_f)}{\partial t} + \nabla \cdot (\rho_f \phi_f \mathbf{V}_f) = \Gamma_{plag}^D + \Gamma_{plag}^P \quad (C1)$$

$$\frac{\partial[\rho_s \phi_{plag}^D]}{\partial t} + \nabla \cdot [\rho_s \phi_{plag}^D \mathbf{V}_s] = -\Gamma_{plag}^D \quad (C2)$$

$$\frac{\partial[\rho_s \phi_{plag}^P]}{\partial t} + \nabla \cdot [\rho_s \phi_{plag}^P \mathbf{V}_s] = -\Gamma_{plag}^P \quad (C3)$$

where Γ_{plag}^i is the bulk dissolution/reprecipitation rate for the plagioclase, with the superscript D or P indicating whether the plagioclase is dissolving or precipitating; $\rho_s \phi_n$ is the mass fraction of phase n in the mush zone (ρ_s is the density of the solid and ϕ is the volume fraction); and $\mathbf{V}_f$ and $\mathbf{V}_s$ are the velocities of the melt and solid, respectively. The mass conservation equation for a trace element of interest in the melt (concentration C_f), dissolving plagioclase (C_{plag}^D) and reprecipitating plagioclase (C_{plag}^P) are

$$\begin{aligned} \rho_f \phi_f \frac{\partial C_f}{\partial t} + \rho_f \phi_f \mathbf{V}_f \cdot \nabla C_f &= \nabla \cdot [\rho_f \phi_f \mathbf{D}_f \nabla C_f] \\ &+ \rho_s \phi_{plag}^D \mathfrak{R}_{plag}^D (C_{plag}^D - k_{plag}^D C_f) + C_{plag}^D \Gamma_{plag}^D \\ &+ \rho_s \phi_{plag}^P \mathfrak{R}_{plag}^P (C_{plag}^P - k_{plag}^P C_f) + (k_{plag}^P - 1) C_f \Gamma_{plag}^P \end{aligned} \quad (C4)$$

$$\frac{\partial C_{plag}^D}{\partial t} + \mathbf{V}_s \cdot \nabla C_{plag}^D = -\mathfrak{R}_{plag}^D (C_{plag}^D - k_{plag}^D C_f), \quad (C5)$$

$$\rho_s \phi_{plag}^P \frac{\partial C_{plag}^P}{\partial t} + \rho_s \phi_{plag}^P \mathbf{V}_s \cdot \nabla C_{plag}^P = -(\rho_s \phi_{plag}^P \mathfrak{R}_{plag}^P + \Gamma_{plag}^P)(C_{plag}^P - k_{plag}^P C_f). \quad (C6)$$

where $\mathbf{D}_f$ is the diffusion coefficient of the trace element of interest in the melt; $\mathfrak{R}_{plag}^i$ is the diffusive crystal-melt exchange rate for the trace element of interest; and k_{plag}^D and k_{plag}^P are the partition coefficients for the element for dissolving and precipitating plagioclases, respectively. The first term on the right-hand side of Eq. C4 accounts for diffusive (and dispersive) transport in the melt; the second and fourth terms on the right-hand side of Eq. C4 are due to diffusive exchange within the dissolving and precipitating plagioclases, respectively. The third term describes the concentration change due to dissolution of plagioclase, while the fifth term accounts for reprecipitation, which removes the trace element according the partition coefficient. The right-hand side of Eq. C5 accounts for diffusive exchange between the dissolving plagioclase and the melt, while Eq. C6 includes also the effect of the ongoing reprecipitation.

Eqs. C1-C6 form a complete set of mass conservation equations for a trace element of interest in the crystal-melt mush. They can be solved once the velocities and volume fractions of mineral or melt phases are given. In this study, we take a simpler approach by considering spatially averaged quantities for the crystal-melt mush, as these will give us some first order insights into the dissolution-reprecipitation processes.

Integrating the one-dimensional version of Eqs. C4-C6 over a vertical column of height L , and neglecting diffusive fluxes in and out of the system we have

$$\begin{aligned} \frac{d\bar{C}_f}{dt} = & \frac{V_f^{in}}{L} (C_f^{in} - \bar{C}_f) + \frac{\rho_s \bar{\phi}_{plag}^D}{\rho_f \bar{\phi}_f} \mathfrak{R}_{plag}^D (\bar{C}_{plag}^D - k_{plag}^D \bar{C}_f) + (\bar{C}_{plag}^D - \bar{C}_f) \frac{\Gamma_{plag}^D}{\rho_f \bar{\phi}_f} \\ & + \frac{\rho_s \bar{\phi}_{plag}^P}{\rho_f \bar{\phi}_f} \mathfrak{R}_{plag}^P (\bar{C}_{plag}^P - k_{plag}^P \bar{C}_f) + (k_{plag}^P - 1) \bar{C}_f \frac{\Gamma_{plag}^P}{\rho_f \bar{\phi}_f}, \end{aligned} \quad (C7)$$

$$\frac{d\bar{C}_{plag}^D}{dt} = -\Re_{plag}^D (\bar{C}_{plag}^D - k_{plag}^D \bar{C}_f), \quad (C8)$$

$$\frac{d\bar{C}_{plag}^P}{dt} = -\left(\Re_{plag}^P + \frac{\Gamma_{plag}^P}{\rho_s \bar{\phi}_{plag}^P} \right) (\bar{C}_{plag}^P - k_{plag}^P \bar{C}_f). \quad (C9)$$

Eqs. C7-C9 can be non-dimensionalized by choosing the melt transport time scale

$t = \frac{L}{V_f^{in}} t'$, where V_f^{in} is the melt velocity at the base of the mush column. After dropping

the prime for t' , we have

$$\begin{aligned} \frac{d\bar{C}_f}{dt} = & (C_f^{in} - \bar{C}_f) + M_{\gamma_f} w_{plag}^D \mathcal{D}_a^D (\bar{C}_{plag}^D - k_{plag}^D \bar{C}_{plag}) + (\bar{C}_{plag}^D - \bar{C}_f) \Theta_{plag}^D, \\ & + M_{\gamma_f} w_{plag}^P \mathcal{D}_a^P (\bar{C}_{plag}^P - k_{plag}^P \bar{C}_{plag}) + (k_{plag}^P - 1) \bar{C}_f \Theta_{plag}^P, \end{aligned} \quad (C10)$$

$$\frac{d\bar{C}_{plag}^D}{dt} = -\mathcal{D}_a^D (\bar{C}_{plag}^D - k_{plag}^D \bar{C}_f), \quad (C11)$$

$$\frac{\partial \bar{C}_{plag}^P}{\partial t} = -\left(\mathcal{D}_a^P + \frac{\Theta_{plag}^P}{M_{\gamma_f} w_{plag}^P} \right) (\bar{C}_{plag}^P - k_{plag}^P \bar{C}_f), \quad (C12)$$

where the non-dimensional parameters are defined as follows

$$w_{plag}^D = \frac{\rho_s \bar{\phi}_{plag}^D}{\rho_f (1 - \bar{\phi}_f)}, \quad w_{plag}^P = \frac{\rho_s \bar{\phi}_{plag}^P}{\rho_f (1 - \bar{\phi}_f)}, \quad M_{\gamma_f} = \frac{\rho_s (1 - \bar{\phi}_f)}{\rho_f \bar{\phi}_f}, \quad (C13a,b,c)$$

$$\mathcal{D}_a^i = \frac{\Re_{plag}^i L}{V_f}, \quad (C14)$$

$$\Theta_{plag}^i = \frac{\Gamma_{plag}^i L}{\rho_f \bar{\phi}_f V_f}, \quad (C15)$$

$\mathcal{D}_a^i$ is a measure of the relative rate of diffusive exchange rate in the plagioclase to the rate of melt percolation in the mush; and Θ_{plag}^i a measure of the relative rate of plagioclase dissolution or precipitation to the rate of melt percolation in the mush. Each

trace element is assigned a different $\mathcal{D}_a^i$ related to its diffusivity in the mineral, while each solid phase has a different Θ_{plag}^i , which is effectively the amount of each solid added to (or subtracted from) the melt. $\mathfrak{R}_{plag}^i$ is itself a function of grain size r , geometry β and diffusivity D_n of the trace element of interest in the solid and is approximated using the simple relationship, $\mathfrak{R}_{plag}^i = \beta D_n / r^2$ (Liang, 2003).

Eqs. C10-C12 were solved numerically for a given set of dimensionless parameters (Table 3.3), and results are given in the text and Table 3.1 and illustrated in Figures 3.3 and 3.4. To gain further insight into dissolution-reprecipitation processes, we consider a special case in which we neglect diffusion of major elements in the solid phases. Eq. C10 then takes the form

$$\frac{d\bar{C}_f}{dt} = (C_f^{in} - \bar{C}_f) + \Theta_{plag}^D (\bar{C}_{plag}^D - \bar{C}_f) + \Theta_{plag}^P (\bar{C}_{plag}^P - \bar{C}_f) \quad (C16)$$

which can be solved by an integration, giving

$$\begin{aligned} \bar{C}_f^i = & \frac{C_f^{in} + \Theta_{plag}^D \bar{C}_{plag}^D + \Theta_{plag}^P \bar{C}_{plag}^P}{1 + \Theta_{plag}^D + \Theta_{plag}^P} \\ & + \left[\bar{C}_f^0 - \frac{C_f^{in} + \Theta_{plag}^D \bar{C}_{plag}^D + \Theta_{plag}^P \bar{C}_{plag}^P}{1 + \Theta_{plag}^D + \Theta_{plag}^P} \right] \exp \left[-(1 + \Theta_{plag}^D + \Theta_{plag}^P)t \right]. \end{aligned} \quad (C17)$$

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APPENDIX D

Supplementary Material to Chapter 4

Extended Methods

The synthetic silicate melt was prepared using a sol-gel method [Cooper and Kohlstedt, 1984] incorporating organometallic sources for silica and titania with nitrate sources for other cations. The composition of the synthetic basalt is (wt%) 49.9 SiO₂, 5.6 TiO₂, 12.7 Al₂O₃, 15.8 MgO, 7.6 FeO, 8.4 CaO with trace Na₂O and La₂O₃ (Table C1) and was designed to resemble that used by Spandler and O'Neill [2010]. The composition is notable for its high (~5 wt%) TiO₂ and has an activity a_{TiO_2} of 0.1 [Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995]. Pulverized San Carlos olivine (~Fo₉₀; ~20μm grain size) was added before gelling such that the basalt was 10 wt% (oxide equivalent) of the final mixture. We calculate $a_{\text{TiO}_2} = 0.0035$ in the olivine [Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995]. After drying overnight on a stirring hot plate, the gel was fired at 650°C in argon for 20 hours for calcining. The resultant olivine + oxide powder was cold-pressed (1500 lb. load in Carver press), then vacuum sintered (f_{O_2} ~Ni-NiO) at 1260°C for 4 h before quenching and sectioning. The melt was designed to be in equilibrium with the olivine for major elements, but it is possible that a small amount of dissolution of the olivine took place at the start of the experiment.

Small sections of the sintered samples were reheated in a CO-CO₂ or H₂-CO₂ (the latter being diluted with Ar) gas atmosphere for 48-50 h at 1310°C or 1410°C (Table D2). Water fugacity ($f_{\text{H}_2\text{O}}$) was calculated for the experiments buffered by H₂-CO₂ and is greater at higher f_{O_2} . Experiments were quenched by removal of the sample from the furnace and immersion in water; the samples reached room temperature within <30 s of being taken out of the hot spot.

Thin sections of the experimental samples were prepared for scanning electron microscopy (SEM) with chemical analysis done using energy-dispersive X-ray spectrometry (EDS). TEM foils on Cu grids were made from thin sections after mechanical thinning and polishing, and final thinning was done by ion milling (Ar^+) at 5 keV at low angle ($<8^\circ$) followed by finishing at 3 keV.

We used the LEO 1530VP SEM at Brown University for backscattered electron imaging (BEI) and for EDS. Transmission electron microscopy was performed at Brown University on the CM20 (200kV), which includes an EDS detector; HRTEM was accomplished using the JEOL 2010 (200kV, 103 μA) at Brown University, and on the JEOL 2010 Field Emission Gun Analytical Electron Microscope (AEM) at MIT (200kV). The AEM is equipped for EDS X-ray analysis, along with a Gatan image filter (GIF) for electron energy-loss spectrometry (EELS) and energy filtered imaging. Select element maps were obtained using the three-window method. Fast Fourier Transforms (FFTs) and lattice fringe measurements were done using ImageJ software [*Rasband*, 1997].

Table D1 — Composition of synthetic basalt.

Oxide	Wt% ^a
SiO ₂	49.90
TiO ₂	5.60
Al ₂ O ₃	12.66
MgO	15.82
FeO	7.61
CaO	8.41
Na	486 ppm
La	260 ppm
α_{TiO_2}	0.1 ^b

^a Estimated from starting material^b *Asimow and Ghiorso* [1998]; *Ghiorso and Sack* [1995]**Table D2 — Experimental run conditions.**

Sample	Temperature (°C)	Duration (h)	f_{O_2} (atm)	ΔQFM	$f_{\text{H}_2\text{O}}$ (atm)	Environment
M0	1260	4	--	~+1	--	vacuum
M1	1310	48.5 h	5×10^{-7}	+1	--	CO-CO ₂
M2	1310	50	2×10^{-6}	+1.7	--	CO-CO ₂
M3	1410	50	7×10^{-6}	+2	--	CO-CO ₂
M4	1310	49	5×10^{-7}	+1	5×10^{-9}	H ₂ -CO ₂
M5	1310	49	8×10^{-10}	-2	2×10^{-10}	H ₂ -CO ₂

Figure D1

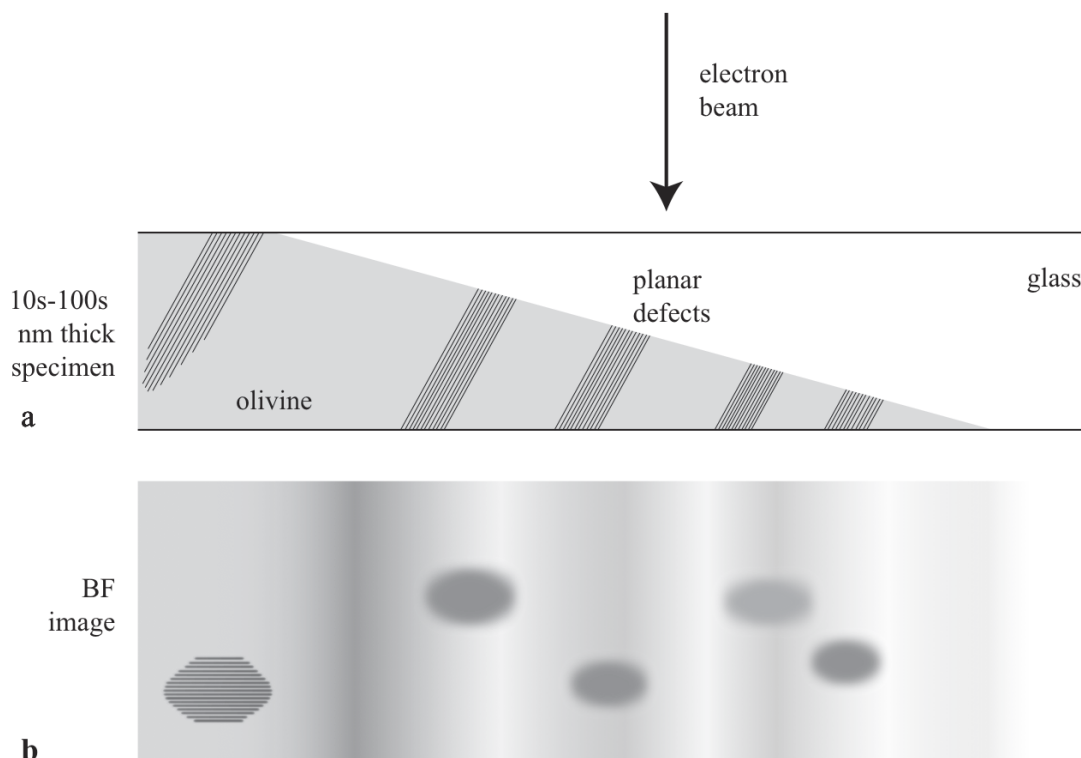


Figure D1: Schematic illustrating the specimen orientation relative to the electron beam in Fig. 4.1c and location of defect superstructures within the olivine. (a) The olivine-glass boundary is angled relative to the electron beam (viewing direction). The defect planes extend into the olivine, possibly through the entire specimen in places. (b) The associated bright-field (BF) image example shows the defect-rich olivine as regions of high-contrast. The lattice superstructure may be viewable where the electron beam passes through olivine only (i.e., no glass is present in the specimen above or below the olivine wedge), if the zone axis lies on $\{101\}$, as illustrated by the “striped” defect at the far left.

Figure D2

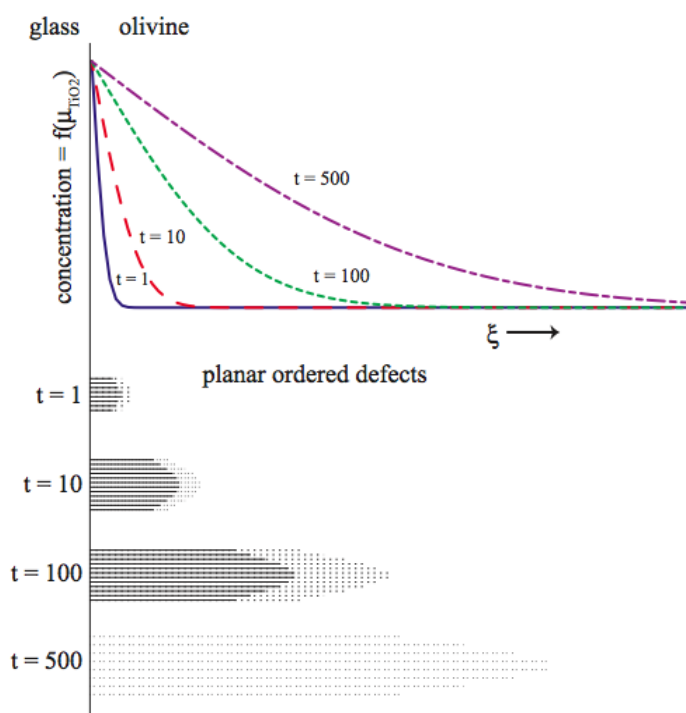


Figure D2: Schematic illustrating the role of chemical potential gradient in planar defect transience. Time is non-dimensional. At the beginning of the experiment, the driving force for Ti^{4+} inclusion in the olivine, which is the chemical potential gradient (here shown in terms of concentration), is very large. Similar to the mechanism proposed to drive chemically induced grain boundary migration (CIGM) [Hay and Evans, 1987], the rapid incorporation of Ti^{4+} into the crystal structure, even at levels below the solubility limit, may cause enough strain for reordering of the structure. Here, instead of moving a grain boundary to reduce the strain, the charged defects ($\text{Ti}_{\text{Mg}}^{\bullet\bullet}$ ^a and $\text{V}_{\text{Mg}}^{//}$) are ordered into a superstructure of extended planar defects. While the driving force, or slope of the concentration with depth, is great, ordered defects are formed in the olivine. The extended defects dissolve at depth and with time as the gradient becomes too low to sustain them, and “free” point defects, sustained by the entropy of mixing, become the equilibrium defect structure. The smooth transition between the defect superstructures and surrounding defect-free olivine when viewing the $\{101\}$ lattice fringes indicates the ease of such dissolution of the ordered structure.

The real dimensions of the extended defect structures reach at least 160 nm after 50 hours. The characteristic diffusion coefficient for this diffusion distance (i.e., the concentration gradient would be steep to this depth from the interface) is $\sim 1.5 \times 10^{-19} \text{ m}^2/\text{s}$, but it is possible that the measured length does not represent the longest dimension. The defects may also be dissolving at the stage captured by these experiments.

^a In Kröger-Vink notation, the subscript indicates the lattice site and the superscript refers to the real defect charge (x is neutral, prime is a negative charge, and a dot is a positive charge). Thus $\text{V}_{\text{Mg}}^{//}$ indicates a vacancy on an octahedral cation site usually occupied by Mg or Fe and having a charge of 2-, and $\text{Ti}_{\text{Mg}}^{\bullet\bullet}$ is Ti^{4+} replacing Mg^{2+} or Fe^{2+} and thus having a charge of 2+.

References

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APPENDIX E

Olivine—Ti-Oxide Experiments

1. Introduction and Motivation

The dynamics of diffusion-couple experiments, where the driving force for incorporation of ions into another material is large, do not always show Fickian lattice diffusion profiles, and structures such as extended planar defects can form that enhance diffusion, as demonstrated by the high-TiO₂ basalt—olivine experiments described in Chapter 4 of this dissertation. The use of different starting materials in the diffusion-couple changes the activity of the diffusing ion and thus the chemical potential gradient that is the driving force. Continuing with our examination of Ti⁴⁺ in olivine, we performed experiments using the same powdered olivine as in the melt-olivine experiments, now combined with synthetic ilmenite (TiO₃).

2. Methods

The olivine-oxide starting material, polycrystalline San Carlos olivine (~20 μm grain size; ~Fo₉₀) with 24 wt% synthetic ilmenite (99.8% metals basis; ~10 μm grain size), was mechanically mixed then cold-pressed (dry, 1500 lb. load in Carver press) and vacuum sintered at 1290°C for 4 hours. Assuming the presence of both ilmenite and armalcolite (discussed further in Section 3), a_{TiO_2} is 0.2.

Small sections of the sintered sample were reheated in a H₂-CO₂ (diluted with Ar) gas atmosphere for 48-50 h at 1310°C (Table E1). Samples were held at one log unit above and two log units below the fayalite-magnetite-quartz (QFM) buffer, well within the stability field of Fo₉₀ olivine. Water fugacity ($f_{\text{H}_2\text{O}}$) was calculated for the experiments and is greater at higher f_{O_2} . Experiments were quenched by removing the sample from the furnace and placing it quickly in water; the samples reached room temperature within ~30 s of being taken out of the hot spot.

Table E1 — Experimental run conditions.

Sample	Temperature (°C)	Duration (h)	f_{O_2} (atm)	ΔQFM	f_{H_2O} (atm)	Environment
O0	1290	4	--	$\sim +1$	--	vacuum
O1	1310	48.5	5×10^{-7}	+1	5×10^{-9}	H ₂ -CO ₂
O2	1310	48	8×10^{-10}	-2	2×10^{-10}	H ₂ -CO ₂

Thin sections of the experimental samples were prepared for scanning electron microscopy (SEM) with chemical analysis done using energy-dispersive X-ray spectrometry (EDS). Major element compositions were obtained by wavelength-dispersive X-ray spectroscopy (WDS) analysis, performed on a Cameca SX100 electron microprobe. TEM foils on Cu grids were made from thin sections after mechanical thinning and polishing, and final thinning was done by ion milling (Ar⁺) at 5 keV followed by finishing at 3 keV.

We used the LEO 1530VP SEM at Brown University for backscattered electron imaging (BEI) and for EDS. Transmission electron microscopy was performed at Brown University on the CM20 (200kV), which includes an EDS detector; HRTEM was accomplished using the JEOL 2010 (200kV) at Brown University and on the JEOL 2010 Field Emission Gun Analytical Electron Microscope (AEM) at MIT. The AEM is equipped for EDS X-ray analysis, along with a Gatan image filter (GIF) for electron energy-loss spectrometry (EELS) and energy filtered imaging and 3 CCD cameras. Most filtered imaging was done in zero-loss mode (blocking inelastically scattered electrons), but select element maps were obtained using the three-window method. Fast Fourier Transforms (FFTs) and lattice fringe measurements were done using ImageJ software [Rasband, 1997].

Identification of phases was done both through compositional data and indexing selected area electron diffraction (SAED) patterns. To efficiently index the diffraction patterns, the author developed several simple MATLAB codes to first calculate the d-spacings for each mineral suspected in the sample and the length ratios and angles between planes that are the data obtained from SAED patterns. The data from individual patterns were then used to search the tables for the matching planes. Where FFTs and lattice fringes were present from the same regions, they were used for confirmation of the d-spacing of the indexed plane. The tables and MATLAB codes can be made available upon request.

3. Results

The olivine-ilmenite reaction specimens show extensive exchange of Fe and Mg amongst the phases, as expected, as well as significant incorporation of TiO_2 into the olivine. Olivine grains from both samples are homogeneous in major elements and have Mg# 85 (i.e., the olivine has evolved to Fo_{85} from the starting material of $\sim\text{Fo}_{90}$). The olivine grains show a large variation in TiO_2 content as measured by microprobe/WDS (Fig. E1). Most data cluster between 0.1 and 0.4 wt% TiO_2 , and but TiO_2 content reaches as much as 0.9 wt% in the olivine with no change in SiO_2 , which would indicate overlap with an oxide in the excitation volume. Profiles from oxide grains into and across olivine grains show no diffusion profiles of any component, although it is possible that profiles that extend less than a couple microns would not be recognized (e.g., as for Si).

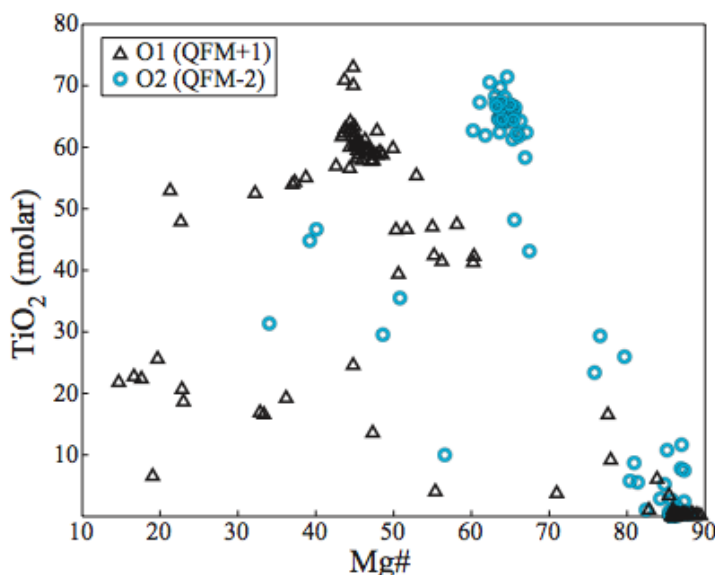


Figure E1: Plot of TiO_2 (molar) versus $\text{Mg\#}$ in samples O1 and O2. The high- TiO_2 measurements indicate the presence of armalcolite; the $\text{Mg\#}$ of the armalcolite in the oxidized sample O1 is lower than that for O2. A second, lower TiO_2 , high FeO oxide is present in both samples. The very low (but non-zero) TiO_2 measurements are from olivine grains in the samples; the olivine has $\text{Mg\#} \sim 85$. Measurements falling on a mixing line between olivine and the oxides are due to beam size larger than oxide grains and thus, contamination. It is unclear if the high and low- TiO_2 oxides form a continuum or distinct phases. Totals have been renormalized from microprobe data assuming the presence of SiO_2 , TiO_2 , MgO and $\text{FeO}^T = \text{FeO}$; a significant amount of an Fe_2O_3 component is likely present in the oxides in sample O1.

Microprobe/WDS data indicate a range of $\text{Ti}/(\text{Fe}+\text{Mg})$ in the oxides in both samples O1 and O2, corroborated by the differences in brightness between grains (Fig. E2). The experiments initially contained ilmenite, but the largest grains in both specimens are predominantly armalcolite ($(\text{Fe,Mg})\text{Ti}_2\text{O}_5$); the small grains in sample O1 (QFM+1) generally have lower $\text{Ti}/(\text{Fe}+\text{Mg})$ and approach pseudobrookite bulk composition (Fe_2TiO_5) (Fig. E1). A bright oxide is also present along some olivine grain boundaries, but grains are too small for measurement in the microprobe. The armalcolite in sample O2 (QFM-2) has higher $\text{Mg\#}$ than the oxidized sample (~ 65 versus ~ 45 in O1). A second (lower Ti) phase is also present in the sample, but the grains are too small for measurement without olivine contamination. The identification of armalcolite was

confirmed structurally using selected area electron diffraction (SAED) patterns; it is the stable Ti-bearing oxide at low pressure in the presence of olivine and pyroxene [Thacker *et al.*, 2009]. Ilmenite, although confirmed by XRD as the starting material, was not uniquely identified.

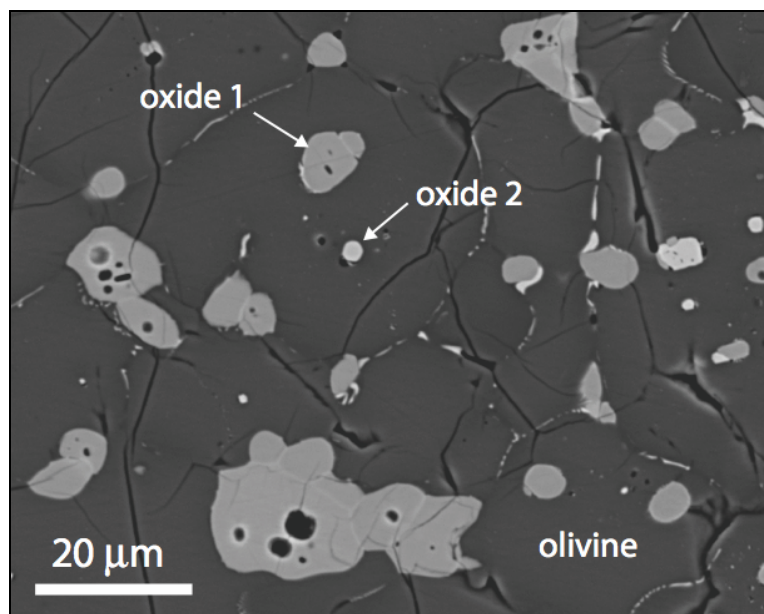


Figure E2: SEM/BEI image of olivine-titanium oxide reaction specimen O1 (QFM+1). The dark grains are olivine (Mg# 85), and the bright grains are Fe and Ti rich oxides. Microprobe/WDS data indicate a range of Ti/(Fe+Mg) in the oxides, corroborated by the differences in brightness between grains. The experiment initially contained ilmenite, but the largest grains are predominantly armalcolite ((Fe,Mg)Ti₂O₅); the small grains generally have lower Ti/(Fe+Mg) and approach pseudobrookite bulk composition (Fe₂TiO₅). Pyroxene was not detected in SEM images, but was identified in TEM.

Pyroxene is not clearly observed in either SEM/BEI or microprobe data (no high-SiO₂ phase), but is identified from SAED patterns. TEM/EDS indicates that the pyroxene is very high Fe compared to the olivine; the precise amount of Ti in the pyroxene grains cannot be determined from the available data, but energy-filtered imaging indicates that it is well ordered (and negatively correlated with Fe) along (100)_{pyx}.

TEM/EDS measurements of olivine indicate qualitatively the presence of Ti^{4+} even at depths several microns from any phase or grain boundary (Fig. E3). For comparison, an olivine measurement from sample M1 (olivine + high-Ti basalt, QFM+1; Ch. 4 of this dissertation) is also shown; while qualitatively similar, there is no visible Ti peak. Differences in Fe and Mg between the two samples is expected due to the reaction with ilmenite and lowering of the Mg# in sample O1.

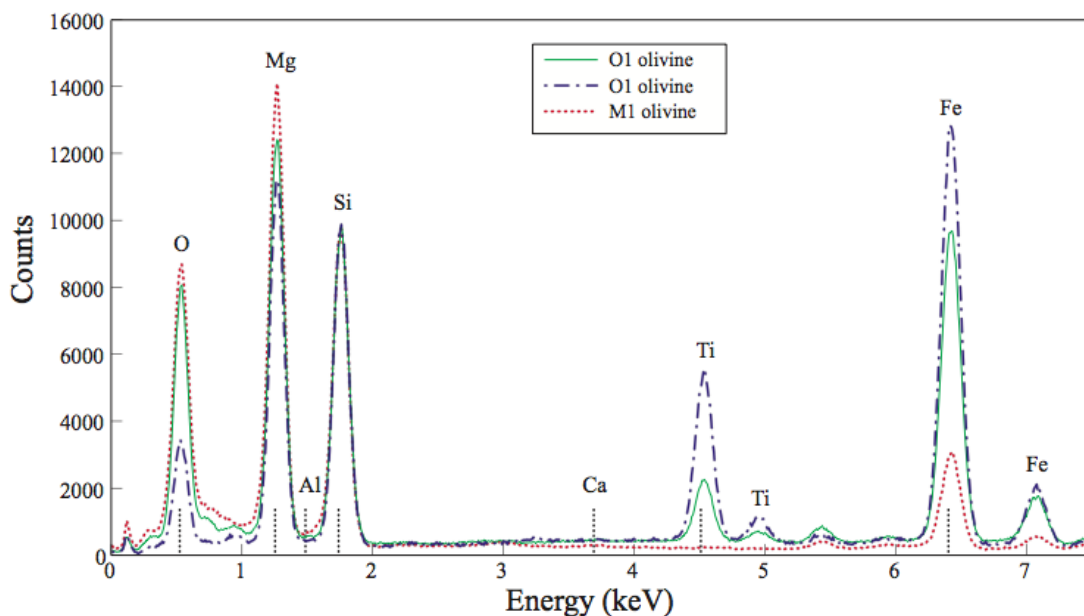


Figure E3: TEM/EDS data from olivine grains. There is a clear Ti peak at ~ 4.5 keV, indicating the presence of Ti in the olivine from sample O1 (QFM+1) even far from phase boundaries. For comparison, an olivine from an olivine-melt specimen (M1; Ch. 4) has no visible Ti peak. The spectra were normalized to have the same Si peak height; higher Fe and lower Mg in the olivines from sample O1 is expected due to the reaction with ilmenite.

Regions near the interfaces between olivine and oxide grains do not exhibit the larger high-contrast regions seen in olivine near olivine-glass interfaces, and no defects were recognized along $(101)_{\text{ol}}$. However, HRTEM imaging of sample O1 (QFM+1) shows that the lattice fringe spacing in olivine near some phase boundaries changes from $d(001)_{\text{ol}} = 0.6$ nm (Fig. E4, right inset) in far-field olivine to $d(001) = 1.1$ or 1.3 nm near the interface (left inset) viewed along the $[\bar{2}10]$ zone axis of olivine. These defects were

not observed in sample O2 (QFM-2). Optimally oriented olivine grains were difficult to find in the electron-transparent regions of the samples, and we are unable to make any estimate of defect ubiquity or density.

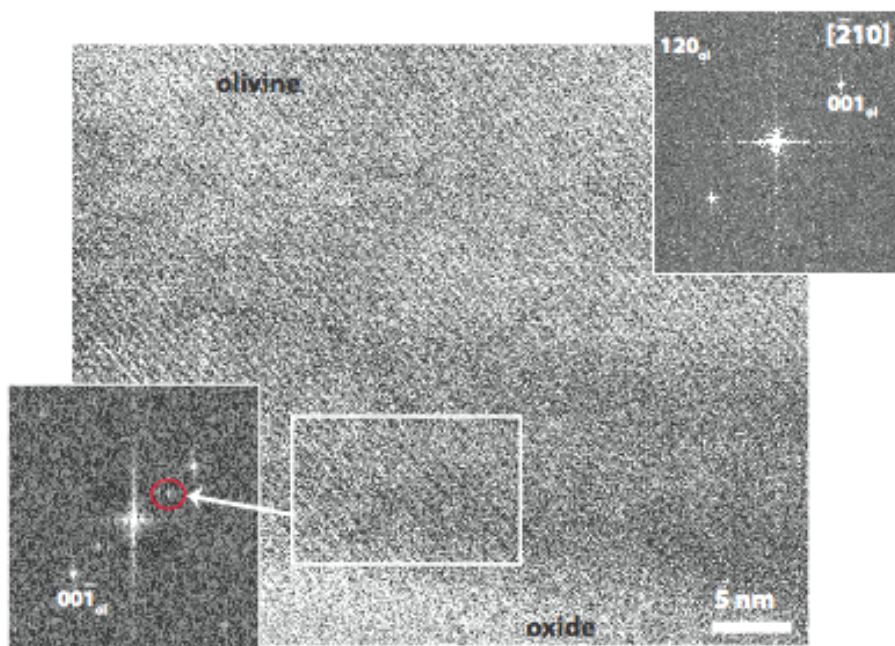


Figure E4: HRTEM image of olivine-titanium oxide reaction specimen O1 (QFM+1), showing irregular lattice fringe spacing parallel to $(001)_{ol}$ near an olivine-Ti oxide phase boundary. The inset to the left shows the FFT of the highlighted region with extra spots related to the presence of the defects, while the inset to the upper right shows the FFT for the upper part of the image and lacks the excess spots due to a superlattice structure. The olivine zone axis is $[210]$.

4. Comments

It is possible that some of our microprobe analyses are contaminated by “phantom” Ti due to stray electrons or fluorescence from background Bremsstrahlung radiation, which was noted in Ti-olivine solubility experiments with ubiquitous Ti-oxides [Hermann *et al.*, 2005]. However, the TiO_2 concentration in some of our olivine data is much greater than the assumed “phantom” signal measured by Hermann *et al.* [2005]. We also have TEM/EDS data for several olivine grains from sample O1 that show large Ti peaks and for which the contamination issue should be much less.

The lack of observed (101)_{ol}-type planar defects in the O-series samples is interesting given their high a_{TiO_2} . However, as mentioned above, a reaction took place between the ilmenite and olivine originally present in the sample, and while the samples still contained large olivine grains, we also formed pyroxene and armalcolite. Although olivine and ilmenite are stable together in the absence of pyroxene [Thacker *et al.*, 2009], San Carlos olivine, used as our starting material, is equilibrated with pyroxene, which is enough to effect the given reaction of ilmenite to armalcolite. If the pyroxene formed as a reaction rim on the olivine, which is likely given the slow diffusivity of Si^{4+} , any defect clusters that did form as Ti^{4+} reacted with the olivine lattice could have been wiped-out by later reactions. Interfaces between olivine and pyroxene were difficult to observe in the TEM and were recognized based on changes in the SAED pattern rather than phase contrast in the image. As such, the extent of reaction and amount of pyroxene present cannot be estimated.

References

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APPENDIX F

Supplementary TEM Images

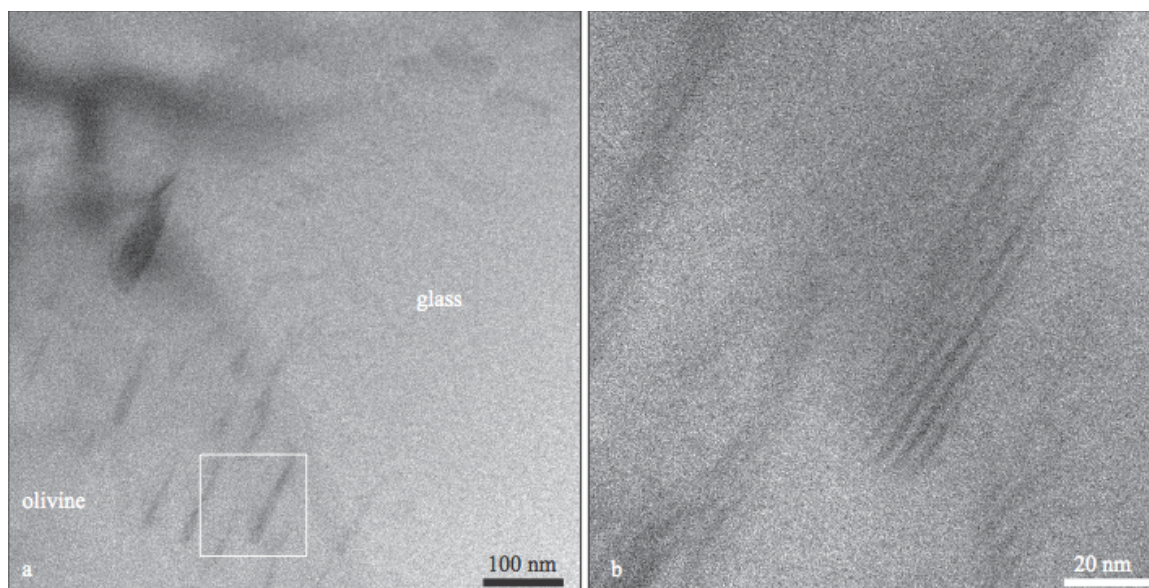


Figure F1: TEM BF images from specimen M1 (1310°C, QFM+1). (a) Elongate, high-contrast defects are present in olivine along a glass-olivine phase boundary. (b) Higher magnification view of highlighted region in (a). Interference fringes are created by the presence of the superstructure, but lattice fringe spacing is not visible.

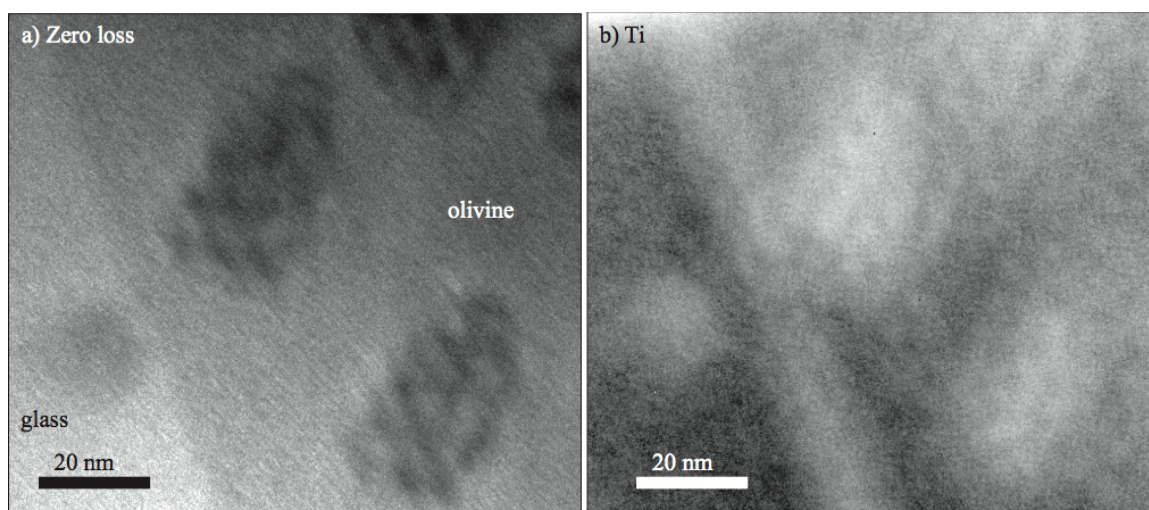


Figure F2: (a) Zero-loss energy filtered image of specimen M1 (1310°C, QFM+1). High-contrast defects are present in olivine. The defect to the far left is in olivine where glass is also present in the specimen cross-section. (b) Ti element map (35 eV) showing relative increase in Ti in defects relative to surrounding olivine and glass. The olivine-glass phase boundary also has a high-Ti boundary layer.

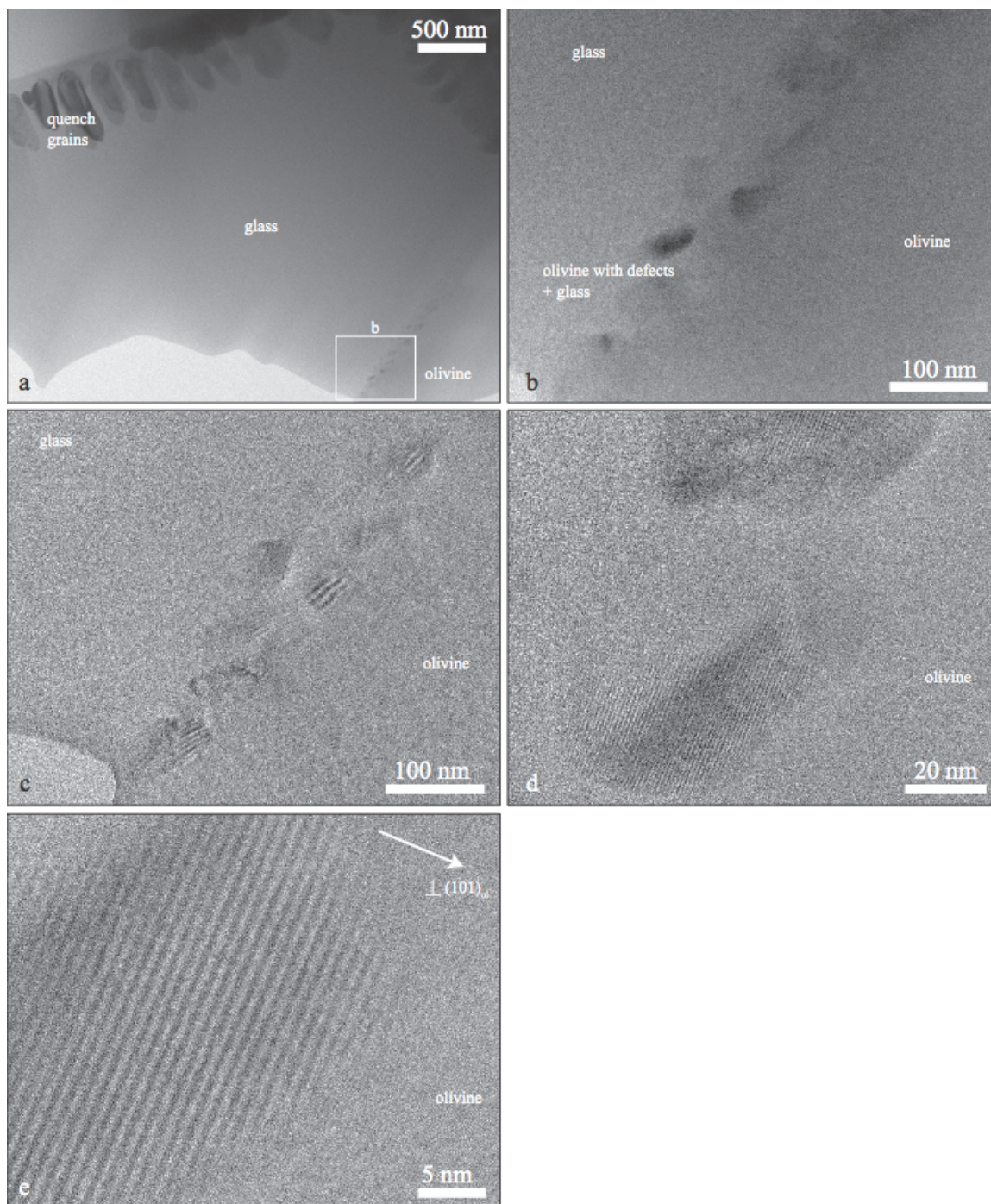


Figure F3: TEM BF images of specimen M2 (1310°C, QFM+2) at increasing magnification. (a) Melt pocket between two olivine grains. Oxide quench grains are present near one boundary; small defects are present in the olivine to the right. (b) Image of highlighted region in (a). (c) Same region as above, but contrast is different because specimen tilt has been changed. (d)-(e) The lattice superstructure of the defects is visible and shows the planar defects parallel to $(101)_{ol}$.

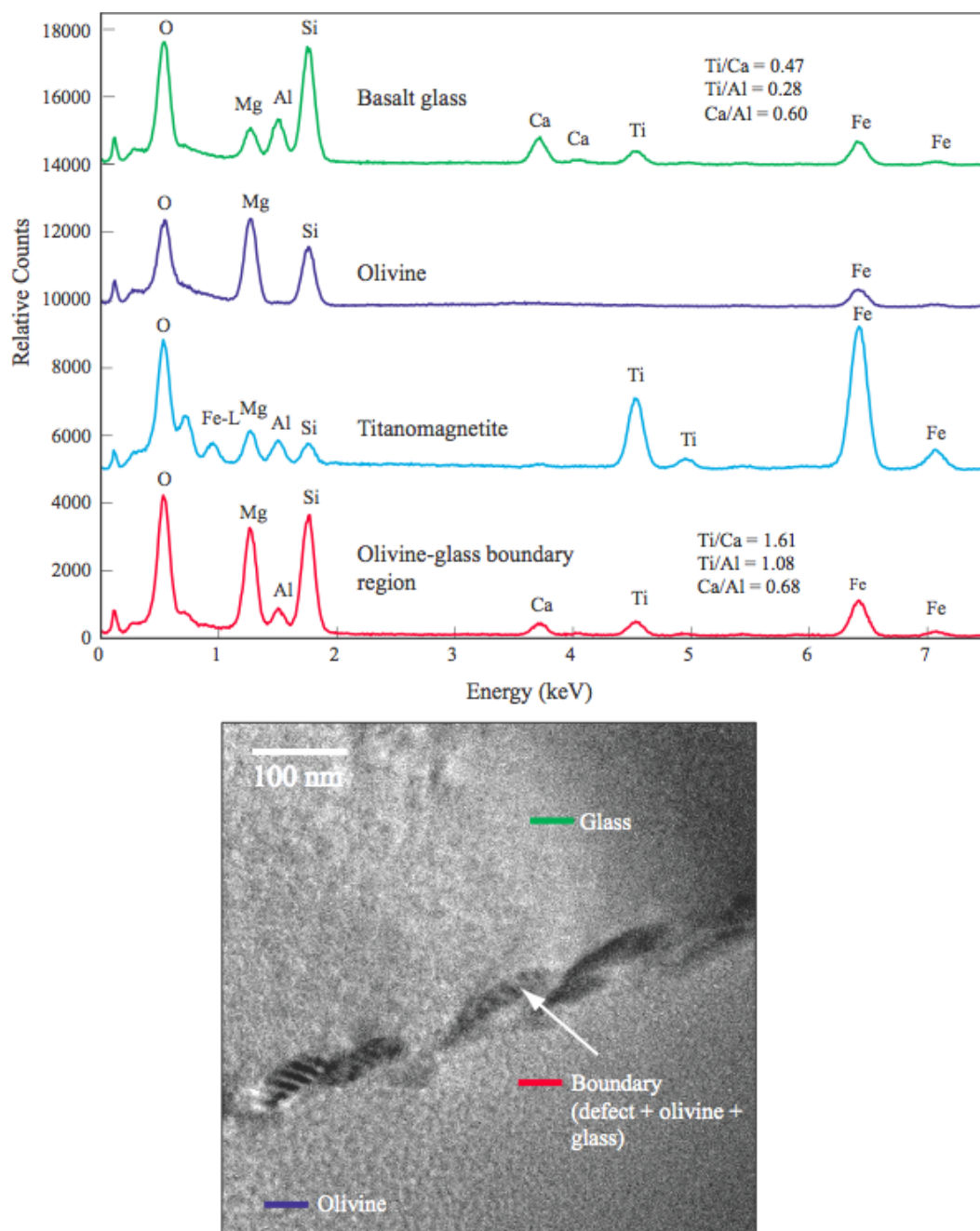


Figure F4: TEM/EDS spectra from specimen M2 (1310°C, QFM+2) for several different regions as noted in the associated image. Elemental abundances are qualitative, but comparison of peak height ratios can show relative changes. Ti, Ca, and Al are not present above the EDS detection limit in defect-free olivine; thus a region where defect-free olivine and glass are both present within the electron beam and contributing to the spectrum would have the same Ti/Ca, Ti/Al, and Ca/Al ratios as the glass. The increase in Ti/Ca and Ti/Al indicates an increase in Ti in the olivine-glass boundary region where defects are present. The titanomagnetite spectrum likely includes a small glass signature, and the oxide itself may not match the true end-member composition. The spectra are offset for clarity.

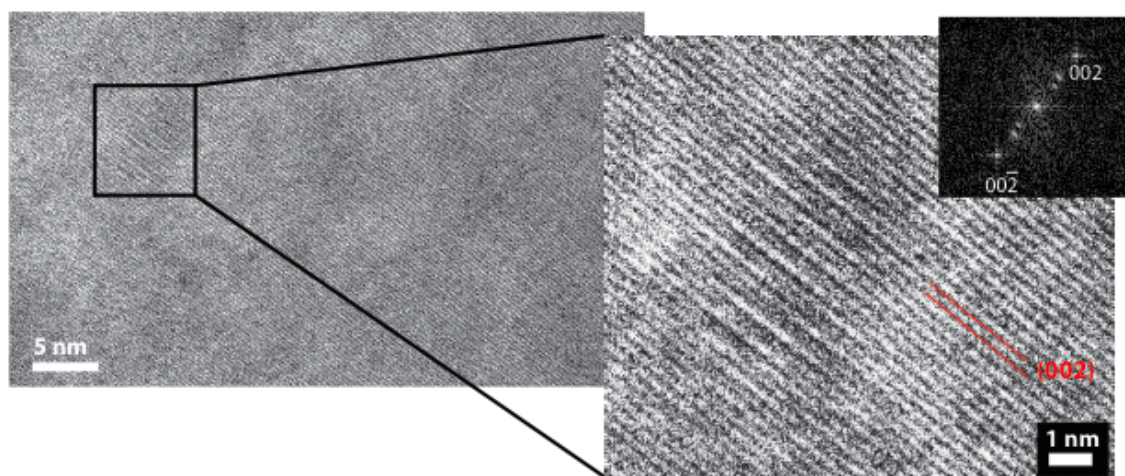
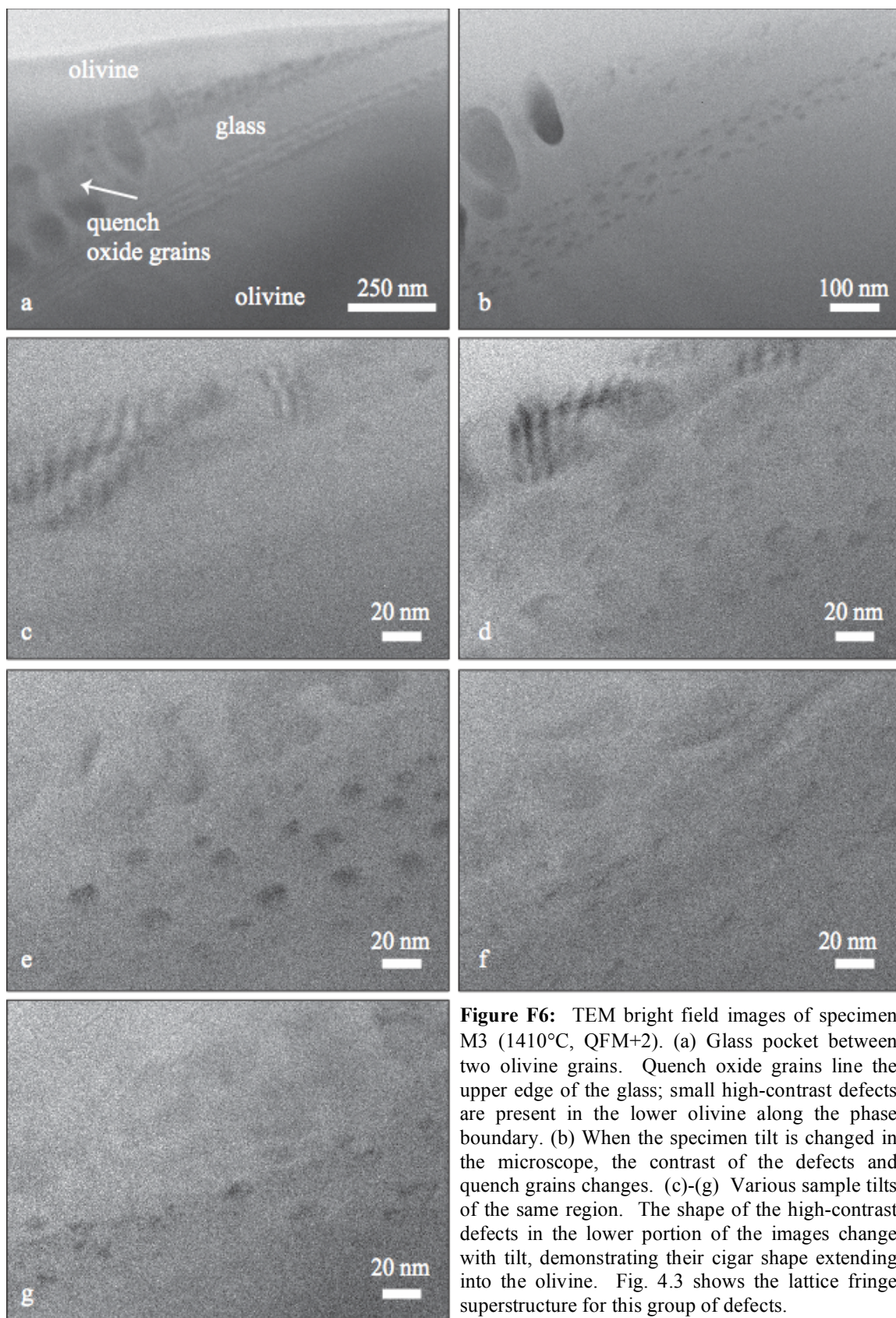


Figure F5: HRTEM image of specimen M2 (1310°C, QFM+2) showing irregular lattice fringe spacing parallel to $(002)_{ol}$. The extra spots in the FFT (inset) have spacings of 0.54 and 0.76 nm; by contrast, $d_{(002)ol} = 0.3$ nm. Planar defects with this orientation are found only in samples reacted at QFM+2 (M2 and M3) and are likely related to laihunite-type defects.



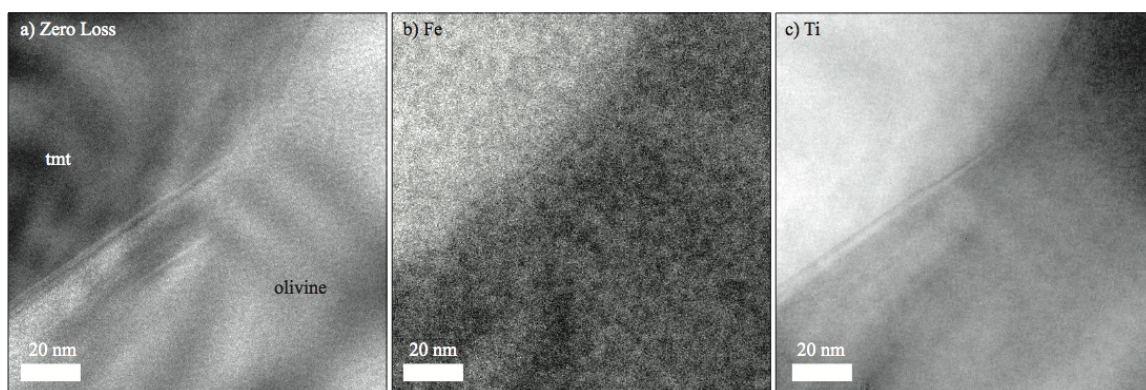


Figure F7: Energy-filtered images of specimen M3 (1310°C, QFM+2). (a) Zero-loss image of a titanomagnetite (tmt) grain in olivine. (b) Fe map and (c) Ti map showing the elevated Fe and Ti in the tmt. The tmt grain is not associated with any basaltic glass and confirms the presence of Ti far from phase boundaries where it can effect tmt nucleation.

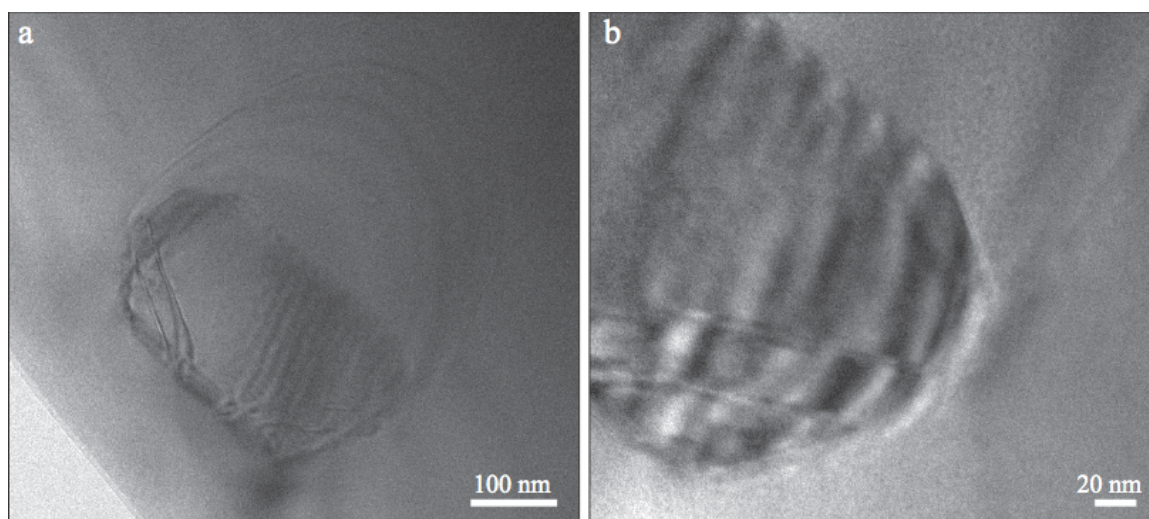


Figure F8: BF TEM images of specimen M3 (1310°C, QFM+2) showing a small, internally-nucleated titanomagnetite grain in olivine. An amorphous region is also present in the olivine due to the reaction. Dislocations (?) and other strain-induced features are observed in the titanomagnetite grains due to the mismatch between the olivine and oxide lattices.

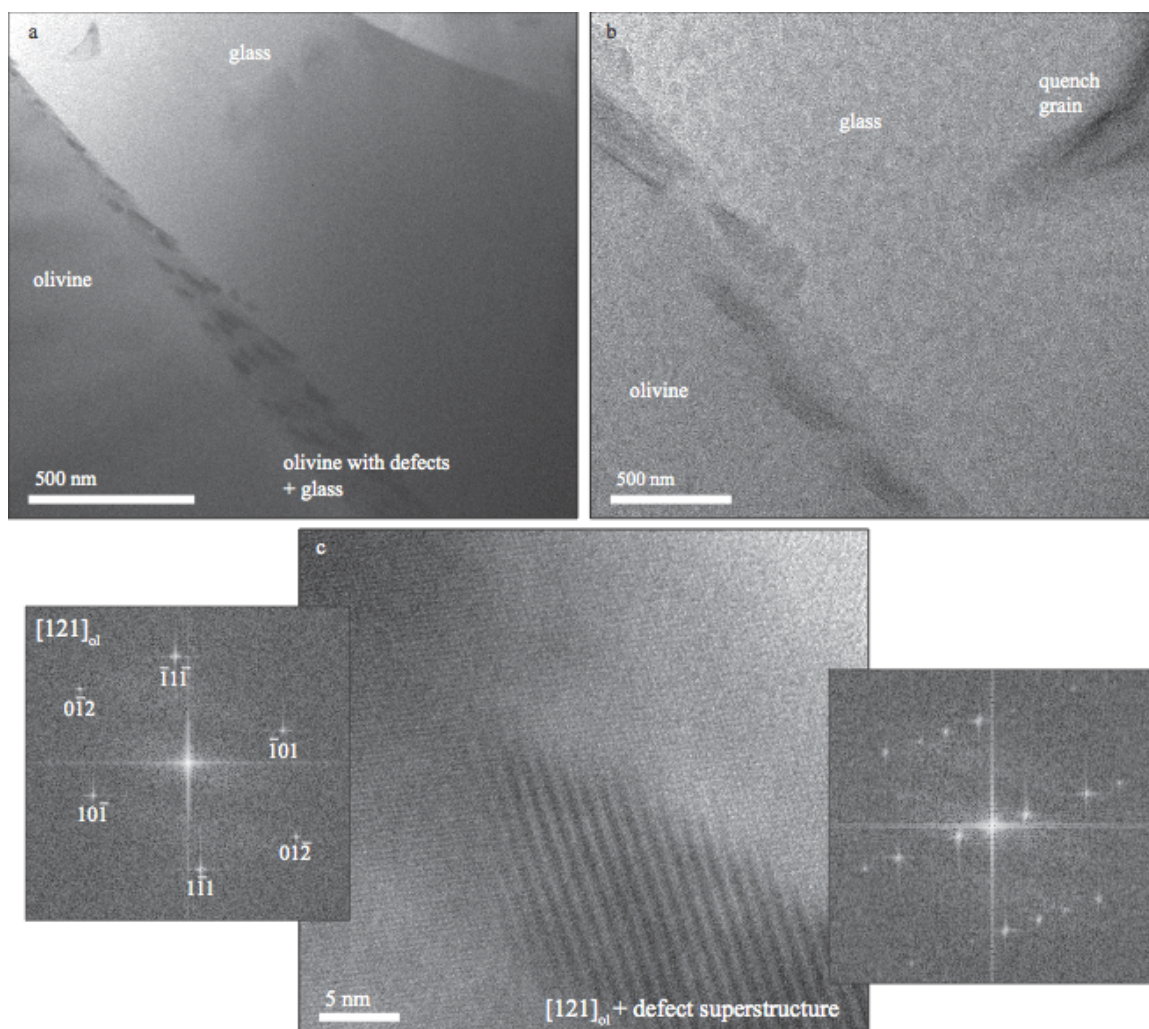


Figure F9: TEM images of specimen M4 (1310°C, QFM+1) showing the presence of defects in olivine along an olivine-glass phase boundary. (a) The small regions of ordered defects cover a significant portion of this phase boundary. (b) Tilting the specimen alters the contrast of the defect-rich regions. (c) HRTEM image of the defect superstructure showing the change in lattice spacing parallel to $(101)_{ol}$, as apparent in the right FFT. The FFT on the left shows the defect-free olivine. Zone axis is $[121]_{ol}$.

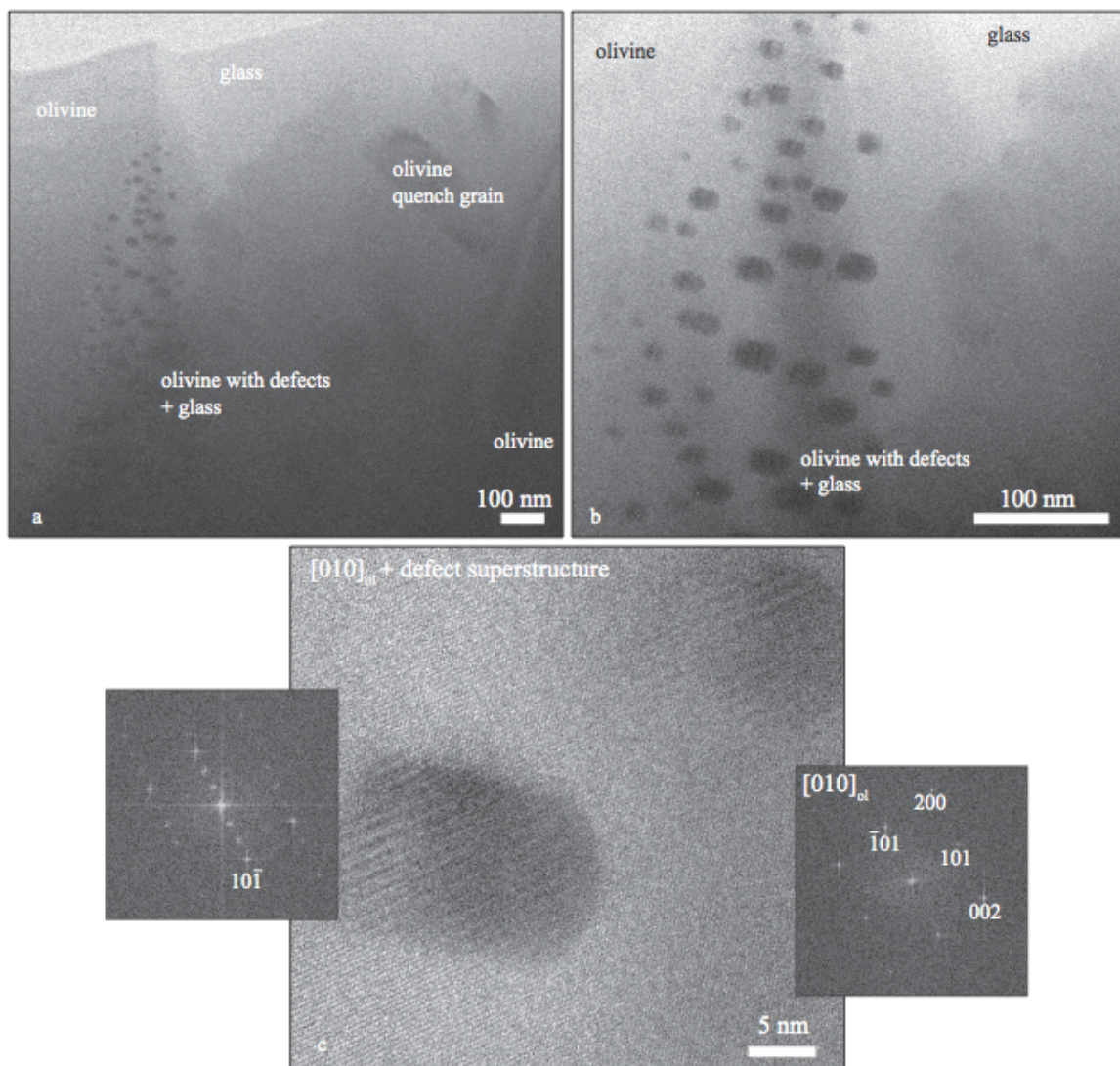


Figure F10: TEM images from specimen M5 (1310°C, QFM-2). (a) Glass/melt pocket between olivine grains. Defects are present in the olivine to the left; olivine quench grains are in the glass to the right side. (b) The defects are present in the olivine both where glass is not present in the specimen cross-section and in the olivine “behind” the glass in the cross-section. (c) HRTEM image showing the defect-free olivine lattice fringes (right FFT) and the tripling of spacing parallel to $(101)_{ol}$ in the defect-rich region (left FFT). Zone axis $[101]_{ol}$.

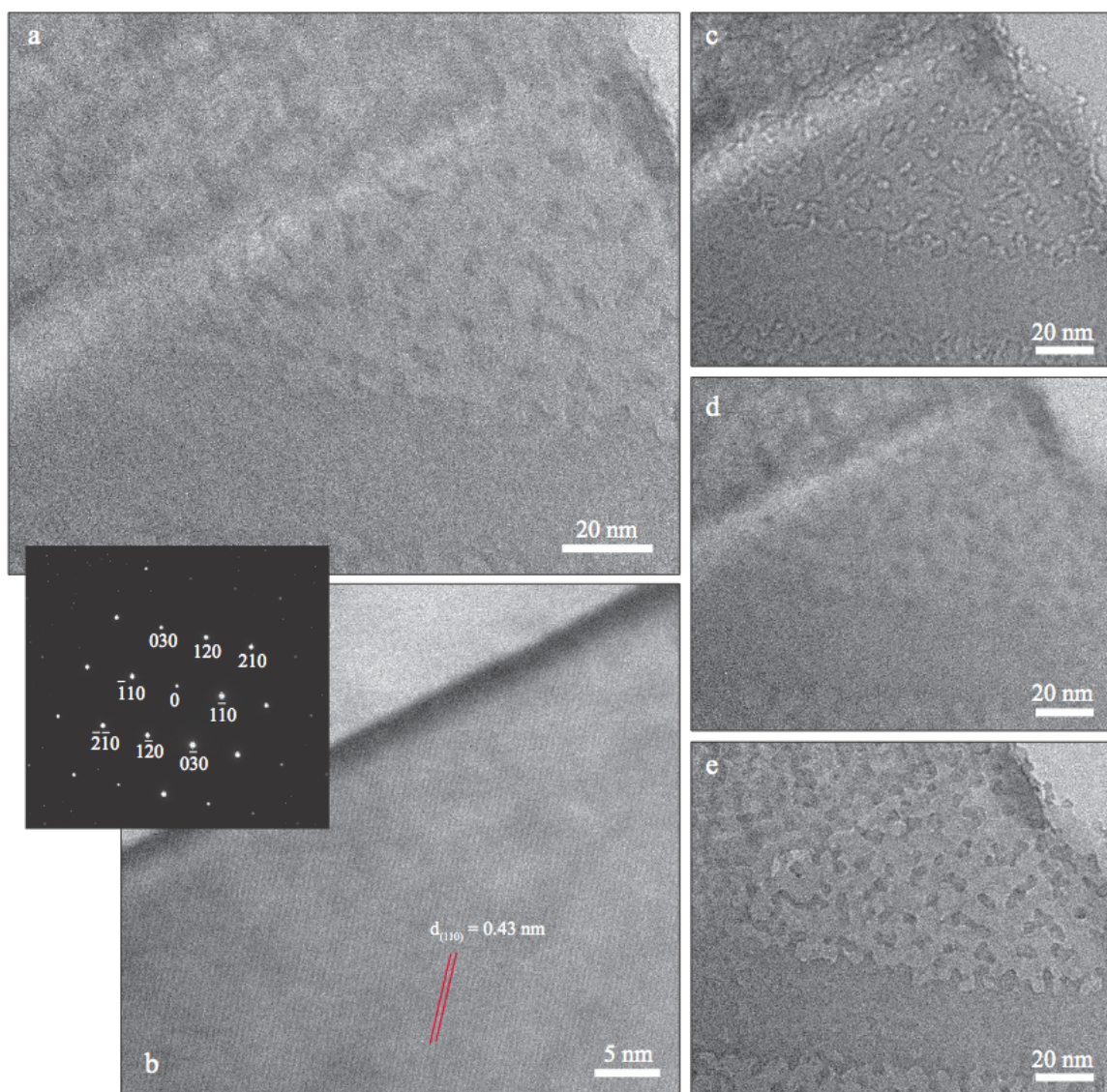


Figure F11: TEM images of specimen O1 (olivine+Ti-oxide, QFM+1). (a) Two olivine grains show spinodal decomposition textures. (b) The $(110)_{ol}$ lattice fringes are identifiable and extend through the apparently phase separated olivine. The specimen tilt is not the same as in (a). (c)-(e) A through-focus series of the grain boundary, which highlights the band of olivine lacking the lighter phase. This sample went through several reactions including alteration of ilmenite to armalcolite and formation of pyroxene (Appendix E). No compositional data were obtained for this specific location within the specimen, and the texture is unexplained.

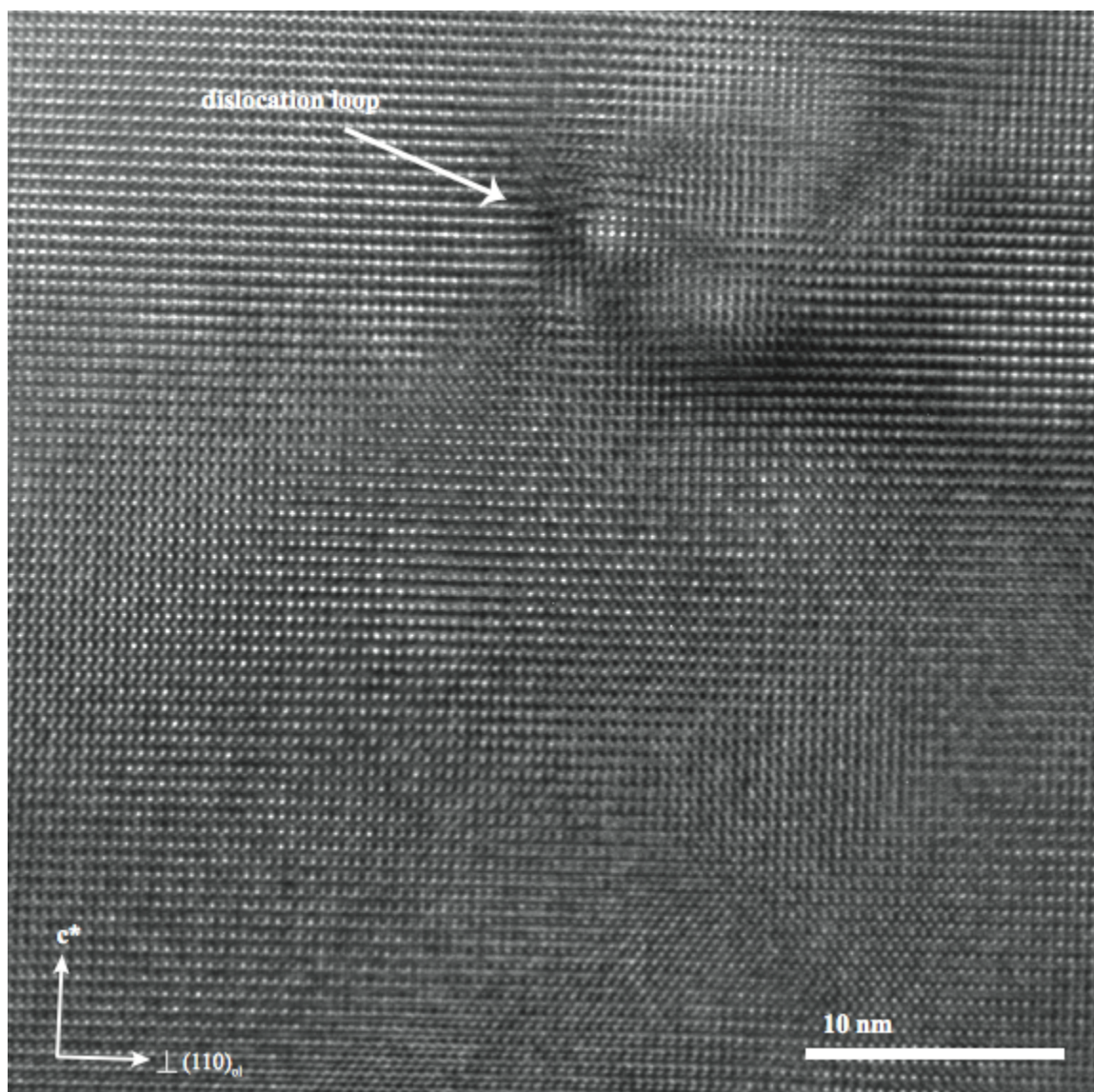


Figure F12: HRTEM image of sample O1 (olivine+ilmenite, 1310°C, QFM+1) showing a dislocation loop in olivine. Zone axis $[\bar{1}01]_{ol}$.

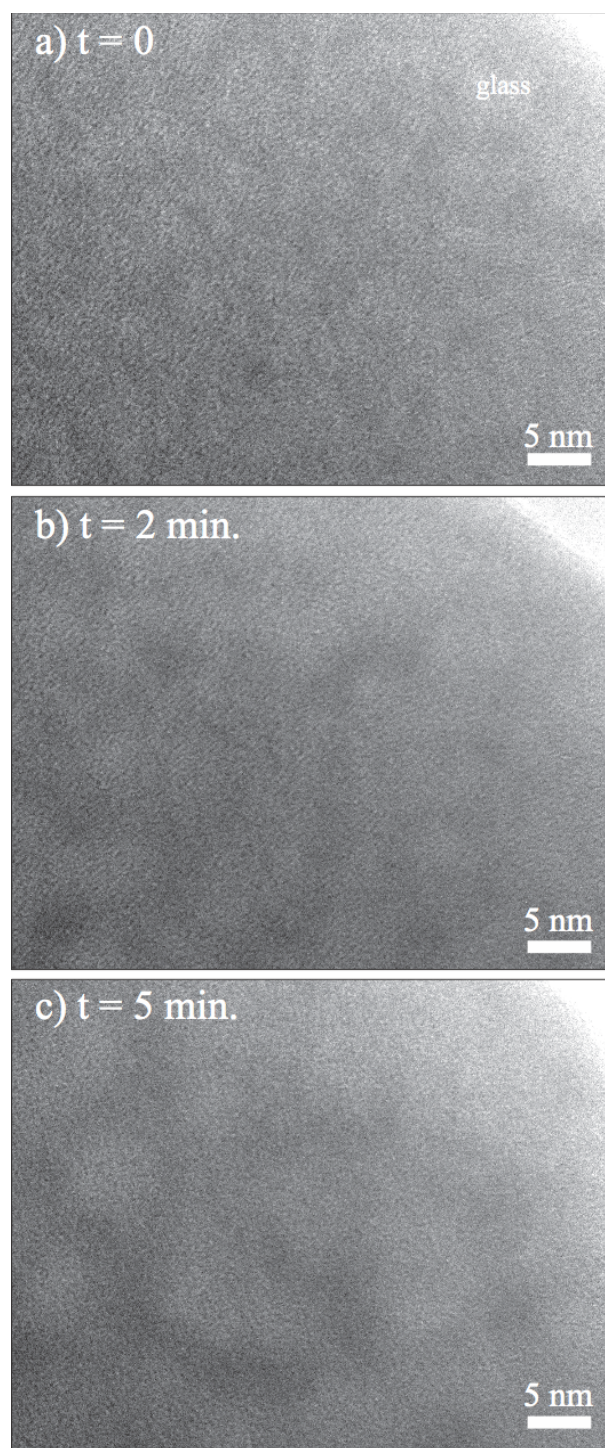


Figure F13: Time series of glass undergoing spinodal decomposition in the electron beam (200kV), with coarsening of the emulsion evident after only a couple minutes. A similar process was observed in basaltic glass in Chapter 2. The glass is an olivine-hosted basaltic melt inclusion from the Siqueiros Fracture Zone (courtesy of A. Saal). The specimen was prepared using the FIB.

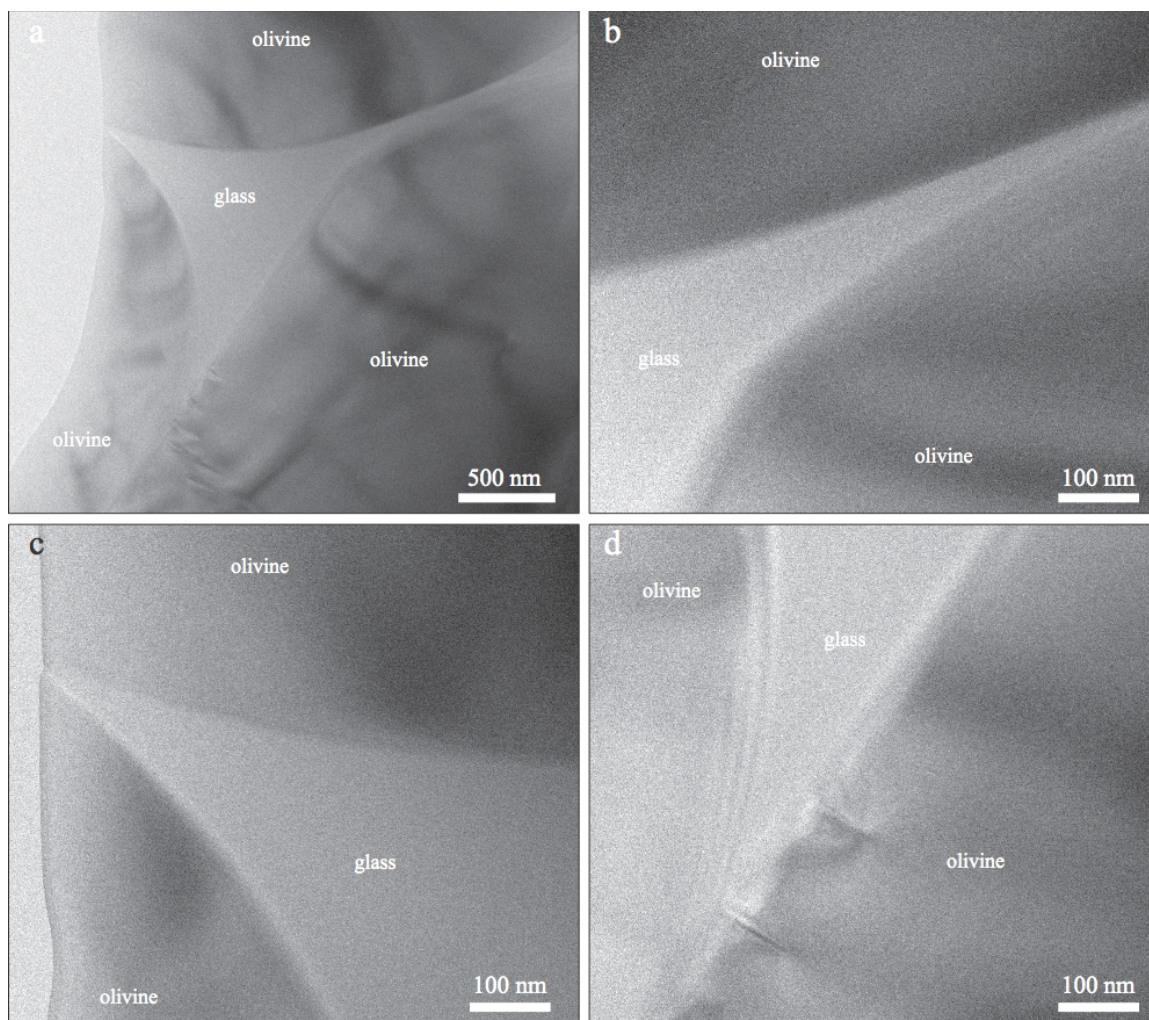


Figure F14: BF TEM images from sample J1, a sintered olivine + low-Ti basalt sample (courtesy of J. Beaulieu). Although classic triple junctions and melt pockets are identifiable, none show the presence of extended defects as were seen in the high-Ti samples.