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UNIVERSITY OF CALIFORNIA
RIVERSIDE

California Petrology - From Basaltic Volcanoes to Lithium-Bearing Minerals

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Geological Sciences

by

Jen Humphreys

September 2023

Dissertation Committee:

Dr. Maryjo Brounce, Chairperson
Dr. Heather Ford
Dr. Michael A. McKibben
Dr. Timothy Lyons

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2023

The Dissertation of Jen Humphreys is approved:

Committee Chairperson

University of California, Riverside

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My journey up to this point has been a rollercoaster, and, just like how you are never alone on a roller coaster, I would have never made it this far without all the people in my life.

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And finally, I want to thank second chances – it is never too late to start something new.

Never give up, never surrender!

ABSTRACT OF THE DISSERTATION

California Petrology - From Basaltic Volcanoes to Lithium-Bearing Minerals

by

Jen Humphreys

Doctor of Philosophy, Graduate Program in Geological Sciences

University of California, Riverside, September 2023

Dr. Maryjo Brounce, Chairperson

California is geologically complex because of a long history of changing tectonic environments in the last ~300 my. Currently, the tectonic environments of California can be broadly split between subduction-driven in the north and transform motion-driven in the south, with the current transition between the two occurring ~325 kms northwest of San Francisco, at the Mendocino Triple Junction. Around 12 Ma, this transition location was in what is now Southern California and Northern Mexico. The full subduction of the Farallon plate under the North American plate and resulting attachment of the Pacific plate to the western edge of the North American plate led to the formation of the oblique-transform San Andreas fault system as well as

the northern migration of the Mendocino Triple Junction. These different tectonic environments are evident through petrologic investigations of the rocks. Northern California has active subduction zone volcanism, the southern most active volcano being Lassen Peak. Southern California contains the western edge of the Basin and Range Province, where propagation of volcanism across the American Southwest has been attributed to lithospheric thinning and/or decompression melting. In the southernmost part of Southern California, where the San Andreas Fault system begins, ongoing continental rifting connected with the opening of the Gulf of California occurs beneath thick layers of Colorado River deposited sediments. This thesis reports microanalytical, geochemical analyses of various volcanic systems throughout California. Olivine hosted melt inclusions from the Basalts of Round Valley Butte, a basaltic cinder cone about 40 km east of Lassen Peak, were analyzed to evaluate the use of these investigative tools for pre-eruptive processes. The knowledge gained from Basalts of Round Valley Butte were then used on olivine hosted melt inclusions, melt embayments, and matrix glasses to characterize the melts beneath Pisgah Crater in the Mojave Desert to better constrain the mantle melting conditions that led to the formation of Basin and Range mafic volcanism. Finally, this study examines the effects of continental rifting heat sources on the mineralogy of the Salton Sea Geothermal Field and specifically how this heat source has affected the distribution of lithium between geothermal brines and minerals.

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INTRODUCTION

Since 12 Ma, the western edge of the North American tectonic plate has been transitioning from a convergent tectonic margin to a right-lateral, strike-slip tectonic margin (e.g., Atwater, 1970; Mammerickx and Klitgord, 1982; Stock and Hodges, 1989). In California, this change corresponds with the northward migration of the Mendocino triple junction, where subduction of the Juan de Fuca plate meets the San Andreas fault system. The ways in which volcanism and related processes manifest in California are intimately tied to their tectonic environment. In Northern California, volcanism is driven by subduction, where surface derived materials are thrust beneath the overriding North American plate. Melting of the North American plate is initiated via the release of fluids from the underlying Juan de Fuca plate due to the lowering of the peridotite solidus in the presence of H_2O . This process produces relatively hydrated and oxidized basaltic magmas compared to those generated at mid-ocean ridges (e.g., Muth and Wallace, 2021; Walowski et al., 2016, 2015). The first chapter of this dissertation examines more closely the relationship between the oxidized subducting plate and associated volcanic products erupted onto the surface as a consequence of subduction.

Basalt Round Valley Butte is a basaltic cinder cone in Northern California that is located about 40 km east of Lassen Peak, the southernmost active volcano in the Cascades volcanic range. A longstanding observation of basalts generated due to subduction is that they are more oxidized than mid-ocean ridge basalts (e.g., Berry et al., 2018; Bézoz et al., 2021; Bézoz and Humler, 2005; Brounce et al., 2014; Carmichael, 1991; Christie et al., 1986; Cottrell and Kelley, 2011; Kelley and Cottrell, 2012, 2009; O'Neill et al., 2018) despite both being generated via melting of the

asthenosphere. However, the cause of this difference in oxidation state between the basalts is debated. One school of thought is that these basalts are oxidized through fractional crystallization since minerals like olivine take in Fe^{2+} , driving up the relative abundance of Fe^{3+} in the remaining melt (e.g., Chin et al., 2018; Farner and Lee, 2017; Lee, 2005; Lee et al., 2012, 2010; Tang et al., 2019, 2018). Another school of thought is that subduction related basalts are more oxidized because the subducting plate is oxidized due to contact with the surface of the Earth prior to subduction and the fluids originating from the subducting slab impart this oxidized signature onto the melts that they generate (e.g., Brounce et al., 2015, 2014; Cottrell and Kelley, 2011; Kelley and Cottrell, 2012, 2009). Complicating this debate is the fact that the tools we use to understand the oxidation state of these basalts, olivine hosted melt inclusions, are susceptible to modification prior to eruption (e.g., Anderson, 1974; Barth et al., 2019; Bucholz et al., 2013; Cottrell et al., 2002; Danyushevsky et al., 2002, 2000; Gaetani and Watson, 2000; Hauri, 2002; Le Voyer et al., 2015; Lloyd et al., 2013; Miyashiro, 1974; Newcombe et al., 2020, 2014; Portnyagin et al., 2008; Qin et al., 1992; Roedder, 1979; Spandler and O'Neill, 2010). One known modification that affects olivine hosted melt inclusions is the loss of water from these entrapped magmas through their host olivine via the diffusive loss of hydrogen (e.g., Barth et al., 2019; Bucholz et al., 2013; Chen et al., 2011; Gaetani et al., 2012; Hauri, 2002; Lloyd et al., 2013; Massare et al., 2002; Portnyagin et al., 2008). This study examines how the oxidation state recorded by these melt inclusions is similarly affected by diffusion by comparing the oxidation state of iron and vanadium in the same suite of olivine hosted melt inclusions. This comparison is useful because the valence state of vanadium (and thus the partitioning behavior of vanadium between the host olivine and related melt) in basaltic systems is

similarly affected by changes in the oxidation state of a magma as Fe is; however, vanadium diffuses through the host olivine crystal on time scales much greater than that of iron (e.g., Bucholz et al., 2013; Cottrell et al., 2002; Gaetani et al., 2012), thus making possible the comparisons between these two oxybarometer proxies and extrapolating those changes out to timescales relevant to magmatic processes.

To the south of the Mendocino Triple Junction, the drivers of volcanism in California (and the greater Basin and Range Province) are less well understood than Basalt of Round Valley Butte and for subduction related volcanism more broadly. Volcanism in the Basin and Range Province has been attributed to lithospheric thinning associated with motion along the San Andreas fault (e.g., Atwater, 1970; Fitton et al., 1991; Leeman and Harry, 1993; Nicholson et al., 1994) as well as upwelling and resultant decompression melting of deeper, hotter mantle rocks due to the disappearance of the Farallon plate after subduction ceased in this region (Humphreys et al., 2003; Humphreys, 1995; Lee, 2005). The second chapter of this dissertation investigates the causes and depths associated with mafic volcanism at Pisgah Crater, a mafic volcano in the Lavic Lake volcanic field in the Mojave Desert, by untangling the various post entrapment processes that have affected Pisgah Crater olivine hosted melt inclusions.

Pisgah Crater melt inclusions have been subjected to and corrected for a wide range of post entrapment processes. Firstly, these melt inclusions show evidence of experiencing “Fe-loss,” a process through which after entrapment, melt inclusions first crystallize olivine out of the inclusions onto the interface between the inclusion and the host olivine (Danyushevsky et al., 2000). Given sufficient time, newly crystallized olivine will diffusively equilibrate with the composition of the

host olivine and the composition of the melt inclusion will in turn diffusively equilibrate with the composition of the olivine at the host-inclusion interface. The result of this process is a net loss of Fe out of the melt inclusion and net gain of Mg into the melt inclusion (Danyushevsky et al., 2000). Because any form of post entrapment crystallization affects the density (and thus pressure) of the entrapped melt (i.e., post entrapment crystallization affects the mass and volume of the entrapped melt), the solubility of the entrained volatiles is similarly affected by post entrapment processes (e.g., Dixon et al., 1995). For instance, the solubility of CO₂ is highly sensitive to pressure (i.e., it is the first volatile to degas as magma ascends) and thus diffuses into a vapor bubble when pressure drops in a melt inclusion (Anderson, 1974; Rasmussen et al., 2020; Roedder, 1979). Relatedly, all Pisgah Crater melt inclusions contain CO₂ vapor bubbles. Because Pisgah Crater melt inclusions contain multiple lines of evidence that point to their being affected by post entrapment processes, these processes are corrected for prior to using these melt inclusions as a tool to geochemically investigate crustal and lithospheric thicknesses beneath Pisgah Crater and the cause of mafic volcanism in the Mojave Desert and Basin and Range Province more widely.

In the southernmost part of California, volcanism in the Salton Trough is related to continental rifting at the southern end of the San Andreas fault system which caused the opening of the Gulf of California immediately following the cessation of subduction of the Farallon slab around 12 Ma (e.g., Atwater, 1970; Mammerickx and Klitgord, 1982; Stock and Hodges, 1989). By ~4 Ma, not only did the Gulf of California fully open into the Salton Trough but the Colorado River formed a delta which isolated the Salton Trough from the rest of the Gulf of California (e.g., Lonsdale, 1989; Winker and Kidwell, 1986). As a result of this isolation, the Salton Trough became

an evaporitic basin. Periodical flooding of the Colorado River would re-route the Colorado River northward, flooding the Salton Trough, but once the Colorado River began to drain back into the Gulf of California, within ~60 years the flood waters in the Salton Trough would completely evaporate (e.g., Philibosian et al., 2011; Rockwell et al., 2022; Tompson, 2016; Van De Kamp, 1973; Waters, 1983; Wilke, 1976). This cyclical flooding and evaporation of Colorado River flood waters in the Salton Trough happened at least seven times in the past 2 Ka. This cyclicity happened frequently enough that the Cahuilla people, who still live in the region and for which Lake Cahuilla is named, have an oral history of these floods (as quoted in MacDougal, 1914).

The rate of sedimentation in the Salton Trough due to this periodic flooding is similar to the rate of subsidence due to rifting (e.g., Lonsdale, 1989), which keeps the Salton Trough at a relatively constant elevation compared to sea level, despite the ever-thickening layers of sediments deposited into and evaporites formed in this basin (e.g., Elders and Sass, 1988; Lonsdale, 1989). Because of the rifting, there is also a heat source beneath the Salton Trough which has driven periodic rhyolitic volcanism in the region for at least the past 400 Ka and led to the formation of the Salton Sea Geothermal Field that is hosted in the buried evaporitic and sedimentary rocks previously deposited by the Colorado River (e.g., Brothers et al., 2022; Coplen, 1976; McKibben et al., 1988; Rex, 1983; Robinson et al., 1976; Schmitt et al., 2019; Schmitt and Hulen, 2008; Waters, 1983; Wright et al., 2015). Domestic interest in the Salton Sea Geothermal field has increased in the past several years due to the presence of lithium (Li) in the geothermal brine and the increased importance of Li batteries in decarbonizing the global transportation network and long-term green energy storage goals (e.g., Ambrose and Kendall, 2020; U.S.G.S., 2022). The behavior of lithium

during interactions between the brine and host rocks of the Salton Sea Geothermal Field is poorly constrained. Because of this, the total size of the recoverable Li reservoir after a Li-depleted geothermal brine is reinjected into the Salton Sea Geothermal Field because of how it could interact with the reservoir rocks at depth is uncertain. The third chapter of this dissertation investigates bulk rock and brine Li concentrations and $\delta^7\text{Li}$ along with *in situ* Li concentration measurements of rocks and minerals from the deep portions of the California State 2-14 scientific drilling core and a few commercial wells in the Salton Sea Geothermal Field to (1) characterize the dominant mineral hosts of Li and (2) constrain the behavior of Li during brine-rock interaction at depth.

Chapter one of this dissertation and its associated appendix was published in 2022 in Earth and Planetary Science Letters. Chapter two of this dissertation is being prepared for publication in the Journal of Petrology. Chapter three of this dissertation and its associated appendices is in review with the Department of Energy Geothermal Technologies Division and will be published as a chapter in a larger report about the Lithium Valley Quantification Project. Additionally, a conference paper related to chapter three was published by the Stanford Geothermal Workshop and will be published by the Geothermal Rising Conference. A longer version of Chapter three is being prepared for publication in a special edition of Economic Geology.

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CHAPTER ONE

DIFFUSIVE EQUILIBRATION OF H₂O AND OXYGEN FUGACITY IN NATURAL OLIVINE-HOSTED MELT INCLUSIONS

J. Humphreys, M. Brounce, K. Walowski

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Abstract

Arc basalts are oxidized relative to mid-ocean ridge basalts; however, the mechanism through which arc basalts gain this elevated oxidative state is debated. This observation has been extended to include Fe³⁺/ΣFe measurements from olivine-hosted melt inclusions enclosed in relatively Fo-rich olivines (i.e., which have presumably trapped relatively unevolved liquid compositions as melt inclusions). Experimental data suggest, however, that Fe³⁺/ΣFe recorded by melt inclusions can diffusively equilibrate with the host magma on short timescales, perhaps as rapidly as timescales relevant for H⁺ diffusive equilibration. Here, we present major, minor, and trace element concentrations, H₂O concentrations, and Fe³⁺/ΣFe of naturally glassy olivine-hosted melt inclusions from the Basalt of Round Valley Butte, a cinder cone in the Lassen Region of northern California. These melt inclusions record H₂O loss through diffusion of H⁺ and can be used to constrain the extent of Fe³⁺/ΣFe equilibration in a suite of natural melt inclusions. The H₂O concentrations of Basalt of Round Valley Butte melt inclusions decrease with decreasing melt inclusion radius,

consistent with diffusive H^+ loss. The $Fe^{3+}/\Sigma Fe$ do not correlate with H_2O or inclusion diameter, suggesting that $Fe^{3+}/\Sigma Fe$ equilibration does not occur on the same timescale as H^+ diffusion. Calculated oxygen fugacities (fO_2) from the partitioning of vanadium between olivine and melt are ~ 1 log unit higher than those calculated from $Fe^{3+}/\Sigma Fe$. One explanation for these combined observations is that $Fe^{3+}/\Sigma Fe$ of the Basalt of Round Valley Butte melt inclusions diffusively equilibrated with a host magma at low pressure on shorter timescales than H^+ diffusion. This scenario requires that the host magma decreased in fO_2 after the time of melt inclusion entrapment to explain the offset between fO_2 constraints from $Fe^{3+}/\Sigma Fe$ of the melt inclusions and the partitioning of vanadium between olivine and melt. One volcanological process known to result in a decrease in fO_2 of magmas stored at shallow pressure is the degassing of S, CO_2 , and H_2O . We show that reasonable estimates for the extent of degassing of Basalt of Round Valley Butte magma, coupled with diffusive equilibration of both H^+ and $Fe^{3+}/\Sigma Fe$, can reconcile Fe- and V-proxies for fO_2 . Additionally, we have compared estimates of fO_2 from vanadium abundances of melt inclusions and their olivine hosts with recently reported measurements of $Fe^{3+}/\Sigma Fe$ of the melt inclusions for several Mariana arc volcanoes and conclude that this process – small decreases in host magma fO_2 driven by degassing and rapid equilibration of the $Fe^{3+}/\Sigma Fe$ of olivine-hosted melt inclusions with this host magma – may be a widespread phenomenon.

1.1. Introduction

Submarine pillow glasses and naturally glassy melt inclusions with relatively high MgO contents (i.e., >6.0 wt%) from the Mariana arc record higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ (ratio of oxidized Fe relative to total Fe, i.e., $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$) and oxygen fugacities ($f\text{O}_2$) that are calculated from those ratios than do mid-ocean ridge basalts (MORBs; e. g., Berry et al., 2018; Bézoz et al., 2021; Bézoz and Humler, 2005; Brounce et al., 2014; Carmichael, 1991; Christie et al., 1986; Cottrell and Kelley, 2011; Kelley and Cottrell, 2012, 2009; O'Neill et al., 2018). However, the mechanisms by which arc basalts gain elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $f\text{O}_2$ remains actively debated (Brounce et al., 2014; Chin et al., 2018; Cottrell and Kelley, 2011; Evans et al., 2012; Farner and Lee, 2017; Gaetani, 2016; Grocke et al., 2016; Kelley and Cottrell, 2012, 2009; Lee et al., 2012, 2010, 2005; Mallmann and O'Neill, 2009; Stolper and Bucholz, 2019; Tang et al., 2019, 2018; Tollan and Hermann, 2019). Many trace element proxies (e.g., V/Sc, Zn/Fe, Cu, Eu) suggest that the $f\text{O}_2$ of mantle sources beneath arcs and mid-ocean ridges are similar, and that the difference in the $f\text{O}_2$ measured in eruptive products at these two tectonic settings arises during magma storage and ascent through thick arc crust (e. g., Lee et al., 2012, 2010, 2005; Tang et al., 2018). For example, in arcs where the overriding crust is >40 km, some portion of the crystallization history of the transiting magma takes place at high enough pressures for Fe^{2+} -bearing garnet fractionation. This fractionation process is hypothesized to increase the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the residual liquid (Chin et al., 2018; Farner and Lee, 2017; Tang et al., 2019, 2018). In contrast, observations of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in back-arc spreading center submarine glasses from the Mariana trough range from similar to more oxidized than MORB (Kelley and Cottrell, 2009; Cottrell and Kelley, 2011; Brounce et al., 2014), even though the thickness of the crust along the

Mariana trough is similar, and similar to that of mid-ocean ridges (Bown and White, 1994; Kitada et al., 2006). Because this crust is too thin for garnet fractionation to occur, it demonstrates that additional processes can create oxidized back-arc lavas in oceanic settings. Additionally, elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ in melt inclusions from relatively magnesian olivines (i.e., $\text{Mg}/(\text{Mg}+\text{Fe}^{2+}) > 0.70$) and submarine pillow glasses indicate that crystallization (olivine + pyroxene $\pm$ plagioclase $\pm$ magnetite) and degassing ($\text{H}_2\text{O}+\text{CO}_2\pm\text{S}$) lead to a decrease in melt $\text{Fe}^{3+}/\Sigma\text{Fe}$ of Mariana arc magmas by ~ 0.1 units (absolute) due to the reducing power of the conversion of sulfide dissolved in the melt to SO_2 in the gas phase, and cannot explain the offset between $\text{Fe}^{3+}/\Sigma\text{Fe}$ of arc basalts and MORBs with similar MgO contents (Brounce et al., 2015, 2014; Carmichael, 1991; Christie et al., 1986; Kelley and Cottrell, 2012, 2009). The trace element $f\text{O}_2$ proxy V/Yb, which is not fractionated during olivine + plagioclase $\pm$ clinopyroxene crystallization, is in general agreement with the increase in oxidation state from MORB to back-arc basin basalts to arc basalts (Laubier et al., 2014). Furthermore, $\text{Fe}^{3+}/\Sigma\text{Fe}$ in pillow glass from MORB, Mariana trough, and Mariana arc volcanoes and in olivine-hosted melt inclusions from Mariana arc volcanoes correlate positively with trace element proxies for slab influence (e.g., Ba/La; Brounce et al., 2015, 2014; Cottrell and Kelley, 2011; Kelley and Cottrell, 2012, 2009).

Implicit to the interpretation that melt inclusion compositions represent melt compositions at the time of entrapment is the assumption that once trapped, olivine-hosted melt inclusions are isolated from any compositional changes experienced by the external host magma via continued differentiation, such as through fractional crystallization and volcanic degassing (e.g., Anderson, 1974). However, this compositional change imposes gradients in the chemical potentials

of major, minor, trace and volatile elements which can drive diffusive equilibration of the melt inclusion with the external magma through the host olivine (e.g., Anderson, 1974; Bucholz et al., 2013; Cottrell et al., 2002; Danyushevsky et al., 2002, 2000; Gaetani and Watson, 2000; Hauri, 2002; Le Voyer et al., 2014; Lloyd et al., 2013; Miyashiro, 1974; Newcombe et al., 2014; Portnyagin et al., 2008; Qin et al., 1992; Roedder, 1979; Spandler and O'Neill, 2010). The timescales over which these processes operate range from hours (e.g., H^+) to hundreds to thousands of years (e.g., rare earth elements) and depend on the diameter of the melt inclusion, the size of the olivine host, and the diffusivities and concentrations of the elements involved (e.g., Cottrell et al., 2002; Qin et al., 1992; Barth et al., 2019; Bucholz et al., 2013; Gaetani et al., 2012; Hauri, 2002; Lloyd et al., 2013; Portnyagin et al., 2008).

In particular, the H_2O concentrations of olivine-hosted melt inclusions have been demonstrated experimentally to diffusively equilibrate with an external magma on the order of ~10s of hours (Barth et al., 2019; Bucholz et al., 2013; Chen et al., 2011; Gaetani et al., 2012; Hauri, 2002; Lloyd et al., 2013; Massare et al., 2002; Portnyagin et al., 2008). Dehydration experiments that placed melt inclusions with initial H_2O contents of ~4 wt% and $\delta D_{VSMOW} \sim 16\text{‰}$ in a $CO-CO_2$ gas mix at 1 atm, 1250°C and $f_{O_2} \sim NNO$ (oxygen fugacity relative to the nickel-nickel oxide buffer) show a decrease in H_2O contents from 4.89 to 0.06 wt% and an increase in δD_{VSMOW} from -2.4‰ to 450‰ over the course of 1-18 hours (Bucholz et al., 2013; Gaetani et al., 2012). The diffusive equilibration of H_2O is proposed to start (or end) with the growth (or dissolution) of fayalite at the olivine-melt inclusion interface and incorporation of H_2O into the olivine through the creation of metal vacancies (a missing Mg^{2+} or Fe^{2+} on the octahedral site, effectively a negative two charge

within the crystal lattice) and 2OH^- (Gaetani et al., 2012). Since $^1\text{H}^+$ diffuses more rapidly through olivine than $^2\text{H}^+$, diffusive loss of H_2O from the melt inclusion leaves the melt inclusion relatively enriched in $^2\text{H}^+$ (leading to a high $\delta\text{D}_{\text{VSMOW}}$ relative to the initial value of the melt inclusion at the time of entrapment, where $\delta\text{D}_{\text{VSMOW}} = 1,000 \times [(D/H)_{\text{sample}} - (D/H)_{\text{VSMOW}}] / (D/H)_{\text{VSMOW}}$, V_{SMOW} is Vienna standard mean ocean water with $\delta\text{D} = 0\text{‰}$; Bucholz et al., 2013; Gaetani et al., 2012; Hauri, 2002). Conversely, gain of H_2O into the melt inclusion should leave the melt inclusion enriched in $^1\text{H}^+$ relative to $^2\text{H}^+$, leading to a lighter $\delta\text{D}_{\text{VSMOW}}$ relative to the initial value of the melt inclusion at the time of entrapment (Bucholz et al., 2013; Gaetani et al., 2012; Hauri, 2002).

The $f\text{O}_2$ calculated from the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of olivine-hosted melt inclusions has been shown experimentally to diffusively equilibrate under experimental conditions on similarly short timescales as H_2O diffusive equilibration. These experiments demonstrate reduction in $\text{Fe}^{3+}/\Sigma\text{Fe}$ of natural olivine-hosted melt inclusions from Cerro Negro from 0.64 to 0.23 within 24 hours (Bucholz et al., 2013; Gaetani et al., 2012). The $f\text{O}_2$ of the melt inclusion is proposed to diffusively equilibrate with a reduced external melt through the growth of olivine at the host-inclusion interface coupled with the oxidation of two Fe atoms at an octahedral lattice site and creation of a metal vacancy (Nakamura and Schmalzried, 1983). The reverse condition, where the $f\text{O}_2$ diffusively equilibrates with an oxidized external melt is proposed to take place through the dissolution of olivine at the host-inclusion interface coupled with the reduction of two Fe atoms at an octahedral lattice site and destruction of a metal vacancy (Nakamura and Schmalzried, 1983). Because the equilibration of hydrogen and $\text{Fe}^{3+}/\Sigma\text{Fe}$ are rate limited by the diffusion of metal vacancies within the olivine lattice, both are expected to equilibrate on similar timescales (Gaetani et al., 2012). This

experimental result suggests that $\text{Fe}^{3+}/\Sigma\text{Fe}$ recorded by melt inclusions can be altered through diffusive equilibration on the order of hours.

These experiments (Bucholz et al., 2013; Gaetani et al., 2012; Hauri et al., 2006) were used to calibrate a model that could relate the creation of metal vacancies in olivine to the diffusive equilibration of H_2O and $f\text{O}_2$ in olivine-hosted melt inclusion with the external melt (Bucholz et al., 2013). This model couples the metal vacancy diffusion mechanism (Gaetani et al., 2012) with radial diffusion through a spherical olivine (Qin et al., 1992). The fractionation of hydrogen is modeled using Graham's law of diffusion for gasses where the ratio of the diffusivity of two isotopes is inversely proportional to their masses:

$$\frac{D_{^2\text{H}^+}}{D_{^1\text{H}^+}} = \left(\frac{m_{^1\text{H}^+}}{m_{^2\text{H}^+}}\right)^\beta$$

where D_i is the diffusivity of each isotope, m_i is the mass of each species, and $\beta=0.3$ has been fit to previous experimental results ($\beta=0.5$ in an ideal gas; Gaetani et al., 2012; Hauri, 2002). This model builds upon previous work that characterized the relationship between Fe^{3+} , Fe^{2+} , and $f\text{O}_2$; experimentally determined hydrogen and metal vacancy diffusivities; the concentration of metal vacancies in olivine with respect to the $f\text{O}_2$, composition, and temperature for anhydrous olivine; the diffusion of elements between the inclusion and external melts through the host olivine; and the partitioning of hydrogen between olivine and basaltic melt in order to calculate the compositional changes to a melt inclusion as it undergoes diffusive equilibration of H_2O and/or $f\text{O}_2$ (Kress and Carmichael, 1991; Qin et al., 1992; Wanamaker, 1994; Demouchy and Mackwell, 2006; Hauri et al., 2006; Dohmen and Chakraborty, 2007). In contrast, diffusion of V is expected to

be relatively slow (e.g., Cottrell et al., 2002). Because the oxidation state of V varies in silicate systems (V^{2+} to V^{5+}) as a function of fO_2 , the partitioning behavior of V between a silicate melt and olivine varies as well. For instance, as fO_2 increases, V increases in incompatibility in olivine, leading to a decrease in $D_V^{olv/melt}$ (partitioning of V between olivine and melt; e.g., Canil, 1997; Mallmann and O'Neill, 2013). The combination of fO_2 -sensitivity and long timescale for equilibration means that the V contents of melt inclusions and their olivine hosts may offer a useful constraint on the fO_2 at the time of olivine crystallization that is not reset on such rapid timescales as for H^+ and $Fe^{3+}/\Sigma Fe$.

This study will examine the timescales of the diffusive equilibration of fO_2 and H^+ in natural olivine-hosted melt inclusions from the Basalt of Round Valley Butte, a cinder cone in the Lassen Region of Northern California (Fig. 1.1; Clynne and Muffler, 2010; Walowski et al., 2015) using an

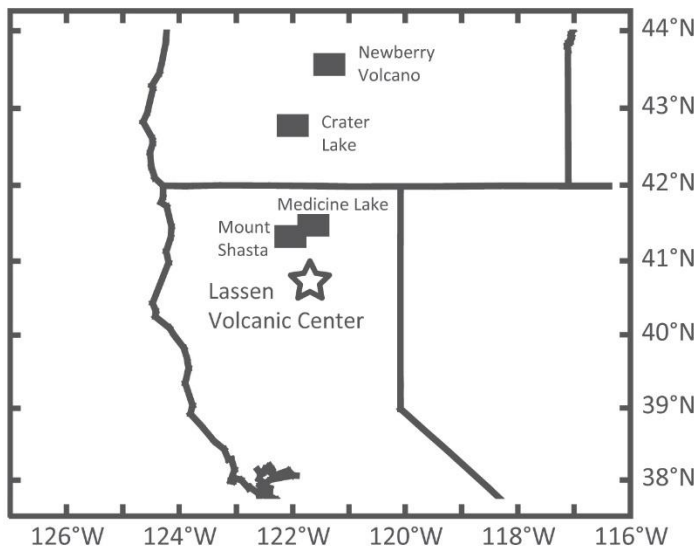


Figure 1.1. Locality map for the samples in this study. Lassen Volcanic Center, where the samples were collected, is represented by the star.

updated version of the diffusive equilibration model of Bucholz et al. (2013) that has been adjusted to impose an external boundary condition for D/H (Bucholz, pers comm). The hydrogen isotopic compositions of melt inclusions from Basalt of Round Valley Butte tephra are negatively correlated with H_2O concentrations,

consistent with model predictions for ~2.7 wt% diffusive loss of hydrogen through the host olivine (Walowski et al., 2015; Bucholz et al., 2013). This correlation is similar to observations of melt inclusions subjected to dehydration experiments which found that $\text{Fe}^{3+}/\Sigma\text{Fe}$ recorded by melt inclusions decreased with increased heating time and $\delta\text{D}_{\text{VSMOW}}$ compositions, making the diffusive equilibration model developed from those experiments an ideal tool to investigate the timescales of diffusive equilibration in natural samples (Bucholz et al., 2013; Gaetani et al., 2012).

1.2. Geologic Setting

Lassen Peak is the southernmost active volcano in the Cascadia subduction zone (Fig. 1.1). The Lassen volcanic region overlies where the Gorda microplate, composed of relatively young and warm oceanic lithosphere, is being subducted beneath the North American plate. A field of basaltic cinder cones surrounds Lassen Peak (Clynne and Muffler, 2010; Guffanti et al., 1990), the development of which is likely associated with a broad zone of extensional faulting which impinges on the arc axis from the east (Guffanti et al., 1990). Basalts in this region are wetter (~3 wt% H_2O) and variably enriched in subducted slab components (e.g., Ba, Th, Pb) when compared to MORB (Carmichael, 1991; Plank et al., 2013; Walowski et al., 2016, 2015). The Basalt of Round Valley Butte cone and associated lava flows lie roughly 40 km east of Lassen Peak (Fig. 1.1; Clynne and Muffler, 2010; Macdonald, 1965).

1.3. Materials and Methods

The tephra sampled in this study was collected from a quarry-exposed section of the Basalt of Round Valley Butte cone and are the same bulk tephra sample from previous studies (Fig. 1.1; Walowski et al., 2016, 2015). Olivine grains (2-0.8 mm in size) coated in black glass were

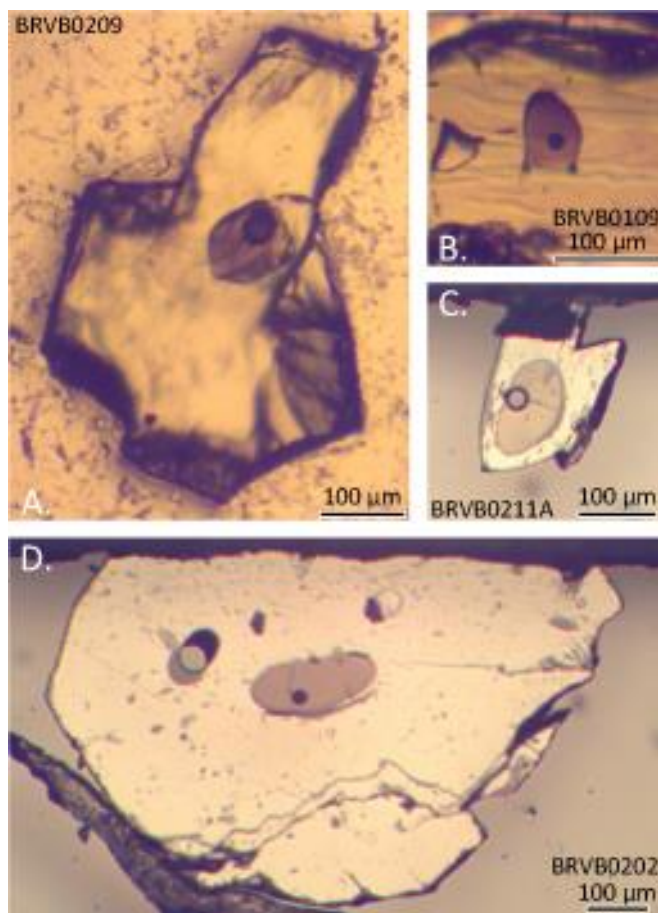


Figure 1.2. Representative photomicrographs of the melt inclusions in this study. (A) Sample BRVB0209 under transmitted light in single polish preparation stage. (B) Sample BRVB0109 under transmitted light in single polish preparation stage. (C) Sample BRVB0211 under reflective light, double polished. (D) Sample BRVB0202 under reflective light, double polished.

two melt inclusions did not contain spinel inclusions and one contained a spinel inclusion in a neck off the main inclusion body (Table 1A.3.3; Fig. 1.2B).

Major element analyses were conducted at the California Institute of Technology Division of Geological and Planetary Sciences Analytical Facility using a JEOL JXA-8200 electron

handpicked from the sieved tephra for analysis. A total of 13 melt inclusions were prepared for major element analysis, 6 of which were analyzed via μ -XANES and subsequently had their chemistries corrected for post-entrapment crystallization (Table 1.1, discussed in section 4. *Results*, below). All six of these post-entrapment crystallization corrected melt inclusions contained one vapor bubble. Some melt inclusions are adjacent to or encapsulate a spinel inclusion. Of the six post-entrapment crystallization corrected melt inclusions measured,

Table 1.1. Basalt of Round Valley Butte melt inclusion major elements, H_2O , $Fe^{3+}/\Sigma Fe$, and fO_2

Sample	PEC %	SiO ₂ (wt%)	1 σ (wt%)	TiO ₂ (wt%)	1 σ (wt%)	Al ₂ O ₃ (wt%)	1 σ (wt%)	FeO* (wt%)	1 σ (wt%)	Fe ₂ O ₃ ** (wt%)	FeO** (wt%)
BRV/B0105	---	48.45	0.94	1.31	0.01	16.67	0.17	8.60	0.11	ND	ND
BRV/B0108	---	47.85	0.93	1.36	0.01	17.42	0.17	9.24	0.13	1.90	7.53
BRV/B0108	0.90%	47.78	0.93	1.35	0.01	17.26	0.17	9.31	0.13	1.89	7.61
BRV/B0109	---	49.03	0.95	1.41	0.01	18.43	0.18	8.49	0.12	1.96	6.73
BRV/B0109	2.30%	48.83	0.95	1.38	0.01	18.02	0.18	8.65	0.12	1.91	6.93
BRV/B0112A	---	48.68	0.94	1.52	0.01	18.43	0.18	7.92	0.11	1.67	6.42
BRV/B0112A	0.80%	48.61	0.94	1.51	0.01	18.28	0.18	7.98	0.11	1.66	6.49
BRV/B0112B	---	46.94	0.91	1.61	0.02	18.53	0.19	7.86	0.10	ND	ND
BRV/B0202	---	48.97	0.95	1.30	0.01	16.87	0.17	8.87	0.12	1.86	7.20
BRV/B0202	1.20%	48.86	0.95	1.29	0.01	16.67	0.17	8.94	0.12	1.84	7.29
BRV/B0204	---	48.10	0.94	1.43	0.01	17.81	0.18	9.47	0.13	ND	ND
BRV/B0205B	---	48.10	0.94	1.40	0.01	16.62	0.17	8.92	0.12	ND	ND
BRV/B0208	---	48.79	0.95	1.41	0.01	17.50	0.18	8.05	0.11	ND	ND
BRV/B0209	---	47.53	0.93	1.58	0.01	18.42	0.19	7.97	0.11	1.72	6.42
BRV/B0209	0.00%	47.53	0.93	1.58	0.01	18.42	0.19	7.97	0.11	1.72	6.42
BRV/B0211A	---	49.22	0.96	1.36	0.01	17.33	0.17	8.87	0.12	1.87	7.19
BRV/B0211A	0.00%	49.22	0.96	1.36	0.01	17.33	0.17	8.87	0.12	1.87	7.19
BRV/B0211B	---	48.57	0.95	1.38	0.01	17.44	0.18	9.33	0.12	ND	ND
BRV/B0212	---	48.34	0.94	1.41	0.01	17.78	0.18	9.37	0.12	ND	ND

* = total Fe content reported as FeO

** = calculated value from FeO* and Fe³⁺/ Σ Fe

1 Mallmann and O'Neill, 2013

2 Jayasuriya et al., 2004

3 Kress and Carmichael, 1991

4 O'Neill et al. 2018

5 Borisov et al., 2017

MgO (wt%)	1 σ (wt%)	CaO (wt%)	1 σ (wt%)	Na ₂ O (wt%)	1 σ (wt%)	K ₂ O (wt%)	1 σ (wt%)	H ₂ O (wt%)	1 σ (wt%)	Total (%)
6.24	0.14	9.81	0.04	3.17	0.02	0.86	0.01	ND	ND	95.12
6.12	0.17	10.94	0.05	3.87	0.02	1.10	0.01	0.32	+0.06/-0.09	100.13
6.47	0.17	10.84	0.05	3.84	0.02	1.09	0.01	0.32	+0.06/-0.09	98.26
5.20	0.16	10.78	0.05	4.26	0.02	1.01	0.01	0.37	+0.08/-0.19	100.94
6.10	0.16	10.54	0.05	4.16	0.02	0.99	0.01	0.36	+0.08/-0.19	99.03
5.88	0.16	10.44	0.05	3.57	0.02	1.05	0.01	1.23	+0.08/-0.02	100.39
6.20	0.16	10.36	0.05	3.54	0.02	1.04	0.01	1.22	+0.08/-0.02	98.75
5.73	0.13	10.67	0.05	3.81	0.02	1.08	0.01	ND	ND	96.24
6.03	0.16	10.00	0.04	3.59	0.02	0.90	0.01	1.84	+0.21/-0.13	100.23
6.49	0.16	9.88	0.04	3.55	0.02	0.89	0.01	1.82	+0.21/-0.13	98.39
5.83	0.14	10.00	0.05	3.52	0.02	1.05	0.01	0.75	+0.21/-0.24	97.96
6.14	0.14	9.49	0.04	3.42	0.02	0.95	0.01	ND	ND	95.04
6.02	0.14	9.97	0.05	3.31	0.02	0.99	0.01	ND	ND	96.05
6.77	0.16	10.32	0.05	3.78	0.02	1.07	0.01	0.72	$\pm$ 0.01	98.15
6.77	0.16	10.32	0.05	3.78	0.02	1.07	0.01	0.72	$\pm$ 0.01	98.15
6.15	0.15	9.89	0.04	3.35	0.02	0.94	0.01	1.34	+0.10/-0.06	98.45
6.15	0.15	9.89	0.04	3.35	0.02	0.94	0.01	1.34	+0.10/-0.06	98.45
6.44	0.15	9.83	0.04	3.45	0.02	0.99	0.01	1.75	+0.07/-0.23	99.19
5.72	0.13	9.97	0.05	3.58	0.02	1.08	0.01	0.85	+0.08/-0.16	98.11

$\text{Fe}^{3+}/\Sigma\text{Fe}$	1σ	$f\text{O}_2^1$ ΔNNO	$f\text{O}_2^2$ ΔNNO	$f\text{O}_2^3$ ΔNNO	$f\text{O}_2^4$ ΔNNO	$f\text{O}_2^5$ ΔNNO
ND	ND	ND	ND	ND	ND	ND
0.19	0.026	0.82	-0.89	-0.42	0.19	0.01
0.18	0.026	0.78	-0.88	-0.45	0.17	-0.05
0.21	0.026	0.88	-0.66	-0.14	0.42	0.40
0.20	0.026	0.77	-0.65	-0.22	0.38	0.25
0.19	0.026	0.13	-0.63	-0.29	0.33	0.27
0.19	0.026	0.09	-0.64	-0.33	0.31	0.22
ND	ND	ND	ND	ND	ND	ND
0.19	0.026	0.86	-0.78	-0.27	0.36	0.23
0.18	0.026	0.83	-0.77	-0.32	0.34	0.17
ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND
0.19	0.026	1.12	-0.51	-0.24	0.37	0.22
0.19	0.026	1.12	-0.51	-0.24	0.37	0.22
0.19	0.026	ND	-0.63	-0.20	0.43	0.29
0.19	0.026	ND	-0.63	-0.20	0.43	0.29
ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND

microprobe operated at 10nA, 15kV, and with a 10 μm beam diameter. Major element concentrations can be found in Table 1.1. Dissolved H_2O concentrations in the melt inclusions were measured at the University of California Riverside using a Thermo Scientific Nicolet iS50 Fourier-transform infrared spectrometer coupled with a Nicolet Continuum Fourier-transform infrared microscope attachment. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 6 melt inclusions were analyzed *in situ* using micro X-ray absorption near edge structure spectroscopy ($\mu\text{-XANES}$) at the Advanced Photon Source, Argonne National Laboratory at the University of Chicago's GeoSoilEnviroCARS at Beamline 13-ID-E. Trace element abundances for 6 melt inclusions and corresponding olivine hosts were analyzed at

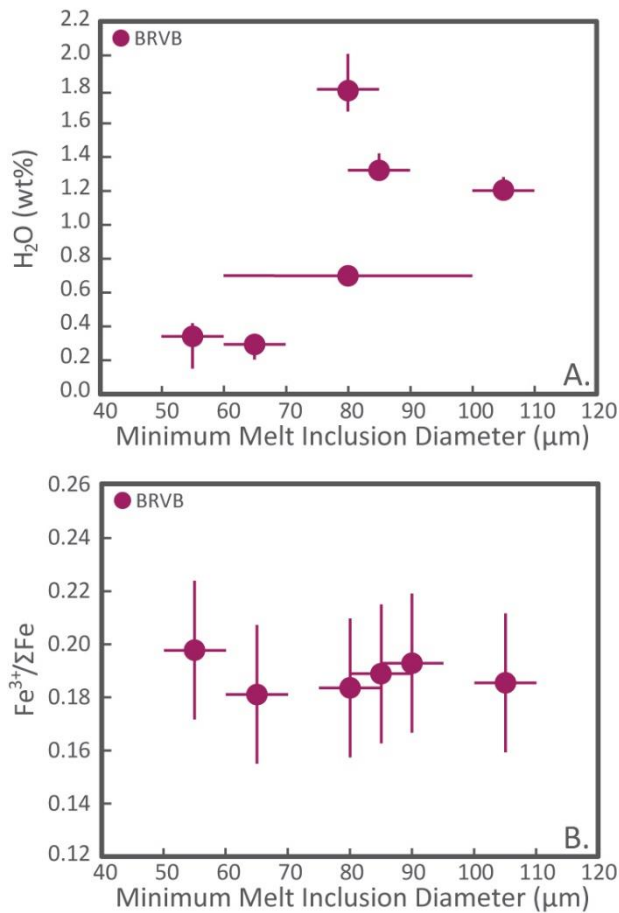


Figure 1.3. Variations in H_2O content (A) and $\text{Fe}^{3+}/\Sigma\text{Fe}$ (B) with minimum melt inclusion diameter.

the Lyons ICP Facility at the University of California Riverside via laser-ablation inductively coupled plasma mass spectrometry using an Agilent Technologies 7900 quadrupole mass spectrometer that is coupled to a short pulse width coherent 193 nm ArF excimer laser. Detailed information about the samples and analyses are available in the supplement.

1.4. Results

Olivine hosts range in composition from Fo_{84} to Fo_{86}

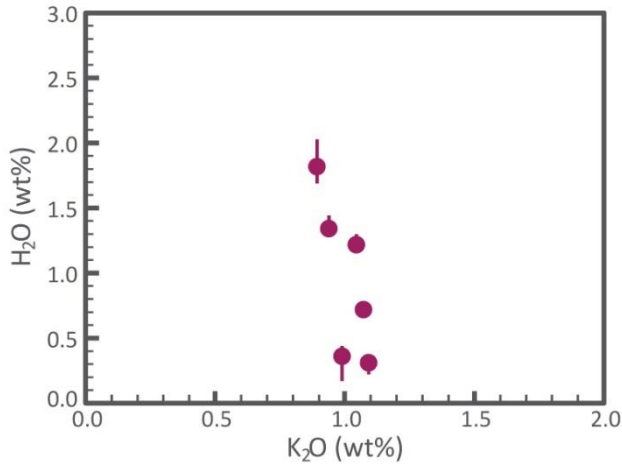


Figure 1.4. Variations in H₂O and K₂O content of Basalt of Round Valley Butte melt inclusions.

($Fo_{\#} = \text{Mg}/(\text{Mg} + \text{Fe}) \times 100$). Six melt inclusions with measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Table 1.1) were post-entrapment crystallization-corrected by incrementally adding 0.1 wt% of equilibrium composition olivine until equilibrium with the host olivine was reached (e.g., when the predicted $Fo_{\#}$ of

the olivine equaled the measured $Fo_{\#}$ of the olivine host). We assumed Fe^{3+} and Fe^{2+} are conserved and used a calculated $K_D = 0.27\text{--}0.29$ (Toplis, 2005) for each melt inclusion. The melt inclusions required between 0 and 2.3 wt% post-entrapment crystallization correction. Prior to post-entrapment crystallization correction, the uncorrected major element analyses overlap with previous work on melt inclusions from the same site (Table 1.1; Fig. 1A.2; Walowski et al., 2016; Muth and Wallace, 2021). The six melt inclusions which were post-entrapment crystallization corrected contain H₂O concentrations between 0.3–1.8 wt% H₂O, which are weakly positively correlated with melt inclusion diameter and SiO₂ concentration (Table 1.1; Fig. 1.3; Fig. 1A.3; Fig. 1A.6) and vary across a near constant K₂O ($\bar{x}=1.0$, $1\sigma=0.1$; Fig. 1.4). Olivine-liquid equilibria temperatures for the corrected melt inclusions range from ~1080–1105°C (Table 1A.3.3; Putirka et al., 2007). Five of the six corrected melt inclusions were analyzed for minor and trace elements. These samples contain ~220–260 ppm V (Table 1A.3.2), consistent with previous work (Walowski

et al., 2015; Muth and Wallace, 2021). The olivine hosts contain 5.2-9.8 ppm V (Table 1A.3.1), yielding a $D_V^{\text{olv/melt}}$ of 0.02-0.04 for these olivine-melt inclusion pairs.

The $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the six post-entrapment crystallization corrected inclusions vary between 0.18 and 0.20 (uncorrected values vary between 0.19-0.21, consistent with previous work; Muth and Wallace, 2021). The $f\text{O}_2$ recorded by these melt inclusions is calculated using major element compositions and either: 1) $\text{Fe}^{3+}/\Sigma\text{Fe}$ or 2) $D_V^{\text{olv/melt}}$. The $f\text{O}_2$ calculated from the $\text{Fe}^{3+}/\Sigma\text{Fe}$ proxies in Basalt of Round Valley Butte samples ranges from an average value of $\Delta\text{NNO}=-0.68$ (Table 1.1; Jayasuriya et al., 2004) for the most reduced calculations to $\Delta\text{NNO}=+0.33$ (Table 1.1; O'Neill et al. 2018) for the most oxidized calculations. These values are more reduced than the average value given by $D_V^{\text{olv/melt}}$ ($\Delta\text{NNO}=0.72$; Table 1.1; Mallmann and O'Neill, 2013) by a minimum average difference of ~ 0.4 log units and a maximum average difference of ~ 1.4 log units (Table 1.1). The $f\text{O}_2$ of the melt inclusions calculated from $D_V^{\text{olv/melt}}$ (Mallmann and O'Neill, 2013) is consistently higher than that calculated from $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 1.5), consistent with previously observed offsets between these two methods of $f\text{O}_2$ calculations (Brounce, 2014; Kelley and Cottrell, 2012). This offset is systematic and exceeds the stated error of each empirical calibration (Fig. 1.5; Kress and Carmichael, 1991; Jayasuriya et al., 2004; Mallmann and O'Neill, 2013; Borisov et al., 2018; O'Neill et al., 2018). It is also possible that this offset between two independent $f\text{O}_2$ proxies (i.e., Fe-based and V-based) points to inaccuracies in one or both of these proxies. We cannot rule this possibility out; however, we note that all calibrations for both proxies yield the same direction and a similar magnitude of offset. If this is due to inaccuracy in one or both proxies, this suggests a fundamental flaw in the experimental campaigns for one or both proxies, the nature of which is currently unclear.

Here, we demonstrate that simple and rapid volcanological processes present a plausible explanation for this observed offset assuming that both proxies are reasonably accurate (i.e., there are no major flaws in either experimental campaign) and each proxy records the fO_2 at different stages of petrogenesis.

The time scale of equilibration for Fe (hours to days; Bucholz et al., 2013; Gaetani et al., 2012) is faster than for V (hundreds to thousands of years; Cottrell et al., 2002; Qin et al., 1992).

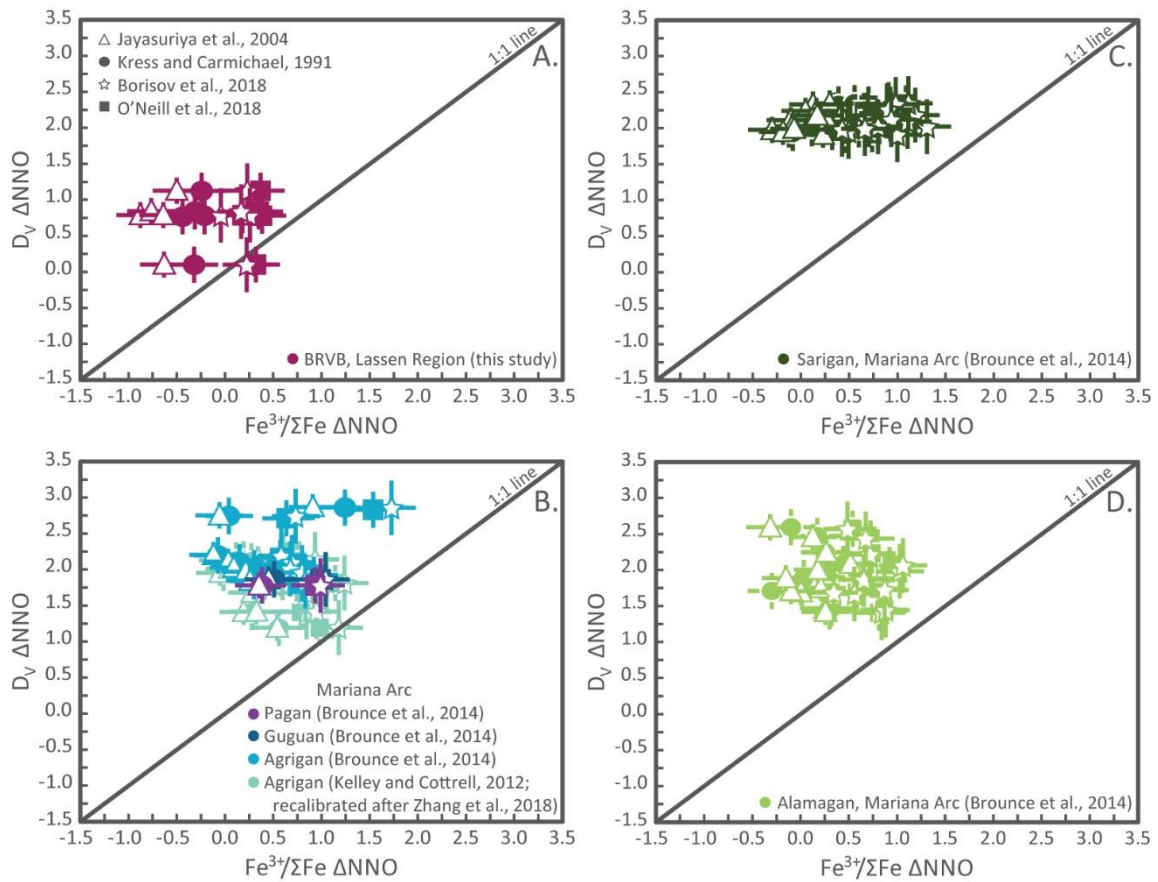


Figure 1.5. Offset in calculated fO_2 using $Fe^{3+}/\Sigma Fe$ (Borisov et al., 2018; Jayasuriya et al., 2004; Kress and Carmichael, 1991; O'Neill et al., 2018) and $D_v^{olv/melt}$ (Mallmann and O'Neill, 2013) set with respect to the NNO buffer. A) Offset for Basalt of Round Valley Butte samples. B) Offset for Pagan (Brounce et al., 2014), Guguan (dark blue; Brounce et al., 2014), and Agrigan (blue, Brounce et al., 2014; light blue, Kelley and Cottrell, 2012 recalibrated after Zhang et al., 2018) samples. C) Offset for Sarigan (Brounce et al., 2014) samples. D) Offset for Alamagan (Brounce et al., 2014) samples.

The fO_2 calculated from $D_V^{olv/melt}$ is consistently higher than the fO_2 calculated from $Fe^{3+}/\Sigma Fe$ in the same samples, no matter which $Fe^{3+}/\Sigma Fe$ proxy for fO_2 is applied (Fig. 1.5; Kress and Carmichael, 1991; Jayasuriya et al., 2004; Borisov et al., 2018; O'Neill et al., 2018). While each proxy has associated uncertainties in both precision and accuracy, the difference between the fO_2 s yielded by each compositional parameter (Fe and V) exceeds these uncertainties. This suggests that the offset in fO_2 s may not be an artifact of the uncertainties of the various experimental calibrations involved and is perhaps driven by a natural process experienced by all the Basalt of Round Valley Butte melt inclusions studied here. The offset suggests a process that would change the fO_2 of the magma in between the time of olivine crystallization and the time of eruption. The constancy of $Fe^{3+}/\Sigma Fe$ in our melt inclusions (Fig. 1.3) indicates that equilibration of $Fe^{3+}/\Sigma Fe$ in our melt inclusions was sufficiently rapid to result in a homogeneous reset of the melt inclusion $Fe^{3+}/\Sigma Fe$ to reflect a magmatic fO_2 different from that at the time of V partitioning during olivine crystallization. One such process that is known to change the fO_2 of silicate magmas prior to and during eruption is volcanic degassing of combinations of CO_2 , H_2O , and sulfur (e.g., Kelley and Cottrell, 2012; Brounce et al., 2014; Helz et al., 2017; Shorttle et al., 2015; Brounce et al., 2017; Hartley et al., 2017; Moussallam et al., 2019, 2016, 2014; Cottrell et al., 2020).

1.5. Discussion

1.5.1 Crystallization, degassing, and diffusion – Basalt of Round Valley Butte

Melt inclusions in this study record a narrow range in MgO concentrations (Table 1.1). We used MELTs to estimate the effects of fractional crystallization on major element chemistry at pressures equal to 3000, 2000, 1000, and 750 bar and a starting fO_2 of either the value indicated by

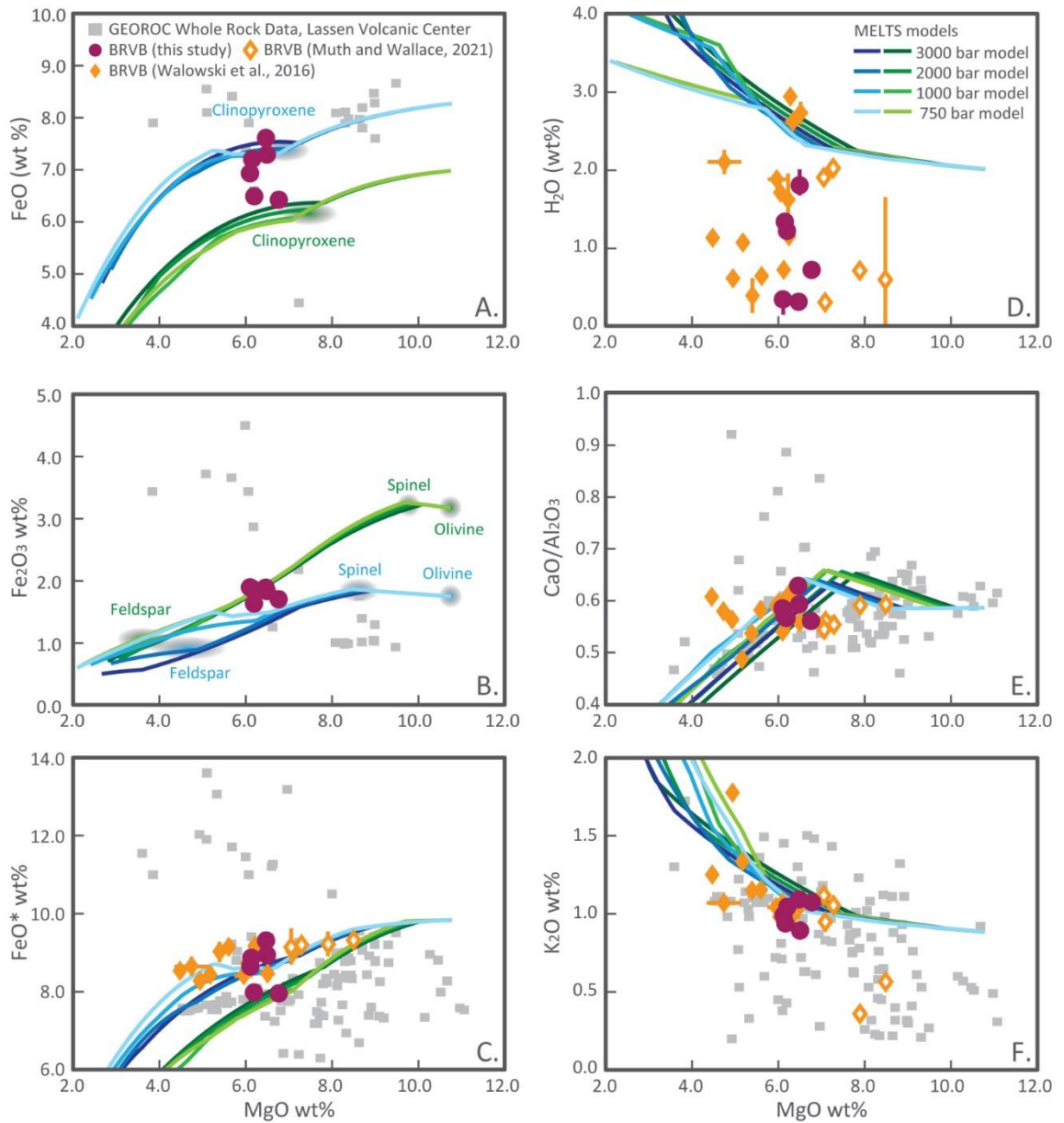
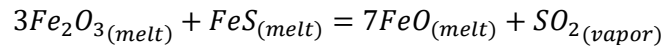


Figure 1.6. Major element variations for Basalt of Round Valley Butte samples (purple circles). Blue curves are MELTS models run for Lassen Volcanic Center with a starting $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.18$ and variable pressures ranging from 3000 bar, dark blue, to 750 bar, light blue. Green curves are MELTS models run for Lassen Volcanic Center with a starting $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.29$ and variable pressures ranging from 3000 bar, dark green, to 750 bar, light green. Orange diamonds are previous melt inclusion measurements from the Basalt of Round Valley Butte (closed diamonds, Walowski et al., 2016; open diamonds, Muth and Wallace, 2021). Grey squares are whole rock data for the Lassen Volcanic Center taken from GEOROC.

$\text{Fe}^{3+}/\Sigma\text{Fe}$ of the melt inclusions ($\text{Fe}^{3+}/\Sigma\text{Fe}=0.18$; Fig. 1.6A-E, blue curves) or the value indicated by $D_V^{\text{olv/melt}}$ ($D_V^{\text{olv/melt}}=0.02$, $\text{Fe}^{3+}/\Sigma\text{Fe}=0.29$; Fig. 1.6A-E, green curves). At these pressures and starting $f\text{O}_2$ s, a modeled melt with an initial major element composition slightly more magnesian than recorded by the melt inclusions crystallizes olivine + spinel +/- clinopyroxene, broadly consistent with observations of spinel inclusions within the studied olivine (see section 3.1, above). The major element compositions of melt inclusions in this study can be reproduced in these models from ~15% mass spinel + olivine crystallization in 3:10 proportions at 750 bar to ~20% mass spinel + olivine + clinopyroxene crystallization in 4:9:8 proportions at 3000 bar for the more oxidized melt inclusions and from ~20% mass spinel + olivine + clinopyroxene crystallization in 6:8:5 proportions at 750 bar to ~25% mass spinel + olivine ± clinopyroxene crystallization in 6:7:12 proportions at 3000 bar for the more reduced melt inclusion compositions, indicating limited extents of fractional crystallization at the time of entrapment (Fig. 1.6). Modeled olivine compositions for the more oxidized melt (initial $\text{Fe}^{3+}/\Sigma\text{Fe}=0.29$) range from Fo_{85} – Fo_{83} , broadly consistent with olivines in this study (Fo_{86-84}). The compositions of the olivines for a starting $\text{Fe}^{3+}/\Sigma\text{Fe}=0.18$ range from Fo_{83} – Fo_{81} , lower than measured in this study.

The K_2O contents of melt inclusions range from 0.9–1.1 wt% (Fig. 1.4, Table 1.1), consistent with limited extents of fractional crystallization at the time of entrapment; however, the H_2O concentrations vary more widely (0.3–1.8 wt%; Fig. 1.4, 6D). In the absence of substantial fractional crystallization, this variation in H_2O concentrations is likely driven by either 1) volcanic degassing of H_2O at the time of melt inclusion entrapment or 2) diffusive loss of H_2O from the inclusions at some time after entrapment. We assess these possibilities below.

Natural magmatic systems degas combinations of CO₂, H₂O, and sulfur. The relative abundance of these volatile species determines the extent to which volcanic degassing affects magmatic fO_2 (Brounce et al., 2017). For example, the fO_2 of ocean island basalts, such as Hawaii, Erebus, or Laki, decreases as the result of degassing roughly 1 wt% H₂O and 2000 ppm S (Brounce et al., 2017; Hartley et al., 2017; Helz et al., 2017; Moussallam et al., 2016, 2014). Typical arc basalts, on the other hand, have much higher H₂O concentrations at similar sulfur abundances to ocean island basalts (4 wt% H₂O, ~2000 ppm S), and thus, the fO_2 for these residual magmas decreases less during degassing when compared to ocean island basalts (Brounce et al., 2017, 2014; Kelley and Cottrell, 2012). The reduction of residual magmas has been hypothesized to take place through mechanisms such as:



(Anderson and Wright, 1972; Brounce et al., 2017, 2021; Carmichael and Ghiorso, 1986; Gaillard et al. 2011; Hartley et al., 2017; Helz et al., 2017; Mousallam et al., 2014, 2016, 2019; Shorttle et al., 2015; Novella et al., 2020). Detailed discussion of this mechanism and demonstrations of the decrease in magmatic fO_2 during volcanic degassing in a variety of melt inclusion and submarine glass studies can be found in these references.

We used D-Compress (Burgisser et al., 2015) to model the expected change in H₂O contents during volcanic degassing for Basalt of Round Valley Butte magmas using the major element composition of melt inclusion BRVB0202 (Table 1.1) and starting H₂O and CO₂ contents of 3.8 wt% and ~500 ppm respectively (Table 1A.3.5; Walowski et al., 2016, 2015). We modeled

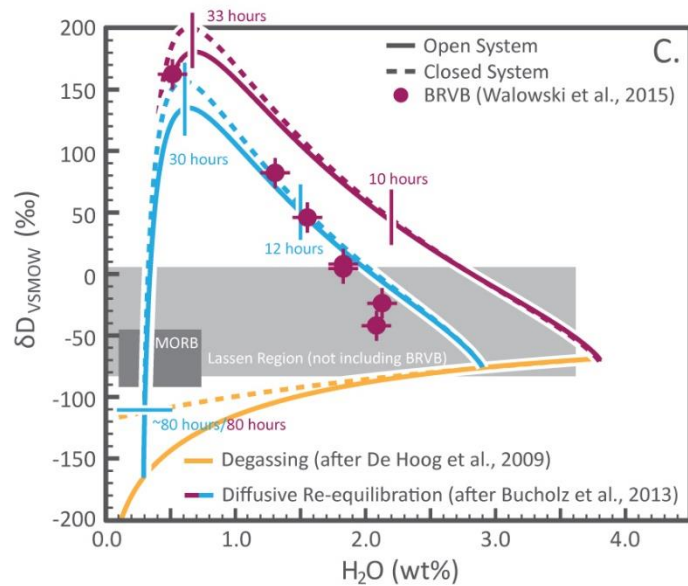
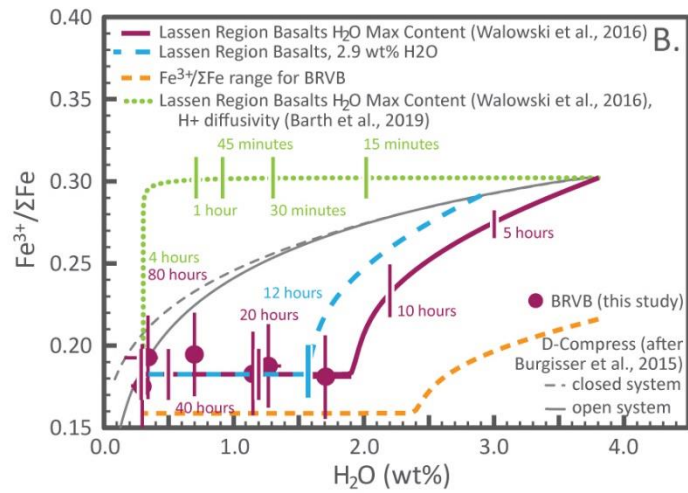
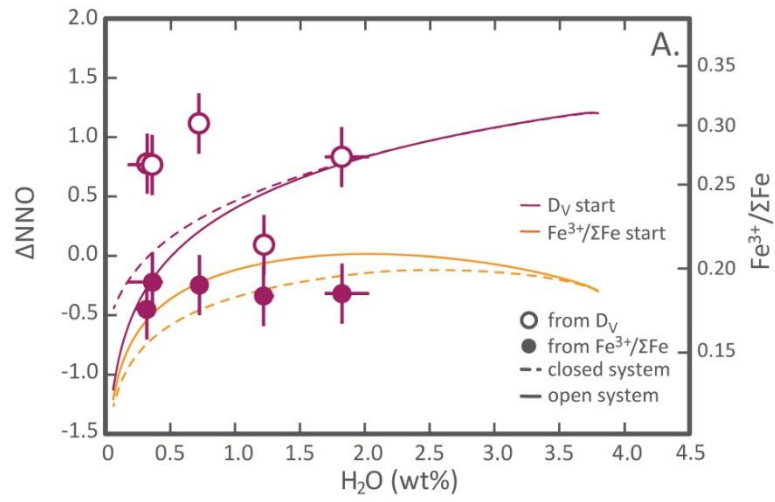


Figure 1.7. A) Variation in H₂O concentration and fO_2 (open circle calculated from Mallmann and O'Neill, 2013; closed circle calculated from Kress and Carmichael, 1991) for melt inclusions from Basalt of Round Valley Butte samples. Purple curves are D-Compress (Burgisser et al., 2015) model runs with initial H₂O = 3.8 wt%, CO₂ = 550 ppm, P = 1800, T = 1100°C, $fO_2 = \Delta NNO = +1.2$, and major element composition of sample BRVB0202. Orange curves are D-Compress model runs with initial H₂O = 3.8 wt%, CO₂ = 500 ppm, P = 1800 bar, T = 1100°C, $fO_2 = \Delta NNO = -0.3$, and major element composition of sample BRVB0202. B) Diffusive equilibration model curves (Bucholz et al., 2013) for an 85 μ m melt inclusion of same composition as (A) with an initial $fO_2 = \Delta NNO = +1.2$ (purple solid curve, green dotted curve), $fO_2 = \Delta NNO = +1.06$ (blue dashed curve) and H₂O = 2.9, or $fO_2 = \Delta NNO$ (orange dashed curve) and an external $fO_2 = \Delta NNO = -0.36$ (purple solid curve, blue dashed curve, green dotted curve) or $\Delta NNO = -0.7$ (orange dashed curve). D-Compress model runs are the same as in (A; grey). C) Degassing (orange; De Hoog et al., 2009) and diffusive equilibration (purple and blue, Bucholz et al., 2013) model curves for H₂O and hydrogen isotopic composition. Initial composition for the degassing model (orange; De Hoog et al., 2009) is the same as in (B, purple solid curve) with an initial $\delta D = -70\%$. Light grey box is range in H₂O concentration and H₂O composition for Lassen Volcanic Center samples (Walowski et al., 2015) and dark grey box is range in H₂O and hydrogen isotopic composition for MORB samples (e.g., Clog et al., 2013; Kyser and O'Neil, 1984).

open and closed system degassing using the maximum fO_2 calculated from $Fe^{3+}/\Sigma Fe$ in this study (Table 1A.3.5; Fig. 1.7A, orange curves; Kress and Carmichael, 1991). The models show that magmas degas from their initial H_2O and CO_2 contents at 1800 bars (initial S = 3016 ppm) to <0.1 wt% H_2O , negligible CO_2 contents, and 691 ppm S concentrations at 1 bar of total pressure. Simultaneously, these magmas reduce from a starting fO_2 of $\Delta NNO = -0.3$ to a final fO_2 of $\Delta NNO = -1.2$ (closed system, curves). We also modeled open and closed system degassing starting at the fO_2 indicated by the maximum fO_2 calculated from $D_V^{olv/melt}$ ($fO_2 = \Delta NNO = +1.2$; Table 1A.3.5; Fig. 1.7A, purple curves; initial $CO_2 = 550$ ppm; Mallmann and O'Neill, 2013). These degassing models are similar to those based on starting fO_2 from $Fe^{3+}/\Sigma Fe$, except that they reduce to a final fO_2 of $\Delta NNO = -0.4$ (closed system, Fig. 1.7A, purple dashed curve) or $\Delta NNO = -1.1$ (open system; Fig. 1.7A, purple solid curve). The decrease in fO_2 of these modeled degassed magmas demonstrates that the difference in fO_2 between the undegassed and fully or partially degassed magmas (from $fO_2 = \Delta NNO = +1.2$ to $\Delta NNO = -0.4$) presents a driving force for equilibration of fO_2 in olivine-hosted melt inclusions within natural magmatic systems. Interestingly, we find models initiated at the highest fO_2 indicated by $D_V^{olv/melt}$ from the Basalt of Round Valley Butte data set reduce to an fO_2 near that indicated by $Fe^{3+}/\Sigma Fe$ (average of $\Delta NNO = -0.3$; Kress and Carmichael, 1991) as the result of degassing H_2O , CO_2 , and S contents.

The D-Compress models do not describe the relationship between the H_2O contents and fO_2 in the Basalt of Round Valley Butte melt inclusion dataset well (e.g., fig 7A). In the model starting with the higher fO_2 , the open and closed system degassing models (purple curves, Fig 7A) do not replicate the near constant fO_2 calculated from $Fe^{3+}/\Sigma Fe$ for these samples. In the case where

the D-Compress model starts with an initial fO_2 calculated from $Fe^{3+}/\Sigma Fe$, the open and closed system degassing model curves (orange solid and dashed curve, Fig 7A) generally fall below the values calculated from $D_v^{olv/melt}$ and do not replicate the near constant fO_2 across nearly 2 wt% H_2O calculated from $Fe^{3+}/\Sigma Fe$ in these samples.

The effect of degassing on δD compositions were modeled (De Hoog et al., 2009) using the same initial H_2O contents as the D-Compress models (3.8 wt%) and with $\delta D_{initial} = -70\text{‰}$ (Fig. 1.7C, orange curves). The hydrogen isotopic composition models (De Hoog et al., 2009) were calculated following the H_2O concentration steps of the D-Compress model. These models demonstrate that with increased volcanic degassing, the δD composition of the melt becomes increasingly lighter in both open and closed systems (Fig. 1.7C, orange curves). This decrease in δD arises because the fractionation factor between the vapor phase (H_2O and OH) and the melt ($\alpha_{vapor-melt}$) is greater than 1 ($\alpha_{vapor-melt} = 1 + \Delta D_{vapor-melt} / (\delta D_{melt} + 1000)$ and $\Delta D_{vapor-melt} = 44.53 \times (C_{H_2O}/7.03 + 1)^{-1.2}$; De Hoog et al., 2009). Thus, the relationship between δD and H_2O concentration of melt inclusions trapped along a degassing path is expected to be positively correlated in both open and closed systems (De Hoog et al., 2009).

In contrast to the expected positive relationship between H_2O concentrations and δD compositions due to degassing, Basalt of Round Valley Butte melt inclusions record a negative correlation (Fig. 1.7C; Walowski et al., 2015). This observation, paired with the observed offset in fO_2 calculated from $D_v^{olv/melt}$ (Fig. 1.5), constant $Fe^{3+}/\Sigma Fe$, and a positive correlation between SiO_2 and H_2O (Fig. 1A.6; Portnyagin et al., 2019) may reflect variable extents of diffusive H_2O loss and $Fe^{3+}/\Sigma Fe$ equilibration from these inclusions through their host olivine with an external melt that

has partially or fully degassed. In this scenario, a melt inclusion could have been trapped in an olivine growing at sufficiently high pressures to predate significant low pressure volcanic degassing. This olivine and melt inclusion pair would record the entrapment fO_2 of the melt through $D_V^{olv/melt}$ and $Fe^{3+}/\Sigma Fe$ in the melt inclusion. Upon ascent to lower pressures, where the host magma would be subject to degassing and concomitant reduction in fO_2 (Fig. 1.7A), the more hydrous and oxidized melt inclusion would be subject to diffusive equilibration, which has been shown to occur on short time scales at magmatic temperatures for $Fe^{3+}/\Sigma Fe$ and H_2O (e.g., 10s of hours; Bucholz et al., 2013), and longer timescales for V (e.g., 100s of years; Cottrell et al., 2002). Upon eruption, the melt inclusion would then have $Fe^{3+}/\Sigma Fe$ and H_2O values that reflect late-stage diffusive equilibration at low pressures and $D_V^{olv/melt}$ that reflects the fO_2 at the time of olivine crystallization.

We explore the possibility of diffusive equilibration of H_2O and $Fe^{3+}/\Sigma Fe$ quantitatively using the model of Bucholz et al. (2013) that has been adjusted to impose an external boundary condition for D/H (Bucholz, pers comm), beginning with a melt inclusion of the same starting composition as that used in the D-Compress model ($H_2O=3.8$ wt%, $fO_2=\Delta NNO=+1.2$). This modeled melt inclusion is held in a host magma with fO_2 calculated from $Fe^{3+}/\Sigma Fe$ ($\Delta NNO=-0.36$). Due to the negligible impact of CO_2 on fO_2 (Brounce et al., 2017) we did not include the presence of a vapor bubble in our $Fe^{3+}/\Sigma Fe$ fO_2 calculations. The model results show that a melt inclusion of 85 μm diameter in 1 mm diameter olivine host will lose 3.5 wt% H_2O in ~80 hours. At the same time, $Fe^{3+}/\Sigma Fe$ recorded by the melt inclusion will change from ~0.3 to ~0.18 in a little over 10 hours, fully diffusively equilibrating with the host magma while H_2O continues to diffuse (Fig. 1.7B). This diffusion model agrees well with the observed negative correlation between δD and H_2O

concentrations in this same suite of melt inclusions and demonstrates that the full range in observed δD concentrations can be matched by a diffusively equilibrating melt inclusion (starting $\delta D = -75\text{‰}$) with external melt conditions in about 30 hours (external melt $\delta D = -110\text{‰}$; Fig. 1.7C; Walowski et al., 2015). In contrast, a model of the same major element composition as BRVB0202 with a starting fO_2 from the higher end of the range recorded by samples in this study ($Fe^{3+}/\Sigma Fe = 0.21$) equilibrates with an external melt with $Fe^{3+}/\Sigma Fe = 0.16$ in less than 10 hours (Fig. 1.7B, orange dashed curve). When starting and ending at the same H_2O concentration and δD composition this model fully overlaps with the previous model (Fig. 1.7C, purple curves) but does not overlap with the fO_2 recorded by $D_V^{olv/melt}$ of these same melt inclusions. While more than one model explains some facets of the observed data, the only model that describes all three observations ($D_V^{olv/melt}$, $Fe^{3+}/\Sigma Fe$, and H_2O) of Basalt of Round Valley Butte samples indicates that these melt inclusions were trapped at fO_2 recorded by $D_V^{olv/melt}$, then diffusively equilibrated with a reduced, degassing/degassed magma within ~ 40 hours of eruption, based on the preserved δD in these same melt inclusions.

The relationship between melt inclusion position within the host olivine and orientation with respect to the crystallographic axes has been shown to affect the timescale of diffusive H_2O loss from the melt inclusion (Barth et al., 2019). Not accounting for crystallographic orientation of the host olivine when making melt inclusion H_2O observations during dehydration experiments yields H^+ diffusivities that are generally expected from the metal vacancy diffusion method; however, when accounting for crystallographic orientation, H^+ is observed to be preferentially diffusing at higher rates along the a-axis (Ferriss et al., 2018; Barth et al., 2019). To examine how this relationship would appear in our measurements, we explore the possibility of diffusive

equilibration of H_2O and $\text{Fe}^{3+}/\Sigma\text{Fe}$ quantitatively using the proton-polaron diffusivity of H^+ (Barth et al., 2019) in the Bucholz et al. (2013) model, using the same starting parameters as above. The model results show that a modeled melt inclusion of 85 μm diameter in a 1 mm olivine host will lose 3.5 wt% H_2O in ~ 4 hours, an order of magnitude faster than in the metal vacancy model. Because the diffusive equilibration of $\text{Fe}^{3+}/\Sigma\text{Fe}$ is still taking place via the metal vacancy mechanism in this model, the change in $\text{Fe}^{3+}/\Sigma\text{Fe}$ is unchanged from the initial model run (Fig. 1.7B, green dotted curve). While this model does not fit with the observed correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and H_2O , this diffusion model agrees well with the observed negative correlation between δD and H_2O concentrations, albeit on a much shorter diffusive equilibration timescale (4 hours vs 80 hours; Fig. 1.7C, green curves with green text; Walowski et al., 2015). Since the diffusive equilibration model is isotropic, the green curve model result underestimates the time taken for diffusive equilibration for a-axis diffusivity. Similarly, the Bucholz et al. (2013) model is likely an incomplete description of equilibration processes because it assumes constant boundary conditions. An actively degassing magma will produce an external melt boundary condition that evolves during the process of degassing. Studies have shown that multiple diffusive mechanisms working simultaneously describe the movement of H^+ through an olivine, and that these various mechanisms are dependent on the composition of and number of vacancies within the host olivine (Ferriss et al., 2018; Jollands et al., 2019). Examining the potential for anisotropic diffusive equilibration under evolving external boundary conditions is an important avenue for future research.

1.5.2 Implications for Mariana Island Arc Basalts and fO_2 of the mantle wedge

Because of the short timescale, diffusive equilibration of $Fe^{3+}/\Sigma Fe$ in olivine-hosted melt inclusions may be a more universal phenomenon. For instance, melt inclusions from Mariana arc basalts (Brounce, 2014; Brounce et al., 2014) reveal similar offset between the fO_2 calculated from $D_V^{olv/melt}$ and $Fe^{3+}/\Sigma Fe$ (average offset of the $D_V^{olv/melt}$ oxybarometer ranges from 1.2-1.9 log units higher than the Fe oxybarometers; Fig. 1.8B-C). As in the case for Basalt of Round Valley Butte inclusions, we explore the combined effects of volcanic degassing and diffusive equilibration of fO_2 , H_2O , and δD in the Mariana arc melt inclusions, using D-Compress (Burgisser et al., 2015) and a diffusive equilibration model (Bucholz et al., 2013). These models were run using a starting major element composition from Sarigan and Agrigan (Tables 2A.3.5), a starting fO_2 calculated using $D_V^{olv/melt}$ from these same volcanos, and the highest H_2O concentrations measured from each volcano (Table 1A.3.5; Brounce, 2014). The ending fO_2 used in the diffusive equilibration model (Bucholz et al., 2013) was calculated from the recalibrated (Zhang et al., 2018) $Fe^{3+}/\Sigma Fe$ from these volcanos (Table 1A.3.5; Brounce et al., 2019, 2014). Similar to the degassing model results for the Basalt of Round Valley Butte magma, Mariana Island arc volcano melts with an initial fO_2 recorded by $D_V^{olv/melt}$ can reach lower fO_2 than recorded by $Fe^{3+}/\Sigma Fe$ (Fig. 1.8B-C solid and dashed curves) through volcanic degassing.

The offset between the fO_2 described by $Fe^{3+}/\Sigma Fe$ and $D_V^{olv/melt}$ in Sarigan melt inclusions by ~ 1.5 log units can be explained by the same process that affects the Basalt of Round Valley Butte melt inclusions (see section 5.1), where diffusive equilibration of H_2O and fO_2 in melt inclusions

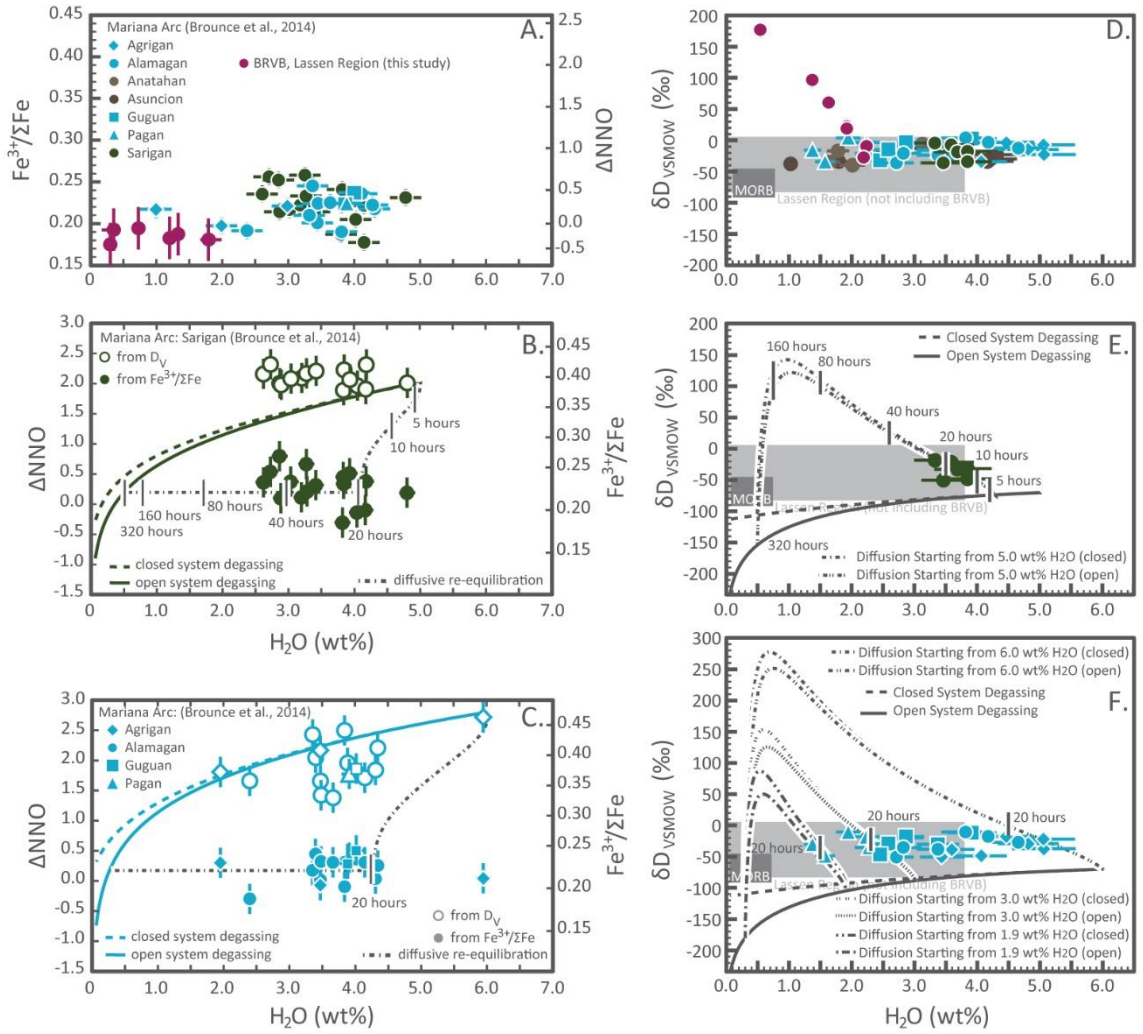


Figure 1.8. A) Variation H_2O concentration and $\text{Fe}^{3+}/\Sigma\text{Fe}$ for Basalt of Round Valley Butte samples (purple circles) and Mariana Arc (blue, grey, and green symbols; Brounce et al., 2014) samples. B) Variation in H_2O concentration and $f\text{O}_2$ for Sarigan samples (Brounce et al., 2014). Green curves are open (solid) and closed (dashed) system D-Compress (Burgisser et al., 2015) model runs with initial $\text{H}_2\text{O} = 5 \text{ wt\%}$, $\text{CO}_2 = 1200 \text{ ppm}$, $P = 3000 \text{ bar}$, $T = 1020^\circ\text{C}$, and $f\text{O}_2 = \Delta\text{NNO} = +2.0$. Grey curve is a diffusive equilibration model (Bucholz et al., 2013) for an $85 \mu\text{m}$ melt inclusion of same composition as in the D-Compress (Burgisser et al., 2015) model with an initial $f\text{O}_2 = \Delta\text{NNO} = +2.0$ and external $f\text{O}_2 = \Delta\text{NNO} = +0.2$. C) Variation in H_2O concentration and $f\text{O}_2$ for Mariana Arc samples (Agrigan, Guguan, Pagan, and Alamagan; Brounce et al., 2014). Blue curves are open (solid) and closed (dashed) system D-Compress (Burgisser et al., 2015) model runs with initial $\text{H}_2\text{O} = 6 \text{ wt\%}$, $\text{CO}_2 = 280 \text{ ppm}$, $P = 3000 \text{ bar}$, $T = 1030^\circ\text{C}$, and $f\text{O}_2 = \Delta\text{NNO} = +2.8$. Grey curve is a diffusive equilibration model (Bucholz et al., 2013) for an $85 \mu\text{m}$ melt inclusion of same composition as in the D-Compress (Burgisser et al., 2015) model with an initial $f\text{O}_2 = \Delta\text{NNO} = +2.8$ and external $f\text{O}_2 = \Delta\text{NNO} = +0.3$. D) Variation in H_2O concentration and hydrogen isotopic composition for Basalt of Round Valley Butte (purple circles) and Mariana Arc (green, blue, and grey symbols; Shaw et al., 2008) samples. Light grey box is range in H_2O concentration and H_2O composition for Lassen Volcanic Center samples (Walowski et al., 2015) and dark grey box is range in H_2O concentration and hydrogen isotopic composition for MORB samples (e.g., Clog et al., 2013; Kyser and O'Neil, 1984). E) Degassing (solid and dashed grey curves; De Hoog et al., 2009) and diffusive equilibration (dotted-dashed curves, Bucholz et al., 2013) model curves for H_2O and hydrogen isotopic composition. Initial composition for the degassing model (solid and dashed grey curves; De Hoog et al., 2009) is the same as in (B, grey curve) with an initial $\delta\text{D} = -70\text{‰}$. F) Degassing (solid and dashed grey curves; De Hoog et al., 2009) and diffusive equilibration (dotted-dashed curves, Bucholz et al., 2013) model curves for H_2O and hydrogen isotopic composition. Initial composition for the degassing model (solid and dashed grey curves; De Hoog et al., 2009) is the same as in (C, grey curve) with an initial $\delta\text{D} = -70\text{‰}$.

with a partially degassed external magma takes place on the order of <48 hours (Fig. 1.8B-C, grey dashed curve). In contrast to the case for Basalt of Round Valley Butte, the offset of H₂O diffusive loss in the Sarigan samples is less readily apparent for δD (Fig. 1.7C; fig 8E). In this case, Sarigan melt inclusions capture a short interval of diffusive H₂O loss, consistent with previous interpretations of Mariana melt inclusion δD values (Shaw et al., 2008). If Sarigan melt inclusions equilibrated with an external melt with a lower fO_2 due to CO₂, H₂O, and sulfur degassing (as in the scenario explored in section 5.1, above), then they would only need ~20 hours to fully equilibrate Fe³⁺/ΣFe while mostly preserving the initial δD . The combination of H₂O, δD , and Fe and V constraints on the fO_2 could be indicative of diffusive equilibration taking place between the trapped un-degassed melt and a partially degassed external melt, which we show would be sufficient to explain the offset in fO_2 from the elevated values recorded by $D_V^{olv/melt}$ and the lower values recorded by Fe³⁺/ΣFe. The remainder of the recorded H₂O, δD , and Fe and V concentrations for Mariana melt inclusions (i.e., samples from Agrigan, Alamagan, Guguan, and Pagan) could be explained by a combination of melt inclusion entrapment along a degassing path and diffusive equilibration (Fig. 1.8 C&F), similarly to Sarigan and Basalt of Round Valley Butte melt inclusions (Fig. 1.8 B & E and Fig. 1.7 A&C, respectively). Despite the range in ~5 wt% H₂O, diffusive equilibration of H⁺ taking place on the order of ~20 hours, would be insufficient to overwrite the H isotopic trend for degassing (Fig. 1.8F), preserving this isotopic trend and offsetting it to elevated δD . This minimal loss of H⁺ is consistent with previous observations of Mariana subaerial arc volcanoes (Shaw et al., 2008). While diffusive equilibration may affect the oxidation state of arc melt inclusions as recorded by Fe³⁺/ΣFe, it may not fully erase the characteristically elevated fO_2 of

arc basalts relative to MORBs. Instead, diffusive equilibration may lower the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded by arc melt inclusions, but trace element records of slab influence (e.g., Ba/La; Elliot et al., 1997) remain unchanged. The result is that a positive correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and Ba/La persists in the record of measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ of melt inclusions and their corresponding $f\text{O}_2$ calculated from those measurements, but the $f\text{O}_2$ indicated by $D_V^{\text{olv/melt}}$ in those same melt inclusion-olivine pairs records a magmatic condition unaffected by diffusive equilibration (Fig. 1A.9). In the case of Basalt of Round Valley Butte and Mariana arc melt inclusions examined here, the $f\text{O}_2$ recorded by $D_V^{\text{olv/melt}}$ is higher than that recorded by direct measurements of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the melt inclusions, and we suggest this may reflect the impact of volcanic degassing and the relatively short timescale of redox equilibration in olivine-hosted melt inclusions.

1.6. Conclusions

This study of olivine-hosted melt inclusions from the Basalt of Round Valley Butte examines the offset between calculated $f\text{O}_2$ using $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Borisov et al., 2018; Jayasuriya et al., 2004; Kress and Carmichael, 1991; O'Neill et al., 2018) and $D_V^{\text{olv/melt}}$ (Mallmann and O'Neill, 2013) as oxybarometers. The near constant K_2O despite a change of ~2 wt% in H_2O concentrations, combined with negatively correlated δD and H_2O indicate that this suite of melt inclusions has undergone partial diffusive equilibration of H_2O trapped in the melt inclusions with the ambient melt via the diffusion of H^+ through the host olivine. The near constant $\text{Fe}^{3+}/\Sigma\text{Fe}$ of melt inclusions from this same suite indicates that if $\text{Fe}^{3+}/\Sigma\text{Fe}$ is diffusively equilibrating with the degassing melt, then it is doing so on a faster timescale than H^+ .

The offset in fO_2 between $Fe^{3+}/\Sigma Fe$ (Borisov et al., 2018; Jayasuriya et al., 2004; Kress and Carmichael, 1991; O'Neill et al., 2018) and $D_V^{olv/melt}$ (Mallmann and O'Neill, 2013) calculations can be replicated via diffusive equilibration with a nearly fully degassed magma that started at 3.8 wt% H_2O , 550 ppm CO_2 , fO_2 of $\Delta NNO=+1.2$, and 1800 bars (Table 1A.3.5). Diffusive equilibration of $Fe^{3+}/\Sigma Fe$ in these modeled samples takes place in under 20 hours whereas full diffusive equilibration of H_2O could take upwards of 40 hours in this same suite. This same offset between calculated fO_2 using $Fe^{3+}/\Sigma Fe$ (Kress and Carmichael, 1991) and $D_V^{olv/melt}$ (Mallmann and O'Neill, 2013) can be observed in samples from Mariana arc volcanoes. Notably, diffusive equilibration models (Bucholz et al., 2013) show that Sarigan melt inclusion $Fe^{3+}/\Sigma Fe$ can equilibrate with a degassed and reduced magma in about 20 hours compared to 100s of hours for H_2O .

Previous work has used the fO_2 calculated from $Fe^{3+}/\Sigma Fe$ measured in olivine-hosted melt inclusions to describe the oxidation state of the Earth's sub-arc mantle (Brounce et al., 2014; Kelley and Cottrell, 2012, 2009). However, this ratio is likely altered on magmatically short timescales (under one day), and because of the reducing nature of volcanic degassing, may underestimate the fO_2 of the mantle sources of the magmas represented by the melt inclusions. Use of $D_V^{olv/melt}$ proxies for fO_2 may avoid this rapid, very late-stage modification and for this reason, may be better applied (relative to direct measurements of $Fe^{3+}/\Sigma Fe$ of melt inclusions) for those seeking to constrain mantle fO_2 in any setting. The use of $D_V^{olv/melt}$ fO_2 proxies indicates that the mantle beneath arc volcanoes may be somewhat more oxidized than previously thought, from $\sim\Delta NNO=+0.4$ (Brounce et al., 2014; Kelley and Cottrell, 2012, 2009) to $\sim\Delta NNO=+2.1$.

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CHAPTER ONE APPENDIX

DIFFUSIVE EQUILIBRATION OF H₂O AND OXYGEN FUGACITY IN NATURAL OLIVINE-HOSTED MELT INCLUSIONS

J. Humphreys, M. Brounce, K. Walowski

1A.1. Materials and Methods

1A.1.1. Sample Description and Preparation

The tephra sampled in this study was collected from a quarry-exposed section of the Basalt of Round Valley Butte cone and are the same bulk tephra sample from previous studies (Fig. 1.1; Walowski et al., 2016, 2015). These tephra range in color from black to bright rust red or dull yellow, are vesiculated (upwards of 50% of sample surface), and angular. The tephra was washed in de-ionized water, dried, and progressively sorted by size using metal sieves of size No. 10, 20, and 200 mesh. Olivine grains (2-0.8 mm in size) coated in a black glass were handpicked from the sieved tephra for analysis. These olivine grains were immersed in HBF₄ to remove the glass coating prior to identifying melt inclusions for study following the methods from Luhr (2001).

Olivines in the tephra are subhedral to anhedral, contain abundant small (<25 µm) opaque spinel inclusions, and are predominantly encrusted in matrix glass. Melt inclusions which are spherical to oblate, naturally glassy, pale to dark brown in color, and range in diameter from 10 µm to 200 µm (Fig. 1.2) are typical in these olivines. Naturally glassy melt inclusions (>45 µm in diameter) were selected for analysis in this study. A total of 13 melt inclusions were prepared for major element analysis, 6 of which were analyzed via µ-XANES and subsequently had their chemistries corrected for post-entrapment crystallization (Table 1.1, discussed in 1.4. Results, main

text). All six of these post-entrapment crystallization corrected melt inclusions contained one vapor bubble. Some melt inclusions are adjacent to or encapsulate a spinel inclusion. Of the six post-entrapment crystallization corrected melt inclusions measured, two melt inclusions did not contain spinel inclusions and one contained a spinel inclusion in a neck off the main inclusion body (Table 1A.3; Fig. 1.2B).

1A.1.2. EPMA

Melt inclusions and their olivine hosts were mounted in epoxy within 0.7 cm-round brass spacers cut to be 0.6 cm in length, exposed on one side, and polished for major elements analysis. These analyses were conducted at the California Institute of Technology Division of Geological and Planetary Sciences Analytical Facility using a JEOL JXA-8200 electron microprobe operated at 10nA, 15kV, and with a 10 μ m beam diameter. Magnesium, chromium, potassium, aluminum, manganese, sodium, titanium, calcium, silicon, and iron were measured with 20 s peak count times. Primary calibration standards for olivines and melt inclusions included forsteritic olivine (Si in the olivine, Mg), Cr₂O (Cr), microcline (K), Al₂O₃ (Al in olivine), anorthite (Al in the melt inclusions, Ca), Mn olivine (Mn), Albite (Na), TiO₂ (Ti), Fayalite (Ca), and VG-2 glass (Si in the melt inclusion), and fayalitic olivine (Fe; Jarosewich et al., 1980). Secondary calibration standards measured included United States Geological Survey BHVO g, BCR-2 g, and BIR-1 g glasses as well as VG-2 and A-99 glasses (Jarosewich et al., 1980). Major element concentrations can be found in Table 1.1.

1A.1.3. FTIR

After electron microprobe analysis, all 13 samples were re-polished to remove EPMA analysis activation volumes. The newly polished surface was then superglued to a glass slide and polished from the opposite side to doubly expose the melt inclusion for further analyses. Doubly exposed melt inclusions ranged in thickness from 13-23 μm .

Dissolved H₂O concentrations in the melt inclusions were measured at the University of California Riverside using a Thermo Scientific Nicolet iS50 Fourier-transform infrared spectrometer coupled with a Nicolet Continuum Fourier-transform infrared microscope attachment. Infrared spectra were collected between 600 and 6000 cm^{-1} . Aperture dimensions used in analysis ranged from $\sim 15 \times 15 \mu\text{m}$ to $\sim 40 \times 40 \mu\text{m}$, depending on the size of each individual melt inclusion. Total H₂O concentrations were calculated from the absorption feature measured at the 3530 cm^{-1} band. Conversion of the 3530 cm^{-1} absorption feature into total H₂O concentration was performed using Beer's Law in conjunction with glass densities and absorption coefficients calculated from the methods of Dixon et al. (1995) and Luhr (2001). Sample thicknesses were calculated using the interference spectra present in the 2000 to 2700 cm^{-1} band using the relationship:

$$t = \lambda / 2n$$

where t = sample thickness, λ = wavelength, and $n = 1.546$.

1A.1.4. μ -XANES

The Fe³⁺/ Σ Fe of 6 melt inclusions were analyzed in situ using micro X-ray absorption near edge structure spectroscopy (μ -XANES) at the Advanced Photon Source, Argonne National

Laboratory at the University of Chicago's GeoSoilEnviroCARS at Beamline 13-ID-E. Spectra were collected in fluorescence mode from 7012 eV to 7356 eV with a Vortex ME4 silicon-drift diode detector array coupled to a high-speed digital spectrometer system and a defocused beam diameter of 10 x 10 μm . Six layers of aluminum foil were placed in the path of the incident photon beam to decrease beam intensity and prevent auto-oxidation of the Fe species present in the hydrous glass (Cottrell et al., 2018). The photon flux of the beam was $\sim 2 \times 10^9$ photons/s with a flux density of $\sim 2 \times 10^7$ photons/s/ μm . Spectra were collected from 7012 to 7101 eV in 2.5 eV steps, 7101 to 7120 eV in 0.1 eV steps, and 7120 to 7355 eV in 2.3 $\text{\AA}$ steps using 1 second per point dwell times in accordance with the procedures described in Cottrell et al. (2018). Spectra were normalized to the energy of the EXAFS region between 7120 and 7355 eV and fit following the techniques from Cottrell et al. (2009) and Zhang et al. (2018). The spectra were checked for influences from the olivine host and/or small crystals contained in the glass by examining the spectral forms in the energy region of 7120-7150 eV where olivine interference will produce a secondary peak in the EXAFS region (Fig. 1.S1). Any spectra showing these influences were discarded from further analysis.

1A.1.5. LA-ICP-MS

Trace element abundances for 6 melt inclusions and corresponding olivine hosts were analyzed at the Lyons ICP Facility at the University of California Riverside via laser-ablation inductively coupled plasma mass spectrometry using an Agilent Technologies 7900 quadrupole mass spectrometer that is coupled to a short pulse width coherent 193 nm ArF excimer laser. Three melt inclusions and host olivines (BRVB 0209, 0108, and 0202; Tables 1A.1, 1A.2) were analyzed

for 20 trace elements (Sc, V, Sr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, and U) while BRVB 0109, 0112, and 0211 olivines and melt inclusion glasses as well as olivine BRVB 0108 and 0202 were analyzed for 37 trace elements (Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Th, and U; Tables 1A.1, 1A.2). Spot sizes ranged from 25-50 μm . A repeat rate of 5 Hz and energy on sample surface of 0.037 – 0.144 mJ per area was used. The same analyses were performed on the melt inclusions and the olivine hosts, normalizing to ^{43}Ca for the melt inclusions and ^{26}Mg for the olivine host. United State Geological Survey glass standards BIR-1 g, BCR-2 g, and BHVO-2 g and Max Planck Institute glass standards KL2-G, ML3B-G, StHls-G, GOR-128-G, GOR-132-G, ATHO-G, and T1-G were used to create linear calibration curves ($R^2 > 0.999$) for each analytical session (Jochum et al., 2000; Kelley et al., 2003). Counting statistics were examined carefully for each element and those elements that did not return strong signals for the entire length of the ablation period were discarded.

1A.2. Figures

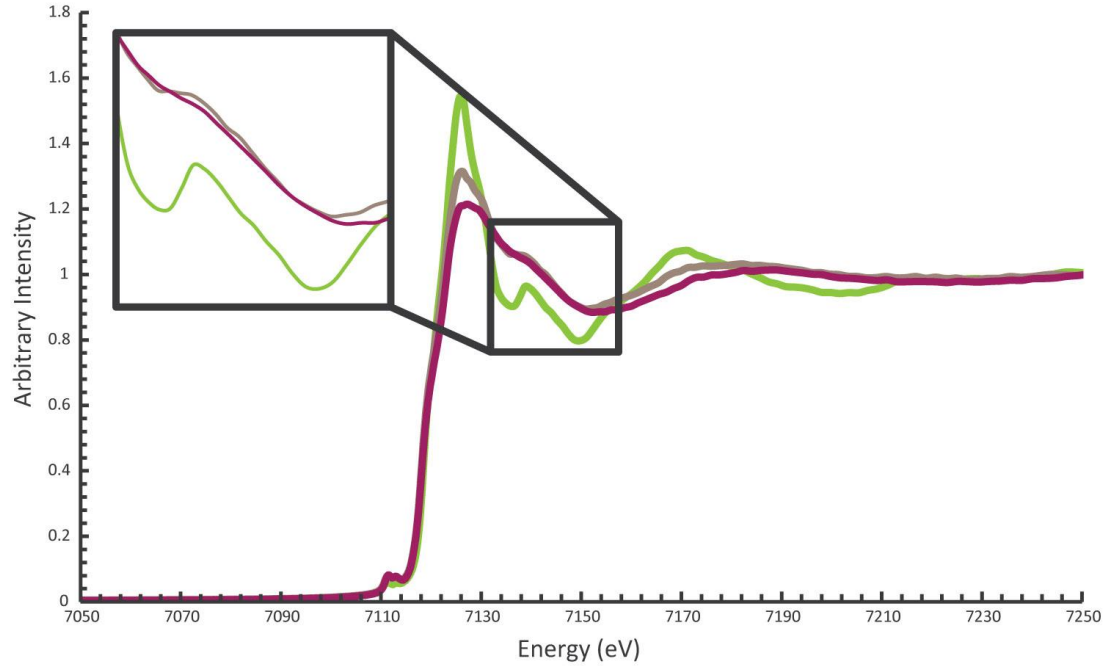


Figure 1A.1. Example Fe- μ -XANES spectra for olivine (green curve), melt inclusion with olivine interference (grey curve), and melt inclusion without olivine interference (purple curve) from sample BRVB0209. Inset image shows doublets in the 7130-7150 eV range when olivine is present in the spectra.

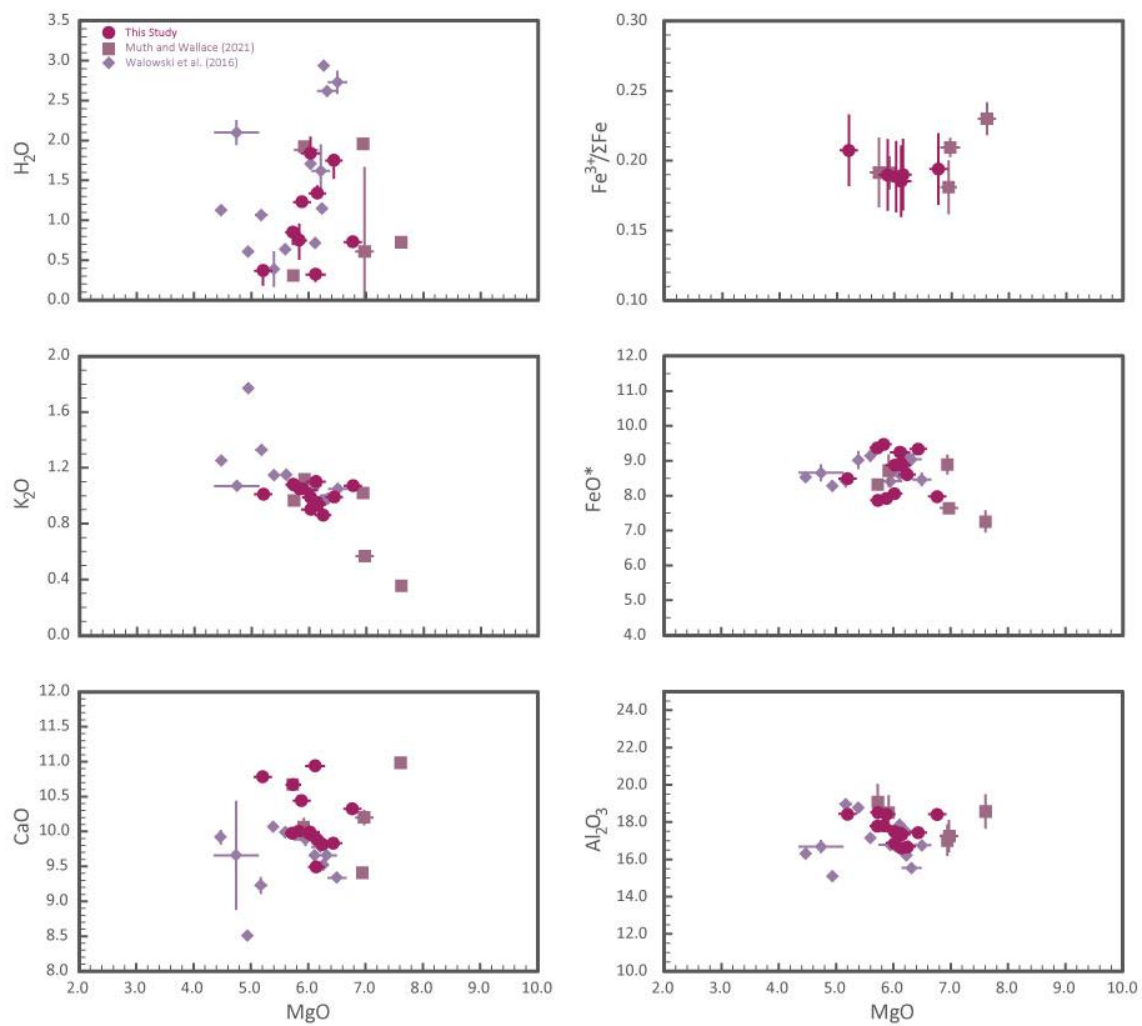


Figure 1A.2. Major element variations in melt inclusions from Basalt of Round Valley Butte that have not been corrected for post-entrapment crystallization (this study; Muth and Wallace, 2021; Walowski et al., 2016).

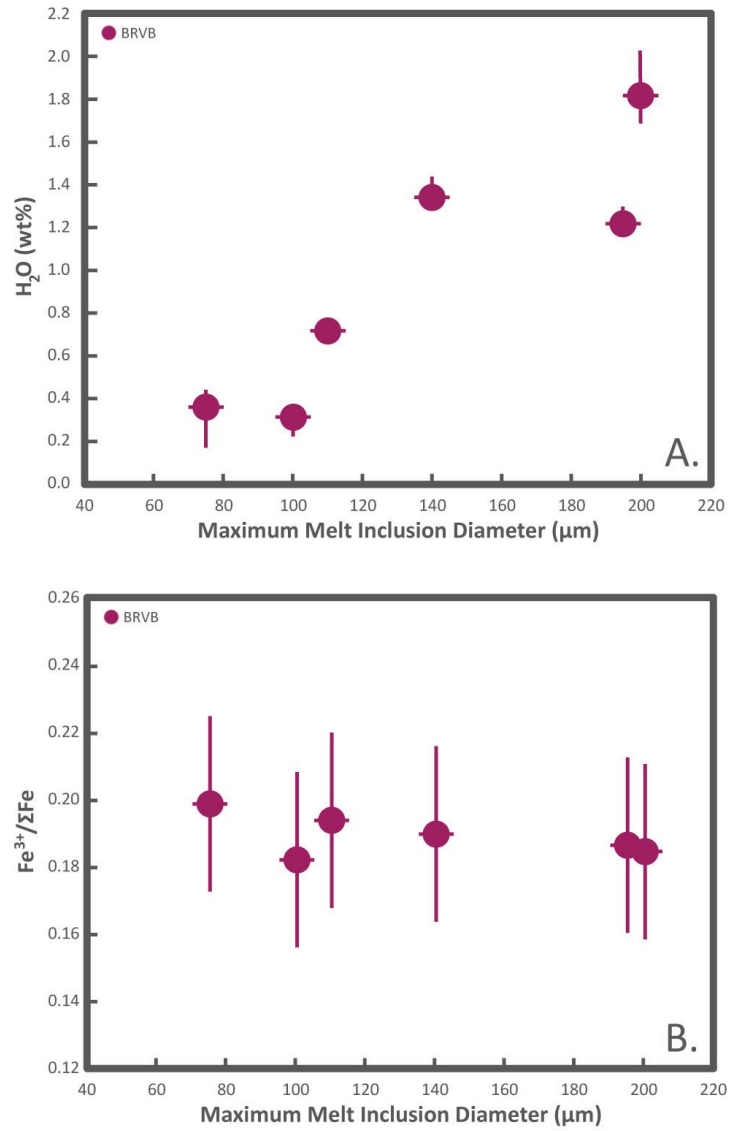


Figure 1A.3. Variations in (A) H₂O content and (B) Fe³⁺/ΣFe with maximum melt inclusion diameter.

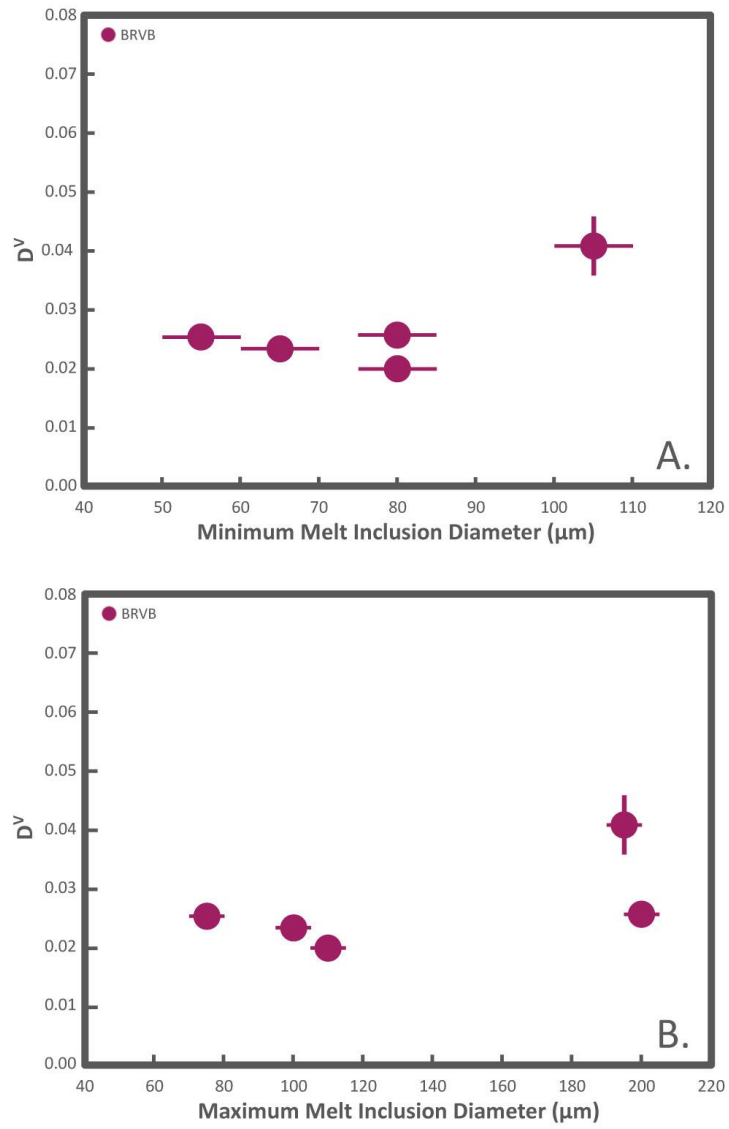


Figure 1A.4. Variations in $D_v^{olv/melt}$ with (A) minimum and (B) maximum melt inclusion diameter.

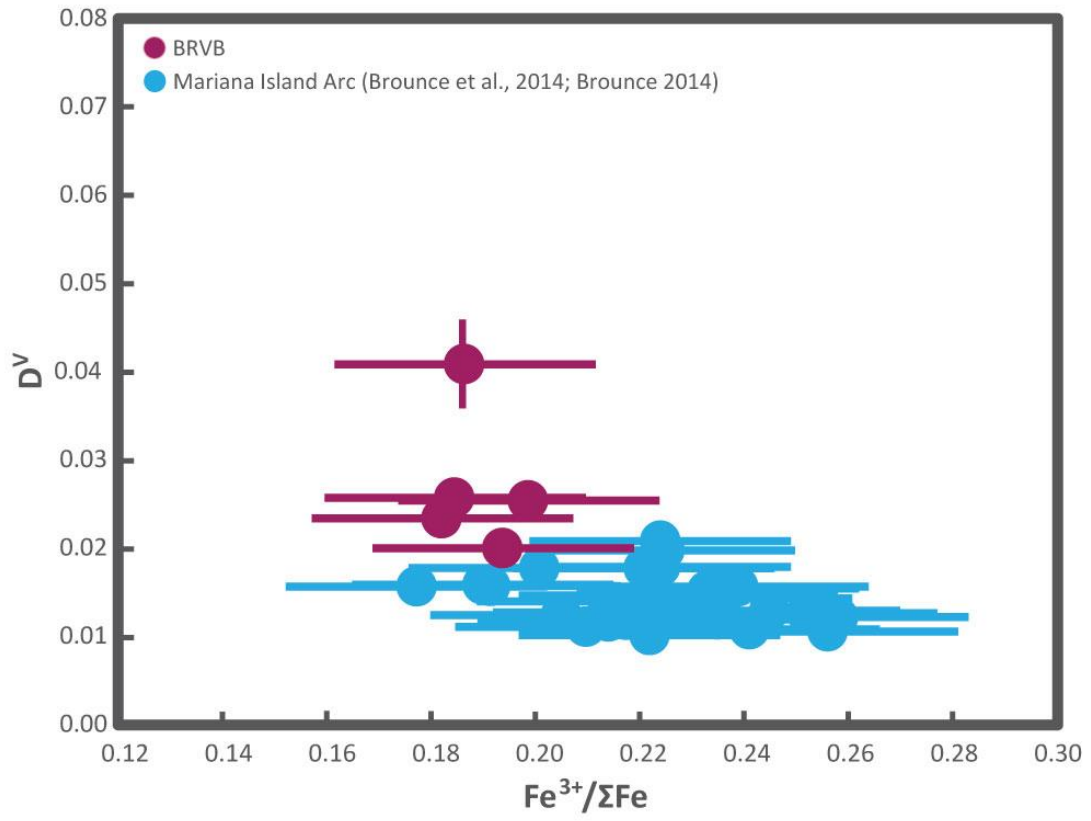


Figure 1A.5. Variations in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio with $D_v^{\text{oliv/melt}}$ for Basalt of Round Valley Butte (purple circles) and Mariana Island Arc (blue circles) melt inclusions.

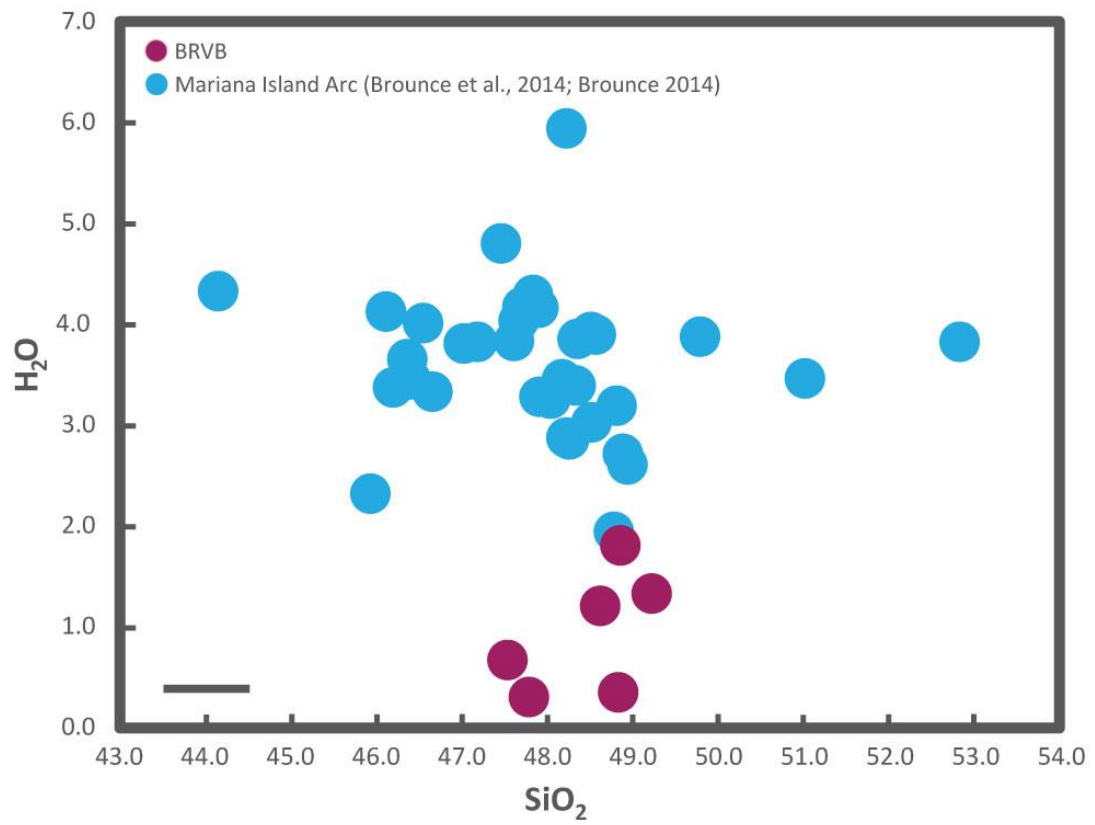


Figure 1A.6. Variations in SiO₂ with H₂O for Basalt of Round Valley Butte (purple circles) and Mariana Island Arc (blue circles) melt inclusions. Grey bar in lower left corner is max error for SiO₂. Circles are taller than the max error on H₂O.

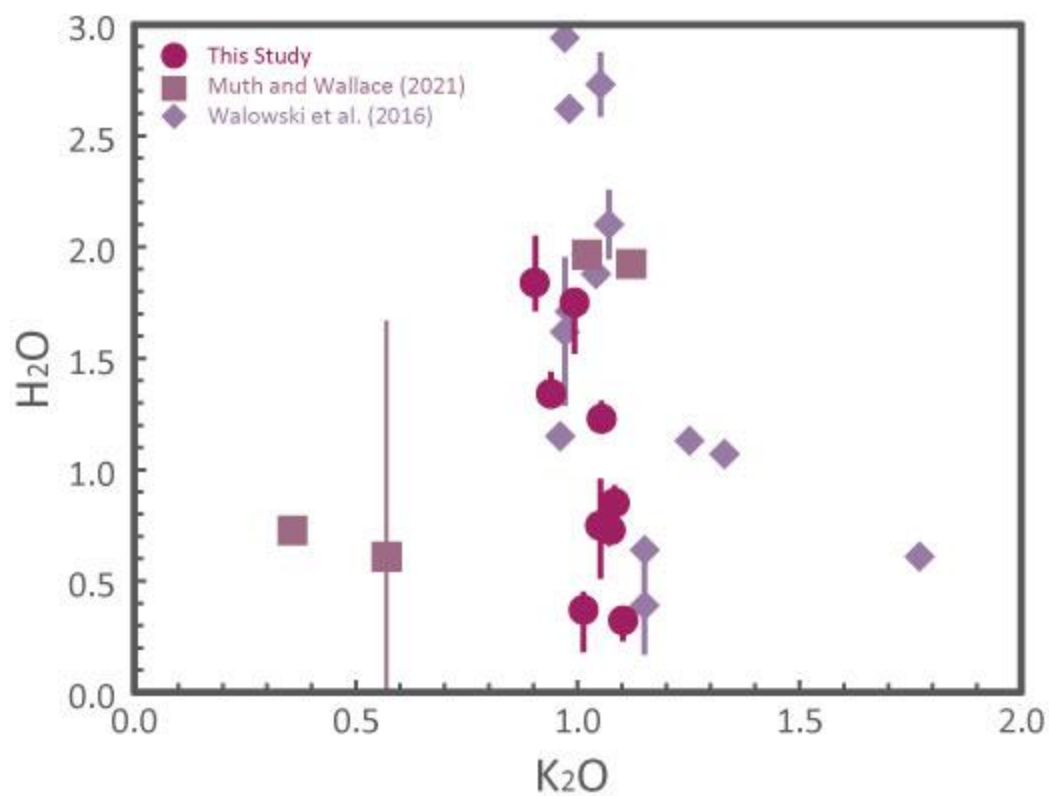


Figure 1A.7. Variations in non-post entrapment crystallization corrected H₂O content and K₂O content of Basalt of Round Valley Butte melt inclusions (this study; Muth and Wallace, 2021; Walowski et al., 2016).

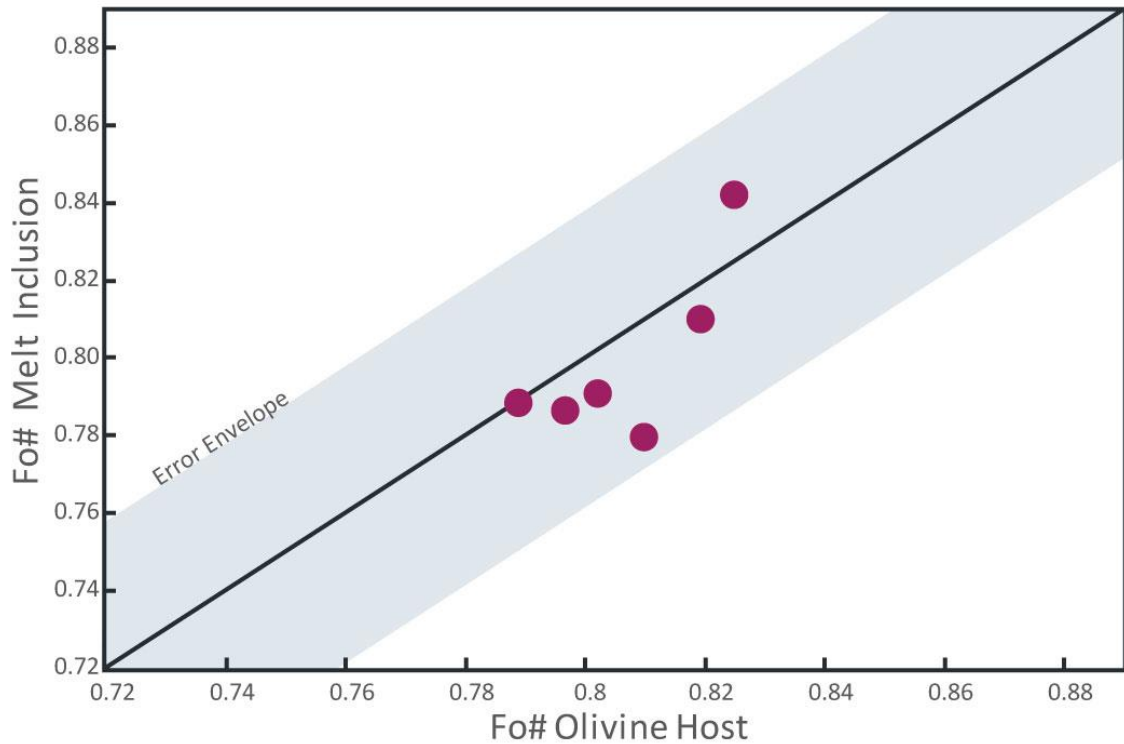


Figure 1A.8. Calculated Fo# of an equilibrium olivine host for each melt inclusion included in this study, using $KD = 0.27-0.29$ (Toplis, 2005) vs. the measured Fo# of the olivine host. Solid black line is a 1:1 relationship. Grey region represents the error envelope of the equilibrium Fo# calculation. The error envelope is calculated by propagating the average analytical error for FeO^* and MgO through the equations for calculating equilibrium Fo#. Any melt inclusion that falls below the 1:1 line is subject to post entrapment crystallization correction described in the main text, until the melt inclusion composition is in equilibrium with the composition of its olivine host. Any melt inclusion composition that falls above the 1:1 line, but lies within the error envelope, is left uncorrected.

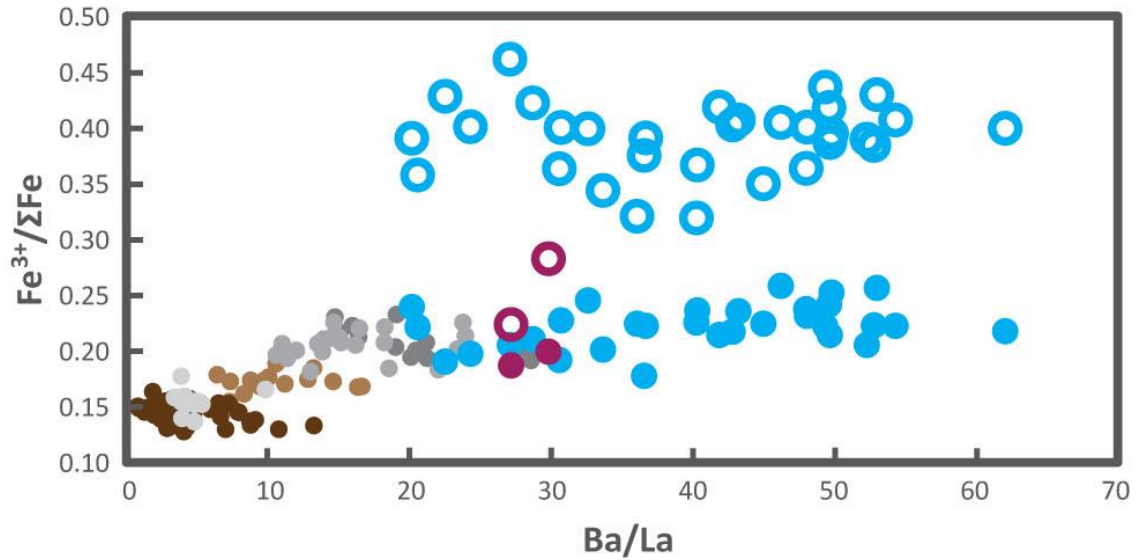


Figure 1A.9. Variations in Ba/La with $\text{Fe}^{3+}/\Sigma\text{Fe}$ for Basalt of Round Valley Butte (purple circles) and Mariana arc (blue circles; Brounce et al., 2014; Kelley and Cottrell, 2009, 2012; Zhang et al., 2018) melt inclusions. Closed circles are measured values and open circles are the values calculated from DVolv/melt. Light grey circles are forearc basaltic glasses from the Mariana Islands, medium grey is low silica boninite glasses, dark grey is high silica boninite glasses (Brounce et al., 2021; Coulthard et al., 2021), dark brown circles are MORB glasses (Kelley and Cottrell, 2009; Zhang et al., 2018), light brown circles are back-arc basin basalt glasses (Brounce et al., 2014; Kelley & Cottrell, 2009; Cottrell & Kelley, 2011, 2013; recalibrated after Zhang et al., 2018).

1A.3 Tables

Table 1A.3.1. Major and Trace Elements for olivines from the Basalt of Round Valley Butte

Olivine	BRVB 0105	BRVB 0108	BRVB 0109	BRVB 0112	BRVB 0202	BRVB 0204	BRVB 0205	BRVB 0208	BRVB 0209	BRVB 0211	BRV B0212
Major											
SiO ₂	39.09	38.72	39.04	39.75	39.96	39.30	39.30	39.46	39.35	39.11	39.41
Elements	1σ	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
FeO	13.89	14.46	13.93	13.37	14.53	15.04	15.01	14.17	13.17	15.00	15.06
1σ	0.68	0.71	0.68	0.66	0.71	0.74	0.74	0.70	0.65	0.74	0.74
MgO	45.17	45.40	45.32	45.50	44.52	43.91	45.28	44.94	46.03	44.40	44.36
1σ	0.005	0.005	0.005	0.005	0.004	0.004	0.005	0.004	0.005	0.004	0.004
CaO	0.10	0.10	0.11	0.11	0.11	0.11	0.11	0.12	0.10	0.12	0.11
1σ	0.09	0.08	0.09	0.09	0.09	0.09	0.10	0.10	0.08	0.10	0.09
MnO	0.22	0.22	0.22	0.18	0.25	0.22	0.23	0.21	0.20	0.23	0.24
1σ	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.02	0.02
Fo#	0.85	0.85	0.85	0.86	0.85	0.84	0.84	0.85	0.86	0.84	0.84
Trace											
Li	ND	2.91	3.83	5.24	3.51	ND	ND	ND	ND	4.32	ND
Elements	(± ppm)	0.27	0.55	0.52	-0.86	---	---	---	---	0.52	---
Sc	ND	7.02	11.32	10.72	8.73	ND	ND	ND	6.54	15.14	ND
(± ppm)	---	+0.76	0.81	0.62	+0.91	---	---	---	0.24	0.81	---
V	ND	5.93	5.80	9.82	5.73	ND	ND	ND	5.22	8.16	ND
(± ppm)	---	+0.60	0.55	0.58	+2.67	---	---	---	0.19	0.58	---
Cr	ND	183.56	206.17	310.65	159.11	ND	ND	ND	ND	151.79	ND
(± ppm)	---	-0.48	5.08	4.47	-0.98	---	---	---	---	4.03	---
Co	ND	231.95	181.96	210.91	199.22	ND	ND	ND	ND	208.32	ND

(± ppm)	---	1.95	3.06	2.67	+13.86 -15.41	---	---	---	---	---	2.93	---
Ni (ppm)	ND	2050.3	2243.1	3208.8	1679.6 +199.6	ND	ND	ND	ND	ND	1232.4	ND
(± ppm)	---	12.48	23.16	22.51	193.04	---	---	---	---	---	15.27	---
Cu (ppm)	ND	3.11	3.12	3.66	2.84 +1.03	ND	ND	ND	ND	ND	49.45	ND
(± ppm)	---	0.44	0.80	0.68	-0.89	---	---	---	---	---	2.68	---
Zn (ppm)	ND	128.47	147.53	184.36	150.47 +23.68	ND	ND	ND	ND	ND	139.38	ND
(± ppm)	---	3.47	6.62	5.97	-19.13	---	---	---	---	---	5.74	---
Ga (ppm)	ND	0.26	11.03	0.96	0.41 +0.67	ND	ND	ND	ND	ND	15.29	ND
(± ppm)	---	0.07	0.78	0.19	0.31	---	---	---	---	---	0.83	---
As (ppm)	ND	14.82	416.50	26.94	15.12 +20.91	ND	ND	ND	ND	ND	649.52	ND
(± ppm)	---	1.15	10.74	2.22	-13.24	---	---	---	---	---	12.00	---
Rb (ppm)	ND	0.28	11.92	0.73	0.48 +1.42	ND	ND	ND	ND	ND	14.92	ND
(± ppm)	---	0.07	0.76	0.16	0.45	---	---	---	---	---	0.76	---
Sr (ppm)	ND	0.21	15.03	3.83	1.36 +3.37	ND	ND	ND	ND	0.19	16.59	ND
(± ppm)	---		0.82	0.34	-1.26	---	---	---	---	0.03	0.77	---
Y (ppm)	ND	0.09	0.79	0.23	0.16 +0.15	ND	ND	ND	ND	0.11	0.53	ND
(± ppm)	---	0.04	0.20	0.09	-0.09	---	---	---	---	0.03	0.14	---
Zr (ppm)	ND	0.50	64.95	2.11	1.24 +1.97	ND	ND	ND	ND	ND	34.69	ND
(± ppm)	---	0.13	2.69	0.39	1.08	---	---	---	---	---	1.76	---
Nb (ppm)	ND	ND	0.23	ND	ND	ND	ND	ND	ND	ND	ND	ND
(± ppm)	---	---	0.11	---	---	---	---	---	---	---	---	---

Ba	(ppm)	ND	1.65	105.90	12.24	3.28	ND	ND	ND	ND	11.80	ND
	(± ppm)	---	0.40	5.57	1.53	+4.83 -2.86	---	---	---	---	1.66	---
La	(ppm)	ND	ND	0.80	0.18	0.09	ND	ND	ND	0.03	ND	ND
	(± ppm)	---	---	0.17	0.07	+0.10 -0.06	---	---	---	0.01	---	---
Ce	(ppm)	ND	0.05	1.46	0.42	0.17	ND	ND	ND	0.02	0.21	ND
	(± ppm)	---	0.01	0.23	0.10	+0.20 -0.15	---	---	---	0.01	0.08	---
Pr	(ppm)	ND	ND	0.16	ND	0.04	ND	ND	ND	ND	ND	ND
	(± ppm)	---	---	0.07	---	0.02	---	---	---	---	---	---
Hf	(ppm)	ND	ND	1.08	0.60	0.26	ND	ND	ND	ND	ND	ND
	(± ppm)	---	---	0.36	0.22	+0.13 -0.12	---	---	---	---	---	---
²⁰⁶ Pb	(ppm)	ND	0.88	ND	ND	ND	ND	ND	ND	1.02	ND	ND
	(± ppm)	---	0.11	---	---	---	---	---	---	0.12	---	---
²⁰⁷ Pb	(ppm)	ND	0.17	ND	ND	ND	ND	ND	ND	2.94	ND	ND
	(± ppm)	---	2.16	---	---	---	---	---	---	0.23	---	---
²⁰⁸ Pb	(ppm)	ND	1.26	8.12	1.79	5.43	ND	ND	ND	2.05	11.37	ND
	(± ppm)	---	0.21	0.72	0.27	+19.23 -4.93	---	---	---	0.12	0.76	---
Th	(ppm)	ND	ND	0.25	0.12	0.06	ND	ND	ND	ND	ND	ND
	(± ppm)	---	---	0.10	0.06	+0.04 -0.02	---	---	---	---	---	---
U	(ppm)	ND	ND	0.20	ND	0.04	ND	ND	ND	ND	0.17	ND
	(± ppm)	---	---	0.08	---	+0.02 -0.01	---	---	---	---	0.07	---

Table 1A.3.2. Trace elements for melt inclusions from Basalt of Round Valley Butte

Sample	Li		Be		Sc		V		Cr		Co	
	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)
BRV/B0108	ND	---	ND	---	29.81	0.65	252.71	2.82	ND	---	ND	---
BRV/B0109	9.21	0.79	ND	---	28.75	1.28	228.23	5.45	61.07	3.52	27.86	1.17
BRV/B0112A	7.99	-0.01	1.18	0.56	27.38	-1.62	240.28	-12.44	68.94	-4.49	28.41	-1.73
BRV/B0202	ND	---	ND	---	28.82	-0.65	222.62	-6.96	ND	---	ND	---
BRV/B0209	ND	---	ND	---	25.67	0.73	260.57	3.58	ND	---	ND	---
BRV/B0211A	ND	---	ND	---	ND	---	ND	---	ND	---	ND	---

Sample	Ni		Cu		Zn		Ga		As		Rb	
	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)
BRV/B0108	ND	---	ND	---	ND	---	ND	---	ND	---	ND	---
BRV/B0109	50.05	3.11	24.52	1.96	108.61	5.68	57.12	1.91	ND	---	21.21	1.01
BRV/B0112A	79.99	-8.77	77.55	-30.98	96.05	-12.99	54.45	-4.14	6.17	1.18	18.59	-2.51
BRV/B0202	ND	---	ND	---	ND	---	ND	---	ND	---	ND	---
BRV/B0209	ND	---	ND	---	ND	---	ND	---	ND	---	ND	---
BRV/B0211A	ND	---	ND	---	ND	---	ND	---	ND	---	ND	---

Sample	Sr		Y		Zr		Nb		Cs		Ba	
	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)
BRV/B0108	469.01	4.74	23.35	0.52	ND	---	ND	---	ND	---	ND	---
BRV/B0109	566.07	12.10	25.74	1.12	168.77	5.24	9.11	0.64	0.54	0.11	436.57	13.50
BRV/B0112A	574.78	+49.92	23.74	+3.18	162.79	+12.02	9.61	+1.47	0.39	+0.14	424.43	+42.96
		-47.73		-3.00		11.41		-1.37		-0.13		-40.88
BRV/B0202	446.43	+14.81	21.66	+0.79	ND	---	ND	---	ND	---	ND	---
BRV/B0209	551.18	-13.36	24.20	-0.74	ND	---	ND	---	ND	---	ND	---
BRV/B0211A	ND	6.82	ND	0.66	ND	---	ND	---	ND	---	ND	---

Sample	La		Ce		Pr		Nd		Sm		Eu	
	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)
BRV/B0108	15.91	0.36	38.14	0.60	5.08	0.17	22.16	0.85	4.96	0.43	1.54	0.12
BRV/B0109	14.63	0.70	35.38	1.19	4.56	0.33	20.45	+2.86	4.70	+0.98	1.58	+0.34
BRV/B0112A	15.61	+1.62	36.55	+3.67	5.10	+0.54	21.11	-2.09	4.94	-0.78	1.58	-0.32
		-1.53		-3.49		-0.50		+4.68		+1.47		0.43
BRV/B0202	13.97	+1.21	32.04	+2.62	4.05	+0.27	18.11	-3.56	4.24	-1.33	1.18	+0.17
BRV/B0209	18.30	1.26	42.82	-2.66	5.58	-0.06	24.19	+1.97	5.16	-0.77	1.63	-0.14
		0.49		0.80		0.22		-1.93		0.54		0.15
BRV/B0211A	ND	---	ND	---	ND	---	ND	---	ND	---	ND	---

Sample	Gd		Tb		Dy		Ho		Er		Tm	
	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)
BRV/B0108	5.10	0.45 +1.09	0.73	0.07	4.04	0.31	0.87	0.07	2.25	0.20	0.34	0.05
BRV/B0109	5.08	-0.89 +1.04	0.70	0.14 +0.23	4.16	0.67 +0.99	0.96	0.17 +0.19	2.35	0.45 +0.64	0.25	0.09 +0.16
BRV/B0112A	4.69	-1.03 +0.87	0.74	-0.20 +0.11	4.37	-0.91 +0.79	0.88	-0.18 +0.25	2.45	-0.58 +0.57	0.36	0.14 +0.09
BRV/B0202	3.93	-0.72	0.62	-0.09	3.65	-0.60	0.80	-0.18	2.12	-0.38	0.34	0.07
BRV/B0209	5.58	0.58	0.78	0.08	4.39	0.40	0.88	0.09	2.44	0.26	0.34	0.06
BRV/B0211A	ND	---	ND	---	ND	---	ND	---	ND	---	ND	---

Sample	Yb		Lu		Hf		Ta		Pb		Th	
	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)
BRV/B0108	2.17	0.24	0.35	0.05	ND	---	ND	---	7.92	+0.67 -0.96	1.65	0.11
BRV/B0109	1.91	0.48 +0.52	0.30	0.09 +0.11	2.88	0.54 +0.67	0.36	0.11 +0.14	11.19	0.80	1.44	0.23 +0.34
BRV/B0112A	2.29	-0.55 +0.55	0.31	-0.10 +0.07	3.17	-0.62	0.53	0.13	ND	---	1.77	-0.31 +0.28
BRV/B0202	2.15	-0.38	0.31	-0.05	ND	---	ND	---	10.22	-6.64	1.75	-0.31
BRV/B0209	2.26	0.30	0.37	0.06	ND	---	ND	---	4.66	0.58	1.86	0.15
BRV/B0211A	ND	---	ND	---	ND	---	ND	---	ND	---	ND	---

Sample	U (ppm)	U ($\pm$ ppm)
BRV/B0108	0.58	0.06
BRV/B0109	0.46	0.12 +0.15 -0.14 +0.08 -0.07
BRV/B0112A	0.56	
BRV/B0202	0.58	
BRV/B0209	0.59	0.07
BRV/B0211A	ND	---

Table 1A.3.3. Calculated and non-elemental values from melt inclusion compositions

	D _v	T* °C	T* (no PEC) °C	min. diameter μ m	max. diameter μ m	vapour bubble (Y/N)	phases in MI (Y/N)
BRV/B0108	0.02	1104	1089	65	100	y	N
BRV/B0109	0.03	1091	1055	55	75	y	Y
BRV/B0112A	0.04	1079	1080	105	195	y	Y
BRV/B0202	0.03	1084	1090	80	200	y	Y
BRV/B0209	0.02	1104	1109	80	110	y	N
BRV/B0211A	ND	1081	1095	85	140	y	Y

Table 1A.3.4. Major and trace elements for Mariana Arc olivines from (Brounce, 2014)

Volcano	Olivine Sample	Major Elements					
		SiO ₂ (wt%)	FeO (wt%)	MnO (wt%)	MgO (wt%)	NiO (wt%)	Fo#
Sarigan	SAR115-04-03	39.46	13.69	0.24	45.45	0.11	0.86
	SAR115-04-07	39.30	13.19	0.20	45.59	0.12	0.86
	SAR115-04-11	39.85	14.67	0.26	44.74	0.10	0.84
	SAR115-04-15	39.40	15.66	n.d.	44.42	0.10	0.83
	SAR115-04-17	40.08	14.30	n.d.	45.67	0.10	0.85
	SAR115-04-18	39.99	13.07	n.d.	46.47	0.12	0.86
	SAR115-04-19	39.98	13.39	n.d.	46.40	0.12	0.86
	SAR115-04-21	39.72	14.43	n.d.	45.28	0.11	0.85
	SAR115-04-22	39.72	15.01	n.d.	45.01	0.10	0.84
	SAR115-04-23	39.99	13.35	n.d.	46.19	0.11	0.86
	SAR115-04-24	40.20	12.90	n.d.	47.04	0.12	0.87
	SAR115-04-25	39.61	14.09	n.d.	45.48	0.11	0.85
	SAR115-04-27	39.67	13.45	n.d.	46.81	0.11	0.86
	SAR115-04-29	39.75	13.08	n.d.	47.03	0.13	0.87
	SAR115-04-31A	39.91	13.24	n.d.	46.64	0.11	0.86
SAR115-04-33	39.16	16.96	n.d.	43.94	0.09	0.82	
SAR115-04-34	39.97	13.57	n.d.	46.48	0.10	0.86	
Guagan	GUG11-02	39.87	14.35	n.d.	45.47	0.10	0.85
	GUG11-04	39.77	15.89	n.d.	44.71	0.09	0.83
Pagan	PAGA8-2	39.83	14.82	n.d.	45.02	0.11	0.84
Alamagan	ALA-02-01	39.66	12.74	n.d.	47.45	0.12	0.87
	ALA-02-03	39.33	15.14	n.d.	45.31	0.10	0.84
	ALA-02-04	39.57	14.28	n.d.	45.79	0.11	0.85
	ALA-02-05	39.65	15.25	n.d.	45.95	0.12	0.84
	ALA-02-07	39.61	15.16	n.d.	45.66	0.09	0.84
	ALA-02-08	39.88	12.47	n.d.	47.57	0.13	0.87

	ALA-02-09	39.50	14.69	n.d.	45.49	0.10	0.85
	ALA02-11	39.89	12.44	n.d.	47.00	0.11	0.87
	ALA02-15	39.85	13.06	n.d.	46.96	0.12	0.87
	ALA02-16A	38.20	23.90	n.d.	37.57	0.05	0.74
	ALA-03-01	39.59	15.34	n.d.	45.27	0.08	0.84
	ALA-03-02	38.61	21.02	n.d.	40.58	0.03	0.77
	ALA-03-08	38.21	19.82	n.d.	40.69	0.08	0.79
Agrigan	AGR07-04	38.93	18.65	0.32	42.43	0.03	0.80
	AGR07-06	39.15	18.94	n.d.	42.41	0.03	0.80
	AGR07-09	38.84	18.59	n.d.	42.45	0.03	0.80
	AGR07-15A	38.95	19.12	n.d.	42.22	0.03	0.80
	AGR07-15B	38.95	19.12	n.d.	42.22	0.03	0.80
	AGR05-01	37.98	24.54	n.d.	38.22	0.03	0.74
	AGRI04-05	39.43	17.50	n.d.	43.37	0.04	0.82
	AGRI04-07	39.60	18.52	n.d.	41.93	0.04	0.80
	AGRI04-11	39.42	18.48	n.d.	41.54	0.04	0.80
	AGRI04-12	39.24	19.84	n.d.	40.76	0.03	0.79
	AGRI04-13	39.05	18.90	n.d.	41.45	0.02	0.80
	AGRI04-14	39.03	16.96	n.d.	43.17	0.05	0.82

Trace Elements										
Li (ppm)	Sc (ppm)	V (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)
0.87	9.03	3.08	60.54	185.25	846.88	3.36	99.15	0.04	0.04	0.03
0.84	8.79	2.79	68.69	190.69	943.71	3.24	82.74	0.16	0.04	0.03
0.94	8.80	3.16	43.65	185.96	761.32	3.46	86.57	-0.11	0.05	0.07
1.25	7.52	3.81	49.47	220.75	853.38	4.08	112.41	0.01	0.04	0.03
0.71	9.96	3.97	45.19	215.22	856.49	3.60	112.08	0.00	0.05	0.01
1.08	6.81	3.10	82.44	198.18	966.47	3.77	102.07	0.05	0.03	0.02
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

1.09	7.41	3.76	49.71	215.70	882.02	4.03	101.01	0.10	0.04	0.03
1.42	7.10	4.09	65.80	222.72	940.36	4.77	128.24	0.15	0.05	0.03
1.11	7.42	3.00	65.33	200.09	885.92	3.57	99.10	0.02	0.05	0.01
0.86	9.18	2.63	75.70	181.54	924.19	3.08	86.18	0.01	0.05	0.02
1.02	7.99	3.18	35.24	197.17	816.50	3.70	84.52	0.08	0.06	0.02
1.14	7.35	3.37	72.98	202.66	921.59	3.80	95.89	0.06	0.04	0.01
1.10	6.80	2.82	139.61	190.38	1033.69	3.82	88.46	0.08	0.03	0.01
0.84	8.96	3.07	64.87	181.68	887.96	3.07	75.53	0.03	0.04	0.04
0.93	9.48	3.37	30.68	197.69	696.06	3.87	109.82	0.03	0.05	0.02
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
0.76	10.63	3.43	34.19	184.75	623.16	2.56	82.49	0.03	0.07	0.00
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2.56	10.49	6.70	72.03	220.56	659.79	8.40	155.83	0.14	0.12	0.09
1.03	7.31	3.76	33.30	214.67	831.21	2.95	111.93	0.11	0.05	0.03
1.49	8.27	4.30	39.36	217.87	732.43	3.39	123.03	0.00	0.06	0.03
1.14	7.97	4.19	20.78	221.67	796.10	2.79	117.46	0.03	0.04	0.03
1.08	8.31	2.62	51.41	169.56	781.48	2.15	69.40	0.01	0.04	0.02
0.95	9.08	3.94	22.99	209.94	803.20	2.64	105.82	0.00	0.04	0.05
1.05	8.06	2.97	32.09	178.81	712.43	2.35	77.77	0.02	0.05	0.01
1.06	7.82	3.04	31.45	188.27	735.17	3.03	87.74	0.02	0.04	0.01
0.97	8.51	3.79	18.72	193.07	659.15	2.35	90.05	0.00	0.04	0.01
1.22	7.51	3.49	91.44	181.06	913.40	2.41	76.23	0.18	0.04	0.03
1.09	7.45	4.04	29.87	209.62	759.80	2.71	94.32	0.01	0.04	0.01
0.81	10.20	3.68	48.42	206.98	891.12	2.41	100.24	0.01	0.05	0.09
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1.14	11.45	4.20	19.82	213.04	280.51	2.65	101.36	0.04	0.09	0.02
0.93	10.52	3.94	9.94	234.35	244.83	3.50	101.14	0.02	0.08	0.04
1.14	11.45	4.20	19.82	213.04	280.51	2.65	101.36	0.04	0.09	0.02
0.93	10.52	3.94	9.94	234.35	244.83	3.50	101.14	0.02	0.08	0.04
0.93	10.52	3.94	9.94	234.35	244.83	3.50	101.14	0.02	0.08	0.04

1.75	11.74	5.26	8.96	230.17	177.48	3.60	137.78	0.03	0.11	0.05
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1.35	9.47	3.81	19.48	217.67	252.76	9.02	86.84	0.24	0.14	0.21
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1.29	10.36	4.06	15.39	206.04	228.22	3.14	83.98	0.07	0.07	0.04
1.26	9.01	5.07	23.27	214.27	451.69	3.55	85.74	0.58	0.07	0.18

Table 1A.3.5. Values for DCompress (Burgisser et al., 2015) and Bucholz et al. (2013) model runs

	Modeled Sample	BRVB	BRVB	BRVB	BRVB
DCompress Initial values	Degassing Style	Closed	Open	Closed	Open
	Chemical System	C-S-O-H	C-S-O-H		
	ΔNNO	1.2	1.2	---	---
	H ₂ O (wt%)	3.8	3.8	---	---
	CO ₂ (ppm)	550	550	---	---
	S (ppm)*	2145	2145	---	---
	P (bars)	1800	1800	---	---
DCompress Output at 1 bar	T (°C)	1100	1100	---	---
	ΔNNO	-0.44	-1.12	---	---
	H ₂ O (wt%)	0.06	0.06	---	---
	CO ₂ (ppm)	0	0	---	---
	S (ppm)	613	929	---	---
	P (bars)	1	1	---	---
Bucholz Input	T (°C)	1100	1100	1100	1100
	H ₂ O (wt%, internal)	3.8	3.8	2.9	2.9
	H ₂ O (wt%, external)	0.3	0.3	0.3	0.3
	ΔNNO (internal)	1.2	1.2	1.06	1.06
	ΔNNO (external)	-0.36	-0.36	-0.36	-0.36
	D/H (internal)	1.448568*10 ⁻⁰⁴	1.448568*10 ⁻⁰⁴	1.440780*10 ⁻⁰⁴	1.440780*10 ⁻⁰⁴
	D/H (external)	1.378476*10 ⁻⁰⁴	1.300596*10 ⁻⁰⁴	1.378476*10 ⁻⁰⁵	1.300596*10 ⁻⁰⁵
	Olivine radius (μm)	500	500	500	500
	Melt Inclusion radius (μm)	42.5	42.5	42.5	42.5

* initial value calculated by D-Compress

BRVB	BRVB	Sarigan	Sarigan	Agrigan	Agrigan
Closed	Open	Closed	Open	Closed	Open
C-S-O-H	C-S-O-H	C-S-O-H	C-S-O-H	C-S-O-H	C-S-O-H
-0.3	-0.3	2	2	2.8	2.8
3.8	3.8	5	5	6	6
500	500	1200	1200	280	280
3016	3016	2974	2974	2895	2895
1800	1800	3000	3000	3000	3000
1100	1100	1020	1020	1030	1030
-1.27	-1.22	-0.30	-0.90	0.32	-0.74
0.06	0.06	0.06	0.06	0.06	0.06
0	0	0	0	0	0
691	938	636	933	590	910
1	1	1	1	1	1
1100	1100	1020	1020	1030	1030
3.8	3.8	5	5	6	6
0.3	0.3	0.5	0.5	0.3	0.3
0	0	2	2	2.8	2.8
-0.7	-0.7	0.2	0.2	0.3	0.3
1.448568*10^-04	1.448568*10^-04	1.44078*10^-04	1.44078*10^-04	1.44857*10^-04	1.44857*10^-04
1.378476*10^-04	1.300596*10^-04	1.39405*10^-04	1.31617*10^-04	1.38626*10^-04	1.27723*10^-04
500	500	500	500	500	500
42.5	42.5	42.5	42.5	42.5	42.5

Agrigan	Closed	CO ₂ (melt) (ppm)	1200	1162	1126	1093	1060	993	958
		S _(melt) (ppm)	2974	2973	2972	2972	2971	2969	2968
		P (bar)	3000	2976	2949	2925	2901	2851	2824
		fO ₂	1.36E-07	1.35E-07	1.34E-07	1.32E-07	1.31E-07	1.28E-07	1.27E-07
		H ₂ O (melt) (wt%)	6.00	5.98	5.96	5.95	5.93	5.88	5.85
	Open	CO ₂ (melt) (ppm)	280	258	236	218	202	172	159
		S _(melt) (ppm)	2895	2891	2886	2882	2877	2867	2860
		P (bar)	3000	2976	2949	2925	2901	2851	2824
		fO ₂	1.36E-07	1.35E-07	1.34E-07	1.33E-07	1.31E-07	1.29E-07	1.27E-07
		H ₂ O (melt) (wt%)	6.00	5.98	5.96	5.95	5.93	5.89	5.87
		CO ₂ (melt) (ppm)	280	256	233	213	194	157	140
		S _(melt) (ppm)	2895	2891	2886	2882	2878	2869	2863

1625	1600	1576	1551	1525	1500	1475	1450	1426	1400
2.88E-08	2.88E-08	2.87E-08	2.87E-08	2.86E-08	2.85E-08	2.84E-08	2.83E-08	2.82E-08	2.8E-08
3.78	3.77	3.77	3.76	3.75	3.75	3.74	3.73	3.72	3.70
384	362	341	319	297	276	256	236	218	200
2143	2143	2142	2142	2141	2140	2139	2138	2137	2136
1625	1600	1576	1551	1525	1500	1475	1450	1426	1400
2.89E-08	2.88E-08	2.88E-08	2.88E-08	2.87E-08	2.87E-08	2.86E-08	2.86E-08	2.85E-08	2.84E-08
3.78	3.78	3.77	3.77	3.77	3.76	3.76	3.75	3.75	3.74
381	358	336	313	290	267	245	223	202	180
2144	2143	2143	2143	2142	2142	2141	2141	2140	2140
1625	1600	1576	1551	1525	1500	1475	1450	1426	1400
9.38E-10	9.42E-10	9.47E-10	9.52E-10	9.58E-10	9.64E-10	9.71E-10	9.79E-10	9.87E-10	9.97E-10
3.77	3.77	3.76	3.76	3.75	3.74	3.73	3.72	3.70	3.69
337	316	295	275	254	234	216	197	181	165
2999	2995	2991	2986	2981	2975	2968	2960	2952	2943
1625	1600	1576	1551	1525	1500	1475	1450	1426	1400
9.35E-10	9.38E-10	9.42E-10	9.45E-10	9.49E-10	9.53E-10	9.57E-10	9.62E-10	9.68E-10	9.74E-10
3.78	3.77	3.77	3.77	3.76	3.76	3.75	3.74	3.74	3.73
333	311	289	267	244	222	200	178	158	137
3001	2999	2996	2993	2990	2986	2982	2978	2973	2968
2800	2774	2750	2726	2700	2676	2649	2625	2601	2575
1.51E-08	1.51E-08	1.5E-08	1.5E-08	1.49E-08	1.49E-08	1.48E-08	1.48E-08	1.47E-08	1.46E-08
4.97	4.96	4.96	4.95	4.95	4.94	4.94	4.93	4.92	4.92
932	899	869	840	808	779	749	721	694	665
2966	2965	2963	2962	2960	2958	2957	2955	2953	2950
2800	2774	2750	2726	2700	2676	2649	2625	2601	2575
1.51E-08	1.51E-08	1.51E-08	1.5E-08	1.5E-08	1.5E-08	1.49E-08	1.49E-08	1.49E-08	1.48E-08
4.97	4.97	4.96	4.96	4.96	4.95	4.95	4.94	4.94	4.93
927	892	862	831	798	769	736	707	679	647
2967	2966	2965	2964	2962	2961	2960	2959	2958	2956

2800	2774	2750	2726	2700	2676	2649	2625	2601	2575
1.25E-07	1.24E-07	1.22E-07	1.2E-07	1.19E-07	1.17E-07	1.15E-07	1.13E-07	1.12E-07	1.1E-07
5.83	5.80	5.78	5.75	5.72	5.69	5.66	5.63	5.60	5.57
148	137	128	120	112	106	99	94	89	84
2855	2848	2842	2835	2828	2822	2814	2807	2800	2792
2800	2774	2750	2726	2700	2676	2649	2625	2601	2575
1.26E-07	1.25E-07	1.23E-07	1.22E-07	1.2E-07	1.19E-07	1.17E-07	1.15E-07	1.14E-07	1.12E-07
5.84	5.82	5.80	5.77	5.74	5.72	5.69	5.66	5.63	5.60
125	111	98	87	76	67	58	51	44	38
2858	2852	2847	2841	2835	2828	2821	2815	2808	2800

1375	1351	1325	1301	1276	1250	1225	1200	1175	1151
2.79E-08	2.77E-08	2.75E-08	2.73E-08	2.7E-08	2.67E-08	2.64E-08	2.61E-08	2.57E-08	2.54E-08
3.69	3.67	3.66	3.64	3.61	3.59	3.56	3.53	3.50	3.47
182	167	151	138	125	113	102	93	84	77
2134	2133	2130	2128	2126	2123	2120	2116	2112	2108
1375	1351	1325	1301	1276	1250	1225	1200	1175	1151
2.84E-08	2.83E-08	2.82E-08	2.8E-08	2.79E-08	2.77E-08	2.75E-08	2.72E-08	2.69E-08	2.65E-08
3.73	3.72	3.71	3.70	3.69	3.67	3.65	3.63	3.60	3.57
158	138	117	97	79	60	44	31	20	13
2139	2138	2137	2136	2135	2133	2131	2128	2125	2121
1375	1351	1325	1301	1276	1250	1225	1200	1175	1151
1.01E-09	1.02E-09	1.03E-09	1.04E-09	1.06E-09	1.07E-09	1.08E-09	1.1E-09	1.11E-09	1.13E-09
3.67	3.65	3.63	3.61	3.58	3.55	3.53	3.49	3.46	3.43
149	136	123	112	101	92	83	76	69	63
2932	2922	2909	2897	2883	2868	2854	2838	2822	2807
1375	1351	1325	1301	1276	1250	1225	1200	1175	1151
9.81E-10	9.89E-10	9.99E-10	1.01E-09	1.02E-09	1.04E-09	1.06E-09	1.08E-09	1.11E-09	1.13E-09
3.72	3.71	3.70	3.68	3.66	3.64	3.61	3.58	3.55	3.51
117	98	79	62	47	34	23	15	10	6
2961	2954	2946	2936	2924	2909	2892	2873	2853	2832
2551	2524	2500	2474	2450	2426	2400	2375	2349	2324
1.46E-08	1.45E-08	1.44E-08	1.44E-08	1.43E-08	1.42E-08	1.41E-08	1.4E-08	1.39E-08	1.38E-08
4.91	4.90	4.89	4.88	4.87	4.86	4.85	4.84	4.83	4.81
639	612	587	560	537	514	489	467	445	423
2948	2946	2943	2940	2937	2934	2931	2927	2923	2919
2551	2524	2500	2474	2450	2426	2400	2375	2349	2324
1.48E-08	1.47E-08	1.47E-08	1.46E-08	1.46E-08	1.45E-08	1.45E-08	1.44E-08	1.44E-08	1.43E-08
4.93	4.92	4.92	4.91	4.91	4.90	4.90	4.89	4.88	4.87
619	589	561	531	505	478	450	423	396	370
2955	2953	2952	2950	2948	2947	2945	2943	2941	2939

2551	2524	2500	2474	2450	2426	2400	2375	2349	2324
1.08E-07	1.07E-07	1.05E-07	1.03E-07	1.02E-07	9.99E-08	9.82E-08	9.65E-08	9.49E-08	9.32E-08
5.54	5.51	5.48	5.44	5.41	5.38	5.35	5.31	5.28	5.25
79	75	71	68	65	62	59	56	54	51
2785	2777	2770	2762	2755	2747	2739	2731	2723	2715
2551	2524	2500	2474	2450	2426	2400	2375	2349	2324
1.1E-07	1.08E-07	1.07E-07	1.05E-07	1.03E-07	1.02E-07	9.97E-08	9.8E-08	9.63E-08	9.46E-08
5.57	5.54	5.51	5.47	5.44	5.41	5.38	5.34	5.31	5.27
33	29	25	21	19	16	14	12	10	9
2793	2786	2778	2770	2763	2755	2747	2739	2731	2723

1126	1101	1076	1050	1025	1001	976	950	925	901
2.5E-08	2.46E-08	2.42E-08	2.38E-08	2.33E-08	2.29E-08	2.24E-08	2.2E-08	2.15E-08	2.1E-08
3.43	3.40	3.36	3.32	3.28	3.24	3.20	3.15	3.11	3.06
70	64	58	54	49	45	42	38	36	33
2104	2099	2094	2089	2083	2078	2071	2065	2058	2051
1126	1101	1076	1050	1025	1001	976	950	925	901
2.61E-08	2.56E-08	2.51E-08	2.46E-08	2.41E-08	2.37E-08	2.31E-08	2.26E-08	2.21E-08	2.16E-08
3.53	3.48	3.44	3.40	3.35	3.30	3.26	3.21	3.16	3.11
8	5	3	2	1	1	0	0	0	0
2117	2112	2107	2102	2097	2091	2085	2079	2073	2067
1126	1101	1076	1050	1025	1001	976	950	925	901
1.14E-09	1.15E-09	1.17E-09	1.18E-09	1.19E-09	1.2E-09	1.21E-09	1.22E-09	1.23E-09	1.24E-09
3.39	3.36	3.32	3.28	3.24	3.20	3.16	3.11	3.07	3.03
58	53	49	45	42	39	36	33	31	28
2790	2774	2757	2740	2722	2706	2688	2670	2652	2635
1126	1101	1076	1050	1025	1001	976	950	925	901
1.16E-09	1.19E-09	1.22E-09	1.24E-09	1.27E-09	1.3E-09	1.33E-09	1.35E-09	1.38E-09	1.41E-09
3.47	3.43	3.39	3.34	3.30	3.26	3.21	3.17	3.12	3.07
4	3	2	1	1	0	0	0	0	0
2809	2787	2765	2742	2721	2700	2678	2656	2635	2615
2299	2275	2251	2224	2200	2175	2149	2124	2100	2075
1.37E-08	1.36E-08	1.34E-08	1.33E-08	1.32E-08	1.3E-08	1.29E-08	1.27E-08	1.26E-08	1.24E-08
4.80	4.78	4.77	4.75	4.74	4.72	4.70	4.68	4.66	4.64
403	384	366	347	331	314	298	282	269	255
2915	2911	2906	2901	2896	2890	2884	2878	2872	2866
2299	2275	2251	2224	2200	2175	2149	2124	2100	2075
1.43E-08	1.42E-08	1.41E-08	1.4E-08	1.4E-08	1.39E-08	1.38E-08	1.37E-08	1.36E-08	1.34E-08
4.87	4.86	4.85	4.84	4.83	4.82	4.81	4.80	4.78	4.77
345	320	296	271	249	226	203	181	161	142
2936	2934	2931	2928	2926	2922	2919	2915	2911	2906

2299	2275	2251	2224	2200	2175	2149	2124	2100	2075
9.16E-08	9E-08	8.85E-08	8.68E-08	8.54E-08	8.38E-08	8.22E-08	8.07E-08	7.92E-08	7.78E-08
5.21	5.18	5.15	5.11	5.08	5.05	5.01	4.98	4.94	4.91
49	47	45	43	42	40	38	37	35	34
2707	2699	2691	2682	2675	2666	2658	2649	2641	2633
2299	2275	2251	2224	2200	2175	2149	2124	2100	2075
9.29E-08	9.13E-08	8.97E-08	8.79E-08	8.64E-08	8.48E-08	8.32E-08	8.16E-08	8.01E-08	7.86E-08
5.24	5.21	5.17	5.14	5.11	5.07	5.03	5.00	4.96	4.93
8	7	6	5	4	4	3	3	2	2
2715	2707	2699	2690	2682	2673	2665	2656	2648	2640

875	851	825	800	775	750	725	701	675	651
2.06E-08	2.01E-08	1.96E-08	1.91E-08	1.86E-08	1.81E-08	1.76E-08	1.71E-08	1.66E-08	1.61E-08
3.02	2.97	2.92	2.87	2.82	2.77	2.72	2.67	2.62	2.56
31	28	26	24	23	21	20	18	17	16
2044	2036	2028	2020	2011	2002	1993	1983	1973	1962
875	851	825	800	775	750	725	701	675	651
2.11E-08	2.06E-08	2.01E-08	1.95E-08	1.9E-08	1.85E-08	1.8E-08	1.74E-08	1.69E-08	1.64E-08
3.06	3.01	2.96	2.91	2.86	2.81	2.75	2.70	2.64	2.59
0	0	0	0	0	0	0	0	0	0
2060	2054	2047	2040	2033	2025	2017	2009	2001	1992
875	851	825	800	775	750	725	701	675	651
1.25E-09	1.25E-09	1.26E-09	1.26E-09	1.27E-09	1.27E-09	1.27E-09	1.27E-09	1.27E-09	1.27E-09
2.98	2.94	2.89	2.84	2.79	2.74	2.69	2.64	2.59	2.54
26	25	23	21	20	18	17	16	15	14
2616	2598	2579	2561	2542	2522	2503	2483	2462	2442
875	851	825	800	775	750	725	701	675	651
1.43E-09	1.46E-09	1.48E-09	1.5E-09	1.53E-09	1.55E-09	1.57E-09	1.59E-09	1.61E-09	1.63E-09
3.02	2.98	2.93	2.88	2.83	2.78	2.72	2.67	2.62	2.56
0	0	0	0	0	0	0	0	0	0
2594	2574	2553	2532	2512	2492	2471	2451	2429	2409
2051	2025	2000	1974	1951	1924	1900	1875	1851	1826
1.23E-08	1.21E-08	1.19E-08	1.17E-08	1.16E-08	1.14E-08	1.12E-08	1.1E-08	1.08E-08	1.07E-08
4.62	4.59	4.57	4.54	4.52	4.49	4.47	4.44	4.41	4.38
243	230	219	207	198	187	178	170	162	154
2859	2852	2845	2837	2830	2821	2813	2806	2797	2789
2051	2025	2000	1974	1951	1924	1900	1875	1851	1826
1.33E-08	1.32E-08	1.3E-08	1.28E-08	1.27E-08	1.25E-08	1.23E-08	1.21E-08	1.18E-08	1.16E-08
4.75	4.73	4.72	4.69	4.67	4.65	4.62	4.59	4.56	4.53
124	106	90	75	63	51	42	33	27	21
2902	2896	2890	2883	2877	2868	2860	2852	2843	2833

2051	2025	2000	1974	1951	1924	1900	1875	1851	1826
7.64E-08	7.49E-08	7.34E-08	7.2E-08	7.06E-08	6.92E-08	6.78E-08	6.65E-08	6.52E-08	6.38E-08
4.88	4.84	4.80	4.77	4.74	4.70	4.66	4.63	4.59	4.56
33	32	30	29	28	27	26	25	24	24
2624	2616	2607	2598	2590	2581	2572	2563	2555	2546
2051	2025	2000	1974	1951	1924	1900	1875	1851	1826
7.71E-08	7.55E-08	7.4E-08	7.25E-08	7.12E-08	6.96E-08	6.82E-08	6.69E-08	6.55E-08	6.41E-08
4.90	4.86	4.82	4.79	4.75	4.71	4.68	4.64	4.61	4.57
2	2	1	1	1	1	1	1	1	1
2631	2623	2614	2605	2597	2588	2579	2570	2562	2553

626	600	576	550	526	500	475	450	426	400
1.56E-08	1.51E-08	1.46E-08	1.4E-08	1.36E-08	1.3E-08	1.25E-08	1.2E-08	1.14E-08	1.09E-08
2.51	2.45	2.40	2.34	2.28	2.22	2.15	2.09	2.02	1.95
15	14	13	12	11	10	9	8	8	7
1951	1939	1928	1914	1901	1887	1872	1857	1841	1823
626	600	576	550	526	500	475	450	426	400
1.58E-08	1.53E-08	1.48E-08	1.42E-08	1.37E-08	1.31E-08	1.25E-08	1.2E-08	1.14E-08	1.08E-08
2.53	2.47	2.42	2.35	2.29	2.23	2.17	2.10	2.04	1.96
0	0	0	0	0	0	0	0	0	0
1984	1974	1964	1954	1944	1932	1921	1908	1896	1882
626	600	576	550	526	500	475	450	426	400
1.27E-09	1.26E-09	1.26E-09	1.25E-09	1.24E-09	1.23E-09	1.21E-09	1.19E-09	1.17E-09	1.15E-09
2.48	2.42	2.37	2.31	2.25	2.19	2.13	2.07	2.00	1.93
13	12	11	10	10	9	8	7	7	6
2421	2399	2378	2354	2332	2307	2284	2259	2235	2207
626	600	576	550	526	500	475	450	426	400
1.64E-09	1.66E-09	1.67E-09	1.68E-09	1.69E-09	1.7E-09	1.7E-09	1.71E-09	1.7E-09	1.7E-09
2.51	2.45	2.39	2.33	2.28	2.21	2.15	2.09	2.02	1.95
0	0	0	0	0	0	0	0	0	0
2389	2367	2346	2324	2302	2280	2257	2233	2210	2185
1800	1775	1751	1726	1700	1675	1651	1625	1601	1575
1.05E-08	1.03E-08	1.01E-08	9.91E-09	9.72E-09	9.53E-09	9.35E-09	9.16E-09	8.98E-09	8.79E-09
4.35	4.32	4.29	4.26	4.23	4.20	4.17	4.14	4.10	4.07
146	140	133	127	121	115	110	105	100	96
2780	2771	2762	2753	2743	2734	2724	2714	2705	2694
1800	1775	1751	1726	1700	1675	1651	1625	1601	1575
1.14E-08	1.11E-08	1.09E-08	1.07E-08	1.04E-08	1.02E-08	9.95E-09	9.71E-09	9.49E-09	9.26E-09
4.50	4.46	4.43	4.40	4.36	4.32	4.29	4.25	4.21	4.18
17	13	10	8	6	5	4	3	3	2
2823	2812	2802	2791	2780	2769	2758	2746	2735	2724

1800	1775	1751	1726	1700	1675	1651	1625	1601	1575
6.25E-08	6.12E-08	5.99E-08	5.87E-08	5.74E-08	5.61E-08	5.49E-08	5.37E-08	5.25E-08	5.13E-08
4.52	4.48	4.45	4.41	4.37	4.34	4.30	4.26	4.23	4.19
23	22	21	20	20	19	18	18	17	17
2537	2528	2519	2510	2500	2491	2482	2472	2463	2453
1800	1775	1751	1726	1700	1675	1651	1625	1601	1575
6.28E-08	6.14E-08	6.01E-08	5.88E-08	5.75E-08	5.62E-08	5.5E-08	5.37E-08	5.25E-08	5.12E-08
4.53	4.50	4.46	4.43	4.39	4.35	4.31	4.27	4.24	4.20
0	0	0	0	0	0	0	0	0	0
2544	2535	2526	2517	2508	2498	2489	2480	2471	2461

376	350	325	300	275	251	225	200	175	150
1.04E-08	9.81E-09	9.27E-09	8.72E-09	8.18E-09	7.63E-09	7.06E-09	6.48E-09	5.91E-09	5.32E-09
1.89	1.81	1.74	1.66	1.58	1.50	1.41	1.32	1.23	1.12
6	6	5	5	4	4	3	3	3	2
1805	1786	1765	1742	1718	1692	1663	1631	1595	1555
376	350	325	300	275	251	225	200	175	150
1.03E-08	9.69E-09	9.1E-09	8.51E-09	7.92E-09	7.32E-09	6.69E-09	6.06E-09	5.43E-09	4.79E-09
1.90	1.82	1.75	1.67	1.59	1.51	1.42	1.32	1.23	1.13
0	0	0	0	0	0	0	0	0	0
1868	1852	1836	1818	1800	1780	1757	1732	1705	1675
376	350	325	300	275	251	225	200	175	150
1.12E-09	1.1E-09	1.07E-09	1.04E-09	1E-09	9.67E-10	9.26E-10	8.81E-10	8.33E-10	7.8E-10
1.87	1.79	1.72	1.65	1.57	1.49	1.40	1.31	1.21	1.11
6	5	5	4	4	3	3	3	2	2
2181	2151	2120	2087	2053	2016	1975	1930	1881	1827
376	350	325	300	275	251	225	200	175	150
1.69E-09	1.67E-09	1.65E-09	1.63E-09	1.6E-09	1.56E-09	1.51E-09	1.46E-09	1.39E-09	1.32E-09
1.88	1.81	1.73	1.66	1.58	1.50	1.41	1.32	1.22	1.12
0	0	0	0	0	0	0	0	0	0
2160	2133	2106	2078	2048	2017	1982	1946	1906	1862
1551	1525	1500	1476	1450	1425	1400	1376	1351	1325
8.62E-09	8.43E-09	8.25E-09	8.08E-09	7.9E-09	7.72E-09	7.55E-09	7.39E-09	7.22E-09	7.05E-09
4.04	4.00	3.97	3.93	3.90	3.86	3.83	3.79	3.75	3.72
92	88	84	80	77	73	70	67	64	61
2685	2674	2664	2654	2643	2632	2621	2610	2599	2588
1551	1525	1500	1476	1450	1425	1400	1376	1351	1325
9.04E-09	8.82E-09	8.59E-09	8.39E-09	8.17E-09	7.96E-09	7.76E-09	7.56E-09	7.37E-09	7.16E-09

4.14	4.10	4.06	4.03	3.99	3.95	3.91	3.87	3.83	3.79
2	1	1	1	1	1	0	0	0	0
2713	2701	2689	2678	2666	2654	2642	2631	2619	2606
1551	1525	1500	1476	1450	1425	1400	1376	1351	1325
5.02E-08	4.9E-08	4.79E-08	4.68E-08	4.56E-08	4.45E-08	4.34E-08	4.24E-08	4.14E-08	4.03E-08
4.15	4.11	4.07	4.03	4.00	3.96	3.92	3.88	3.84	3.80
16	15	15	14	14	13	13	12	12	12
2444	2434	2424	2414	2404	2394	2384	2374	2364	2354
1551	1525	1500	1476	1450	1425	1400	1376	1351	1325
5.01E-08	4.89E-08	4.77E-08	4.66E-08	4.54E-08	4.42E-08	4.31E-08	4.21E-08	4.1E-08	3.99E-08
4.16	4.12	4.08	4.04	4.00	3.96	3.93	3.89	3.85	3.81
0	0	0	0	0	0	0	0	0	0
2452	2442	2433	2423	2413	2404	2394	2384	2374	2364

126	100	75	51	25	1	---	---	---	---
4.73E-09	4.09E-09	3.43E-09	2.73E-09	1.88E-09	5.77E-10	---	---	---	---
1.01	0.89	0.76	0.61	0.41	0.06	---	---	---	---
2	1	1	1	0	0	---	---	---	---
1508	1452	1382	1289	1137	613	---	---	---	---
126	100	75	51	25	1	---	---	---	---
4.13E-09	3.45E-09	2.74E-09	2E-09	1.16E-09	1.18E-10	---	---	---	---
1.02	0.89	0.76	0.60	0.40	0.06	---	---	---	---
0	0	0	0	0	0	---	---	---	---
1640	1597	1545	1475	1362	929	---	---	---	---
126	100	75	51	25	1	---	---	---	---
7.21E-10	6.53E-10	5.74E-10	4.79E-10	3.47E-10	8.65E-11	---	---	---	---
1.00	0.88	0.75	0.60	0.40	0.06	---	---	---	---
2	1	1	1	0	0	---	---	---	---
1765	1691	1601	1483	1297	691	---	---	---	---
126	100	75	51	25	1	---	---	---	---
1.23E-09	1.11E-09	9.78E-10	8.07E-10	5.62E-10	9.7E-11	---	---	---	---
1.01	0.89	0.75	0.60	0.40	0.06	---	---	---	---
0	0	0	0	0	0	---	---	---	---
1812	1753	1683	1591	1447	938	---	---	---	---
1300	1275	1250	1225	1200	1175	1151	1125	1101	1076
6.88E-09	6.72E-09	6.55E-09	6.39E-09	6.23E-09	6.07E-09	5.92E-09	5.77E-09	5.62E-09	5.47E-09
3.68	3.64	3.60	3.56	3.52	3.48	3.44	3.40	3.36	3.32
59	56	54	52	49	47	45	43	41	40
2576	2565	2553	2542	2530	2517	2505	2493	2481	2468
1300	1275	1250	1225	1200	1175	1151	1125	1101	1076
6.97E-09	6.78E-09	6.59E-09	6.41E-09	6.23E-09	6.04E-09	5.87E-09	5.7E-09	5.53E-09	5.36E-09
3.75	3.71	3.67	3.63	3.58	3.54	3.50	3.46	3.42	3.37
0	0	0	0	0	0	0	0	0	0
2594	2582	2570	2558	2545	2532	2520	2507	2495	2482

1300	1275	1250	1225	1200	1175	1151	1125	1101	1076
3.92E-08	3.82E-08	3.72E-08	3.62E-08	3.53E-08	3.43E-08	3.33E-08	3.24E-08	3.15E-08	3.06E-08
3.76	3.72	3.68	3.63	3.59	3.55	3.51	3.47	3.42	3.38
11	11	10	10	10	9	9	9	8	8
2343	2332	2322	2311	2300	2289	2278	2267	2256	2244
1300	1275	1250	1225	1200	1175	1151	1125	1101	1076
3.88E-08	3.78E-08	3.67E-08	3.57E-08	3.47E-08	3.37E-08	3.27E-08	3.17E-08	3.08E-08	2.98E-08
3.76	3.72	3.68	3.64	3.60	3.56	3.52	3.47	3.43	3.39
0	0	0	0	0	0	0	0	0	0
2354	2343	2333	2323	2312	2301	2291	2280	2269	2258

1051	1025	999	976	950	926	900	875	850	825
2.96E-08	2.87E-08	2.78E-08	2.7E-08	2.61E-08	2.53E-08	2.44E-08	2.36E-08	2.28E-08	2.2E-08
3.34	3.29	3.24	3.20	3.15	3.11	3.06	3.01	2.97	2.92
8	7	7	7	7	6	6	6	6	5
2232	2220	2208	2196	2183	2171	2158	2145	2132	2119
1051	1025	999	976	950	926	900	875	850	825
2.89E-08	2.79E-08	2.7E-08	2.62E-08	2.52E-08	2.44E-08	2.35E-08	2.26E-08	2.18E-08	2.1E-08
3.34	3.29	3.25	3.21	3.16	3.11	3.06	3.02	2.97	2.92
0	0	0	0	0	0	0	0	0	0
2247	2235	2223	2212	2200	2188	2176	2164	2151	2138

800	776	751	726	701	675	651	626	600	575
2.12E-08	2.04E-08	1.97E-08	1.89E-08	1.81E-08	1.74E-08	1.67E-08	1.59E-08	1.52E-08	1.45E-08
2.87	2.82	2.77	2.72	2.66	2.61	2.56	2.50	2.44	2.39
5	5	5	4	4	4	4	4	3	3
2105	2091	2077	2063	2048	2032	2017	2001	1984	1967
800	776	751	726	701	675	651	626	600	575
2.02E-08	1.94E-08	1.86E-08	1.78E-08	1.7E-08	1.62E-08	1.55E-08	1.48E-08	1.4E-08	1.33E-08
2.87	2.82	2.77	2.72	2.67	2.61	2.56	2.50	2.45	2.39
0	0	0	0	0	0	0	0	0	0
2125	2113	2099	2086	2072	2057	2043	2028	2013	1997

550	525	501	476	451	426	401	375	351	325
1.38E-08	1.32E-08	1.25E-08	1.19E-08	1.12E-08	1.06E-08	9.91E-09	9.27E-09	8.66E-09	8.05E-09
2.33	2.27	2.21	2.15	2.08	2.02	1.95	1.88	1.81	1.74
3	3	3	3	2	2	2	2	2	2
1950	1932	1914	1895	1875	1855	1833	1810	1787	1762
550	525	501	476	451	426	401	375	351	325
1.26E-08	1.19E-08	1.13E-08	1.06E-08	9.94E-09	9.29E-09	8.66E-09	8.01E-09	7.41E-09	6.81E-09
2.33	2.27	2.21	2.15	2.09	2.02	1.95	1.88	1.81	1.74
0	0	0	0	0	0	0	0	0	0
1981	1965	1948	1931	1913	1895	1876	1855	1835	1813

301	275	250	226	201	176	150	126	101	76
7.46E-09	6.85E-09	6.27E-09	5.71E-09	5.14E-09	4.58E-09	4.01E-09	3.47E-09	2.91E-09	2.36E-09
1.66	1.58	1.50	1.42	1.32	1.23	1.12	1.02	0.90	0.76
1	1	1	1	1	1	1	1	0	0
1736	1707	1677	1645	1610	1571	1526	1477	1418	1346
301	275	250	226	201	176	150	126	101	76
6.23E-09	5.64E-09	5.07E-09	4.53E-09	3.99E-09	3.46E-09	2.93E-09	2.43E-09	1.93E-09	1.45E-09
1.66	1.58	1.50	1.42	1.32	1.23	1.12	1.02	0.89	0.76
0	0	0	0	0	0	0	0	0	0
1791	1766	1740	1714	1684	1653	1617	1578	1532	1477

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51	25	1	1	1	1
4.27E-10	2.81E-10	6.61E-11	6.61E-11	6.61E-11	6.61E-11
0.60	0.41	0.06	0.06	0.06	0.06
1	1	0	0	0	0
1358	1192	636	636	636	636
51	25	1	1	1	1
2.49E-10	1.43E-10	1.51E-11	1.51E-11	1.51E-11	1.51E-11
0.60	0.40	0.06	0.06	0.06	0.06
0	0	0	0	0	0
1514	1388	933	933	933	933

51	25	1
1.8E-09	1.17E-09	3.56E-10
0.61	0.41	0.06
0	0	0
1251	1099	590
51	25	1
9.83E-10	5.08E-10	3.09E-11
0.61	0.41	0.06
0	0	0
1407	1297	910

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CHAPTER TWO

VOLATILES AND $f\text{O}_2$ FROM OLIVINE HOSTED MELT INCLUSIONS, EMBAYMENTS, AND MATRIX GLASSES AT PISGAH CRATER, MOJAVE DESERT, CALIFORNIA

J. Humphreys and M. Brounce

Abstract

The growth of continental lithosphere along Western North America has occurred through both tectonic accretion and magmatic addition during convergent margin tectonics. The margin transitioned from convergent to translation-extensional, and it is unknown the extent to which this extensional motion may thin and/or destroy the lithosphere. To place constraints on mechanisms of melt generation and storage and thus constrain crustal and lithospheric thicknesses in the Mojave block of this region, we present major, minor, and volatile element concentrations, $\text{S}^{6+}/\Sigma\text{S}$, and $\text{Fe}^{3+}/\Sigma\text{Fe}$ of naturally glassy olivine-hosted melt inclusions (Fo_{82-85}), embayments (melt inclusions that are not fully, physically isolated from the external melt), and matrix glass from Pisgah crater, a Quaternary-aged volcano in the Mojave Desert, California. Melt inclusions corrected for “Fe-loss” and the presence of a vapor bubble have 5.4 – 6.8 wt% MgO, 0.2 – 1.8 wt% H_2O , 940 – 5500 ppm CO_2 , 1090 – 1980 ppm S, 0.1 – 1.0 $\text{S}^{6+}/\Sigma\text{S}$ (corresponding to oxygen fugacities, or $f\text{O}_2$ s denoted relative to the quartz fayalite magnetite oxygen buffer, or ΔQFM , of +0.1 to +1.0), and 0.19 – 0.21 $\text{Fe}^{3+}/\Sigma\text{Fe}$ (ΔQFM = +0.4 to +0.9). Pisgah embayments have 2.6 – 4.6 wt% MgO, 0.2 – 1.0 wt% H_2O , 770 – 1900 ppm S, and 0.0 – 0.2 $\text{S}^{6+}/\Sigma\text{S}$ (ΔQFM = 0 to +0.2). Matrix glasses adhered to the outside of olivine crystals have 3.5 – 4.3 wt% MgO, 0.2 – 0.4 wt% H_2O , 0 – 640 ppm S, 0.0 $\text{S}^{6+}/\Sigma\text{S}$, and 0.29 – 0.35 $\text{Fe}^{3+}/\Sigma\text{Fe}$. Water, CO_2 and S relationships are broadly consistent with H_2O

degassing and possible magma mixing, though scatter in H₂O-CO₂ contents and variable H₂O at roughly constant K₂O may allow for the possibility of H⁺ loss from the inclusions after entrapment. Volatile contents are assumed to be representative of magmas stored in the crust, placing a minimum estimate of crustal thickness at 15 – 20 km. Estimates from Fo₉₀ calculations indicate that these melts last equilibrated with mantle peridotite at 78 – 87 km depth and 1323 – 1334°C. Trace element concentrations of these melt inclusions are enriched compared to E-MORB and trace element patterns are smooth, indicating that Pisgah magmas are generated by small degrees of melting of the mantle and that simple melting of peridotite is the primary control on the distribution of trace elements in this region. Calculated melt fraction calculations from modeled primary melt compositions indicate as low as 1.6 – 2.6 % melting. Mantle source H₂O concentrations calculated from the same modeled primary melt compositions indicate a maximum of ~580 ppm H₂O, similar to that of enriched MORB mantle (660 ± 184 ppm H₂O), and mantle source CO₂ concentrations at least as high as 321 ppm (though CO₂ degassing likely obscures the initial CO₂ composition of Pisgah magmas). The CO₂/Ba in Pisgah melt inclusions ranges from 2.0 – 38.8, where the range is driven by CO₂ degassing. None of our measurements reveal CO₂ undersaturated compositions, even after correcting for the presence of CO₂ in the vapor bubble. If we assume that the initial CO₂/Ba is equivalent to that found in depleted MORB mantle (120), then the CO₂ concentration of the mantle source of Pisgah magmas could be as high as 979 ppm. The elevated H₂O, CO₂, and trace element concentrations for Pisgah magmas, together with our calculated pressures and temperatures of melting, indicate that melting of a depleted mantle source in this region at somewhat cooler-than-ambient mantle potential temperatures is facilitated by

source mantle enrichments in volatiles, particularly CO₂. Depending on the exact concentration of CO₂ in the mantle source rock, melting may have initiated from as shallow as 85 km depth to 175 km depth. It is likely that mafic volcanism in the Basin and Range province is due to source mantle enrichments in CO₂.

2.1. Introduction

Earth is unique in the solar system in having high-standing continental lithosphere that contrasts with low-lying oceanic lithosphere, the latter of which is more like the lithospheres of other planets in this solar system. This continental lithosphere is thought to grow in the present day through ongoing tectonic accretion of oceanic plateaus, island arcs (e.g., Saleeby, 1983) onto the edges of cratonic lithosphere that formed early in Earth history through a style of petrogenesis that may no longer be taking place today but shares some compositional similarities with modern day subduction zone volcanism (e.g., Rudnick, 1995). Although subduction zone petrogenetic processes have left obvious marks on the western edge of North America (e.g., the Sierra Nevada batholith), the dominant mode of continental growth along the entire margin has been through tectonic accretion. This tectonic accretion and subduction zone magmatism occurred from the Jurassic to Cretaceous (~200 – 65 Ma; Saleeby, 1983) but today the margin is no longer convergent, and the lithosphere is possibly thinning in the southwest in response to microplate rotations and extension from transform motion (e.g., Atwater, 1970; Nicholson *et al.*, 1994). Once assembled, major uncertainties exist about the strength and durability of continental lithosphere, and the recent lithospheric deformation of Western North America provides an excellent natural laboratory to place constraints on lithospheric thickness, including changes in lithospheric thickness through time during transitions between convergent and non-convergent tectonics. Here we focus on young volcanism in the Mojave Desert block, specifically Pisgah Crater to determine the conditions of melt generation in the asthenosphere and magma storage in the lithosphere prior to eruption.

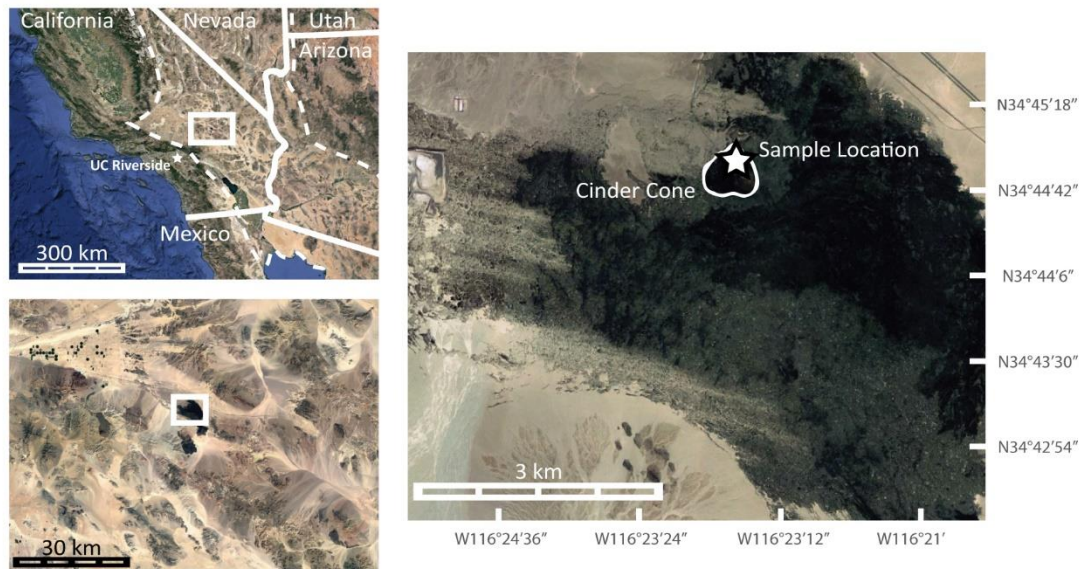


Figure 2.1. (A) Regional map of the southwestern North American Continent. United States State Borders and United States – Mexico borders are solid white lines. The Basin and Range Province is outlined in a white dashed line. Lavic Lake Volcanic Field in the Mojave Desert is outlined by the white, rectangular box. (B) Inset map from A. showing partial area of the Lavic Lake Volcanic field with Pisgah Crater at the center, outlined in white, rectangular box. (C) Inset map from B. showing an aerial view of Pisgah Crater with the cinder cone portion outlined in white. The sampling location is indicated with a star.

The cause of volcanism in the Mojave Desert and the greater Basin and Range Province (dashed lines, Fig. 2.1.A.) is thought to be driven by upwelling of asthenosphere to accommodate lithospheric thinning and subsequent decompression melting. Tectonically this region is complex, with the Basin and Range Province constituting a diffuse boundary between the North American and Pacific Plates (e.g., Atwater, 1970). Subduction beneath the Mojave Desert ended ~15-20 Ma (Atwater, 1970) but from ~15 Ma to ~5 Ma, mafic volcanic rocks from both the Mojave and greater Basin and Range Province retained chemical signatures of subduction, such as enrichments in large ion lithophile elements like Ba compared to the rare earth elements (e.g., high Ba/La) and depletions in high field strength elements (e.g., Nb, Ta, Ti, Hf, U, Lu, Y, Eu, La; Fitton *et al.*, 1991) compared

to melts derived solely through partial melting of peridotite outside of subduction zones. At ~5 Ma, strike-slip motion between the Pacific and North American Plates began (Atwater, 1970), and volcanic rocks erupted since then lack the enrichments in large ion lithophile elements and depletions in high field strength elements of the older rocks, indicating that the source of Basin and Range lavas (including those erupted at Pisgah) transitioned from dominantly subduction related prior to 5 Ma, to mixtures of an asthenospheric melt with some assimilation of a mafic lithosphere mantle or crust after 5 Ma (e.g., Fitton *et al.*, 1991; Glazner *et al.*, 1991).

Primary melts (i.e., modeled partial melts of the mantle asthenosphere in equilibrium with peridotite bearing olivine of Fo₉₀ composition) in the Basin and Range Province contain on average >1 wt% H₂O (Big Pine, Amboy, Pisgah, Snow Canyon, and Western Grand Canyon; Plank and Forsyth, 2016). This is higher than expected from ~dry decompression melting under spreading ridges in the ocean - primary Mid-Ocean Ridge Basalts (MORB) have 0.12 – 0.51 wt% H₂O (Sobolev, 1996). The elevated H₂O contents of Basin and Range magmas compared to MORB magmas could be explained by the following:

- 1) Low degrees of melting of a ~dry, low carbon mantle. Since H₂O is incompatible in mantle minerals and thus will preferentially enter a melt (e.g., Foley *et al.*, 2009; Rosenthal *et al.*, 2015; Adam *et al.*, 2016), low degree melting leads to melts of higher concentrations of all incompatible elements, including H₂O, than higher degree melts. The mantle may melt to a lower degree in the Basin and Range compared to at a Mid-Ocean Ridge because the continental lithosphere is relatively thick, necessitating that the asthenosphere melts at higher overall pressures, and ceases deeper (at the deep, continental lithosphere-asthenosphere boundary) than at a Mid-

Ocean Ridge. From the lithosphere-asthenosphere boundary, these melts would move into the lithosphere and H₂O contents would increase during fractional crystallization and/or decrease during volcanic degassing to the atmosphere.

2) Assimilation: The lithosphere may contain hydrated mineral assemblages from the long history of subduction in this region (Glazner *et al.*, 1991; Humphreys *et al.*, 2003). The mantle source may be dry like depleted MORB mantle and melt to a similar degree as at a Mid-Ocean Ridge, leading to primary melts of similar H₂O and CO₂ contents. Upon percolation through the lithosphere these melts may interact with Jurassic-aged hydrated and carbonated mineral assemblages in the lithosphere and perhaps assimilate these materials, increasing in H₂O contents during low pressure differentiation (Glazner *et al.*, 1991).

3) The mantle source itself may be more hydrous and/or carbonated than depleted MORB mantle and may melt to similar or lower degrees than at Mid-Ocean Ridge, which will yield primary Basin and Range melts of higher H₂O contents than Mid-Ocean Ridge. In this scenario, the mantle source would be presumed to be elevated in H₂O and/or CO₂ because of the long history of subduction in this region (e.g., Atwater, 1970; Saleeby, 1983). Melting in this region could initiate from the upwelling of a mantle asthenosphere due to the creation of accommodation space, either from the loss of the Farallon Slab from this region (e.g., Humphreys, 1995; Humphreys *et al.*, 2003; Lee, 2005) or from upwelling of mantle asthenosphere due to lithospheric deformation/thinning of the Basin and Range Province in response to motion along the San Andreas fault system (e.g., Atwater, 1970; Fitton *et al.*, 1991; Leeman and Harry, 1993; Nicholson *et al.*, 1994). Alternatively, decompression of the asthenosphere may not be substantial, and melting could be driven primarily

by the movement of remnant H₂O and/or CO₂ and associated depression of the ~dry peridotite solidus.

The solubility of H₂O and CO₂ in silicate magmas is proportional to the pressure and temperatures of the magma (Dixon *et al.*, 1995), such that as magmas approach 1 atmosphere of pressure and cool, H₂O and CO₂ will exsolve as a vapor phase and degas from the magmatic system. At surface pressures and temperatures, the volatile contents of subaerially erupted basalts will have degassed most of their H₂O and CO₂ and thus volatile measurements on basaltic glasses erupted into the atmosphere cannot be used to determine pre-eruptive volatile contents (Dixon and Stolper, 1995). Olivine-hosted melt inclusions can circumvent this problem since they are packets of magma which were trapped at the relatively higher pressures of olivine crystallization and isolated by the strength of the olivine from ambient magmatic decompression to 1 atmosphere during eruption. Thus glassy melt inclusions may be representative of magmatic compositions which have not yet degassed all the elevated volatile contents (e.g., Kelley *et al.*, 2006; Plank *et al.*, 2013; Brounce *et al.*, 2021; Muth and Wallace, 2021). However, melt inclusions are not immune to modification processes, including processes that are critical for this study's goals, such as H⁺ diffusion (Hauri, 2002; Portnyagin *et al.*, 2008; Gaetani *et al.*, 2012; Bucholz *et al.*, 2013; Lloyd *et al.*, 2013) and the formation of vapor bubbles by CO₂ exsolved during small pressure changes communicated through the olivine host (e.g., Anderson, 1974; Roedder, 1979). Investigating the volatile content of melt inclusions, including correcting for post-entrapment processes is a valuable tool that can provide constraints on the pressures and temperatures of melt generation and storage, and thus crust and lithosphere thickness, in the Basin and Range Province. This study examines the compositions

(including volatile contents) and oxidation states of olivine hosted melt inclusions, olivine hosted embayments, and corresponding matrix glasses of one Basin and Range Province volcano, Pisgah Crater, to characterize the volatile contents of these lavas. Through volatile characterization, the source of these elevated volatile contents and thus lithospheric evolution in the Basin and Range Province can be further constrained.

2.2. Geologic Background

Volcanism throughout the Mojave Desert began about 20 million years ago (Armstrong and Higgins, 1973). Pisgah crater, a cinder cone located in the Southwestern portion of the Mojave Desert (Fig. 2.1. C.; Wise, 1969; Glazner *et al.*, 1991) in the western part of the Basin and Range Province (e.g. Fitton *et al.*, 1991) erupted basaltic to basanitic magmas three times over the course of ~10-20 years from paleomagnetic data (quoted in (Glazner *et al.*, 1991). Cosmogenic ^{36}Cl and varnish dating both put the age of the oldest of the 3 eruptions at Pisgah at ~20 – 25 ka (Liu, 2003; Phillips, 2003). These eruptions roughly align with NW-SE faults in the area (Wise, 1969; Glazner *et al.*, 1991). As the eruptions decrease with age, the lavas trend increasingly crystalline rich and increasingly basaltic (i.e., less alkali rich) in whole rock composition (Glazner *et al.*, 1991).

2.3. Samples and Methods

2.3.1. Sample Description and Preparation

The tephra sampled in this study were collected from an exposed bed on the northwest, interior-facing side of Pisgah Crater (Fig. 2.1. C.). This tephra was washed in de-ionized water, dried, and progressively sorted by size using metal sieves of size No. 10, 20, and 200 mesh. Olivine grains coated in a black glass were handpicked from the sieved tephra for analysis and were

immersed in HBF_4 to remove the glass coating prior to identifying melt inclusions for study following the methods from Luhr (2001). Olivine grains in the tephra are subhedral to anhedral in habit, contain abundant small ($<25\text{ }\mu\text{m}$) opaque spinel inclusions, and are predominantly encrusted in matrix glass. The naturally glassy melt inclusions analyzed in this study are spherical to oblate in shape, pale to dark brown in color, and range in diameter from $34\times42\text{ }\mu\text{m}$ to $120\times490\text{ }\mu\text{m}$. Eight melt inclusions were excluded from further study based physical characteristics (e.g., presence of another crystal or sulfide phase, angular shape, opaque) indicative of complex post-entrapment processes affecting the melt inclusion that we wish to avoid. Of the remaining melt inclusions, all inclusions contained a vapor bubble. These vapor bubbles ranged in size from 10 to $110\text{ }\mu\text{m}$ in diameter, 0 – 13% of total inclusion volume with one outlier with 69% of total inclusion volume (Table 2A.2.3.).

2.3.2. Electron Microprobe Analysis

A total of 53 melt inclusions, 11 matrix glasses, and 15 melt embayments were prepared for major element, S, and Cl analysis via Electron Microprobe. These samples and their associated olivine grains were mounted in epoxy within 0.7 cm-round brass spacers cut to be 0.6 cm in length, exposed on one side, and polished for major elements analysis. These analyses were conducted at the University of California Los Angeles Electron MicroProbe Laboratory using a JEOL JXA-8200 electron microprobe. Olivine analyses were performed at 15 nA, 15 kV, and with a focused beam. Three olivine grains were analyzed in a separate session using the same settings as were used for glass major element analyses. Glass major element analyses were conducted at 15 nA, 15 kV, and with a $10\text{ }\mu\text{m}$ beam diameter. Glass analyses of S and Cl were performed separately and operated at

80nA, 15 kV, and with a 10 μm beam diameter with 100 s count times and 25 s background count times. Pyrite, barite, and apatite were used as the primary calibration standards. For the olivine grains, Si and Mg were measured with 30 s peak count times and Ni and Fe with 120 s peak count times. For the glasses, Si, Na, and K were measured with 20 s peak count times; Ca, Fe, Al, and Mg were measured with 30 s peak count times; and Ti, Mn, and P were measured with 40 s peak count times. Primary calibration standards for olivine grains and melt inclusions included forsteritic olivine (Si in the olivine, Mg in both), K-feldspar (K), anorthite (Al, Ca, and Si in the glass), manganese (Mn), albite (Na), sphene (Ti), fayalite (Ca), anorthite (Si in the melt inclusion), Durango apatite (P), Ni-olivine (Ni), and magnetite (Fe). San Carlos Olivine and A-99 glass was monitored as a secondary standard. After electron microprobe analysis, all samples were re-polished to remove EPMA analysis activation volumes. The newly polished surface was then superglued to a glass slide and polished from the opposite side to doubly expose the melt inclusion for further analyses. The doubly exposed melt inclusions ranged from 13-96 μm in thickness.

2.3.3. Fourier Transform Infrared Spectroscopy

A total of 15 melt inclusions, 4 matrix glasses, and 6 embayments were analyzed for H_2O and CO_2 via Fourier Transform Infrared Spectroscopy. Dissolved H_2O concentrations in the melt inclusions were measured at the University of California Riverside using a Thermo Scientific Nicolet iS50 Fourier-transform infrared spectrometer coupled with a Nicolet Continuum Fourier-transform infrared microscope attachment. Infrared spectra were collected between 600 and 6000 cm^{-1} . Aperture dimensions used in analysis ranged from $\sim 12 \times 12 \mu\text{m}$ to $\sim 40 \times 40 \mu\text{m}$, depending on the size of each individual melt inclusion. Total H_2O concentrations were calculated from the

absorption feature measured at the 3530 cm^{-1} band and total CO_2 concentrations were calculated from the absorption feature measured at the 1515 and 1435 cm^{-1} band. Conversion of the 3530 cm^{-1} and 1515 and 1435 cm^{-1} absorption features into total H_2O concentration was performed using Beer's Law in conjunction with glass densities and absorption coefficients calculated from the methods of Dixon et al. (1995) and Luhr (2001). Sample thicknesses were calculated using the interference spectra present in the 2000 to 2700 cm^{-1} band using the relationship $t=\lambda/2n$, where t = sample thickness, λ = wavelength, and $n = 1.546$.

2.3.4. *S* μ -XANES

The $\text{S}^{6+}/\Sigma\text{S}$ of 33 melt inclusions, 8 matrix glasses, and 11 embayments were analyzed via *S* micro-X-ray absorption near edge structure spectroscopy (μ -XANES) at beamline 13-IDE, Advanced Photon Source, Argonne National Laboratory. Spectra were collected in fluorescence mode from 2447 to 2544 eV with a Vortex ME4 silicon-drift diode detector array coupled to a high-speed digital spectrometer system and a defocused beam diameter of 20x20 μm in one session and of 15x15 μm in the other session. All analyses were done in a helium atmosphere, to avoid interaction between the incident photon beam and atmosphere. As with iron, to avoid significant beam damage during analysis, the beamline hardware was tuned so that the incident photon beam intensity was on the order of 10^9 - 10^{10} photons/s, and together with the defocused beam yielded photon flux density of $10^6 - 10^7$ photons/s/ μm^2 . Spectra were collected from 2447 to 2462 eV in 1.5 eV steps, 2462 to 2487 eV in 0.1 eV steps, and 2487 to 2544 eV in 1.5 steps using a 2 second dwell time. Spectra were normalized to the energy of the EXAFS region between 2487 to 2544 eV. Fityk, an open source curve and peak fitting software (Wojdyr, 2010), was used for peak area analysis

(Konecke *et al.*, 2017) with the EMG function positioned at 2485 eV for all samples and 3 to 4 Gaussian functions fit separately to the S^{6+} , S^{4+} , and S^{2-} peaks, when present. An empirical polynomial relationship between the peak areas and corresponding correction for the presence of S^{4+} as a result of beam damage was used to convert the peak areas into $S^{6+}/\Sigma S$ (Lerner *et al.*, 2021). We estimate that the uncertainty on these sulfur XANES measurements is ± 0.01 (absolute), based on the reproducibility of spectra from individual natural samples measured in Brounce *et al.* (2017).

2.3.5. Fe μ -XANES

The $Fe^{3+}/\Sigma Fe$ of 12 melt inclusions and 2 matrix glasses were analyzed in situ using micro X-ray absorption near edge structure spectroscopy (μ -XANES), also at beamline 13-IDE, Advanced Photon Source, Argonne National Laboratory. Spectra were collected in fluorescence mode from 7012 eV to 7484 eV with a Vortex ME4 silicon-drift diode detector array coupled to a high-speed digital spectrometer system and a defocused beam diameter of 10 x 10 μm . Aluminum foil of 100 μm thickness was placed in the path of the incident photon beam to decrease beam intensity and prevent auto-oxidation of the Fe species present in the hydrous glass (Cottrell *et al.*, 2018). The photon flux prior to interaction with the sample surface was $\sim 2 \times 10^9$ photons/s, and together with the defocused beam yielded a photo flux density of $\sim 10^7$ photons/s/ μm^2 . Spectra were collected from 7012 to 7102 eV in 2.5 eV steps, 7102 to 7132 eV in 0.1 eV steps, and 7132 to 7484 eV in 2 Å steps using 2 second per point dwell times in accordance with the procedures described in Cottrell *et al.* (2018). Spectra were normalized to the energy of the EXAFS region between 7120 and 7355 eV and fit following the techniques from Cottrell *et al.* (2009) and Zhang *et al.* (2018). The spectra were checked for influences from the olivine host and/or small crystals contained in the glass by

examining the spectral forms in the energy region of 7120-7150 eV where olivine interference will produce a secondary peak in the EXAFS region. Any spectra showing these influences were discarded from further analysis.

2.3.6. LA-ICP-MS

Trace element abundances for the volcanic glasses and corresponding olivine hosts were analyzed at the Lyons ICP-MS Facility at the University of California Riverside via laser-ablation inductively coupled plasma mass spectrometry using an Agilent Technologies 7900 quadrupole mass spectrometer that is coupled to a short pulse width coherent 193 nm ArF excimer laser. These samples were analyzed for 38 trace elements (Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Bi, Th, U). Analyses were performed with a spot size of 30 μm , a repeat rate of 5 Hz, and energy on the sample surface between 0.050 – 0.052 mJ. The same analyses were performed on the melt inclusions, embayments, matrix glasses, and the olivine hosts, normalizing to ^{43}Ca for the volcanic glasses and ^{26}Mg for the olivine host. United States Geological Survey glass standards BIR-1 g, BCR-2 g, and BHVO-2 g and Max Planck Institute glass standards KL2-G, ML3B-G, StHls-G, GOR-128-G, GOR-132-G, ATHO-G, and T1-G were used to create linear calibration curves ($R^2 > 0.999$) for each analytical session (Jochum et al., 2000; Kelley et al., 2003). Counting statistics were examined carefully for each element and those elements that were below the detection limit or had accumulated counting errors $> 50\%$ for the analyzed length of the ablation period were discarded.

Table 2.1: Corrected for "Fe-loss" melt inclusion major, minor, and volatile concentration analysis.

Sample	Olivine % added	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	FeO* (wt%)	FeO** (wt%)	Fe ₂ O ₃ ** (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	P ₂ O ₅ (wt%)
P17_20_01	3.7	44.9	2.4	16.5	9.7	7.7	2.2	0.1	5.6	9.0	4.1	1.9	0.6
P17_20_03	6.8	45.9	2.6	16.8	9.8	7.8	2.2	0.1	6.0	9.9	4.1	1.8	0.6
P17_20_04	2.9	46.3	2.6	17.7	10.1	8.0	2.3	0.1	5.4	10.0	4.3	1.8	0.7
P17_20_05	5.6	46.2	2.5	16.9	9.8	7.8	2.2	0.1	6.0	9.6	4.1	1.7	0.6
P17_20_06	5.9	45.7	2.6	16.8	9.9	7.9	2.3	0.1	6.1	9.4	4.2	1.9	0.7
P17_20_06B	6.2	46.4	2.5	16.8	9.9	7.9	2.3	0.1	6.1	9.7	4.0	1.7	0.5
P17_20_08A	6.6	46.1	2.5	16.5	9.8	7.8	2.2	0.1	6.4	9.1	4.0	1.9	0.6
P17_20_10A	8.4	45.7	2.6	16.6	9.8	7.8	2.2	0.1	6.2	9.8	4.2	1.8	0.7
P17_20_10B	8.0	45.4	2.6	16.7	9.9	7.9	2.3	0.1	6.5	9.7	4.1	1.8	0.6
P17_20_11	6.2	44.7	2.7	17.1	9.8	7.8	2.2	0.1	5.9	9.4	4.3	2.0	0.7
P17_20_13B	6.0	45.7	2.6	16.9	9.9	7.9	2.3	0.1	6.1	9.3	4.3	2.0	0.7
P17_20_15	4.2	46.1	2.6	17.0	9.9	7.9	2.3	0.1	5.8	9.7	4.1	1.8	0.6
P17_AL_01A	9.1	46.2	2.4	16.2	9.8	7.8	2.2	0.1	6.5	9.7	3.8	1.7	0.6
P17_AL_03	10.3	43.9	2.6	16.3	9.7	7.7	2.2	0.1	6.8	9.3	4.1	1.9	0.6
P17_AL_04	10.8	45.5	2.7	16.6	9.8	7.8	2.2	0.1	6.4	10.3	4.0	1.6	0.8
P17_AL_05	5.9	46.1	2.5	16.6	9.9	7.8	2.2	0.1	6.3	9.8	4.0	1.8	0.6
P17_AL_07A	4.5	45.9	2.6	16.9	9.9	7.9	2.3	0.1	5.9	9.3	4.4	2.1	0.6
P17_AL_07B***	4.0	46.6	2.5	16.8	9.9	7.8	2.2	0.1	5.9	9.1	4.3	2.0	0.6
P17_AL_10	3.6	46.8	2.4	16.9	9.9	7.9	2.3	0.1	5.5	9.6	3.9	1.7	0.6
P17_JAH_03	4.8	45.8	2.6	16.8	9.9	7.8	2.2	0.1	5.7	9.4	4.2	2.0	0.7
P17_JAH_04	3.9	46.1	2.5	17.0	9.9	7.9	2.3	0.1	5.6	9.5	4.3	1.9	0.5
P17_JAH_08	3.2	45.5	2.6	16.9	9.9	7.9	2.3	0.1	5.7	9.5	4.2	1.9	0.6
P17_JAH_09	6.8	45.6	2.6	16.6	9.7	7.7	2.2	0.1	6.6	9.3	3.9	1.9	0.5

P17_JAH_10A****	6.2	45.9	2.4	16.6	9.8	7.8	2.2	0.1	6.2	9.7	4.0	1.6	0.5
P17_JAH_10B	6.1	45.9	2.5	16.7	9.8	7.8	2.2	0.1	6.2	9.6	4.0	1.6	0.5
P17_JAH_11	7.8	45.2	2.6	16.6	9.8	7.8	2.2	0.1	6.7	9.2	4.2	2.0	0.7
P17_N_20_02	7.0	45.7	2.5	16.3	9.8	7.8	2.2	0.1	6.4	9.3	4.1	1.9	0.6
P17_N_20_03	4.8	45.9	2.6	16.8	9.7	7.7	2.2	0.1	5.7	9.9	4.0	1.7	0.6
P17_N_20_04A	4.5	46.0	2.5	16.4	9.8	7.8	2.2	0.2	6.2	9.2	4.4	1.9	0.7
P17_N_20_04B	6.5	45.0	2.7	16.8	9.8	7.8	2.2	0.1	6.1	9.5	4.2	2.0	0.7
P17_N_20_05	1.9	45.7	2.4	16.6	9.7	7.8	2.2	0.1	5.6	9.7	4.2	1.9	0.6
P17_N_20_10	8.8	45.4	2.6	16.5	9.9	7.9	2.3	0.1	6.8	9.3	4.1	1.9	0.6
P17_N_20_11	5.3	45.5	2.6	16.9	9.9	7.8	2.2	0.1	5.7	9.2	4.2	2.0	0.7
P17_N_20_12	3.2	45.9	2.6	16.8	10.0	8.0	2.3	0.2	5.7	9.7	4.6	2.0	0.6
P17_N_20_14A	7.0	45.5	2.5	16.7	9.8	7.8	2.2	0.1	6.7	9.7	4.0	1.8	0.5
P17_N_20_14B	7.9	45.6	2.5	16.8	9.8	7.8	2.2	0.1	6.6	9.7	4.0	1.7	0.5
P17_N_20_17	6.3	45.1	2.6	16.6	9.7	7.7	2.2	0.1	5.9	9.6	4.2	1.9	0.7
P17_N_20_18A	3.7	45.6	2.6	16.8	9.7	7.7	2.2	0.1	5.6	9.5	4.0	1.8	0.6
P17_N_20_18B	3.7	44.7	2.6	17.0	9.7	7.7	2.2	0.1	5.4	9.4	4.3	2.0	0.7
P17_N_20_21	5.9	46.0	2.5	17.0	9.9	7.9	2.3	0.1	5.6	9.6	4.1	1.8	0.6
P17_N_20_22	3.8	45.5	2.6	16.9	9.8	7.8	2.2	0.1	5.7	9.3	4.2	2.0	0.6

*Total Fe content (Fe₂O₃ + FeO) calculated as FeO

** = calculated value from FeO* and average Fe₃+/ Σ Fe

***Sample was predominately a vapor bubble

****Vapor bubble present but size is not resolvable in photograph

¹Vapor bubble correction from Rasmussen et al., 2020

²Vapor bubble correction from Tucker et al., 2019, using the equation of state for CO₂ from Duan and Zhang, 2006

³Helz and Thornber, 1987

⁴Toplis, 2005

⁵Newman & Lowenstern, 2002

⁶Calculated using the equation $P = gph$ using a depth to the crust-mantle boundary = 20 km, $\rho_{crust} = 2.8 \text{ g/cm}^3$, $\rho_{crust} = 3.25 \text{ g/cm}^3$

OOB = Out of Bounds of either the 5000 bar or 10,000 ppm CO₂ limits of VolatileCalc

S	Cl	H ₂ O	CO ₂ ¹	CO ₂ ²	D ^v	Fe ³⁺ /ΣFe	T ³	K _D ⁴	P ^{1,5}	D ^{1,6}	P ^{2,5}	D ^{2,6}	CO ₂ /Ba _{avg}	
(ppm)	(ppm)	(wt%)	(ppm)	(ppm)		(average)	(°C)		(GPa)	(km)	(GPa)	(km)	CO ₂ ¹	CO ₂ ²
1713	0.04	1.34		4052	0.028	0.205	1141	0.28			0.32	11.8		9.9
1811	0.04	0.77	1251	3304	0.022	0.205	1160	0.28	0.12	4.3	0.28	10.2	3.1	8.1
1839	0.04			2925		0.205	1155	0.27			0.25	9.1		7.2
1511	0.04			2400		0.205	1170	0.27			0.21	7.8		5.9
1822	0.05			2735		0.205	1173	0.27			0.24	8.6		6.7
1748	0.04			8576		0.205	1171	0.27			OOB	OOB		21.0
1638	0.04	1.27		1866	0.028	0.205	1163	0.28			0.05	2.0		4.6
1667	0.04			3310		0.205	1175	0.27			0.27	10.0		8.1
1690	0.04	1.54	3904	9480		0.205	1162	0.28	0.32	11.6	OOB	OOB	9.6	23.2
1939	0.05			811		0.205	1170	0.27			0.11	3.9		2.0
1714	0.05	1.38	4394	4630		0.205	1158	0.28	0.36	13.0	0.37	13.6	10.8	11.3
1714	0.04	1.16	4233	5412		0.205	1150	0.28	0.36	13.3	0.44	16.1	10.4	13.3
1616	0.04			10599		0.205	1180	0.28			OOB	OOB		26.0
1771	0.05			6416		0.205	1190	0.27			0.48	17.5		15.7
1982	0.05			7627		0.205	1177	0.27			OOB	OOB		18.7
1360	0.04			5879		0.205	1177	0.27			0.45	16.2		14.4
1909	0.04			3509		0.205	1170	0.27			0.29	10.5		8.6
1262	0.04					0.205	1170	0.27						
1702	0.04			5111		0.205	1153	0.28			0.39	14.4		12.5
1793	0.05			6078		0.205	1163	0.27			0.46	16.7		14.9
1477	0.05			5763		0.205	1160	0.27			0.44	16.0		14.1
1450	0.05	1.45	1823	2385		0.205	1144	0.28	0.17	6.3	0.22	7.8	4.5	5.8
1298	0.06	1.41	2015	1598		0.205	1166	0.28	0.19	6.8	0.16	5.7	4.9	3.9
1205	0.04					0.205	1173	0.27						

1233	0.04			6296		0.205	1173	0.27			0.47	17.2		15.4
1740	0.04	0.59	2027	4413		0.205	1182	0.27	0.16	5.8	0.32	11.7	5.0	10.8
1242	0.06	1.42	2587	15816	0.033	0.205	1162	0.28	0.24	8.6	OOB	OOB	6.3	38.7
1686	0.05			974		0.205	1161	0.27			0.12	4.3		2.4
1741	0.05			1308		0.205	1178	0.27			0.14	5.1		3.2
1865	0.05			4153		0.205	1175	0.27			0.33	12.0		10.2
1481	0.05	1.84		1606		0.205	1137	0.28			0.16	5.9		3.9
1092	0.04	1.70		15741		0.205	1169	0.28			OOB	OOB		38.6
1779	0.04			1836	0.026	0.205	1163	0.27			0.18	6.4		4.5
1584	0.05			2346		0.205	1167	0.27			0.21	7.7		5.7
1408	0.04	0.91	937	6355	0.024	0.205	1175	0.28	0.09	3.2	0.45	16.5	2.3	15.6
1343	0.04	0.20		10925		0.205	1181	0.27			OOB	OOB		26.8
1739	0.05			5383		0.205	1169	0.27			0.41	15.0		13.2
1634	0.04			1197		0.205	1157	0.27			0.13	4.9		2.9
1826	0.05			2196		0.205	1157	0.27			0.20	7.3		5.4
1571	0.04			1590		0.205	1161	0.27			0.16	5.8		3.9
1779	0.04	1.73	5497	5412	0.022	0.205	1141	0.28	0.43	15.7	0.42	15.5	13.5	13.3

2.4. Results

Olivine hosts range in composition from Fo₈₂ to Fo₈₅ ($Fo_{\#} = Mg/(Mg + Fe) \times 100$; Table 2A.2.1). One olivine (P17_AL_03) is Fo₈₅ in composition near the melt inclusion, and Fo₈₂ in composition at the edge (near the matrix glass) of the olivine grain, indicating normal

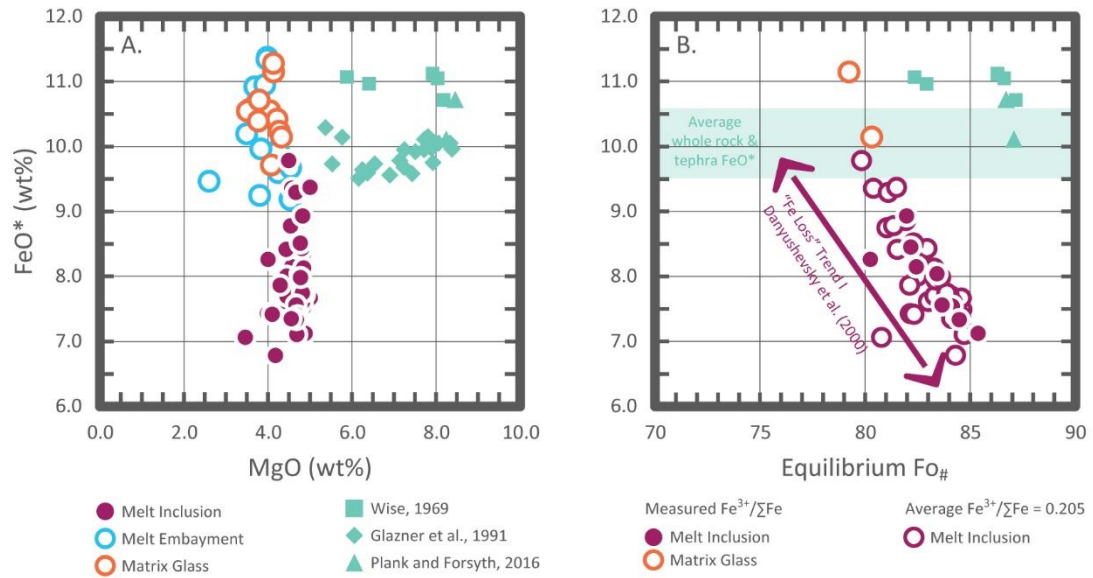


Figure 2.2. (A) Plot of measured FeO* versus MgO for olivine hosted melt inclusions (purple closed circles, this study), olivine hosted melt embayments (blue open circles, this study), and matrix glass (orange open circles, this study). Also plotted are Pisgah Crater whole rock (blue-green closed squares; Wise, 1969; blue-green closed diamonds; Glazner et al., 1991) and whole tephra (blue-green closed triangles; Plank and Forsyth, 2016) analyses. (B) Plot of measured FeO* versus Fo_# for olivine in equilibrium with melt inclusions using calculated K_D for each melt inclusion (K_D = 0.26 – 0.27; Table 2A.2.2) along with corresponding measured values for Fe³⁺/ΣFe (purple closed circles) and the average measured value for Fe³⁺/ΣFe (purple open circles) as well as matrix glass using measured values for Fe³⁺/ΣFe (orange open circles) in this study. Whole rock and whole tephra measurements of FeO* and calculated equilibrium olivine using the average K_D (0.266) calculated from the melt inclusions in this study and Fe³⁺/ΣFe calculated from measured Fe₂O₃ and FeO (blue-green closed squares; Fe³⁺/ΣFe = 0.194 – 0.248; Wise, 1969) and Fe³⁺/ΣFe calculated from $D_v^{olivine/whole\ tephra}$ (blue-green closed triangles; Fe³⁺/ΣFe = 0.19; Plank and Forsyth, 2016). Average whole rock (Wise, 1969; Glazner et al., 1991) and whole tephra (Plank and Forsyth, 2016) FeO* concentration (10.1 wt%, 1σ = 0.48 wt%) is plotted in the light blue-green field. The relationship between melt inclusions and whole rock form an “Fe-loss” triangle as described by Danyushevsky et al., 2000.

compositional zoning, consistent with previous work on olivine grains from Pisgah Crater (Plank and Forsyth, 2016). Pisgah melt inclusions, embayments, and matrix glasses are basanitic in composition (Fig. 2A.1.1.). Melt inclusions from this study have a wide range in FeO* content (6.8 – 10.9 wt%) and a relatively narrow range in MgO content (3.5 – 5.0 wt%; Fig. 2.2.A. & Fig. 2A.1.2. A; Table 2A.2.2). Measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Table 2A.2.2) and calculated K_D ($K_D^{\text{Mg-Fe}} = \frac{x_{\text{melt}}^{\text{Mg}}/x_{\text{olivine}}^{\text{Mg}}}{x_{\text{melt}}^{\text{Fe}^{2+}}/x_{\text{olivine}}^{\text{Fe}^{2+}}}$, where X is the mol fraction of the respective element; $K_D = 0.26 - 0.27$; Table 2A.2.2; Toplis, 2005) were used to calculate the $\text{Fo}_\#$ of an olivine in equilibrium with the associated melt inclusion (Table 2A.2.2). A negative relationship between the fictive “equilibrium” $\text{Fo}_\#$ olivine and the measured FeO* of the melt inclusion extends from the average whole rock/tephra FeO* (10.1 wt%, $1\sigma = 0.5$ wt%) to lower FeO* contents in inclusions with higher equilibrium $\text{Fo}_\#$ s (Fig. 2.2. B.). These observations indicate that “Fe-loss” may have modified the compositions of Pisgah Crater melt inclusions after entrapment (Danyushevsky *et al.*, 2000). “Fe-loss” is a process by which (1) melt inclusions undergo post-entrapment crystallization of olivine out of the melt inclusion at the melt inclusion-olivine interface, and then (2) that post-entrapment-crystallized olivine diffusively equilibrates with the composition of the host olivine through diffusion of Fe out of and diffusion of Mg into the melt inclusion. This process keeps the melt inclusion and post-entrapment-crystallized olivine host in chemical equilibrium with each other (e.g., the calculated equilibrium $\text{Fo}_\#$ and the measured olivine $\text{Fo}_\#$ are the same; Fig. 2A.1.3.), occurs on timescales of <2 years (Danyushevsky *et al.*, 2002), and produces melt inclusion glass compositions that are modified in FeO* and MgO from the initial values at the time of entrapment (Danyushevsky *et al.*, 2000). All of

the melt inclusions in this study appear to be affected by this “Fe-loss” process, and were corrected for this process using the software program MIMiC (Rasmussen *et al.*, 2020). We used an initial FeO* equal to the average FeO* recorded by the whole rock and tephra (10.1 wt%, $1\sigma = 0.5$; Wise, 1969; Glazner *et al.*, 1991; Plank and Forsyth, 2016), $\text{Fe}^{3+}/\Sigma\text{Fe}$ equal to the average measured in the melt inclusions ($\text{Fe}^{3+}/\Sigma\text{Fe} = 0.205$, $1\sigma = 0.01$; Table 2.1), $K_D = 0.26 - 0.27$ calculated for each inclusion-olivine pair (Toplis, 2005), the minimum measured diameter of each melt inclusion in this study (20-220 μm ; Table 2A.2.3), and an olivine host diameter of 1000 μm to correct for “Fe-loss”. Between 2 and 11 % olivine was added back into the melt inclusions as a result of this correction. These “Fe-loss” corrected melt inclusions have 9.7 – 10.0 wt% FeO (Table 2.1) and a relatively narrow range in MgO content (5.4 – 6.8 wt%; Table 2.1). The “Fe-loss” corrected compositions will be referred to for the remainder of this contribution.

The range of measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ for the melt inclusions (0.188 – 0.214, Table 2A.2.2) is narrow (average = 0.205, $1\sigma = 0.01$; Table 2.1), while the range of measured $\text{S}^{6+}/\Sigma\text{S}$ for the melt inclusions is wide (0.08 – 1.0; Table 2A.2.2). This range in $\text{S}^{6+}/\Sigma\text{S}$ does not correlate with any major element, minor element, or volatile element concentrations in either the measured values or “Fe-loss” corrected values. Two melt embayments have elevated $\text{S}^{6+}/\Sigma\text{S}$ compared to the majority of melt embayments (0.18 & 0.20 compared to 0 – 0.02 for the remainder of melt embayments; Table 2A.2.2). These same embayments have lower FeO* concentrations (7.5 – 7.7 wt%, similar to those of pre-“Fe-loss” corrected melt inclusions; Table 2A.2.2) than the rest of the melt embayments (FeO* = 9.2 – 11.4; Table 2A.2.2) but no other noticeable differences between $\text{S}^{6+}/\Sigma\text{S}$ and major

Table 2.2: Oxygen Fugacity from measured and "Fe-loss" corrected analysis.

Sample	fO_2 (ΔQFM) [*]						fO_2 (ΔQFM) ^{**} Calculated Via:					
	Fe ¹	Fe ²	Fe ³	Fe ⁴	D _V ⁵	S ⁶⁺ /ΣS ⁶	Fe ¹	Fe ²	Fe ³	Fe ⁴	D _V ⁵	
Melt Inclusions												
P17_20_01	0.61	0.66	0.55	0.81	1.17	0.74	0.66	0.70	0.55	0.71	1.01	
P17_20_03	0.39	0.46	0.33	0.76	1.58		0.61	0.67	0.52	0.74	1.30	
P17_20_04						0.74	0.61	0.66	0.56	0.84		
P17_20_05							0.64	0.72	0.59	0.86		
P17_20_06							0.62	0.69	0.59	0.81		
P17_20_06B							0.64	0.72	0.53	0.86		
P17_20_08A	0.61	0.68	0.57	0.87	1.18	0.72	0.68	0.74	0.60	0.72	0.92	
P17_20_10A						0.87	0.59	0.67	0.56	0.80		
P17_20_10B						1.07	0.65	0.69	0.57	0.64		
P17_20_11							0.59	0.64	0.60	0.77		
P17_20_13B	0.24	0.32	0.36	0.53		0.91	0.64	0.68	0.59	0.66		
P17_20_15						0.86	0.65	0.69	0.53	0.72		
P17_AL_01A						1.03	0.65	0.73	0.57	0.86		
P17_AL_03						1.08	0.61	0.68	0.63	0.75		
P17_AL_04							0.60	0.70	0.66	0.83		
P17_AL_05						0.66	0.62	0.70	0.57	0.83		
P17_AL_07A						1.61	0.59	0.65	0.53	0.78		
P17_AL_07B							0.63	0.70	0.58	0.84		
P17_AL_10							0.66	0.73	0.55	0.92		
P17_JAH_03						0.90	0.60	0.66	0.57	0.82		
P17_JAH_04							0.60	0.65	0.47	0.82		
P17_JAH_08	0.68	0.71	0.51	0.83		0.62	0.63	0.66	0.46	0.67		
P17_JAH_09						0.85	0.69	0.72	0.58	0.68		

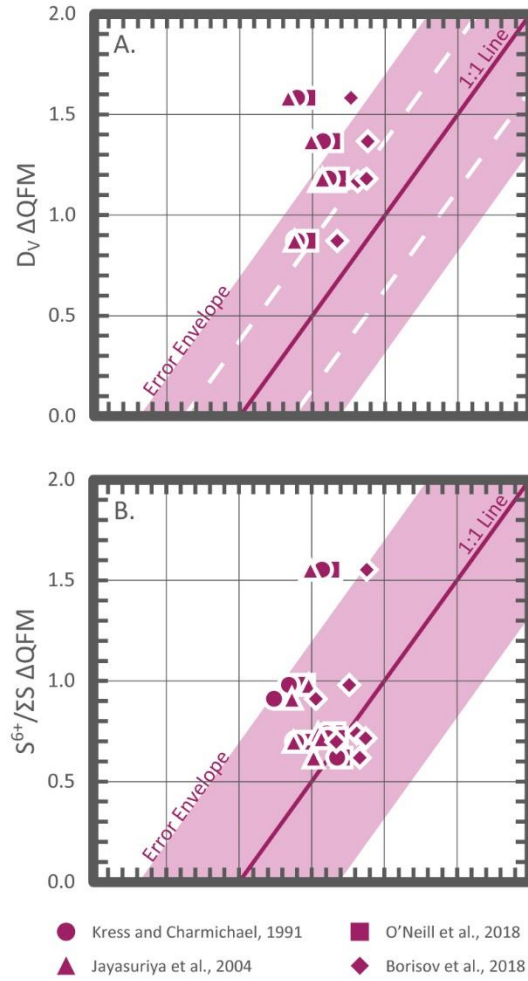


Figure 2.3. Offset in calculated fO_2 amongst a selection of oxybarometer proxies. Solid purple line is the 1:1 line in which the oxybarometer proxies would calculate identical values for ΔQFM . Solid light purple error envelop is the uncertainty reported for the whole data set used by Borisov et al., 2018 to convert $Fe^{3+}/\Sigma Fe$ to fO_2 (0.38). Dashed white line is the uncertainty reported by Mallmann and O'Neill, 2013 to convert $D_V^{olivine/melt}$ to fO_2 (0.24). (A) Offset for measured melt inclusion compositions for $Fe^{3+}/\Sigma Fe$ (Kress and Carmichael, 1991; Jayasuriya et al., 2004; Borisov et al., 2018; O'Neill et al., 2018) and $D_V^{olivine/melt}$ (Mallmann and O'Neill, 2013) set with respect to the QFM buffer. (B) Offset for measured melt inclusion compositions for $Fe^{3+}/\Sigma Fe$ (Kress and Carmichael, 1991; Jayasuriya et al., 2004; Borisov et al., 2018; O'Neill et al., 2018) and $S^{6+}/\Sigma S$ (Jugo et al., 2010) set with respect to the QFM buffer.

element, minor element, and volatile concentrations. There is no relationship between measured $S^{6+}/\Sigma S$ in matrix glasses (0 – 0.3; Table 2A.2.2) and major element, minor element, and volatile concentrations.

The oxygen fugacity (fO_2) recorded by the melt inclusions in this study is calculated three ways: 1) $Fe^{3+}/\Sigma Fe$ together with using “Fe-loss” corrected major element compositions, 2) $S^{6+}/\Sigma S$ or 3) $D_V^{olv/melt}$ (partitioning of V between the host olivine and entrapped melt; Table 2.1). The $\log fO_2$ calculated from $Fe^{3+}/\Sigma Fe$ range from $\Delta QFM = +0.53$ to $+0.69$ (Table 2.2; Kress and Carmichael, 1991), $+0.59$ to $+0.73$ (Table 2.2; Berry *et al.*, 2018; O’Neill *et al.*, 2018), $+0.37$ to $+0.63$ (Table 2.2; Jayasuriya *et al.*, 2004), and $+0.65$ to $+0.95$ (Table 2.2; Borisov *et al.*, 2018). These values are in broad general agreement with the $\log fO_2$ calculated from $D_V^{olv/melt}$ ($\Delta QFM = +0.63$ to $+1.37$; Fig. 2.3.A.; Table 2.2; Mallmann and O’Neill, 2013). The $\log fO_2$ calculated from the measured $S^{6+}/\Sigma S$ range from $\Delta QFM = +0.51$ to $+1.61$ (Table 2.2; Jugo *et al.*, 2010) and are also in broad general agreement with the $Fe^{3+}/\Sigma Fe$ and $D_V^{olv/melt}$ oxybarometers, though it extends to higher values (Fig. 2.3.B.; Table 2.2).

Measured H_2O (0.2 to 1.9 wt%; Table 2A.2.2), CO_2 (594 to 3725 ppm; Table 2A.2.2), and S (1204 to 2224 ppm; Table 2A.2.2) are in general agreement with previous measurements of these volatiles in Pisgah melt inclusions ($H_2O = 0.0 - 1.9$ wt%, $CO_2 = 16 - 3832$ ppm, and $S = 55 - 1872$ ppm; Fig. 2A.1.7; Plank and Forsyth, 2016). The CO_2 contents of all of the melt inclusions in this study were corrected for the presence of vapor bubbles two ways: 1) using the MIMiC algorithm (Rasmussen *et al.*, 2020) and 2) melt inclusion vapor bubble size along with a CO_2 equation of state (Duan and Zhang, 2006; Tucker *et al.*, 2019). The MIMiC-corrected compositions of these melt

inclusions have 0.2 – 1.8 wt% H₂O, 937 – 5497 ppm CO₂, and 1092 – 1982 ppm S (Table 2.1). The range in vapor bubble CO₂ corrected melt inclusions using vapor bubble size along with a CO₂ equation of state is 848 – 16,577 ppm (Table 2.1). Here, the CO₂ concentration calculated using MIMiC (Rasmussen *et al.*, 2020) is treated as a minimum estimate for CO₂ concentration and the corrections calculated using vapor bubble size along with a CO₂ equation of state (Duan and Zhang, 2006; Tucker *et al.*, 2019) are treated as maximum estimates for CO₂ concentration.

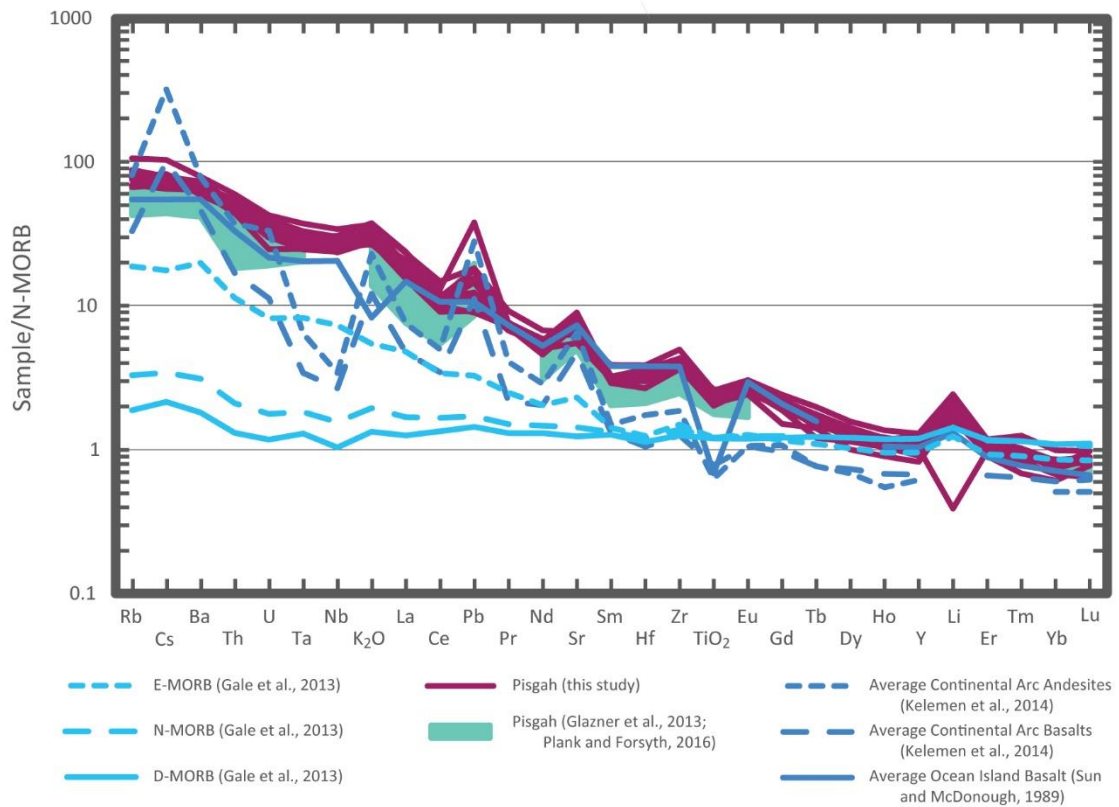


Figure 2.4. Trace element diagram for Pisgah Crater glasses (melt inclusion, melt embayment, and matrix glass) in this study (purple lines) compared to previous Pisgah whole rock and whole tephra measurements (blue-green field; Glazner, 1991; Plank and Forsyth, 2016), average continental arc andesites and basalts (dashed blue lines; Kelemen *et al.*, 2014), average ocean island basalt (solid blue line; Sun and McDonough, 1989), and E-MORB, N-MORB, and D-MORB (light blue lines; Gale *et al.*, 2013). Concentrations are normalized to N-MORB (Arevalo Jr. & McDonough, 2010).

Trace element concentrations for Pisgah melt inclusions are enriched in the most incompatible trace elements compared to normal MORB (Arevalo Jr and McDonough, 2010) and enriched MORB (Gale *et al.*, 2013), and the degree of enrichment decreases as incompatibility of the element decreases. These melt inclusions are moderately enriched in the light rare earth elements, but similar to MORB in the heavy rare earth elements (Fig. 2.4.). Pisgah samples have small positive anomalies in K₂O, Pb, and Zr, and a small negative anomaly in Sm.

2.5. Discussion

2.5.1. Crystallization

Melt inclusions have major element concentrations which are distinct from those recorded by melt embayments and matrix glasses in this study (Fig. 2.5). We used MELTs (Gualda *et al.*, 2012; Ghiorso and Gualda, 2015) to estimate the effects of fractional crystallization on major and minor element chemistry of a cooling melt of a composition similar to that of previous whole rock measurements at a constant pressure equal to 500 bar and an initial $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.2$ (Fig. 2.5., black curve and closed star; Wise, 1969; Glazner *et al.*, 1991; Plank and Forsyth, 2016). At this pressure and starting $\text{Fe}^{3+}/\Sigma\text{Fe}$, a modeled melt crystallizes olivine (starting at $T = 1,190^\circ\text{C}$), plagioclase (starting at $T = 1,138^\circ\text{C}$), clinopyroxene (starting at $T = 1,145^\circ\text{C}$), and spinel (starting at $T = 1,119^\circ\text{C}$) as it cools from 1191°C to 1091°C , which is consistent with observations of these phases in Pisgah lavas. The major element compositions of melt inclusions in this study can be reproduced in these models with up to ~15% mass of olivine + plagioclase + clinopyroxene crystallization in 32:20:48 proportions at temperatures between 1129°C and 1165°C , indicating relatively limited extents of fractional crystallization at the time of entrapment (Fig. 2.5.). Modeled olivine

compositions for the melt range from Fo₈₀–Fo₈₃, which overlap with the lower range of Fo₈s measured for Pisgah Crater olivines (Fo₇₉₋₈₅; this study; Plank and Forsyth, 2016). These temperatures align with those calculated from the MgO concentration in the “Fe-loss” corrected melt inclusions (1119–1148°C; Table 2.1; Helz and Thornber, 1987).

2.5.2. Volatiles and fO_2

The melt inclusions in this study have a narrow range of K₂O concentrations (average = 1.9 wt%, 1σ = 0.1 wt%) and a wide range in H₂O concentrations (~2 wt%; Fig. 2.6.A.; Table 2.1). This relationship is commonly interpreted as indicating that either (1) these melt inclusions were entrapped from a magma undergoing H₂O loss to a vapor phase and concomitant minimal fractional crystallization, or (2) these melt inclusions entrapped a magma undersaturated with respect to H₂O and undergoing minimal fractional crystallization, but then were transported in a magma that degassed its H₂O, causing diffusive water loss from the melt inclusions through their olivine hosts. Diffusive H₂O loss is a process which can affect melt inclusions on timescales as short as hours to days because it involves the loss of H⁺ from the melt inclusion through diffusion through the olivine host (Hauri, 2002; Portnyagin *et al.*, 2008; Gaetani *et al.*, 2012; Bucholz *et al.*, 2013; Lloyd *et al.*, 2013; Barth *et al.*, 2019; Humphreys *et al.*, 2022). One way to check for the extent of H⁺ loss from melt inclusions is correlations between measured H₂O content and melt inclusion diameters, where the smallest diameter melt inclusions would be most impacted by this process and thus contain the lowest measured H₂O concentrations. Melt inclusions in this study do not show this relationship, which we take as evidence against H⁺ diffusive loss from our inclusion compositions.

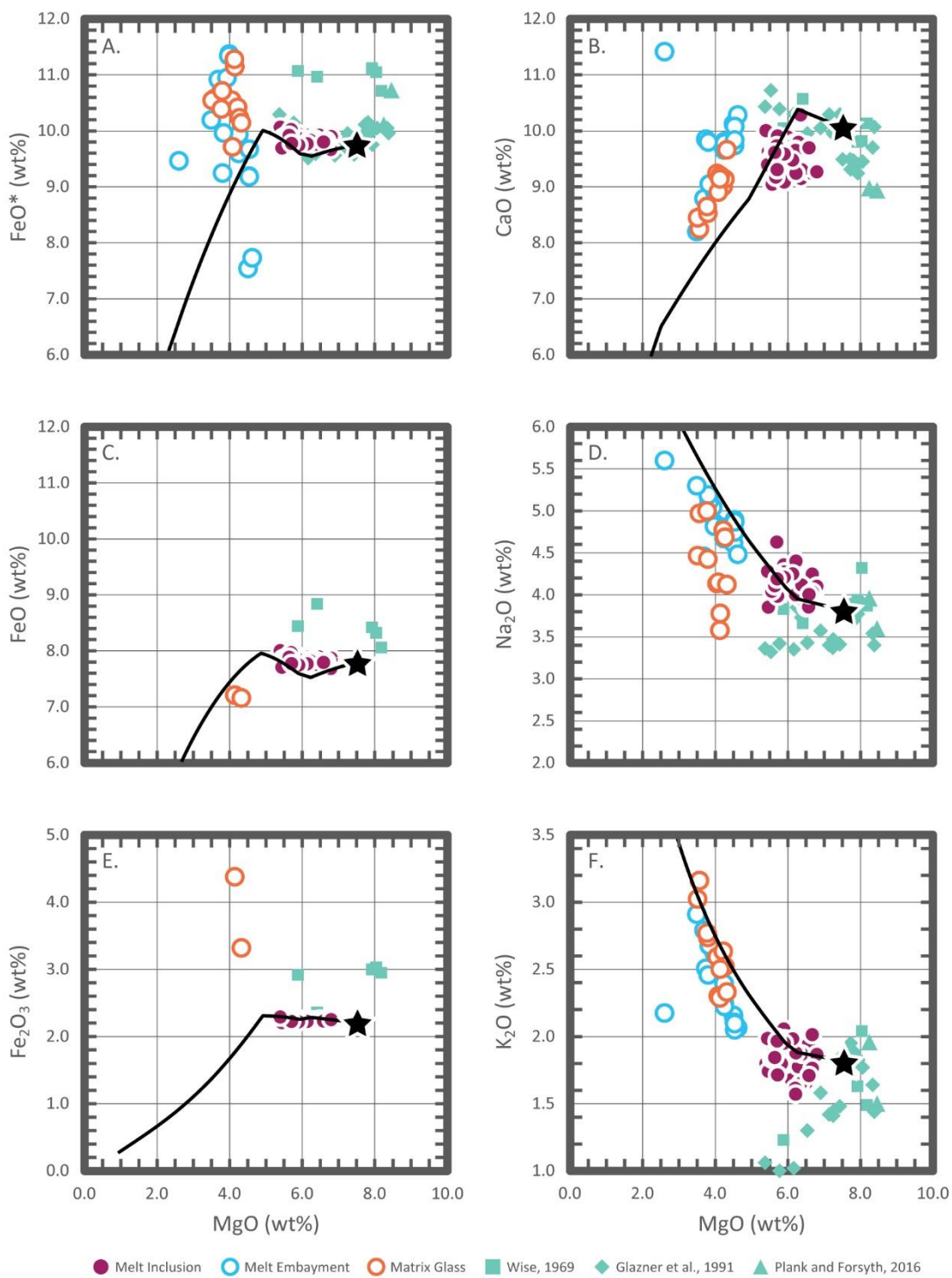


Figure 2.5. Major element variations for Pisgah Crater melt inclusion (purple closed circles), melt embayment (blue open circles), and matrix glass (orange open circle) compositions from this study and previous measurements of Pisgah Crater whole rock (blue-green closed squares; Wise, 1969; and blue-green closed diamonds; Glazner et al., 1991) and whole rock tephra (blue-green closed triangles; Plank and Forsyth, 2016). The melt inclusions in this study have been corrected for “Fe-loss” (Danyushevsky et al., 2000) using MIMiC (Rasmussen et al., 2020) with initial FeO^* equal to the average FeO^* recorded by the whole rock and tephra (10.10 wt%, $1\sigma = 0.48$) and a fixed $\text{Fe}^{3+}/\Sigma\text{Fe}$ equivalent to the average measured melt inclusion value ($\text{Fe}^{3+}/\Sigma\text{Fe} = 0.205$, $1\sigma = 0.01$). Calculations were performed using the model from Toplis (2005) to calculate KD, the minimum measured diameter of each melt inclusion in this study (20-220 μm), and an olivine host diameter of 1000 μm . Black curve is an isobaric MELTS (Gualda et al., 2012; Ghiorso and Gualda, 2015) model run for Pisgah Crater starting from the composition denoted by the star with a starting $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.205$ and $P = 500$ bar.

Additionally, K_2O and CO_2 concentrations in Pisgah Crater melt inclusions display the same relationship as K_2O and H_2O (Fig. 2.6. A. & B.), further indicating that entrapment along a degassing path is the more likely interpretation of the relationship between H_2O and K_2O . However, because the diffusion of H^+ is also tied to the proximity of the melt inclusion to the edge of the olivine (e.g., Qin *et al.*, 1992; Bucholz *et al.*, 2013; Lloyd *et al.*, 2013; Cottrell *et al.*, 2018), and the orientation of the inclusion with respect to the crystallographic axes of the olivine host (Le Voyer *et al.*, 2014; Barth *et al.*, 2019), this interpretation is tentative. Measurements of the isotopic composition of hydrogen in Pisgah melt inclusions is necessary to confirm our interpretation (e.g., Gaetani *et al.*, 2012; Walowski *et al.*, 2015; Humphreys *et al.*, 2022).

The relative abundance of magmatic volatiles dissolved in silicate magmas decreases with decreasing pressure, and the relationship between H_2O , CO_2 and pressure are generally well

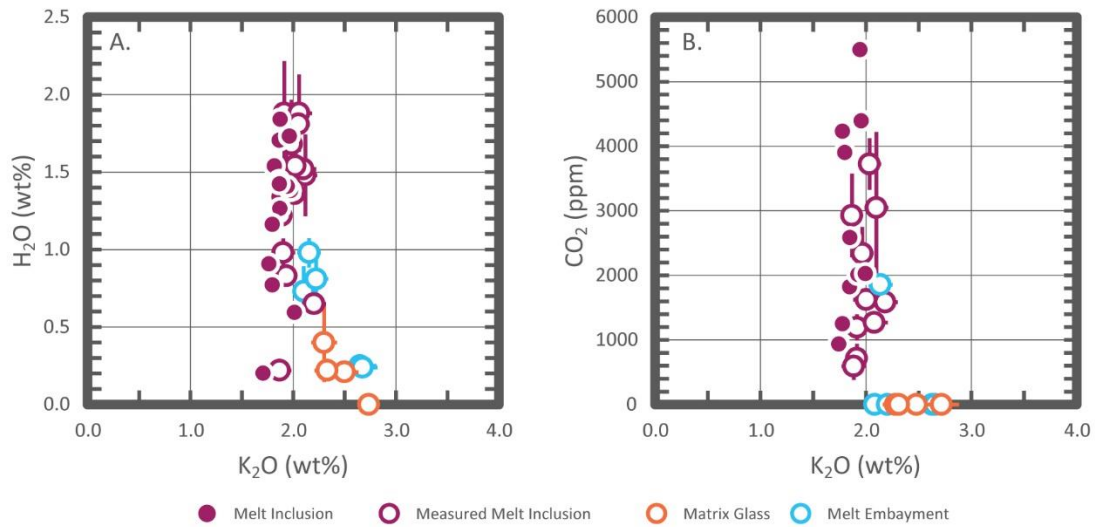


Figure 2.6. (A) Plot of H_2O vs. K_2O for Pisgah Crater measured “Fe-loss” corrected (Danyushevsky *et al.*, 2000; Rasmussen *et al.*, 2020) melt inclusion (purple closed circles), melt embayment (blue open circles), matrix glass (orange open circle), and measured melt inclusion (purple open circles) compositions from this study. (B) Plot of H_2O vs. K_2O for Pisgah Crater samples. Symbols are the same as in A.

calibrated as functions of magma major element composition, and temperature (Dixon and Stolper, 1995; Dixon *et al.*, 1995). Thus, the relative abundances of H₂O and CO₂ measured in glassy melt inclusions can be used to calculate the pressures at which melt inclusions were trapped in their olivine hosts (Table 2.1; Dixon and Stolper, 1995; Dixon *et al.*, 1995; Newman and Lowenstern, 2002). Entrapment depths for Pisgah magmas were calculated with “Fe-loss” and vapor bubble corrected melt inclusion compositions using MIMiC (Table 2.1; Rasmussen *et al.*, 2020) as well as with the same “Fe-loss” corrected compositions that have been paired with vapor bubble corrected CO₂ concentrations calculated from the CO₂ equation of state (Duan and Zhang, 2006; Tucker *et al.*, 2019). Entrapment pressures for Pisgah melt inclusions were then calculated from these paired H₂O and CO₂ concentrations using VolatileCalc2 (Newman and Lowenstern, 2002) and the assumption that all melt inclusions in this study were entrapped in the crust.

In the case of the vapor bubble corrected melt inclusions using an equation of state CO₂ approach, some of the CO₂ concentrations exceeded the limits of the VolatileCalc2 calibration (>10,000 ppm CO₂; Newman and Lowenstern, 2002) and thus were not considered further. We also discarded analyses that returned pressures >5000 bar, as this pressure also exceeds the limits of the VolatileCalc2 calibration (Newman and Lowenstern, 2002). Melt inclusion entrapment depths were also not calculated for melt inclusions that did not have a paired H₂O and CO₂ measurement before “Fe-loss” corrections, as the estimated CO₂ did not include CO₂ that was in the glass, only CO₂ in the vapor bubble or there was no corresponding H₂O concentration. The eight samples for which VolatileCalc2 could be used to calculate entrapment depths (CO₂-H₂O pairs where CO₂ < 10,000 ppm and calculated P < 5,000 bar) were used to calculate a linear regression model relating

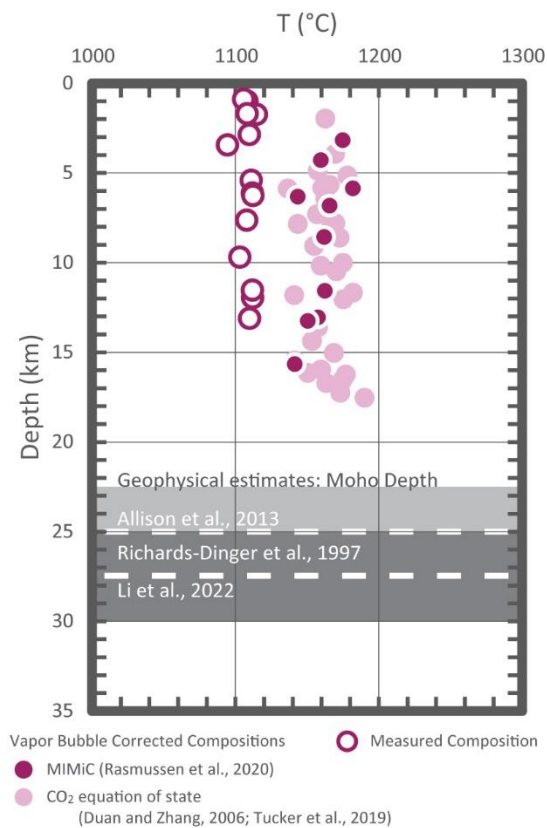


Figure 2.7. Plot of calculated melt inclusions entrapment depths (Newman and Lowenstern, 2002) versus calculated temperature (Helz and Thornber, 1987) for measured as well as “Fe-loss” (Danyushevsky et al., 2000) and vapor bubble corrected compositions from this study. Dark purple, open circles are calculated from the measured melt inclusion compositions for Pisgah Crater. Dark purple, closed circles are vapor bubble corrected melt inclusions calculated using MIMiC (Rasmussen et al., 2020). Light purple, closed circles are vapor bubble corrected melt inclusions calculated using a CO₂ equation of state (Duan and Zhang, 2006; Tucker et al., 2019). Also plotted are the estimated depths to the Mohorovičić discontinuity (Moho; crust-mantle boundary) beneath Pisgah Crater from geophysical models (Richards-Dinger and Shearer, 1997; Allison et al., 2013; Li et al., 2022).

CO₂ and depth (pressure = $0.6664x + 541.85$, $R^2 = 0.972$). This equation was used to calculate a minimum depth of entrapment for the remainder of the equation of state vapor bubble corrected melt inclusions in this study. This entrapment depth estimates are a minimum estimate because the amount of CO₂ remaining in the melt inclusions after the formation of the vapor bubble is unknown. Because of these limitations, entrapment depth calculations in this study using the equation of state correction should be taken as minimum depths of entrapment.

Melt inclusions with entrapment depths calculated via MIMiC with VolatileCalc2 have entrapment depths from 3 to 16 km (dark purple closed circles, Fig. 2.7; Table 2.1; Newman and Lowenstern, 2002; Rasmussen *et al.*, 2020). Melt inclusions with entrapment depths calculated from CO₂ corrections via vapor bubble size and CO₂

equation of state have entrapment depths from 2 to 18 km (6 to 17 km for depth calculated for samples with measured H₂O and CO₂ contents; light purple closed circles, Fig. 2.7; Table 2.1; Newman and Lowenstern, 2002; Duan and Zhang, 2006; Tucker *et al.*, 2019). Both correction methods are in general agreement that entrapment of these melts likely began around a minimum of ~15 – 20 km depth, with the majority of the melt inclusions being entrapped between 5 and 18 km (Fig. 2.7.). Assuming that olivine is crystallized from Pisgah parental magmas upon cooling in the crust, we take the deepest calculated entrapment depth of 18 km as the minimum estimate of the thickness of the crust, and the 5 – 15 km entrapment depth of the majority of the melt inclusions as the depth of a main magma storage body at Pisgah volcano. Because we observe that some melt inclusions have equation of state-corrected CO₂ concentrations >10,000 ppm and/or some have calculated entrapment pressures >5,000 bar, it is plausible that some melt inclusions may be trapped at depths >20 km. This extends the start of olivine crystallization to >20 km depth, and the minimum estimate of the depth of the crust-mantle boundary extending to these depths as well. This is in agreement with geophysical models based on receiver functions, ambient noise tomography, and seismic waveform stacking (PmP waves) in the Mojave Desert which indicate depths to the crust-mantle boundary are between 22.5 and 30 km (Fig. 2.7; Richards-Dinger and Shearer, 1997; Allison *et al.*, 2013; Li *et al.*, 2022). Given the large range in entrapment depths, it may be that the magmatic plumbing system beneath Pisgah Crater is complex, including storage locations that span much of the crust in this region. Further discussions of CO₂ contents our inclusions will focus on the MIMiC (Rasmussen *et al.*, 2020) corrected data.

The concentration of CO₂ in Pisgah melt inclusions broadly decreases with decreasing H₂O (Fig. 2.8.A.). We used VolatileCalc2 (Newman and Lowenstern, 2002) and D-Compress (Burgisser *et al.*, 2015) to examine the effect of volcanic degassing on our measurements. Isopleths (constant equilibrium vapor molar H₂O), isobars (constant pressure), and degassing trajectories were calculated using VolatileCalc2 and D-Compress. Pisgah melt inclusions do not plot along H₂O

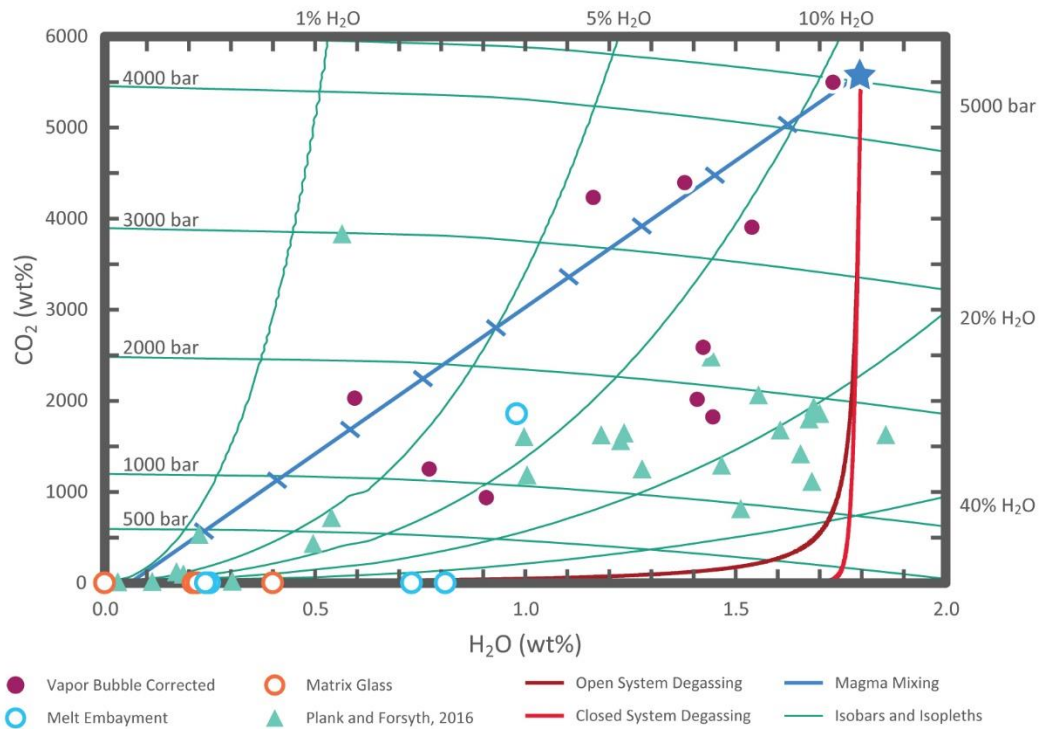


Figure 2.8. Plot of “Fe-loss” (Danyushevsky *et al.*, 2000) and vapor bubble corrected (Rasmussen *et al.*, 2020) CO₂ and H₂O concentrations for olivine hosted melt inclusions (purple closed circles), melt embayments (blue open circles), and matrix glasses (orange open circles) from this study as well as previous measurements of Pisgah melt inclusions (blue-green closed triangles; Plank and Forsyth, 2016). Open (dark red line) and closed (red line) system D-Compress (Burgisser *et al.*, 2015) degassing models were run at a starting pressure of 4400 bars, temperature of 1135°C, f_{O_2} of $\Delta NNO = +1.25$, H₂O concentration of 1.8 wt%, CO₂ concentration of 5600 ppm, and S concentration of 1825 ppm (blue closed star). Degassing models were run until the magma was fully depressurized to 1 bar. The mixing model represents mixing between the initial and end state of the D-Compress model runs with the tick marks representing 10% increments of mixing. Isobars and isopleths (blue-green, thin lines) are calculated in VolatileCalc (Newman and Lowenstern, 2002) at 45.58 wt% SiO₂ and 1165°C.

isopleths (blue-green lines, Fig. 2.8.A.), nor do they plot along an isobar (blue-green lines, Fig. 2.8.A.), nor along a simple degassing trajectory (red and dark red lines, Fig. 2.8.A.). We conclude that this suite of melt inclusions did not sample a simple ascending magma degassing $\text{H}_2\text{O}+\text{CO}_2$. We calculated a mixing model between a fictive “undegassed” magma containing the highest H_2O and CO_2 concentrations we measured and a fictive “degassed” magma (both open and closed system degassing in this case end at similar H_2O and CO_2 compositions) in accordance with D-Compress calculations for a degassing trajectory (dark blue line, Fig. 2.8.A.). Pisgah melt inclusions plot between the mixing line and the degassing trajectories, suggesting either (1) a complex combination of CO_2 +/- H_2O degassing and mixing between relatively undegassed and degassed magmas or (2) a combination of CO_2 +/- H_2O degassing and small amounts of H^+ diffusive loss from some melt inclusions. We tentatively rule out option (2) based on a lack of correlation between measured H_2O and melt inclusion diameter as well as the relationship between K_2O and both H_2O and CO_2 (Fig. 2.6.). In option (1), a magma might buoyantly ascend through the crust until it reaches a depth where it is neutrally buoyant and will have degassed some of the dissolved H_2O and CO_2 in proportion to the pressure at which it stalled. As the stalled magma continues to cool conductively against the surrounding crust, it would become dense and sink in the magmatic plumbing system. As this cooler, less volatile rich magma sinks, it would begin to mix with the warmer more volatile rich magmas. This mixing would generate a new volatile composition that could be sampled as melt inclusions during concomitant olivine crystallization, and the volatile concentrations recorded in these melt inclusions would reflect both the extent of degassing of the

stalled magma and the degree of mixing taking place between a partially degassed and relatively undegassed magma.

While the lack of relationship between melt inclusion diameter and H₂O concentration potentially rules out the possibility diffusive H⁺ loss from the melt inclusions in this study (though we stress the tentative nature of this simple interpretation), two additional lines of evidence suggest that it is possible that some non-zero extents of diffusive re-equilibration of H₂O may have taken place. First, these melt inclusions had sufficient time to undergo “Fe-loss,” (see Results, above) and they record a wide range of entrapment depths that suggest magma transport times from the time of initial olivine crystallization to eruption of greater than a few days (the timescales of H⁺ and *f*O₂ equilibration, e.g., Humphreys *et al.*, 2022). Second, the magma stalling-mixing scenario described

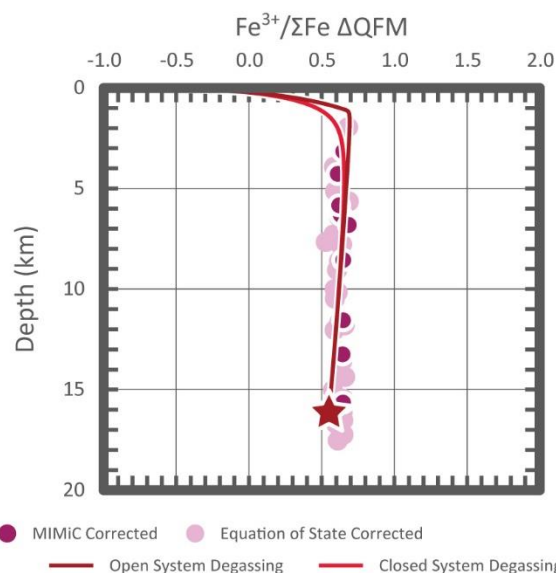


Figure 2.9. Plot depth and ΔQFM . Red and dark red curves are the same D-Compress (Burgisser *et al.*, 2015) degassing models as were run in Fig. 2.8. Closed purple star denotes the initial conditions of D-Compress (Burgisser *et al.*, 2015) degassing model. Purple closed circle and light purple closed circle symbols are the same as in Fig. 2.7.

in the previous paragraph suggests the transport of olivine grains in magmas of variable H₂O-CO₂ contents. Humphreys *et al.* (2022) suggests that incongruence between Fe- and V-based oxybarometers is associated with melt inclusions that experience significant H⁺ diffusive loss (because the timescales of *f*O₂ equilibration is as fast/faster than H⁺ diffusion through olivine; Bucholz *et al.*, 2013). In this study we find broad agreement between Fe-, S-, and V-

based oxybarometers (Fig. 2.3. A. & B.), all of which indicate average fO_2 s of Pisgah magmas between $\Delta QFM = +0.55$ (Borisov *et al.*, 2018) and $+1.05$ (Mallmann and O'Neill, 2013) at the time of olivine crystallization and melt inclusion entrapment. However, we emphasize that our Pisgah melt inclusions have S concentrations $> \sim 1100$ ppm and are not likely saturated with respect to a S-rich volatile phase. Although H_2O and CO_2 degassing are thought to drive small increases in the fO_2 of degassing magmas (Brounce *et al.*, 2017), the magnitude of this change for the Pisgah compositions captured by melt inclusions in this study is smaller than 0.2 log units (Fig. 2.9.), which is less than the precision of available oxybarometers at the time of writing. The large changes in fO_2 for degassing magmas observed in magmas such as is the case in Hawaiian magmas is thought to be driven by the addition of sulfur to the degassing vapor (Brounce *et al.*, 2017). The presence of a sulfide bleb in melt inclusions in the Pisgah olivines (Table 2A.2.4), indicates that the magma(s) sampled by the melt inclusions in this study were sulfide saturated and likely not degassing sulfur to a vapor phase. Therefore, though the congruence between Fe-, S-, and V-based oxybarometers would suggest that H^+ diffusive loss from the melt inclusions measured in this study did not occur, we emphasize that large changes in magmatic fO_2 would not be expected in magmas degassing only moderate amounts of H_2O and CO_2 , and suggest that studies of the hydrogen isotopic composition of Pisgah magmas would be strong evidence for or against substantial diffusive loss of H^+ .

From these observations, we conclude that the melt inclusion compositions with the highest MgO contents (> 6.0 wt%), the highest measured concentrations of H_2O (> 1.3 wt%) and/or CO_2 (2867 ppm) are most relevant to least degassed, parental magma compositions at Pisgah volcano. These compositions suggest minimum crustal thickness of 18 km and a complex network

of magma storage conditions, with potentially complex interactions between batches of magmas moving through the crust. We now use these compositions to calculate model primary melt compositions to place constraints on the conditions of melt generation in the asthenosphere, and the depth of the lithosphere asthenosphere boundary.

2.5.3. Primary Melts

We calculate primary melt (i.e., silicate melt in equilibrium with its peridotite source rock) compositions from our measured values assuming that the only crystal phase fractionating out of the magma is olivine. Because our MELTS models indicate that plagioclase and clinopyroxene were co-crystallizing in the compositional range of our melt inclusion measurements, this “olivine-only” calculation will be inaccurate to the degree to which the unaccounted-for plagioclase and clinopyroxene crystallization would have affected the measured melt inclusion compositions. For instance, in our MELTs models, plagioclase of 73-76% anorthite content ($\text{CaAl}_2\text{Si}_2\text{O}_8$) joins the liquidus assemblage when the melt reaches ~5.9 wt% MgO (our “Fe-loss” corrected melt inclusions have 5.4 – 6.8 wt% MgO). As plagioclase fractionally crystallizes from the magma, it will incorporate primarily Al_2O_3 and CaO into its crystal structure, decreasing the concentrations of these oxides in the melt, while all other oxides (such as FeO and Fe_2O_3) increase in the magma. Clinopyroxene ($\text{Ca, Mg, Fe})_2\text{Si}_2\text{O}_6$ joins the liquidus assemblage when the melt reaches 6.26 wt% MgO, which will decrease the concentrations of CaO, MgO, and FeO in the melt as they are incorporated into the clinopyroxene crystal structure, while simultaneously increasing the concentrations of other oxides, such as Na_2O and K_2O . Clinopyroxene also can incorporate Fe_2O_3 into its crystal lattice, which will cause a decrease in the melt $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio.

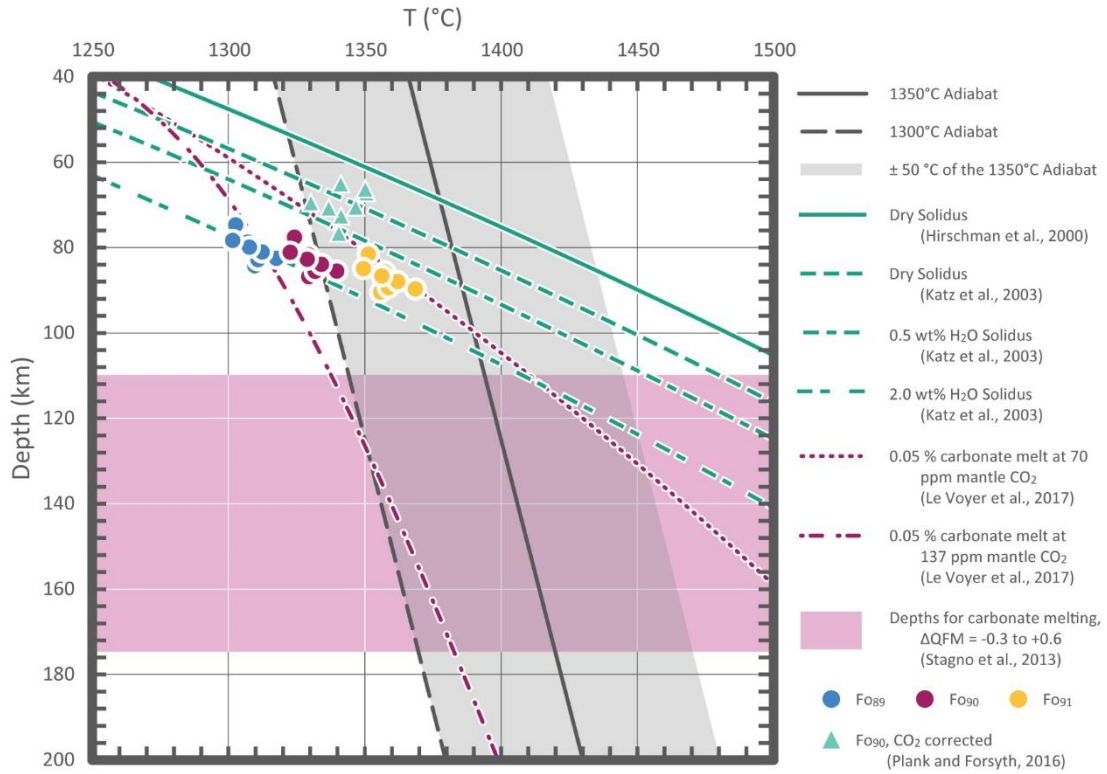


Figure 2.10. Plot of depth and temperature that melt inclusion compositions with the highest “Fe-loss” corrected MgO concentrations and assigned highest H_2O and CO_2 concentrations ($H_2O_{max} = 1.84$ wt%, $CO_{2-max} = 5497$ and $15,816$ ppm) were last in chemical equilibrium with the mantle. Closed circles are samples with depth and temperature corrections to account for the presence of CO_2 in the melt (Plank and Forsyth, 2016). Yellow circles are those samples that have had equilibrium olivine added back into the melt inclusion composition until the resultant melt composition is in equilibrium with Fo_{91} olivine. Purple circles are calculated to be in equilibrium with Fo_{90} olivine. Blue circles are calculated to be in equilibrium with Fo_{89} olivine. Blue-green triangles are calculated to be in equilibrium with Fo_{90} olivine (Plank and Forsyth, 2016). Solid blue-green line is the dry solidus as determined by Hirschman et al. (2000). Dashed blue-green lines are the dry, 0.5 wt% H_2O , and 2.0 wt% H_2O solidus as determined by Katz et al. (2003). Solid grey line is 1350°C mantle adiabat (e.g., Lee et al., 2009) with grey dashed lines being the ± 50 °C range for the adiabat. Pink field is the range in depths for carbonate melting in the mantle when mantle fO_2 is between $\Delta QFM = -0.3$ and $+0.6$ (Stagno et al., 2013). Dotted purple lines are where 0.05 wt% carbonate melt would be present when the source mantle has 70 and 137 ppm CO_2 .

We take our least fractionated melt inclusion measurements (“Fe-loss” corrected melt inclusion compositions with MgO > 6.44 wt% - melt inclusions higher than one standard deviation above the average MgO concentration in this study) to avoid the effects of plagioclase and clinopyroxene crystallization described in the previous paragraph and assign those the highest H₂O and CO₂ concentrations from this study (H₂O = 1.84 wt%; MIMiC CO₂ = 5497 ppm; equation of state CO₂ = 15,816 ppm). We then add equilibrium composition olivine back into the composition in incremental steps until we obtain a magma composition that is in equilibrium with olivine that has the same Fo_# presumed for olivine in the mantle source(s) of Pisgah lavas. In this study, we use the Fo_#s of olivines contained in peridotitic xenoliths from nearby Dish Hill (Fo₈₈₋₉₁; as compiled by (Wang *et al.*, 2002), a mafic volcano that is ~40 km south-east of Pisgah Crater. Accordingly, we calculate primary melt compositions in equilibrium with Fo₈₉, Fo₉₀, and Fo₉₁ olivine (Fig. 2.10. A; Table 2.3). These primary melts have higher MgO (Fo₈₉ = 9.8 – 10.7 wt%, Fo₉₀ = 11.0 – 12.0 wt%, Fo₉₁ = 12.9 – 13.9 wt%; Table 2.3) and FeO* (Fo₈₉₋₉₁ = 9.8 – 10.2 wt%; Table 2.3) and lower H₂O (Fo₈₉₋₉₁ = 1.6 – 1.7 wt%; Table 2.3), and Fe³⁺/ΣFe (Fo₈₉ = 0.175 – 0.183, Fo₉₀ = 0.173 – 0.180, Fo₉₁ = 0.166 – 0.174; Table 2.3) than the “Fe-loss” corrected melt inclusion compositions (Table 2.3).

Pressures and temperatures for equilibrium melts were calculated using the thermobarometer of Lee et al. (2009) as modified by Plank and Forsyth (2016) and range from 1302 – 1369°C and 2.3 – 2.8 GPa (1323 – 1340°C and 2.4 – 2.7 GPa for melts in equilibrium with Fo₉₀ olivine; Fig. 2.10.; Table 2.3). We estimate that these pressures correspond to depth in the Earth of 75 – 90 km (78 – 84 km for melts in equilibrium with Fo₉₀ olivine; purple closed circles, Fig. 2.10; Table 2.3) assuming a crustal thickness of 20 km (between the deepest melt inclusion entrapment

depths calculated in this study and the shallowest estimated depth from geophysics models (Allison *et al.*, 2013); with a density of 2.80 gcm^{-3} as well as a mantle density of 3.25 gcm^{-3} . Assuming that melt generation occurs in the asthenosphere, we take these pressures and temperatures as minimum estimates to the depth of the lithosphere-asthenosphere boundary under Pisgah volcano. These estimates are $\sim 10 \text{ km}$ deeper than what was calculated for Pisgah previously (65 – 77 km; blue-green closed triangles, Fig. 2.10.; Plank and Forsyth, 2016) and consistent with estimates from receiver function analysis and Rayleigh surface wave tomography (75 – 90 km; Plank and Forsyth, 2016).

Using these modelled primary melt compositions, we also calculated the degree of melting of depleted harzburgitic mantle rock and mantle source H_2O concentrations following the methods of Kelley *et al.* (2006). Using primary melt TiO_2 concentrations, an assumed TiO_2 of the mantle source equal to that of the depleted MORB mantle ($\text{TiO}_2 = 0.133 \text{ wt\%}$; Kelley *et al.*, 2006), and bulk partition coefficient during melting of peridotite for TiO_2 of 0.04, we estimate that Pisgah magmas are produced by 1.7 – 2.8 % melting of peridotite. These degrees of melting are $\sim$ half or lower than the expected extent of melting under mid-ocean ridge spreading centers (4 – 17%; e.g., Plank and Langmuir, 1992) and likely drive the enriched nature of Pisgah trace element patterns relative to normal MORB. Using these melt fractions, calculated primary melt H_2O contents of 1.1 – 1.5 wt% for melts in equilibrium with Fo_{90} olivines, and bulk partition coefficient during melting of peridotite for H_2O of 0.012 (Kelley *et al.*, 2006), we estimate that the source mantle peridotite with Fo_{90} olivine for Pisgah magmas contains up to 579 ppm H_2O (Fig. 2.10. C; Table 2.3). This H_2O concentration is $\sim$ 3-10 times higher than that expected for a nominally anhydrous depleted upper

Table 2.3: Melt inclusion composition in equilibrium with Fo_{89-91} olivine from melt inclusions in this study with the highest MgO concentrations.

Samples	Fo#	Olivine % Added	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	FeO* (wt%)	Fe ₂ O ₃ (wt%)	FeO (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	P ₂ O ₅ (wt%)
Fo₈₉														
P17_20_10B	89		11.6	44.8	2.3	15.0	10.2	2.0	10.7	0.1	10.7	8.7	3.7	1.6
P17_AL_01A	89		10.4	45.6	2.2	14.7	10.1	2.0	10.7	0.1	10.3	8.8	3.5	1.5
P17_AL_03	89		8.0	43.6	2.4	15.1	9.9	2.0	10.7	0.1	9.8	8.6	3.8	1.7
P17_JAH_09	89		10.6	45.1	2.3	15.0	10.0	2.0	10.7	0.1	10.5	8.4	3.5	1.8
P17_JAH_11	89		9.4	44.8	2.4	15.2	10.0	2.0	10.7	0.1	10.2	8.4	3.9	1.8
P17_N_20_10	89		9.9	44.9	2.3	15.0	10.1	2.1	10.7	0.1	10.4	8.4	3.7	1.7
P17_N_20_14A	89		9.9	45.0	2.3	15.2	10.1	2.0	10.7	0.1	10.3	8.8	3.7	1.6
P17_N_20_14B	89		9.7	45.2	2.3	15.4	10.0	2.0	10.7	0.1	10.2	8.8	3.6	1.6
Fo₉₀														
P17_20_10B	90		15.4	44.7	2.2	14.5	10.2	2.0	9.8	0.1	11.9	8.4	3.5	1.6
P17_AL_01A	90		14.1	45.5	2.1	14.2	10.1	2.0	9.8	0.1	11.6	8.5	3.4	1.4
P17_AL_03	90		11.3	43.5	2.3	14.6	9.9	2.0	9.8	0.1	11.0	8.4	3.7	1.7
P17_JAH_09	90		14.4	44.9	2.3	14.5	10.0	1.9	9.8	0.1	11.7	8.1	3.4	1.7
P17_JAH_11	90		13.0	44.7	2.3	14.7	10.0	2.0	9.8	0.1	11.4	8.2	3.8	1.8
P17_N_20_10	90		13.6	44.8	2.3	14.5	10.1	2.0	9.8	0.1	11.7	8.2	3.6	1.6
P17_N_20_14A	90		13.5	44.9	2.2	14.7	10.1	2.0	9.8	0.1	11.5	8.5	3.6	1.6
P17_N_20_14B	90		13.3	45.0	2.2	14.9	10.0	2.0	9.8	0.1	11.4	8.6	3.5	1.5
Fo₉₁														
P17_20_10B	91		20.3	44.5	2.1	13.9	10.2	1.9	8.8	0.1	13.5	8.1	3.4	1.5
P17_AL_01A	91		18.7	45.3	2.1	13.7	10.0	1.9	8.8	0.1	13.1	8.2	3.2	1.4
P17_AL_03	91		15.6	43.4	2.2	14.1	9.8	1.9	8.8	0.1	12.4	8.1	3.5	1.6
P17_JAH_09	91		19.1	44.8	2.2	13.9	10.0	1.9	8.8	0.1	13.2	7.8	3.2	1.6
P17_JAH_11	91		17.5	44.5	2.2	14.1	10.0	1.9	8.8	0.1	12.9	7.9	3.6	1.7

P17_N_20_10	91	18.3	44.7	2.2	13.9	10.1	1.9	8.8	0.1	13.2	7.8	3.5	1.6	0.5
P17_N_20_14A	91	18.1	44.7	2.1	14.1	10.0	1.9	8.8	0.1	13.0	8.2	3.4	1.5	0.4
P17_N_20_14B	91	17.8	44.9	2.1	14.3	10.0	1.9	8.8	0.1	12.9	8.2	3.4	1.5	0.5

¹Vapor bubble correction from Rasmussen et al., 2020

²Vapor bubble correction from Tucker et al., 2019, using the equation of state for CO₂ from Duan and Zhang, 2006

³Melt fractionation calculation using equation 9 and DMM TiO₂ = 0.133 from Kelley et al., 2006

⁴Source mantle H₂O calculation using equation 10 and the given DH₂O = 0.012 from Kelley et al., 2006

⁵Source mantle CO₂ calculation using equation 10 and DCO₂ = 0.00055 (Rosenthal et al., 2015) from Kelley et al., 2007

⁶Kress and Carmichael, 1991

⁷O'Neill et al. 2018 with Fe³⁺/ΣFe correction via Berry et al., 2018

⁸Jayasuriya et al., 2004

⁹Borisov et al., 2017

¹⁰Pressure and temperature of the melt's last equilibration with mantle peridotite using equations 1 and 2 from Plank and Forsyth, 2016

¹¹Calculated using the equation $P = \rho gh$ using a depth to the crust-mantle boundary = 20 km, $\rho_{\text{crust}} = 2.8 \text{ g/cm}^3$, $\rho_{\text{crust}} = 3.25 \text{ g/cm}^3$

¹²Pressure and temperature correction for the presence of CO₂ using equation 3 from Plank and Forsyth, 2016

H ₂ O (wt%)	S (ppm)	CO ₂ ¹ (ppm)	CO ₂ ² (ppm)	Fe ³⁺ /ΣFe	F ³	H ₂ O _{source} ⁴ (wt%)	H ₂ O _{source} ⁴ (ppm)	CO _{2-source} ^{1,5} (ppm)	CO _{2-source} ^{2,5} (ppm)	fO ₂ ⁶	fO ₂ ⁷	fO ₂ ⁸	fO ₂ ⁹
1.65	1514	4926	14172	0.178	0.019	0.05	500	91	263	-0.12	0.54	0.05	-0.43
1.67	1464	4979	14326	0.179	0.021	0.05	546	105	302	-0.11	0.57	-0.01	-0.36
1.70	1640	5090	14645	0.175	0.016	0.05	475	82	236	-0.14	0.43	0.02	-0.44
1.66	1173	4970	14300	0.183	0.017	0.05	488	87	251	-0.11	0.62	0.01	-0.40
1.68	1591	5025	14457	0.180	0.017	0.05	479	84	241	-0.13	0.52	0.04	-0.43
1.68	993	5002	14392	0.183	0.018	0.05	493	88	254	-0.09	0.60	0.03	-0.39
1.68	1281	5002	14392	0.183	0.018	0.05	504	92	264	-0.11	0.60	-0.02	-0.40
1.68	1225	5011	14418	0.183	0.018	0.05	507	93	266	-0.11	0.61	0.00	-0.37
1.60	1464	4764	13706	0.173	0.021	0.05	515	98	282	0.04	0.50	0.27	-0.33
1.61	1416	4818	13862	0.175	0.023	0.06	562	112	321	0.05	0.56	0.21	-0.26
1.65	1591	4939	14211	0.180	0.018	0.05	490	88	254	0.02	0.56	0.23	-0.34
1.61	1134	4805	13825	0.174	0.020	0.05	504	94	271	0.05	0.54	0.23	-0.30
1.63	1540	4865	13997	0.177	0.019	0.05	495	91	261	0.03	0.53	0.26	-0.32
1.62	961	4839	13923	0.176	0.020	0.05	509	95	274	0.07	0.55	0.25	-0.29
1.62	1241	4843	13935	0.176	0.020	0.05	520	98	283	0.05	0.54	0.20	-0.30
1.63	1186	4852	13960	0.177	0.020	0.05	522	99	285	0.06	0.55	0.22	-0.27
1.53	1404	4569	13147	0.166	0.023	0.05	534	106	306	0.21	0.45	0.50	-0.24
1.55	1362	4631	13325	0.169	0.026	0.06	580	119	343	0.22	0.51	0.45	-0.16
1.59	1532	4755	13682	0.174	0.020	0.05	508	96	276	0.20	0.52	0.48	-0.23
1.55	1090	4616	13280	0.168	0.022	0.05	522	102	293	0.22	0.49	0.47	-0.21
1.57	1481	4678	13461	0.171	0.021	0.05	513	98	283	0.21	0.49	0.50	-0.22
1.56	923	4647	13370	0.170	0.022	0.05	528	103	297	0.25	0.51	0.49	-0.20
1.56	1192	4655	13392	0.170	0.023	0.05	538	106	306	0.22	0.49	0.45	-0.20
1.56	1140	4666	13426	0.170	0.023	0.05	540	107	307	0.23	0.51	0.46	-0.17

P ¹⁰ (GPa)	D ¹¹ (km)	T ¹⁰ (°C)	P ^{10,12} (GPa)	D ¹¹ (km)	T ^{10,12} (°C)
2.6	84	1352	2.5	83	1318
2.3	76	1330	2.3	75	1303
2.7	86	1346	2.6	84	1310
2.5	80	1337	2.4	79	1307
2.6	84	1344	2.6	83	1311
2.5	82	1344	2.5	81	1312
2.5	81	1340	2.5	80	1308
2.5	80	1333	2.4	78	1302
2.7	87	1376	2.6	86	1340
2.4	79	1353	2.4	78	1324
2.7	89	1367	2.7	87	1329
2.6	83	1361	2.5	82	1329
2.7	87	1367	2.6	86	1332
2.6	85	1367	2.6	84	1334
2.6	84	1363	2.6	83	1329
2.5	83	1356	2.5	81	1323
2.8	91	1406	2.8	90	1369
2.6	83	1382	2.5	82	1351
2.9	92	1395	2.8	90	1356
2.7	87	1391	2.6	86	1357
2.8	91	1395	2.8	89	1359
2.8	90	1397	2.7	88	1362
2.7	88	1392	2.7	87	1356
2.7	86	1384	2.6	85	1350

mantle that feeds the mid ocean ridge spreading system (e.g., 59-160 ppm H₂O; yellow field and orange open circles plus orange field, Fig. 2.10. C.; Workman and Hart, 2005; Shimizu *et al.*, 2016) and about half the estimated maximum H₂O storage capacity of peridotite at ~2 GPa (~1000 ppm; (Hauri *et al.*, 2006). This H₂O concentration is within the estimated range of enriched MORB mantle (660 ± 184 ppm; blue open circle and corresponding blue field, Fig. 2.10. C; Shimizu *et al.*, 2016).

The concentration of CO₂ decreases across a near constant Ba concentration for primary melt, indicating that the melt inclusions were entrapped as CO₂ was degassing from the melt (Fig. 2.10.B.). Using the above melt fractions, calculated primary melt CO₂ contents of 1534 – 4682 ppm (from MIMiC vapor bubble corrections; Rasmussen *et al.*, 2020) or 1363 – 13893 ppm (from equation of state vapor bubble corrections; Duan and Zhang, 2006; Tucker *et al.*, 2019) for melts in equilibrium with Fo₉₀ olivines, and bulk partition coefficient during melting of peridotite for CO₂ of 0.00055 (Rosenthal *et al.*, 2015), we estimate source mantle peridotite with Fo₉₀ olivine for Pisgah magmas (Fig. 2.10.C; Table 2.3). If the MIMiC (Rasmussen *et al.*, 2020) CO₂ vapor bubble correction is the more accurate correction, then Pisgah Crater melt inclusions have similar CO₂ (CO_{2-max} = 112 ppm) concentrations to depleted MORB mantle (purple circles, Fig. 2.11. A; Workman and Hart, 2005; Shimizu *et al.*, 2016, 2023). If the equation of state (Duan and Zhang, 2006; Tucker *et al.*, 2019) CO₂ vapor bubble correction is the more accurate correction then the Pisgah Crater source mantle has H₂O and CO₂ (CO_{2-max} = 321 ppm) concentrations similar to those of enriched depleted MORB mantle source rocks (light purple circles, Fig. 2.11. A; Workman and

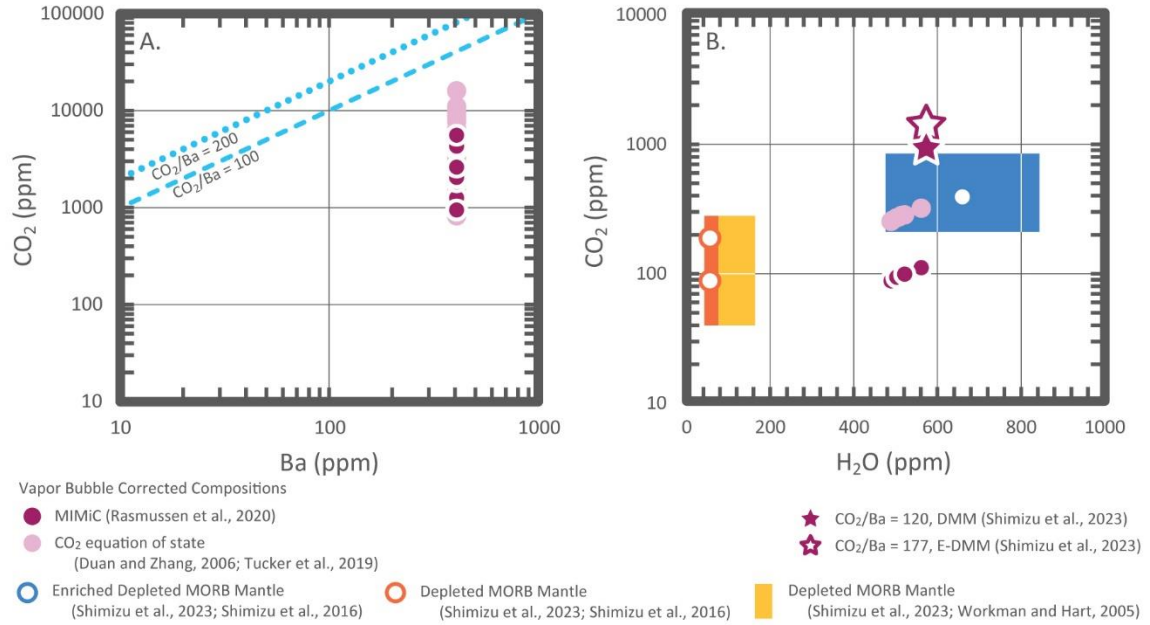


Figure 2.11. (A) Plot of Ba and CO_2 . Purple closed circles are MIMiC (Rasmussen et al., 2020) vapor bubble corrected melt inclusion CO_2 concentrations and average measured Ba (408 ppm) in this study. Light purple closed circles are equation of state (Duan and Zhang, 2006; Tucker et al., 2019) corrected melt inclusion CO_2 concentrations and average measured Ba (408 ppm) in this study. Blue lines are for constant CO_2/Ba : dashed line is $\text{CO}_2/\text{Ba} = 100$ and dotted line is $\text{CO}_2/\text{Ba} = 200$. B. Plot of H_2O and CO_2 for mantle sources. Purple closed circles are calculated source H_2O and CO_2 from the volatile contents of the closed purple circles in Fig. 2.10 and associated CO_2 vapor bubble corrections from MIMiC (Rasmussen et al., 2020) and a CO_2 equation of state (Duan and Zhang, 2006; Tucker et al., 2019). Blue open circle is the H_2O (Shimizu et al., 2016) and CO_2 (Shimizu et al., 2023) concentration for enriched MORB source mantle. Blue field is the extent of the uncertainty for this concentration. Orange open circles are H_2O (Shimizu et al., 2016) and CO_2 (Shimizu et al., 2023) concentrations for depleted MORB source mantle. Orange field is the extent of the uncertainty for these concentrations. Yellow field is the H_2O (Workman and Hart, 2005) and CO_2 (Shimizu et al., 2023) concentration for depleted MORB source mantle and associated uncertainty. Purple closed star is the possible mantle source H_2O and CO_2 from the highest calculated mantle source H_2O in this study for melts in equilibrium with Fo₉₀ olivines and a CO_2 concentration calculated from the depleted MORB source, $\text{CO}_2/\text{Ba} = 120$ when Ba = 408 ppm (average measured Ba for Pisgah melt inclusions in this study). Purple open star is the possible mantle source H_2O and CO_2 from the highest calculated mantle source H_2O in this study for melts in equilibrium with Fo₉₀ olivines and a CO_2 concentration calculated from the enriched MORB source, $\text{CO}_2/\text{Ba} = 177$ when Ba = 408 ppm (average measured Ba for Pisgah melt inclusions in this study).

Hart, 2005; Shimizu *et al.*, 2016, 2023). However, if the initial CO₂/Ba was either the same as that in depleted or enriched MORB mantle (120 and 177, respectively; Shimizu *et al.*, 2023), then the source mantle may have had as high as 979 (depleted MORB mantle) – 1444 (enriched MORB mantle) ppm CO₂ prior to melting, a higher CO₂ concentration than enriched MORB mantle source rock. It is also possible that melt fractions are even lower than calculated. If only 1% of depleted mantle containing 150 ppm CO₂ melted, that would be sufficient to generate a melt with 14,000 ppm CO₂, the high range of primary melt CO₂ estimates from this study (Table 2.3). The source of this possible CO₂ and H₂O enrichment is unknown; however, the long history of subduction during the Jurassic and Cretaceous in this region is a likely candidate.

The conditions of melting are consistent with an asthenosphere that is on the cooler side of, if not even slightly cooler than, the range of estimated mantle potential temperatures today (1300-1400°C; e.g., Lee *et al.*, 2009) and situate the melt at the lithosphere-asthenosphere boundary between the 0.5 and 2.0 wt% H₂O solidus (Fig. 2.10.); however these water contents are much higher than calculated for Pisgah source mantle (~0.05 wt%, Table 2.3) indicating that CO₂ likely plays a role in generating melt beneath Pisgah Crater. To assess the importance of the role of CO₂ in melt generation, two considerations must be made: (1) the fO_2 of the mantle, which controls whether carbon in the mantle will be speciated as graphite/diamond ($fO_2s < \Delta QFM-2$; immobile phases which will not lower the peridotite solidus; Stagno *et al.*, 2013) or carbonate ($fO_2s > \Delta QFM-2$; a flux in the mantle which dramatically lowers the peridotite solidus (Dasgupta *et al.*, 2013) and (2) the depth at which this melting could initiate. At the fO_2s calculated for melts in equilibrium with mantle peridotite in this study ($\Delta QFM = -0.3 - +0.6$; Table 2.3), carbonate-induced peridotite

melting initiates beneath Pisgah Crater at depths as deep as 110 ($\Delta QFM \approx -0.3$) – 175 ($\Delta QFM \approx +0.6$) km, where mantle carbon is oxidized from graphite/diamond into carbonate (Stagno *et al.*, 2013). The exact depth of melt generation, and whether it takes place at these, or shallower, depths is dependent on the initial CO₂ concentration of the mantle. At depths ranging from where melt might be first generated (~175 km) and where the melt last equilibrated with the mantle (~85 km), carbonate melts can become interconnected at melt fractions of ~0.05 % carbonate; Minarik and Watson, 1995) with as little as 70 – 137 ppm CO₂ in the source mantle rock (purple dotted and dot-dashed lines, Fig. 2.10; Le Voyer *et al.*, 2017). Since CO_{2-max} = ~110 or 320 ppm, depending on the correction method, for Pisgah Crater source mantle, the presence of CO₂ in the mantle is the likely cause of melt generation beneath Pisgah.

There are two ways in which carbonate melting beneath Pisgah Crater could generate magmas: 1) melting at ~85 km, where the mantle adiabat intersects an interconnected melt line for carbonate melts, or 2) a combination of melting at depths greater than 85 km and upwelling of that melt to ~85 km where it pools and equilibrates with the mantle at that depth. In the first scenario, the source mantle would have somewhere between 70 and 137 ppm CO₂ (purple dotted and dot-dashed lines, Fig. 2.10; Le Voyer *et al.*, 2017) but because the mantle is relatively cool beneath Pisgah Crater (adiabat is ~1300°C; grey dashed line, Fig. 2.10), sufficient melt generation for the melts to become interconnected would not be possible until ~85 km, where the 0.05 % melt fraction for the source mantle CO₂ concentration intersects the mantle adiabat. In this scenario, the presence of volatiles in the mantle beneath Pisgah Crater would be solely responsible for generating melt. In the second scenario, the mantle would have sufficient CO₂ for melting to initiate at some depth

below where the melts pooled, up to ~175 km depth (pink field, Fig. 2.10; Stagno *et al.*, 2013). If the mantle has 137 ppm CO₂, melting in this scenario could have initiated at some depth > 130 km. By 130 km, melting in a mantle with a potential temperature of 1300°C would have become interconnected (intersection of grey dashed line with purple dot-dashed line, Fig. 2.10). At this point, the melt and associated rocks would then rise along the mantle adiabat (grey dashed line, Fig. 2.10) until ~85 km depth where the melt pools and equilibrates with the surrounding mantle peridotite. This scenario would require mantle upwelling of anywhere from ~20 – 90 km and would necessitate a mechanism for decompression in the Mojave Desert, either from crustal thinning associated with motion along the San Andreas fault (e.g., Atwater, 1970; Fitton *et al.*, 1991; Leeman and Harry, 1993; Nicholson *et al.*, 1994) or the loss of the Farallon slab from beneath the Basin and Range Province (e.g., Humphreys, 1995; Humphreys *et al.*, 2003; Lee, 2005). Since the mantle beneath Pisgah Crater has at a minimum ~110 or ~320 ppm CO₂ (depending on the vapor bubble correction method; Table 2.3), either of the above two scenarios presents a possible explanation for melt generation. As this study is unable to sort between these two melting scenarios, electrical conductivity studies (in which 0.05 wt% carbonate melt should be conductive; e.g., Le Voyer *et al.*, 2017) would be a useful next step for determining the depth of melt generation beneath Pisgah Crater.

An enrichment in source mantle CO₂ concentration (Fig. 2.11.B; Table 2.3) is the likely cause of low degree melting beneath Pisgah Crater. If this CO₂ enrichment exists for the entire mantle beneath the Mojave Desert and the greater Basin and Range Province (and has a similar fO_2), then this enrichment is the likely cause of melt generation for the region. The origin of this

CO₂ enrichment may be from the long history of subduction in this region (e.g., Atwater, 1970; Saleeby, 1983) but further isotopic analyses of the volatiles would be necessary to test this hypothesis. After subduction ceased (along with associated volcanism), melt generation in this region would take place through low degrees of melting of the source mantle due to the oxidation of carbon into carbonate. This process would transition the cause of volcanism in the region from subduction driven to low degrees of asthenosphere melting due to volatile enrichments and could explain the change in chemical signatures of Basin and Range mafic volcanism away from subduction related chemistries at ~5 Ma (Fitton *et al.*, 1991).

After the melt was generated, it eventually ascended through the lithosphere until it reached the crust-mantle boundary (≥ 20 km depth) where it began to entrap melt inclusions within olivine crystals. The crustal magmatic plumbing system beneath Pisgah Crater is complex with magma mixing taking place between magmas that have equilibrated from depths of ~5 – 20 km. Melt inclusion entrapment depths reflect this history with some inclusions showing entrapment along a degassing trajectory, some showing entrapment along a mixing trajectory, and most being entrapped between a mix of degassing and magma mixing. After entrapment, these melt inclusions resided in the crust for a sufficient amount of time to undergo “Fe-loss” (up to two years for full equilibration; Danyushevsky *et al.*, 2002) as well as for the host olivines to become zoned. The long residence time of olivine hosted melt inclusions in the crust is further supported by the increasing phenocryst size of Pisgah lavas with each successive eruption and that the melt inclusions record basaltic compositions (the same as the earliest erupted compositions at Pisgah; Wise, 1969) and not the basaltic composition of the lava that they erupted with.

2.6. Conclusions

Pisgah magmas were first generated as a result of ~2% melting of the asthenosphere in the presence of ~580 ppm H₂O and, at a minimum, 110 ppm CO₂. The presence of CO₂ in the mantle source rocks significantly suppressed the peridotite solidus, allowing for carbonate melt generation either at or below ~85 km depth, depending on the initial concentration of CO₂ in the mantle (Fig. 2.10.). These magmas then rose through the lithosphere and pooled at or near the crust mantle boundary (≥ 20 km depth) with entrapment of the melts taking place in a degassing and mixing magma between ~5 and 20 km depth (Fig. 2.7). This variably mixed magma resided within the crust for up to 2 years and underwent “Fe-loss” as a result (Danyushevsky *et al.*, 2000). There was little change to the oxidation state of the magma during this residence time due to minimal sulfur degassing at the entrapment depths recorded by melt inclusions.

In the past 5 Ma, mafic volcanism in the Basin and Range province ceased to retain geochemical signatures related to subduction, instead having geochemical signatures of low degree asthenosphere melting (Fitton *et al.*, 1991). Pisgah Crater demonstrates that low degree of mantle melting is possible in the Basin and Range province with a carbonated asthenosphere (Fig. 2.10.). These findings allow for the possibility that asthenosphere upwelling, regardless of the tectonic cause, is responsible for magmatism in the Basin and Range Province since 5 Ma (e.g., Atwater, 1970; Fitton *et al.*, 1991; Leeman and Harry, 1993; Nicholson *et al.*, 1994; Humphreys *et al.*, 2003; Lee, 2005); however, it is equally likely that magmatism is due to the enrichment in CO₂ with melting that may have taken place at depths as shallow as ~85 km (where Pisgah Crater melts were last in chemical equilibrium with the mantle).

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CHAPTER TWO

VOLATILES AND $f\text{O}_2$ FROM OLIVINE HOSTED MELT INCLUSIONS, EMBAYMENTS, AND MATRIX GLASSES AT PISGAH CRATER, MOJAVE DESERT, CALIFORNIA

J. Humphreys and M. Brounce

2A.1. Figures

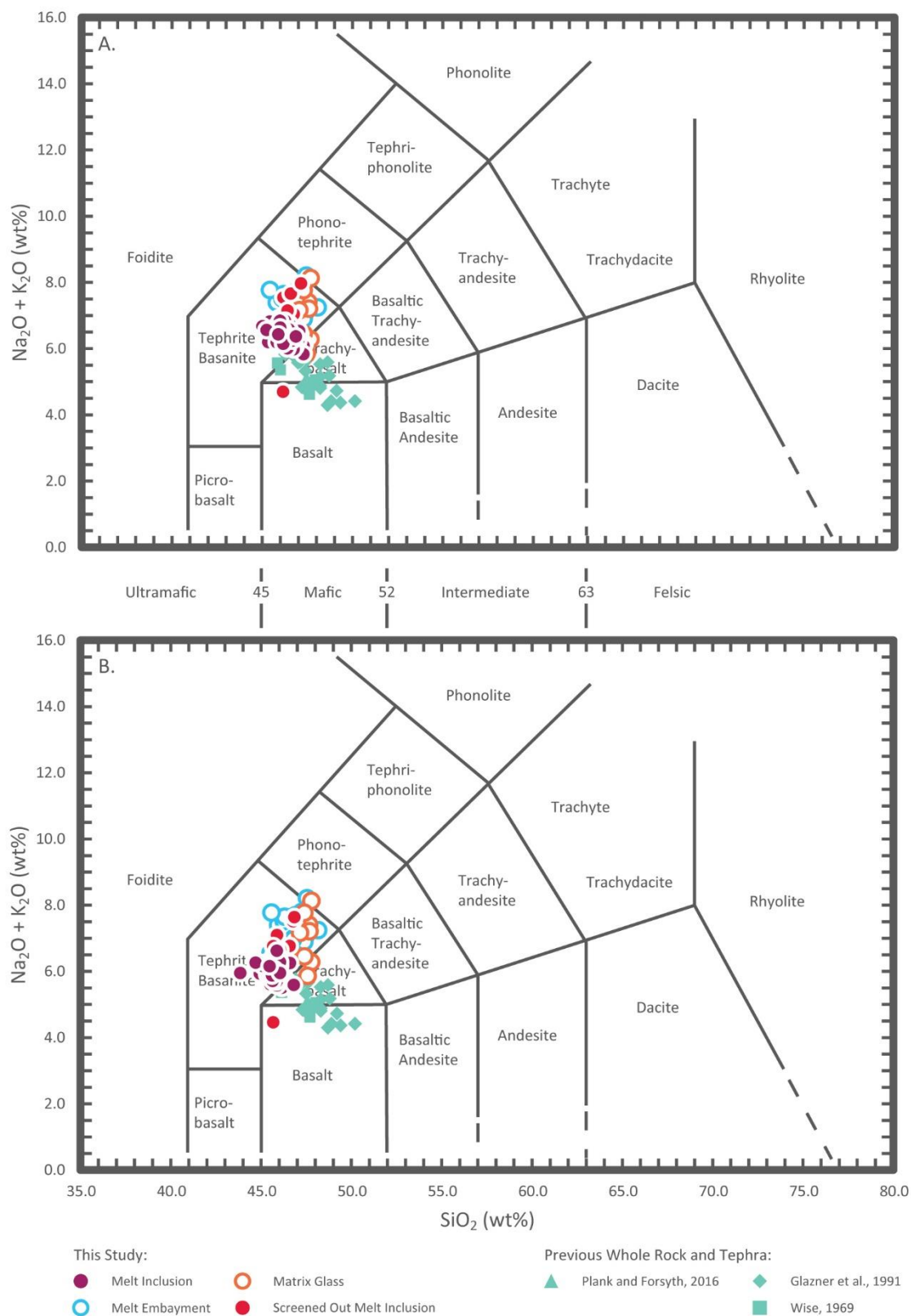


Figure 2A.1.1. Total Alkali Silica (TAS) diagram (modified from (Bas et al., 1986). (A) Pisgah Crater measured melt inclusion (purple closed circles), melt embayment (blue open circles), matrix glass (orange open circle), and screened out melt inclusion (red closed circles) compositions from this study. Previous measurements of Pisgah Crater whole rock (blue-green diamonds; (Wise, 1969); and blue-green closed circles; (Glazner, 1991) and Pisgah and Amboy whole rock tephra (brown closed circles for Pisgah and brown diamonds for Amboy; (Plank and Forsyth, 2016). (B) Pisgah Crater “Fe-loss” corrected (Danyushevsky et al., 2000; Rasmussen et al., 2020) melt inclusion (purple closed circles) and screened out melt inclusion (red closed circles) compositions from this study. All other symbols are the same as they are in A.

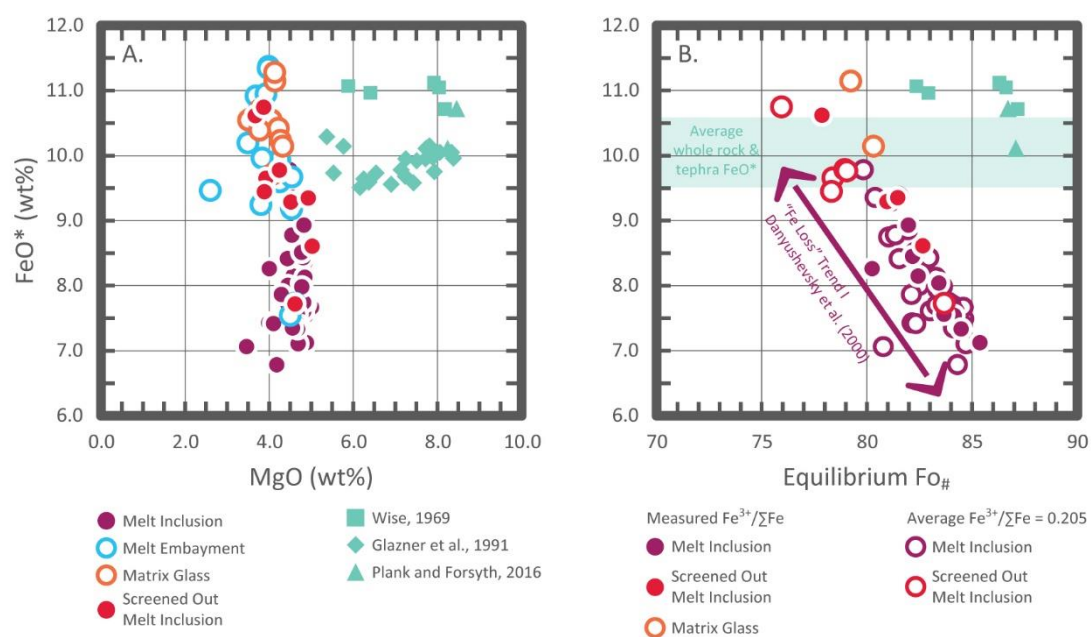


Figure 2A.1.2. (A) Figure 2. A. from the main text with the addition of screened out Pisgah Crater melt inclusion compositions from this study (red closed circles). B. Figure 2. (B) from the main text with the addition of screened out Pisgah Crater melt inclusion compositions from this study (red closed circles).

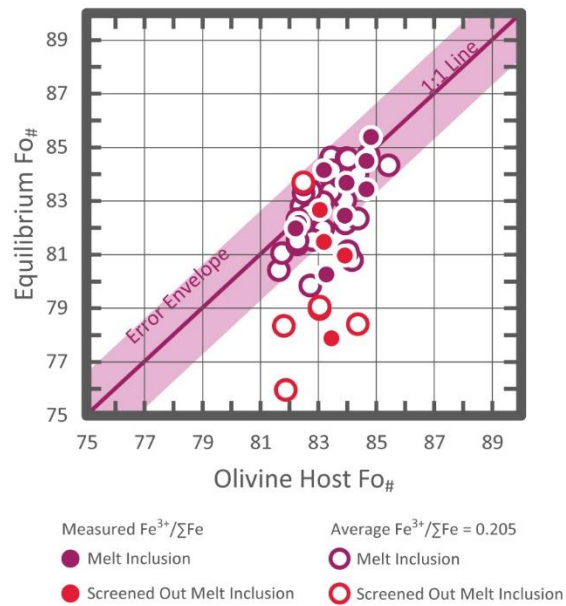


Figure 2A.1.3. Measured olivine host $\text{Fo}_{\#}$ compared to calculated equilibrium $\text{Fo}_{\#}$ for the melt inclusion compositions in this study. Melt inclusion symbols are the same as in Supplemental Figure 2. B. Solid purple line is the 1:1 relationship. The light purple field is the error envelope for the $\text{Fo}_{\#}$ calculations calculated by propagating the average analytical error for FeO^* and MgO through the equations for calculating equilibrium $\text{Fo}_{\#}$ (Supplemental Table 2). Most of the melt inclusion compositions measured in this study plot within the 1:1 field, expected for melt inclusions that have undergone “Fe loss.”

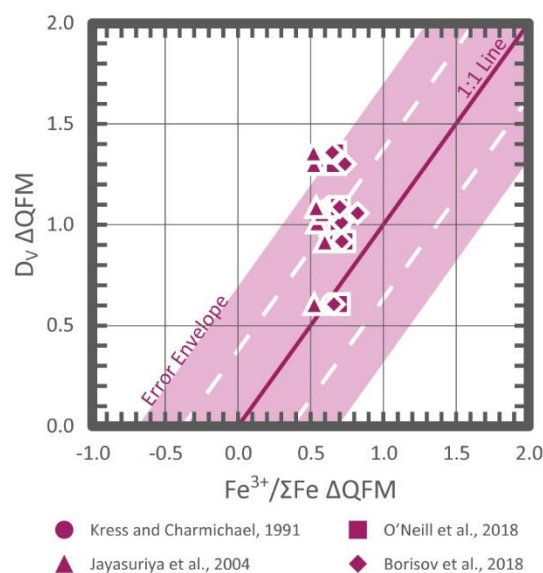


Figure 2A.1.4. Offset for “Fe-loss” corrected (Rasmussen et al., 2020) melt inclusion compositions for $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Kress and Carmichael, 1991; Jayasuriya et al., 2004; Borisov et al., 2018; O'Neill et al., 2018) and $D_v^{\text{olivine/melt}}$ (Mallmann and O'Neill, 2013) set with respect to the QFM buffer. Solid purple line is the 1:1 line in which the oxybarometer proxies would calculate identical values for ΔQFM . Solid light purple error envelope is the uncertainty reported for the whole data set used by Borisov et al., 2018 to convert $\text{Fe}^{3+}/\Sigma\text{Fe}$ to $f\text{O}_2$ (0.38). Dashed white line is the uncertainty reported by Mallmann and O'Neill, 2013 to convert $D_v^{\text{olivine/melt}}$ to $f\text{O}_2$ (0.24).

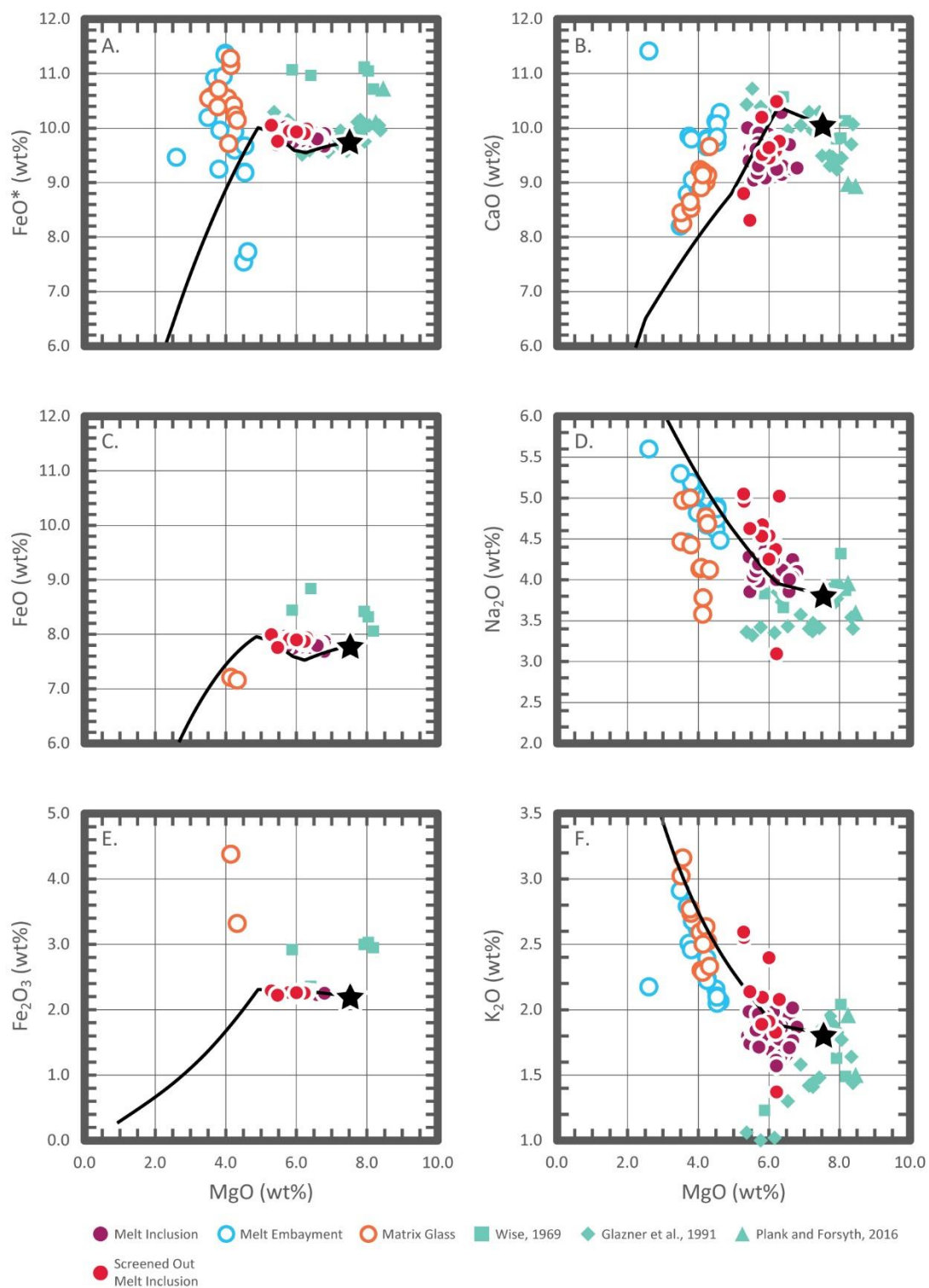


Figure 2A.1.5. Fig. 2.5. from the main text with the addition of screened out Pisgah Crater melt inclusion compositions from this study (red closed circles).

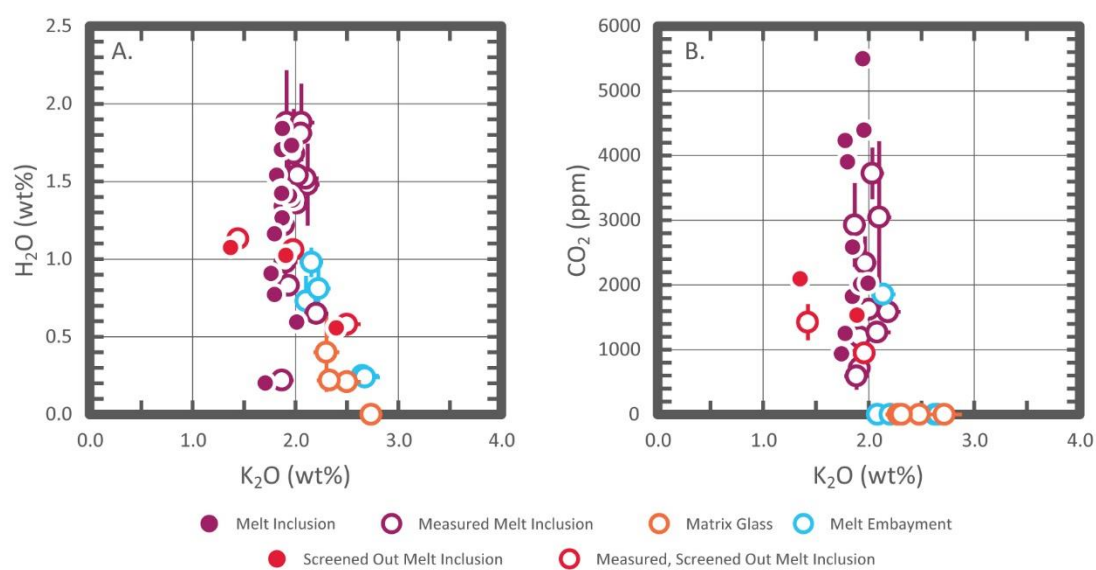


Figure 2A.1.6. Fig. 2.6. from the main text with the addition of screened out Pisgah Crater melt inclusion compositions from this study (red closed circles, “Fe-loss” corrected compositions; red open circles, measured compositions).

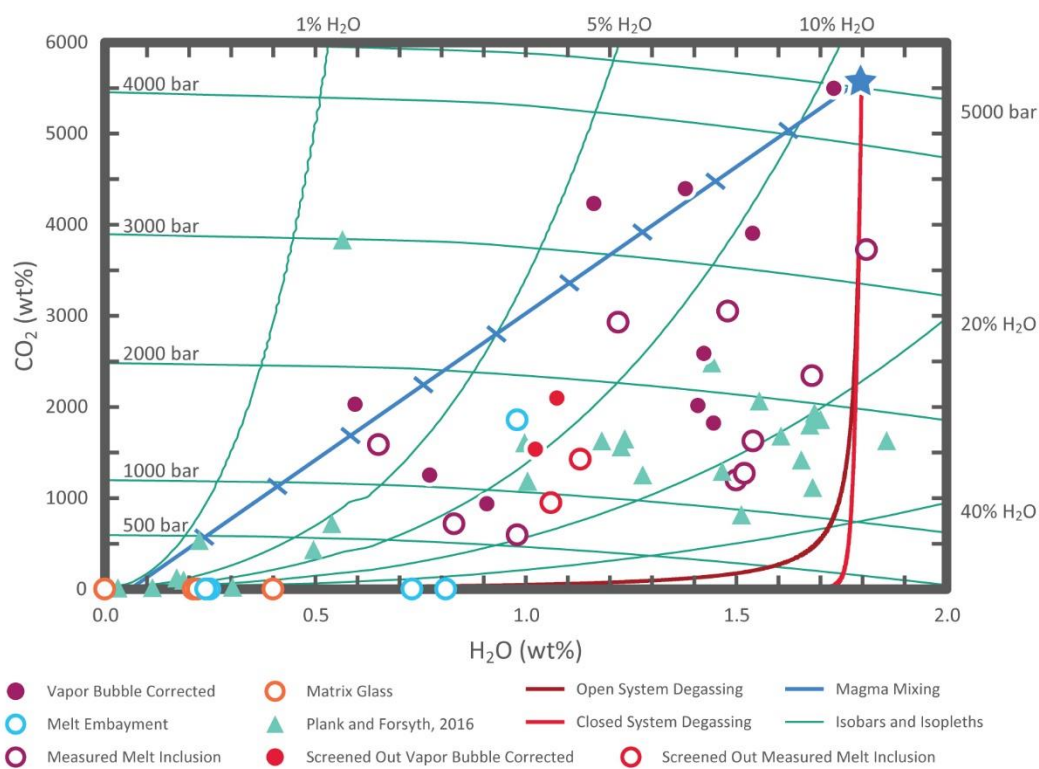


Figure 2A.1.7. Fig. 2.8. from the main text with the addition of screened out (red closed circles, “Fe-loss” corrected compositions; red open circles, measured compositions) and measured (purple open circles) Pisgah Crater melt inclusion compositions from this study.

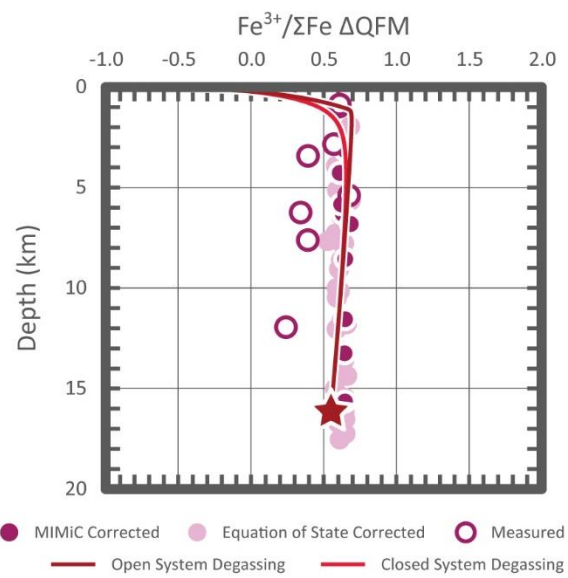


Figure 2A.1.8. Fig. 2.9. from the main text with the addition of measured (purple open circles) Pisgah Crater melt inclusion compositions from this study.

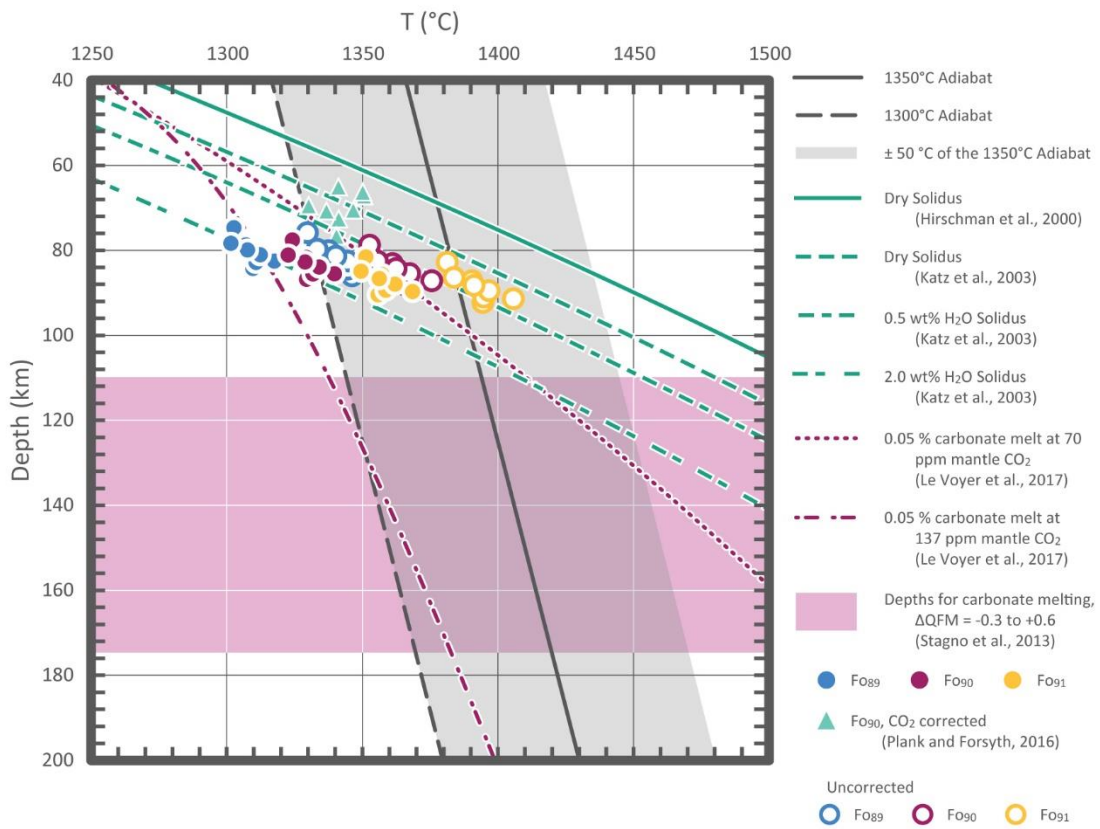


Figure 2A.1.9. Fig. 2.10. from the main text with the addition of calculated depth and temperatures for samples that were not corrected for the presence of CO₂ in the source mantle (open circles).

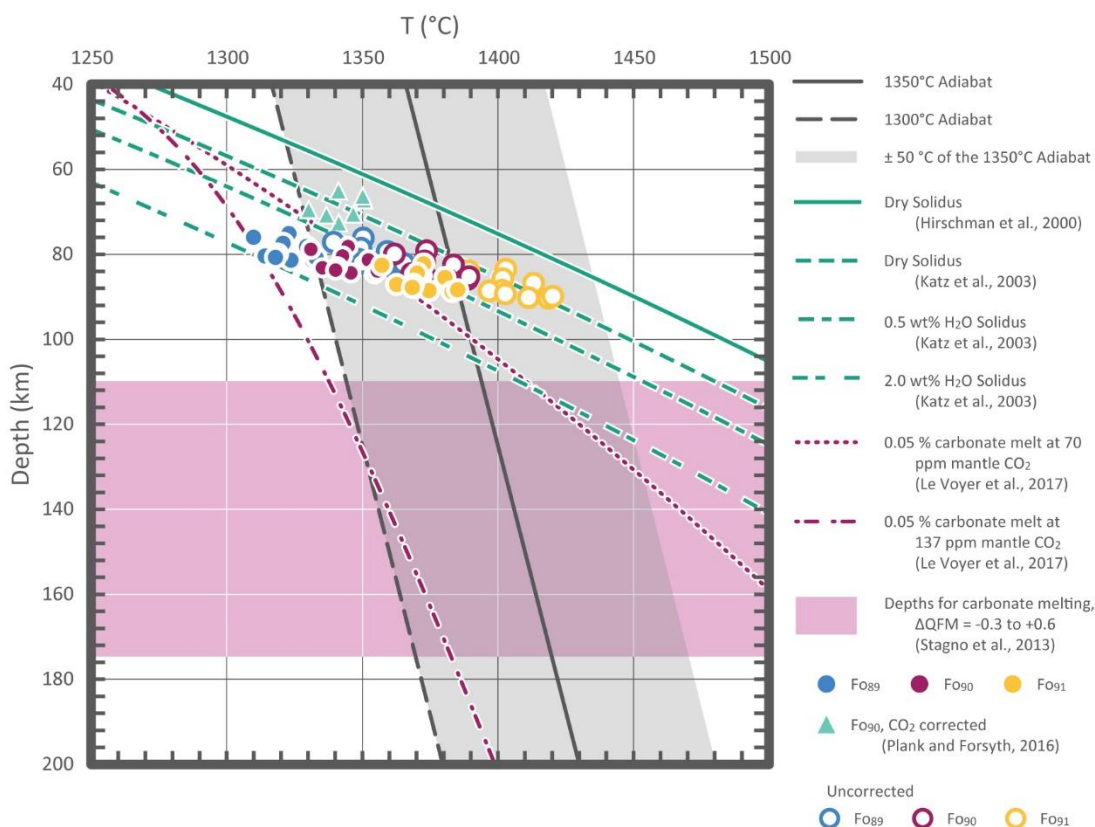


Figure 2A.1.10. Open and closed circles are the least degassed ($\text{H}_2\text{O} > 1.25$ wt%) melt inclusions in this study which then had their compositions corrected to be in equilibrium with Fo_{89-91} olivine. Closed circles are samples which have had calculated depth and temperature corrected for the presence of CO_2 . Open circles are uncorrected depth and temperature. All other symbols are the same as they are in the main text Fig. 2.10. and Fig. 2A.9.

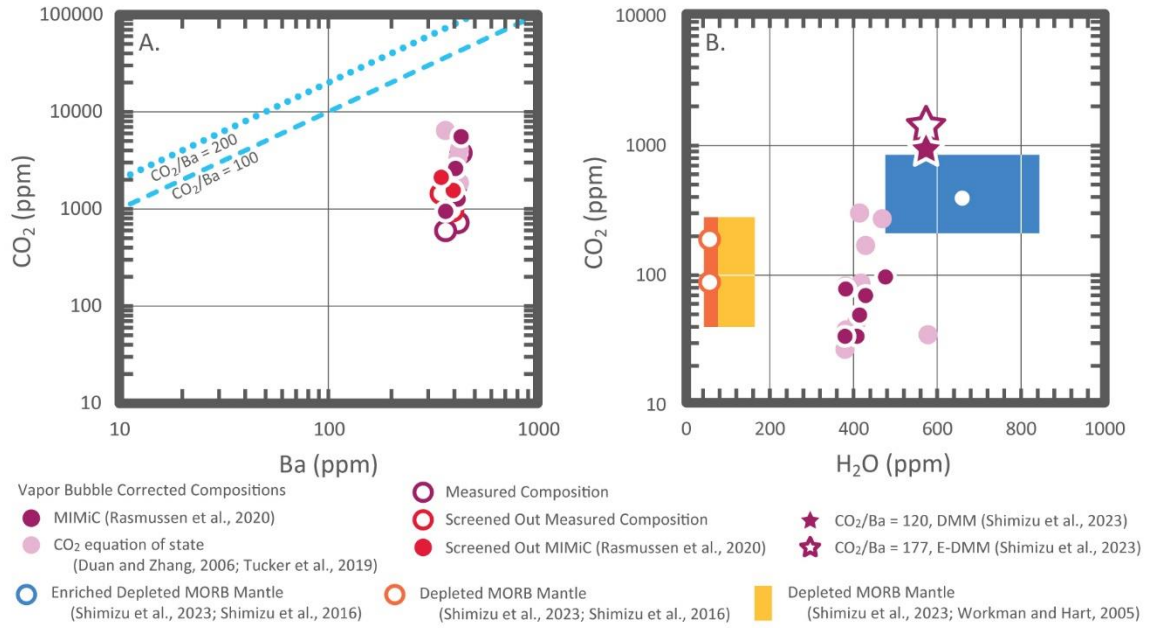


Figure 2A.1.11. (A) Plot of Ba and CO_2 . Purple closed circles are MIMiC (Rasmussen et al., 2020) vapor bubble corrected melt inclusion CO_2 concentrations and measured Ba in this study. Light purple closed circles are equation of state (Duan and Zhang, 2006; Tucker et al., 2019) corrected melt inclusion CO_2 concentrations and measured Ba in this study. Red closed circles are MIMiC (Rasmussen et al., 2020) vapor bubble corrected melt inclusion CO_2 concentrations and measured Ba in this study. Purple open circles are measured melt inclusion CO_2 and Ba concentrations in this study. Red open circles are screened out, measured CO_2 and Ba in this study. Blue lines are for constant CO_2/Ba : dashed line is $\text{CO}_2/\text{Ba} = 100$ and dotted line is $\text{CO}_2/\text{Ba} = 200$. (B) Plot of H_2O and CO_2 for mantle sources. Purple (MIMiC corrected; Rasmussen et al., 2020) and light purple (equation of state corrected; Duan and Zhang, 2006; Tucker et al., 2019) closed circles are calculated source H_2O and CO_2 from the volatile contents of the closed purple and light purple circles in Fig. 2A.1.10. Purple closed star is the possible mantle source H_2O and CO_2 from the highest calculated mantle source H_2O in this study for melts in equilibrium with Fo90 olivines and a CO_2 concentration calculated from the depleted MORB source, $\text{CO}_2/\text{Ba} = 120$ when Ba = 408 ppm (average measured Ba for Pisgah melt inclusions in this study). All other symbols are the same as in Fig. 2.11.

2A.2. Tables

Table 2A.2.1. Olivine Major and Minor Element Analysis.

Sample	SiO ₂		MgO		NiO		FeO		MnO		Fo _#
	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(%)
P17_20_01_OLV	38.7	0.4	42.8	0.4	0.1	0.0	16.4	0.1			82.3
P17_20_02_OLV	39.6	0.4	44.3	0.4	0.2	0.0	15.7	0.1			83.4
P17_20_03_OLV	39.5	0.4	44.5	0.4	0.2	0.0	15.9	0.1			83.3
P17_20_04_OLV	39.6	0.4	43.6	0.4	0.1	0.0	17.5	0.2			81.6
P17_20_05_OLV	39.9	0.4	44.6	0.4	0.2	0.0	15.8	0.1			83.4
P17_20_06_OLV	39.6	0.4	44.6	0.4	0.2	0.0	15.7	0.1			83.5
P17_20_06_OLVB	39.7	0.4	44.7	0.4	0.2	0.0	15.8	0.1			83.5
P17_20_07_OLV	39.4	0.4	44.2	0.4	0.2	0.0	15.9	0.1			83.2
P17_20_08_OLV	39.6	0.4	44.4	0.4	0.2	0.0	15.2	0.1			83.9
P17_20_10_OLV	39.7	0.4	44.9	0.4	0.2	0.0	15.3	0.1			83.9
P17_20_11_OLV	39.6	0.4	44.3	0.4	0.2	0.0	15.7	0.1			83.4
P17_20_13_OLV	39.6	0.4	44.2	0.4	0.2	0.0	15.9	0.1			83.2
P17_20_14_OLV	39.5	0.4	44.0	0.4	0.2	0.0	15.9	0.1			83.1
P17_20_15_OLV	39.6	0.4	44.0	0.4	0.1	0.0	16.7	0.1			82.4
P17_AL_01_Olv	39.7	0.4	44.9	0.4	0.2	0.0	14.8	0.1			84.4
P17_AL_03_Olv_center	39.3	0.4	45.5	0.4	0.2	0.0	13.8	0.1			85.4
P17_AL_03_Olv_edge	38.6	0.4	43.1	0.4	0.2	0.0	16.6	0.1			82.2
P17_AL_04_Olv	39.5	0.4	44.8	0.4	0.2	0.0	15.0	0.1			84.2
P17_AL_05_Olv	39.6	0.4	44.9	0.4	0.2	0.0	15.3	0.1			84.0
P17_AL_06	40.1	0.3	44.5	0.1	0.2	0.0	16.2	0.0			83.1
P17_AL_07_Olv	39.6	0.4	44.5	0.4	0.2	0.0	16.1	0.1			83.2
P17_AL_08_Olv	39.2	0.4	44.1	0.4	0.2	0.0	15.1	0.1			83.9

P17_AL_08_OlvB	39.0	0.4	43.5	0.4	0.2	0.0	16.1	0.1				82.8
P17_AL_09_Olv	39.9	0.4	43.9	0.4	0.2	0.0	16.3	0.1				82.8
P17_AL_10_Olv	39.0	0.4	42.4	0.4	0.1	0.0	16.9	0.1				81.8
P17_JAH_03_Olv	39.7	0.4	43.7	0.4	0.2	0.0	16.3	0.1				82.7
P17_JAH_04	40.1	0.3	43.8	0.1	0.1	0.0	16.8	0.0				82.3
P17_JAH_08	39.8	0.3	44.0	0.1	0.1	0.0	16.9	0.0				82.2
P17_JAH_09*	39.6	0.3	45.3	0.1			15.0	0.0	0.2	0.0	84.4	
P17_JAH_10	40.0	0.3	44.8	0.1	0.2	0.0	15.5	0.0				83.8
P17_JAH_11_Olv	39.9	0.4	45.3	0.4	0.2	0.0	14.4	0.1				84.8
P17_JAH_11_OlvB	40.0	0.4	45.3	0.4	0.2	0.0	14.6	0.1				84.7
P17_N_20_01_Olv	39.4	0.4	44.2	0.4	0.2	0.0	15.6	0.1				83.5
P17_N_20_02*	39.3	0.3	44.9	0.1			15.3	0.0	0.2	0.0	84.0	
P17_N_20_03_Olv	39.2	0.4	43.6	0.4	0.2	0.0	16.1	0.1				82.8
P17_N_20_04_Olv	39.8	0.4	45.0	0.4	0.2	0.0	15.2	0.1				84.0
P17_N_20_05	39.5	0.3	43.8	0.1	0.1	0.0	16.8	0.0				82.3
P17_N_20_06_OLVA	39.8	0.4	43.3	0.4	0.1	0.0	17.1	0.2				81.9
P17_N_20_06_OLVB	39.3	0.4	43.4	0.4	0.1	0.0	17.2	0.2				81.8
P17_N_20_08	39.2	0.4	43.5	0.4	0.2	0.0	16.5	0.1				82.4
P17_N_20_10	39.8	0.3	45.4	0.1	0.2	0.0	14.6	0.0				84.7
P17_N_20_11_Olv	39.2	0.4	43.4	0.4	0.2	0.0	16.2	0.1				82.7
P17_N_20_12_Olv	39.5	0.4	44.0	0.4	0.2	0.0	16.4	0.1				82.7
P17_N_20_14*	39.4	0.3	45.0	0.1			14.5	0.0	0.2	0.0	84.7	
P17_N_20_16	39.2	0.4	43.9	0.4	0.1	0.0	16.6	0.1				82.5
P17_N_20_17_Olv	39.4	0.4	44.3	0.4	0.2	0.0	15.6	0.1				83.5
P17_N_20_18_Olv	39.1	0.4	43.6	0.4	0.2	0.0	16.5	0.1				82.5
P17_N_20_19_Olv	39.0	0.4	42.9	0.4	0.1	0.0	17.1	0.2				81.7
P17_N_20_21_Olv	39.4	0.4	43.7	0.4	0.2	0.0	16.6	0.1				82.4

P17_N_20_22_OlvA	39.3	0.4	43.8	0.4	0.1	0.0	16.8	0.1			82.3
P17_N_20_22_OlvB	39.3	0.4	43.6	0.4	0.1	0.0	17.0	0.1			82.1
P17_N_20_22_OlvC	39.3	0.4	43.9	0.4	0.1	0.0	16.4	0.1			82.7

* Analyzed in a separate session where Mn was analyzed instead of Ni

Table 2A.2. Measured glass major, minor, and volatile concentration analysis.

Sample	SiO ₂		TiO ₂		Al ₂ O ₃		FeO*		FeO**		Fe ₂ O ₃ **		MnO		MgO	
Melt Inclusion	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ
P17_20_01	45.5	0.6	2.6	0.02	17.2	0.3	8.4	0.1	6.7	0.1	2.0	0.1	0.04	0.1	4.7	0.1
P17_20_03	46.7	0.6	2.8	0.03	18.0	0.4	8.3	0.1	6.6	0.1	1.8	0.1	0.05	0.1	4.0	0.1
P17_20_04	46.6	0.6	2.7	0.02	18.2	0.4	9.4	0.1		0.1		0.1	0.05	0.1	4.6	0.1
P17_20_05	47.2	0.6	2.6	0.02	18.1	0.4	7.5	0.1		0.1		0.1	0.04	0.1	4.9	0.1
P17_20_06	46.7	0.6	2.8	0.03	18.0	0.4	7.7	0.1		0.1		0.1	0.04	0.1	4.8	0.1
P17_20_06B	47.5	0.6	2.7	0.02	18.1	0.4	7.6	0.1		0.1		0.1	0.04	0.1	4.7	0.1
P17_20_08A	46.9	0.6	2.6	0.02	17.7	0.4	8.1	0.1	6.4	0.1	1.9	0.1	0.05	0.1	4.6	0.1
P17_20_10A	46.8	0.6	2.8	0.03	18.2	0.4	7.4	0.1		0.1		0.1	0.04	0.1	4.0	0.1
P17_20_10B	46.4	0.6	2.8	0.03	18.3	0.4	7.6	0.1		0.1		0.1	0.04	0.1	4.4	0.1
P17_20_11	45.6	0.6	2.9	0.03	18.4	0.4	7.7	0.1		0.1		0.1	0.04	0.1	4.5	0.1
P17_20_13B	46.6	0.6	2.8	0.03	18.1	0.4	7.5	0.1	6.1	0.1	1.6	0.1	0.04	0.1	4.9	0.1
P17_20_15	46.8	0.6	2.7	0.02	17.8	0.4	8.4	0.1		0.1		0.1	0.04	0.1	4.9	0.1
P17_AL_01A	47.4	0.6	2.7	0.02	17.9	0.4	7.4	0.1		0.1		0.1	0.04	0.1	4.1	0.1
P17_AL_03	45.2	0.6	2.9	0.03	18.2	0.4	6.8	0.1		0.1		0.1	0.03	0.1	4.2	0.1
P17_AL_04	46.8	0.6	3.0	0.03	18.7	0.4	7.1	0.1		0.1		0.1	0.03	0.1	3.5	0.1
P17_AL_05	47.1	0.6	2.7	0.02	17.8	0.4	7.7	0.1		0.1		0.1	0.04	0.1	5.0	0.1
P17_AL_07A	46.6	0.6	2.7	0.03	17.8	0.4	8.4	0.1		0.1		0.1	0.04	0.1	4.8	0.1
P17_AL_07B	47.2	0.6	2.6	0.02	17.6	0.4	8.9	0.1		0.1		0.1	0.05	0.1	4.8	0.1
P17_AL_10	47.4	0.6	2.5	0.02	17.6	0.4	8.7	0.1		0.1		0.1	0.05	0.1	4.6	0.1
P17_JAH_03	46.7	0.6	2.8	0.03	17.8	0.4	7.9	0.1		0.1		0.1	0.04	0.1	4.7	0.1
P17_JAH_04	46.6	0.3	2.6	0.01	17.8	0.3	8.8	0.1		0.1		0.1	0.04	0.1	4.5	0.1
P17_JAH_08	45.9	0.3	2.7	0.01	17.5	0.3	8.9	0.1	7.0	0.1	2.1	0.1	0.03	0.1	4.8	0.1
P17_JAH_09	46.5	0.3	2.8	0.01	17.9	0.3	7.7	0.1		0.1		0.1	0.03	0.1	4.9	0.1
P17_JAH_10A	47.0	0.3	2.6	0.01	17.8	0.3	7.6	0.1		0.1		0.1	0.03	0.1	4.8	0.1

P17_JAH_10B	46.9	0.3	2.7	0.01	17.9	0.3	7.7	0.1				0.1	0.03	4.8	0.1
P17_JAH_11	46.4	0.6	2.8	0.03	18.2	0.4	7.1	0.1	5.7	1.6		0.1	0.04	4.9	0.1
P17_N_20_02	46.7	0.3	2.7	0.01	17.7	0.3	7.6	0.1	6.1	1.7		0.1	0.03	4.7	0.1
P17_N_20_03	46.5	0.6	2.8	0.03	17.8	0.4	8.4	0.1				0.1	0.04	4.4	0.1
P17_N_20_04A	46.5	0.6	2.6	0.02	17.2	0.3	9.3	0.1				0.2	0.05	4.7	0.1
P17_N_20_04B	46.0	0.6	3.0	0.03	18.1	0.4	7.4	0.1				0.1	0.03	4.7	0.1
P17_N_20_05	45.9	0.3	2.5	0.01	17.0	0.3	9.4	0.1				0.1	0.03	5.0	0.1
P17_N_20_10	46.6	0.3	2.8	0.01	18.1	0.3	7.1	0.1				0.1	0.02	4.7	0.1
P17_N_20_11	46.3	0.6	2.7	0.03	18.0	0.4	8.0	0.1				0.1	0.04	4.4	0.1
P17_N_20_12	46.1	0.6	2.7	0.02	17.3	0.4	9.8	0.1				0.2	0.06	4.5	0.1
P17_N_20_14A	46.3	0.3	2.7	0.01	18.0	0.3	8.0	0.1	6.3	1.9		0.1	0.03	4.8	0.1
P17_N_20_14B	46.8	0.3	2.8	0.01	18.4	0.3	7.3	0.1	5.8	1.7		0.1	0.03	4.7	0.1
P17_N_20_17	46.1	0.6	2.8	0.03	17.9	0.4	7.3	0.1				0.1	0.04	4.6	0.1
P17_N_20_18A	46.3	0.6	2.7	0.02	17.6	0.4	8.1	0.1				0.1	0.04	4.8	0.1
P17_N_20_18B	45.4	0.6	2.8	0.03	17.8	0.4	8.0	0.1				0.1	0.04	4.8	0.1
P17_N_20_21	47.0	0.6	2.7	0.02	18.2	0.4	7.9	0.1				0.1	0.04	4.3	0.1
P17_N_20_22	46.0	0.6	2.7	0.03	17.7	0.4	8.5	0.1				0.1	0.05	4.8	0.1
Matrix Glass															
P17_AL_01_matrix	47.8	0.6	3.3	0.03	16.3	0.3	10.6	0.1				0.2	0.06	3.6	0.1
P17_AL_03_matrix	46.3	0.6	3.2	0.03	16.2	0.3	10.5	0.1				0.2	0.06	4.1	0.1
P17_AL_05_matrix	47.7	0.6	3.1	0.03	16.3	0.3	10.4	0.1				0.2	0.06	4.2	0.1
P17_AL_07_matrix	47.7	0.6	3.1	0.03	16.5	0.3	10.2	0.1				0.2	0.06	4.3	0.1
P17_AL_08_matrix	47.8	0.6	3.1	0.03	15.8	0.3	11.1	0.1	7.2	4.4		0.2	0.06	4.1	0.1
P17_AL_09_matrix	46.5	0.6	3.0	0.03	16.3	0.3	9.7	0.1				0.2	0.06	4.1	0.1
P17_AL_10_matrix	47.6	0.6	3.4	0.03	15.3	0.3	11.3	0.1				0.2	0.06	4.1	0.1
P17_JAH_11_matrix	47.4	0.6	3.1	0.03	16.5	0.3	10.1	0.1	7.2	3.3		0.2	0.06	4.3	0.1
P17_N_20_01_matrix	47.0	0.6	3.3	0.03	16.3	0.3	10.5	0.1				0.2	0.06	3.5	0.1

P17_N_20_02_matrix	47.2	0.3	3.3	0.01	16.1	0.2	10.7	0.2			0.1	0.04	3.8	0.1
P17_N_20_04_matrix	47.4	0.6	3.3	0.03	16.2	0.3	10.4	0.1			0.2	0.07	3.8	0.1
Embayment														
P17_20_02EMBY	48.2	0.6	3.4	0.03	16.5	0.3	10.9	0.1			0.2	0.06	3.7	0.1
P17_20_04EMBYA	45.9	0.6	3.4	0.03	16.8	0.3	11.4	0.1			0.2	0.07	4.0	0.1
P17_20_04EMBYB	47.3	0.6	3.4	0.03	16.3	0.3	11.3	0.1			0.2	0.06	4.0	0.1
P17_20_07EMBY	46.5	0.6	2.8	0.03	18.0	0.4	7.5	0.1			0.1	0.04	4.5	0.1
P17_20_14EMBY	47.5	0.6	2.7	0.03	17.6	0.4	9.6	0.1			0.2	0.05	4.3	0.1
P17_AL_01EMBY	46.3	0.6	2.8	0.03	17.4	0.4	10.7	0.1			0.2	0.06	3.7	0.1
P17_AL_05EMBY	47.1	0.6	2.9	0.03	17.0	0.3	9.9	0.1			0.2	0.06	4.2	0.1
P17_AL_09EMBYA	46.8	0.6	2.7	0.02	18.1	0.4	9.2	0.1			0.2	0.05	4.5	0.1
P17_AL_09EMBYB	47.4	0.6	2.9	0.03	17.1	0.3	9.9	0.1			0.2	0.05	4.3	0.1
P17_JAH_04EMBY	46.9	0.3	3.3	0.01	16.6	0.2	10.9	0.2			0.1	0.04	3.9	0.1
P17_N_20_08EMBY	47.3	0.6	3.3	0.03	16.6	0.3	10.0	0.1			0.2	0.06	3.8	0.1
P17_N_20_17EMBY	45.5	0.6	2.8	0.03	17.7	0.4	7.7	0.1			0.1	0.04	4.6	0.1
P17_N_20_17EMBYA	46.3	0.6	2.7	0.03	17.8	0.4	9.2	0.1			0.2	0.05	3.8	0.1
P17_N_20_17EMBYB	47.6	0.6	3.2	0.03	16.5	0.3	10.2	0.1			0.2	0.07	3.5	0.1
P17_N_20_19EMBY	45.6	0.6	2.8	0.03	17.5	0.4	9.5	0.1			0.2	0.05	2.6	0.0
P17_N_20_22EMBYA	46.1	0.6	2.6	0.02	17.4	0.4	9.7	0.1			0.2	0.05	4.5	0.1
P17_N_20_22EMBYB	46.8	0.6	2.6	0.02	17.6	0.4	9.2	0.1			0.1	0.05	4.5	0.1

*Total Fe content (Fe₂O₃ + FeO) calculated as FeO

** = calculated value from FeO* and Fe³⁺/ΣFe

***Equilibrium Fo# calculated from the average measured Fe³⁺/ΣFe (0.205)

¹Helz and Thornber, 1987

²Toplis, 2005

³Newman & Lowenstern, 2002

⁴Calculated using the equation P = gph using a depth to the crust-mantle boundary = 20 km, ρcrust = 2.8 g/cm³, ρcrust = 3.25 g/cm³

⁵Uncertainty of sulfur XANES measurements based on reproducibility from Brounce et al., 2015

⁶Total uncertainty in temperature (±10°C) as reported in Helz and Thornber, 1987

CaO		Na ₂ O		K ₂ O		P ₂ O ₅		S		Cl		H ₂ O		CO ₂	
(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(ppm)	1σ	(ppm)	1σ	(wt%)	1σ	(ppm)	1σ
9.4	0.2	4.3	0.4	1.9	0.1	0.7	0.1	1789	341	0.04	0.002	1.40	0.10		
10.6	0.2	4.4	0.4	1.9	0.1	0.7	0.1	1948	372	0.05	0.003	0.83	0.04	717	223
10.3	0.2	4.4	0.4	1.9	0.1	0.7	0.1	1898	362	0.05	0.002				
10.2	0.2	4.3	0.4	1.8	0.1	0.6	0.1	1616	308	0.04	0.002				
10.1	0.2	4.5	0.4	2.0	0.1	0.7	0.1	1953	373	0.05	0.003				
10.4	0.2	4.3	0.4	1.8	0.1	0.6	0.1	1878	358	0.04	0.002				
9.8	0.2	4.3	0.4	2.0	0.1	0.7	0.1	1760	336	0.05	0.003	1.36	0.05		
10.7	0.2	4.6	0.4	2.0	0.1	0.7	0.1	1829	349	0.05	0.003				
10.6	0.2	4.5	0.4	2.0	0.1	0.7	0.1	1844	352	0.05	0.003	1.68	0.29	2342	409
10.2	0.2	4.7	0.4	2.2	0.1	0.8	0.1	2084	398	0.05	0.003				
10.0	0.2	4.6	0.4	2.1	0.1	0.7	0.1	1839	351	0.05	0.003	1.48	0.26	3050	1171
10.2	0.2	4.3	0.4	1.9	0.1	0.6	0.1	1799	343	0.05	0.002	1.22	0.07	2929	646
10.8	0.2	4.2	0.4	1.8	0.1	0.6	0.1	1785	340	0.04	0.002				
10.4	0.2	4.6	0.4	2.1	0.1	0.7	0.1	1987	379	0.05	0.003				
11.5	0.2	4.4	0.4	1.8	0.1	0.9	0.1	2224	424	0.05	0.003				
10.5	0.2	4.3	0.4	1.9	0.1	0.7	0.1	1458	278	0.05	0.003				
9.8	0.2	4.6	0.4	2.2	0.1	0.7	0.1	2012	384	0.04	0.002				
9.5	0.2	4.5	0.4	2.1	0.1	0.7	0.1	1320	252	0.05	0.003				
10.0	0.2	4.0	0.4	1.8	0.1	0.6	0.1	1775	339	0.04	0.002				
10.0	0.2	4.5	0.4	2.1	0.1	0.7	0.1	1898	362	0.05	0.003				
9.9	0.2	4.5	0.3	2.0	0.1	0.6	0.1	1544	321	0.05	0.000				
9.8	0.2	4.4	0.3	1.9	0.1	0.6	0.1	1504	313	0.05	0.000	1.50	0.21	1196	201
10.0	0.2	4.2	0.3	2.1	0.1	0.6	0.1	1400	291	0.06	0.000	1.52	0.01	1271	7
10.4	0.2	4.3	0.3	1.7	0.1	0.5	0.1	1296	270	0.04	0.000				
10.4	0.2	4.3	0.3	1.7	0.1	0.5	0.1	1324	275	0.04	0.000				
10.1	0.2	4.6	0.4	2.2	0.1	0.7	0.1	1903	363	0.05	0.002	0.65	0.04	1585	167

10.1	0.2	4.5	0.3	2.0	0.1	0.6	0.1	1344	280	0.07	0.000	1.54	0.13	1625	139
10.5	0.2	4.2	0.4	1.8	0.1	0.7	0.1	1780	340	0.05	0.003				
9.7	0.2	4.6	0.4	2.0	0.1	0.7	0.1	1824	348	0.05	0.003				
10.2	0.2	4.6	0.4	2.1	0.1	0.7	0.1	2012	384	0.05	0.003				
9.9	0.2	4.3	0.3	1.9	0.1	0.6	0.1	1512	314	0.05	0.000	1.88	0.34		
10.2	0.2	4.5	0.3	2.1	0.1	0.6	0.1	1204	250	0.05	0.000	1.88	0.25		
9.8	0.2	4.5	0.4	2.1	0.1	0.7	0.1	1893	361	0.05	0.003				
10.0	0.2	4.8	0.5	2.1	0.1	0.7	0.1	1636	312	0.05	0.003				
10.4	0.2	4.4	0.3	1.9	0.1	0.6	0.1	1520	316	0.04	0.000	0.98	0.09	594	211
10.6	0.2	4.4	0.3	1.9	0.1	0.6	0.1	1468	305	0.04	0.000	0.22	0.02		
10.3	0.2	4.5	0.4	2.1	0.1	0.7	0.1	1873	357	0.05	0.000				
9.9	0.2	4.2	0.4	1.9	0.1	0.7	0.1	1710	326	0.04	0.000				
9.8	0.2	4.5	0.4	2.1	0.1	0.7	0.1	1913	365	0.05	0.000				
10.3	0.2	4.4	0.4	2.0	0.1	0.6	0.1	1681	321	0.04	0.000				
9.7	0.2	4.4	0.4	2.1	0.1	0.6	0.1	1859	355	0.05	0.000	1.81	0.07	3725	399
8.2	0.2	5.0	0.5	3.2	0.2	0.9	0.1								
9.2	0.2	4.1	0.4	2.6	0.1	0.8	0.1	638	122	0.05	0.003				
9.0	0.2	4.8	0.5	2.6	0.1	0.8	0.1	203	39	0.05	0.003				
9.1	0.2	4.7	0.5	2.5	0.1	0.8	0.1								
9.2	0.2	3.8	0.4	2.5	0.1	0.8	0.1	247	47	0.03	0.002	0.21	0.03	0	
8.9	0.2	4.1	0.4	2.3	0.1	0.8	0.1	272	52	0.06	0.003	0.40	0.25	0	
9.1	0.2	3.6	0.3	2.3	0.1	0.8	0.1	306	58	0.04	0.002				
9.7	0.2	4.1	0.4	2.3	0.1	0.8	0.1	311	59	0.05	0.003	0.22	0.05	0	
8.4	0.2	4.5	0.4	3.0	0.2	0.9	0.1	227	43	0.06	0.003				
8.5	0.2	4.4	0.3	2.7	0.2	0.8	0.1	228	47	0.08	0.001	0.00		0	
8.6	0.2	5.0	0.5	2.8	0.1	0.8	0.1	193	37	0.05	0.000				

8.8	0.2	4.5	0.4	2.8	0.1	0.9	0.1	272	52	0.06	0.003						
8.9	0.2	4.9	0.5	2.5	0.1	0.8	0.1	1310	250	0.06	0.003						
8.9	0.2	4.8	0.5	2.6	0.1	0.8	0.1	1384	264	0.06	0.003						
10.1	0.2	4.6	0.4	2.2	0.1	0.7	0.1	1844	352	0.05	0.003	0.98	0.09	1857	871		
9.8	0.2	4.8	0.5	2.2	0.1	0.7	0.1	774	148	0.05	0.003						
9.8	0.2	5.0	0.5	2.5	0.1	0.7	0.1	1604	306	0.05	0.003						
9.7	0.2	4.7	0.4	2.4	0.1	0.7	0.1	786	150	0.05	0.003						
9.7	0.2	4.9	0.5	2.1	0.1	0.7	0.1	1139	217	0.03	0.002	0.73	0.16	0			
9.8	0.2	4.7	0.5	2.2	0.1	0.7	0.1	786	150	0.05	0.003	0.81	0.14	0			
9.0	0.2	5.0	0.3	2.6	0.2	0.7	0.1	960	200	0.06	0.000	0.25	0.04	0			
9.0	0.2	5.1	0.5	2.7	0.1	0.8	0.1	539	103	0.05	0.003	0.24	0.07	0			
10.3	0.2	4.5	0.4	2.1	0.1	0.7	0.1	1888	360	0.05	0.003						
9.8	0.2	5.2	0.5	2.5	0.1	0.7	0.1	949	181	0.05	0.003						
8.2	0.2	5.3	0.5	2.9	0.2	1.0	0.2	143	27	0.06	0.003						
11.4	0.2	5.6	0.5	2.2	0.1	0.7	0.1	1873	357	0.05	0.003						
10.1	0.2	4.7	0.5	2.0	0.1	0.6	0.1	1713	327	0.05	0.003						
9.8	0.2	4.9	0.5	2.1	0.1	0.6	0.1	1092	208	0.05	0.003						

$S^{6\gamma}/S$		$Fe^{3\gamma}/SFe$		$Fo_{\#}$		T^1		K_F^2		P^3		D^4	
$(\pm)^5$		1σ		Equilibrium		$(^{\circ}C)$		$(\pm^{\circ}C)^6$		(GPa)		(km)	
0.19	0.01	0.208	0.006	82.2		1108	10	0.271	0.02	1.0			
1.00	0.01	0.200	0.002	80.3		1095	10	0.266	0.08	3.4			
0.19	0.01			80.4***		1106	10	0.267					
				84.6***		1113	10	0.268					
				84.1***		1111	10	0.265					
				83.8***		1109	10	0.268					
0.18	0.01	0.211	0.001	82.4		1106	10	0.270	0.02	0.9			
0.30	0.01			82.2***		1094	10	0.262					
0.53	0.01			83.0***		1103	10	0.267	0.25	9.7			
				83.3***		1104	10	0.260					
0.34	0.01	0.188	0.006	84.1		1112	10	0.268	0.31	12.0			
0.29	0.01			82.8***		1112	10	0.271	0.30	11.5			
0.48	0.01			82.3***		1097	10	0.266					
0.54	0.01			84.3***		1098	10	0.257					
				80.8***		1084	10	0.262					
0.14	0.01			84.6***		1115	10	0.267					
0.93	0.01			83.0***		1111	10	0.263					
1.00	0.01			81.0***		1110	10	0.266					
				81.0***		1106	10	0.273					
0.33	0.01			83.4***		1109	10	0.265					
				81.4***		1105	10	0.266					
0.12	0.01	0.214	0.019	82.0		1111	10	0.270	0.13	5.4			
0.28	0.01			84.0***		1112	10	0.270	0.15	6.1			
				84.2***		1111	10	0.268					
				83.9***		1111	10	0.268					

0.42	0.01	0.200	0.011	85.4	1112	10	0.262	0.16	6.3
0.16	0.01	0.199	0.003	83.7	1108	10	0.268	0.19	7.6
				81.5***	1103	10	0.268		
				81.1***	1108	10	0.262		
				84.6***	1109	10	0.261		
				81.5***	1115	10	0.272	0.04	1.7
				84.7***	1108	10	0.267	0.04	1.7
0.57	0.01			82.5***	1103	10	0.264		
				79.8***	1104	10	0.260		
0.91	0.01	0.211	0.007	83.4	1110	10	0.266	0.07	2.9
		0.212		84.5	1108	10	0.265		
0.48	0.01			84.1***	1106	10	0.263		
0.08	0.01			83.3***	1111	10	0.269		
0.13	0.01			83.6***	1110	10	0.263		
0.19	0.01			82.1***	1100	10	0.267		
0.21	0.01			82.3***	1110	10	0.270	0.35	13.1
0.00	0.01				1090	10	0.260		
					1086	10	0.253		
0.00	0.01				1096	10	0.264		
0.03	0.01				1099	10	0.259		
0.03	0.01	0.353	0.009	79.2	1100	10	0.261		
0.01	0.01				1097	10	0.268		
					1096	10	0.267		
0.01	0.01	0.294	0.009	80.3	1097	10	0.273		
0.02	0.01				1101	10	0.265		
0.02	0.01				1107	10	0.262		

Table 2A.2.3. Melt inclusion and vapor bubble dimensions.

Sample	Melt Inclusion diameter (μm)		ϕ^1	Vapor Bubble diameter (μm)	
	minimum	maximum		minimum	maximum
P17_20_01	89	146	0.034	37	
P17_20_03	79	118	0.022	27	
P17_20_04	71	86	0.025	23	
P17_20_05	50	66	0.020	16	
P17_20_06	65	81	0.023	21	
P17_20_06B	34	50	0.072	17	
P17_20_08A	44	116	0.015	19	
P17_20_10A	55	89	0.028	21	
P17_20_10B	43	56	0.061	19	
P17_20_11	96	175	0.007	25	
P17_20_13B	72	91	0.015	20	
P17_20_15	46	74	0.022	16	
P17_AL_01A	37	76	0.089	24	
P17_AL_03	32	66	0.054	18	
P17_AL_04	50	57	0.064	21	
P17_AL_05	123	492	0.049	97	
P17_AL_07A	123	198	0.029	49	
P17_AL_07B	115	136	0.694	111	
P17_AL_10	59	76	0.043	24	
P17_JAH_03	64	109	0.051	31	
P17_JAH_04	41	81	0.048	21	
P17_JAH_08	57	61	0.010	13	
P17_JAH_09	60	191	0.003	17	

P17_JAH_10A*	54	67	---	0
P17_JAH_10B	34	42	0.053	14
P17_JAH_11	59	133	0.025	26
P17_N_20_02	69	245	0.119	68
P17_N_20_03	43	57	0.008	10
P17_N_20_04A	66	90	0.011	17
P17_N_20_04B	102	150	0.035	41
P17_N_20_05	37	48	0.013	10
P17_N_20_10	54	106	0.131	39
P17_N_20_11	59	99	0.015	19
P17_N_20_12	46	60	0.020	14
P17_N_20_14A	146	194	0.048	61
P17_N_20_14B	57	106	0.092	36
P17_N_20_17	61	204	0.045	42
P17_N_20_18A	43	89	0.010	14
P17_N_20_18B	40	59	0.018	13
P17_N_20_21	56	71	0.013	15
P17_N_20_22	46	46	0.015	11
Screened Out				
P17_20_08B	22	66	0.000	0
P17_20_13A	55	60	0.000	0
P17_AL_01B	56	56	0.000	0
P17_AL_06A	86	97	0.021	25
P17_AL_06B	0	0	0.000	0
P17_AL_06C	0	0	0.000	0
P17_N_20_01	120	126	0.000	0
P17_N_20_06A	19	87	0.000	0

P17_N_20_06B	49	57	0.044	19
P17_N_20_16	34	69	0.010	11

¹V Volume Fraction

*Vapor bubble present but size is not resolvable in photograph

Table 2A.2.4. Measured and "Fe-loss" corrected major, minor, and volatile concentrations of melt inclusions screened out from this study.

Sample Measured	Olivine (% added)	SiO ₂ (wt%)	1σ	TiO ₂ (wt%)	1σ	Al ₂ O ₃ (wt%)	1σ	FeO* (wt%)	1σ	FeO** (wt%)	Fe ₂ O ₃ ** (wt%)	MnO (wt%)	1σ	MgO (wt%)	1σ
P17_20_08B		46.3	0.6	2.5	0.0	17.1	0.3	9.3	0.1	7.2	2.3	0.2	0.3	4.5	0.1
P17_20_13A		46.5	0.6	2.5	0.0	17.2	0.3	9.4	0.1	7.5	2.0	0.2	0.3	4.9	0.1
P17_AL_01B		46.3	0.6	2.6	0.0	17.3	0.4	9.7	0.1			0.2	0.3	3.9	0.1
P17_AL_06A		46.3	0.3	2.9	0.0	17.9	0.3	8.6	0.1	6.7	2.1	0.1	0.0	5.0	0.1
P17_AL_06B		46.9	0.3	2.7	0.0	17.2	0.2	9.8	0.1			0.1	0.0	4.3	0.1
P17_AL_06C		46.4	0.3	2.6	0.0	17.6	0.2	9.8	0.1			0.1	0.0	4.3	0.1
P17_N_20_01		46.1	0.6	2.7	0.0	17.6	0.4	10.6	0.1	7.2	3.8	0.2	0.3	3.7	0.1
P17_N_20_06A		46.7	0.6	3.1	0.0	17.3	0.4	10.7	0.1			0.2	0.3	3.9	0.1
P17_N_20_06B		47.3	0.6	3.0	0.0	17.4	0.4	9.4	0.1			0.2	0.3	3.9	0.1
P17_N_20_16		46.5	0.6	2.7	0.0	18.3	0.4	7.7	0.1			0.1	0.3	4.6	0.1
"Fe-loss" Corrected															
P17_20_08B	4.8	45.9		2.4		16.3		9.9		7.8	2.2	0.2		6.2	
P17_20_13A	3.3	46.1		2.5		16.6		9.9		7.9	2.3	0.2		6.0	
P17_AL_01B	6.3	45.9		2.5		16.3		10.0		7.9	2.3	0.1		6.3	
P17_AL_06A	4.6	45.7		2.7		17.0		9.9		7.9	2.3	0.1		6.2	
P17_AL_06B	4.1	46.6		2.6		16.6		10.0		7.9	2.3	0.1		5.8	
P17_AL_06C	3.9	46.1		2.5		17.0		9.9		7.9	2.3	0.1		5.8	
P17_N_20_01	4.9	46.1		2.6		16.9		9.9		7.9	2.3	0.2		6.0	
P17_N_20_06A	2.6	46.8		3.0		17.0		10.0		8.0	2.3	0.2		5.3	
P17_N_20_06B	4.1	46.8		2.9		16.7		10.0		8.0	2.3	0.1		5.3	
P17_N_20_16	4.6	45.7		2.5		17.3		9.8		7.8	2.2	0.1		5.5	

- *Total Fe content ($\text{Fe}_2\text{O}_3 + \text{FeO}$) calculated as FeO
- ** = calculated value from FeO^* and average $\text{Fe}^{3+}/\Sigma\text{Fe}$
- ¹Helz and Thornber, 1987
- ²Toplis, 2005
- ³Uncertainty of sulfur XANES measurements based on reproducibility from Brounce et al., 2015
- ⁴Total uncertainty in temperature ($\pm 10^\circ\text{C}$) as reported in Helz and Thornber, 1987
- ⁵Vapor bubble correction from Rasmussen et al., 2020
- ⁶Vapor bubble correction from Tucker et al., 2019, using the equation of state for CO_2 from Duan and Zhang, 2006
- ⁷Newman & Lowenstern, 2002
- ⁸Calculated using the equation $P = \text{gph}$ using a depth to the crust-mantle boundary = 20 km, $\rho_{\text{crust}} = 2.8 \text{ g/cm}^3$, $\rho_{\text{crust}} = 3.25 \text{ g/cm}^3$

	CaO		Na ₂ O		K ₂ O		P ₂ O ₅		S		Cl		H ₂ O		CO ₂	
	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(wt%)	1σ	(ppm)	1σ	(ppm)	1σ	(wt%)	1σ	(ppm)	1σ
10.1	0.2	4.6	0.4	1.9	0.1	0.6	0.2	1794	342	0.04	0.002					
9.8	0.2	4.7	0.5	2.0	0.1	0.6	0.2	1814	346	0.04	0.002	1.06	0.03	948	63	
10.4	0.2	5.3	0.5	2.2	0.1	0.6	0.2	1809	345	0.05	0.003					
11.0	0.2	3.3	0.2	1.4	0.1	0.6	0.1	1140	237	0.04	0.000	1.13	0.03	1426	278	
9.9	0.2	4.9	0.3	2.2	0.1	0.6	0.1	1180	245	0.04	0.000					
10.6	0.2	4.7	0.3	2.0	0.1	0.6	0.1	1232	256	0.04	0.000					
10.0	0.2	4.4	0.4	2.5	0.1	0.7	0.2	1740	332	0.05	0.003	0.58	0.07			
8.9	0.2	5.1	0.5	2.6	0.1	0.7	0.2	880	168	0.05	0.003					
9.2	0.2	5.3	0.5	2.7	0.1	0.8	0.2	381	73	0.05	0.003					
8.8	0.2	4.9	0.5	2.3	0.1	0.9	0.2	1834	350	0.06	0.003					
																CO ₂ ⁵ (ppm)
9.6		4.4		1.8		0.6		1707		0.04						CO ₂ ⁶ (ppm)
9.5		4.5		1.9		0.6		1751		0.04		1.02		915	1535	
9.8		5.0		2.1		0.6		1702		0.04						
10.5		3.1		1.4		0.5		1083		0.04		1.07		1355	2096	
9.5		4.7		2.1		0.5		1134		0.04						
10.2		4.5		1.9		0.5		1185		0.04						
9.6		4.3		2.4		0.7		1669		0.05		0.56				
8.8		5.0		2.6		0.7		863		0.05						
8.8		5.0		2.6		0.8		365		0.05						
8.3		4.6		2.1		0.8		1734		0.05						

S^{6+}/Σ	$Fe^{3+}/\Sigma Fe$	T^1	K_D^2	$Fo_{\#}$	Reason Screened			
$(\pm)^3$	1σ	(°C)	$(\pm^{\circ}C)^4$	Equilibrium				
0.03	0.01	0.221	0.001	1105	10	0.26	81.0	Angular shape
0.01	0.01	0.194	0.002	1113	10	0.27	81.5	No vapor bubble
0.02	0.01			1093	10	0.25	78.4***	Angular shape
0.01	0.01	0.219	0.004	1115	10	0.28	82.7	Sulfide bleb present in melt inclusion
				1099	10	0.26	79.0***	Interstitial melt between olivine grains
				1100	10	0.26	79.1***	Interstitial melt between olivine grains
0.01	0.01	0.323	0.006	1088	10	0.26	77.9	Smearred shape, not translucent
0.01	0.01			1092	10	0.26	76.0***	Oblong shape may have been a melt embayment before entrapment
0.04	0.01			1092	10	0.26	78.3***	Contains crystal inclusion
0.23	0.01			1107	10	0.26	83.7***	Angular shape, possibly contains co-entrapped or daughter phase spinel
average								
		0.205		1139		0.27		p^7
		0.205		1135		0.27	0.15	D^8
		0.205		1141		0.26		(km)
		0.205		1139		0.29	0.19	
		0.205		1131		0.27		
		0.205		1131		0.27		
		0.205		1135		0.27		
		0.205		1121		0.26		
		0.205		1120		0.26		
		0.205		1124		0.27		

Table 2A.2.5. Melt inclusion composition in equilibrium with Fo89-91 olivine from the least degassed melt inclusions in this study.

Samples	Fo#	Olivine (% Added)	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	FeO* (wt%)	Fe ₂ O ₃ (wt%)	FeO (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	P ₂ O ₅ (wt%)
Fo ₈₉														
P17_20_01	89	14.0	44.4	2.1	14.5	10.1	1.9	10.7	0.1	10.6	7.9	3.6	1.6	0.6
P17_20_08A	89	11.7	45.5	2.2	14.7	10.1	2.0	10.7	0.1	10.6	8.2	3.6	1.7	0.5
P17_20_10B	89	11.5	44.8	2.3	15.0	10.2	2.0	10.7	0.1	10.7	8.7	3.7	1.6	0.6
P17_20_13B	89	13.1	45.1	2.3	14.9	10.3	2.0	10.7	0.1	10.8	8.2	3.8	1.7	0.6
P17_JAH_08	89	14.8	44.8	2.3	14.7	10.3	2.0	10.7	0.1	10.9	8.3	3.7	1.6	0.5
P17_JAH_09	89	9.6	45.1	2.4	15.1	10.0	2.0	10.7	0.1	10.1	8.5	3.5	1.8	0.5
P17_N_20_02	89	10.9	45.2	2.3	14.7	10.0	2.0	10.7	0.1	10.4	8.4	3.7	1.7	0.5
P17_N_20_05	89	14.0	45.1	2.1	14.6	10.2	1.9	10.7	0.1	10.6	8.5	3.7	1.6	0.5
P17_N_20_10	89	9.7	45.0	2.3	15.0	10.1	2.1	10.7	0.1	10.4	8.4	3.7	1.7	0.5
P17_N_20_22	89	13.5	44.9	2.3	14.9	10.2	2.0	10.7	0.1	10.6	8.2	3.7	1.7	0.5
Fo ₉₀														
P17_20_01	90	18.0	44.2	2.1	14.0	10.1	1.9	9.8	0.1	11.9	7.7	3.5	1.6	0.5
P17_20_08A	90	15.5	45.3	2.1	14.3	10.1	1.9	9.8	0.1	11.9	7.9	3.5	1.6	0.5
P17_20_10B	90	15.3	44.7	2.2	14.5	10.2	2.0	9.8	0.1	11.9	8.4	3.5	1.6	0.6
P17_20_13B	90	17.1	44.9	2.2	14.4	10.3	1.9	9.8	0.1	12.1	8.0	3.6	1.7	0.6
P17_JAH_08	90	18.8	44.7	2.2	14.2	10.3	1.9	9.8	0.1	12.2	8.0	3.6	1.6	0.5
P17_JAH_09	90	13.2	45.0	2.3	14.6	10.0	2.0	9.8	0.1	11.4	8.2	3.4	1.7	0.5
P17_N_20_02	90	14.7	45.0	2.2	14.2	10.0	1.9	9.8	0.1	11.7	8.1	3.6	1.6	0.5
P17_N_20_05	90	17.9	44.9	2.1	14.1	10.2	1.9	9.8	0.1	11.9	8.2	3.6	1.6	0.5
P17_N_20_10	90	13.3	44.8	2.3	14.5	10.1	2.0	9.8	0.1	11.6	8.2	3.6	1.6	0.5
P17_N_20_22	90	17.4	44.7	2.2	14.4	10.2	1.9	9.8	0.1	11.8	7.9	3.6	1.7	0.5
Fo ₉₁														
P17_20_01	91	22.9	44.1	2.0	13.4	10.1	1.8	8.8	0.1	13.4	7.4	3.3	1.5	0.5
P17_20_08A	91	20.3	45.2	2.0	13.7	10.1	1.9	8.8	0.1	13.4	7.6	3.3	1.6	0.5

P17_20_10B	91	20.2	44.6	2.1	13.9	10.2	1.9	8.8	0.1	13.5	8.1	3.4	1.5	0.5
P17_20_13B	91	22.1	44.7	2.1	13.8	10.2	1.9	8.8	0.1	13.7	7.6	3.5	1.6	0.6
P17_JAH_08	91	24.0	44.5	2.1	13.6	10.3	1.8	8.8	0.1	13.8	7.7	3.4	1.5	0.5
P17_JAH_09	91	17.6	44.8	2.2	14.1	10.0	1.9	8.8	0.1	12.8	7.9	3.3	1.7	0.5
P17_N_20_02	91	19.4	44.9	2.1	13.7	10.0	1.9	8.8	0.1	13.2	7.8	3.4	1.6	0.5
P17_N_20_05	91	22.8	44.8	2.0	13.5	10.1	1.8	8.8	0.1	13.4	7.9	3.4	1.5	0.5
P17_N_20_10	91	17.9	44.7	2.2	14.0	10.1	1.9	8.8	0.1	13.1	7.9	3.5	1.6	0.5
P17_N_20_22	91	22.3	44.6	2.1	13.8	10.1	1.8	8.8	0.1	13.4	7.6	3.4	1.6	0.5

¹Vapor bubble correction from Rasmussen et al., 2020

²Vapor bubble correction from Tucker et al., 2019, using the equation of state for CO₂ from Duan and Zhang, 2006

³Melt fractionation calculation using equation 9 and DMM TiO₂ = 0.133 from Kelley et al., 2006

⁴Source mantle H₂O calculation using equation 10 and the given DH₂O = 0.012 from Kelley et al., 2006

⁵Source mantle CO₂ calculation using equation 10 and DCO₂ = 0.00055 (Rosenthal et al., 2015) from Kelley et al., 2007

⁶Kress and Carmichael, 1991

⁷O'Neill et al. 2018 with Fe³⁺/ΣFe correction via Berry et al., 2018

⁸Jayasuriya et al., 2004

⁹Borisov et al., 2017

¹⁰Pressure and temperature of the melt's last equilibration with mantle peridotite using equations 1 and 2 from Plank and Forsyth, 2016

¹¹Calculated using the equation $P = \rho_{\text{gph}}$ using a depth to the crust-mantle boundary = 20 km, $\rho_{\text{crust}} = 2.8 \text{ g/cm}^3$, $\rho_{\text{crust}} = 3.25 \text{ g/cm}^3$

¹²Pressure and temperature correction for the presence of CO₂ using equation 3 from Plank and Forsyth, 2016

H ₂ O (wt%)	S (ppm)	CO ₂ ¹ (ppm)	CO ₂ ² (ppm)	Fe ³⁺ /ΣFe	F ³	H ₂ O _{source} ⁴ (wt%)	H ₂ O _{source} ⁴ (ppm)	CO _{2-source} ^{1,5} (ppm)	CO _{2-source} ^{2,5} (ppm)
1.18	1502		3555	0.172	0.023	0.04	408		82
1.13	1466		1671	0.178	0.021	0.04	373		35
1.38	1515	3502	8502	0.179	0.018	0.04	417	65	157
1.22	1515	3885	4094	0.175	0.019	0.04	371	73	77
1.26	1263	1588	2078	0.171	0.020	0.04	398	32	41
1.29	1184	1838	1458	0.183	0.017	0.04	370	31	25
1.28	1120	2333	14262	0.180	0.020	0.04	404	46	282
1.62	1299		1409	0.172	0.023	0.06	563		33
1.55	995		14349	0.183	0.018	0.05	455		252
1.53	1567	4843	4769	0.173	0.019	0.05	463	90	89
1.14	1452		3434	0.166	0.025	0.04	419		87
1.10	1418		1616	0.172	0.023	0.04	384		38
1.34	1465	3386	8222	0.173	0.020	0.04	431	70	169
1.18	1464	3753	3954	0.169	0.021	0.04	383	78	82
1.22	1221	1534	2008	0.165	0.022	0.04	410	34	44
1.24	1146	1780	1412	0.177	0.019	0.04	382	34	27
1.24	1083	2256	13789	0.173	0.022	0.04	416	49	301
1.56	1256		1363	0.166	0.025	0.06	579		35
1.50	964		13893	0.177	0.019	0.05	470		271
1.48	1515	4682	4610	0.168	0.021	0.05	478	97	95
1.09	1394		3297	0.160	0.028	0.04	432		92
1.05	1361		1551	0.166	0.026	0.04	397		40
1.28	1406	3248	7887	0.166	0.023	0.04	446	75	183
1.13	1404	3599	3792	0.163	0.023	0.04	397	85	89

1.17	1169	1470	1924	0.159	0.025	0.04	425	36	48
1.20	1104	1713	1359	0.170	0.021	0.04	395	36	29
1.19	1040	2167	13247	0.167	0.024	0.04	430	53	324
1.50	1206		1308	0.160	0.028	0.06	597		37
1.45	926		13351	0.170	0.022	0.05	487		294
1.42	1454	4495	4426	0.161	0.023	0.05	495	105	103

fO_2^6	fO_2^7	fO_2^8	fO_2^9	P^{10} (GPa)	D^{11} (km)	T^{10} (°C)	$P^{10,12}$ (GPa)	D^{11} (km)	$T^{10,12}$ (°C)
-0.18	0.49	0.01	-0.45	2.4	79	1359	2.4	78	1329
-0.11	0.58	0.06	-0.34	2.3	76	1350	2.3	75	1323
-0.12	0.55	0.06	-0.40	2.6	83	1358	2.5	81	1323
-0.14	0.50	0.08	-0.42	2.6	83	1365	2.5	81	1331
-0.16	0.45	-0.02	-0.46	2.5	82	1365	2.5	81	1333
-0.11	0.61	0.02	-0.34	2.4	77	1339	2.3	76	1310
-0.15	0.56	-0.02	-0.39	2.4	79	1349	2.4	77	1320
-0.20	0.44	-0.08	-0.50	2.5	81	1348	2.5	80	1318
-0.09	0.60	0.03	-0.38	2.5	82	1346	2.5	80	1314
-0.17	0.48	-0.01	-0.47	2.5	82	1350	2.5	81	1318
-0.02	0.44	0.23	-0.35	2.5	83	1384	2.5	81	1352
0.05	0.53	0.27	-0.24	2.4	79	1374	2.4	78	1345
0.04	0.50	0.28	-0.30	2.6	86	1381	2.6	84	1346
0.02	0.46	0.29	-0.32	2.7	86	1389	2.6	84	1354
-0.01	0.40	0.20	-0.37	2.6	85	1389	2.6	84	1355
0.06	0.56	0.24	-0.23	2.5	80	1362	2.4	79	1331
0.01	0.51	0.21	-0.29	2.5	82	1373	2.5	80	1342
-0.04	0.40	0.14	-0.40	2.6	84	1372	2.6	83	1341
0.07	0.56	0.25	-0.28	2.6	85	1368	2.6	83	1335
-0.01	0.43	0.22	-0.37	2.6	85	1373	2.6	84	1340
0.15	0.40	0.46	-0.26	2.7	87	1414	2.6	85	1380
0.22	0.49	0.51	-0.15	2.6	83	1403	2.5	82	1372
0.21	0.45	0.51	-0.21	2.8	90	1412	2.7	88	1374
0.19	0.41	0.53	-0.23	2.8	90	1419	2.7	89	1383

0.16	0.35	0.44	-0.28	2.8	90	1421	2.7	88	1385
0.23	0.52	0.47	-0.13	2.6	84	1390	2.5	82	1357
0.19	0.47	0.45	-0.19	2.6	86	1402	2.6	84	1370
0.13	0.35	0.38	-0.31	2.7	88	1402	2.7	87	1369
0.25	0.51	0.49	-0.18	2.7	89	1397	2.7	87	1362
0.16	0.39	0.45	-0.27	2.8	89	1403	2.7	88	1368

Table 2A.2.6. Olivine Trace Element Analysis.

Sample	Li		Sc		V		Cr		Co	
	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)
P17_20_01_OLV	2.9	0.4	11.7	0.5	6.2	0.4	135.4	2.7	172.1	2.0
P17_20_03_OLV	2.6	0.3	11.5	0.3	5.8	0.2	150.1	2.2	185.1	1.1
P17_20_07_OLV	2.5	0.3	11.5	0.3	6.3	0.2	152.5	1.3	167.7	1.0
P17_20_08_OLV_B	2.3	0.3	10.7	0.4	6.3	0.3	151.4	2.2	179.0	1.6
P17_20_08_OLV_A	3.0	0.4	13.5	0.5	6.7	0.3	151.7	2.3	191.0	1.9
P17_20_10_OLV_A	1.7	0.3	10.9	0.4	9.1	0.4	90.4	1.9	176.2	1.7
P17_20_13_OLV_B	2.5	0.2	10.7	0.3	7.0	0.2	122.4	1.7	160.3	1.2
P17_20_15_OLV	2.8	0.3	11.5	0.4	6.0	0.3	134.7	2.5	173.9	1.4
P17_AL_06_OLV_A	2.4	0.2	12.8	0.3	6.4	0.2	151.0	1.7	174.0	1.1
P17_AL_07_OLV_MATRIX	2.9	0.3	13.3	0.3	5.8	0.2	107.0	1.4	187.7	0.8
P17_AL_08_OLV_MATRIX	2.5	0.3	13.3	0.4	6.8	0.3	172.4	2.1	176.0	1.4
P17_AL_09_OLV	2.6	0.2	12.0	0.3	5.1	0.2	99.7	1.4	170.1	1.2
P17_AL_09_OLV_EMBY_A	2.7	0.3	11.3	0.4	5.8	0.2	133.3	1.6	194.0	1.3
P17_AL_09_OLV_EMBY_B	3.3	0.4	13.7	0.5	6.3	0.3	122.6	2.0	193.9	1.8
P17_JAH_03_OLV	2.8	0.3	15.0	0.4	5.9	0.2	159.4	1.6	166.3	1.2
P17_JAH_04_OLV_EMBY	2.6	0.2	14.4	0.3	5.9	0.2	111.1	1.8	192.9	0.9
P17_JAH_08_OLV	2.9	0.2	14.0	0.3	5.2	0.2	114.0	1.1	172.5	0.8
P17_JAH_09_OLV	2.7	0.2	13.4	0.3	6.1	0.2	128.2	1.2	161.1	0.9
P17_JAH_11_OLV	2.2	0.2	12.1	0.3	6.5	0.2	168.3	1.6	159.0	1.1
P17_JAH_11_OLV_MATRIX	2.7	0.2	12.6	0.3	8.5	0.2	189.8	1.4	169.0	0.8
P17_N_20_01_OLV	1.6	0.3	12.9	0.5	6.3	0.3	158.7	2.3	153.3	1.7
P17_N_20_01_OLV_MATRIX	1.8	0.4	13.0	0.5	5.4	0.3	132.7	2.1	173.4	1.7
P17_N_20_02_OLV	2.6	0.2	11.4	0.3	7.5	0.2	154.1	2.1	165.6	1.0
P17_N_20_02_OLV_MATRIX	2.4	0.2	11.4	0.3	6.9	0.2	136.4	1.7	177.8	1.0

P17_N_20_05_OLV	2.4	0.3	10.3	0.3	5.2	0.3	116.6	2.1	172.9	1.3
P17_N_20_06_OLV_A	2.4	0.4	9.9	0.4	13.1	0.4	334.0	3.2	172.2	1.5
P17_N_20_08_OLV	2.9	0.2	10.8	0.2	6.7	0.2	127.2	1.5	188.5	0.9
P17_N_20_10_OLV	2.6	0.3	11.2	0.3	6.3	0.2	159.3	1.8	155.2	1.1
P17_N_20_11_OLV	2.2	0.2	9.6	0.3	6.0	0.3	157.2	2.0	159.4	1.3
P17_N_20_14_OLV_A	2.8	0.3	10.9	0.3	6.2	0.2	142.3	2.0	191.7	1.0
P17_N_20_14_OLV_B	2.2	0.2	9.8	0.2	7.5	0.2	161.9	1.7	166.6	0.9
P17_N_20_16_OLV	2.9	0.3	12.8	0.4	6.0	0.3	174.3	2.3	150.1	1.3
P17_N_20_22_OLV	2.5	0.4	10.9	0.3	5.5	0.2	122.3	2.2	171.0	1.1

Sample ending in "_A" or "_B" are designating the respective melt inclusion or embayment that the olivine measurement was taken near

Samples ending in "_MATRIX" are olivine samples measured towards the edge of the olivine, near the matrix glass

Samples ending in "_EMBY" are olivine samples measured near the designated melt embayment in the olivine

Ni		Cu		Zn		Ga		As		Rb		Sr	
(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)	(ppm)	($\pm$ ppm)
1138.1	10.6	10.5	1.0	225.3	6.9	0.3	0.1	4.0	1.0	0.2	0.1	1.0	0.1
1329.2	6.2	33.2	1.0	240.2	4.3	0.2	0.0			0.2	0.1	0.2	0.0
1534.9	5.9	1.6	0.2	152.1	3.0	0.2	0.0					0.6	0.0
1351.1	9.1	1.3	0.3	148.2	4.6	0.3	0.1	21.4	1.6	0.2	0.1	0.9	0.1
1462.4	10.6	1.4	0.4	176.3	5.6	0.3	0.1			0.2	0.1	0.4	0.1
1015.8	8.4	1.0	0.3	121.5	4.3	0.2	0.1						
1461.0	7.4	3.2	0.4	151.6	3.6	0.2	0.0					0.1	0.0
1137.3	7.1	8.5	0.6	192.3	4.4	0.1	0.1	2.8	0.6			0.7	0.1
1225.0	6.0	1.3	0.2	171.9	3.6	0.3	0.0	2.0	0.4	0.1	0.1	0.8	0.1
1075.8	4.1	2.4	0.2	177.7	3.3	0.2	0.0			0.1	0.1	1.6	0.1
1333.3	7.9	1.8	0.3	159.3	4.1	0.2	0.1	2.2	0.6			0.7	0.1
1000.8	5.7	1.4	0.2	168.9	3.5	0.1	0.0						
1104.9	6.5	1.5	0.2	186.3	4.0	0.2	0.0	1.4	0.4			0.7	0.1
1073.6	8.6	2.2	0.4	181.6	5.6	0.2	0.1	3.4	0.8			0.5	0.1
1596.8	7.4	1.6	0.3	168.3	3.6	0.2	0.0						
1020.9	4.4	1.6	0.2	179.3	3.1	0.2	0.0						
1124.3	4.2	1.5	0.3	156.6	3.0	0.2	0.0					0.4	0.0
1405.3	5.5	1.3	0.2	153.6	3.2	0.2	0.0	0.8	0.3			0.5	0.0
1592.5	7.3	1.7	0.3	138.4	3.6	0.2	0.0	0.6	0.3			1.6	0.1
1543.6	4.8	2.2	0.2	149.2	3.0	0.6	0.1	3.0	0.4	0.4	0.1	5.4	0.1
1479.3	10.6	6.7	0.7	196.2	5.7	0.2	0.1	1.8	0.7			0.4	0.1
1294.3	9.7	3.5	0.5	187.0	5.8	0.1	0.1						
1429.6	5.9	1.2	0.2	149.1	3.0	0.4	0.1	1.2	0.4	0.2	0.1	3.6	0.1
1208.1	5.3	1.2	0.2	173.8	3.6	0.2	0.0	2.6	0.5	0.2	0.1	1.3	0.1
1029.9	6.3	1.4	0.3	147.6	4.0	0.1	0.0						
956.2	7.4	1.1	0.3	170.7	5.4	1.3	0.2			0.2	0.1	4.8	0.2

	Y		Zr		Nb		Ba		La		Ce		Nd	
	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)
0.1	0.0	4.7	0.41	0.7	0.12	1.9	0.5				0.1	0.04		
0.1	0.0	0.2	0.04											
0.2	0.0	0.3	0.05			0.2	0.1				0.1	0.02		
0.2	0.0	1.1	0.15	0.1	0.03	1.4	0.3				0.1	0.03		
0.2	0.0	0.5	0.12			0.7	0.3				0.1	0.03		
0.2	0.0													
0.2	0.0	0.2	0.05											
0.2	0.0	0.5	0.09	0.1	0.03	0.6	0.2				0.1	0.03		
0.2	0.0	0.7	0.09	0.1	0.02	0.8	0.2		0.02	0.1	0.1	0.02		
0.2	0.0	0.9	0.07	0.2	0.02	1.4	0.2	0.1	0.02	0.3	0.03	0.1	0.0	
0.2	0.0	0.4	0.09	0.1	0.02	0.7	0.2				0.1	0.03		
0.2	0.0	0.1	0.03											
0.1	0.0	0.5	0.09	0.1	0.02	0.7	0.2	0.1	0.02	0.1	0.02			
0.2	0.0	0.6	0.12	0.1	0.03	0.8	0.3				0.1	0.03		
0.1	0.0													
0.2	0.0	0.1	0.02											
0.2	0.0	0.2	0.04	0.1	0.01	0.3	0.1				0.1	0.01		
0.1	0.0	0.3	0.05	0.1	0.02	0.4	0.1	0.1	0.01	0.1	0.02			
0.2	0.0	0.7	0.09	0.2	0.03	1.4	0.2	0.1	0.02	0.2	0.03			
0.3	0.0	2.2	0.11	0.5	0.04	3.6	0.3	0.3	0.03	0.8	0.04	0.4	0.1	
0.2	0.1	0.9	0.15			0.5	0.2	0.2	0.05					
0.2	0.1													
0.3	0.0	1.5	0.12	0.3	0.04	2.5	0.3	0.2	0.03	0.4	0.04	0.1	0.0	
0.2	0.0	0.8	0.08	0.1	0.02	1.1	0.2	0.1	0.02	0.2	0.03	0.1	0.0	
0.2	0.0	0.1	0.04											
0.3	0.1	2.2	0.21	0.4	0.07	2.7	0.4	0.3	0.05	0.6	0.07	0.3	0.1	

0.2	0.0	0.0	0.5	0.06	0.1	0.02	0.9	0.1	0.1	0.02	0.2	0.02			
0.1	0.0		0.1	0.03											
0.2	0.0		2.0	0.18	0.1	0.02	5.6	0.6			0.1	0.02			
0.2	0.0		0.1	0.03			0.2	0.1							
0.3	0.0		1.1	0.09	0.2	0.03	1.3	0.2	0.2	0.02	0.3	0.03			
0.2	0.0		0.1	0.05											
0.2	0.0		0.2	0.05											

	Sm		Gd		Yb		Hf		Pb		Th		U	
	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)
									4.7	0.4			0.2	0.06
									33.9	0.6				
									0.4	0.1				
									0.5	0.1				
									3.2	0.3				
									0.3	0.1				
									0.3	0.1				
					0.1	0.05			0.3	0.1				
									0.9	0.1				
									0.4	0.1				
					0.1	0.03			0.1	0.1				
									0.1	0.0				
									0.3	0.1				
									0.1	0.0				
					0.1	0.03								
					0.1	0.03			0.1	0.0	0.0	0.01		
									0.1	0.0				
									0.3	0.1				
									1.1	0.1	0.0	0.01		
0.1	0.04	0.1	0.0	0.1	0.03				6.9	0.4	0.1	0.04	0.2	0.05
							0.3	0.1	8.2	0.4			0.1	0.04
									0.2	0.0				
									0.1	0.0				
					0.1	0.03			0.4	0.1				

Table 2A.2.7. Measured glass trace element concentration analysis.

Sample	CO ₂ /Ba			Li		Be		Sc		V		Cr	
Melt Inclusion	A	B	C	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(± ppm)	
P17_20_01_MI			9.6	6.9	0.6	1.6	0.5	27.4	0.8	220.8	3.7	70.0	3.2
P17_20_03_MI	1.7	3.0	7.9	8.8	0.4	1.9	0.3	32.5	0.5	260.5	1.9	54.8	2.6
P17_20_08_MI_A			4.7	7.5	0.7	1.9	0.5	24.0	0.8	238.1	3.9	79.0	3.5
P17_N_20_02_MI	4.0	6.4	0.0	8.8	0.4	2.0	0.4	30.7	0.6	226.1	2.3	61.9	1.6
P17_N_20_11_MI			4.3	8.5	0.7	2.2	0.6	26.6	0.9	228.1	3.8	50.8	2.4
P17_N_20_14_MI_A	1.6	2.6	17.5	8.2	0.6	2.4	0.4	27.7	0.5	259.2	2.2	44.5	1.8
P17_N_20_22_MI	8.6	12.7	12.5	7.6	0.5	1.9	0.4	27.4	0.6	244.6	2.7	49.6	1.7
Matrix Glass													
P17_AL_07_MATRIX				9.9	0.4	2.2	0.3	34.1	0.4	242.8	1.8	75.5	1.6
P17_AL_08_MATRIX				1.7	0.3	2.1	0.4	32.1	0.6	263.9	2.9	61.4	1.9
P17_JAH_11_MATRIX				9.2	0.4	2.1	0.3	34.0	0.4	249.0	1.9	55.0	1.6
P17_N_20_02_MATRIX				8.4	0.7	1.8	0.5	35.0	0.8	233.1	3.2	50.8	2.3
Melt Embayment													
P17_20_07_EMBY				8.1	0.5	2.1	0.4	28.5	0.7	234.7	2.8	61.5	1.9
P17_AL_09_EMBY_B				9.7	0.6	2.1	0.5	33.5	0.9	229.8	3.4	67.7	1.9
P17_N_20_08_EMBY				10.4	0.4	2.8	0.4	29.2	0.5	290.6	2.5	29.5	1.5
Screened Out Melt Inclusions													
P17_20_13_MI_A	2.4	3.9		10.4	0.5	1.7	0.4	28.4	0.6	226.1	2.5	66.6	1.6
P17_AL_06_MI_A	4.1	6.1		7.3	0.5	1.6	0.3	27.5	0.6	262.2	2.7	59.7	1.8
P17_N_20_01_MI				2.6	0.5	2.2	0.7	26.1	0.9	242.8	4.5	57.2	2.4

Sample ending in " _A" or " _B" are designating the respective melt inclusion or embayment that the olivine measurement was taken near

A is CO₂/Ba calculated from measured CO₂ and measured Ba

B is CO₂/Ba calculated from MIMiC corrected (Rasmussen et al., 2020) CO₂ and measured Ba

C is CO₂/Ba calculated from equation of state (Duan and Zhang, 2006; Tucker et al., 2019) corrected CO₂ and measured Ba

Co		Ni		Cu		Zn		Ga		As		Rb	
(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)	(ppm)	(± ppm)
26.8	0.8	35.4	1.9	33.3	1.7	85.7	4.5	35.4	1.1	2.8	0.9	37.6	1.0
30.3	0.4	43.8	1.0	62.4	1.2	117.7	3.1	41.3	0.5	2.1	0.4	43.5	0.5
28.2	0.9	38.1	2.0	18.1	1.3	91.5	5.1	36.5	1.1			44.6	1.1
23.2	0.5	40.8	1.3	19.1	0.8	98.0	3.5	31.3	0.6	1.8	0.5	39.1	0.7
27.1	0.9	63.3	2.6	583.0	10.8	712.3	15.2	28.4	0.9	5.8	1.6	39.3	1.1
27.7	0.5	52.0	1.2	44.6	1.1	98.1	3.4	30.7	0.5	1.9	0.6	40.5	0.6
27.6	0.6	37.2	1.4	23.5	1.0	87.6	3.2	31.0	0.7	6.6	0.9	45.0	0.8
31.0	0.4	31.3	0.8	51.4	1.0	120.0	3.4	41.3	0.5	1.9	0.4	45.2	0.5
27.2	0.6	16.7	0.8	28.5	1.1	129.0	3.9	37.3	0.7	3.3	0.9	42.4	0.7
28.1	0.4	19.5	0.6	48.2	1.0	110.3	3.1	47.9	0.6	2.7	0.4	47.9	0.5
43.5	0.9	96.2	2.6	53.9	1.8	136.1	4.7	29.2	0.8	109.9	3.8	49.8	1.0
29.0	0.7	89.4	2.3	27.9	1.2	95.9	3.8	37.5	0.8	2.3	0.7	47.5	0.9
33.4	0.9	63.9	2.3	52.7	2.0	111.6	4.8	36.2	1.0	2.7	0.8	42.4	1.0
27.8	0.5	24.8	0.8	89.9	1.6	129.8	3.6	36.8	0.6	1.7	0.7	60.0	0.7
32.2	0.6	69.6	1.8	53.1	1.5	129.0	3.6	32.9	0.7	6.5	0.8	39.6	0.7
28.9	0.6	38.1	1.3	46.8	1.4	152.2	4.3	39.8	0.8	1.4	0.5	33.6	0.6
26.6	1.0	14.9	1.4	53.6	2.6	137.7	6.3	34.6	1.2	1.9	0.8	47.1	1.3

Sr		Y		Zr		Nb		Cs		Ba		La	
ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm
702.8	10.2	25.3	0.7	274.0	4.7	58.8	1.3	0.5	0.1	423.9	9.0	43.0	1.0
763.8	5.0	30.1	0.4	296.7	2.3	60.9	0.6	0.5	0.0	416.5	4.1	46.5	0.5
661.4	9.7	22.9	0.7	268.8	4.7	56.3	1.2	0.6	0.1	393.1	8.6	38.8	0.9
753.5	6.7	29.1	0.5	268.6	2.9	54.9	0.8	0.5	0.1	405.2	5.4	47.0	0.6
756.7	11.1	30.0	0.8	280.5	4.9	57.7	1.3	0.6	0.1	424.4	9.2	47.2	1.1
698.4	5.2	29.2	0.4	269.7	2.4	58.1	0.7	0.5	0.0	363.1	4.2	41.6	0.5
742.5	7.3	28.3	0.5	318.9	3.7	66.3	0.9	0.5	0.1	431.3	6.2	50.0	0.7
608.4	4.1	32.5	0.4	308.5	2.4	63.0	0.6	0.6	0.0	403.2	3.9	49.6	0.5
495.6	5.0	28.5	0.5	280.9	3.3	55.5	0.8	0.6	0.1	375.5	5.5	41.7	0.6
642.7	4.3	28.9	0.4	280.3	2.2	69.9	0.7	0.6	0.0	443.3	4.3	48.1	0.5
578.4	7.1	35.2	0.7	316.2	4.4	71.7	1.2	0.6	0.1	463.5	7.8	59.7	1.0
809.0	8.4	30.0	0.6	291.8	3.6	70.8	1.1	0.5	0.1	439.9	6.8	52.0	0.8
739.5	9.6	29.5	0.7	275.3	4.3	64.4	1.2	0.5	0.1	465.0	8.7	50.0	1.0
588.6	4.7	36.1	0.5	367.8	3.3	80.0	0.8	0.7	0.1	503.2	5.4	58.4	0.6
733.3	7.0	28.0	0.5	262.0	3.0	59.4	0.8	0.4	0.1	395.0	5.7	46.0	0.7
659.6	6.1	26.9	0.5	295.5	3.3	56.0	0.8	0.4	0.1	346.3	5.1	42.9	0.6
629.0	10.3	28.7	0.9	287.8	5.6	62.1	1.5	0.5	0.1	482.8	11.2	44.1	1.1

Ce		Pr		Nd		Sm		Eu		Gd		Tb	
ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm
74.6	1.4	9.5	0.3	35.1	1.9	7.9	0.8	2.7	0.3	6.9	0.7	0.8	0.1
87.2	0.7	10.0	0.2	40.1	1.0	8.5	0.4	2.7	0.1	7.3	0.3	1.1	0.1
68.3	1.3	9.3	0.3	33.4	1.9	7.6	0.8	2.5	0.2	5.5	0.6	0.9	0.1
85.2	1.0	8.9	0.2	39.0	1.3	7.7	0.5	2.6	0.2	7.1	0.4	1.1	0.1
89.8	1.7	9.3	0.4	39.7	2.1	8.5	0.9	2.5	0.2	7.3	0.7	0.9	0.1
79.7	0.8	9.2	0.2	36.9	1.0	7.7	0.4	2.6	0.1	6.9	0.4	1.0	0.1
86.3	1.1	9.9	0.2	41.4	1.4	8.4	0.6	2.7	0.2	7.1	0.5	1.0	0.1
91.3	0.8	10.1	0.2	42.6	1.0	8.5	0.4	2.8	0.1	8.1	0.3	1.2	0.1
78.6	1.0	9.4	0.2	36.8	1.3	8.1	0.6	2.6	0.2	7.2	0.5	1.0	0.1
85.1	0.7	10.1	0.2	40.2	1.0	8.5	0.4	2.8	0.1	7.6	0.3	1.1	0.1
98.3	1.4	10.0	0.3	43.0	1.7	8.2	0.7	2.6	0.2	7.8	0.6	1.1	0.1
90.5	1.2	9.8	0.3	41.8	1.6	8.2	0.6	2.8	0.2	7.2	0.5	1.0	0.1
84.8	1.4	9.2	0.3	42.2	1.9	8.4	0.8	2.8	0.2	7.7	0.6	1.0	0.1
111.1	1.0	12.2	0.2	49.3	1.2	10.2	0.5	3.1	0.1	8.9	0.4	1.3	0.1
84.4	1.0	9.0	0.2	35.9	1.3	7.6	0.5	2.5	0.2	7.0	0.4	1.0	0.1
80.8	1.0	10.3	0.2	41.4	1.4	8.7	0.6	2.8	0.2	7.0	0.4	1.0	0.1
83.2	1.8	11.1	0.4	38.2	2.3	8.8	1.0	2.9	0.3	7.6	0.8	1.0	0.1

Dy		Ho		Er		Tm		Yb		Lu		Hf	
ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm
5.1	0.5	1.0	0.1	2.8	0.3	0.4	0.1	2.0	0.3	0.3	0.1	6.6	0.6
5.8	0.3	1.2	0.1	2.7	0.2	0.4	0.0	2.6	0.2	0.4	0.0	6.1	0.3
4.5	0.5	0.9	0.1	2.7	0.3	0.3	0.1	1.8	0.3	0.4	0.1	5.5	0.5
5.6	0.3	1.1	0.1	2.8	0.2	0.4	0.0	2.3	0.2	0.4	0.0	6.1	0.3
5.6	0.5	1.2	0.1	3.0	0.3	0.4	0.1	2.5	0.4	0.3	0.1	6.5	0.6
5.8	0.3	1.1	0.1	2.8	0.2	0.4	0.0	2.5	0.2	0.4	0.0	5.8	0.3
5.6	0.4	1.1	0.1	3.5	0.2	0.5	0.1	2.5	0.2	0.4	0.0	7.4	0.4
6.4	0.2	1.2	0.1	3.0	0.2	0.4	0.0	2.6	0.2	0.4	0.0	6.9	0.3
5.8	0.3	1.2	0.1	2.9	0.2	0.4	0.0	2.3	0.2	0.4	0.0	6.7	0.4
5.3	0.2	1.2	0.1	3.2	0.2	0.4	0.0	2.5	0.2	0.4	0.0	6.6	0.3
6.1	0.4	1.2	0.1	3.0	0.3	0.4	0.1	2.6	0.3	0.4	0.1	6.3	0.4
6.1	0.4	1.1	0.1	3.5	0.3	0.4	0.1	2.5	0.3	0.4	0.1	7.5	0.4
6.2	0.5	1.0	0.1	3.0	0.3	0.4	0.1	2.6	0.3	0.4	0.1	6.7	0.5
7.1	0.3	1.4	0.1	3.5	0.2	0.6	0.0	3.0	0.2	0.4	0.0	7.9	0.3
5.0	0.3	1.1	0.1	2.7	0.2	0.4	0.0	2.5	0.2	0.3	0.0	5.8	0.3
5.7	0.4	1.1	0.1	3.1	0.2	0.4	0.0	2.5	0.2	0.4	0.0	6.9	0.4
5.4	0.6	1.2	0.1	3.3	0.4	0.3	0.1	2.0	0.4	0.4	0.1	6.7	0.6

Ta		Pb		Th		U	
ppm	± ppm	ppm	± ppm	ppm	± ppm	ppm	± ppm
3.5	0.2	2.7	0.3	5.5	0.3	1.4	0.1
4.0	0.1	4.7	0.2	5.5	0.2	1.6	0.1
3.3	0.2	2.8	0.3	5.3	0.3	1.2	0.1
3.7	0.1	3.3	0.2	5.4	0.2	1.5	0.1
4.2	0.3	81.8	2.0	5.9	0.3	1.5	0.2
3.5	0.1	3.1	0.2	5.1	0.2	1.6	0.1
4.2	0.2	5.3	0.3	6.2	0.2	1.7	0.1
4.1	0.1	3.7	0.2	6.2	0.2	1.8	0.1
3.3	0.1	4.4	0.2	5.6	0.2	1.4	0.1
4.1	0.1	3.3	0.2	6.5	0.2	1.7	0.1
4.0	0.2	11.5	0.5	5.7	0.3	1.7	0.1
4.4	0.2	3.4	0.2	6.5	0.3	1.9	0.1
4.3	0.2	3.7	0.3	6.3	0.3	1.8	0.2
4.9	0.1	5.5	0.2	7.2	0.2	2.0	0.1
3.8	0.2	6.9	0.3	5.4	0.2	1.7	0.1
3.1	0.1	464.3	4.7	5.4	0.2	1.2	0.1
3.2	0.3	3.9	0.4	5.5	0.4	1.3	0.2

Table 2A.2.8. Sulfur peak conversion to $S^{6+}/\Sigma S$.

Sample	Peak Areas1					Calculations				
	~2482	~2477.7	~2476.4	~2469.1	$\Sigma I [S^{6+}]^*$	$I[S^{6+}]/\Sigma I[ST]^{**}$	$S^{6+}/\Sigma S^{***}$	$[S^{6+}/\Sigma S]_{avg}$		
Melt Inclusions	6+	4+	2-	2-						
P17_20_01	4.97	0.09	6.14	0.38	5.08	0.44	0.19	N/A		
P17_20_03	10.12	0.48		0.02	10.69	1.00	1.00	N/A		
P17_20_04	5.92	0.26	7.49	0.17			0.19	N/A		
P17_20_08A	4.65	0.15	6.22	0.51	4.83	0.42	0.18	N/A		
P17_20_08B	2.03		8.94	1.20	2.03	0.17	0.03	N/A		
P17_20_10A	5.92	0.16	4.60	0.41	6.12	0.55	0.30	N/A		
P17_20_10B	30.31		11.62		30.31	0.72	0.53	N/A		
P17_20_13A	1.15		9.11	0.64	1.15	0.11	0.01	N/A		
P17_20_13B	6.10	0.14	4.16	0.29	6.27	0.58	0.34	N/A		
P17_20_15	5.69	0.13	4.72	0.33	5.85	0.54	0.29	N/A		
P17_AL_01A	6.98	0.76	3.51	0.07	7.89	0.69	0.48	N/A		
P17_AL_01B	1.60		9.75	0.47	1.60	0.14	0.02	N/A		
P17_AL_03	9.41		3.42	0.06			0.54	N/A		
P17_AL_05	4.23	0.09	6.71	0.56	4.34	0.37	0.14	N/A		
P17_AL_06	1.43		14.90	0.74			0.01	N/A		
P17_AL_07A	9.46	0.69	0.39	0.03	10.29	0.96	0.93	N/A		
P17_AL_07B	11.15	0.59	0.00	0.03	11.86	1.00	1.00	N/A		
P17_JAH_03	6.14	0.33	4.75	0.13	6.55	0.57	0.33	N/A		
P17_JAH_08	4.86	0.19	9.42	0.22	5.09	0.35	0.12	N/A		
P17_JAH_09	4.85	0.26	4.22	0.40	5.16	0.53	0.28	N/A		
P17_JAH_11	6.32	0.27	3.39	0.26	6.64	0.65	0.42	N/A		
P17_N_20_01	1.35		9.64	1.02	1.35	0.11	0.01	N/A		
P17_N_20_02a	5.87		8.56	0.20			0.16	0.16		

P17_N_20_02b	5.84		8.41	0.19			0.16	---
P17_N_20_06A	1.05		13.33	0.30			0.01	N/A
P17_N_20_06B	3.30		13.15	0.21			0.04	N/A
P17_N_20_11	7.82	0.59	2.71	0.06	8.53	0.76	0.57	N/A
P17_N_20_14_Aa	10.09	0.09	0.49	0.04	10.19	0.95	0.91	0.91
P17_N_20_14_Ab	9.61	0.03	0.46	0.04	9.65	0.95	0.91	---
P17_N_20_16	5.00	0.35	5.59	0.39	5.42	0.48	0.23	N/A
P17_N_20_17a	7.76	0.23	3.50	0.09	8.04	0.69	0.48	0.48
P17_N_20_17b	7.84	0.39	3.79	0.07	8.31	0.68	0.47	---
P17_N_20_17c	7.66	0.66	3.73	0.09	8.44	0.69	0.48	---
P17_N_20_18A	2.96	0.20	7.92	0.51	3.21	0.28	0.08	N/A
P17_N_20_18B	3.85	0.35	7.25	0.33	4.28	0.36	0.13	N/A
P17_N_20_21a2	5.85	0.14	7.40	0.45	6.02	0.43	0.19	0.19
P17_N_20_21b2	5.76	0.26	7.24	0.44	6.08	0.44	0.20	---
P17_N_20_21c2	5.26	0.97	8.04	0.64	6.43	0.43	0.18	---
P17_N_20_22a	4.84	0.23	5.79	0.35	5.12	0.45	0.21	N/A
Matrix Glass								
P17_AL_01matrix	0.14		12.69	0.30	0.14	0.01	0.00	N/A
P17_AL_05matrix	0.60		12.28	1.81	0.60	0.04	0.00	N/A
P17_AL_07matrix	1.98		9.15	0.89	1.98	0.16	0.03	N/A
P17_AL_08matrix	2.26		10.03	1.17	2.26	0.17	0.03	N/A
P17_AL_09matrix	1.69		14.14	0.46	1.69	0.10	0.01	N/A
P17_JAH_11matrix	0.97		9.90	1.10	0.97	0.08	0.01	N/A
P17_N_20_01matrix	2.03		11.01	3.33	2.03	0.12	0.02	N/A
P17_N_20_02matrixa	0.82		3.83	0.75			0.02	N/A
Melt Embayments								
P17_20_04EmbyAa	0.00		12.58	0.24			0.00	0.00

P17_20_04EmbyAb			12.74	0.21				0.00	---
P17_20_04EmbyBa			12.83	0.22				0.00	0.00
P17_20_04EmbyBb			12.49	0.23				0.00	---
P17_20_07Embya	5.17	0.37	7.49	0.11	5.62		0.43	0.18	N/A
P17_AL_01Embya	0.93		9.75	0.91	0.93		0.08	0.01	0.00
P17_AL_01Embyb	0.64		11.19	0.65	0.64		0.05	0.00	---
P17_AL_01Embyc	0.41		11.50	0.61	0.41		0.03	0.00	---
P17_AL_01Embyd	0.30		11.76	0.50	0.30		0.02	0.00	---
P17_AL_01Embye	0.25		11.61	0.52	0.25		0.02	0.00	---
P17_AL_01Embyf			11.57	0.73	0.00		0.00	0.00	---
P17_AL_09EmbyBa	0.49		12.79	0.36	0.49		0.04	0.00	N/A
P17_N_20_08Emby	0.03		12.89	0.26	0.03		0.00	0.00	N/A
P17_N_20_17Emby	5.77		7.15	0.21				0.19	N/A
P17_N_20_17EmbyAa	0.89		13.41	0.29				0.00	0.00
P17_N_20_17EmbyAb	0.86		13.72	0.25				0.00	---
P17_N_20_17EmbyBa	2.49		13.11	3.58				0.02	N/A
P17_N_20_19Embya			11.94	0.64				0.00	0.00
P17_N_20_19Embyb			11.99	0.61				0.00	---
P17_N_20_22EmbyB	0.99	0.00	10.97	0.37	0.99		0.08	0.01	N/A

[†]Peak area analysis from Konecke et al., 2017

^{*}Equation 2 using the given scaling factor of 1.2 from Lerner et al., 2021

^{**}Equation 3 from Lerner et al., 2022

^{***}Equation 1 from Lerner et al., 2023

N/A is for samples where averaging is not applicable because there is only one measurement

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CHAPTER THREE

DISTRIBUTION AND ISOTOPIC COMPOSITION OF LI IN THE SALTON SEA GEOTHERMAL FIELD

J. Humphreys, M. Brounce, M. A. McKibben, P. Dobson, N. Planavsky, B. Kalderon-Asael

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Abstract

The behavior of lithium (Li) during interactions between geothermal brine and the host rocks of the Salton Sea Geothermal Field are poorly constrained. Because of this, how the recoverable Li reservoir may evolve after Li-depleted brine is reinjected and reacts with the Li-bearing reservoir rocks at depth is uncertain. Here, we present bulk rock and brine Li concentration and $\delta^7\text{Li}$ along with *in situ* Li concentration measurements of rocks and minerals from the deep portions of the California State 2-14 scientific drilling core and a few commercial wells in the Salton Sea Geothermal Field to (1) characterize the dominant mineral hosts of Li and (2) constrain the behavior of Li during brine-rock interaction at depth.

Li concentrations are highest in authigenic chlorite and Li concentration in chlorite decreases with increasing depth (270-580 ppm at ~2358 m and 70-100 ppm at ~2882 m); groundmass containing chlorite has up to 250 ppm Li at ~2358 m. Chlorite from ~2358 m depth is observed to encase pyrite in anhydrite-bearing rocks, indicating that specific brine-mineral reactions are important to fixing Li in the rocks at these depths. Metasediments have $\delta^7\text{Li}$ (relative to Li-SVEC) = +1.8 - +7.9‰. Below 1.5 km depth, there is a positive correlation between depth

(and temperature) and $\delta^7\text{Li}$ such that rocks from the chlorite-calcite metamorphic zone have $\delta^7\text{Li} = +2.0$ to $+4.3\text{‰}$ and rocks from the deeper and hotter biotite metamorphic zone have $\delta^7\text{Li} = +4.3$ to $+7.9\text{‰}$. Conversely, whole rock Li concentration decreases with depth from ~ 80 ppm at ~ 2358 m to ~ 10 ppm at ~ 2882 m. The geothermal brines have $\delta^7\text{Li} = +3.7$ to $+4.7\text{‰}$. The values of the rocks and brines overlap with the known $\delta^7\text{Li}$ of many Li-bearing fluids and solid Earth reservoirs of Li, obscuring the origin of Li in the Salton Sea Geothermal Field. The difference in Li concentration and $\delta^7\text{Li}$ between chlorite-bearing rocks at depth suggests that the partitioning of Li in chlorite between the brine and rock is temperature dependent – lithium becomes more incompatible in chlorite in the biotite metamorphic zone, indicating an important control of temperatures above and below 325°C on the behavior of Li upon brine-rock interaction. It is critical to test this hypothesis by examining rocks at shallower depths from the State 2-14 drill core, where we expect lithium to become less incompatible in chlorite, and perhaps more significant major mineral hosts of lithium will become clear at both higher and lower temperatures.

3.1. Introduction

Lithium (Li) is desirable for use in multiple applications (e.g., lubricants, ceramics, flux powders; U.S.G.S., 2023). Of particular note is the steadily increasing demand for Li as a component in batteries for short term energy storage and electric vehicles (Ambrose and Kendall, 2020). Currently, lithium mining, refining, and battery assembly is an environmentally damaging process that requires energy- and water-rich mining and processing techniques as well as long distances and international supply chains (Sun et al., 2017; Olivetti et al., 2017; Liu and Agusdinata, 2020; Kelly et al., 2021; Chordia et al., 2022). With efforts to combat climate change focusing on the utilization of renewable energy resources and the decarbonization of transportation, the demand for Li-batteries as an efficient means for short term energy storage has increased, along with interest in establishing large, reliable domestic sources of lithium ores. Lithium is thus considered a critical mineral by the United States Department of Interior (U.S.G.S., 2022).

The Salton Sea Geothermal brines contain ~200 ppm Li (Dobson and McKibben, in review). There has long been interest in recovering Li from these brines (along with other precious metals; e.g., Maimoni, 1982), but until recently it was not considered cost-effective given the substantial challenges of managing such metal-rich brines at near-boiling temperatures. Given the demand of the green energy transition and interest in developing domestic sources of Li, plans to extract Li from the brines contained in the Salton Sea Geothermal Field are now moving forward. Beyond developing a domestic supply, there are additional advantages – because DLE technology builds upon pre-existing geothermal energy extraction infrastructure and technology, the physical footprint on the surface of the Earth for this form of Li-extraction is much smaller than the

traditionally employed methods – thus less water would be consumed and less carbon released during geothermal extraction compared to the more traditional methods (Kumar et al., 2022; Liu and Agusdinata, 2020; Kelly et al., 2021; Chordia et al., 2022).

As one of the lightest elements on the periodic table, lithium has a large relative difference in the mass between its two stable isotopes, ^6Li and ^7Li (~17%), which leads to large fractionations at low temperatures (<250°C; e.g., Chan et al., 1994; Wunder et al., 2007; Millot et al., 2010), such that as the temperature of the fluid decreases, the difference between $\delta^7\text{Li}$ ($\delta^7\text{Li} =$

$$\left[\frac{(^7\text{Li}/^6\text{Li})_{\text{sample}}}{(^7\text{Li}/^6\text{Li})_{\text{standard}}} - 1 \right] * 10^3$$

of the host fluid and the secondary minerals forming from that same fluid increases. For instance, weathering at ambient atmospheric temperatures typically increases the $\delta^7\text{Li}$ of river water ($\delta^7\text{Li}_{\text{avg}} = +23\text{‰}$; Huh et al., 1998) and seawater ($\delta^7\text{Li}_{\text{avg}} = +31\text{‰}$; Millot et al., 2004) compared to both the rocks being weathered (e.g., upper continental crust has a $\delta^7\text{Li}_{\text{avg}} = +0.6\text{‰}$; Sauzéat et al., 2015) and the minerals forming due to weathering (e.g., global average seafloor sediment, also known as GLOSS-II, has a $\delta^7\text{Li}_{\text{avg}} = +0.2\text{‰}$; Plank, 2014). The fractionation of Li isotopes during fluid-rock interactions occurs because of the preferential incorporation of ^7Li into lower coordination environments (e.g., Wunder et al., 2007; Penniston-Dorland et al., 2017 and references therein). Lithium in aqueous fluids is typically in 4-fold, tetrahedral coordination and many mineral hosts contain Li in a higher 6-fold, octahedral coordination (Fig. 3.1.). When a fluid containing Li interacts with a rock to precipitate new Li-bearing minerals, ^6Li will partition preferentially into the mineral host because of a preference for a higher coordination environment. This process leaves the fluid enriched in ^7Li and the new mineral depleted in ^7Li . When the fluid and

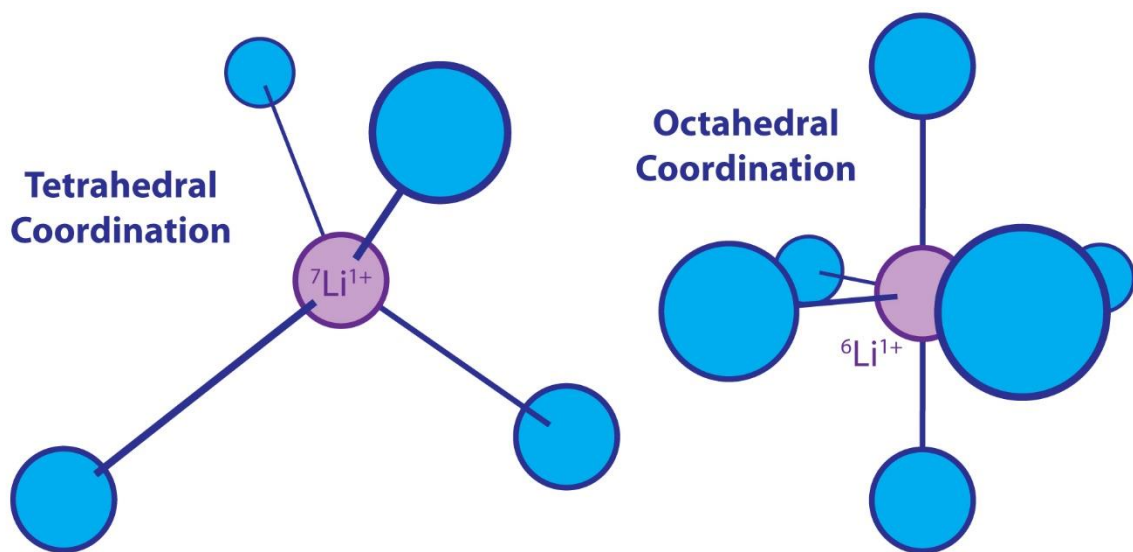


Figure 3.1. Tetrahedral and octahedral coordination of Li. Tetrahedral coordination is preferred by ${}^7\text{Li}$ (e.g., Wunder et al., 2007; Penniston-Dorland et al., 2017 and references therein).

mineral share the same coordination environment (e.g., quartz), the fractionation of Li isotopes is minimized (e.g., Schauble, 2004; Penniston-Dorland et al., 2017 and references therein), as is also the case when fluid-rock interactions occur at progressively higher temperatures (i.e., fractionation is larger at 260°C than it is at 400°C; e.g., Chan et al., 2002; Schauble, 2004; Millot et al., 2010). Lithium isotopes are also susceptible to fractionation due to diffusion on relatively rapid timescales (e.g., Lynton et al., 2005; Marschall and Tang, 2020). For example, Li isotopes between both muscovite and quartz and a chloride-bearing fluid diffusively fractionate between the host fluid and mineral on a timescale of about 30-60 days at high temperatures (400-500°C; Lynton et al., 2005).

Because of these fractionation behaviors, Li isotopes are useful for constraining the extent of interactions between surface and near-surface waters and rocks, such as in the Rhine Graben geothermal brines (Sanjuna et al., 2016), the Qaidam Basin on the northern Tibetan Plateau in China (He et al., 2020), the Central Andes (Godfrey et al., 2013; Munk et al., 2018; Garcia et al.,

2020; Godfrey and Álvarez-Amado, 2020), and in the United States (Munk et al., 2011; Araoka et al., 2014). Generally, studies of surface brines compare measured $\delta^7\text{Li}$ and Li concentration of the surface reservoir with surrounding aqueous sources feeding the reservoir to narrow down the potential origins of the Li in the surface brine along with observations of other elements and isotopic systems (e.g., Munk et al., 2011; Godfrey et al., 2013; Munk et al., 2018; He et al., 2020). Other studies add to these observations with measurements of brines at depth (Garcia et al., 2020) or use models to study how fractionation and mixing would change the $\delta^7\text{Li}$ of the surface Li reservoirs (Araoka et al., 2014; Godfrey and Álvarez-Amado, 2020). Modeling of Li isotopic fractionation of subsurface brines calculated between a solution and solid at a given temperature ($\Delta_{\text{solution} - \text{solid}} = 7847/T(\text{K}) - 8.093$; Millot et al., 2010) has been used on the hottest Rhine Graben geothermal brines ($\delta^7\text{Li} = +1.0$ to $+1.7\text{‰}$) to demonstrate that they are in equilibrium with sedimentary carbonate rocks found within the reservoir due to the calculated fractionation of Li isotopes between the brine and a rock in equilibrium with the brine, necessitating that the rock to have $\delta^7\text{Li} = -6.7$ to -6.0‰ . This value is too light to be from the granitic rocks in the Rhine Graben reservoir but overlaps with known values for carbonate-bearing sediments (Coplen, 2002) and thus indicated that the hottest geothermal brines in the Rhine Graben are from the carbonate reservoir rocks (Sanjuan et al., 2016). By constraining the behavior of Li isotopic fractionation for the sources and sinks of Li within saline systems, as is the case in the Salton Sea Geothermal Field, reservoir rocks and brines can (1) provide the record of extent of interactions between surface and near-surface fluids and source rocks in the past, and (2) predict changes in behavior of Li in the future, for example in response to chemical perturbations to the system in the case of extracting Li from a

Li-rich geothermal brine and then reinjecting that Li-poor brine back into the geothermal reservoir. This study will combine petrography and analytical geochemistry to identify the dominant mineral hosts of Li in the source rocks in the Salton Sea Geothermal Field and assess the extent to which Li may be further recovered from the source rocks after reaction with the reinjected, Li-poor brines.

3.2. Geologic History

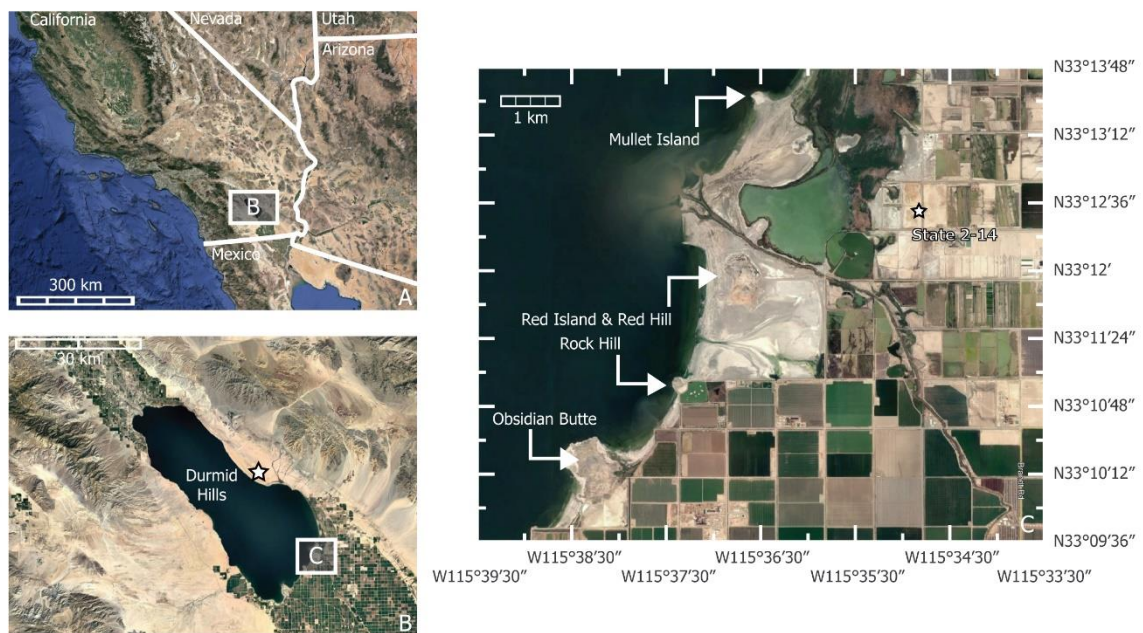


Figure 3.2. (A) Regional map of southern California. (B) Map of Salton Sea. The sampling location for the Durmid Hills is labeled with a star. (C) Map of the northern part of the Salton Sea Geothermal Field. Rhyolitic domes are labeled and indicated with arrows. The location of the State 2-14 well is labeled and indicated with a star.

The Salton Sea Geothermal Field is located in southern California, 60 km north of the United States-Mexico border, on the southeastern shore of the Salton Sea (Fig. 3.2.). This region is shaped by a variety of tectonic processes related to the subduction of the Farallon slab (until ~12 Ma) and change from subduction to the strike-slip and ongoing extensional motion (e.g., Atwater, 1970; Mammerickx and Klitgord, 1982; Stock and Hodges, 1989). At present, the Salton Sea is

underlain by a series of transform faults and pull-apart basins that formed as a consequence of the rifting associated with the opening of the Gulf of California (e.g., Elders et al., 1972; Han et al., 2016).

The Gulf of California opened into western North America around 6 Ma (e.g., Matti et al., 1985; Oskin and Stock, 2003; Dorsey et al., 2007). This opening caused the Colorado River to begin depositing sediments into the Gulf of California, which created a delta that eventually isolated the northern part of the rift, the Salton Trough, from the remainder of the Gulf of California by ~4 Ma (e.g., Winker and Kidwell, 1986; Lonsdale, 1989). Today, the Colorado River predominately drains southwards into the Gulf of California, but historically has periodically re-routed northwards, filling the Salton Trough with water and eroded sediments of the Colorado Plateau. This process created repeating instances of terminal lakes in the Salton Trough basin (e.g., Van De Kamp, 1973; Wilke, 1976; Waters, 1983; Philibosian et al., 2011; Tompson, 2016; Rockwell et al., 2022). These ancient evaporative lakes are collectively referred to as Lake Cahuilla, after the Cahuilla people who live in the Salton Trough (MacDougal, 1914). When the Colorado River would eventually route back to draining southwards into the Gulf of California, Lake Cahuilla would evaporate over the course of ~60 years (Wilke, 1976; Waters, 1983), producing saline lakes and then sequences of evaporite and sedimentary deposits (Van De Kamp, 1973; Rex, 1983). This filling-evaporation cycle took place 7 times in the past 2,500 years (Rockwell et al., 2022), and is believed to have been ongoing since ~4 Ma (Winker and Kidwell, 1986). During this time, sedimentation has kept pace with the subsidence caused by rifting beneath the Salton Trough (e.g., Lonsdale, 1989) producing thick sections of sedimentary rocks rich in evaporite minerals (2-4 km thick; e.g., Elders and Sass, 1988).

The sedimentary units within the Salton Sea Geothermal Field have been heated from depth due to prolonged rifting in the trough and associated silica-rich magmatism (Elders et al., 1972; Han et al., 2016). This heating yields hot, advecting brine and progressive metamorphic grade rocks -for example, in the State 2-14 drill core, these metamorphic grades are a chlorite-calcite zone from ~610-2,480 m depth & from ~180-325°C, a biotite zone from ~2,480-3,000 m depth & from ~325-350°C, and a clinopyroxene zone from ~3,000-3,180 m depth & with temperatures >~350°C; which correspond with the first appearance of the characteristic minerals for that grade (Cho et al., 1988; Sass et al., 1988). Previous studies on rocks in the Salton Trough have noted the appearance of chlorite coincides with the disappearance of kaolinite, ankerite, dolomite, calcite, and quartz (Muffler and White, 1969; Cho et al., 1988) and chlorite has also been observed as replacing plagioclase in thin sections (McDowell and Elders, 1980). These previously observed minerals are similar to the minerals proposed in Na/Li thermobarometry to form and break down to equilibrate Na and Li concentrations with each other (Sanjuan et al., 2014; Sanjuan et al., 2022).

Surface expressions of this subsurface heating and magmatism can be seen on the southeastern shore of the Salton Sea, where five rhyolitic domes that are ~2,000-12,000 years old (range in ages reflects uncertainties related to dating method) are located (Fig. 3.2.C; Robinson et al., 1976; Wright et al., 2015; Schmitt et al., 2019). Beneath these domes, starting at ~1,500 m depth, are a series of buried extrusive and intrusive rhyolites that are ~450,000 years old (Schmitt and Hulen, 2008). The repeated episodes of volcanism in this region are the shallow expression of the long-standing nature of the deep magmatic activity taking place under the Salton Sea Geothermal Field and the associated extensional plate tectonic related heat source. This unique focus of tectonic,

hydrological, and geomorphological events resulted in the sediments, host rocks, and pore waters that exist at depth beneath the Salton Sea today, including the source of the geothermal brines currently being used to power the Salton Sea Geothermal Field (e.g., Coplen, 1976; Rex, 1983; Waters, 1983; McKibben et al., 1988a; Brothers et al., 2022).

Currently within the Salton Sea Geothermal Field are two immiscible, density-stratified and distinct fluids: (1) a cooler, lower salinity (<10 wt% total dissolved solids, $\rho = 0.85$ g/cm³) fluid on top and (2) an underlying hot, hypersaline ($>20\%$ total dissolved solids, $\rho = 1.0$ g/cm³) brine (Williams and McKibben, 1989; Williams, 1997). The interface between the lower salinity fluid and the hypersaline brine approximately follows the depth of the 250°C isotherm in the geothermal field, such that in locations where the 250°C isotherm is shallowest, so too is the depth to the low salinity-hypersaline-brine interface (Williams and McKibben, 1989). This relationship between the brine boundary layer and the 250°C isotherm connects the existence of this hypersaline, geothermal (and lithium-bearing) brine to the heat source in this region (Williams and McKibben, 1989). Previous studies of the Salton Sea Geothermal Field hypersaline brines have found that these brines contain on average ~ 200 ppm Li (Skinner et al., 1967; Helgeson, 1968; Maimoni, 1982; Williams and McKibben, 1989; McKibben and Hardie, 1997).

3.3. Sample Descriptions and Methods

3.3.1. Sample Description

Samples in this study include igneous and sedimentary surface rocks, geothermal brines collected from 22 commercial wells in the Salton Sea Geothermal Field, as well as previously analyzed commercial drill cuttings (Schmitt and Hulen, 2008), newly analyzed commercial drill

cuttings, and State 2-14 drill core specimens (e.g., McKibben et al., 1988a; McKibben et al., 1988b; Elders and Sass, 1988; Herzig et al., 1988; Herzig and Elders, 1988). Surface igneous samples were collected from Obsidian Butte and Rock Hill (Robinson et al., 1976; Herzig and Jacobs, 1994). Unmetamorphosed sedimentary and evaporitic samples were collected from surface exposures of the Durmid Hills (Babcock, 1974).

Surface rhyolitic samples collected for analysis in this study include spherulitic obsidian from Obsidian Butte (Fig. 3A.1.). The spherulites in this sample are centered around fine grained, subhedral to anhedral phenocrysts of plagioclase and are composed of radiating, acicular crystals of feldspar and quartz. Sparse (<1% of the thin section area), fine grained, subhedral clinopyroxene phenocrysts can be found at the center of some spherulites, adjacent to the larger fine grained plagioclase phenocrysts. Medium grey, vesicular, aphanitic to glassy rhyolite was collected from Rock Hill (Fig. 3A.2.A.). Within this sample are sparse (<1% of the thin section area) amounts of fine grained euhedral-subhedral, plagioclase, clinopyroxene, and Fe-Ti oxide crystals. Also collected from Rock Hill are dark grey, vesicular, glassy rhyolite (Fig. 3A.2.B). Sparse (<1% of the thin section area) amounts of fine grained subhedral and rounded plagioclase, clinopyroxene, and Fe-Ti oxide crystals are present within the rhyolite. Vesicles within this sample are elongated in one direction.

Four outcrop samples were collected from the Durmid Hills, representing unmetamorphosed equivalents of the geothermal reservoir rocks. One sample is a light grey mudstone (Fig. 3A.3) with minor amounts of fine to medium grained pyrite crystals. Also collected is a grey-translucent gypsum (Fig. 3A.4.A. & B.) with light grey, interbedded mudstone. The gypsum beds range from very fine-grained layers of a few mm in thickness to coarser grained, acicular blocks

of about 1 cm in thickness. Additionally, white, cryptocrystalline gypsum (Fig. 3A.5.) was collected.

A light to medium grey, calcite-cemented, fine-grained sandstone (Fig. 3A.6.) was also collected.

Subsurface samples from the State 2-14 drill core have previously been described in the literature (e.g., McKibben et al., 1988b; Charles et al., 1988; Cho et al., 1988; Elders and Sass, 1988; Herzig et al., 1988; Herzig and Elders, 1988). This study adds to those descriptions using microanalytical analyses (see Scanning Electron Microscope, below). The specific State 2-14 drill core samples analyzed (Fig. 3A.7. – 15.) include samples from ~1866 m depth (flow zone ejecta; Charles et al., 1988), ~2358 m depth, ~2485 m depth, ~2745 m depth, ~2819 m depth, and ~2882 m depth. The sample from ~1866 m depth is a monomineralic, interlocking, very fine grained, granular, subhedral epidote (Fig. 3A.7.). The sample from ~2358 m depth is an interbedded grey-green mudstone and white, coarse to fine-grained anhydrite with medium to fine-grained pyrite intermittently present near the mudstone-anhydrite interfaces (Fig. 3A.8.). The sample from ~2485 m depth is an interbedded medium-grey mudstone and light grey to light green epidotized mudstone (Fig. 3A.9; Cho et al., 1988). The sample from ~2745 m depth is a medium grey, interbedded mudstone and white, very coarse grained to fine grained, angular anhydrite (Fig. 3A.10.). The sample from ~2819 m depth is a dark green epidotized mudstone with light green veins and spots of larger fine-grained minerals of epidote, quartz, and anhydrite (Fig. 3A.11.). The sample from ~2882 m depth is a brecciated diabase and mudstone (Fig. 3A.12; Herzig and Elders, 1988).

Three additional drill core samples (2 samples were from State 2-14) were analyzed for Li isotopes (and one for whole rock Li concentration) during this study. These samples are from depths of ~1039 m (massive anhydrite with < ~10% grey-green mudstone interlayered within the

anhydrite collected from well Magma-max-11; Fig. 3A.13; McKibben et al., 1988a), ~1294 m (epidotized metasedimentary mudstone; Fig. 3A.14.), and ~1427 m (metasedimentary mudstone with hematite veins; Fig. 3A.15.) from well State 2-14.

3.3.2. *Sample Preparation*

Samples were sawn with a diamond-coated blade and washed in de-ionized water before being sent for commercial polished thin section preparation by Burnham Petrographics, LLC. Drill cuttings were mixed with Petropoxy 154 and mounted within 0.7 cm-round brass spacers cut to be 0.6 cm in length. Brass spacer mounted samples were polished using progressively finer grain sized polish paper down to 0.25 μm until the samples were exposed on one side with areas of optically smooth surface. These exposed samples along with previously analyzed State 2-14 samples and newly created thin sections of State 2-14 and surface samples were then carbon coated in preparation for Scanning Electron Microscope (SEM) analysis.

3.3.3. *Scanning Electron Microscope*

Carbon-coated samples were analyzed at the Brounce Geochemical Laboratory at the University of California, Riverside on a JEOL JCM-7000 NeoScope Benchtop scanning electron microscope equipped with a mapping stage using an accelerating voltage of 15 kV in high vacuum mode. Elemental and back-scattered electron maps of the samples in this study were analyzed to identify major mineral phases in conjunction with visible light petrographic observations. Selected regions of interest were analyzed *in situ* for major and trace element concentrations via laser ablation induced coupled plasma mass spectrometry (LA-ICP-MS).

3.3.4. Laser Ablation Inductively Coupled Mass Spectrometry

Trace element abundances for the samples in this study were analyzed at the Lyons ICP-MS Facility at the University of California, Riverside via LA-ICP-MS using an Agilent Technologies 7900 single quadrupole mass spectrometer that is coupled to a short pulse width coherent 193 nm ArF excimer laser. Samples in this study were analyzed for 60 major, minor, and trace elements of which ^7Li , ^{23}Na , ^{26}Mg , ^{27}Al , ^{29}Si , ^{39}K , ^{44}Ca , ^{55}Mn , and ^{56}Fe are presented in this study. Spot sizes analyzed ranged from 25-30 μm in diameter. A repeat rate of 5 Hz and energy on sample surface of 0.040 – 0.052 mJ was used. United States Geological Survey glass standards BIR-1 g, BCR-2 g, and BHVO-2 g; Max Planck Institute glass standards KL2-G, ML3B-G, StHls-G, GOR-128-G, GOR-132-G, ATHO-G, and T1-G; and National Institute of Science and Technology Standard Reference Material glasses 610 and 612 were used to create linear calibration curves ($R^2 > 0.999$) for each analytical session (Pearce et al., 1997; Jochum et al., 2000; Kelley et al., 2003). Counting statistics were examined carefully for each element and those elements that did not return strong signals for the entire length of the ablation period were discarded. Samples with two distinct, strong signals during the ablation period had both signals analyzed and sample names were amended to include the interval period in their name (e.g., sample 9005m_Aa_10-14 and 9005m_Aa_18-21 are from one analysis period). For minerals where sulfur and/or carbon was a major elemental constituent (i.e., pyrite, anhydrite, gypsum, and calcite), analyses were normalized to either ^{44}Ca (for anhydrite, gypsum, and calcite) or ^{56}Fe (for pyrite) using an assumed calculated CaO or FeO stoichiometric concentration (41.3 wt% CaO for anhydrite, 32.6 wt% CaO for gypsum, 56.0 wt% CaO for calcite, and 59.9 wt% FeO for pyrite). Since this method calculates the values of Si, Ca, and Fe using identical

standard measurements (e.g., KL2-G SiO_2 = 50.3 wt% for both ^{28}Si and ^{29}Si), ^{29}Si , and ^{56}Fe were chosen to calculate elemental abundances. Samples with major element totals less than 95% were discarded from analysis.

3.3.5. *Lithium Isotopes*

Lithium isotopic compositions of brines and selected rock powders were analyzed at the Geochemistry Center at Yale University via a Thermo Finnigan Neptune Plus ICP-MS using the methods of Kalderon-Asael et al. (2021). For the brines, an aliquot of 1 mL of each sample was dried at 93°C into a pre-acid-cleaned Teflon beaker. The aliquots were subsequently digested with aqua regia (200 microliters of distilled HNO_3 and 600 microliters of distilled HCl), capped and left on a hotplate at 130°C for 48 hours, and dried again. At a second digestion step, 1 mL of distilled HNO_3 and three drops of H_2O_2 were added to each sample, capped and left on a hotplate at 130°C for 48 hours, and dried again. The samples were then redissolved in 10 mL of 6N HCl . Splits were taken for lithium column procedure. The rock samples were digested using the total digest protocol. At the end, the samples were redissolved in 5 mL of 6N HCl . The few evaporitic samples were dissolved in Milli-Q H_2O . Splits were taken for the lithium column procedure.

3.3.6. *Whole Rock Lithium Analysis*

Whole rock powders were dissolved using Environmental Protection Agency Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils using a temperature of 220°C for ~15 minutes. Lithium concentrations of selected rock powders were analyzed at the Lawrence Berkeley National Laboratory via an Agilent 8900 triple quadrupole ICP-MS (Agilent 8900 QQQ ICP-MS) which has been used to measure the concentrations of 36

elements simultaneously for environmental samples, of which Li (measured using standard no gas mode) is reported here. The instrument settings and analytical methods are similar to those reported by Belkouteb et al. (2023) and Agilent application notes (Agilent, 4th Edition). All samples were prepared/diluted with 2% (v/v) ultrapure nitric acid in Milli-Q water (18.2 mΩ·cm) and analyzed under a rigorous quality assurance and quality control (QA/QC) process.

3.4. Results

3.4.1. Surface Samples

Rhyolitic samples. Surface rhyolitic rocks were collected from Obsidian Butte and Rock Hill (Fig. 3.2.C.). Lithium concentrations of these rocks vary depending on mineralogy ($1.1 \pm 0.3 - 91 \pm 2.3$ ppm for the various minerals from Obsidian Butte and $13 \pm 0.5 - 90 \pm 1.9$ ppm for the various minerals from Rock Hill; Humphreys et al., 2023). The highest Li concentrations are found in volcanic glass (Obsidian Butte, 91 ± 2.3 ppm, Humphreys et al., 2023) and plagioclase (Rock Hill, 90 ± 1.9 ppm, Humphreys et al., 2023). Whole rock Li isotopic concentrations vary for these rocks (Obsidian Butte has $\delta^7\text{Li} = +3.5 \pm 0.04 - +3.8 \pm 0.02$ ‰ and Rock Hill has $\delta^7\text{Li} = +8.1 \pm 0.03 - +10.3 \pm 0.03$ ‰, Humphreys et al., 2023). Buried, hydrothermally-altered rhyolitic rocks from commercial drill wells in the Salton Sea Geothermal Field and from depths ranging from 1573 m (5160 ft) – 2655 m (8710 ft; Schmitt and Hulen, 2008) have Li concentrations that range from $2 \pm 0.9 - 68 \pm 2.0$ ppm (Humphreys et al., 2023) and $\delta^7\text{Li} = +6.4 \pm 0.03$ to $+7.6 \pm 0.03$ ‰, with quartz having the highest Li concentrations (highest = 68 ± 2.0 ppm with an average = 42 and a standard deviation = 13 ppm; Humphreys et al., 2023).

Sedimentary and evaporitic samples. Surface sedimentary and evaporitic rocks were collected from the Durmid Hills (Fig. 3.2.B; Babcock, 1974). The Li contents of the Durmid Hills surface sedimentary and evaporitic rocks vary by rock type. Sandstone has low concentrations of Li (0.8 ± 0.3 ppm, Humphreys et al., 2023) and has $\delta^7\text{Li} = +5.2 \pm 0.08\text{‰}$ (Humphreys et al., 2023). The groundmass of the mudstone rock and the mudstone that is interbedded with gypsum has relatively high lithium concentrations ($142 \pm 2.45 - 177 \pm 5.11$ ppm, Humphreys et al., 2023); these values are slightly higher than the reported Li concentrations (104 – 136 ppm) measured in the clay-size fraction of near-surface sediments from the Salton Sea (Sturz, 1989) and the whole rock measurements from this study ($97 \pm 5.1 - 115 \pm 4.8$ ppm, Humphreys et al., 2023). Durmid Hills mudstones have $\delta^7\text{Li} = +1.5 \pm 0.3\text{‰}$ (Humphreys et al., 2023), interbedded mudstone and gypsum whole rock have $\delta^7\text{Li} = +5.5 \pm 0.5 - +6.0 \pm 0.06\text{‰}$ (Humphreys et al., 2023). Lithium contents for the cryptocrystalline gypsum are $<1 \pm 0.1$ ppm (Humphreys et al., 2023) and have $\delta^7\text{Li} = -9.1 \pm 0.06\text{‰}$ (Humphreys et al., 2023).

3.4.2. Subsurface Samples

State 2-14 Rock Samples and Geothermal Brines. Like the surface samples, the Li concentrations and isotopic compositions of the metasedimentary rocks vary according to the mineralogy of the rock and, because mineralogy is tied to metamorphic grade, with depth. Metasedimentary mudstones found at depths from ~1290-1430 m have $\delta^7\text{Li} = 1.8 \pm 0.04\text{‰}$ for the epidotized mudstone (~1290 m depth, Humphreys et al., 2023) and have $\delta^7\text{Li} = +5.7 \pm 0.04 - +6.3 \pm 0.03\text{‰}$ for the mudstone with hematite veins (~1430 m depth; Humphreys et al., 2023). Vein material was not analyzed in either of these metasedimentary rocks, and care was taken to only

sample the mudstone in these cores. Monomineralic epidote ejecta from a flow-test at 1866 m has <1 ppm Li and has $\delta^7\text{Li} = +2.7 \pm 0.05 - +3.3 \pm 0.03\text{‰}$ (Humphreys et al., 2023). Interbedded anhydrite and shale have whole rock Li concentrations of $79.2 \pm 2.9 - 83.9 \pm 6.6$ ppm (Humphreys et al., 2023). Spot analysis Li concentrations for this sample range from $<1 \pm 0.1 - 581 \pm 12.17$ ppm (Humphreys et al., 2023) with chlorite grains consistently yielding the highest Li concentrations for this section ($269 \pm 2.58 - 581 \pm 12.17$ ppm, Humphreys et al., 2023). An epidotized metasedimentary rock from ~2485 m depth has $\delta^7\text{Li} = +2.0 \pm 0.03 - 4.3 \pm 0.04\text{‰}$ (Humphreys et al., 2023); an epidote grain in this rock has 2.7 ± 0.3 ppm Li (Humphreys et al., 2023). Whole rock interbedded anhydrite and mudstone from ~2745 m depth has 34.2 ± 3.2 ppm Li (Humphreys et al., 2023) and a range from $<1 \pm 0.1 - 87 \pm 1.6$ ppm Li for spot analyses in the minerals and the heterogeneous, fine-grained matrix (Humphreys et al., 2023). An epidotized mudstone from ~2819 m depth has $<1 \pm 0.2 - 18 \pm 0.7$ ppm Li (Humphreys et al., 2023) and whole rock $\delta^7\text{Li} = +6.2 \pm 0.05 - +7.9 \pm 0.04\text{‰}$ (Humphreys et al., 2023). The deepest rocks studied are recovered from ~2882 m depth and have a whole rock Li concentration of $6.7 \pm 1.6 - 12.3 \pm 2.5$ ppm (Humphreys et al., 2023) and $\delta^7\text{Li} = +4.1 \pm 0.03 - +5.1 \pm 0.03\text{‰}$ (Humphreys et al., 2023). Spot analyses of chlorite yield $70 \pm 1.3 - 104 \pm 22.2$ ppm Li, alkali feldspar yield $2 \pm 0.4 - 19 \pm 0.6$ ppm Li, and groundmass yields $3 \pm 0.3 - 43 \pm 0.8$ ppm Li (Humphreys et al., 2023). Geothermal brines recovered from multiple geothermal wells in the Salton Sea Geothermal Field have $\delta^7\text{Li} = +3.7 \pm 0.04 - +4.5 \pm 0.05\text{‰}$ (Humphreys et al., 2023) and have previously been measured to have Li concentrations from 117-245 ppm (Skinner et al., 1967; Helgeson, 1968; Maimoni, 1982; Williams and McKibben, 1989; McKibben and Hardie, 1997).

3.5. Discussion

All but one of the rocks measured in this study have whole rock $\delta^7\text{Li} = +1.5$ to $+10.3\text{‰}$ (the one outlier has $\delta^7\text{Li} = -9.1\text{‰}$; Humphreys et al., 2023). The Salton Sea Geothermal Field brines in this study have $\delta^7\text{Li} = +3.7$ to $+4.5\text{‰}$ (Humphreys et al., 2023), overlapping with that of the rocks, but with less variation. This is consistent with narrow ranges of O and H isotopic measurements of the brine ($\delta^{18}\text{O} = 0$ to $+3.3\text{‰}$ and $\delta\text{D} = -68$ to -75‰) implying that the brine reservoir is internally convecting and well-mixed (Williams and McKibben, 1989). The geothermal brine samples and host rocks in this study overlap in $\delta^7\text{Li}$ of many potential source materials (Fig. 3.3.), including MORB ($\delta^7\text{Li} = +1.5$ to $+5.6\text{‰}$; Moriguti and Nakamura, 1998; Chan et al., 2002; Elliott et al., 2006; Nishio et al., 2007; Tomascak et al., 2008), upper continental crust ($\delta^7\text{Li} = -2.9$ to $+4.7\text{‰}$; Teng et al., 2004; Sauzéat et al., 2015), and rivers (suspended and dissolved load, $\delta^7\text{Li} = -5.9$ to $+43.7\text{‰}$; Huh et al., 1998; Huh et al., 2001; Kısakürek et al., 2005; Pogge Von Strandmann et al., 2006; Vigier et al., 2009; Pogge Von Strandmann et al., 2010; Lemarchand et al., 2010; Liu et al., 2015; Pogge Von Strandmann and Henderson, 2015; Dellinger et al., 2015; Pogge Von Strandmann et al., 2020). The samples in this study (brine and rock) also overlap with previous measurements of $\delta^7\text{Li}$ in Li-rich deposits (Fig. 3.3.), including salar brines from the Andes ($\delta^7\text{Li} = +3.7$ - $+12.6\text{‰}$; Godfrey et al., 2013; Munk et al., 2018; Garcia et al., 2020; Godfrey and Álvarez-Amado, 2020) and Nevada ($\delta^7\text{Li} = -1$ - $+8\text{‰}$; Araoka et al., 2014) and spodumene Li mines in Australia, Canada, China, the United States, and Zimbabwe ($\delta^7\text{Li} = -2.83$ - $+14.7\text{‰}$; Magna et al., 2016; Fan et al., 2020; Desautly et al., 2022). The brines in this study are heavier in $\delta^7\text{Li}$ composition than those reported for Li-bearing geothermal brines from the Rhine Graben ($\delta^7\text{Li} = +1.0$ - $+1.7\text{‰}$, 168-190 ppm; Fig. 3.3; Sanjuan et al., 2016)

and are lighter in $\delta^7\text{Li}$ composition than oil field related brines from the Rhine Graben ($\delta^7\text{Li} = 7.0 - 12.6\text{‰}$, 6.9 – 72.0 ppm; Fig. 3.3; Sanjuan et al., 2016) and the Tibetan Plateau ($\delta^7\text{Li} = 31.3 - 32.6\text{‰}$, 14.4 – 97.5 ppm; Fig. 3.3; He et al., 2020). The brine in this study is also lighter isotopically than non-oil field well brines in the Tibetan Plateau (meteoric: $\delta^7\text{Li} = 31.3 - 32.6\text{‰}$, 14.4 – 97.5 ppm; ancient brine lake and mountain recharge: $\delta^7\text{Li} = 9.2 - 21.2\text{‰}$, 8.7 – 408.8 ppm; Fig. 3.3; He et al.,

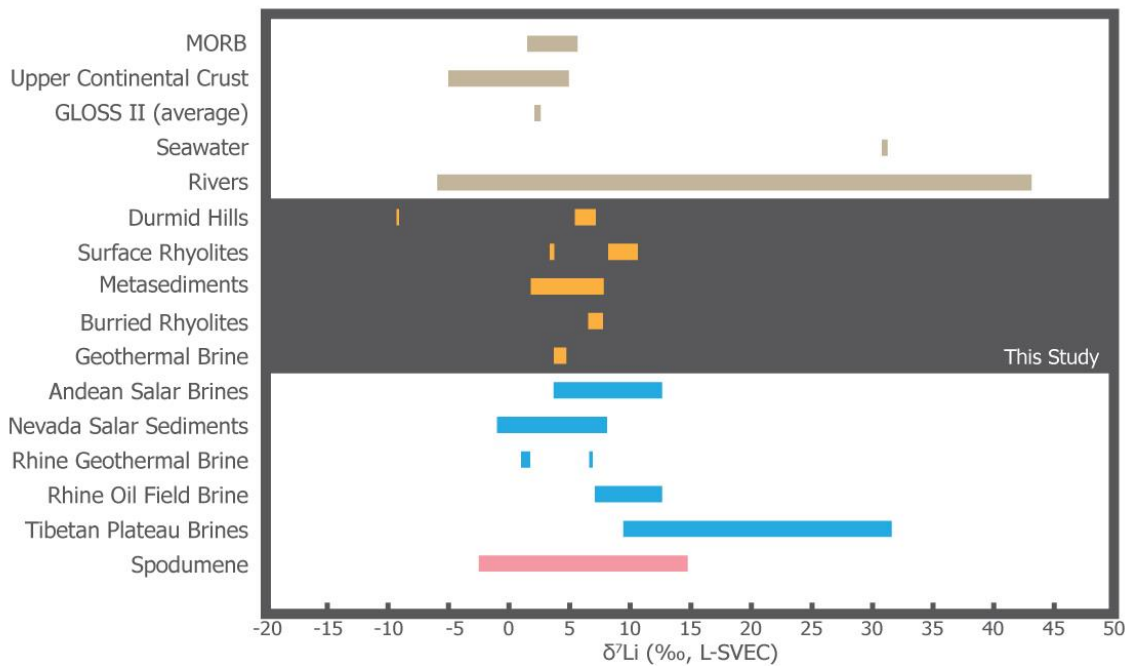


Figure 3.3. The Li isotopic composition for rocks and brines in this study compared to other Li-bearing reservoirs (modified after Penniston-Dorland et al., 2017). Brown bars represent known global ranges for Mid-ocean Ridge Basalt (Moriguti and Nakamura, 1998; Chan, 2002; Elliott et al., 2006; Nishio et al., 2007; Tomascak et al., 2008), the upper continental crust (Teng et al., 2004; Sauzéat et al., 2015), seawater (Millet et al., 2004), and rivers (suspended and dissolved load; Huh et al., 1998; Huh et al., 2001; Kısakürek et al., 2005; Pogge Von Strandmann et al., 2006; Vigier et al., 2009; Pogge Von Strandmann et al., 2010; Lemarchand et al., 2010; Liu et al., 2015; Pogge Von Strandmann and Henderson, 2015; Dellinger et al., 2015). Orange bars represent the rock and brine values measured in this study. Blue bars represent known Li-bearing, location specific isotopic data for the Andean salar brines, Nevada salar sediments, Rhine Graben geothermal brines, Rhine Graben oil field brines (Godfrey et al., 2013; Araoka et al., 2014; Sanjuan et al., 2016; Munk et al., 2018; Garcia et al., 2020; He et al., 2020; Godfrey and Álvarez-Amado, 2020; Desaulty et al., 2022). The Pink bar is for the range in known spodumene isotopic values (Magna et al., 2016; Fan et al., 2020; Desaulty et al., 2022).

2020). The wide range in geologic settings and potential Li-rich reservoirs that overlap with the isotopic composition of Salton Sea Geothermal Field rocks and brine in this study necessitates careful quantitative modeling of isotopic fractionation between the brines and the rocks that the brine is in contact with to identify the possible source(s) of the Li to Salton Sea Geothermal Field brines. It is possible that modern hydrothermal metamorphism has altered and obscured the original Li isotopic signatures in these samples

State 2-14 rock samples in this study come from the chlorite-calcite (~610-2480 m, ~180-325°C) and biotite (~2480-3000 m, ~325-350°C) metamorphic zones (Cho et al., 1988; Sass et al., 1988). The minerals with the highest measured Li concentrations of any phase in this study are relatively large chlorite grains which encase authigenic pyrite grains (rims of chlorite range in thickness from ~40 to 400 μm in diameter) from the calcite-chlorite metamorphic zone (269-581 ppm; Humphreys et al., 2023) that are observed encasing skeletal pyrite grains at ~2358 m depth (Fig. 3.4.). Pyrite grains in the host rocks of the Salton Sea Geothermal Field are authigenic, formed during diagenetic sulfide mineralization at temperatures <250°C and metamorphic sulfide mineralization at temperatures >250°C (McKibben and Elders, 1985; McKibben et al. 1988b). As temperature increases above 250°C with increased depth, porphyroblastic pyrite grows, then decomposes into skeletal aggregates upon reaction with the geothermal brine (McKibben and Elders, 1985). Since the pyrite grains encased by Li-bearing chlorite measured in this study are skeletal, we interpret these pyrites as in the process of dissolution via reaction with the brine in which Fe is mobilized out of the pyrite (McKibben and Elders, 1985). This dissolution process happens in tandem with hornfelsic recrystallization of the silicate minerals (e.g., quartz and

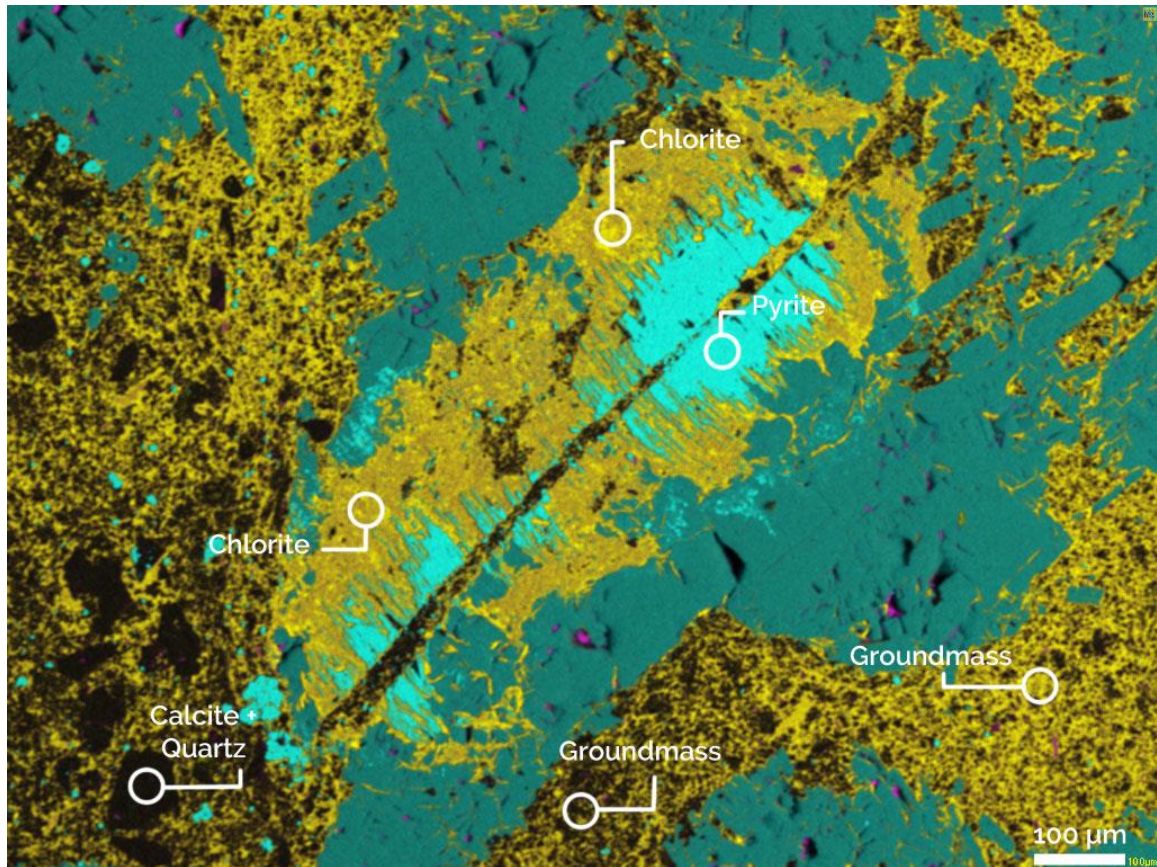


Figure 3.4. Back Scatter Electron map of metasedimentary anhydrite and mudstone from ~2358 m depth. Relatively aluminum rich regions are represented by magenta, relatively sulfur rich regions are represented by cyan, and relatively magnesium rich regions are represented by yellow. Anhydrite is the dark cyan mineral that is unlabeled on the sample. Relatively large authigenic chlorite surrounds skeletal pyrite.

feldspar) at this depth (e.g., McDowell and Elders, 1980; McKibben and Elders, 1985). Additionally, the appearance of chlorite $((\text{Mg,Fe})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot (\text{Mg,Fe})_3(\text{OH})_6)$ coincides with the disappearance of dolomite-ankerite $(\text{Ca}(\text{Fe,Mg,Mn})(\text{CO}_3)_2)$ and has been observed replacing feldspar $(\text{KNaCa}(\text{AlSi})_4\text{O}_8)$ in the Salton Sea Geothermal Field (McDowell and Elders, 1980; Cho et al., 1988). The combination of dolomite-ankerite and feldspar dissolution in conjunction with hydrothermal alteration would provide the necessary elements for the formation of chlorite in this

setting. It is possible that the process of pyrite dissolution and chlorite crystallization is also acting as an oxygen buffer between the host rocks and brine at this depth (McKibben and Elders, 1985).

Chlorite-rich groundmasses (where the chlorites are $<10\ \mu\text{m}$ in diameter; Fig. 3.4.) in these same metasedimentary rocks (at a depth of $\sim 2358\ \text{m}$) also have elevated Li concentrations relative to non-chlorite minerals (e.g., anhydrite and pyrite) from similar depths (48-252 ppm in the groundmass compared to 0-6 ppm for anhydrite and pyrite; Humphreys et al., 2023). This difference along with the observation of elevated Li concentrations in larger chlorite clasts confirms hypotheses based on Na/Li geothermometry involving Li-bearing micas that suggests that chlorite and other octahedral clay minerals are the most likely hosts for Li in the Salton Sea Geothermal Field reservoir rocks (Sanjuan et al., 2022). In both the larger and smaller, groundmass chlorite grains, lithium is incorporated into these grains from the brine in trace quantities within the calcite-chlorite metamorphic zone (i.e., Li is not present as a major element). Li is also present in trace quantities in the surface Durmid Hill mudstones, which have somewhat higher bulk Li concentrations than the chlorite-bearing rocks in the calcite-chlorite zone (compare 97-115 ppm Li in surface mudstones to 79-84 ppm at $\sim 2358\ \text{m}$ depth; Humphreys et al., 2023), suggesting a net loss of Li from the rocks into the brines, and that the Li that remains in the rock is preferentially incorporated into chlorite compared to other mineral indicators of brine-rock reaction. Rocks in the biotite metamorphic zone have even lower Li concentrations than those in the chlorite-calcite zone (7-34 ppm; Humphreys et al., 2023), suggesting that at high temperatures more Li is lost from rocks into the brines. The extent to which this temperature-dependence extends to higher

temperatures (e.g., into the pyroxene-zone at 3000 m depth in State 2-14; (Cho et al., 1988) is critical to test in a future study (see Proposed Future Work, below).

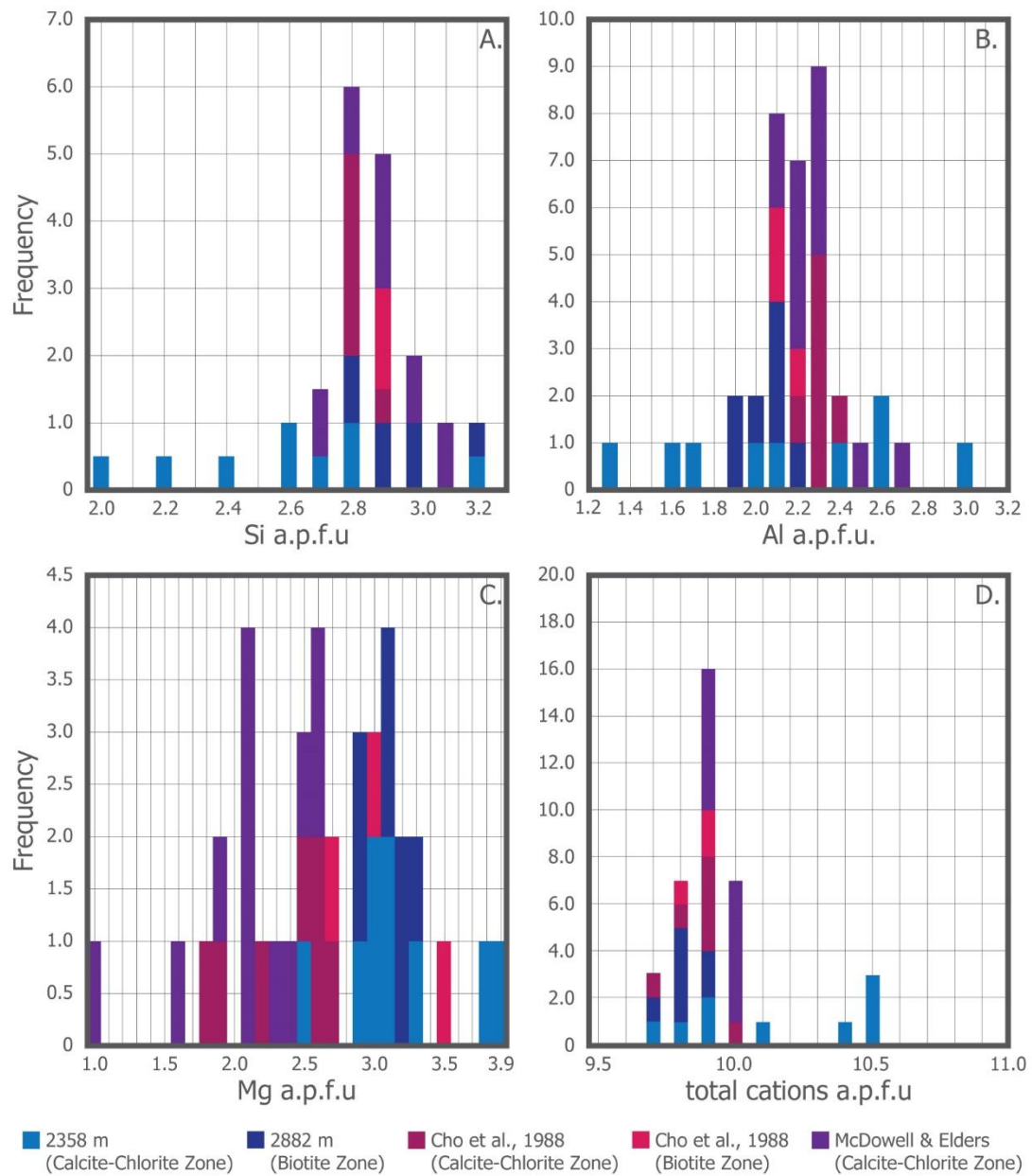


Figure 3.5. Major element comparison of chlorites in this study separated by depth (~2358 m depth, blue; ~2882 m depth, dark blue) with previous studies of the Salton Sea Geothermal Field separated by depth and well (calcite-chlorite zone from State 2-14 (Cho et al., 1988), magenta; biotite zone from State 2-14 (Cho et al., 1988), pink; calcite-chlorite zone from Elmore 1 (McDowell and Elders, 1980) with equivalent depths to the State 2-14 well calculated from reported temperature (Sass et al., 1988), purple. (A) Frequency comparison between samples in this study and previous studies (McDowell and Elders, 1980; Cho et al., 1988) for Si atoms per formula unit (a.p.f.u.). (B) Frequency comparison between samples in this study and previous studies (McDowell and Elders, 1980; Cho et al., 1988) for Al atoms per formula unit (a.p.f.u.) (C) Frequency comparison between samples in this study and previous studies (McDowell and Elders, 1980; Cho et al., 1988) for Mg a.p.f.u. (D) Frequency comparison between samples in this study and previous studies (McDowell and Elders, 1980; Cho et al., 1988) for the sum of all cations (Si + Al + Mg + Fe + Mn + Ti + Na + K + Ca) as a.p.f.u.

The measured major element chemical compositions of the chlorites in this study overlap with previous measurements of chlorites from the Salton Sea Geothermal Field (Fig. 3.5.A – D; Cho et al., 1988). Chlorite compositions in this study were calculated with $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.1$, as has been previously observed for chlorites in the Salton Sea Geothermal field (Dyar et al., 1992) and on a 14-oxygen basis (Cho et al., 1988). There is a positive correlation between Li and Al ($R^2 = 0.777$; Fig. 3.6.A.), a moderately positive correlation between Li and Mn ($R^2 = 0.584$, Fig. 3.6.B.), and a moderately negative correlation between Li and (Mg + Fe^{2+} + Fe^{3+} ; $R^2 = 0.456$; Fig. 3.6.C.) in chlorite

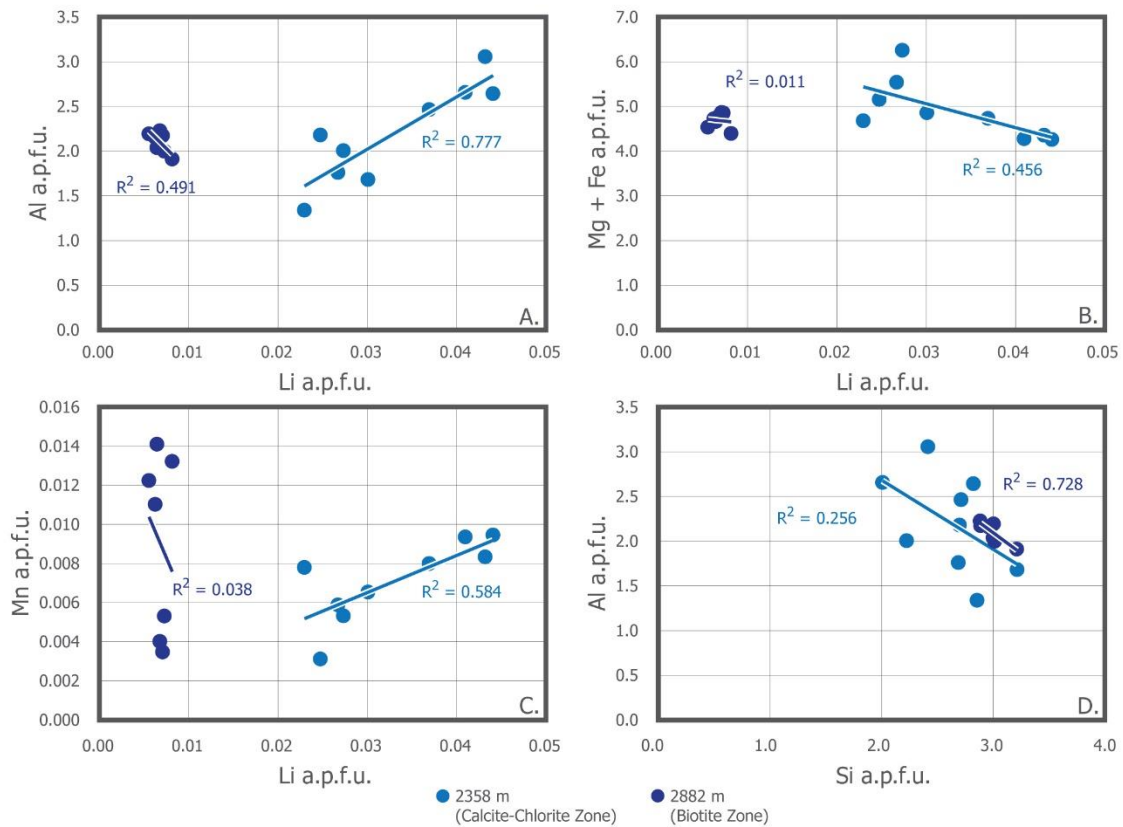


Figure 3.6. Major element comparison of chlorites in this study with Li and Si a.p.f.u. (A) Comparison of Al and Li a.p.f.u. in chlorites found at ~2358 m depth (blue) and ~2882 m depth (dark blue). (B) Comparison of Mg + Fe (Fe^{2+} + Fe^{3+}) and Li a.p.f.u. in chlorites found at ~2358 m depth (blue) and ~2882 m depth (dark blue). (C) Comparison of Mn and Li a.p.f.u. in chlorites found at ~2358 m depth (blue) and ~2882 m depth (dark blue). (D) Comparison of Al and Si a.p.f.u. in chlorites found at ~2358 m depth (blue) and ~2882 m depth (dark blue).

from the chlorite-calcite zone. In contrast, in the biotite metamorphic zone there is a negative correlation between Li and Al ($R^2 = 0.491$; Fig. 3.6.A.) and no other statistically significant relationships between Li and the other major elements in chlorite. In this zone, anhedral chlorite grains are found dispersed amongst xenoblastic alkali feldspar, epidote, and pyrite grains. There is no correlation between Li and Si in chlorite from either metamorphic zone ($R^2 = 0.092$ at ~2358 m depth and $R^2 = 0.262$ at ~2882 m depth). The strong positive relationship between Li and Al in chlorite from the chlorite-calcite zone indicates that Li substitutes into chlorite together with Al, but the lack of correlation between Li and Si in samples from ~2358 m depth ($R^2 = 0.092$) indicates that this coupled substitution with Al is not on the tetrahedral Si^{4+} site, as a charge coupled mechanism in the style of $\text{Al}^{3+} + \text{Li}^+ = \text{Si}^{4+}$. This is supported by the moderately negative correlation between Li and $\text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+}$ (Fig. 3.6.B.), the latter of which are two of the other octahedrally coordinated elements in chlorite. The moderately positive relationship between Mn and Li (Fig. 3.6.C.), further suggests that Li is substituting into an octahedral coordination within chlorite. The partitioning of Li into chlorite is markedly different in the biotite zone - there is no relationship between Si and Al within the calcite-chlorite zone chlorites ($R^2 = 0.256$), there is a strong negative correlation ($R^2 = 0.728$) between Si and Al in chlorite grains found in rocks within the biotite metamorphic zone (Fig. 3.6.D.). Additionally, there is a weak negative correlation ($R^2 = 0.491$) between Li and Al within these same rocks (Fig. 3.6.A.). This suggests that at temperatures $>325^\circ\text{C}$, the incorporation of Al in chlorite occurs in the tetrahedral site, and because these chlorites have lower Li concentrations as well as display a negative correlation between Li and Al, this substitution is not charge-coupled with Li. The result is that Li may be more incompatible in chlorite at

temperatures $>325^{\circ}\text{C}$ in the State 2-14 rocks. We caution that the partitioning behavior of Li in chlorite will depend in detail on fluid and mineral compositions and pressure in addition to temperature and that these relationships will be important to constrain and/or test with additional measurements.

Understanding the primary source for the abundance and isotopic compositions of Li in the Salton Sea Geothermal Field brines is complex, owing to the variety of geologic processes involved in the Salton Trough and length of time in which these processes have been affecting the region (from ~ 4 Ma to present, see above Geologic History; Van De Kamp, 1973; Wilke, 1976; Waters, 1983; Winker and Kidwell, 1986; Lonsdale, 1989; Philibosian et al., 2011; Tompson, 2016; Rockwell et al., 2022). While evaporation of Lake Cahuilla alone likely had little to no effect on the Li isotopic composition of the evaporating lake waters since salt precipitation does not significantly fractionate Li isotopes (e.g., Tomascak et al., 2003; Godfrey et al., 2013), Li more readily fractionates between fluids and minerals at lower temperatures and thus fractionation between pore fluid and associated Li-bearing minerals is expected to be greater at shallower to near-surface depths within the Salton Sea Geothermal Field (e.g., Chan et al., 1994; Chan et al., 2002; Millot et al., 2010). The buried sedimentary and evaporitic rocks are incrementally metamorphosed with increasing depth through hydrothermal interactions until a time when they are in contact with geothermal brines between $330 - 360^{\circ}\text{C}$. Fluid-rock interactions at these and lower temperatures would have driven the recrystallization of clay minerals via reacting with the hot brines at depth (e.g., Helgeson, 1968; Muffler and White, 1969). This process in turn would yield metamorphic mineral assemblages with lighter $\delta^7\text{Li}$ compositions than the brine, and the brine would become progressively heavier in $\delta^7\text{Li}$

as the metamorphic mineral assemblage preferentially incorporates ^6Li into its crystal structures. Metamorphic minerals forming from brines with progressively heavier $\delta^7\text{Li}$ compositions would themselves have heavier $\delta^7\text{Li}$ compositions than minerals formed at earlier stages of this process, though at each stage the metamorphosed clay minerals would be expected to be lighter in $\delta^7\text{Li}$ than the equilibrium compositions brine. Higher temperatures at depth may have caused the initial release of more Li into the brine from the buried sediments and volcanic rocks as they were hydrothermally altered due to the mobilization of Li through interaction with a fluid when the geothermal field was initially forming (e.g., Magenheimer et al., 1995; Chan et al., 2002; Millot et al., 2010; Coffey et al., 2021; Ellis et al., 2022) and even at low temperatures ($< 100^\circ\text{C}$), rocks in the Salton Sea Geothermal Field show signs of alteration (Sturz, 1989). Reactive-transport modeling of the Salton Sea Geothermal Field as a whole suggests that the interaction between the rock and brine is slower than is necessary to affect the Li concentration of re-injected, Li-poor brines on decadal timescales (see Constraints on Lithium Evolution and Reservoir Sustainability in the Salton Sea Geothermal Field From Reactive-Transport Modeling, Sonnenthal et al., in review).

3.6. Conclusions

Lithium concentrations vary with depth and mineralogy within the Salton Sea Geothermal Field. The highest Li concentrations for rocks and minerals are found within mudstones and decrease with depths with surface mudstones containing ~ 106 ppm Li, mudstones at 2358 m containing ~ 82 ppm Li, and mudstones from 2745 m containing ~ 34 ppm Li. At depth, chlorite has the highest concentration of Li, with values as high as ~ 580 ppm found at a depth of ~ 2358 m. Chlorites from deeper in State 2-14 have less lithium within them with a maximum measured

concentration of ~104 ppm. While chlorite has been observed to be the primary mineral host of Li at depth, further analysis work on rocks from deeper (hotter) and shallower (cooler) in the Salton Sea Geothermal Field will be undertaken to test whether the mineral hosts of Li change with changes in temperature and determine how whole rock quantities of Li evolve with depth in the Salton Sea Geothermal Field (see Proposed Future Work, below)

Lithium isotopic compositions for the rocks vary at depths less than 1.5 km ($< \sim 300^{\circ}\text{C}$; Sass et al., 1988) but are consistently lighter than the hypersaline geothermal brine they are in contact with at depths greater than 1,500 m in the chlorite-calcite zone and heavier than the hypersaline geothermal brine within the biotite metamorphic zone ($> 2,480$ m depth and $> 325^{\circ}\text{C}$). Much like previous hydrogen and oxygen isotopic work done on Salton Sea Geothermal brines (Williams and McKibben, 1989), the $\delta^7\text{Li}$ composition is narrowly confined ($\delta^7\text{Li}_{\text{avg}} = +4.1 \pm 0.3$ ‰), indicating a well-mixed brine reservoir.

3.7 Proposed Future Work

This study has revealed a temperature dependence for the incorporation of Li into the crystal structure of chlorite in the Salton Sea Geothermal Field, with a change in Li behavior taking place around 325°C , the transition temperature between the calcite-chlorite and biotite metamorphic zones (Cho et al., 1988; Sass et al., 1988). The clinopyroxene metamorphic zone lies below the biotite metamorphic zone, at even higher temperatures ($> 350^{\circ}\text{C}$; Cho et al., 1988; Sass et al., 1988) but was not sampled during this study. To fully constrain the temperature-dependent behavior of Li within the rocks in the Salton Sea Geothermal Field, rocks from greater depths and temperatures should be sampled to test whether Li partitioning in chlorite changes at higher

temperatures and pressure and/or if there are other mineral hosts of Li in these conditions. Similarly, the mineralogic hosts of Li at shallower depths and lower temperatures have not been identified in this study. What are the Li-bearing minerals prior to the formation of chlorite?

Additionally, contained within the dataset gathered through the study of Li but unexamined to date are determinations for the abundance of other major and trace elements, including USGS-designated critical minerals Co, Ni, Zn, Mn, and the REEs. As is the case for Li described in this study, this unexplored dataset will provide currently unknown but first order constraints on the mineralogical hosts of these elements, as well as describe the behaviors of these elements during brine-rock interactions in the Salton Sea Geothermal Field. Continued examination of the existing data set can answer the question: what are the primary mineralogical hosts of Mn, Zn, Co, Ni, and the REEs in the Salton Sea Geothermal Field source rocks, and what constraints do the observed mineralogical reaction textures place on the nature of Mn, Zn, Co, Ni, and REE mobility during brine-rock reaction at elevated temperatures and depth?

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CHAPTER THREE APPENDIX

DISTRIBUTION AND ISOTOPIC COMPOSITION OF LI IN THE SALTON SEA GEOTHERMAL FIELD

J. Humphreys, M. Brounce, M. A. McKibben, P. Dobson, N. Planavsky, B. Kalderon-Asael

3A.1. Sample Photographs

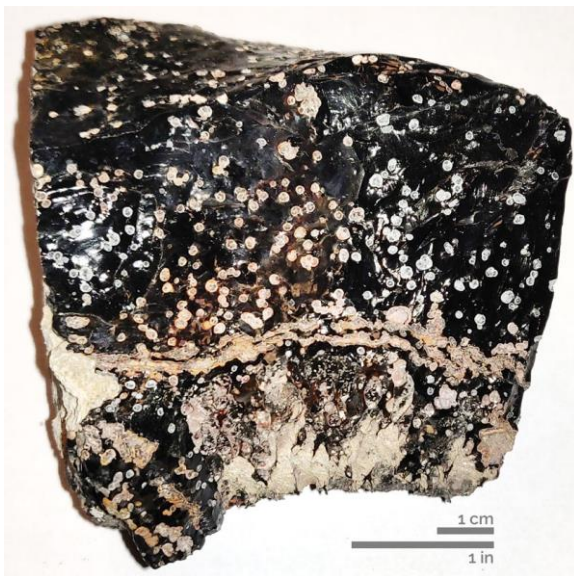


Fig. 3A.1.1. Spherulitic Obsidian from Obsidian Butte (Fig. 1.C.).



Fig. 3A.1.2.A. Glassy rhyolite from Rock Hill (Fig. 1.C.).



Fig. 3A.1.2.B. Glassy rhyolite from Rock Hill (Fig. 1.C.).



Fig. 3A.1.3. Mudstone from the Durmid Hills (Fig. 1.B.).



Fig. 3A.1.4.A. Interbedded gypsum and mudstone from the Durmid Hills (Fig. 1.B.).



Fig. 3A.1.4.B. Interbedded gypsum and mudstone from the Durmid Hills (Fig. 1.B.).

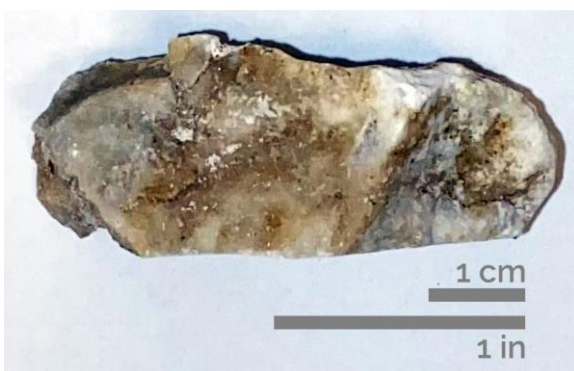


Fig. 3A.1.5. Cryptocrystalline gypsum from the Durmid Hills (Fig. 1.B.).



Fig. 3A.1.6. Sandstone from the Durmid Hills (Fig. 1.B.).



Fig. 3A.1.7. Monomineralic epidote from 1866 m (6122 ft) depth in the State 2-14 drill core (Fig. 1.C.).

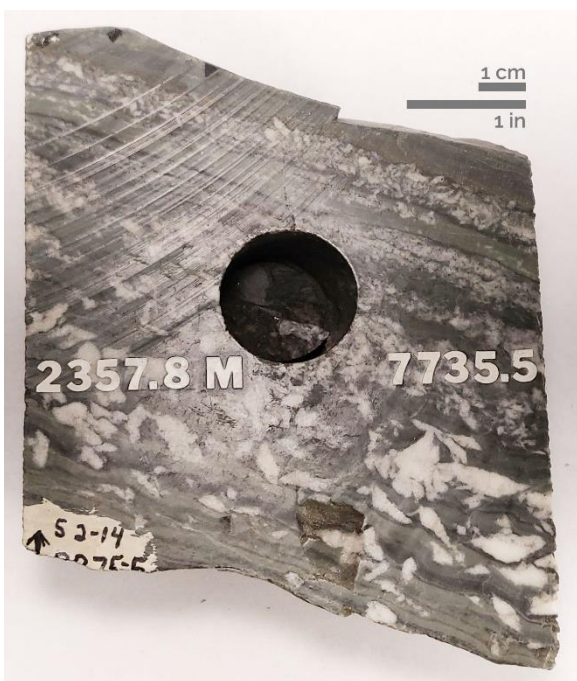


Fig. 3A.1.8. Interbedded mudstone and anhydrite from 2357.8 m (7735.5 ft) depth in the State 2-14 drill core (Fig. 1.C.).



Fig. 3A.1.9. Epidotized mudstone from 2485 m (8153 ft) depth in the State 2-14 drill core (Fig. 1.C.).



Fig. 3A.1.10. Interbedded mudstone and anhydrite from 2744.6 m (9004.6 ft) depth in the State 2-14 drill core (Fig. 1.C.).



Fig. 3A.1.11. Epidotized mudstone from 2818.9 m (9248.4 ft) depth in the State 2-14 drill core (Fig. 1.C.).



Fig. 3A.1.12. Brecciated diabase and mudstone from 2881.99 m (9455 ft) depth in the State 2-14 drill core (Fig. 1.C.).



Fig. 3A.1.13. Interbedded anhydrite and mudstone from the Magmamax 2 drill core (Fig. 1.C.).



Fig. 3A.1.14. Epidotized metasedimentary mudstone from 1293.5 m (4243.7 ft) depth in the State 2-14 drill core (Fig. 1.C.).



Fig. 3A.1.15. Metasedimentary mudstone with hematite veins from 1426.8 m (4681 ft) depth in the State 2-14 drill core (Fig. 1.C.).

3A.2. Internship Activity Report

J. Humphreys, L. English, M. Brounce, M. A. McKibben, P. Dobson, J. Calzada, A. Ramirez, J. Uribe, A. Valdes, B. Wenzel

3A.2.1. Museum Curation Interns

Andrea Valdes and Jesus Uribe worked as museum curation interns. Both interns worked on curating specimens collected from cores in the Salton Sea area for the purpose of scientific research in the 1980s. Curation involved labeling specimens with unique specimen numbers (Fig. 3A.2.1.), adding specimen data (specimen number, specimen description, locality, storage location, etc.) into the museum database (Fig. 3A.2.2.), and researching locality data to ensure its



Figure 3A.2.1. A selection of specimens curated over the course of this project.

completeness and accuracy. The museum database these specimens have been added to is available upon request to any qualified researchers, with plans to make all non-sensitive data freely available online in the future. The work completed by the interns ensures that any future scientists who wish to revisit these specimens for any future studies will be able to easily locate and access them with confidence that the information associated with them is accurate. Uribe additionally volunteered to work with other members of the Lithium Valley Quantification project on community outreach.

The image shows a web-based database interface titled "Rock Collection Database". It has a dark grey background with white text. At the top, there are five tabs: "Specimen", "Stratigraphy", "Provenance", "Storage", and "Misc". The "Specimen" tab is currently selected. Below the tabs, there are several input fields for specimen data. On the left, there are fields for Latitude (33.208145 N), Longitude (-115.580685 W), Uncertainty, Elevation, Datum (NAD83), Country (USA), Province/State (California), County (Imperial), Quad, and Locality Description (State 2-14 Borehole (API 02590632), Southeastern edge of Salton Sea, Imperial County, CA. Sec. 14, T11S, R13E, Depth: 1985.0 ft). On the right, there are fields for Collected by, Collection Date (1980s), Purchased from, Purchase date, Donated by, and Donation date. Further right, there are fields for UCR number, F number, T number, D number, P number, Tunnell number (SSGS-1), and Other numbers.

Figure 3A.2.2. Example of a database entry for a State 2-14 specimen.

3A.2.2. Mineralogic Investigation Interns

HannahRose Hoover and Brianna Wenzel worked as Mineralogic Investigation Interns starting in the Summer of 2022. Javier Calzada, Grace Huseman, and Alejandro Ramirez joined the intern team in the Fall of 2022 to expand upon the research-related activities that the interns were undertaking. All interns investigated Li contents in rock samples from the Salton Sea Geothermal Field using a variety of methods. All students worked on sample preparation and documentation.



Figure 3A.2.3. Photograph of a State 2-14 sample which was taken by an intern who worked on this study.

This work involved photo-documenting samples (Fig. 3A.2.3. & Fig. 3A.1.15.), recording laboratory notes as they worked on the samples (Fig. 3A.2.4.), picking and sorting samples under a microscope, and powdering rock samples for whole rock analyses using an alumina crucible. Additionally, three of the interns analyzed thin sections of rock samples using a Scanning Electron Microscope (SEM; Fig. 3A.2.4.) and Laser Ablation Inductively Coupled Mass Spectrometer (LA-ICP-MS; Fig. 3A.2.4.). Through these tools, the interns investigated Li content variations of textural and mineralogic differences within their thin sections. Calzada investigated mineral

abundances in the thin sections using MATLAB and the SEM backscatter electron maps that were made over the course of this study to extrapolate possible whole rock Li concentrations of the host rocks by pairing the relative abundance of Li-bearing minerals in the rocks with known Li-concentrations for those minerals from the same rocks that were measured in this study via LA-ICP-MS. When examining the sample from ~2358 m depth in the State 2-14 well, the intern found

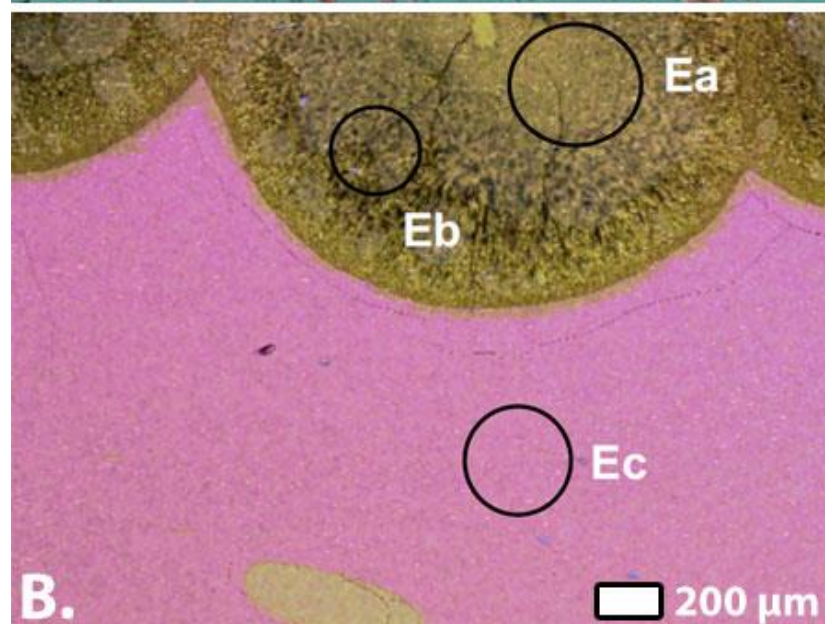
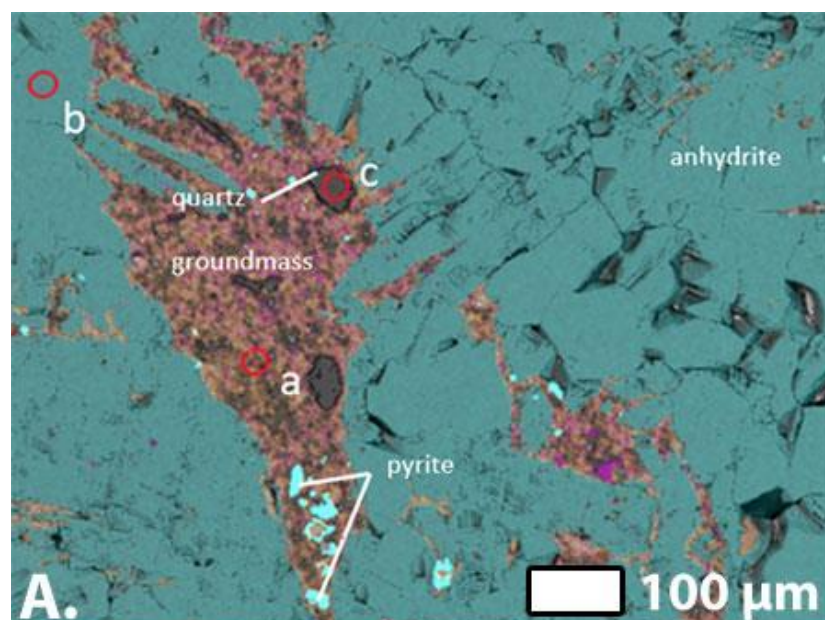


Figure 3A.2.4. Example notes made of some of the samples that the interns worked on in this study for LA-ICP-MS investigation. Through the course of this study, interns who chose to work on thin sections were given a thin section to study. Interns chose the regions to analyze, created backscatter electron maps of those regions, and then specific spots to analyze further via LA-ICP-MS. (A) Back Scatter Electron map of metasedimentary anhydrite and mudstone from ~2358 m depth. Regions relatively high in Mg concentrations are yellow. Regions relatively high in Al concentrations are pink. Regions relatively high in S concentrations are blue. Minerals identified by the intern are labeled on the map. Spots analyzed via LA-ICP-MS are circled in red and annotated with lowercase letters. (B) Back Scatter Electron map of spherulitic obsidian from Obsidian Butte, a surface sample. Regions relatively high in Na concentrations are yellow. Regions relatively high in K concentrations are pink. Regions relatively high in Ca concentrations are blue. Spots analyzed via LA-ICP-MS are circled in black and annotated with both uppercase and lowercase letters.

an average chlorite abundance of ~30% for the regions analyzed. Pairing this with the average observed concentration for Li at this depth being ~410 ppm, the whole rock estimate for the sample from ~2358 m is 125 ppm Li. This value is higher than the average measured whole rock Li concentration in this rock sample, ~82 ppm. Given that the backscatter maps made of this sample for this study were biased in favor of sampling the mudstone heavy regions rather than the anhydrite heavy regions (where the Li concentration is nearly 0 ppm), it is expected that the estimated whole rock Li concentration would be higher than the measured value.

3A.2.3. About the Interns

This work supported researchers at the University of California Riverside, a federally designated HSI- and AANAPISI- serving institution that has been ranked #1 nationally in social mobility by US News and World Report for four consecutive years and for the success with which Pell grant recipients are graduated on 4-year times scales. This specific research was accomplished with the help of 5 undergraduate students from a variety of backgrounds and identities which include students who are the first generation to attend college, non-traditional (i.e., undergraduates

who are older and thus more likely to have increased responsibilities beyond the classroom than the typical undergraduate student), Latina, Chicano, Mexican American, LGBTQ+, second generation immigrants, and from lower socio-economic backgrounds. Several interns have reported that the skills acquired through the course of this internship have been useful in other research projects they have worked on or plan to work on. Another intern reported that working on this project helped ground the theory that they were learning. The interns were actively mentored by two Ph.D. holders and one Ph.D. candidate, one of whom is a woman and two of whom are nonbinary. Following their research experiences, 4 of the interns graduated from their undergraduate programs. Two of the interns are continuing to graduate school and the remaining two interns are either in the process of applying or are considering applying to graduate school in disciplines that are in or adjacent to the earth and environmental sciences.

CONCLUSION

While each of these chapters broadly relates to volcanic and diffusive processes to varying degrees, they each have something new and different to contribute to the geologic history of California. The first chapter of this dissertation investigates how olivine hosted melt inclusions from Basalt of Round Valley Butte underwent diffusive equilibration of H_2O and $f\text{O}_2$ with an ambient, degassed magma prior to eruption. The oxidation state of iron recorded in these entrapped magmas equilibrated with ambient magmatic conditions in less than a day while the H_2O content took up to 80 hours to equilibrate. Since iron in these entrapped magmas became less oxidized through this diffusion process, the difference in oxidation state between arc basalts and mid-ocean ridge basalts is larger than initially believed. The second chapter of this dissertation investigates how post-entrapment processes, like those in chapter one, can be corrected for, to investigate the conditions of melting that produce magmas. By correcting for these post entrapment processes, a minimum geochemical estimate for the depth of the crust-mantle boundary beneath Pisgah Crater was placed at 15 – 20 km while primary melt geochemical estimates indicate that the lithosphere-asthenosphere boundary is at ~80 km depth and 1340°C. Trace element concentrations and modeled primary melt compositions (including volatile contents) indicate that these magmas were formed from low degrees of melting of mantle source with somewhat elevated H_2O and CO_2 contents. The presence of CO_2 in the asthenosphere is likely the driver of volcanism in the Mojave Desert and greater Basin and Range Province.

The third chapter of this dissertation shifted focus to other systems that are impacted by the presence of a magmatic heat source, namely geothermal heat and associated hydrothermal

alteration through the investigation of Li in the Salton Sea Geothermal Field. The highest Li concentrations for rocks and minerals within the Salton Sea Geothermal Field are found within mudstones and decrease with depth. At depth, chlorite has the highest concentration of Li of the minerals investigated in the State 2-14 scientific drill core and the concentration of Li is highest in chlorites from the calcite-chlorite metamorphic zone compared to chlorites in the hotter and deeper biotite metamorphic zone. While geothermal brines have a consistent Li isotopic signature despite the temperature and depth sampled, the Li isotopic signature of the rocks varies with depth and temperature. At depths >1.5 km, in the chlorite-calcite metamorphic zone the rocks are consistently isotopically lighter than the geothermal brine; however, rocks in the biotite metamorphic zone are isotopically heavier than the geothermal brine. Additionally, the incorporation of Li in chlorite changes between these two different metamorphic zones. Taken together, these variations indicate that the behavior of Li at depth in the Salton Sea Geothermal Field is related to temperature. While Chlorite has been observed to be the primary mineral host of Li at depth, further analysis of rocks from deeper (hotter) and shallower (cooler) in the Salton Sea Geothermal Field will be undertaken to test whether the mineral hosts of Li change with changes in temperature to determine how whole rock quantities of Li evolve with depth in the Salton Sea Geothermal Field.

GENERAL APPENDIX

CALIFORNIA PETROLOGY - FROM BASALTIC VOLCANOES TO LITHIUM-BEARING MINERALS

J. Humphreys

GA.1. About

As a non-traditional geoscience student/researcher, I have had a multitude of experiences and gained an assortment of skills beyond those that are taught in the sciences. My first degree was in visual art and my first jobs were in marketing and communication as well as publication. Through these experiences I learned how to tell stories visually, though truth be told I likely gravitated towards these experiences because my brain is more drawn towards the visual rather than the written. I have continued to practice the skills that I gained from my first foray into adulthood as I have gained experience with teaching and research. The below sections are a curated selection of my not-strictly-academic contributions. Many of them are directly related to my first skills set, but others are extensions of research efforts that I hope will aid whoever comes after me.

GA.2. Illustrations and Artwork

The following illustrations and artwork are a curated selection of pieces I made while I was a graduate student at UCR. These illustrations were created for a variety of purposes related to my work at UCR that ranged from conferences to scientific talks that I gave.

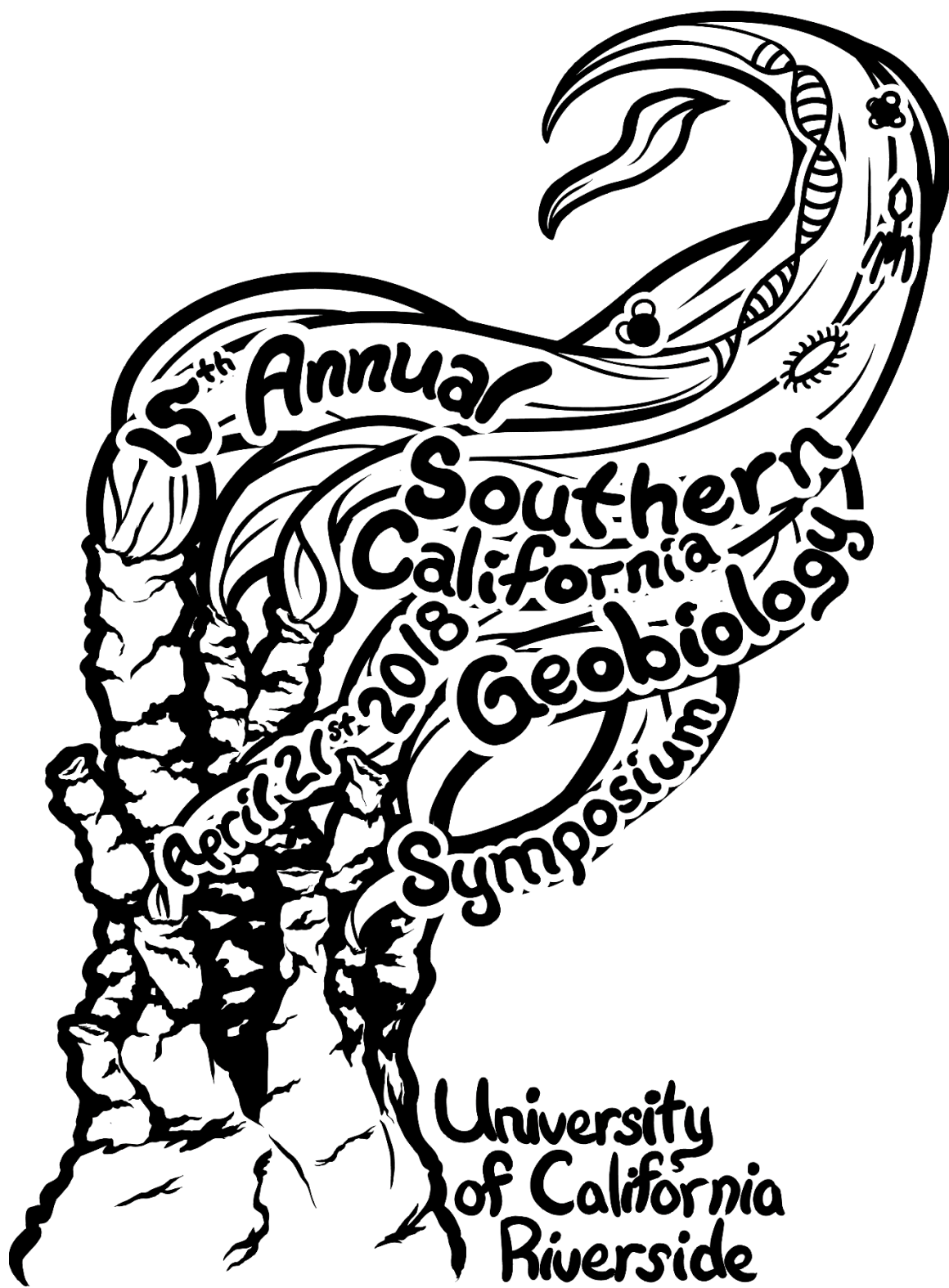


Figure GA.2.1. Pint glass design for the 2018 Southern California Geobiology Symposium.

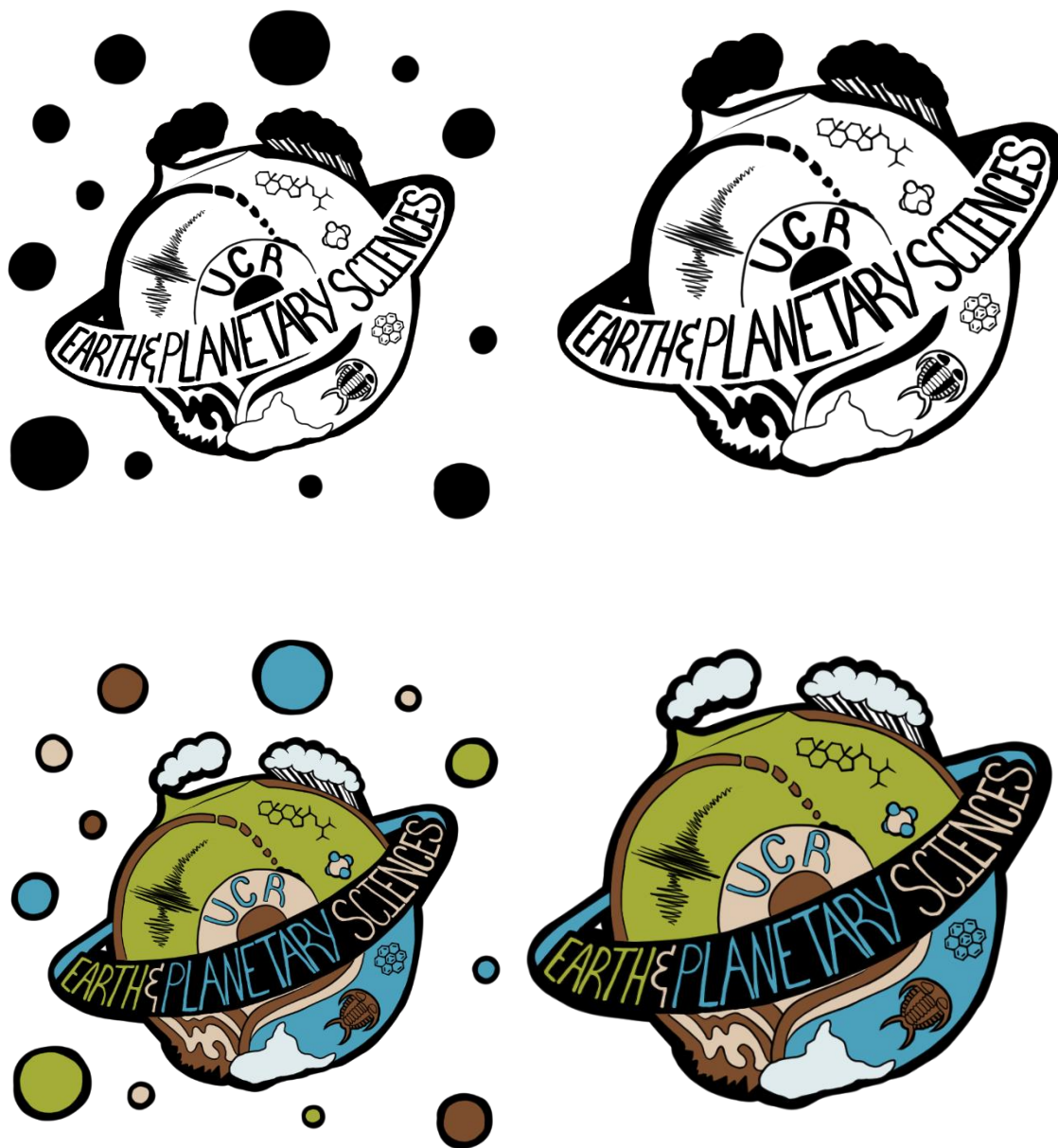


Figure GA.2.2. Re-designed University of California Riverside Earth and Planetary Sciences Department logo. Versions pictured here are black and white as well as color along with including planets versus only the central planet.

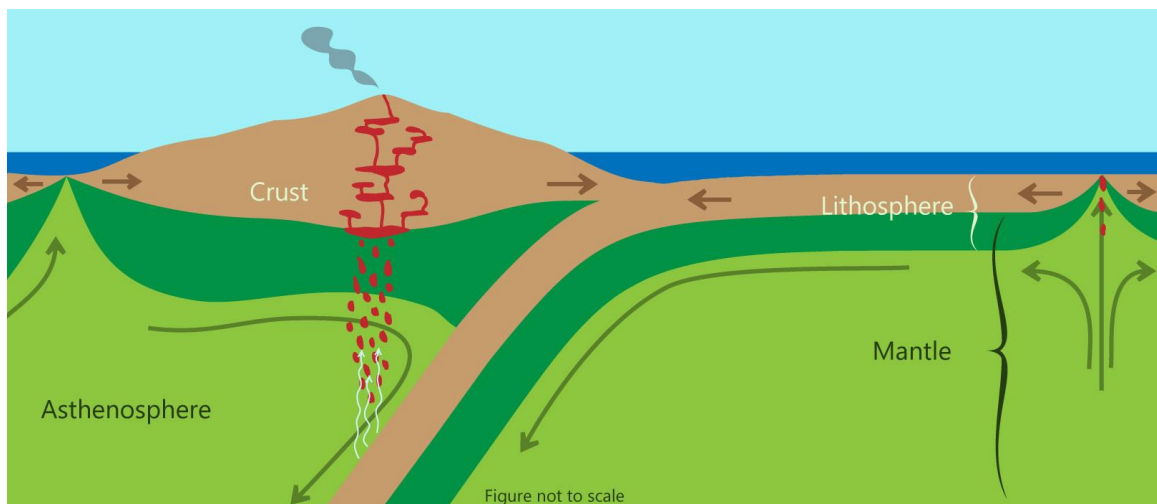


Figure GA.2.3. Scientific illustration of a back arc spreading center, subduction zone, and mid-ocean ridge spreading center with the crust, mantle, lithosphere, and asthenosphere labeled. Arrows denote relative plate motions. White squiggly arrows represent oxidized fluids leaving the subducting plate. Melt generation and migration in the subduction zone and mid-ocean ridge is represented in red.

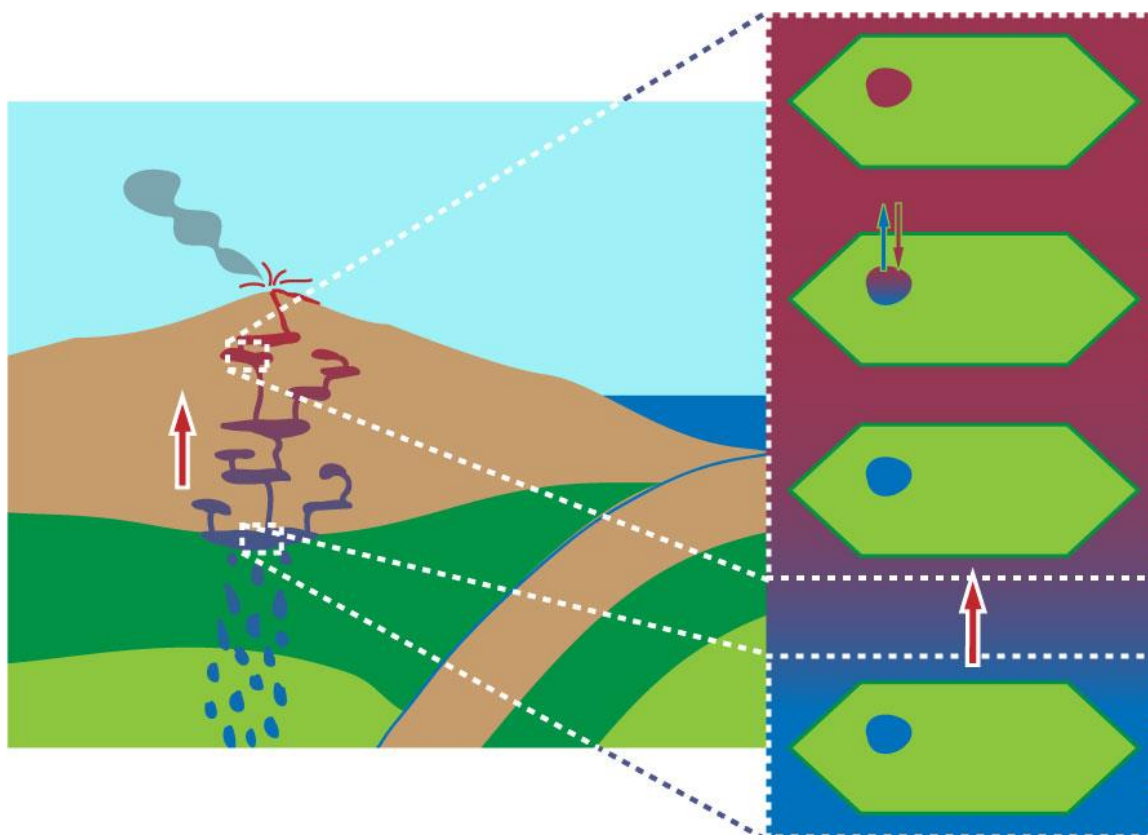


Figure GA.2.4. Scientific illustration of the diffusive process. Melt is entrapped in a melt inclusion at one depth before being transferred to another, shallower, depth (movement direction is denoted by the large, red arrow). Because of the change in pressure with change in depth (shallower depth = lower pressure), volatiles and fO_2 of the external melt change (blue represents the chemical conditions at the depth of entrapment and maroon represents the chemical conditions at the new shallower depth). Diffusion through the olivine host brings the H_2O and fO_2 of the entrapped melt back into equilibrium with the ambient magmatic H_2O and fO_2 conditions at the shallower depth.

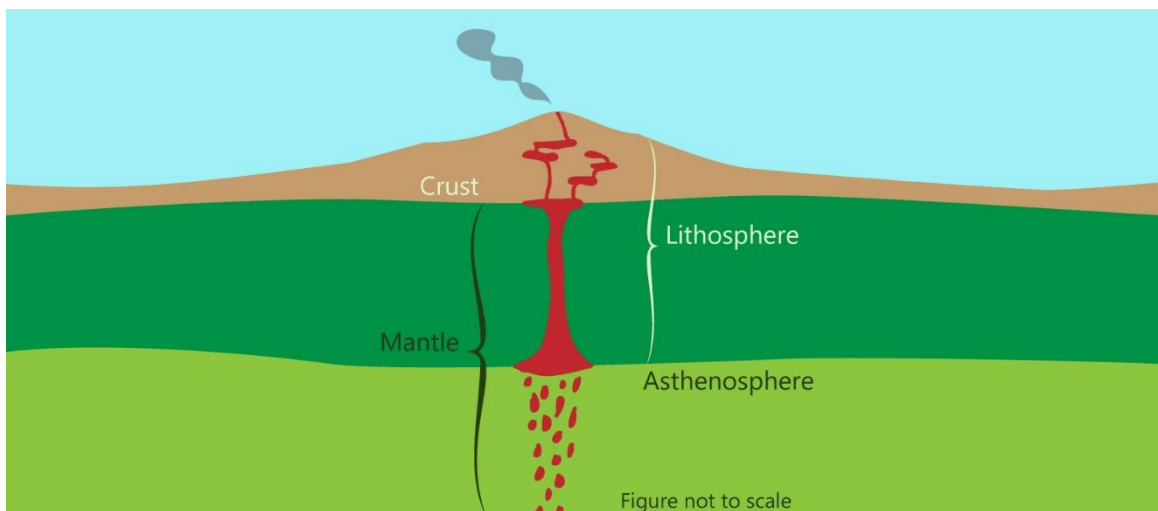


Figure GA.2.5. Scientific illustration of a volcanic plumbing system not related to subduction. Melting initiates at some depth in the asthenosphere and collects around the lithosphere-asthenosphere boundary. This magma migrates up through the lithosphere and crust where it may eventually erupt.



Figure GA.2.6. Scientific illustration of geothermal energy production. Energy is produced in this system by extracting hot, geothermal brines and allowing them to cool to a point that steam is generated. The steam moves a turbine which generates electricity. The brine is further cooled before it is reinjected back into the geothermal reservoir where it heats back up and is re-extracted.



Figure GA.2.7. Same illustration as in GA.2.6. with a potential pathway for Li extraction and re-incorporation in the Salton Sea Geothermal Field (Ch. 3, this work). One of the research questions related to Ch. 3. is if Li is extracted from the geothermal brine, will the Li-poor re-injected brine scavenge Li from the source rock prior to re-extraction.

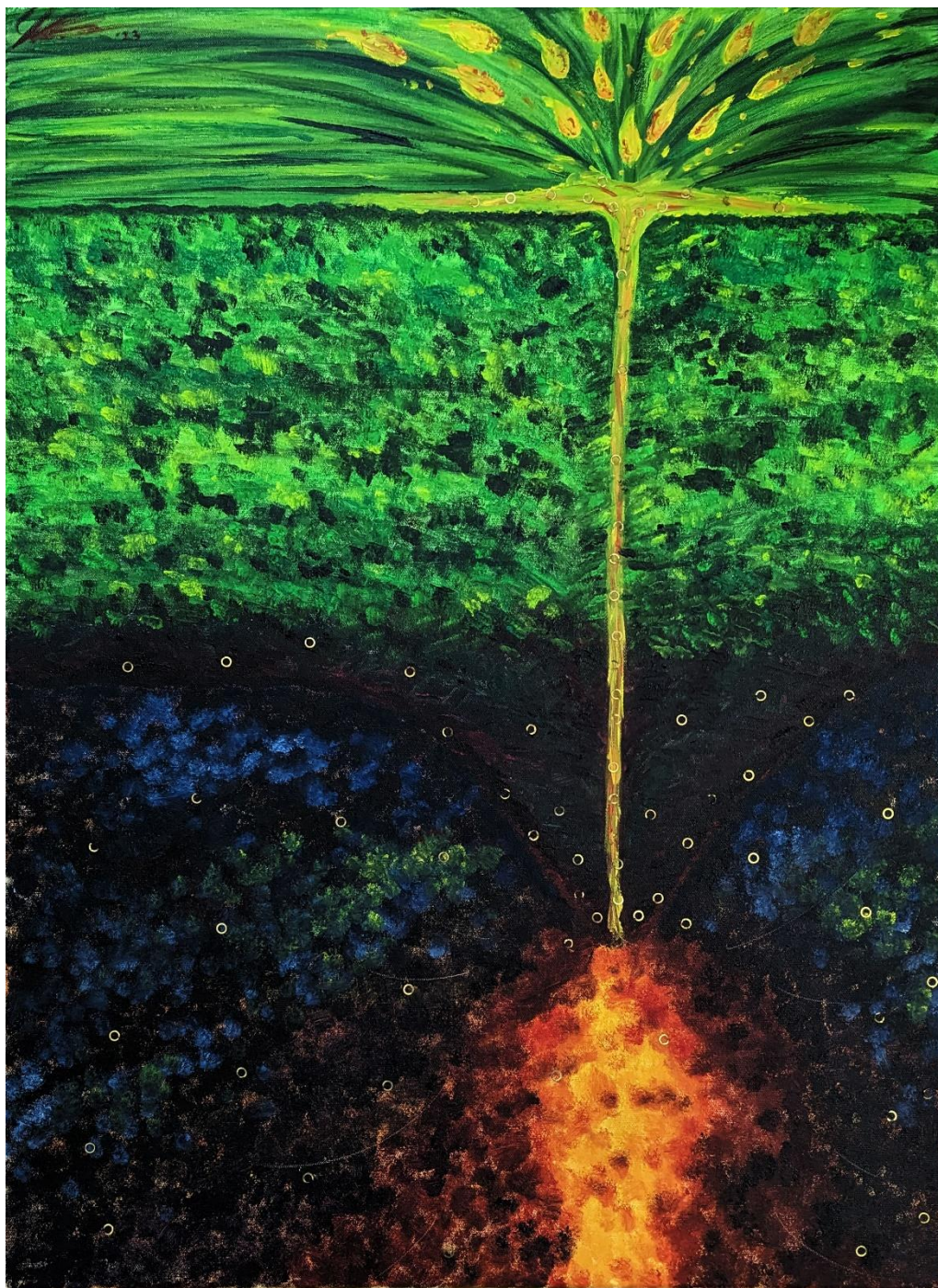


Figure GA.2.8. As Above. Oil and brass on canvas. First of three paintings created as part of Artistic Expressions of Original Research, a 10-week course and gallery exhibition run by SciComm at UCR.



Figure GA.2.9. Let It Flow. Oil on canvas. Second of three paintings created as part of Artistic Expressions of Original Research, a 10-week course and gallery exhibition run by SciComm at UCR.

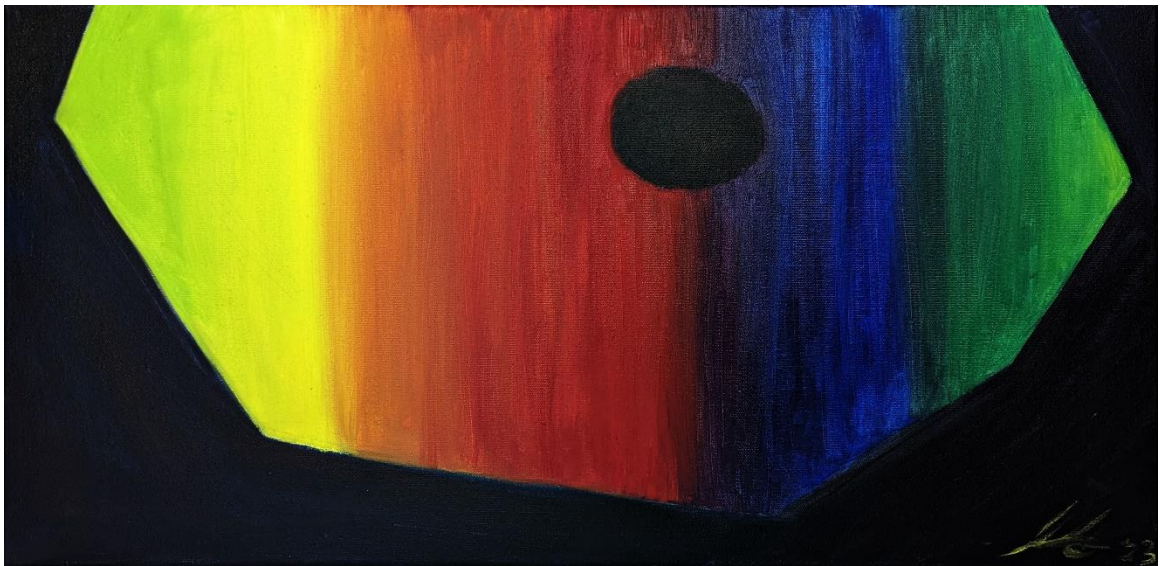


Figure GA.2.10. Wedged. Oil on Canvas. Third of three paintings created as part of Artistic Expressions of Original Research, a 10-week course and gallery exhibition run by SciComm at UCR.

GA.3. Teaching Laboratory Updates

I was the teaching assistant for Geo XXX: Mineralogy and Geo XXX: Igneous and Metamorphic Petrology for five years. During that time, I completely overhauled some of the labs using a combination of student feedback and knowledge gained from the University Teaching Certificate Program at UCR. Below are both the completely overhauled labs that I made as labs which I updated but did not completely overhaul.

GA.3.1. Mineralogy Lab Updates

The following are the long format labs from Mineralogy. I removed the sections that I did not write myself and note where I made modifications rather than fully rewriting a section.

For this appendix, all figures have designations reflecting their position in the General Appendix. In the assignment, these designations do not exist (i.e., a figure captioned “Figure GA.3.1.2.1. Example (<https://skfb.ly/6TBoV>)” in the appendix is captioned “Example (<https://skfb.ly/6TBoV>)” in the assignment).

GA.3.1.1 Lab #1: Introduction to Mineral Identification Part 1

Spend some time familiarizing yourself with the minerals of the hardness set. Practice testing the hardness with your fingernail (for very soft minerals) and a nail or small pocketknife blade. These are the tools you will usually have in the field.

A. Mineral Identification Application

Please form groups of 3-5 students. You will be provided with 15 minerals. Each group will be provided with overlapping but different sets of minerals (i.e; some minerals in your set will be

different from some of the minerals in another group's set). Your task will be to split your minerals into 3 subgroups based on the properties that you are testing. ***You can use any property other than color to form your mineral subgroups.***

Use the following questions to guide your group formation:

- How are these minerals similar to one another?
- How are these mineral different from one another?
- Which properties (not color) are you using to classify your minerals into groups?

B. Mineral Comparison (60pts/5pts per each box)

Answer the following questions based on the groups that you made:

	Group A	Group B	Group C
Which minerals (specimen number) are in each group?			
How are the minerals in this group of minerals similar to one another?			
How are the minerals in this group of minerals different from one another			
Which properties (not color) are you using to classify your minerals into groups?			

GA.3.1.2 Lab #2: Mineralogy and Crystal Symmetry

Thinking in three dimensions is a critical skill necessary in not only mineralogy but many other fields in the Earth and Planetary Sciences. The first step in learning to use symmetry in mineral identification is to recognize orderly external repetition of crystal faces in models idealized “crystals”. Since textbook mineral descriptions usually start by giving the symmetry of the mineral, learning to deduce the macroscopic symmetry of a mineral is an important skill.

A. Definitions

For each question you will define the crystal symmetry term in your own words and then complete the requested actions and questions related to each term.

1. Equivalent Faces –

On the following crystal diagrams, label the equivalent faces using descending letters of the alphabet (i.e., start with “A” then “B” then “C” ...etc.). Equivalent faces to face “A” will be written as “A1, A2, A3, ..., An” and the same will be done for each successive letter of the alphabet.

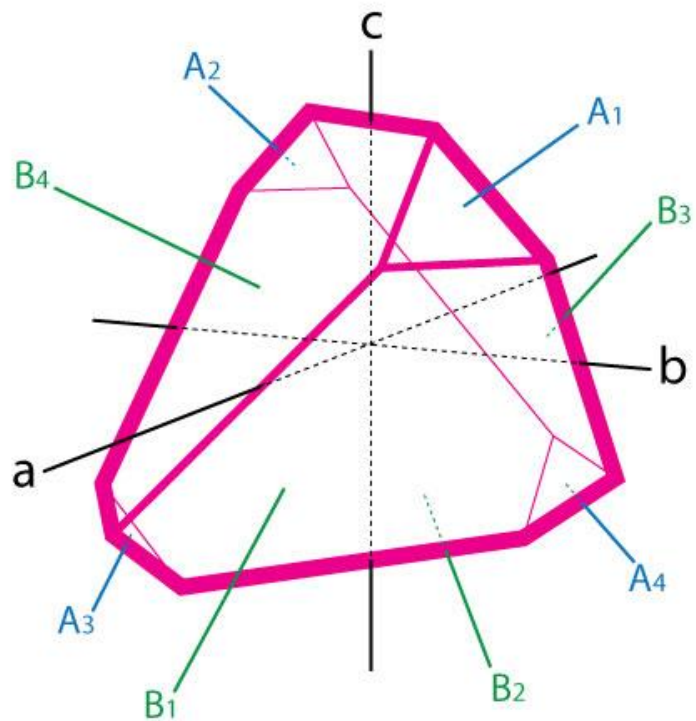


Figure GA.3.1.2.2. Example (<https://skfb.ly/6TBoV>)

Crystals:

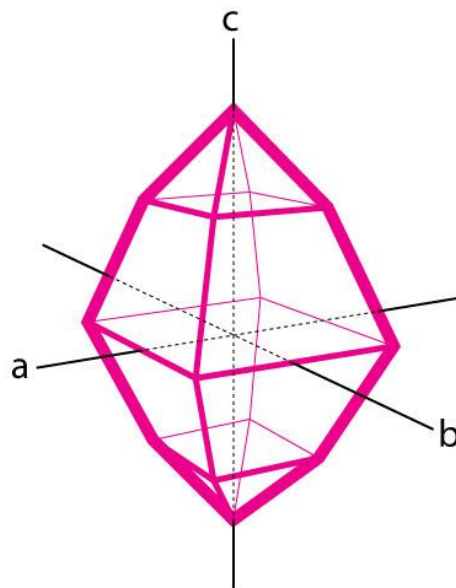


Figure GA.3.1.2.1. Crystal A (Sulfur - <https://skfb.ly/6UsFS>)

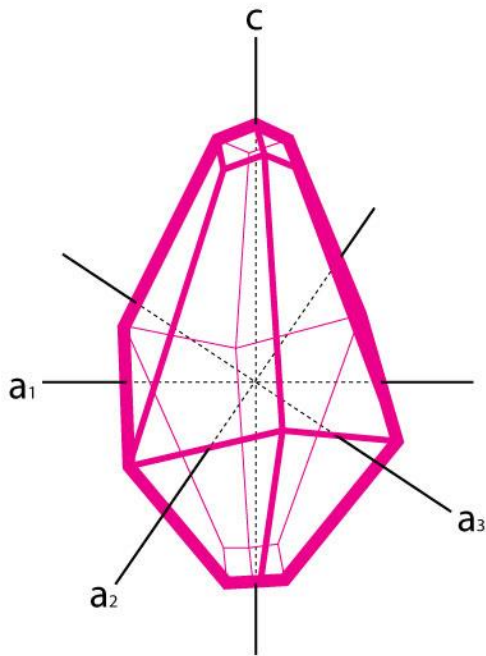


Figure GA.3.1.2.3. Crystal B (Calcite - <https://skfb.ly/6RwXQ>)

2. Rotational Symmetry –

What are the 4 main types of rotational axes that exist in crystals (ignore the 1-fold rotational axis for this question)?

On the following crystal diagrams, draw and label the rotational axes. Please remember that rotational axes are not necessarily the same as crystallographic axes.

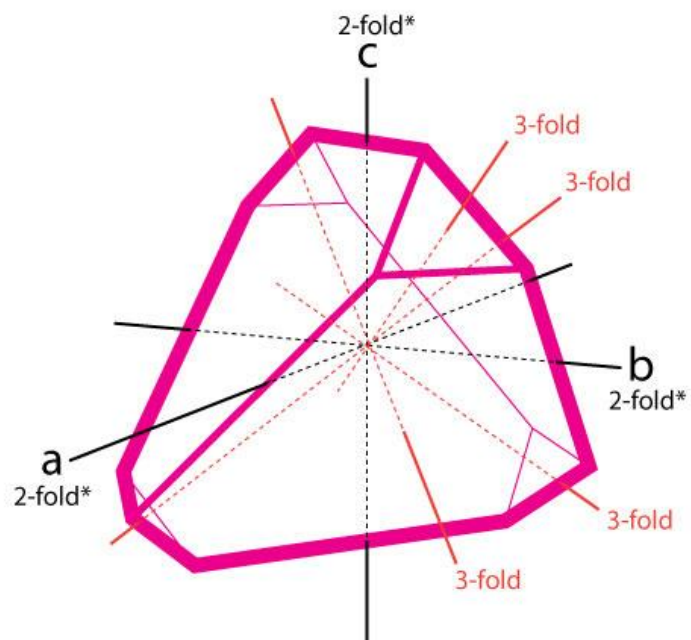


Figure GA.3.1.2.4. Example (<https://skf.ly/6TBoV>)

*Below you will learn about rotoinversion. On first glance, these axes appear to be 2-fold rotational axes. Instead, these axes are 4-fold rotoinversion axes.

Crystals:

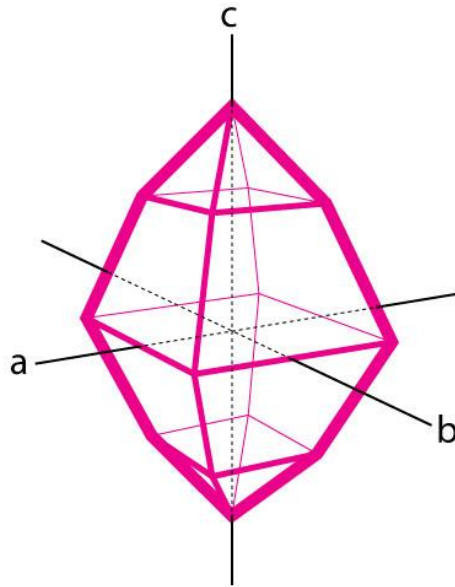


Figure GA.3.1.2.5. Crystal A (Sulfur - <https://skfb.ly/6UsFS>)

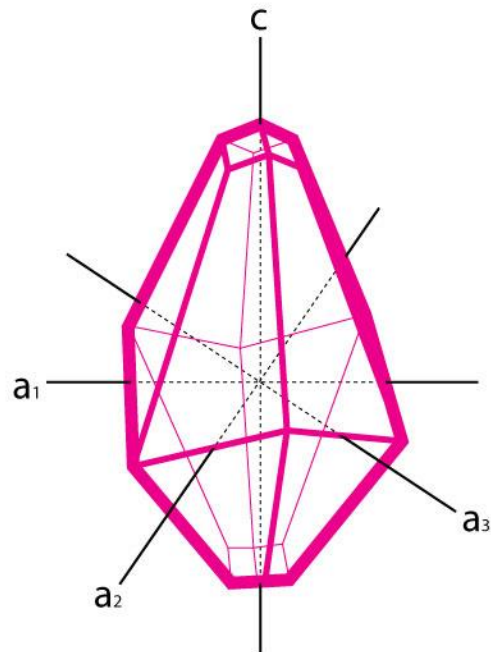


Figure GA.3.1.2.6. Crystal B (Calcite - <https://skfb.ly/6RwXQ>)

3. Mirror Symmetry –

On the following crystal diagrams, draw the mirror planes.

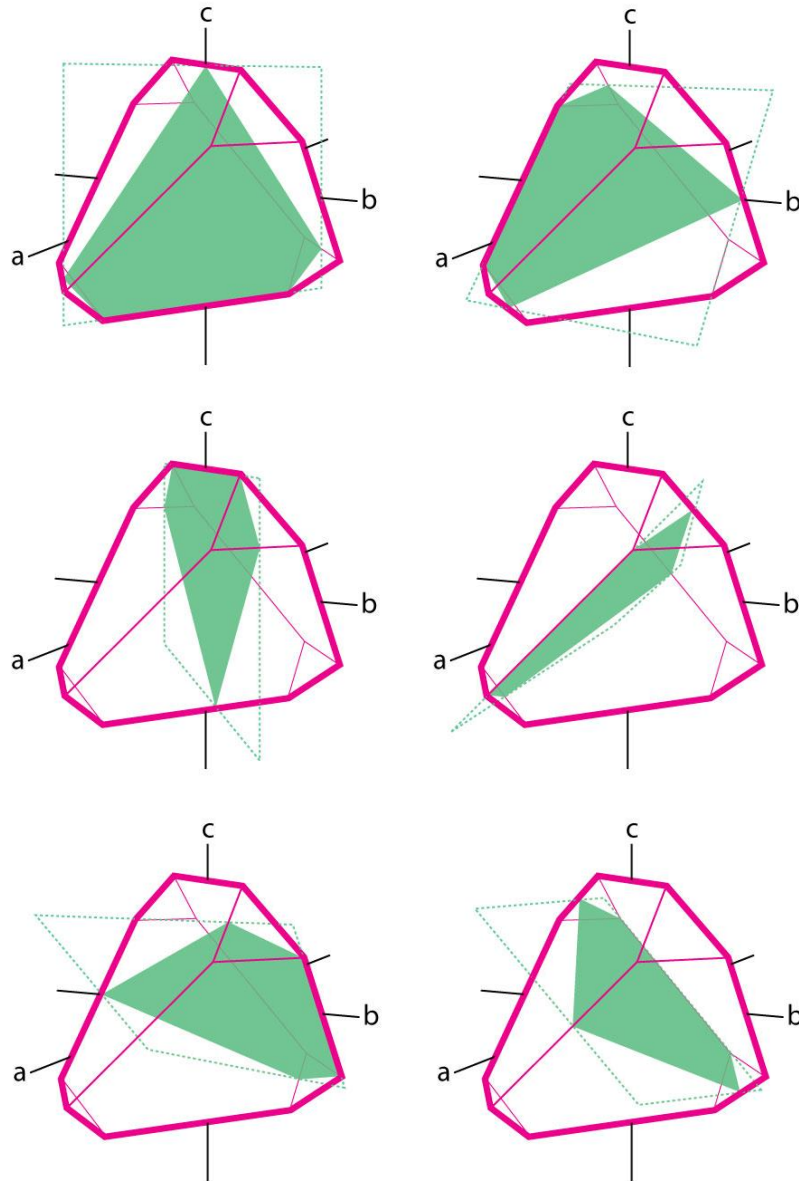


Figure GA.3.1.2.7. Example (<https://skfb.ly/6TBoV>)

Crystals:

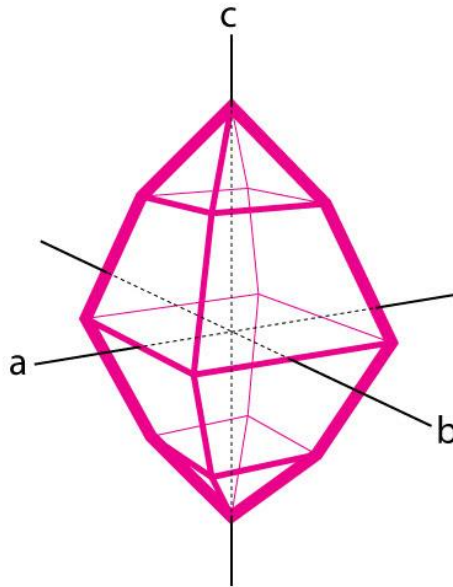


Figure GA.3.1.2.9. Crystal A (Sulfur - <https://skfb.ly/6UsFS>)

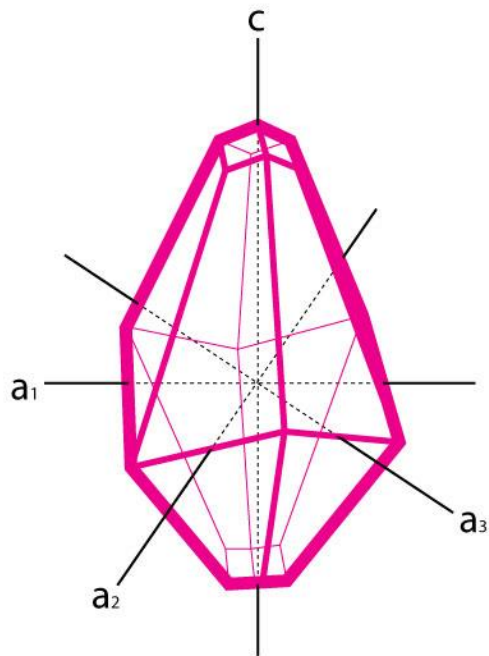
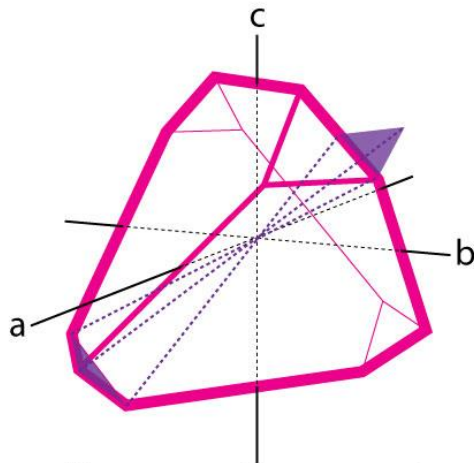


Figure GA.3.1.2.8. Crystal B (Calcite - <https://skfb.ly/6RwXQ>)

4. Center of Symmetry (Inversion) –

On the following crystal diagrams, choose 3 faces on the crystal model and draw out the inversion of this face. Then, indicate whether the crystal has a center of symmetry.



No center of symmetry!

Figure GA.3.1.2.10. Example (<https://skfb.ly/6TBoV>)

Crystals:

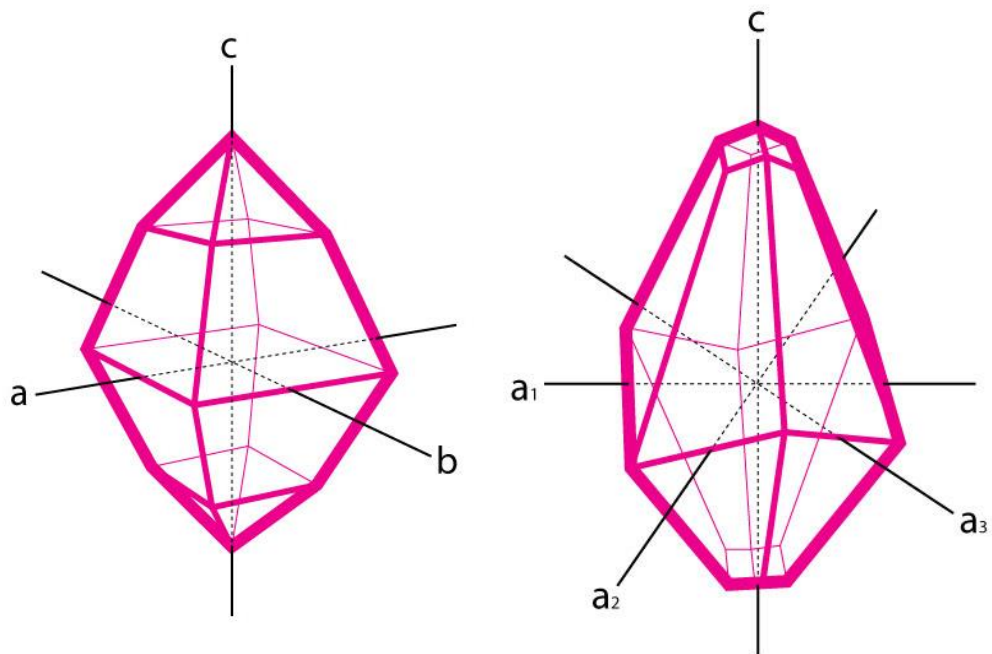


Figure GA.3.1.2.11. Crystal A (Sulfur) and Crystal B (Calcite).

5. Rotoinversion –

Some rotoinversion axes are redundant because they can be reproduced via a combination of the other symmetry elements (hint: you defined these above and a figure in your class textbook has all the answers).

- a. Which rotoinversion axes are redundant and what are they equivalent to?
- b. What rotoinversion axis is unique?

On the following crystal diagrams, draw and label the rotoinversion axes (if present). Hint #1: Look at the other symmetry elements present in these figures, when possible, to help guide you with viewing rotoinversion axes.

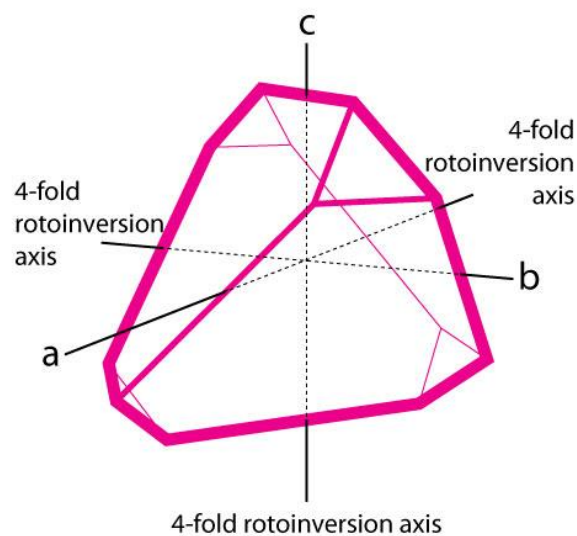


Figure GA.3.1.2.12. Example (<https://skfb.ly/6TBoV>)

Crystals:

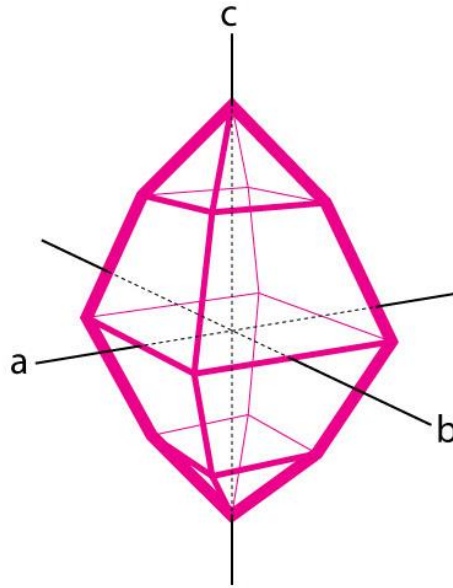


Figure GA.3.1.2.13. Crystal A (Sulfur - <https://skfb.ly/6UsFS>)

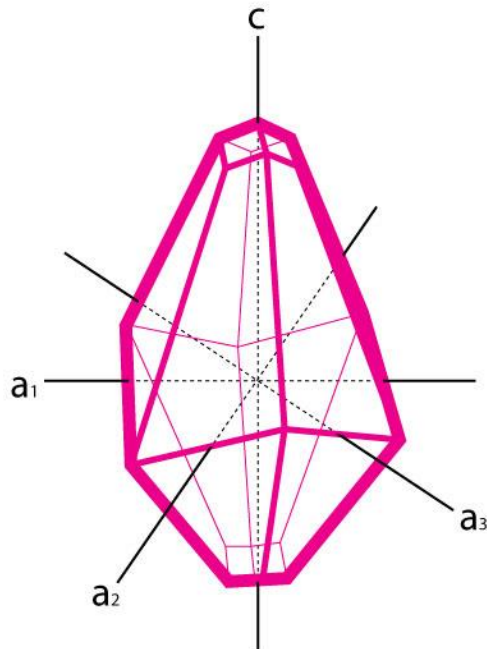


Figure GA.3.1.2.14. Crystal B (Calcite - <https://skfb.ly/6RwXQ>)

GA.3.1.3. Lab #3: More on Crystals

Note: most of this lab has been unaltered from what it was prior to my being a teaching assistant for Mineralogy. The following is my addition to this lab:

Sketch

To the best of your ability, sketch the models you identified in parts A, B, and C from this lab in the space below (and following blank page). Be sure to include your approximation of where the crystallographic axes are. You may also use these sketches as ways to work through the symmetry elements present in each crystal. No extra points will be rewarded for accurate symmetry elements drawn nor will they be deducted for inaccurate symmetry elements drawn on your sketches.

GA.3.1.4. Lab #4: Miller Indices on Crystals

Part I. Introduction to Miller Indices

Label the miller index for each solid orange face. Assume that all planes that are not at 90° to a crystallographic axis and cross that axis at 45°. Please remember that **there is no negative sign** in Miller Indices. For example, instead of writing a Miller index as (1-11), **write it as (1 $\bar{1}$ 1)** for full credit.

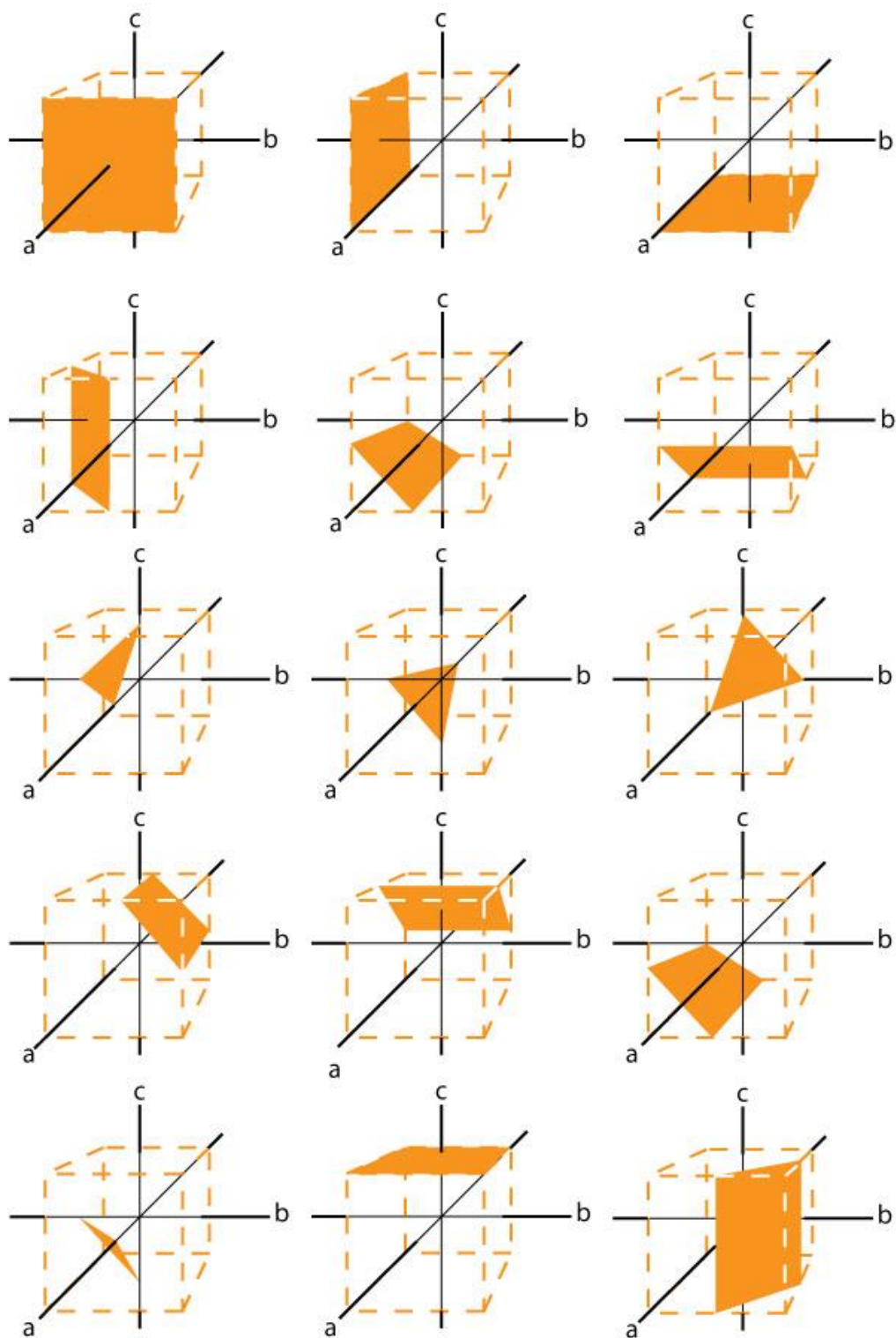


Figure GA.3.1.4.1. Diagrams on which students are to label the miller index of the orange plane. These figures are unlabeled in the assignment.

Part II: Using the crystal diagrams below, label all the faces for each crystal (recall how equivalent faces are labeled) and give the Miller Indices in proper notation. Assume that the faces cut the crystal axes at either 90 or 45 degrees unless otherwise indicated.

Please note that the linked to 3D models contain information about the Miller Indices. These indices are not necessarily accurate for how the axes cross the given models. In other words, **do not trust the information contained on the linked 3D models.**

Anatase

3D model: <https://skfb.ly/6S8KF>

Wooden Block Model #83

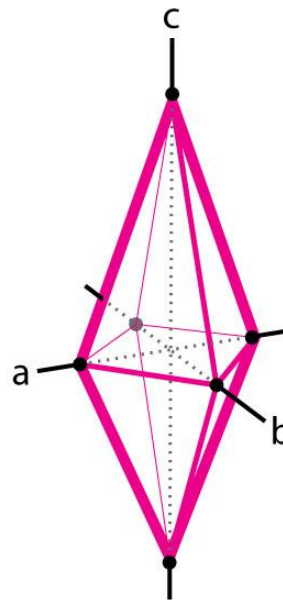


Figure GA.3.1.4.2. This figure does not have a caption in the original assignment.

Brookite

3D model: <https://skfb.ly/6TBoI>

Wooden Block Model #66

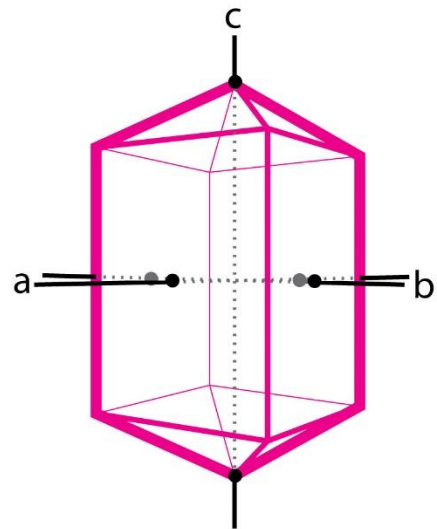


Figure GA.3.1.4.3. This figure does not have a caption in the original assignment.

Diamond

3D model: <https://skfb.ly/6TDuq>

Wooden Block Model #2

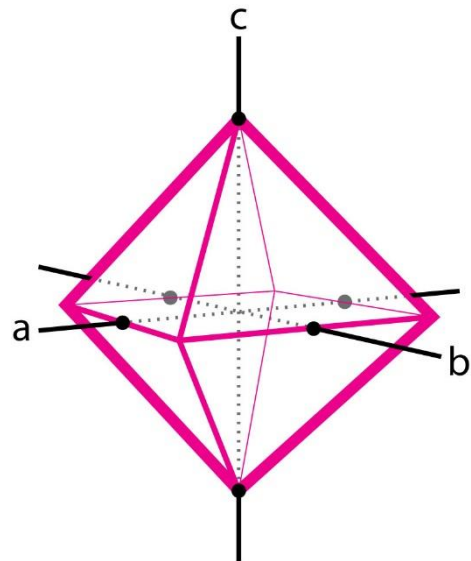


Figure GA.3.1.4.4. This figure does not have a caption in the original assignment.

Forsterite (Olivine)

3D model: <https://skfb.ly/6TDIA>

Plastic Block Models

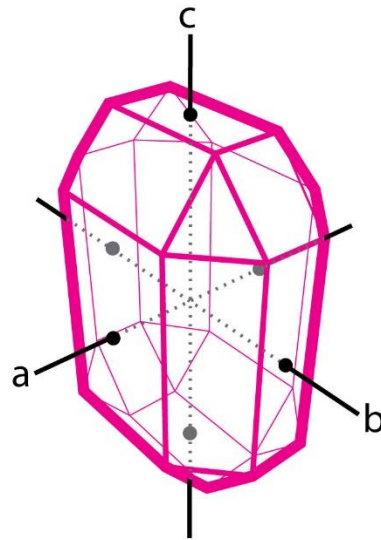


Figure GA.3.1.4.5. This figure does not have a caption in the original assignment.

Part III: Identify the symmetry content and crystal system for each crystal in the above section.

	Anatase	Brookite
Center of Symmetry/Inversion? (Y/N)		
Rotational Axes (number & kind)		
# of Mirror Planes		
Symmetry Content		
Crystal System		

	Diamond	Forsterite
Center of Symmetry/Inversion? (Y/N)		
Rotational Axes (number & kind)		
# of Mirror Planes		
Symmetry Content		
Crystal System		

GA.3.2. Petrology Lab Updates

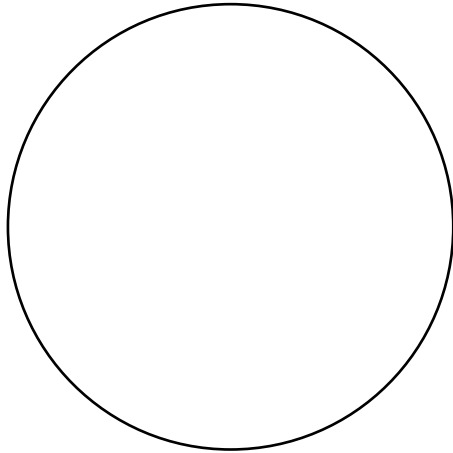
Note: The petrology labs have generally been reworked into a different format from what they were previously. For example, labs were created to introduce igneous and metamorphic rock related vocabulary to the students instead of giving them a sheet of paper with all of the vocabulary they needed to know already defined on it.

The following is an example of how I reworked the rock identification section of the petrology labs to make the use of descriptive vocabulary less intimidating for the student:

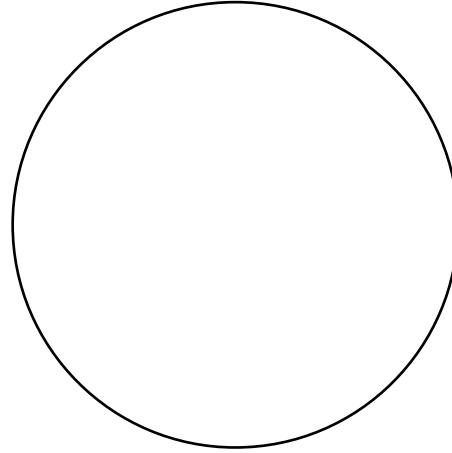
Gabbro

Sample Name: **F-112**

PPL



XPL



Degree of Crystallinity:	Holocrystalline	Hypocrystalline	Holohyaline
General Characteristics:	Leucocratic	Melanocratic	Vesicular
Pyroclastic +		Graphic +	
Orbicular +		Amygdaloidal +	
Mineral Specific Characteristics:		Euhedral +	
Subhedral +		Anhedral +	
Spinifex +		Twinning +	
Skeletal +		Contact +	
Embayed +		Penetration +	
Poikilitic +		Polysynthetic +	
Zoning +		Oscillatory +	
Grain Size (+ which minerals):		Phaneritic:	
Porphyritic		Fine grained +	
Groundmass +		Medium grained +	
Phenocrysts +		Coarse grained +	
Xenocrysts +		Very coarse grained +	
Equigranular +		Inequigranular +	
Aphanitic +		Cryptocrystalline	

Modal Abundance of Minerals Listed:

GA.4. LA-ICP-MS User Manual

The following user manual is intended to be a living document that is added to as researchers in the Brounce lab find details to add, more efficient ways of phrasing specific instructions, and/or take better screenshots of the user interfaces of the LA and ICP programs.

GA.4.1. Glossary of Terms and Definitions

Agilent Technologies 7900 single quadrupole mass spectrometer

The “ICP-MS” part of the analysis process

What you will be using to measure your samples

ELS 193 - Elemental Scientific Laser 193 nm ArF excimer laser

At the time of purchase was called an NWR 193. ESL bought NWR.

The “LA” part of the analysis process

What you will be using to ablate your samples

Tech Support information:

Clerian O'Connor – 402-991-7800

Direct Service – 406-586-3159 (hours 8:30 AM – 5:30 PM Mountain Time)

Parts – 406-640-1271 (hours 8:30 AM – 5:30 PM Mountain Time)

lasersupport@icpms.com

Flow rate – rate of gas flow

Gas Related Terms

ArF – Argon Fluoride, a toxic gas used by the laser cell to create a laser

He – Helium gas

kBar – kilobar, a unit of pressure

kPa – kilopascal, a unit of pressure

N₂ – Nitrogen gas

PSI – Pounds per Square Inch, a unit of pressure

LA-ICP-MS – Laser Ablation Inductively Coupled Plasma Mass Spectrometer

O-ring – this plastic-rubber ring will seal the sample chamber from atmosphere. It will dry out after 3-4 years and need to be replaced.

Push-to-connect – a type of connector where the grey plastic piece around the tube must be depressed before the tube can be pulled out. You cannot pull a tube out from this type of connection without first depressing the surrounding plastic. Inserting a tube simply requires pushing the tube in.

UI – User Interface

GA.4.2. Check 1 Week Prior to Using the LA-ICP-MS

GA.4.2.1. N_2 gas level



Figure GA.4.1. Picture of N_2 tank valves. To open the N_2 valve, rotate the left, silver-colored valve counter-clockwise. Do not touch the pressure regulator valve, the brass valve beneath the gauges. Gauge on the left is the pressure regulator gauge that displays the pressure of the gas leaving the tank. Orange mark denotes where the pressure regulator should be set. The gauge on the right is the tank pressure gauge which shows how much gas is in the tank based on the gas pressure in the tank. White tape with black line marks the tank starting pressure.

- Flow rate increases as gas volume in tank decrease
- Uses ~600 PSI (4000 kPa) per 10 hour session (time starts from when first enter the room)
- Takes 1-5 business days to arrive after ordering
- N_2 is purchased with Maryjo's permission (cc Maryjo on all tank order requests; mbrounce@ucr.edu) through the Lab Coordinator – Currently Ying Lin (yinglin@ucr.edu).

GA.4.2.2. He gas level

- This tank is ordered infrequently



Figure GA.4.2. Picture of He tank valves. Everything is the same as on the N₂ tank photo.

- Pay attention to the gas levels between uses to get a feeling for when to request that Maryjo purchases more He gas
- There is a He shortage, this gas may take some time to arrive but a tank can also last >5 years (depending on usage).

GA.4.2.3. ArF gas level

- This will likely go “bad” before the volume is used up
- Gas can power the laser for 1-2 years before sufficiently degrading to an unusable point
- Pay attention to the number of times a laser cell refresh has taken place in the past. One refresh should last for multiple, consecutive days of lasering. If you are refreshing the laser cell every day during a multi-day, consecutive laser session, the tank ArF quality has degraded, and you should alert Maryjo so that she can order a new tank.



Figure GA.4.3. Picture of ArF tank valves. White valve on the right opens/closes the ArF tank. Middle valve labeled, “Do NOT Touch,” sets the pressure leaving the tank (pressure regulating valve). Black valve on the left opens/closes the path to the laser cell. Pressure in the tank is measured on the right gauge with tape over the starting pressure and red mark on the time to order a new tank pressure. The pressure regulating valve is set to be the pressure of the red mark.

- Maryjo orders this gas through a special process. It can take as long as 3-6 months for a new tank to arrive.

GA.4.2.4. Liquid Ar tank level



- The tank level gauge does not always work. If the gauge is broken, you can use your body weight and strength to check the tank levels (Fig. GA.4.4.).
- If you can rock the tank back and forth with your body weight (do this gently), the tank is low.

Figure GA.4.4. Picture of Ar tank liquid volume gauge. There are multiple different types of gauges that could be used but they are not the most accurate and sometimes fully broken. This gauge is always located at the top of the liquid Ar tank (first tank you will see when you enter the lab space from the hallway).

- If you can rock the tank back and forth with one arm (do this gently), the tank is empty.
- It takes ~3-5 business days for a new tank to arrive.
- Liquid Ar is purchased by the Lyon's Lab Coordinator – Currently Charlie Diamond (cdiam001@ucr.edu).

GA.4.3. Starting the laser

These steps will take you about 30 minutes – 1 hour, depending on if you do a gas exchange and you will have any troubleshooting to work through.

GA.4.3.1. Check the Cones and Glassware

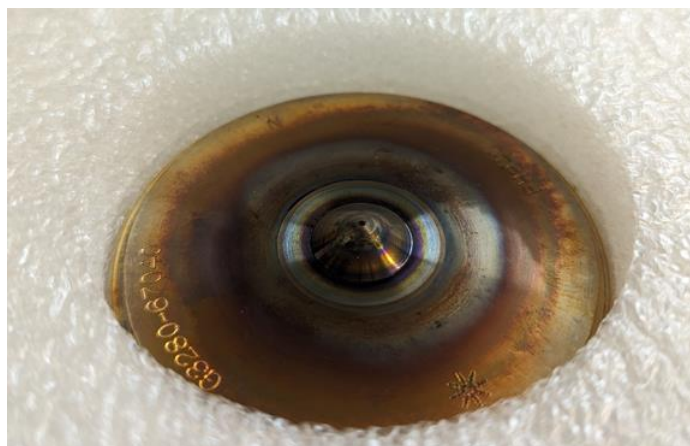


Figure GA.4.5. ICP Sampler Cone.

- WEAR GLOVES!
- Use the sampler (Fig. GA.4.5.) and skimmer (Fig. GA.4.6.) cone in the boxes marked “MJ’s.”

This box has green tape on it.

- Inspect the sampler and skimmer to make sure they are both clean
- If they are dirty, clean them with a Kimtech wipe and some ethanol



Figure GA.4.6. ICP Skimmer Cone.

- To change/swap the cones and skimmers:
 - Locate the box for the set that is currently in the ICP. This will be designated by tape on the ICP black, translucent plasma housing box in the upper left corner of the ICP. The boxes for the skimmer and cone will most likely be on top of or beside the ICP.
 - Maryjo's cone and skimmer will be located on her shelf in the Lyon's ICP room or on top of the ICP.



Figure GA.4.7. ICP with gloved hand on the silver button of the housing box. Red tape on the top left of the housing box denotes which sampler and skimmer are currently in the ICP.

- On the bottom of the casing box on the ICP is a silver button (in the bottom tight corner of box) that does not look like a button. Push it to open the housing box (you will need to rotate the box upwards after it is



Figure GA.4.8. Inside of ICP housing with sampler cone visible. Skimmer cone inside/behind the sampler cone (not visible).

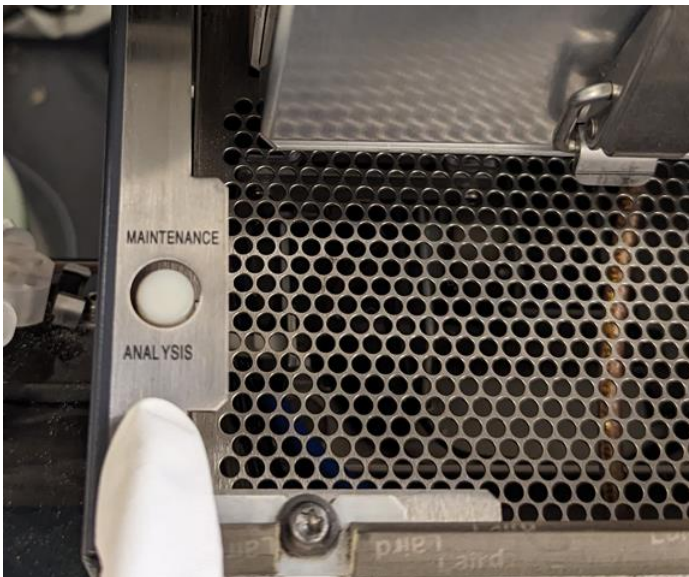
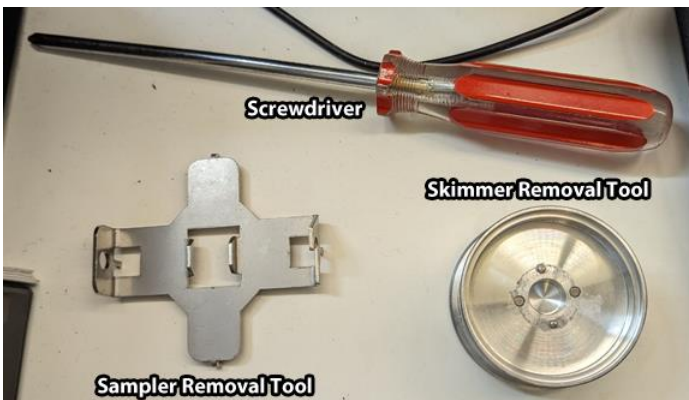


Figure GA.4.10. Gloved finger points towards the ICP maintenance/analysis button.



unlocked; Fig. GA.4.7.). There should be no resistance to you rotating the box up. If there is resistance do not proceed.

- In the front left of the open box is a white “maintenance/analysis” button (Fig. GA.4.9.). Push and hold button until the plasma torch box begins to move out of the way of the cone and skimmer housing area. You can stop pushing the button once the torch box begins to move. DO NOT TOUCH anything while the torch box is still moving. Wait until both the torch box and associated gear noise have stopped before proceeding.

Figure GA.4.9. Tools used to remove and install the sampler and skimmer cones. The screwdriver is inserted into the circular holes on the sampler removal tool to aid in loosening the sampler cone from the ICP.

- Use tools to help you remove the skimmer and cone. You will be shown how to handle these and which tools to use (Fig. GA.4.10.).
- Place skimmer and cone you took out CAREFULLY in the appropriate boxes for them and close the boxes.
- CAREFULLY align the “MJ’s” skimmer and cone in the machine and hand tighten everything. **Do not use excessive forth.**
- Once the “MJ’s” skimmer and cone are installed, press the “maintenance/analysis” button and wait for the torch box and mechanical noise to stop before proceeding further.
- Close the translucent black box cover.

GA.4.3.2. Connect the Laser Tubing to the ICP



Figure GA.4.11. Picture of the Nebulizer and clip attaching the nebulizer to the ICP. Screw under the nebulizer is not in view.

- Unclip the spray chamber nebulizer from the torch inlet (Fig. GA.4.11.).
- Loosen the nebulizer by loosening the screw on the bottom of the chamber and slide it to the left (away from the ICP). Once moved, re-tighten the screw.

- Couple the glass flange (glass end of the split tube; Fig. GA.4.12.) from the laser tubing to the torch inlet using the metal clip that was previously attached to the nebulizer.



Figure GA.4.12. Laser split Teflon tube prior to connection to ICP. Both the glass flange and carrier gas end are in the plastic bag.

- Disconnect the nebulizer tube attached to the “carrier gas” push-to-connect line (Fig. GA.4.13.).
- Connect the Teflon tube end of the split tube to the “carrier gas” push-to-connect line (Fig. GA.4.12.).

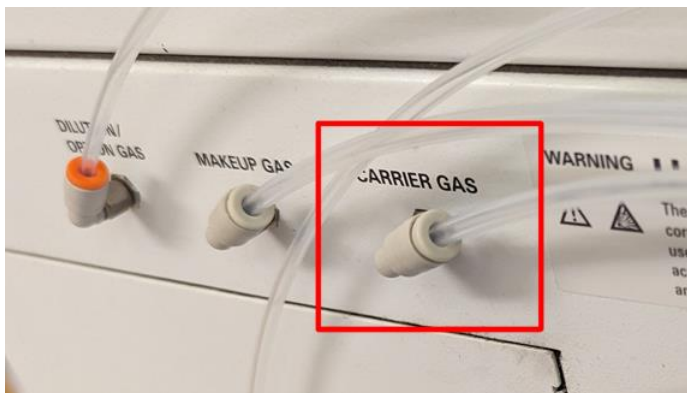


Figure GA.4.13. Picture of different gas connections to the ICP. Red rectangle around the carrier gas connection.

GA.4.3.3. Check the Ar Supply

- Turn on the chiller below the ICP-MS (behind the grey Styrofoam rectangle attached to the table). It will make a loud humming noise when on.
- Always good to double check this tank after a new tank has arrived (see GA.4.2.4; above).

- Open the tank (Fig. GA.4.14.).



Figure GA.4.14. Liquid Ar valves. The tank open/close valve is on the right.

- Gas pressure should be >100 PSI. The ICP needs the pressure to be >80 PSI to run. The plasma will quench if the pressure drops too low (Fig. GA.4.15.).

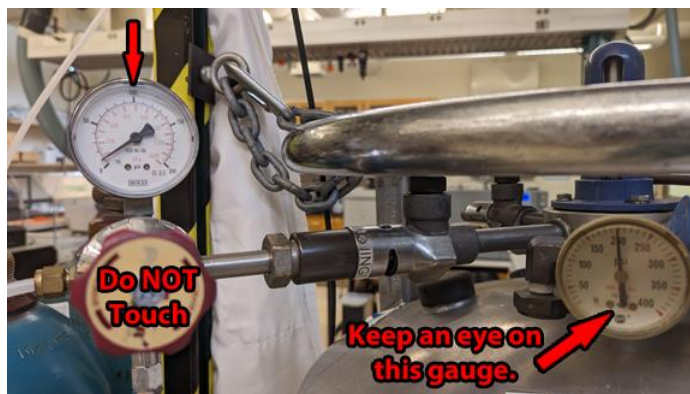


Figure GA.4.15. Liquid Ar pressure gauges. On the left is the pressure regulating gauge with arrow indicating the minimum acceptable run pressure. On the right is the tank pressure gauge.

- Check on the pressure of the Ar tank every hour at a minimum.
- A full tank is more likely to have the tank gas pressure decrease below a viable pressure than a not-full tank because of the smaller volume available for gas expansion. Opening the pressure building valve when the tank gets to ~ 110 - 105 PSI and monitoring the pressure every few minutes afterwards is key to ensuring that the plasma will not quench



Figure GA.4.16. Labeled valves on liquid Ar tank.

on you due to low pressure (see Troubleshooting > Plasma will not stay lit for more information; Fig. GA.4.16.).

- If the gas pressure in the tank starts to drop lower than what the

pressure regulating valve is set to, both will read the same number. This starts to happen around 100 -110 PSI (Fig. GA.4.15.).

- If the pressure in the tank gets too high (> ~235 PSI), the tank will vent from a release pipe to the left of the tank pressure gauge.

GA.4.3.4. Open the N₂ and He tanks behind the fridge (See GA.2.1. & GA.2.2; above)

GA.4.3.5. Open the laser software

- MEOLaser, shortcut symbol has the letters “NWR” on it (Fig. GA.4.17.)
- Click “N₂ Purge” and wait 15 minutes before proceeding (Fig. GA.4.18.).
- During this wait time, you can skip ahead to GA.4.3.8. to load the settings from a previous LA session and to check/the plasma settings before lighting the plasma.

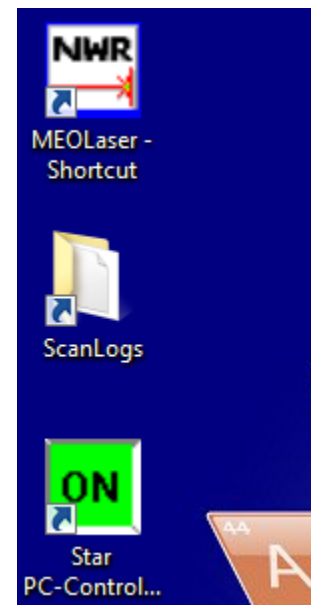


Figure GA.4.17. Cropped view of the desktop GUI for the laser ablation system. The laser software is the top program (MEOLaser - shortcut). The gas control software is the bottom program (Star PC-Control).

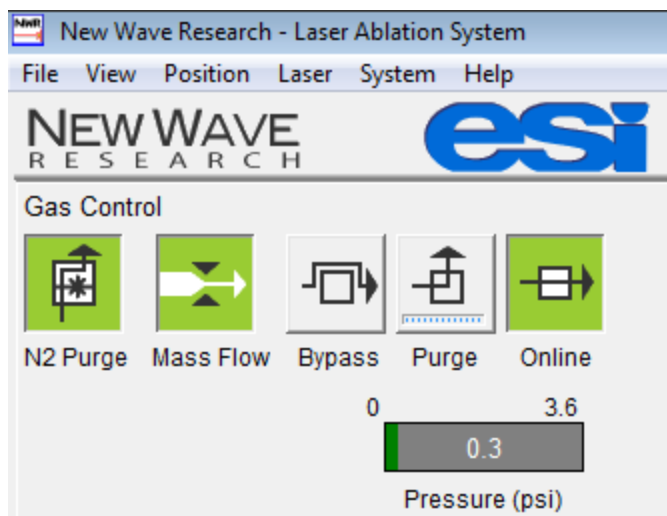


Figure GA.4.18. Gas Control UI in the top left corner of the laser software UI. N₂ Purge, Mass Flow, and Online are all on.

- Check that ball in the top right of the metal laser “cage” is floating (Fig. GA.4.19.).



Figure GA.4.19. N₂ gas flow chamber showing no gas flow. When N₂ is flowing, the small ball will float between the 3-5 marker, depending on the pressure left in the N₂ tank.

GA.4.3.6. Optional: Open ArF tank below the laser

- If the laser has not been run in a while (longer than a month), you will want to perform a Laser Cell Gas Exchange (see GA.4.5.1; below).
- This step can be skipped if the laser was recently run for an analysis session or is running consistently over an extended period.

GA.4.3.7. Mass Flow: He

- Click on “mass flow”
- Set He flow rate to 650 mL/min
- Click outside of the value box but still inside of the prompt box to start the ramp up of He
- Watch the flow rate number climb from 0 to 650 mL/min
- Once the flow rate for He is at 650 mL/min, click “ok” to close the box.
- Click “Purge” and once complete, click “Purge” again
- Click “mass flow,” and set the flow rate for He to 0.
- Switch to the ICP-MS computer

GA.4.3.8. Starting the Plasma (ICP)

The following steps will take you anywhere from 15 minutes to 1 hour, depending on whether troubleshooting is involved.

Quick note before beginning – Agilent includes a bunch of written and video how-to documents with their instruments. These are on the ICP computer. When in doubt about any process, you can always reference these documents to help you run the ICP.

GA.4.3.8.A. Load a previous laser session

This step is so that you can use the same settings as any previous laser ablation session. It'll make the tuning step faster and will make checking the settings before lighting the plasma faster (below).

- “Batch” > “New batch folder” (Fig. GA.4.20.)

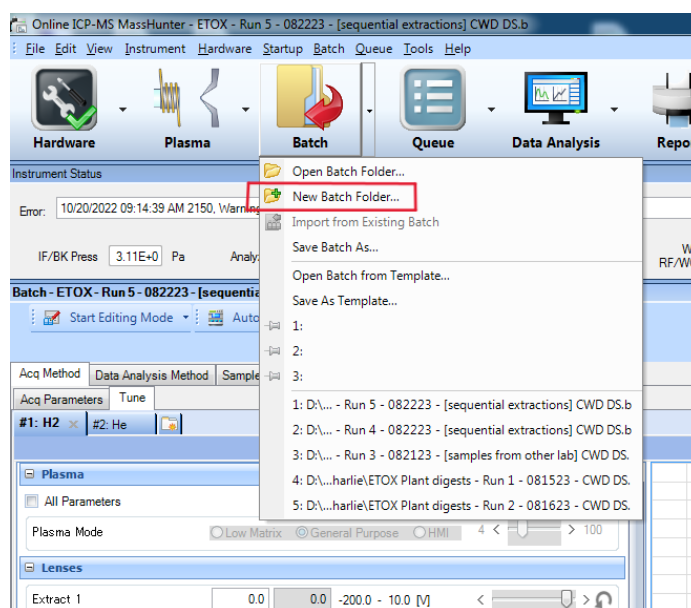


Figure GA.4.20. ICP UI with Batch > New Batch Folder in red box.

- Navigate to the folder you want to save your data in in the “Save in” drop down menu (Maryjo’s folder will be the parent folder)
- In the “Create from” menu select “Existing Batch” option (Fig. GA.4.21.)
 - Click on the Select button
 - Choose the folder from which to import run conditions (recommend one of the most recent runs for the type of laser ablation analysis session you will be doing) from then hit “Open” (Fig. GA.4.22.)

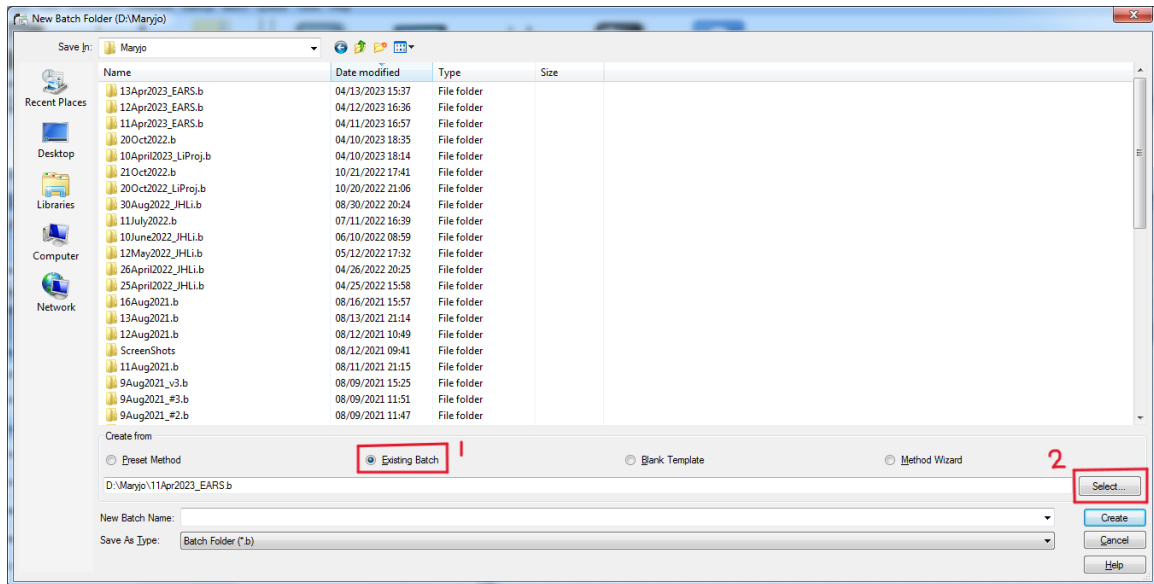


Figure GA.4.22. ICP UI for Batch > New Batch Folder with Create from > Existing Batch (1) and Select button (2) in red boxes.

- Write a file name that includes today's date then hit "Create"

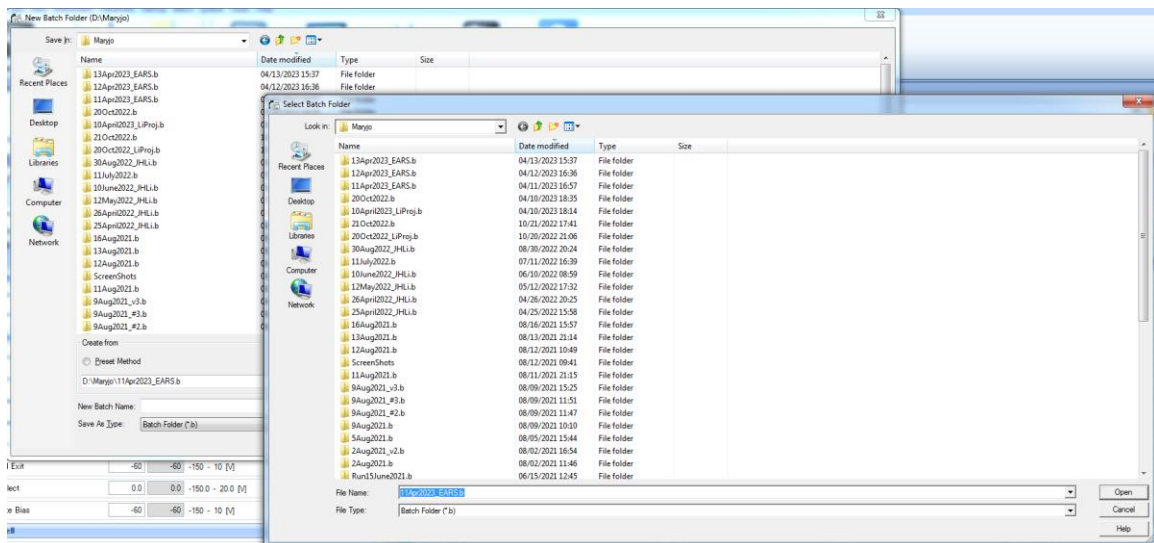


Figure GA.4.21. ICP UI with example of choices to select after Batch > New Batch Folder > Create from Existing Batch > Select has been hit.

GA.4.3.8.B. Create a new file to save the ICP data in

This step is for when you are starting your run completely from scratch. Highly recommend using one of the most recently run laser ablation Batch settings instead of setting everything up from scratch. Everything can be adjusted after importing a Batch file but tuning will take longer with this method.

- “Batch” > “New batch folder”
 - Navigate to the folder you want to save your data in (Maryjo’s folder will be the parent folder)
 - Write a file name that includes today’s date
 - Choose “create from: Method Wizard” and click “create”
 - Choose “low matrix” > “no present method” > “no stock soln” > “no element list” >
 - Turn on elements that you desire to measure
 - Example of standard silicate analysis: K, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, Hf, Ta, W, Tl, Pb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U
 - Put more emphasis on low detection limit than time
 - Click “optimize” > “Finish”
 - “View Task” will open windows
 - “Acq Method” > “Acq Parameters” > Acq mode: TRA
 - In “Acq Method” > Tune

- Under cell deselect “use gas”
- Custom tune: override hardware settings
 - “New batch name” > hit “create”
- Check acquiring methods: “Acq Method” > “Acq parameters” > “Acq mode” > select “TRA”
- To select elements for analysis: click “select elements” > manually select on periodic table
- To configure the tune settings: “Tune way” > “Custom Tune” > “Signal Monitor” > “Show Hardware Settings”

GA.4.3.8.C. Settings to check before lighting the Plasma

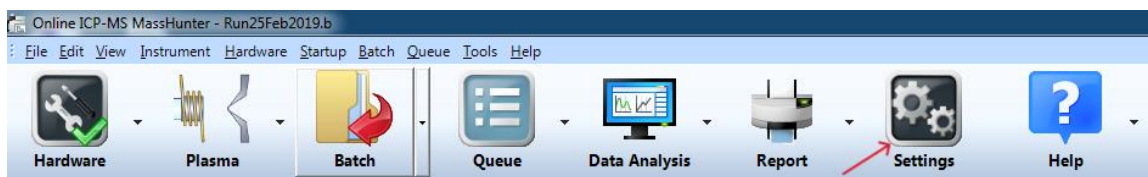


Figure GA.4.23. ICP UI Settings button location in top menu.

- Check that the ICP is set properly for laser calibration before turning on the plasma. **You cannot change this setting once the plasma is lit.**
 - Open Mass Hunter
 - Settings (Fig. GA.4.23.) > Hardware (this button does not look like a button; Fig. GA.4.24.) > Sample Introduction (Fig. GA.4.25.)
 - Uncheck “USE ALS”

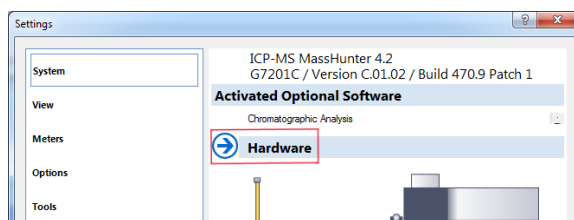


Figure GA.4.24. ICP UI Settings Menu with Hardware button in red box.

- Sample Introduction is set to “LA”
 - Deselect Post PeriPump Rotation and Spray Chamber (SC) Cooling
- Mode is properly set: Acq Method > Tune > uncheck “use gas”

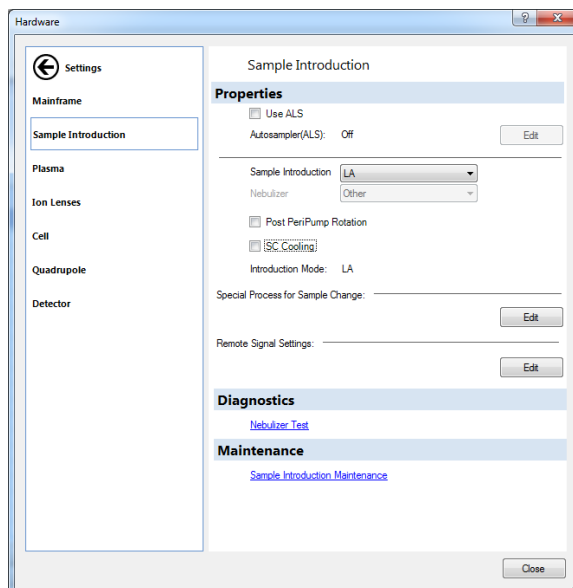


Figure GA.4.25. ICP UI Settings > Hardware

- Data analysis method: Basic menu with LA options set.
- Information > check “FullQuant Analysis”
- Validate method and make sure there are no errors
- Hit “Save batch” when convinced all settings are correct

GA.4.3.8.D. Lighting the Plasma

- Plasma > Plasma On (Fig. GA.4.26.)
- Uncheck “Execute Configured Ignition Sequence”
- Hit “ok”

It really is that easy. Wait ~2 -minutes, listening to the sounds of the ICP, for the plasma to light and remain stable. You will know stability of the plasma is

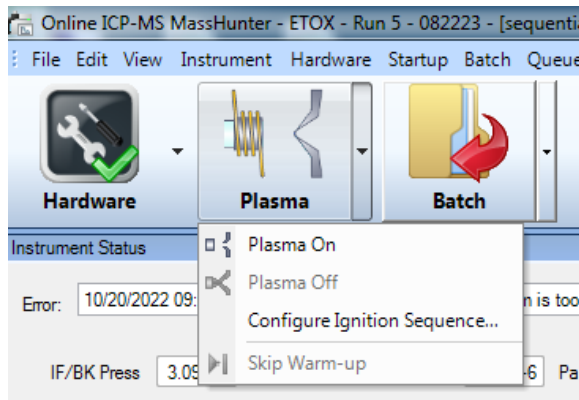


Figure GA.4.26. ICP UI Plasma > Plasma on.

achieved because the yellow blinking light on the outside of the ICP with switch to a solid green light.

Once the plasma is stable, switch to the LA computer.

GA.4.3.8.E. Plasma Warm-up Time

On the LA computer, very slowly increase the flow of He to the from the laser to the plasma:

- Click on Mass Flow
 - Check that the ramp up rate is set to “5”
- If it is not set to “5,” set the ramp up rate to “5”
- Set the He flow rate to 650 mL/min
- Click inside the box (not on any buttons) but outside the text box region
 - You can hit “ok” and close the box but then you can’t monitor the flow of He while the rate ramps up.
 - If the plasma quenches, you want to know where in the ramp-up process the He flow was for troubleshooting purposes, hence the recommendation to not hit “ok.”
- Once the He flow reaches “650 mL/min,” wait 30 minutes for the plasma to warm up before proceeding further.
- **Suggestion:** Use the 30 minutes to set up your sample names or go over your pre-analysis session notes.

GA.4.4. Tuning the Laser Signal

The NIST 612 glass will be used for tuning. You will monitor ^{139}La and ^{88}Sr during this process to ensure the counts on the elements are sufficiently high before you laser the standards and samples for your laser ablation run.

GA.4.4.1. Run a Start-Up Scan

On the ICP Computer

- Go into the window Acq Method > Tune
- When the ICP is running, the gridded field on the right will show the counts for the set elements (counts update dynamically; Fig. GA.4.27.)

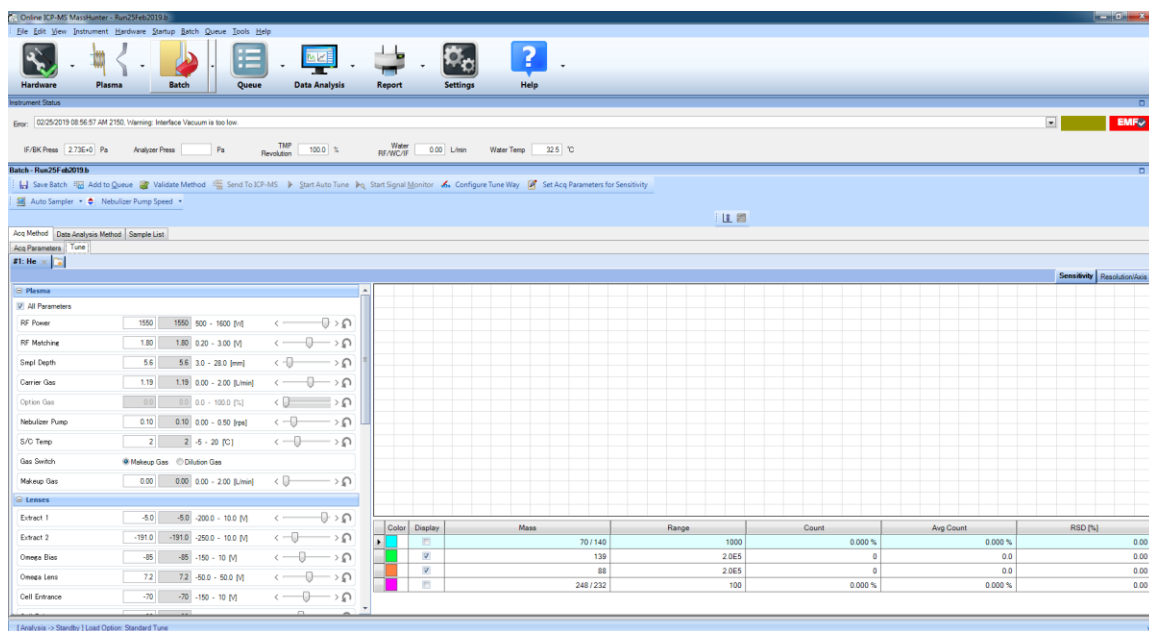


Figure GA.4.27. ICP UI for Acq. Method > Tune with ^{139}La and ^{88}Sr set to be monitored.

- To adjust the elements being monitored: Configure Tune Way > Signal Monitor and set ^{139}La and ^{88}Sr to be monitored (can also monitor ^{238}U)

On LA computer

- Set a line to pass on the sample surface (see GA.4.5.4; below) in the laser software with the following properties:

- Scan speed: 1 $\mu\text{m}/\text{sec}$ Spot size: 60 μm Scan Speed: 1 $\mu\text{m}/\text{sec}$
Output: 65% Rep Rate: 10 Hz Spot Size: 60 μm

- Run the line (see GA.4.5.4; below)

On the ICP computer

- Once you visually see that the laser signal has reached the signal monitor and have visually verified that the signal is stable:

- Generate a tune report: Report > Generate Tune Report
 - Report masses:
 - 139, 88, 238 or 220, 248/232 (Th/Th), 70/140 (Ce++)
 - Report template > Browse
 - Open: en/letter/tune report/tuneReport.xltx
- Make sure you hit the appropriate button to generate the report
- Print the report and compare to previous tune reports
 - Verify with Maryjo the range of acceptable values

GA.4.4.2. *Tuning*

If the tune report is out of the acceptable range for the reported masses, you will need to tune the laser signal. This process involves adjusting the physical relationship between the cones and the plasma.

- The tune menu is on the left side of the UI in Acq Method > Tune
- Tune while the laser is firing so that you can monitor the counts and RSD%
 - You want to maximize counts on Sr and La while minimizing the RSD% (keep RSD% < 1.5)
- Tune in this order:
 - Torch Axis
 - Adjust “Torch H” and “Torch V”
 - These adjust the horizontal and vertical position of the plasma torch in the housing with respect to the cones’ position
 - Plasma
 - Adjust “smpl Depth” and “Carrier Gas”
 - These adjust the proximity of the plasma torch to the cones and the rate of flow of the carrier gas, respectively
 - Lenses
 - Adjust “Extract 1” and “Extract 2”
 - You are adjusting the charge on these lenses which affects how the ions move through the ICP
- Be sure to click “Save Batch” to save all of your changes to the tuning settings
- When you are satisfied that you have min/maxed your tuning settings, re-run a start-up scan

GA.4.5. Troubleshooting & Measurements

GA.4.5.1. Laser Cell Gas Exchange

- You will either perform this:
 - When you first start up the laser after it has been sitting, unrun for over a month
 - when the laser cannot keep a consistent fluence on the sample surface (the fluence will drop slowly after each sample analyzed)
 - when the laser stops firing halfway through a tuning run
- Close the Laser Software
- Open both gas valves
 - Do NOT touch the MIDDLE valve that is attached to the flow regulator and the tank pressure gauge.
- Open the gas exchange software titled – “Star PC-Control V.”
- Click on “Gas Menu” (Fig. GA.4.28.)

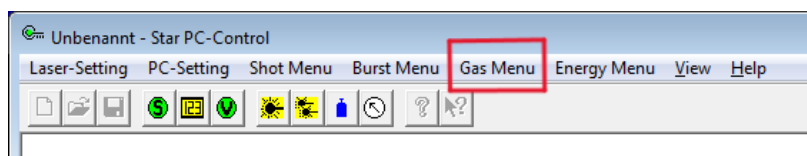


Figure GA.4.28. Screenshot of the PC Star Control UI. The Gas Menu is the fourth option from the right (red box).

- Click on “gas exchange” (Fig. GA.4.29.)
 - This will start the gas exchange process
 - It will take ~5-10 minutes for the process to complete
 - Monitor which valves are opening or closing during the process

- If the process completes pre-maturely, knowing where in the exchange process the error occurred will help with further troubleshooting.

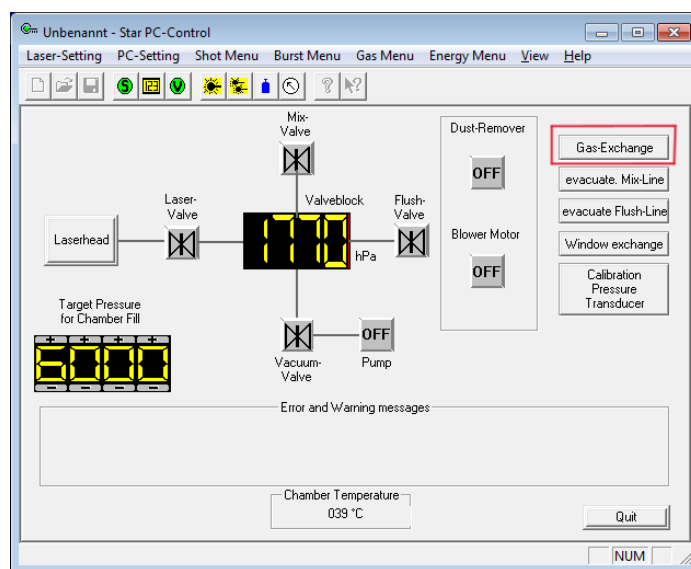


Figure GA.4.29. Gas Menu UI. The Gas Exchange option is on the far right (red box).

- Once completed, exit the gas exchange software and re-launch the laser software
- Run “N₂ Purge” for a few minutes before continuing setting up the laser (see Open Laser Software)

GA.4.5.2. Pre-mix Pressure Too Low

This error pops up after a failed gas exchange when you open the laser software (failed gas exchanges end earlier than they should) and is due to not opening at least one of the two valves that allows ArF to flow from the tank to the laser cell. Make sure both valves are open and re-do the gas exchange (see Laser Cell Gas Exchange).

GA.4.5.3. Sample Exchange

This process is an inevitability when you laser your samples; however, when not done properly can add a significant (>15 minute) delay to your laser session as the plasma will quench.

To exchange samples in the laser ablation chamber:

- Set Mass Flow for He to 0 (ramp up rate does not matter)
- Hit “Bypass” button in Lase Ablation software
- Exchange your samples
- Hit Purge button and when Online button next to Purge is green, hit Purge again and wait for Online to be green.
- Slowly ramp up the flow rate of He back to 650 (see Day of Laser Use > Starting the Plasma > Plasma Warm-up Time)
- Once He flow rate is back at 650 mL/min, continue lasering samples

GA.4.5.4. How to set up laser analyses (spot, line, text, ect...)

You will use these tools (Fig. GA.4.30.) and their settings to set up analysis volumes/areas

- The options menu for the various tools can be found on the lower left of the LA software

UI. Some examples of how to set up analyses using the tools (Fig. GA.4.30.):

- To set a spot, select the spot tool from the tools list. Click on the sample surface in the central view in the UI.

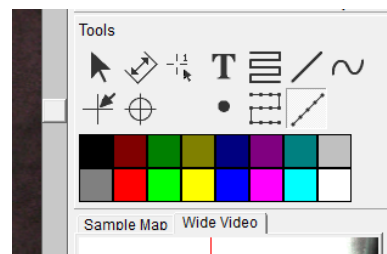


Figure GA.4.30. LA UI. Tools options are above the camera view for the sample stage on the bottom left of the UI.

- To set a line, select the line tool from the tools list. Click on the sample surface where the line should start. Keep clicking on the sample surface at points where you want the line to bend. When your line is set up, right click to finalize the analysis line (Fig. GA.4.31.).

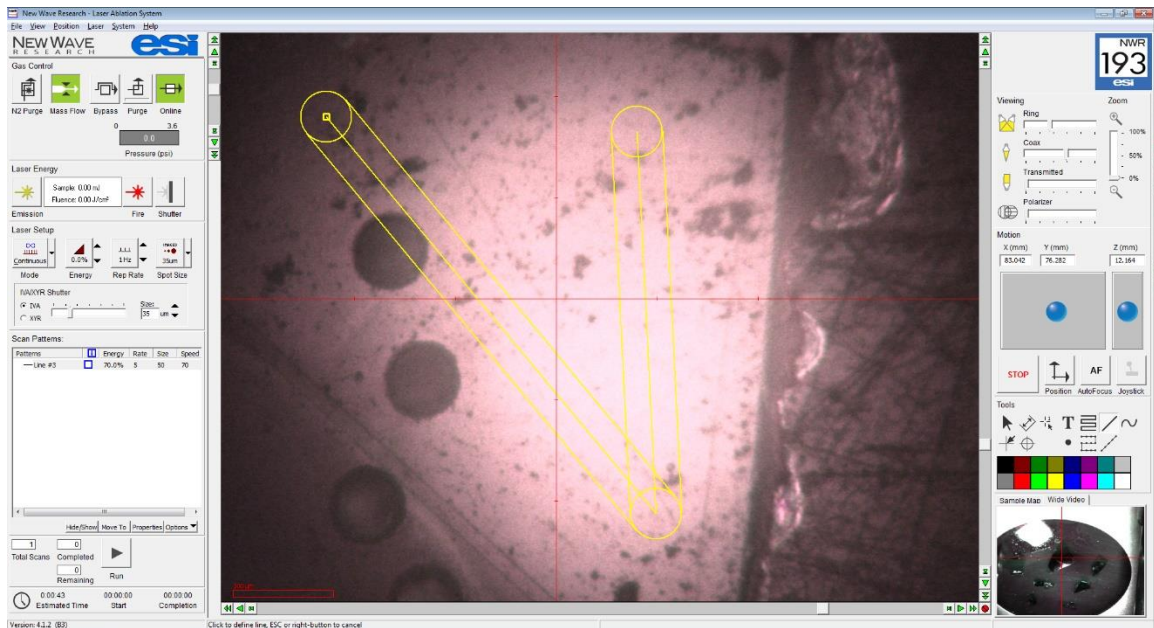


Figure GA.4.31. LA UI with lines set for analysis of sample surface.

- To adjust the analysis properties, right click on the analysis object in the Scan Patterns menu

(Fig. GA.4.32.)

- Select Properties
- Properties not relevant to the type of analysis being performed will be greyed out
- Adjust the properties in this box to be relevant to the type of analysis being performed (Fig. GA.4.33.)

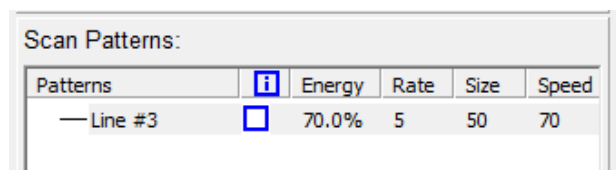


Figure GA.4.32. LA UI, Scan Pattern menu showing one line drawn on sample surface.

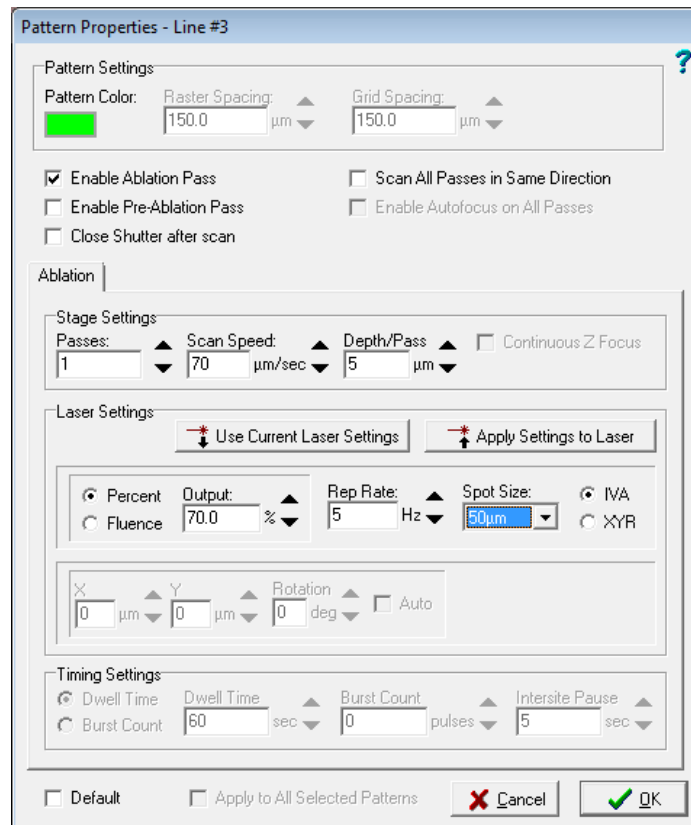


Figure GA.4.33. LA UI, Pattern Properties for a line.

- To run the analysis
 - Right click on the analysis object to run
 - Ensure that “enable laser during scan” is checked
 - Click ok/run

GA.4.5.5. Inconsistent Fluence and/or Energy on the Sample Surface

If you cannot get a good laser signal on samples (e.g., low fluence, jagged excavation pit, inconsistent/low energy on the sample surface), there are two possible causes:

GA.4.5.5.A. O-ring Failure

- When the O-ring has gone bad it lets atmosphere into the sample chamber. Different sample surfaces will ablate differently (e.g., dark vs. light glass)
- Take the sample holder out and inspect the O-ring.
 - If the O-ring is cracked, pitted, or otherwise “stiff” feeling, replace the O-ring.
 - If the O-ring is flexible and appears in one piece, possible issue with the gold focusing mirror located above the sample chamber (see GA.4.5.5.B; below)

GA.4.5.5.B. Gold Mirror Oxidation

- Issues with the gold mirror will be similar to O-ring failure issues (see GA.4.5.5.A; above)
- This issue will require contacting an ESL support technician to resolve (See GA.4.1. ELS 193 > Tech Support Information, above)

GA.4.5.6. No change in ICP signal when laser firing?

Mass flow of He is at 0. Slowly ramp up the flow rate of He back to 650 (see GA.4.3.8.E; above)

GA.4.5.7. Plasma will not stay lit

The plasma is very sensitive to minute changes in operating conditions. The following are a list of reasons/questions for why the plasma will not stay lit:

- Tubing connections are not tightly sealed between the LA and the ICP machines.
- Mass flow of He is not set to “0” while the Plasma is lighting.
- The ramp up rate for He is set to much higher than “5” when He is reintroduced to the plasma. Adding He too quickly will quench the plasma.

- Did you hit “Bypass” before setting the He flow rate back to “0”?
 - If yes, then that is your issue. ALWAYS set the flow rate to “0” and watch to make sure the flow rate is at “0” before bypassing the sample chamber.
 - If no, check the Ar tank pressure
- What is the Ar tank pressure at?
 - Is it below 100 PSI? → Open the Ar pressure building valve
 - Is it at or above 100 PSI? → The Ar tank is likely not the issue
 - There is a balance in how open the pressure building valve is and maintaining pressure adequate pressure to keep the plasma lit in a full tank. If the valve is not open enough, the pressure will continue to drop as the plasma burns. If the valve is too open, the pressure in the tank will build until the tank must release pressure or risk exploding. The release of excess pressure is loud but otherwise uneventful; however, it also uses up a valuable resource. Try to find a balance so that the Ar tank has a consistent pressure for the entire run.

GA.5. Scanning Electron Microscope User Manuals

The following two sections are short documents that were created to orient undergraduate student researchers to how to use a Scanning Electron Microscope. The first section is a brief description of how the focus on an image and the dwell time affect the image quality of mapped sections. The second section details how to set up the SEM to make elemental map scans.

GA.5.1. Example Images

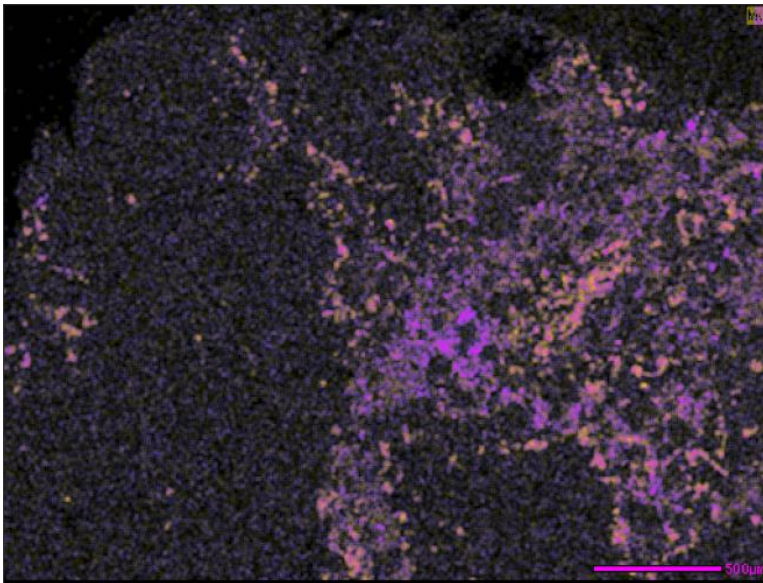


Figure GA.5.1. Example_A
512 x 384 (default)
out of focus
0.02ms dwell time (default)

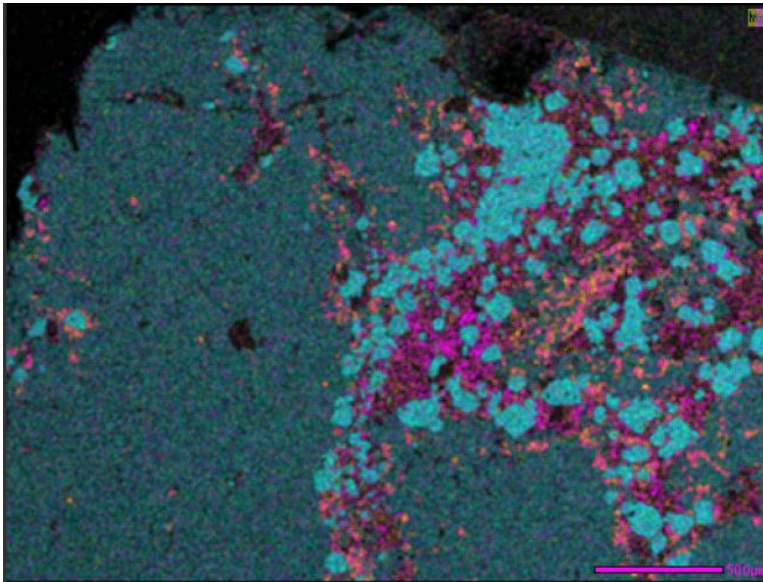


Figure GA.5.2. Example_B (same area as A)
 512 x 384 (default)
 in focus
 0.02ms dwell time (default)

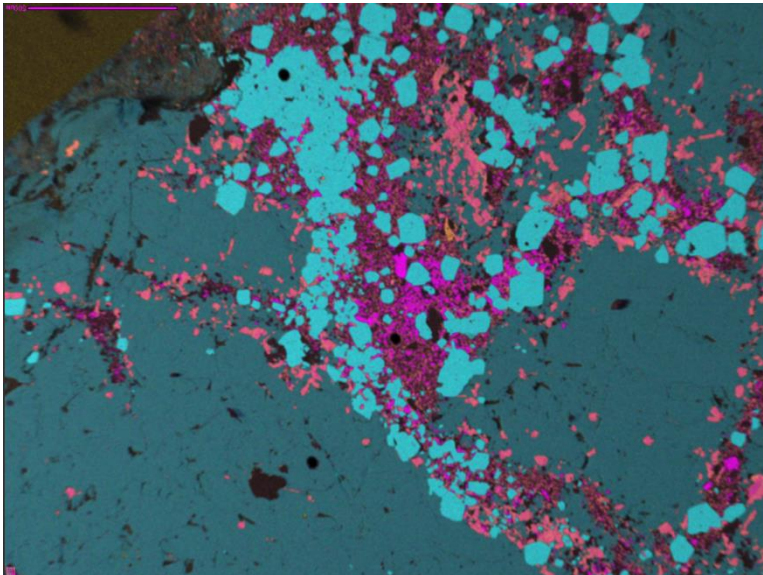


Figure GA.5.3. Example_C (same as A & B)
 1024x768
 in focus (mostly)
 0.5ms dwell time

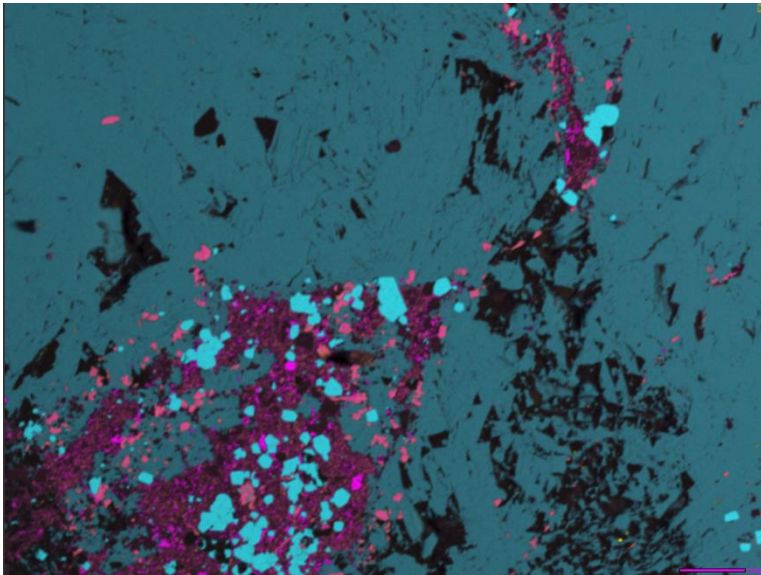


Figure GA.5.4.
Example_D (same sample as A,
B, & C but different area)
1024x768
out of focus
1.0ms dwell time

GA.5.2. How to Run Elemental Map Analyses

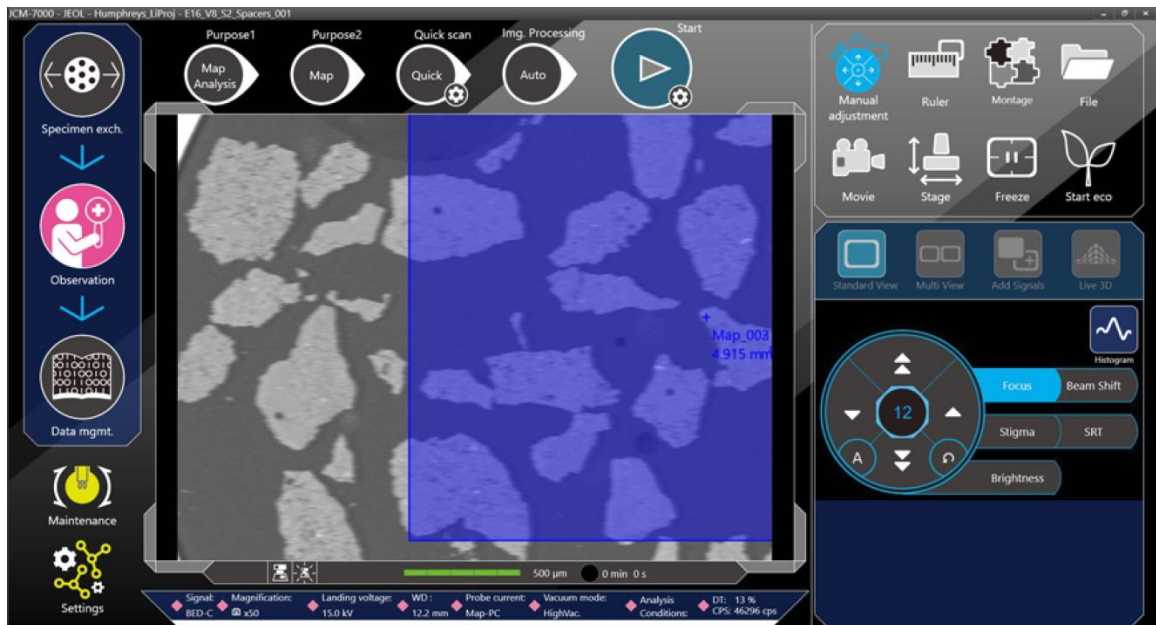


Figure GA.5.5. This is the user interface (UI) for the SEM with “Manual Adjustment” selected in the upper right corner.



Figure GA.5.6. Options for “P1”. You change this when you want to change the type of analysis you will be running.

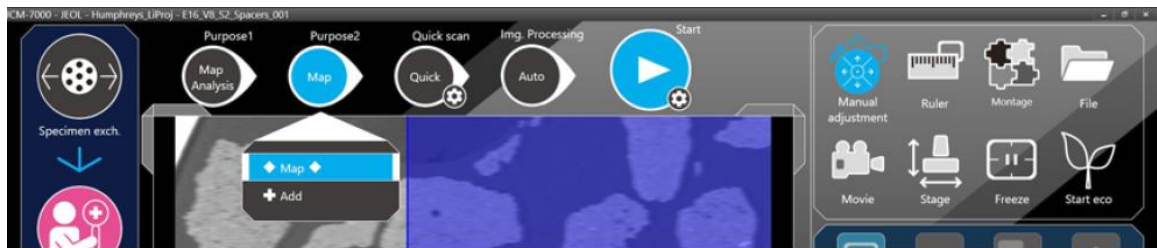


Figure GA.5.7. Options for “P2”. Options change depending on what is selected for “P1” (above).



Figure GA.5.8. Scanning options. Will affect how the sample displays in the large sample viewing section of the UI.

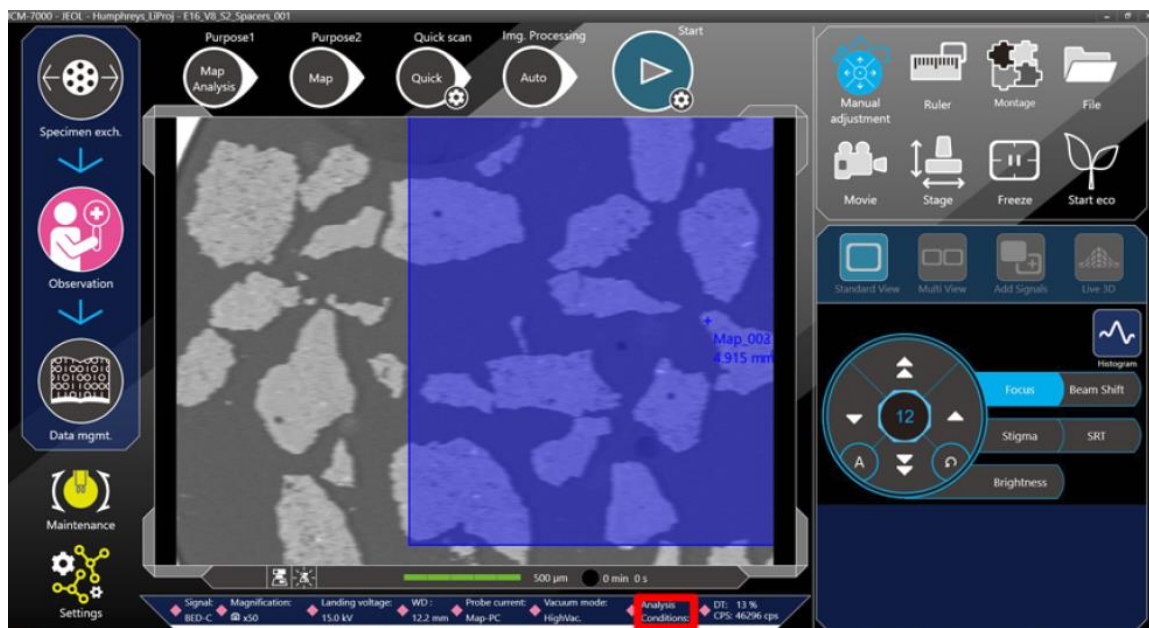


Figure GA.5.9. Before you run any analyses, you'll want to set (and record in you lab notebook) the "Analysis Conditions". To do this you will want to click in the region inside the red box on the image to the left.

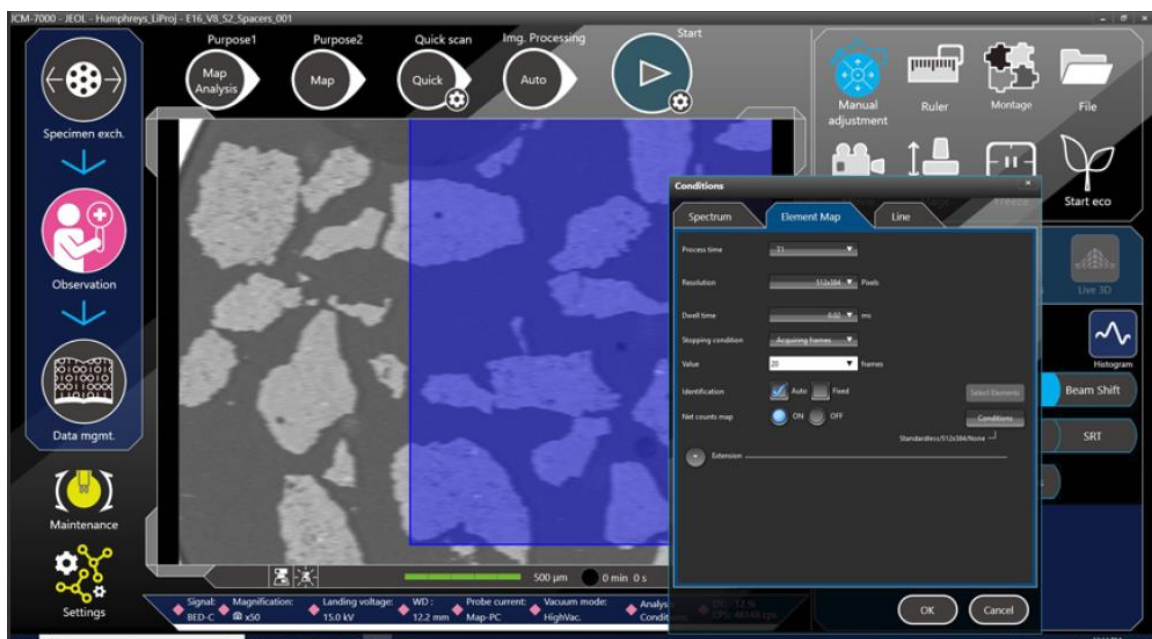


Figure GA.5.10. Upon clicking on “Analysis Conditions,” the “Condition” box will pop up. Here you will set your run conditions. Record everything so that future you or others can independently replicate your observations or re-run your map with adjusted conditions at a future date. Figure GA.5.11. has larger versions of this menu.

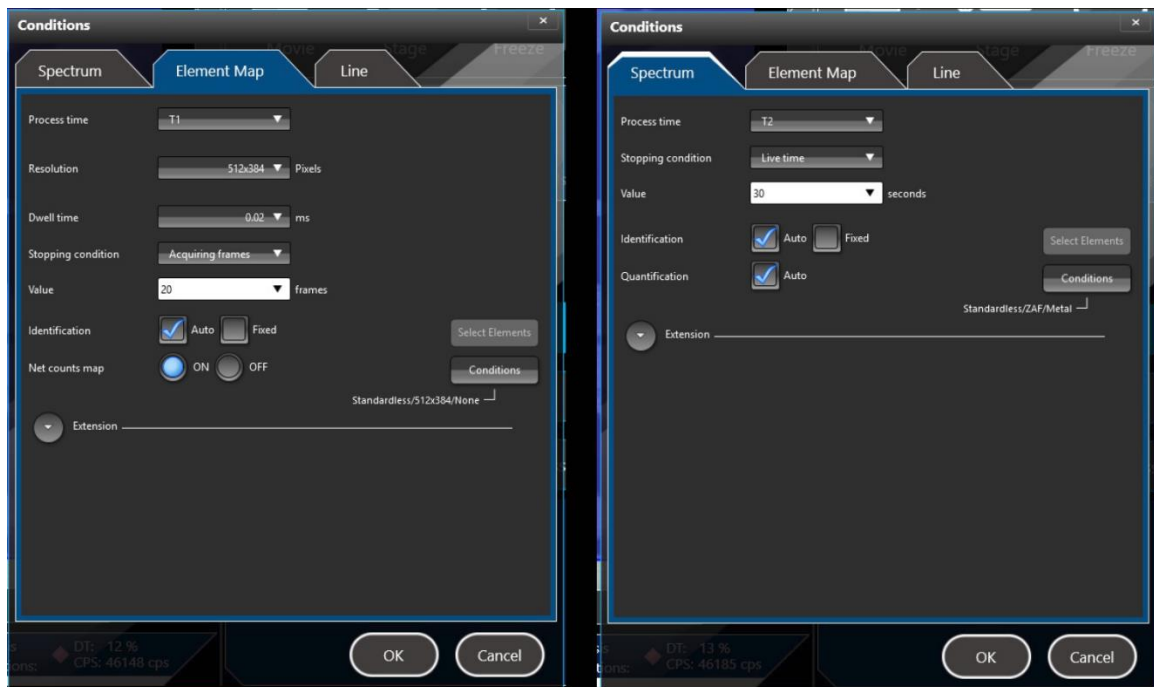


Figure GA.5.11. “Element Map” is for adjusting map settings. “Spectrum” is for setting spot settings.

GA.6. Matlab Codes

The following code allows for the excel output file from rhyolite-MELTS (Gualda et al., 2012; Ghiorso and Gualda, 2015) to be converted into MATLAB charts after being converted into an excel file (Gualda and Ghiorso, 2015). The code also allows for input from a second and third (commented out) file for data to plot alongside the liquid lines of descent. Please feel free to take and modify the code as you see fit. This code is provided free for anyone to use:

```
clear
fileName = '---input_file_path_here---.xlsx'; %replace NAME with
name of file to be read
fileName02 = '---input_file_path_here---.xlsx';
% fileName03 = '---input_file_path_here---.xlsx';

a = xlsread(fileName,'liquid'); %options:
xlsread(filename,sheet,xlRange)
[num,txt,row] = xlsread(fileName,'x_axes');
b = xlsread(fileName02,'WRCompiled');
c = xlsread(fileName02,'FeLoss');
```

```

[row,column] = size(raw); %sets variables for the number of rows
and columns in b array
[rowA,columnA] = size(a);
[rowB,columnB] = size(b);
[rowC,columnC] = size(c);

x = a(:,19); %make original Excel column into 'x', : = all the rows,
MgO
xb = b(:,8);
xc = c(:,8);
y1 = a(:,17); %FeO
ybFeO = b(:,5);
ycFeO = c(:,5);
y2 = a(:,15); %Fe2O3
ybFe2O3 = b(:,4);
ycFe2O3 = c(:,4);
yFeT = a(:,17) + a(:,15)*0.8998; %FeO*, I'm hoping this works
ybFeOT = b(:,6);
ycFeOT = c(:,6);
yTi = a(:,13); %TiO2
ybTi = b(:,2);
ycTi = c(:,2);
y4 = a(:,12); %SiO2
ybSi = b(:,1);
ycSi = c(:,1);
y5 = a(:,14); %Al2O3
ybAl = b(:,3);
ycAl = c(:,3);
y6 = a(:,22); %CaO
ybCa = b(:,9);
ycCa = c(:,9);
y7 = a(:,23); %Na2O
ybNa = b(:,10);
ycNa = c(:,10);
y8 = a(:,24); %K2O
ybK = b(:,11);
ycK = c(:,11);
y9 = a(:,26); %H2O
ybH2O = b(:,18);
ych2O = c(:,18);
for o=1:rowA
    yCaAl(o,1) = y6(o,1)/y5(o,1); %CaO/Al2O3
end
for o=1:rowB
    ybCaAl(o,1) = ybCa(o,1)/ybAl(o,1); %CaO/Al2O3
end
for o=1:rowC
    ycCaAl(o,1) = ycCa(o,1)/ycAl(o,1); %CaO/Al2O3
end

figure('Name','One Diagram')

hold on

```

```

plot(x,y1)
plot(x,y2)
plot(x,yFeT)
plot(x,yTi)
plot(x,y4)
plot(x,y5)
plot(x,y6)
plot(x,y7)
plot(x,y8)
plot(x,y9)
xlabel('MgO wt%')
ylabel('oxide wt%')
axis([0 10 0 inf]) %sets limits for x axis (min max) and then y
axis
for n=3:column
    for m=1:rowA
        if a(m,2) == num(1,n-1)
            mineralName = [raw(1,n),'\downarrow'];
            if mod(m,2) == 0
                text(a(m,19),5,mineralName);
            else
                text(a(m,19),10,mineralName);
            end
        end
    end
end
lgd
legend('FeO','Fe2O3','FeO*','TiO2','SiO2','Al2O3','CaO','Na2O','K
2O','H2O','Location','eastoutside');

hold off

%figure('Name','CaO/Al2O3')
%hold on
%plot(x,yCaAl)
%scatter(xb,ybCaAl,...
%         'MarkerEdgeColor',[0.4666666668653488    0.674509823322296
0.18823529779911])
%hold on
%scatter(xc,ycCaAl,...
%         'MarkerFaceColor',[0.850980401039124    0.325490206480026
0.0980392172932625],...
%         'MarkerEdgeColor','none',...
%         'Marker','diamond')
%hold off
%hold off
%xlabel('MgO wt%')
%ylabel('CaO/Al2O3 wt%')
%lgd2 = legend('CaO/Al2O3','Location','eastoutside');
%disp(yCaAl)

%The REAL plots
figure('Name','Stacked Diagrams')
FeO = subplot(3,4,9); %(rows,column,position)

```

```

hold on
plot(FeO,x,y1)
scatter(FeO,xb,ybFeO,...
        'MarkerEdgeColor',[0.466666668653488
0.18823529779911])
0.674509823322296
hold on
scatter(FeO,xc(1:44),ycFeO(1:44),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
0.325490206480026
hold on
scatter(FeO,xc(45:55),ycFeO(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
0.325490206480026
hold on
scatter(FeO,xc(56:71),ycFeO(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
0.325490206480026
hold off
hold off
hold off
hold off
ylabel(FeO,'FeO wt%')
xlim(FeO,[0 10])
ylim(FeO,[4 12])

Fe2O3 = subplot(3,4,5);
hold on
plot(Fe2O3,x,y2)
scatter(Fe2O3,xb,ybFe2O3,...
        'MarkerEdgeColor',[0.466666668653488
0.18823529779911])
0.674509823322296
hold on
scatter(Fe2O3,xc(1:44),ycFe2O3(1:44),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
0.325490206480026
hold on
scatter(Fe2O3,xc(45:55),ycFe2O3(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
0.325490206480026
hold on
scatter(Fe2O3,xc(56:71),ycFe2O3(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
0.325490206480026

```

```

        'Marker', 'hexagram')
hold off
hold off
hold off
hold off
ylabel(Fe2O3, 'Fe2O3 wt%')
xlim(Fe2O3, [0 10])
ylim(Fe2O3, [0 5])

FeOT = subplot(3,4,1);
hold on
plot(FeOT,x,yFeT)
scatter(FeOT,xb,ybFeOT,...
        'MarkerEdgeColor',[0.4666666668653488
0.18823529779911])
hold on
scatter(FeOT,xc(1:44),ycFeOT(1:44),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
hold on
scatter(FeOT,xc(45:55),ycFeOT(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter(FeOT,xc(56:71),ycFeOT(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
hold off
hold off
hold off
hold off
xlabel(FeOT, 'MgO* wt%')
ylabel(FeOT, 'FeO* wt%')
xlim(FeOT, [0 10])
ylim(FeOT, [6 12])

TiO2 = subplot(3,4,3);
hold on
plot(TiO2,x,yTi)
scatter(TiO2,xb,ybTi,...
        'MarkerEdgeColor',[0.4666666668653488
0.18823529779911])
hold on
scatter(TiO2,xc(1:44),ycTi(1:44),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')

```

```

hold on
scatter(TiO2,xc(45:55),ycTi(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter(TiO2,xc(56:71),ycTi(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
hold off
hold off
hold off
hold off
ylabel(TiO2,'TiO2 wt%')
xlim(TiO2,[0 10])
ylim(TiO2,[1.5 4])

SiO2 = subplot(3,4,2);
hold on
plot(SiO2,x,y4)
scatter(SiO2,xb,ybSi,...
        'MarkerEdgeColor',[0.4666666668653488
0.18823529779911])
hold on
scatter(SiO2,xc(1:44),ycSi(1:44),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
hold on
scatter(SiO2,xc(45:55),ycSi(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter(SiO2,xc(56:71),ycSi(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
hold off
hold off
hold off
hold off
ylabel(SiO2,'SiO2 wt%')
xlim(SiO2,[0 10])
ylim(SiO2,[45 51])

Al2O3 = subplot(3,4,6);
hold on

```

```

plot (Al2O3,x,y5)
scatter (Al2O3,xb,ybAl,...
        'MarkerEdgeColor',[0.466666668653488
0.18823529779911])
hold on
scatter (Al2O3,xc(1:44),ycAl(1:44),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
hold on
scatter (Al2O3,xc(45:55),ycAl(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter (Al2O3,xc(56:71),ycAl(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
hold off
hold off
hold off
hold off
ylabel (Al2O3,'Al2O3 wt%')
xlim (Al2O3,[0 10])
ylim (Al2O3,[15 20])

CaO = subplot(3,4,10);
hold on
plot (CaO,x,y6)
scatter (CaO,xb,ybCa,...
        'MarkerEdgeColor',[0.466666668653488
0.18823529779911])
hold on
scatter (CaO,xc(1:44),ycCa(1:44),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
hold on
scatter (CaO,xc(45:55),ycCa(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter (CaO,xc(56:71),ycCa(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')

```



```

hold off
hold off
hold off
hold off
ylabel(CaO, 'CaO wt%')
xlabel(CaO, 'MgO wt%')
xlim(CaO, [0 10])
ylim(CaO, [6 12])

Na2O = subplot(3,4,7);
hold on
plot(Na2O,x,y7)
scatter(Na2O,xb,ybNa,...
        'MarkerEdgeColor',[0.466666668653488      0.674509823322296
0.18823529779911])
hold on
scatter(Na2O,xc(1:44),ycNa(1:44),...
        'MarkerFaceColor',[0.850980401039124      0.325490206480026
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
hold on
scatter(Na2O,xc(45:55),ycNa(45:55),...
        'MarkerFaceColor',[0.850980401039124      0.325490206480026
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter(Na2O,xc(56:71),ycNa(56:71),...
        'MarkerFaceColor',[0.850980401039124      0.325490206480026
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
hold off
hold off
hold off
hold off
ylabel(Na2O, 'Na2O wt%')
xlim(Na2O, [0 10])
ylim(Na2O, [2 6])

K2O = subplot(3,4,11);
hold on
plot(K2O,x,y8)
scatter(K2O,xb,ybK,...
        'MarkerEdgeColor',[0.466666668653488      0.674509823322296
0.18823529779911])
hold on
scatter(K2O,xc(1:44),ycK(1:44),...
        'MarkerFaceColor',[0.850980401039124      0.325490206480026
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')

```

```

hold on
scatter(K2O,xc(45:55),ycK(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter(K2O,xc(56:71),ycK(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
hold off
hold off
hold off
hold off
ylabel(K2O,'K2O wt%')
xlabel(K2O,'MgO wt%')
xlim(K2O,[0 10])
ylim(K2O,[0 3.5])

H2O = subplot(3,4,4);
hold on
plot(H2O,x,y9)
scatter(H2O,xb,ybH2O,...
        'MarkerEdgeColor',[0.4666666668653488
0.18823529779911])
hold on
scatter(H2O,xc(1:44),ych2O(1:44),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
hold on
scatter(H2O,xc(45:55),ych2O(45:55),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter(H2O,xc(56:71),ych2O(56:71),...
        'MarkerFaceColor',[0.850980401039124
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
hold off
hold off
hold off
hold off
ylabel(H2O,'H2O wt%')
xlim(H2O,[0 10])
ylim(H2O,[0 4])

CaOAl2O3 = subplot(3,4,8);

```

```

hold on
plot(CaOAl2O3,x,yCaAl)
scatter(CaOAl2O3,xb,ybCaAl,...
        'MarkerEdgeColor',[0.4666666668653488      0.674509823322296
0.18823529779911])
hold on
scatter(CaOAl2O3,xc(1:44),ycCaAl(1:44),...
        'MarkerFaceColor',[0.850980401039124      0.325490206480026
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','diamond')
hold on
scatter(CaOAl2O3,xc(45:55),ycCaAl(45:55),...
        'MarkerFaceColor',[0.850980401039124      0.325490206480026
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','pentagram')
hold on
scatter(CaOAl2O3,xc(56:71),ycCaAl(56:71),...
        'MarkerFaceColor',[0.850980401039124      0.325490206480026
0.0980392172932625],...
        'MarkerEdgeColor','none',...
        'Marker','hexagram')
hold off
hold off
hold off
hold off
ylabel(CaOAl2O3,'CaO/Al2O3 wt%')
xlabel(CaOAl2O3,'MgO wt%')
xlim(CaOAl2O3,[0 10])
ylim(CaOAl2O3,[0 1])

legendTile = legend('model','Whole Rock','Pisgah MI','Pisgah
Matrix','Pisgah Embayment','Location',[0.743711988775134
0.235646623094841 0.128661085621582 0.0744849425488153]);

```

GA.7. References

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- Gualda G.A.R., Ghiorso M.S., Lemons R.V., Carley T.L. (2012) Rhyolite-MELTS: A modified calibration of MELTS optimized for silica-rich, fluid-bearing magmatic systems. *Journal of Petrology*, 53, 875-890.