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Physical parameters based on Fe-Ti oxide compositions and their correlation with geochemical signatures of mid-Miocene rhyolites, eastern Oregon

by

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An undergraduate honors thesis submitted in partial fulfillment of the

requirements for the degree of

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and

Geology

Thesis Adviser

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ABSTRACT

Eastern Oregon rhyolites are understood to be associated, spatially and temporally, with the main phase of the Columbia River flood basalt volcanism extending from 16.8 Ma to 15.9 Ma. This study focuses on rhyolitic units found between John Day and Burns, Oregon. While these rhyolites do not cover a wide extent and all erupted within a relatively short period of time, they vary widely in their chemical composition. Some of the rhyolites in this area are classified as A-type, according to the geochemical definition set forth by Whalen and others in 1989, while others are classified as Calc-alkaline (or I) types. Classifying the rhyolites in such a way implies that the chemical variance between the rhyolites is due to a difference in tectonic origin. However, the significantly small spatial and temporal distribution of their emplacement suggests otherwise. To investigate their source and evolution further, I estimate the temperature and oxygen fugacity of their magmas using the Fe-Ti Oxide thermobarometer by Ghiorso and Evans (2008). I compare the estimations between rhyolites designated as A-type, Calc-alkaline type, and a classification I created named 'Borderline'. Characterizing the physical conditions of each of these rhyolites aids in understanding the overall magmatic environment in the region. Using the compositions of titanomagnetite and ilmenite, I estimate that the A-type rhyolites in this region are on average slightly more reduced than Calc-alkaline types. However, all the rhyolites fall within a similar temperature and oxygen fugacity range of $\sim 700\text{-}1100$ °C and $\pm 1 \Delta \text{NNO} \log f\text{O}_2$. Since the rhyolites in eastern Oregon are estimated to form in similar physical conditions, then I cannot support the presumption that the A-type and Calc-alkaline rhyolites are formed by distinctly different processes based on this method. The variation in $f\text{O}_2$ between the types of rhyolites may suggest differing magmatic histories.

INTRODUCTION

Oregon is home to silicic volcanism extending from the Nevada-Oregon border to eastern Idaho and into northeastern Oregon (Figure 1). Recent studies suggest that this magmatic activity may not be formed through intra-plate rifting, but rather associated with the Columbia River Flood Basalt volcanism (Cummings et al., 2000; Hooper et al., 2002, 2007; Camp and Ross, 2004; Pierce and Morgan, 2009). The rhyolitic centers between Baker City and Crowley, Oregon erupted between 17.0 Ma and 15.5 Ma (Streck et al., 2015). Although the rhyolites we find in this area erupted in a relatively short time frame, they vary significantly in chemical composition.

The bulk geochemical signatures of eastern Oregon rhyolites can be defined by the SIAM (Sedimentary – Igneous – Anorogenic – Mantle) granitoid classification compiled in the later 20th century by various researchers (Chappell and White, 1974; Loiselle, M.C.; Wones, 1979; Didier et al., 1982; Whalen et al., 1987). For the purposes of this study, we will classify eastern Oregon rhyolites as either A-type or Calc-alkaline type (I- and S-) type rhyolites. A-type rhyolites, meaning anorogenic, are considered to form in intra-plate tectonic zones similar to the Yellowstone hotspot. Calc-alkaline type rhyolites are conversely considered to form in volcanic arc or subduction dominated tectonic zones (Whalen et al., 1987). Thus, forms our question – why do we see a geochemical range encompassing both types of rhyolites within a similar spatial and temporal area?

To better understand the variation in rhyolite geochemistry within this region, this study estimates the physical parameters of the rhyolitic centers using the iron-titanium Two-Oxide thermo-oxybarometer model (Ghiorso and Evans, 2008). We focus on how these physical parameters, such as temperature and oxygen fugacity (fO_2), may correlate with the bulk geochemical signatures of a given rhyolite. The fO_2 can be equated to the partial pressure of oxygen and therefore the water content of the magma. A-type rhyolites are understood to form from hot and dry magmas whereas Calc-alkaline rhyolites would form from cool and wet magmas due to their associated tectonic province of origin (Whalen et al., 1987). Therefore, the A-type rhyolites in the region should record increased temperatures and lower fO_2 while Calc-alkaline rhyolites should record lower temperatures and higher oxygen content or fO_2 .

GEOLOGIC CONTEXT

The rhyolites of interest reside in eastern Oregon (Figure 2). This region has experienced a complex geologic history involving multiple events such as interaction of the subduction zone and subsequent back-arc rifting, the Yellowstone hotspot, and the silicic and mafic volcanism extensive throughout the region (Cummings et al., 2000; Hooper et al., 2002, 2007; Camp and Ross, 2004; Pierce and Morgan, 2009; Coble and Mahood, 2012).

Tectonics

The Juan de Fuca plate began subducting beneath the North American plate nearly 40 million years ago. Prior to that, the accretion of terranes onto the North American continent led to the migration of the convergent plate boundary from the western edge of Idaho to the western edge of Oregon and Washington. This accreted crust of Oregon and Washington is relatively thin compared to the cratonic crust to the east (Hooper et al., 2007). The oblique subduction of the

Juan de Fuca plate results in north-south compression and consequently east-west extension, thinning the upper crust even further (Hooper et al., 2007).

A mantle plume, known as the Yellowstone hotspot, made contact with the base of the lithosphere underlying Oregon and Washington approximately 17 million years ago (Camp and Ross, 2004; Hooper et al., 2007; Pierce and Morgan, 2009). The head of the mantle plume pierced through the subducting Juan de Fuca plate, which initiated melting resulting in the extensive flood basalt volcanism (Camp and Ross, 2004; Hooper et al., 2007; Pierce and Morgan, 2009). The plume head was later sheared off and pushed along by the subducting plate to create the Yellowstone hotspot track (Pierce and Morgan, 2009).

Flood Basalt Volcanism

The Columbia River flood basalts cover Washington, Oregon, and Idaho in one of the largest outpourings of basalt in a distinctly short amount of time (Figure 1). Nearly all of the basalt erupted between 16.6 Ma and 14 Ma (Camp and Ross, 2004).

The main phase of mafic volcanism lasted from 16.8 Ma to 15.9 Ma and accounts for the majority of the erupted basalt. The Steens Basalt is the oldest of the Columbia River Basalt Group (CRBG) in southeastern Oregon. The Imnaha Basalt covered 50,000 km² of the northeastern Columbia River province from 16.5-15 Ma (Hooper et al., 2007). The Grande Ronde basalt, which is stratigraphically younger than the Imnaha Basalt, was emplaced around the same time and accounts for 60% of the overall flood basalt volume in the PNW. It is composed of tholeiitic basaltic andesites and spans multiple paleo-magnetic intervals (Hooper et al., 2007). Picture Gorge Basalt is thought to mark the end of the main phase of mafic volcanism in the area. It was emplaced over a fairly constricted area in the John Day basin covering 10,680 km² (Hooper et al., 2007).

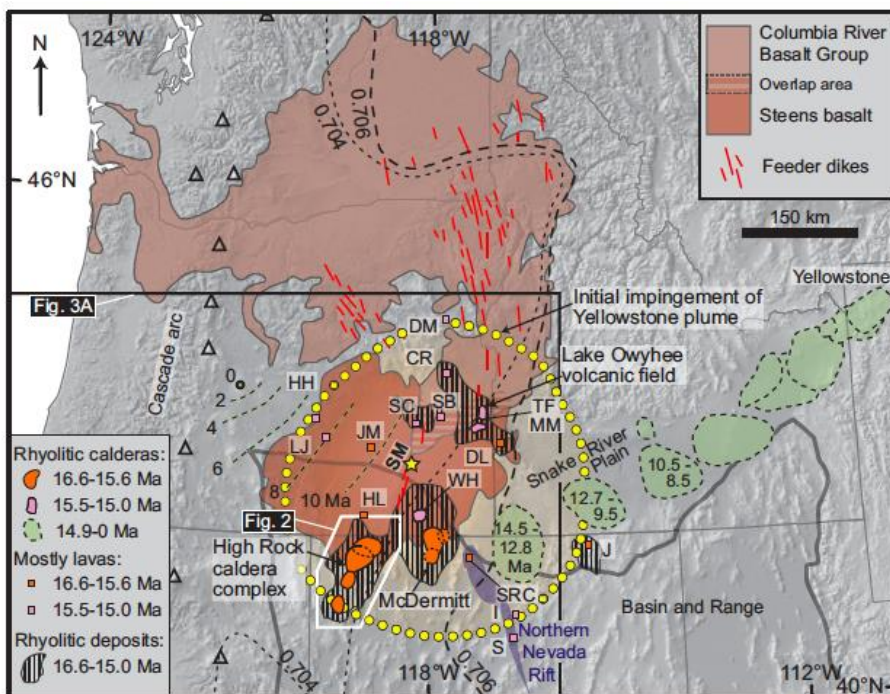


Figure 1: Distribution of basaltic and silicic volcanism in Oregon, Idaho, and Washington in relation to the Yellowstone hotspot track taken from Coble and Mahood (2012). The yellow circle is the approximate location of the plume head during the initial flood basalt eruptions. The orange and pink shaded circles are the centers for the rhyolites of interest. CR – Castle Rock; DL – DeLamar; DM – Dooley Mountain; HH – Horsehead Mountain; HL – Hawks Valley; I – Ivanhoe; J – Jarbidge Rhyolite; JM – Jackass Mountain; LJ – Little Juniper Mountain; MM – Mahogany Mountain; S – Sheep Creek Range; SB – Saddle Butte; SRC – Santa Rosa-Calico; TF – Three Fingers caldera; WH – Whitehorse.

Ekler Mountain Basalt erupted during a time of volcanic quiescence and over a smaller area compared to previous basalt flows. Larger eruptions return with the Wanapum Basalts emplaced from 15.3 to 14.5 Ma. The Saddle Mountain basalt flows, emplaced from 14.5 to 6 Ma, mark the end of mafic volcanism in the Columbia River region (Hooper et al., 2007).

Silicic Volcanism

Roughly 39,000 km³ of magma erupted from the silicic volcanic centers High Rock, McDermitt, and Lake Owyhee from 17.0 Ma to 15.5 Ma, roughly coeval with the main phase CRBG flows (Coble and Mahood, 2012). The erupted units from these centers account for 90% of the silicic volcanism in the region. The flows from the Lake Owyhee volcanic field are metaluminous to weakly peralkaline and account for 1115 km³ of the rhyolite and tuff emplaced. The McDermitt volcanic center erupted from 16.4 to 15.7 Ma and consists of peralkaline rhyolite (Coble and Mahood, 2012).

Recent studies have suggested that the silicic volcanism in the region is more related to the coeval flood basalts than initially thought (Coble and Mahood, 2012; Ferns and McClaughry, 2013; Streck et al., 2015). Rhyolites in the region erupted within the same stratigraphic interval and similar chemical traces (Streck et al., 2015).

GRANITOID GEOCHEMICAL CLASSIFICATION

Granitoid Types

The rhyolites of eastern Oregon can be geochemically defined using the SIAM granitoid classification originally based on the tectonic and petrographic source descriptions of the rock. This classification scheme came about because the traditional TAS and IUGS diagrams did not adequately display the variations in metals and trace elements that may provide greater insight into the origin of these melts.

The S-type (Sedimentary-type) and I-type (Igneous-type) granitoids, also known as Calc-alkaline granitoids, are orogenic rocks thought to form from melting of sedimentary and igneous source rocks respectively (Chappell and White, 1974, 2001). The M-type or mantle-type granitoids are thought to originate from mantle interaction processes (Didier et al., 1982). The A-type or ‘anorogenic’ type granitoids are thought to form in intra-continental zones or anorogenic tectonic environments (Loiselle, M.C.; Wones, 1979). Since A-type granites were first termed, they have also been referred to as alkaline and anhydrous granitoids (Whalen et al., 1987).

These classifications have since been defined in greater geochemical detail rather than simply the tectonic environment in which it is discovered in. Each granitoid type has a general range of major and trace element compositions that can be measured and distinguished. Since these classifications were first identified through petrographic means, the geochemical ranges do overlap some. The granitoids of interest in this study are the Calc-alkaline and the A-type granitoids. These are the most abundant in eastern Oregon, and as such, we will focus on the ways that their physical and chemical characteristics vary.

More recent work has shown what is classified as an A-type does not always occur in interior or extensional settings (Whalen et al., 1987). Instead, the high temperatures at which these rhyolites must form at suggest that partial melting is involved; however, this cannot entirely explain the chemical diversity observed. The Calc-alkaline types are understood to form as ‘cool and wet’ melts as opposed to the ‘hot and dry’ A-type magmas.

A-type rhyolites tend to be more silicic than Calc-alkaline types, however, highly fractionated I- and S-type rhyolites may resemble A-type characteristics. A-types have higher $Ga*1000/Al$ ratios in tandem with high major and trace element contents that include $Fe^{2+/3+}$, Zr^{4+} , $Nb^{2+/4+}$, Y^{3+} , and Ce^{4+} . These rhyolites characteristically have high field strength ions due to forming in hotter and dryer conditions (Whalen et al., 1987). Calc-alkaline rhyolites are less chemically diverse than their A-type counterparts, and thus contain less high field strength ions. Investigations into hydrous mineral content and iron content suggest that A-type magmas have low water content and thus low oxygen fugacity (Loiselle, M.C.; Wones, 1979; Whalen et al., 1987).

Classification Methods

The rhyolites in eastern Oregon involved in this study have yet to be definitively classified as either A-type or Calc-alkaline rhyolites (Figure 2). For the purposes of understanding how the physical and chemical characteristics of these two types vary in the region, we will use the chemical classification scheme as laid out by Whalen and others (1987). They suggest that high $Ga*1000/Al$ ratios are insufficient to truly distinguish the two types. Whalen and others suggest also using major and trace element variation diagrams. The trace element concentrations of Zn^{2+} , Zr^{4+} , $Nb^{2+/4+}$, Y^{3+} , and Ce^{4+} are important in distinguishing A-type and Calc-alkaline type rhyolites (Whalen et al., 1987). These elements and element ratios will be higher in A-types relative to Calc-alkaline types.

Eastern Oregon Rhyolites

Other studies have also used the Whalen compositional framework to classify rhyolites in this area (Hess, 2014; Streck, 2014; Streck et al., 2015). The rhyolite samples were collected in eastern Oregon (Figure 2).

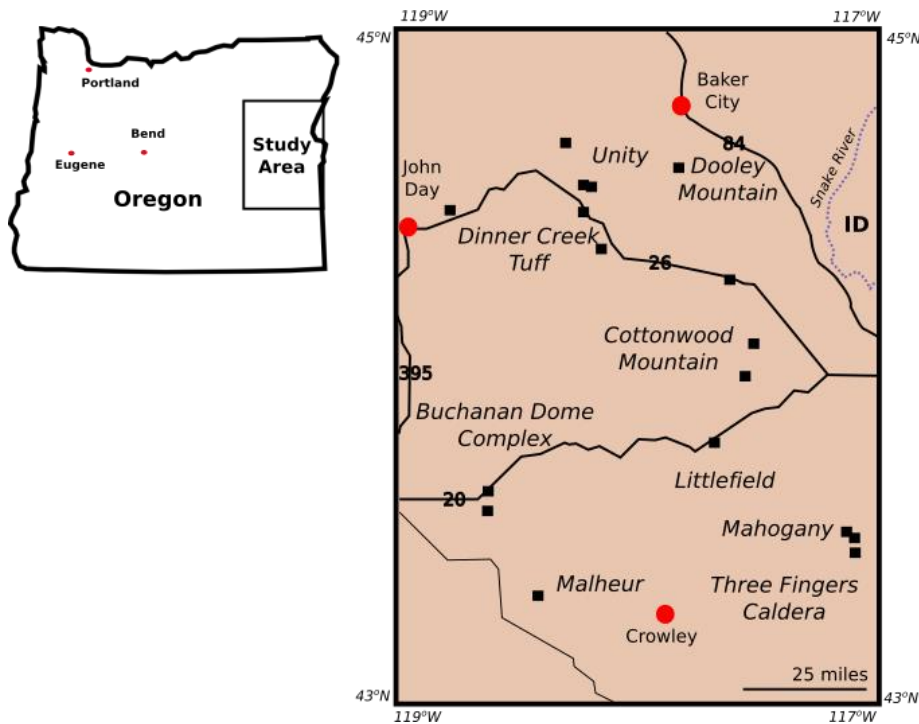


Figure 2: Locations of samples taken from nine total rhyolitic centers in eastern Oregon between Baker City and Crowley. Number of samples taken from each center: Unity (3), Dooley Mountain (1), Dinner Creek Tuff (4), Cottonwood Mountain (2), Buchanan Dome Complex (2), Littlefield (1), Mahogany (3), Three Fingers Caldera (1), Malheur (1). Samples collected between 2008-2014 and are listed in Table 1.

Table 1: List of samples collected between 2008-2014 used in this study. Collection sites shown in Figure 2.

Sample ID	Center	Unit	Unit ID
EJ-12-05B	Malheur	Circle Bar Rhyolite	CBR
CR-U35A	Dinner Creek	Dinner Creek Tuff	DIT
MS-11-20	Dinner Creek	Dinner Creek Tuff	DIT
MS-12-29.1	Dinner Creek	Dinner Creek Tuff	DIT
MS-PCIT 1-A	Dinner Creek	Dinner Creek Tuff	DIT
MS-08-DR2	Dooley	Dooley Mountain Rhyolite	DMR
EJ-12-10	Littlefield	Littlefield	LIR
EJ-12-12	Three Fingers	Old McIntyre Ridge Rhyolite	OMR
EJ-12-16	Cottonwood	Cottonwood	CMR
EJ-12-17	Cottonwood	Rhyolite of Bully Creek	RBC
B010	Buchanan	Buchanan Dome Complex	BDC
B114	Buchanan	Buchanan Dome Complex	BDC
CR-U3A	Unity	Unity	UNI
CR-U4B	Unity	Unity	UNI
MS-12-14b	Unity	Unity	UNI
MS-11-15	Mahogany	Spring Creek Tuff	SCT
MS-13-29	Mahogany	Spring Creek Tuff	SCT
MS-13-24b	Mahogany	Young McIntyre Ridge Rhyolite	YMR

Using the classification scheme defined by Whalen and others (1987) we can split these rhyolites into three categories: A-type, Calc-alkaline type, and ‘Borderline’. The original classification does not include this ‘Borderline’ type in the framework, however some rhyolites display A-type and Calc-alkaline type signatures based on which chemical variation diagram is utilized. Therefore, Borderline indicates that a rhyolite is more difficult to chemically classify and lies in a sort of intermediate zone (Figure 3).

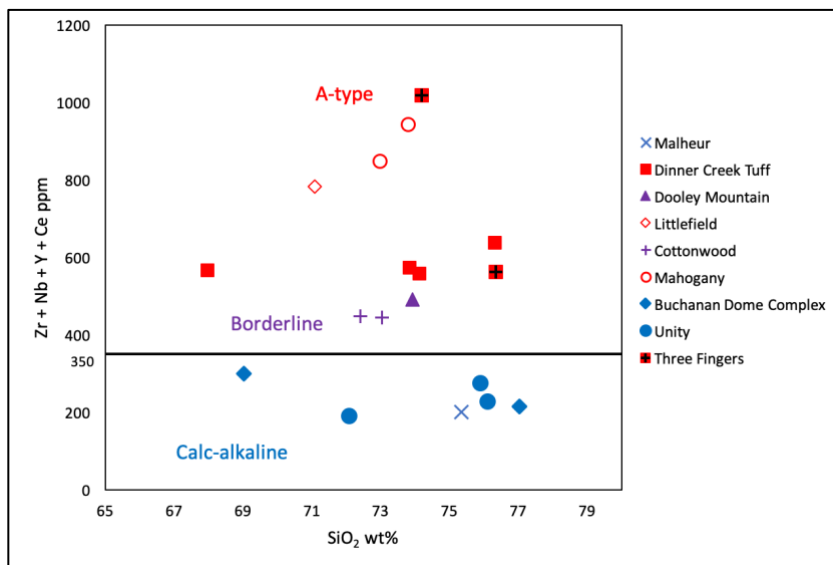


Figure 3: Classifying rhyolites of this study using the bulk concentration of trace elements such as cerium, ytterbium, zinc, and zirconium versus the silica content. A-types are defined as those with a combined trace element concentration greater than 350 ppm shown as the black line. (Whalen et al., 1987). The red color indicates the samples classified as A-type. The purple color indicates the samples classified as Borderline type. The blue color indicates the samples classified as Calc-alkaline type. The shapes are described in the legend where each sample is classified by the rhyolitic center it originates from. A similar symbology is used throughout the rest of the report.

The final classification of rhyolites that will be consistently used throughout the rest of this study are shown in Table 2. The A-types were determined to lie within the geochemical field of the A-types as defined by Whalen and others more than half of the time while the borderline types straddled the line between A-type and Calc-alkaline type.

Table 2: Final classification of samples used in this study. Final classification determined using multiple methods from Whalen and others (only one method shown in Figure 3). (Whalen et al., 1987)

Sample ID	Unit	Classification
EJ-12-05B	CBR	Calc-alkaline
EJ-12-10	LIT	A-type
EJ-12-12	OMR	A-type
EJ-12-16	RCM	borderline
EJ-12-17	RBC	borderline
CR-U3A	UNI	Calc-alkaline
CR-U4B	UNI	Calc-alkaline
MS-12-14b	UNI	Calc-alkaline
CR-U35A	DIT	A-type
MS-PCIT 1-A	DIT	borderline
MS-12-29.1	DIT	A-type
MS-11-20	DIT	borderline
MS-08-DR2	DMR	borderline
MS-11-15	SCT	A-type
MS-13-29	SCT	A-type
MS-12-24B	YMR	A-type
B010	BDC	Calc-alkaline
B114	BDC	Calc-alkaline

METHODS

Sample Collection

Bulk samples of the rhyolite and tuff were collected by Emily Hess, Martin Streck, and Chris Ricker from 2008-2014 (Figure 2). The bulk samples were crushed and sieved to separate fragments smaller than 120 μ m. A magnet was used to separate iron-rich minerals that were then mounted on a thin-section slide with epoxy. Four samples were mounted and polished on each slide to expose a flat surface suitable for analytical analysis. Fifteen samples were adequately exposed to analyze on the electron microprobe (EMP).

Analytical Analysis

The Zeiss Sigma VP FEG SEM located at Portland State University was used to identify, locate, and image iron-titanium crystals ideally with titanomagnetite and ilmenite in close contact. Then, the compositions of oxides from 10 samples (MS-PCIT 1-A, B010, B114, MS-12-14B, MS-11-15, MS-11-20, MS-13-29, MS-12-24B, EJ-12-17, EJ-12-05, CR-U35A, CR-U4B,

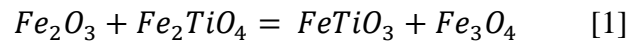
B114, B010) were measured on the Cameca SX100 at the University of Oregon. The EMP analyses were completed during one session at a remote-control location in Portland State University to measure oxide compositions from the mineral separates collected from 10 samples. The beam current for this session was 30nA with a high voltage of 15kV. The major elements we measured for were Fe* and Ti⁴⁺ calibrated against magnetite and ilmenite respectively. We also analyzed for minor elements including Mg²⁺, Al³⁺, Zn²⁺, Cr³⁺, Ca²⁺, Mn²⁺, Si⁴⁺, Na⁺, and V³⁺ calibrated to forsterite, gahnite, chromite, augite, pyroxmangite, anorthoclase, and vanadinite respectively.

Oxide minerals were chosen for analysis based on the previous investigations using the SEM, the polish, and size of the oxide. Points of analysis were chosen to avoid pits in the mineral from polishing errors and rims of crystals that appeared to be altered.

The Iron-Titanium Oxide Model

The thermodynamic model used, the Fe-Ti Oxide model, estimates the temperature and fO_2 of the system when titanomagnetite and ilmenite are at equilibrium (Ghiorso and Evans, 2008). The Fe-Ti Oxide model is based off of the experimental investigations into titanomagnetite and ilmenite phase equilibria by Buddington and Lindsley (1964). These initial investigations show that the chemical compositions of titanomagnetite and ilmenite, in equilibrium, will respond to changing temperature and fO_2 in a predictable way (Buddington and Lindsley, 1964). Using this relationship, they developed the reverse model; where if the composition of titanomagnetite and ilmenite, in close contact and thus assumed to be at equilibrium, is known, then the temperature and fO_2 of the system can be estimated.

The framework for the computational model was first created in 1991 by Ghiorso and Sack where the molar proportions of the ulvöspinel-magnetite solid solution and the hematite-ilmenite solid solutions were used to determine the temperature and the oxygen fugacity of the system assuming equilibrium is reached using the reaction listed below [1].



hematite + ulvöspinel = ilmenite + magnetite

Recently, Ghiorso and Evans (2008) developed a computational model that would more easily and efficiently estimate temperature and oxygen fugacity while taking into account more diverse cations that may be present in the mineral structure and what this may indicate about the equilibrium conditions.

To ensure the two oxides used are in equilibrium, we apply the equilibrium test developed by Bacon and Hirschmann (1988). The test is based on the exchange reaction and equilibrium coefficient (K_D) below [2,3].



$$K_D = (Mg_{mt}/Mn_{mt}) / (Mg_{il}/Mn_{il}) \quad [3]$$

where magnesium and manganese are exchanging in equal amounts during the equilibrium process (Bacon and Hirschmann, 1988). Through applying this concept to real oxide pairs, they developed a regression that most oxide pairs should fall into.

$$\log(Mg_{mt}/Mn_{mt}) = 0.9317(Mg_{il}/Mn_{il}) - 0.0909 \quad [4]$$

Any oxide pair that lies significantly outside of the field of this regression can be assumed to not be in equilibrium.

RESULTS

Compositional Range of Oxides

Oxide chemical compositions were measured using EPMA in a total of 12 samples from seven centers (Buchanan, Mahogany, Dinner Creek, Cottonwood, and Unity). The oxides from these centers display a wide range of compositions (Figure 4).

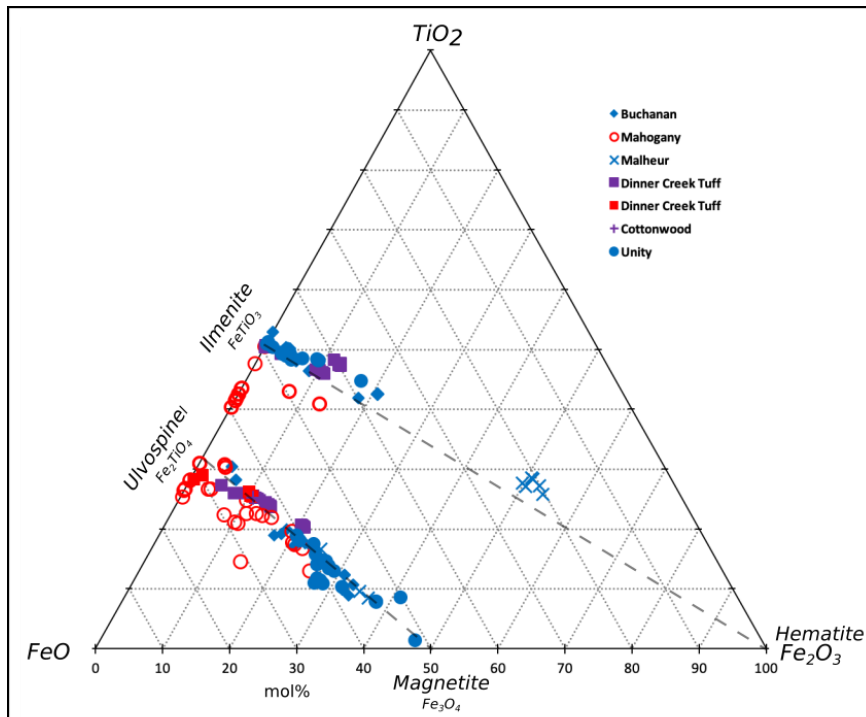


Figure 4: Range of present oxide compositions measured from 12 samples from seven centers. The centers include Buchanan (2 samples), Mahogany (3), Malheur (1), Dinner Creek Tuff (3), Cottonwood (1), and Unity (2). The dashed lines overlaying the ternary diagram show the solid solutions for the ulvöspinel-magnetite system and the hematite-ilmenite system. Red: A-type; Purple: Borderline type; Blue: Calc-alkaline type.

Titanomagnetite oxides and ilmenite oxides are distinguished by their titanium ratios within a given sample where ilmenite oxides will contain higher amounts of TiO_2 . The FeO/Fe_2O_3 ratio was determined using the Carmichael (1967) recalculation. Ilmenites should contain an equal amount of FeO^* and TiO_2 whereas titanomagnetites will contain significantly lower amounts of TiO_2 in a 1:2 ratio to the amount of total iron. In some cases, a sample did not include two populations of oxides with distinct TiO_2 content and instead only contained one oxide or a solution of the two. Samples with only one oxide population present cannot be used in the Fe-Ti Oxide model.

When using the Bacon and Hirschmann (1988) equilibrium test, we see that most of the oxide pairs found are not in equilibrium (Figure 5).

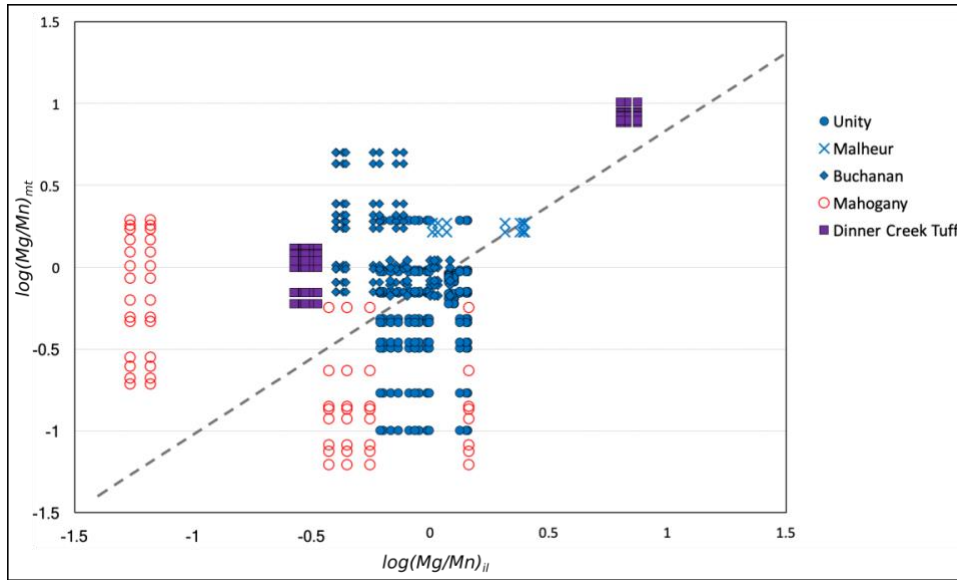


Figure 5: Application of equilibrium test based off the work of Bacon, and Hirschmann (1988). The samples with oxide pairs shown here include rhyolites from Unity (2), Malheur (1), Buchanan (2), Mahogany (2), and Dinner Creek (2). The dashed line is the linear fit provided by the work of Bacon and Hirschmann (1988) which describes the relationship between the magnesium and manganese content in the oxide pair if the two are in equilibrium [4]. Red: A-type; Purple: Borderline type; Blue: Calc-alkaline type.

Oxides that fall within a reasonable range (2σ) from the regression are reasonably assumed to still be in equilibrium (Bacon and Hirschmann, 1988). The oxide pairs that do not fall within a reasonable range of this regression are assumed to not be in equilibrium or have experienced re-equilibration post-emplacment. Although an oxide pair may fall within an acceptable range of this regression, this does not guarantee equilibrium, instead this serves as the first step of a filtering process for oxide compositions. The compositions of oxide pairs determined to be in equilibrium are displayed in another ternary diagram in Figure 6.

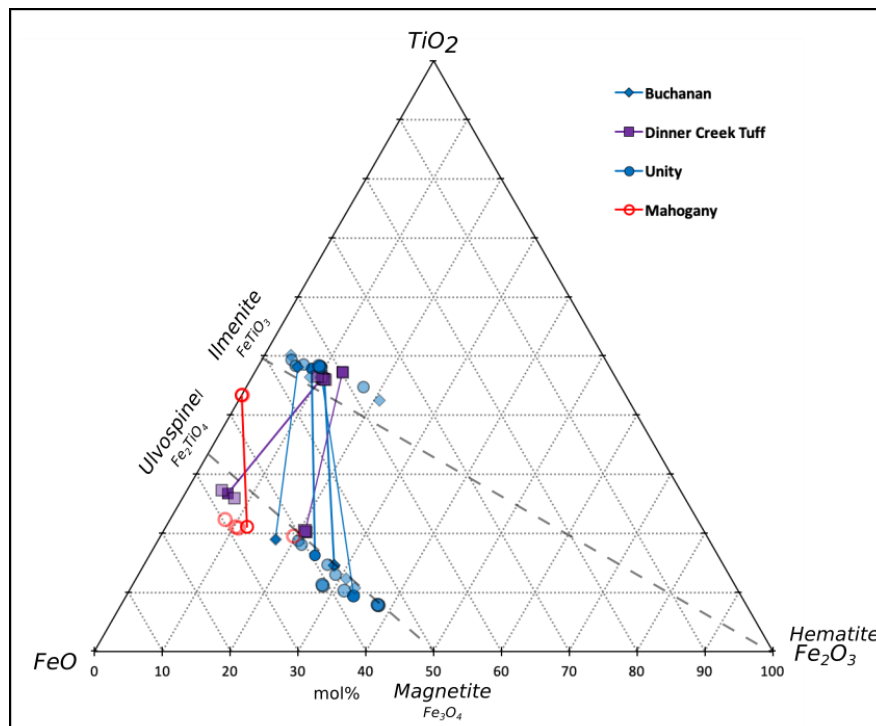


Figure 6: Range of oxide pair compositions in equilibrium. Oxide pairs in equilibrium were found in seven rhyolites from Buchanan (2), Dinner Creek Tuff (2), Unity (2), and Mahogany (1). The average oxide pair compositions from each rhyolite are shown in full color with a line tying the oxide pair together. The individual oxide compositions are shown as more transparent to show the range in a given rhyolite. The dashed lines overlaying the ternary diagram show the solid solutions for the ulvöspinel-magnetite system and the hematite-ilmenite system. Red: A-type; Purple: Borderline type; Blue: Calc-alkaline type.

The range of oxide equilibrium pair compositions is smaller than the overall oxide range, however, this range is still surprisingly high, indicating that these oxides did not always equilibrate or cease pre-eruption alteration at the same time under the same conditions (Figure 6). The Calc-alkaline rhyolites especially have a wide range of titanomagnetite compositions. The A-type rhyolite does not have as wide of a compositional range – however only one A-type sample contained an oxide pair in equilibrium and as such cannot be determined to be representative. On average, A-type oxide pairs contain higher amounts of titanium in the titanomagnetites and higher amounts of Fe²⁺ overall. The Borderline rhyolites are not as distinct as from the A-types or the Calc-alkaline rhyolites but rather fall within both ranges (Figure 6).

Within these rhyolites, it appears that the hematite endmember of the ilmenite solid solution is more common and the titanomagnetites fall more towards the ulvöspinel endmember.

Iron-Titanium Oxide Model Estimations

Oxide pair compositions determined to likely be in equilibrium were used in the Fe-Ti Oxide model to estimate the temperature and oxygen fugacity of the oxide formation, assuming equilibrium conditions (Ghiorso and Evans, 2008). Some oxide pairs used in this model resulted in a “Did not converge” reading, meaning that the resulting temperature was negative and it can be assumed that the oxide pair was not at equilibrium during formation (Ghiorso and Evans, 2008).

The resulting oxide pairs that did converge, according to the model, output a temperature in degrees Celsius and log units of oxygen fugacity relative to the Nickel-Nickel Oxide buffer. The estimations given by the model are corrected with the equation for the Ni-NiO buffer given by Frost (1991) where the pressure (*P*) is assumed to be 200MPa [5].

$$\log f_{O_2} = -\frac{24930}{T} + 9.36 + 0.046 \frac{P-1}{T} \quad [5]$$

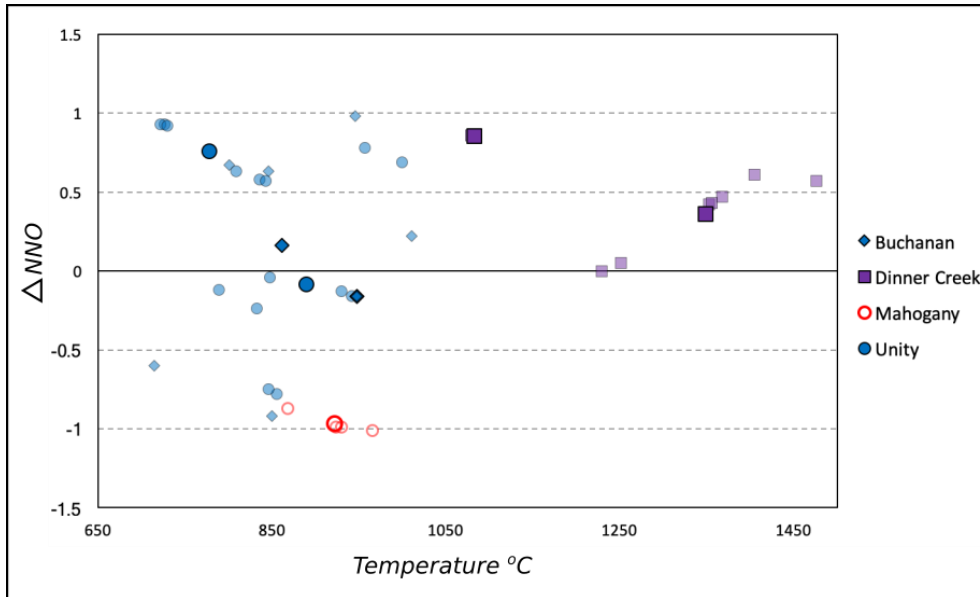


Figure 7: Fe-Ti Oxide model results displayed relative to the Ni-NiO oxygen buffer in log₁₀*f*O₂ units. The temperature and oxygen fugacity could only be estimated for the seven rhyolites containing oxide pairs in equilibrium from centers including Buchanan (2), Dinner Creek (2), Mahogany (1), and Unity (2). The average temperature and *f*O₂ estimations are shown for each sample in full color and the individual oxide pair estimations are shown as more transparent to display the range of conditions recorded. Red: A-type; Blue: Calc-alkaline; Purple: Borderline.

Some of the estimations given by the Fe-Ti Oxide model vastly overestimate the temperature. Namely, one of the samples from Dinner Creek Tuff results in temperatures exceeding 1200°C, which is highly unlikely for a rhyolite or a tuff. The sample from Dinner

Creek Tuff that displays higher temperatures is actually a dacite and may explain the higher temperature estimation. The A-type that did contain an oxide pair in equilibrium is not estimated at higher temperatures than the Calc-alkaline rhyolites, but rather falls within the same range of 650-1000°C. However, on average the A-type rhyolite is far more reduced at $\sim -1 \Delta\text{NNO}$ whereas the Calc-alkaline rhyolites fall within the -0.5 to $+1 \Delta\text{NNO}$ range.

DISCUSSION

Implication of Oxide Compositions

The oxide pair compositions do tend to correlate with the parent rock's geochemical signatures, where A-type rhyolites contain more TiO_2 in their oxides. This indicates that some traces of the overall bulk geochemical signatures are recorded in the composition of the oxide phases. The A-type rhyolites tend to not contain two phases of iron-titanium oxides, primarily only containing ulvöspinel. This suggests that the more oxidized phases of the minerals (magnetite and ilmenite) are not stable during the formation of these rhyolites, suggesting that the A-type rhyolites are in fact more reduced.

It is difficult to argue for more detailed conclusions based on the oxide compositions because of the range we have present (Figure 4). The wide range of compositions should suggest post-emplacement alteration and/or oxides out of equilibrium. However, common post-emplacement alteration would likely follow a straight line showing only an enrichment in TiO_2 and not continue to lie within the solid solution system.

This is further complicated when we see that oxide pairs that can be argued to be in equilibrium (Figure 5) still contain a wide range of compositions (Figure 6). Therefore, this suggests that the oxide pairs may have equilibrated at various points in the cooling process. Another possibility is that the pairs are not in equilibrium and a better discrimination process is needed. Given that one sample from Dinner Creek Tuff recorded temperatures close to 1400°C although the pairs are presumed to be in equilibrium, this may be the case.

Physical Conditions

The estimated temperature of the rhyolite during oxide formation is not vastly different between the A-type rhyolites and the Calc-alkaline rhyolites (Figure 7). The A-type rhyolites are estimated to form in a temperature range of 850-1000°C and the Calc-alkaline rhyolites are estimated to form in a temperature range of 650-1100°C (Figure 7). The Calc-alkaline rhyolite temperatures span the entire range of temperatures estimated for the A-type rhyolites. This may indicate that these rhyolites formed in similar conditions and under similar processes.

However, the A-type rhyolite does appear to be significantly more reduced than the Calc-alkaline rhyolites on average. This, contrary to the temperature estimations, may mean that the A-type rhyolites and the Calc-alkaline rhyolites underwent different evolution or degassing processes where the Calc-alkaline rhyolites record a higher water content.

The classical understanding and definition of A-type vs Calc-alkaline rhyolites claimed that the two rhyolites formed in distinctly different tectonic zones. A-types were assumed to originate in intra-plate tectonic provinces, such as a hotspot. Calc-alkaline rhyolites are assumed to originate in volcanic arc – subduction zone provinces. With this definition, the two rhyolites should come from magmas with distinctly different physical conditions. The Calc-alkaline rhyolites should be colder and wetter (higher f_{O_2}) due to the melting of the cold oceanic lithosphere and the water entrained into the system. The A-types, on the other hand, should be

hotter and dryer (lower fO_2) because intra-plate hot-spot provinces do not have additional water added to the system and the heat originates from the mantle rather than the melting of cold crust. We aren't able to observe a distinct difference between the temperature readings of these two rhyolites using this methodology however the oxygen fugacity tells a different story. The differing oxygen fugacity estimations, where A-types are more reduced than Calc-alkaline rhyolites, suggests that there is a sort of evolutionary distinction between the two types.

The evolution of these rhyolites cannot be singularly parsed out through the estimations given by this model and must be confirmed or improved using mineralogical investigations and separate geothermometers. The lack of ilmenite oxides in A-type rhyolites makes a study such as this even more difficult since we cannot display the full range of physical conditions that may have produced these rhyolites.

CONCLUSIONS

Physical conditions of the magmas for various rhyolites in eastern Oregon was estimated in this study using the Two-Oxide model devised by Ghiorso and Evans (2008) to ultimately correlate with the overall geochemical signatures in a given rhyolite. We determined that the oxide pair compositions, used for the Two-Oxide model, roughly correlate with the overall geochemical signatures; A-type rhyolites contain titanium enriched titanomagnetites whereas the Calc-alkaline rhyolites contained titanium enriched ilmenites and titanium depleted titanomagnetites. The temperature and oxygen fugacity estimations showed similar evidence that the evolution of the A-type and Calc-alkaline type rhyolites is different as the A-types were estimated to form at lower levels of oxygen fugacity than the Calc-alkaline type rhyolites. However, this separation may not have a linear trend with the bulk composition since the borderline rhyolites did not appear to follow a linear path from the A-type to Calc-alkaline type temperature estimations.

The temperatures estimated by the oxide compositions may overestimate a reasonable temperature range. Possible explanations for this may be post-emplacement surficial alteration or oxide disequilibrium. However, we would not expect vastly different post-emplacement processes for the two types of rhyolites meaning that the difference in oxygen fugacity between the two should be approximately preserved. Further research will attempt to account for this through more rigorous filtering of oxide data so as to only include pristine oxide pairs in close enough proximity to be in equilibrium. Further research will also explore more methods to determine or estimate the physical conditions of the rhyolites as using oxide pairs may not be reliable.

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