

AN ABSTRACT OF THE DISSERTATION OF

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Title: The Nature of Sulfate Saturation in Oxidized Arc Magmas: Implications for Magmatic Sulfur Budgets.

Abstract approved:

John H. Dilles

This dissertation is concerned with the behavior of sulfur in intermediate-silicic arc magmas associated with subduction at convergent margins. In particular it focusses on oxidized, sulfur-rich magmas, the conditions at which they might reach sulfate saturation, and implications of sulfate saturation. It is divided into an investigation of natural samples (Chapters II & III) and experimental work (Chapters IV, V and VI). It is motivated by the simple observation that magmatic-hydrothermal ore deposits, particularly porphyry Cu $\pm$ Au $\pm$ Mo deposits, contain large quantities of sulfur, and therefore require sulfur-rich magmas. Since the magmas most commonly associated with porphyry deposits have very little ability to carry dissolved sulfur species, it has been suggested that they must instead store sulfur in the form of the mineral anhydrite. Furthermore it has been suggested that anhydrite is replaced by an immiscible sulfate-melt phase at high temperature, although this has been the subject of little previous study.

In Chapter II I have used automated energy dispersive spectroscopy (EDS) mapping to identify rare inclusions of anhydrite trapped in resistant mineral phases including apatite, amphibole, plagioclase, quartz and titanite. Anhydrite inclusions are identified in samples from five different magmatic-hydrothermal ore deposits and one sulfur-rich volcanic center, suggesting that sulfate saturation may be more common in arcs than is generally thought. Electron probe microanalyzer (EPMA) measurements show that primary magmatic anhydrite has elevated Sr (>2500 ppm) and P (>500 ppm) compared to hydrothermal anhydrite, although in some cases post entrapment exchange between anhydrite and host mineral has

affected the composition. Cathodoluminescence imaging of host mineral zonation, particularly in apatite, can also be used to demonstrate that anhydrite inclusions are of igneous origin.

Analysis of apatite from the same samples (chapter III) shows that in all cases the anhydrite-bearing magmas also produced high-S apatites (>0.3 wt% S). Phenocrystic apatite and apatite inclusions were identified and analyzed by electron probe micro-analyzer (EPMA) for volatile elements (Cl, F, S) and trace elements (Sr, Ce, Na, Si). Host minerals were also analyzed for a range of major and trace elements. Despite a large range in apatite S contents ($\sim 0.05 - 0.5$ wt% S in most samples) there is little correlation between apatite S contents and various proxies for magmatic evolution (including apatite Sr content, apatite volatile content and host mineral crystallization temperature). The observed range of apatite S contents necessitates that magmas underwent either a large ($>200^\circ\text{C}$) change in temperature or the loss of sulfur to a fluid phase. That these processes were not reflected in the data suggests trends may have been obscured by reequilibration and exchange between apatite and host mineral.

The experimental work detailed in chapters IV and V investigates the relative stabilities of immiscible sulfate melt and anhydrite in arc magmas, and characterizes trace element partitioning between silicate melt and both sulfate melt and anhydrite. Experiments were conducted using piston-cylinder and gas-pressurized cold seal apparatus at conditions of $800-1200^\circ\text{C}$, $0.2-1\text{GPa}$ and $f_{\text{O}_2} > \text{NNO}+2$. Synthetic starting materials were based on trachydacite and trachyandesite composition, with 4-7 wt% H_2O and $\sim 8-10$ wt% SO_3 . Experimental results show that in most cases sulfate melt is stable and in equilibrium with anhydrite and silicate melt at temperatures $\geq 1000^\circ\text{C}$, and that it may be present at lower temperatures in alkalic or water rich melts. Furthermore, at temperatures above $\sim 1150-1200^\circ\text{C}$ sulfate melt entirely replaces anhydrite as the stable sulfate phase. EPMA measurements and mass balance calculations provide evidence that sulfate melts are dominated by CaO and SO_3 , but also contain, in order of abundance, Na_2O , K_2O , MgO , FeO , Cl and P_2O_5 .

The trace element content of sulfate melts and coexisting silicate glass, measured using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and secondary ion mass spectrometry (SIMS), is also compared to mass balance calculations. Calculated partition coefficients suggest that large 2+ cations (Ba, Sr, Ca) are particularly compatible in sulfate melts, along with F, Cl, light REE and smaller, highly charged cations Mo and W. When elements are arranged in terms of ionic potential (the ratio of nominal

charge to ionic radius, Z / r) partition coefficients have peaks at Z/r close to that of Ca and S, suggesting that the incorporation of trace elements into the sulfate melt structure is dictated by the ease with which these elements can replace the major cations. Partition coefficients are lower in experiments with more mafic silicate composition (<10 for all elements in one experiment with trachyandesite at $\sim 1200^\circ\text{C}$), and this likely related to depolymerization of the silicate melt.

Anhydrite was also analyzed for trace element composition by SIMS, and 7 sets of anhydrite (Anh) -silicate melt (Sil) partition coefficients are reported covering $900\text{-}1100^\circ\text{C}$, and $0.2\text{ - }1\text{ GPa}$. Nernst-type partition coefficients $D_i^{\text{Anh-Sil}}$ for +2 and +3 cations are a function of both the partition coefficient for Ca ($D_{\text{Ca}}^{\text{Anh-Sil}}$) and the temperature (T, K), consistent with exchange reactions involving the anhydrite Ca site. For practical purposes, the partition coefficients for +2 and +3 cations can be described by semi-empirical equations of the form

$$D_{i(+2)} = e^{\left(\frac{c_1}{T} + c_2\right)} \cdot (\text{CaO}_{\text{Sil}})^{-1} (\text{wt}\%)$$

$$D_{i(+3)} = e^{\left(\frac{c_1}{T} + c_2\right)} \cdot (\text{CaO}_{\text{Sil}})^{-2} (\text{wt}\%)$$

where T is in units of K and CaO_{Sil} is the CaO content of the silicate melt in wt%.

Partition coefficients for +2 and +3 cations also vary systematically with effective ionic radii, and can be described in terms of lattice-strain models. These relate partition coefficients to the elastic strain associated with incorporating a cation of less than optimal ionic radius into a crystal site, in this case, Ca. The Young's modulus calculated for the Ca site by simple "one-site" fits to the partitioning data is 240 ± 25 kbar. However, the calculated partition coefficients are better fit by a "two site" model, with optimum radii for sites at $\sim 1.1\text{\AA}$ and $1.2\text{-}1.3\text{\AA}$, suggesting a change to the anhydrite crystal structure at high temperature and pressure.

Using the temperature and compositionally dependent partition coefficient calculated for Sr, it is possible to model the Sr content of anhydrite precipitating at various stages of magmatic evolution. The Sr content of silicate-hosted anhydrite inclusions from the Luhr Hill granite, Yerington, presented in chapter II ($4000\text{-}5500$ ppm) are consistent with anhydrite crystallizing from a melt with ~ 1000 ppm Sr at $900\text{-}1000^\circ\text{C}$. This suggests that anhydrite was present as a liquidus phase in the Luhr Hill granite and implies magmatic sulfur contents greater than 1200 ppm S.

Finally, experiments described in chapter VI synthesize anhydrite using a molten CaCl_2 flux at temperatures $<950^\circ\text{C}$. Anhydrite crystals were grown up to 2 mm using a

cooling rate of $\sim 2^{\circ}\text{C/hr}$ and were generally free of inclusions of salt flux. Powder XRD results showed that they were also free of any secondary crystalline phases. Anhydrite crystals were doped with Sr (up to 3800 ppm) and P (up to 500 ppm) and were homogenous at the precision available by EPMA. With further work it should be possible to use this technique to synthesize anhydrite for use as standards for in-situ trace element and S-isotope measurements.

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The Nature of Sulfate Saturation in Oxidized Arc Magmas: Implications for
Magmatic Sulfur Budgets

by
Michael C. Hutchinson

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Michael C. Hutchinson, Author

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CONTRIBUTION OF AUTHORS

Chapter II – John Dilles provided samples, contributed to the design of the research and helped to interpret results. Kalin Kouzmanov ran QEMSCAN analyses and assisted in the processing of QEMSCAN data. Kalin Kouzmanov and Farhad Bouzari assisted with the collection of CL images and the interpretation of CL textures.

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Chapter IV – Richard Brooker, John Dilles, Jon Blundy and Brian Tattich contributed to the design of experiments and the interpretation of their results. Richard Brooker assisted with piston cylinder and TZM experiments. Frank Tepley assisted with EPMA analysis. Richard Hinton and Cristina Talavera assisted with the collection and processing of SIMS data. Richard Hinton also contributed to the description of SIMS methods.

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Chapter VI - Richard Brooker assisted with experimental design. Frank Tepley helped to collect EPMA data and Kate Fayloga and Emily McQuarrie assisted with acquiring XRD spectra.

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Chapter I. General Introduction

Sulfur is one of the most abundant magmatic volatile elements and in some magmatic systems is second only to H₂O in its concentration. Sulfur plays a critical role in, amongst other processes, mediating the oxidation state of the mantle wedge above subduction zones (Evans and Tomkins, 2011), controlling chalcophile element abundances in primitive magmas (Mungall and Brenan, 2014) and as a climate forcing agent in the wake of sulfur-rich volcanic eruptions. However despite its significance, the behavior of sulfur in magmas is still not fully understood, in part this is a reflection of sulfur's inherent complexity. Sulfur may be present in magmas as dissolved species, either reduced (S²⁻) or oxidized (S⁶⁺), as solid phases, including pyrrhotite (Fe_(1-x)S) and anhydrite (CaSO₄), as immiscible sulfide or sulfate melts (Jugo et al., 2004, and as shown in this study, chapter IV), or as part of a hydrous fluid phase. Evidence for processes involving sulfur are understandably sparse in the rock record. Fluid and immiscible melt phases are, by their nature, ephemeral and either unmix into solid phases upon cooling or are released from the magma during decompression. Solid sulfide phases are generally significantly denser than their host silicate melt, and as such are generally removed during magmatic fractionation, whereas magmatic anhydrite is soluble in low temperature aqueous fluids and is quickly removed from volcanic rocks at the surface by meteoric fluids (Luhr et al. 1984). Anhydrite may also be removed during routine sample-preparation if a water based polishing medium is used.

One important manifestation of magmatic sulfur in the earth's upper crust comes in the form of magmatic-hydrothermal ore deposits, principally high-sulfidation epithermal Au and porphyry Cu ± Au ± Mo deposits. Although generally valued for their metal endowment, it has been observed that porphyry deposits are actually much greater concentrations of sulfur, with respect to average crustal abundances, than metals. In ore forming systems sulfur plays a crucial role in both complexing metals in solution (e.g. Murakami et al. 2010) and in precipitating metals as sulfide minerals, and deposits may contain as much as 1Gt of sulfur as hydrothermal sulfides and sulfates (Gustafson and Hunt, 1975). The source of the sulfur, as well as most of the metals, H₂O, and Cl needed to produce a porphyry deposit, is understood to be the underlying magmatic system. It has been shown that typical arc magmas should contain enough metal to produce an ore deposit (if efficiently concentrated, Cline and Bodnar, 1991), and that ore forming magmas are generally H₂O-rich (e.g. Richards, 2011). However there is an open question as to whether or not ore-forming magmas are particularly sulfur rich compared to typical arc magmas, and if so, how these fertile, sulfur-rich magmas might be identified.

The key to addressing this question is understanding the distribution of sulfur in the magmatic system, which is closely linked to the solubility of sulfur species in silicate melts, often described in the form of the “sulfur capacity at sulfide saturation” (SCSS, reduced systems) or sulfur capacity at anhydrite saturation” (SCAS, oxidized systems). Broadly, the sulfur capacity is higher in oxidized systems (where $fO_2 \geq NNO+1$), in higher temperature melts, and in more primitive melts (e.g. Zajacz and Tsay, 2019). This raises an apparent dilemma. Porphyry deposits are, in almost all cases, linked to low temperature, intermediate – evolved composition melts, in which, despite being oxidized, the sulfur carrying capacity is low. Simple mass balance calculations show that in many cases the amount of sulfur dissolved in these magmas is more than an order of magnitude too low to produce the overlying ore deposit. One possible explanation invokes underplating mafic magmas as a possible source of sulfur, either by direct mixing (Maughan et al. 2002) or by fluxing of SO_2 gas into the overlying system (Blundy et al. 2015). Mafic melts have the advantage of having a much greater sulfur carrying capacity, and there is evidence of similar processes occurring in volcanic systems (Hattori, 1993). Unfortunately in most cases there is little direct evidence of large volumes of mafic material in association with porphyry deposits.

An alternative explanation is that during the cooling and evolution of a primitive, sulfur-rich magma, anhydrite is precipitated but importantly, due to its low density, is not fractionated from the silicate melt. The magma retains the anhydrite as it ascends through the crust and cools, resulting in an intermediate-evolved composition magma that, despite little ability to carry dissolved sulfur species, contains a significant amount of sulfur as magmatic anhydrite. During degassing this anhydrite then breaks down to provide sulfur to the hydrothermal system above (Chambefort et al. 2008). It is this second explanation, and the implication that ore forming magmas must typically be sulfate saturated during their evolution, that are the motivation for this study.

Chapter II aims to provide direct evidence for anhydrite saturation in ore forming magmas. Although anhydrite has been described as a phenocryst phase in a small number of sulfur rich volcanic eruptions (e.g. Luhr et al. 1984, Pallister et al. 1992), with few exceptions it is conspicuously absent from descriptions of the intrusive rocks commonly associated with ore deposits. As previously noted anhydrite is soluble in low temperature aqueous fluids and is easily removed from the rock record, however previous authors have shown that it may be preserved as inclusions in more resistant phenocrysts (e.g. Audétat et al. 2004, Chambefort et al. 2008). In this chapter I identify anhydrite inclusions in minerals separated from intrusive rocks associated with

5 different ore deposits, indicating that anhydrite saturation was a common feature of these magmas. In addition, measurements of trace element concentrations in anhydrite are presented as a means of distinguishing magmatic anhydrite from hydrothermal anhydrite which is common in porphyry ore deposits.

Chapter III builds on the results of chapter II, with the aim of determining the timing of anhydrite saturation in the studied magmas. This is important because it helps to determine if magmas became anhydrite saturated due to progressive cooling, as suggested, or due to the fluxing of sulfur from another source. To this end I investigated apatite phenocrysts and inclusions from the same, anhydrite saturated samples. Since apatite incorporates S into its crystal structure, along with other volatiles (OH, Cl, F) and trace elements (REE, Na, Si amongst others), it should be possible to track the evolution of the melt sulfur content by correlating apatite S content with various geochemical proxies for cooling, melt evolution or gas fluxing. Although S-rich apatite was present in all samples, apatite S showed little correlation with any of the investigated proxies. The most likely explanation is that reequilibration at low temperature, or exchange between apatite inclusions and their hosts has obscured geochemical trends which may have been originally present.

Chapter IV is the first of two chapters concerning experimental work on sulfate saturated magmas. Previous experimental work (Jugo et al. 2004) has shown that sulfate melt may be present in place of anhydrite at high temperature, and “wormy anhydrite” inclusions described by Chambeffort et al. (2008) are a likely natural analogue. The presence of immiscible sulfate melts would indicate sulfate saturation at high temperature, and therefore high magmatic sulfur contents, however little previous work has been done so far to investigate this phase. I conducted experiments aimed at characterizing the stability and composition of sulfate melts using piston-cylinder and gas pressurized cold-seal experimental apparatus at temperatures between 800 - 1200°C and pressures of 0.2 - 1 GPa. The stability field of sulfate melts and their major element composition is reported in this chapter and suggests a minimum magmatic sulfur content required to produce sulfate melts in natural systems of ~2400 ppm S.

Following on from this, trace element concentrations and partition coefficients for both sulfate melt-silicate melt and anhydrite-silicate melt are reported in Chapter V. Anhydrite partition coefficients can be characterized both in the context of lattice-strain models and as a function of temperature and melt composition. The latter can be used to model the trace element content of anhydrite crystallizing from an evolving melt, and can also provide a temperature estimate for the anhydrite inclusions analyzed in chapter II. Sulfate melt partition coefficients

appear to vary systematically as a function of the ionic potential of elements (the ratio of nominal charge to ionic radius, Z / r) and as a function of silicate melt chemistry, and differ significantly from previously published data.

Finally, in Chapter VI, I detail preliminary work synthesizing trace element doped anhydrite crystals for use as analytical standards. This has been done for the first time using a molten salt flux, and produced large, homogenous anhydrite grains with measurable concentrations of Sr and P. With further development it is likely that this method could be used to grow anhydrite crystals doped with a range of trace elements and with distinct isotopic signatures with broad utility as standards for in-situ measurements.

One of the most important questions this work attempts to address is whether or not the magmas responsible for the formation of ore deposits are anomalously sulfur-rich. This requires the determination of magmatic sulfur budgets, which is often challenging. In part this is because traditional approaches to estimating sulfur budgets, including measuring the sulfur content of melt inclusions, are of limited use in sulfate-saturated systems where the silicate melt may only contain a small fraction of the total sulfur budget. The sulfur content of apatite inclusions, investigated in chapter III, provides some evidence of high magmatic sulfur contents, although, like melt inclusions, only reflects the sulfur contained in the melt. The use of apatite is also limited by the lack of experimental data characterizing sulfur partitioning between apatite and silicate melt.

The relationship between SCAS and temperature is relatively well known (e.g. Zajacz and Tsay, 2019) and if the temperature of sulfate precipitation can be determined then this can provide an estimate of the sulfur content of the coexisting melt. This can then be used as a minimum estimate for the magmatic sulfur budget, with additional sulfur present as anhydrite or sulfate melt.

Chapter IV is the first experimental study of sulfate melts relevant to natural magmatic systems, and provides data on the stability of sulfate melts with respect to pressure, temperature and composition (P-T-X). In this case, the minimum temperature of sulfate melt precipitation can be estimated based on these phase relations and for most magmas, including those which produced “wormy anhydrite” at Yanacocha, is $\sim 1000^{\circ}\text{C}$. This temperature estimate implies a melt sulfur content of ~ 2300 ppm S (although this will also depend on melt composition), such that the discovery of sulfate melts in natural systems indicates a magmatic sulfur budget of >2300 ppm. Although the discovery of sulfate melts in nature is currently limited to Yanacocha it should be

noted that this district hosts the most productive group of epithermal gold deposits in the world (Longo et al. 2010).

By characterizing the partitioning of various trace elements between anhydrite and silicate melt, I have shown that it is also possible to estimate the temperature of anhydrite crystallization. Analyses of the Sr content of anhydrite inclusions from the Luhr Hill granite suggest anhydrite saturation at temperatures of at least 950°C. If this is the case then anhydrite was a liquidus phase in this system and crystallized from a silicate melt containing ~1200 ppm S, indicating a magmatic sulfur budget of >1200 ppm S.

These initial results suggest that ore-forming magmas are indeed sulfur rich. However the application of these methods to a range of sulfate-saturated magmatic systems will be needed in order to determine if ore forming magmas are commonly more S-rich than their barren equivalents. If this turns out to be the case, the identification of S-rich magmatic systems in volcanic arcs may provide a useful exploration tool in the search for both porphyry and high-S epithermal ore deposits.

Chapter II. Evidence for magmatic anhydrite in porphyry copper intrusions

2.1 Abstract

Although magmatic-hydrothermal ore deposits may contain as much as 1 Gt of sulfur as hydrothermal sulfides and sulfates, it is an open question as to whether the genetically related magmas are particularly sulfur-rich. In oxidized melts, the presence of magmatic anhydrite would provide some evidence of this, but its preservation potential in the rock record is low, owing to the high solubility of sulfate in low temperature aqueous fluids. In this study we have examined granitic and porphyry samples from porphyry copper ore deposits using QEMScan and SEM-EDS to identify small and sparse inclusions of anhydrite preserved in a range of igneous minerals including apatite, amphibole, plagioclase, quartz and titanite. In total, anhydrite inclusions were present in 11 different samples from six sulfur-rich magmatic-hydrothermal ore deposits. EMPA analyses of anhydrite inclusions suggests that primary magmatic anhydrite typically has elevated Sr (>2500 ppm) and P (>500 ppm) compared to hydrothermal anhydrite, however in many cases this is obscured by post-entrapment exchange between the inclusion and host mineral or hydrothermal alteration of host minerals. Where the composition of inclusions is inconclusive we have used cathodoluminescence imagery of zoning patterns in host minerals to help distinguish between igneous and hydrothermal origins. This study provides evidence that anhydrite saturation may be a common feature of arc magmas, particularly those associated with ore deposits, even though little evidence of magmatic anhydrite is preserved. Widespread anhydrite saturation has significant implications for any consideration of magmatic sulfur budgets, particularly in low temperature, evolved magmas, which have little capacity to carry sulfur species in the melt.

2.2 Introduction

Sulfur is an important magmatic volatile both as an erupted product and climate-forcing agent and for its role in producing sulfide-rich magmatic-hydrothermal ore deposits. However, the behavior of sulfur during magmatic evolution is complicated; its solubility is sensitive to changes in temperature, melt composition and oxidation state (e.g., Baker and Moretti, 2011), and sulfur may be lost from a melt to either a fluid phase or to sulfides or anhydrite. How sulfur is partitioned between silicate melt, fluid and solid phases has implications for both the trace element evolution of a magma as well as the overall sulfur budget (e.g., Scaillet et al., 1998; Jugo et al., 1999; Simon et al., 2008; Keppler, 2010; Li and Audétat, 2012; Masotta et al., 2016). In an oxidized magma sulfur is dominated by sulfate species (Carroll and Rutherford, 1988; Jugo et al.,

2005; Métrich et al., 2009) and, unless it is lost during degassing, acts incompatibly. Cooling and differentiation should therefore concentrate sulfur in a melt until it saturates in anhydrite, although evidence for this in the geologic record is relatively sparse.

Anhydrite is an orthorhombic mineral with a nominally simple chemical composition of CaSO_4 . Magmatic anhydrite was first observed in products of the 1982 eruption of El Chichon, Mexico (Luhr et al., 1984) and has since been recognized as a primary phase in a number of recent eruptions including at Mount Lamington, Pinatubo, Lascar, Shiveluch and Augustine (Arculus et al., 1983; Pallister et al., 1992; Matthews et al., 1997; Matthews et al., 1999; Dirksen et al., 2006; Larsen et al., 2010) and in older volcanic rocks at Yanacocha, Sutter Buttes and Eagle Mountain (Matthews et al., 1997; Matthews et al., 1999; Parat et al., 2002; Chambefort et al., 2008; Luhr, 2008). It has also been reported as either phenocrysts or as inclusions in several intrusive rocks at Julcani, El Teniente, Santa Rita, Cajon Pass, Bingham, Northparkes and Qulong (Drexler and Munoz, 1985; Barth and Dorais, 2000; Lickfold et al., 2003; Audétat et al., 2004; Stern et al., 2007; Xiao et al., 2012; Zhang and Audétat, 2017). For a comprehensive review see Luhr (2008). It is notable that, except for Cajon Pass, all examples of magmatic anhydrite in plutonic rocks come from intrusions associated with sulfur-rich magmatic-hydrothermal ore deposits.

Despite these examples, magmatic anhydrite features as a primary phase in only a tiny proportion of studied igneous rocks worldwide. In part this reflects the particular set of conditions necessary for sulfate saturation; magmas must be oxidized ($f\text{O}_2 > \text{NNO}+1$, Carroll and Rutherford, 1988; Luhr, 1990, 2008), must be relatively sulfur-rich, and must retain their sulfur until cooling (and to a lesser degree differentiation) leads to a drop in the sulfur carrying capacity of the magma (Baker and Moretti, 2011; Masotta and Keppler, 2015) and anhydrite is precipitated. However, even in magmas which meet these criteria, little evidence of anhydrite saturation may be left in the geologic record. Anhydrite is readily soluble in meteoric water and at El Chichon it was noted that erupted material was effectively stripped of phenocrystic anhydrite within a year of the eruption (Luhr et al., 1984). It is likely that slowly cooled plutonic rocks, particularly those with a long history of magmatic-hydrothermal interaction, also commonly lose most traces of primary anhydrite. In many cases the only readily available evidence of anhydrite saturation may be small ($<10\mu\text{m}$) inclusions of the mineral in more resistant mineral phases. Furthermore, at many localities where anhydrite has been reported in volcanic and plutonic rocks, Luhr (2008) noted that its origin, either igneous or hydrothermal, remains uncertain based on textural and compositional evidence. Determination of igneous origins of anhydrite can be

robustly established by the presence of anhydrite as phenocrysts or as inclusions within other igneous minerals preserving igneous compositional zoning and textures, but we note that anhydrite chemical compositions may also be useful (cf., Chambefort et al., 2008; Xiao et al., 2012).

The main aim of this study is to test the hypothesis that sulfate saturation is a common but poorly preserved and under-reported feature of ore-forming magmas. To this end we have used a range of techniques including automated EDS mapping (QEMScan), cathodoluminescence (CL) imaging, and electron microprobe analysis (EMPA) to find anhydrite inclusions in igneous samples from porphyry copper deposits and to help distinguish between magmatic and hydrothermal anhydrite.

2.3 Methods

2.3.1 Samples

Samples were chosen to maximize the chances of finding igneous anhydrite, and to test the hypothesis presented above. All samples were selected on the basis that they were spatially and temporally associated with porphyry copper deposits, or in the case of Aucanquilcha, samples associated with native sulfur deposits and a large zone of hydrothermal alteration (Clark, 1970; Klemetti and Grunder, 2008). Hand specimen observations, for example visible cleavage in amphibole and twinning in plagioclase, were used to select the least-altered samples available from each site. Details of the samples investigated are presented in Table 2.1 and references therein. Anhydrite inclusions in plagioclase and orthopyroxene from Augustine volcano, previously described by Larsen et al. (2006), were also analyzed as part of this study for comparison.

2.3.2 Sample preparation and identification of anhydrite inclusions

Samples were crushed, sieved, and hand-picked under a binocular microscope. In some cases, heavy mineral separates were obtained either by panning or by using sodium poly-tungstate (SPT) heavy liquid separation. Based on reported anhydrite inclusions in previous work we investigated a range of phases including amphibole, plagioclase, clinopyroxene, titanite and apatite. Crystal separates were mounted in epoxy and polished in oil to minimize any dissolution of anhydrite. Inclusions were then identified by energy dispersive spectroscopy (EDS), either using automated QEMScan mapping (5µm resolution) or manually using an FEI QUANTA 600F SEM at Oregon State University (OSU). Once identified, anhydrite inclusions and their host grains were imaged with color CL using a cold cathode CITL 8200 Mk 5-1 (University of

Geneva) or a CITL Mk 4 (University of British Columbia) mounted on a petrographic microscope.

Microprobe analyses of inclusions were conducted at OSU using a Cameca SX-100 with beam conditions of 15kV, 30nA and a 1 μ m spot diameter (as Chambefort et al., 2008, Table 2.2). This helped to achieve relatively low detection limits for trace elements, including Sr, Fe and P, while maintaining the spatial resolution needed to analyze small, often elongate inclusions.

2.4 Results

2.4.1 Anhydrite-bearing samples

Of the 25 samples investigated, 11 were found to contain anhydrite inclusions (Table 2.1), representing evidence of sulfate saturation at six localities where it had not been previously recognized. Inclusions were most commonly hosted in apatite but were also found in amphibole, titanite, quartz and plagioclase. It has been previously noted that magmatic anhydrite is strongly associated with apatite (Luhr, 2008), possibly due to co-nucleation, and even silicate-hosted anhydrite inclusions in this study were most commonly spatially associated with inclusions of apatite.

Imaging of igneous minerals by reflected light, EDS, and CL methods provides a means of identifying igneous anhydrite inclusions, as exemplified by Figure 2.1. The host igneous minerals display no evidence of subsequent hydrothermal alteration and locally primary igneous compositional zonation is visible (CL images, Figs. 2.1a, d). In most cases, cleavages and cracks in the host mineral do not intersect the anhydrite inclusion but note that some cracks are produced during rock crushing (Fig. 2.1a).

In general, anhydrite inclusions were tabular, locally with rounded edges, and are between 5-120 μ m long. The aspect ratio of inclusions was generally ~1:5 with the exception of those hosted in amphibole from Aucanquilcha, which had a more elongate habit with an average aspect ratio closer to 1:10. Anhydrite exhibits blue-purple-brown colors in CL and in a number of inclusions color zoning was observed, although on a scale too fine to analyze using EMPA (inset, Fig. 2.1b). Characteristic cleavage was also visible in several inclusions using a reflected light microscope, and contrasts with melt-like Ca-sulfate blebs lacking cleavage trapped in Yanacocha high-Al amphibole (Chambefort et al., 2008). In some samples, many inclusions with similar morphology could be seen below the surface of apatite grains (Fig. 2.1c – stacked transmitted light image) and are likely also anhydrite.

In general anhydrite inclusions were exceedingly sparse. Over 60 titanite and over 30 amphibole grains were sectioned and scanned from the Robinson sample to find just one anhydrite inclusion in each mineral. Where anhydrite was present as inclusions in apatite it was generally more abundant than in other phases, although in many samples apatite itself was scarce and relatively small, reducing the chances of finding analyzable anhydrite inclusions.

2.4.2 Anhydrite trace element composition

Since many of the samples investigated are related to ore deposits in which hydrothermal anhydrite is common, chemical composition offers a potential way to distinguish between primary magmatic anhydrite and secondary hydrothermal anhydrite that precipitates at lower temperatures from a fluid phase. Since conditions in these two environments differ significantly, both in bulk composition and temperature, the resulting anhydrite should also exhibit marked differences in its trace element content, assuming no later reequilibration occurs between anhydrite and host mineral. However, assessing the expected differences is difficult because few data currently exist for trace element partitioning between melt or fluid and anhydrite. Xiao et al. (2012) suggested that at Qulong, magmatic anhydrite has lower Sr content (<930 ppm) than its hydrothermal counterpart (850 – 3500 ppm). In contrast, Chambefort et al. (2008) reported compositions of anhydrite from a range of sources and reached an opposite conclusion, that magmatic anhydrite tends to have higher Sr contents (1700 – 7000 ppm) than hydrothermal anhydrite (420 – 2100 ppm) from porphyry environments.

The Sr content of anhydrite analyzed in this study (Figs. 2.2a and b; Table 2.2) ranged from 1250 to 5500 ppm, with silicate-hosted inclusions (Luhr Hill, Aucanquilcha, Veteran pit) having the highest Sr contents (4000 – 5500 ppm), similar to amphibole- and pyroxene-hosted inclusions at Yanacocha. Apatite-hosted inclusions have lower Sr contents (1500 – 3300 ppm) except for those from the Veteran pit, which have similar Sr contents to their silicate-hosted counterparts. Anhydrite inclusions in both plagioclase and orthopyroxene from Augustine Volcano also have relatively low Sr contents (1500 – 2400 ppm), similar to analyses of phenocrysts and amphibole-hosted inclusions from Pinatubo. The P contents of most of the inclusions (Fig. 2.2a; Table 2.2) are between 250 and 1200 ppm, although a number of apatite-hosted inclusions have somewhat elevated P contents, up to ~2500 ppm.

Plagioclase-hosted inclusions from this study, which have been interpreted as hydrothermal (see following section on CL- textures), generally have low Sr and P contents (<2500 ppm Sr, <500 ppm P), similar to hydrothermal anhydrite at Butte, Ajo and El-Salvador

from previous studies (Chambefort et al., 2008). However many igneous anhydrite phenocrysts (Pinatubo) and inclusions (those from Augustine and most apatite-hosted inclusions) also have low Sr and are in many cases compositionally indistinguishable from hydrothermal anhydrite. Of the other elements analyzed, only Ce was commonly above the detection limit with concentrations 300-900 ppm, but Ce showed no obvious difference between hydrothermal and igneous anhydrite or between inclusions trapped in different host minerals.

The low Sr and P of some magmatic anhydrite may reflect crystallization conditions but may also be explained by post-entrapment exchange. Chambefort et al. (2008) suggested that the high Fe content of amphibole- and pyroxene-hosted anhydrite was evidence of sub-solidus exchange and this is supported by our data; all the amphibole- and pyroxene-hosted anhydrite inclusions analyzed for this study have significantly elevated Fe contents compared to those included in plagioclase, apatite or titanite from the same samples (Fig. 2.2b).

In the case of apatite-hosted inclusions, exchange of both Sr and P is likely. Sr^{2+} substitutes for Ca^{2+} in both anhydrite and apatite and should diffuse readily between the two. Even at sub-magmatic temperatures Sr diffusion in apatite is relatively fast ($\sim 1.5 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ at 700°C , Cherniak and Ryerson, 1993) and in metamorphic rocks, exposed to peak temperatures of 660°C for $\sim 10^5$ yr, any Sr zonation in apatite is effectively homogenized. In many cases the magmatic systems associated with porphyry deposits are thought to remain active on timescales of $>10^6$ yr (Chelle-Michou et al. 2017) due to repeated injection of hot material. Apatite-hosted anhydrite inclusions in slowly cooled plutonic rocks are therefore unlikely to preserve their original Sr contents. Certainly apatite-hosted anhydrite inclusions from the Luhr Hill have significantly lower Sr than those hosted in various silicates from the same sample, despite broadly similar conditions of crystallization (Dilles 1987). This difference is not apparent between silicate- and apatite-hosted inclusions from the post-mineral dike at the Veteran pit, Robinson, suggesting that in this case, the intrusion and subsequent rapid cooling of the dike did not allow sufficient time for diffusion.

2.4.3 Use of Cl texture to identify hydrothermal anhydrite

In the absence of a robust geochemical discriminator, we have used host mineral textures to aid in interpreting the origin of the inclusions. As described above, anhydrite hosted in unaltered grains characterized by well-defined igneous growth zoning can be readily interpreted as igneous in origin (Fig. 2.1), whereas anhydrite that is hosted in an igneous mineral that exhibits

fractures and altered zones characterized by patchy or mottled textures may be interpreted as hydrothermal (Fig. 2.3).

In some cases, this zoning (or lack thereof) was obvious in BSE or in reflected light, although for apatite and plagioclase (which host the majority of anhydrite inclusions) color-CL images provided the most detailed evidence of alteration. For example, in the case of plagioclase-hosted anhydrite from El Salvador (K porphyry, Gustafson and Hunt, 1975; Lee et al., 2017), mottled CL textures (Fig. 2.3c) and low Ca in zones hosting anhydrite inclusions (extracted from QEMScan EDS mapping, Fig. 2.3b) strongly suggest these have been altered or precipitated by hydrothermal alteration. This interpretation is supported by low Sr and P in the inclusions, as discussed above. In previous work on CL in apatite, Bouzari et al. (2016) suggested that unaltered apatite from porphyry systems is typically yellow-brown in color and with progressive alteration will tend to green (K-silicate alteration) or grey (sericitic alteration) CL colors.

The apatite imaged for this study ranged widely in color from blue to green to yellow but rarely showed the patchy textures that indicate alteration. Apatite grains separated from porphyry dikes at Encuentro were an exception to this rule. They have a wide range of CL-textures likely related to the hydrothermal alteration. Three different textures are distinguished in Figure 2.4. The first, Ap₁, illustrates primary igneous zoning (Figs. 2.4a and b). It has commonly been replaced by Ap₂ that is characterized by a patchy, mottled texture interpreted to be the result of hydrothermal alteration of primary igneous apatite (Figs. 2.4b and c), similar to that reported by Bouzari et al. (2016). The third, Ap₃, is homogenous and shows neither the primary igneous zoning nor the mottled texture related to alteration (Fig. 2.4d). In figure 2.4a primary growth zoning bands are visible in the Ap₁ core, but this apatite is embayed and growth zones are truncated, suggesting resorption of the crystal before later overgrowth of homogenous and unzoned apatite (Ap₃). Anhydrite inclusions are found in all the textural zones described above but those hosted in homogenous Ap₃ are generally more rounded and are darker in CL compared to those hosted in Ap₁ or Ap₂. We hypothesize that anhydrite hosted in largely unaltered igneous zones, Ap₁ (Fig. 2.4b), are of magmatic origin, those hosted in Ap₂ (Fig. 2.4c) are magmatic in origin but have been modified by hydrothermal alteration, and those hosted in later, apatite overgrowths, Ap₃ (Figs. 2.4a and d), are probably hydrothermal in origin. However, there is no obvious link between the host textural zone and anhydrite trace element compositions.

2.5 Discussion

2.5.1 Implications for magmatic sulfur budgets and ore deposit formation

Magmatic-hydrothermal ore deposits, particularly porphyry and high-sulfidation epithermal deposits, are more significant sulfur anomalies than they are metal anomalies with respect to average crustal abundances (J.P. Hunt, personal communication, in Gustafson, 1979). Furthermore, it has been shown that most arc magmas contain enough metal to produce an ore deposit, assuming efficient concentrating processes (e.g., Dilles, 1987; Cline and Bodnar, 1991; Richards, 2015; Zhang and Audétat, 2017). On the other hand, it is difficult to reconcile the large quantities of sulfur contained in these deposits with the observation that they are primarily associated with more evolved, low temperature magmas, in which the solubility of all sulfur species is low (e.g., Baker and Moretti, 2011; Masotta and Keppler, 2015). A similar problem exists in volcanic systems where measurements of SO₂ emissions are often orders of magnitude greater than the mass of degassed sulfur calculated by the “petrologic method” (Andres et al., 1991). In volcanic systems it is likely that the excess sulfur can be explained by the presence of a sulfur-rich aqueous fluid phase prior to eruption (Westrich and Gerlach, 1992; Hattori, 1993; Wallace, 2001).

In magmatic-hydrothermal ore deposit systems it has been proposed that the excess sulfur must come from a more primitive melt, with a higher sulfur solubility, either by direct mixing or by volatile fluxing at a shallow level in the crust (Hattori and Keith, 2001; Maughan et al., 2002; Blundy et al., 2015). An alternative explanation is that sulfur becomes concentrated during magmatic evolution processes in the deep crust (cf., Chambefort et al., 2008; Loucks, 2014). In this case, a more evolved magma may still have a high bulk sulfur content, despite its low sulfur solubility, with the majority stored as crystalline anhydrite. Indeed, most of the anhydrite inclusions presented in this study were likely trapped at temperatures <900°C (apatite saturation temperatures ~900-930°C, calculated following the method of Piccoli and Candela, 1994, using data from Harrison and Watson, 1984), implying melt sulfur contents <1000 ppm (Masotta and Keppler, 2015). If these magmas contained 1 wt % anhydrite, comparable to erupted products at El Chichon and Pinatubo (Luhr 1990; Pallister et al., 1992), this would account for ~2300 ppm sulfur, more than 2/3 of the bulk sulfur content of the magma.

An important implication of sulfate saturation is that any estimates of melt sulfur content, derived from either melt inclusions, solubility models or from measurements of sulfur in apatite, can only be considered minimum estimates of the bulk sulfur content of the magma, with

additional sulfur being stored as anhydrite. Streck and Dilles (1998) suggested that at Yerington, a drop in the maximum sulfur content of apatite in younger intrusive phases reflected the onset of sulfate saturation, rather than any loss of sulfur from the system. Their conclusion that this was a sign of cryptic anhydrite saturation has been confirmed by this study's discovery of anhydrite inclusions in the Luhr Hill pluton.

Sulfur storage as magmatic anhydrite is also proposed for ore-related magmas at Bingham. Grondahl and Zajacz (2017) argued that syn-mineral latite dikes were formed by fractionation of a parental shoshonitic magma, which could have provided all the necessary sulfur to the system, and that during cooling this magma became saturated in anhydrite. The presence of anhydrite in the latite dikes and the sulfur content of more primitive melt inclusions, which tracks modelled anhydrite solubility (300 – 900 ppm S in melt inclusions with <65 wt % SiO₂), suggests that the magma was continually anhydrite saturated through evolution from 55-65 wt % SiO₂. Alternatively, Zhang and Audétat (2017) suggest that these latite dikes were formed by mixing of end member melanephelinite and rhyolite magmas, with the mafic end member supplying a large part of the sulfur budget. However, they also show that the felsic end member must have contributed a significant amount of sulfur and was likely anhydrite-saturated. Whether the syn-mineral latite dikes were formed by mixing or by evolution from a single source magma, anhydrite forms an important part of the overall magmatic sulfur budget that produced one world's the largest porphyry Cu-Mo-Au deposits (total resource of ca. 28 Mt Cu).

2.5.2 Anhydrite in later stages of ore formation

This study lends weight to the hypothesis that ore-forming magmas are commonly sulfate-saturated, and that magmatic anhydrite may constitute an important sulfur source to mineralizing fluids. Nonetheless, questions remain on the timing of sulfate saturation with respect to the ongoing magmatic evolution of these systems. Do ore-forming magmas begin to crystallize anhydrite as sulfur is added from an external source at shallow levels in the crust (for example underplating mafic magma, Maughan et al. 2002), or in response to recharge, mixing, assimilation and cooling in lower crustal MASH zones (Chambefort et al. 2008)?

In many previous studies, occurrences of magmatic anhydrite are limited to some of the youngest igneous units in a given district, often in syn- or post-mineralization intrusions. This is true of the Bulolo dike at Julcani (Deen et al. 1994), late latite dikes at Bingham (Zhang and Audétat, 2017) and post-mineralization “zero” porphyries at Northparkes (Lickfold et al. 2003). Several of the samples investigated here also support this observation, including at El Salvador,

where anhydrite inclusions were identified in mineral separates from the K-porphyry, associated with waning magmatism and late mineralization, and from latite dikes which postdate mineralization (Lee et al., 2017). At Yerington, anhydrite inclusions were identified in several different minerals from the Luhr Hill granite, the youngest intrusive phase of the Yerington Batholith and the phase most intimately associated with mineralization (Dilles, 1987). At Robinson, anhydrite inclusions were found in a post-mineralization dike which cross cuts pervasively altered syn-mineralization intrusions. At Encuentro, the evidence is less clear, but anhydrite inclusions are present in apatite from the five porphyry intrusion that are directly associated with pulses of hydrothermal alteration and mineralization (Osorio, 2017).

We observe that in many cases sulfur was behaving incompatibly during magmatic evolution, and that later intrusive phases tended to have higher sulfur contents and therefore were more likely to be anhydrite saturated (cf., Streck and Dilles, 1998). This is consistent with the idea that ore-forming magmas typically differentiate relatively deep in the crust (Kay and Mpodozis, 2001; Chambefort et al., 2008; Loucks, 2014; Chiaradia and Caricchi, 2017) where they are water-undersaturated and as such do not lose significant sulfur to degassing. Little experimental data currently exist regarding sulfur partitioning into CO₂-dominated fluids, however melt inclusion data from Mt Etna shows that sulfur degasses at lower pressures than CO₂ and that little sulfur is lost from the melt at pressures above 1500 bars (Spilliaert et al., 2006).

Alternatively, the observation that magmatic anhydrite inclusions are most often reported in later stages of magmatism may be an artefact of the high solubility of anhydrite in aqueous fluids and its resulting low preservation potential. Pervasive hydrothermal alteration, which accompanies mineralization, means that at many ore deposits, the only fresh rocks exposed at the surface are those which post-date ore formation. In a few cases, for example at Yerington, post-emplacement tilting has exposed fresher rocks at the roots of ore forming intrusions, however in most cases these rocks are at considerable depth, well below the limits of drilling. In a number of the more altered samples investigated here, the phases that typically host anhydrite inclusions were either no longer present or had been largely replaced by secondary minerals, making the identification of primary igneous anhydrite impossible. Some long-lived magmatic systems related to ore deposits do preserve anhydrite in early as well as late rocks. At Yanacocha, Peru, unaltered andesite-dacite volcanic rocks are widely preserved, and anhydrite inclusions are found in magmas spanning >3 m.y. that are genetically related the epithermal gold deposits containing about 1 Gt of hydrothermal sulfur (Chambefort et al., 2008).

2.6 Conclusion

Inclusions of anhydrite are important markers for sulfate saturation and, despite their sparsity, they can be identified with careful, oil-based sample preparation and the use of EDS mapping. We suggest that host mineral textures evident in QEMScan element maps and in CL images, and in some cases trace element compositions from EMPA analysis can be used to distinguish between magmatic and hydrothermal anhydrite, although there is clear evidence for post entrapment modification of many inclusions.

Several of the localities investigated here have been well studied, but given the apparent sparsity of inclusions, and the high solubility of anhydrite in cold water, it is no surprise that magmatic anhydrite has not been previously described. The presence of anhydrite inclusions is broadly underreported and anhydrite may be a common, if ephemeral, phase in arc magmas. This being the case, consideration of the sulfur budgets of such magmas must account for the possibility that anhydrite is present, even if not evident from routine petrography.

We have demonstrated in this survey that anhydrite is a commonly present but very rare inclusion in igneous minerals from arc magmas associated with sulfur-rich ore deposits. Anhydrite is a means of storing significant quantities of sulfur in low temperature magmas (~1 vol % anhydrite is approximately 2300 ppm S), and during degassing may breakdown to provide sulfur to magmatic-hydrothermal fluids.

We anticipate that in the future carefully conducted micro-imaging studies will expand the number of examples of anhydrite inclusions in both ore-forming and barren magmas and provide the basis for better understanding the role and origin of sulfur in arc magmas.

2.7 References

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2.8 Figures and tables

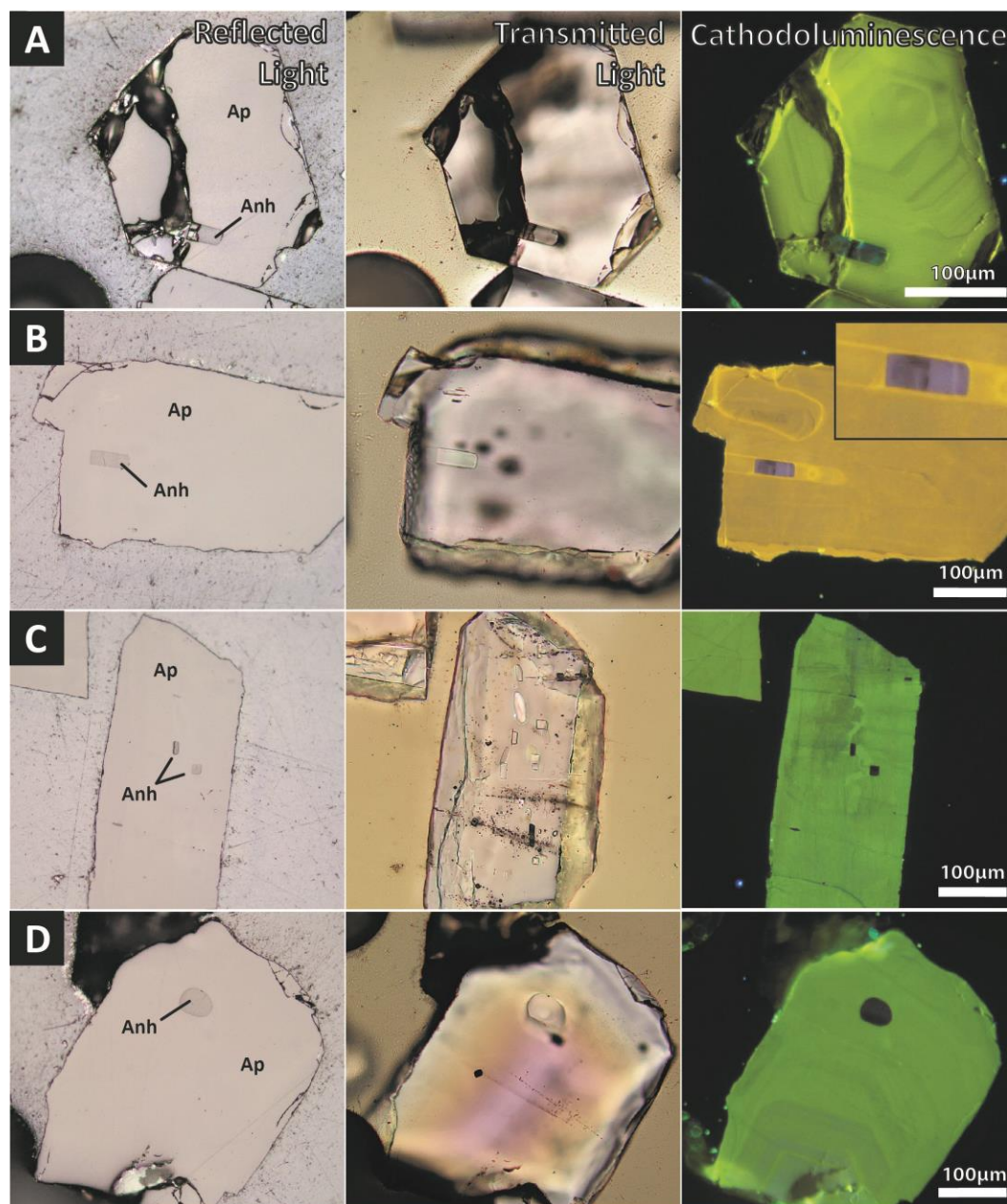


Figure 2.1 Reflected light, transmitted light and CL images of anhydrite inclusions in apatite. A) Apatite from El-Salvador latite dike showing a tabular anhydrite grain present on well-defined igneous growth zoning. B) Apatite from a porphyry dike at Christmas, Arizona, perpendicular to apatite C-axis with tabular anhydrite grain. Inset shows faint zoning in anhydrite inclusion C) Apatite from the Luhr Hill granite, Yerington with two small blocky anhydrite inclusions. More inclusions with similar habit, can be seen below the surface in the stacked transmitted-light image and are also likely anhydrite. D) Also from the Luhr Hill with a larger, rounded anhydrite inclusion. Apatite is mounted with C-axis up and displays well defined igneous growth zones. All CL images here taken using CITL 8200 Mk 5-1 at the University of Geneva.

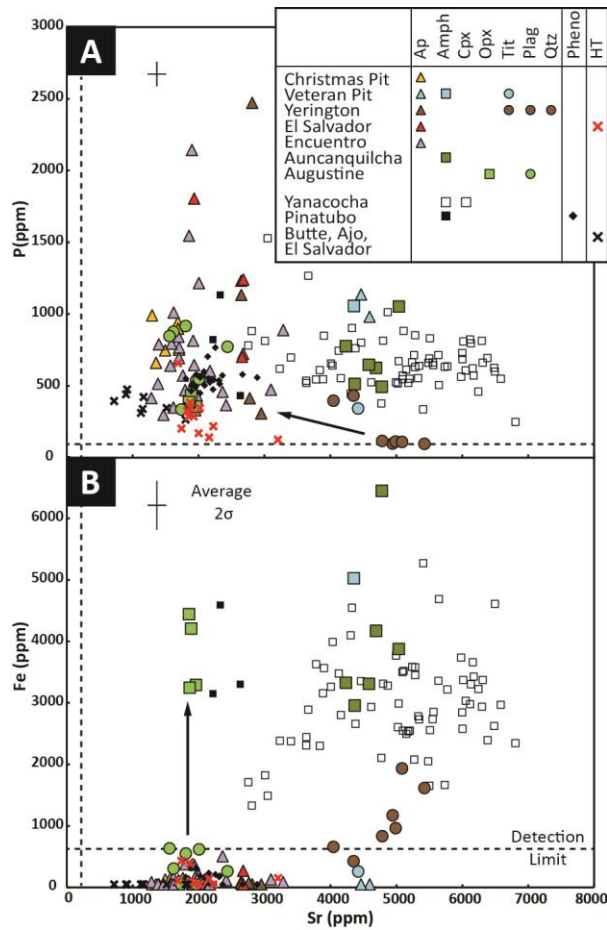


Figure 2.2 Anhydrite compositions by microprobe A) Sr vs P (ppm) B) Sr vs Fe (ppm). Detection limits are 3σ of background counts. Characteristic 2σ uncertainty for analyses are based on either repeat analyses of a standard (Sr, P) or variance of x-ray intensity during individual measurement (Fe). Arrows show likely vectors of post entrapment exchange. Colored symbols are data from this study, black symbols are data from Chambeft et al. (2008). Analyses from Julcani (Chambeft et al., 2008, 10000 – 15000 ppm Sr) are not plotted. Ap – apatite, Amph – amphibole, Cpx – clinopyroxene, Opx – orthopyroxene, Tit – titanite, Plag – plagioclase, Qtz – quartz, Pheno – phenocryst, HT – hydrothermal.

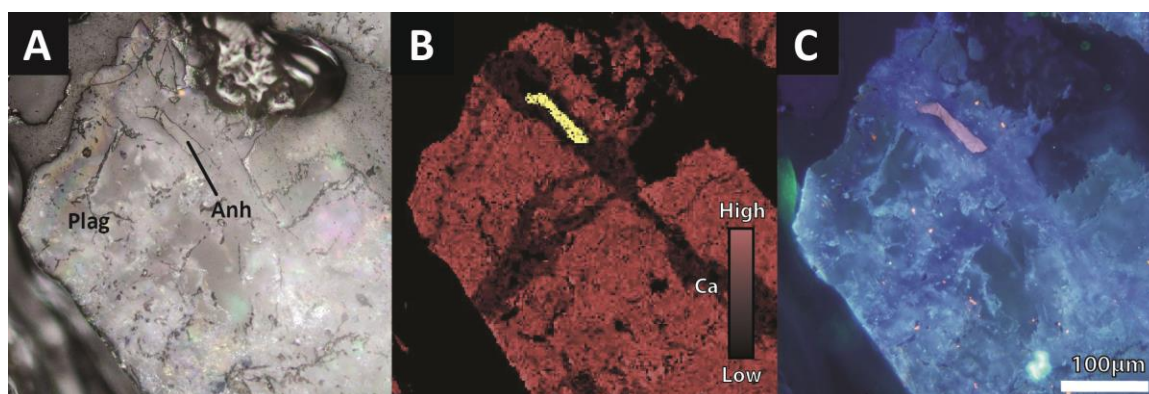


Figure 2.3 Anhedral hydrothermal anhydrite inclusion in plagioclase from K-porphyry at El Salvador. A) Reflected light image B) Map of plagioclase Ca content extracted from QEMScan EDS data, note position of anhydrite in altered, Ca depleted zones of plagioclase C) CL image (CITL 8200 Mk 5-1 University of Geneva) showing mottled, patchy texture in altered plagioclase grain.

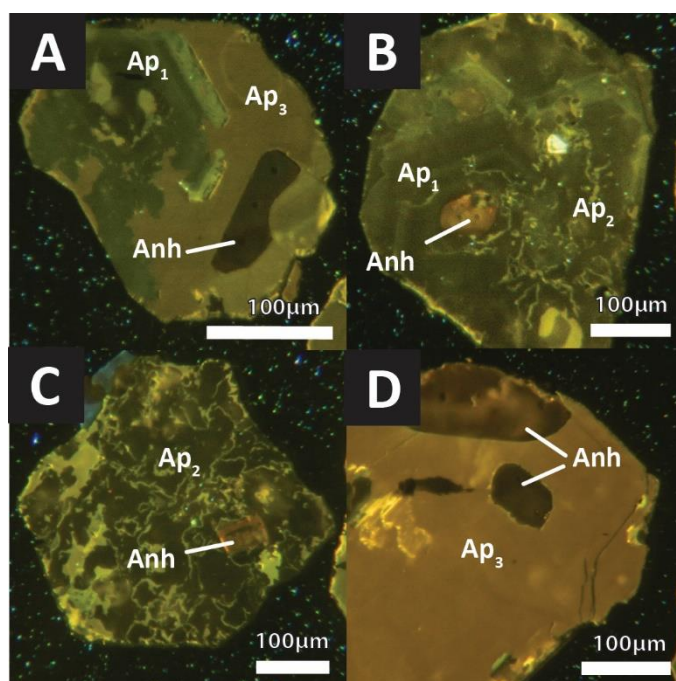


Figure 2.4 CL images of anhydrite inclusions in apatite grains from EEP 4 (b) and EEP-5 (a, c, d) porphyry dikes at Encuentro, Chile. Note wide range of textures in host apatites related to varying degrees of alteration and overgrowth. Images obtained using CITL Mk 4 at University of British Columbia. It should be noted that there is some difference in the color of the images produced by this instrument compared to those in Figure 2.1 but that the same textures were clearly visible in images taken using both instruments.

Table 2.1 List of Anhydrite-bearing samples and localities

Deposit/location	Coordinates (WGS84)			Unit/ sample no.	Lithology	Inclusion host	No. inclusions
	Zone	Easting	Northing				
Aucanquilcha volcanic Center (Chile)	19S	542824	7641521	3,974	AP-07-41	Dacite volcanic rocks	Amphibole 20+
Christmas (Arizona)	12N	523893	3657848	805	CHR-7	Porphyritic dike	Apatite 1
	12N	523420	3658111	902	CHRPIT		Apatite 1
El Salvador (Chile)	19S	443800	7096245	2,476	ES-12792	Latite dike	Apatite 2
	19S	444390	7096420	2,440	ES-12785A	K porphyry	Apatite 3
Encuentro (Chile)	19S	489895	7447649	1,586	EEP-1	Porphyritic dikes	Apatite 4
	19S	489931	7447586	1,613	EEP-2		Apatite 5
	19S	489931	7447586	1,357	EEP-4		Apatite 4
	19S	489931	7447586	1,371	EEP-5		Apatite 4
Robinson (Nevada)	11N	670004	4347769	2,000	VET-2B	Porphyritic dike	Apatite 1
							Amphibole 1
							Titanite 1
Yerington (Nevada)	11N	317338	4314977	1,421	LH-7	Weakly porphyritic granite	Apatite 4
							Titanite 1
							Plagioclase 1
							Quartz 1

Sample references: Aucanquilcha (Walker et al., 2013), El Salvador (Lee et al., 2017), Encuentro (Osorio, 2017), Yerington (Dilles, 1987); samples from Christmas and Robinson deposits were collected by J.H. Dilles (November 2017, and July 1992, respectively)

Table 2.2 Electron microprobe analyses of anhydrite inclusions

Location	Sample	Host mineral	Type ¹	SO ₃	P ₂ O ₅	CaO	FeO	SiO ₂	MnO	SrO	BaO	La ₂ O ₃	Ce ₂ O ₃	Total
Aucanquilcha	AP-07-41	Amphibole	Magmatic	60.25	0.14	40.07	0.54	0.15	0.00	0.55	0.15	0.03	0.04	101.93
Aucanquilcha	AP-07-41	Amphibole	Magmatic	60.10	0.11	39.83	0.83	0.54	0.00	0.57	0.19	0.02	0.04	102.24
Aucanquilcha	AP-07-41	Amphibole	Magmatic	59.29	0.24	40.77	0.50	0.12	0.02	0.60	0.15	0.03	0.03	101.75
Aucanquilcha	AP-07-41	Amphibole	Magmatic	58.86	0.12	41.27	0.38	0.25	0.05	0.52	0.11	0.00	0.03	101.60
Aucanquilcha	AP-07-41	Amphibole	Magmatic	61.37	0.15	40.13	0.43	0.09	0.01	0.54	0.07	0.01	0.00	102.79
Aucanquilcha	AP-07-41	Amphibole	Magmatic	60.91	0.18	39.57	0.43	0.20	0.00	0.50	0.13	0.02	0.02	101.95
Augustine	AUG_HSA2	Orthopyroxene	Magmatic	59.48	0.08	39.39	0.42	0.12	0.04	0.23	0.01	0.00	0.01	99.80
Augustine	AUG_HSA2	Orthopyroxene	Magmatic	58.77	0.09	41.30	0.42	0.06	0.03	0.22	0.01	0.02	0.04	100.95
Augustine	AUG_HSA2	Orthopyroxene	Magmatic	58.34	0.10	41.57	0.54	0.08	0.03	0.22	0.00	0.00	0.02	100.91
Augustine	AUG_HSA2	Orthopyroxene	Magmatic	58.89	0.09	39.81	0.57	0.10	0.04	0.22	0.01	0.04	0.02	99.78
Augustine	AUG_HSA2	Plagioclase	Magmatic	57.73	0.08	39.14	0.00	0.38	0.00	0.21	0.00	0.04	0.00	97.57
Augustine	AUG_QMI	Plagioclase	Magmatic	58.03	0.18	40.85	0.03	0.10	0.00	0.29	0.01	0.01	0.02	99.52
Augustine	AUG_QMI	Plagioclase	Magmatic	57.92	0.21	38.47	0.07	0.82	0.00	0.21	0.01	0.01	0.06	97.79
Augustine	AUG308	Plagioclase	Magmatic	58.79	0.12	40.50	0.01	0.10	0.04	0.23	0.02	0.02	0.03	99.85
Augustine	AUG308	Plagioclase	Magmatic	58.21	0.13	39.99	0.08	0.13	0.04	0.24	0.03	0.00	0.01	98.85
Christmas	CHR-7	Apatite	Magmatic	58.86	0.22	41.33	0.00	0.01	0.00	0.20	0.01	0.03	0.07	100.71
Christmas	CHR-7	Apatite	Magmatic	57.11	0.21	41.28	0.00	0.00	0.03	0.20	0.00	0.03	0.06	98.93
Christmas	CHR-7	Apatite	Magmatic	58.63	0.17	41.05	0.01	0.00	0.05	0.20	0.05	0.03	0.08	100.28
Christmas	CHRPIT	Apatite	Magmatic	55.37	0.23	41.22	0.00	0.00	0.00	0.15	0.04	0.06	0.13	97.20
Christmas	CHRPIT	Apatite	Magmatic	58.10	0.15	40.91	0.00	0.00	0.00	0.16	0.05	0.00	0.04	99.42
Christmas	CHRPIT	Apatite	Magmatic	57.60	0.17	41.15	0.02	0.00	0.03	0.18	0.04	0.01	0.05	99.24
El Salvador	ES-12785A	Apatite	Magmatic	58.55	0.41	40.48	0.00	0.01	0.01	0.23	0.01	0.06	0.05	99.81
El Salvador	ES-12785A	Plagioclase	Hydrothermal	59.47	0.05	40.42	0.06	0.00	0.00	0.21	0.07	0.04	0.05	100.36
El Salvador	ES-12785A	Plagioclase	Hydrothermal	59.85	0.04	40.33	0.00	0.00	0.00	0.24	0.01	0.00	0.05	100.52
El Salvador	ES-12785A	Plagioclase	Hydrothermal	58.82	0.03	40.47	0.02	0.05	0.00	0.26	0.01	0.03	0.01	99.69
El Salvador	ES-12785A	Plagioclase	Hydrothermal	60.06	0.15	39.04	0.01	0.05	0.01	0.20	0.04	0.03	0.03	99.63
El Salvador	ES-12785A	Plagioclase	Hydrothermal	58.45	0.07	41.23	0.01	0.02	0.00	0.23	0.00	0.02	0.04	100.06
El Salvador	ES-12785A	Plagioclase	Hydrothermal	60.57	0.07	39.57	0.00	0.01	0.00	0.22	0.08	0.04	0.06	100.64
El Salvador	ES-12785A	Plagioclase	Hydrothermal	59.44	0.07	39.48	0.00	0.01	0.00	0.22	0.04	0.00	0.03	99.28
El Salvador	ES-12785A	Plagioclase	Hydrothermal	59.38	0.03	39.07	0.02	0.01	0.01	0.38	0.06	0.00	0.00	98.96
El Salvador	ES-12785A	Plagioclase	Hydrothermal	59.95	0.08	40.07	0.00	0.03	0.04	0.24	0.05	0.05	0.04	100.54
El Salvador	ES-12785A	Plagioclase	Hydrothermal	60.45	0.05	39.57	0.00	0.02	0.03	0.26	0.08	0.03	0.01	100.51
El Salvador	ES-12785A	Plagioclase	Hydrothermal	59.77	0.09	40.94	0.05	0.08	0.00	0.22	0.05	0.03	0.07	101.29
El Salvador	ES-12785A	Plagioclase	Hydrothermal	61.25	0.08	39.71	0.01	0.04	0.03	0.22	0.06	0.04	0.06	101.51
El Salvador	ES-12785A	Plagioclase	Hydrothermal	56.00	0.05	42.30	0.03	0.01	0.00	0.21	0.03	0.02	0.04	98.69
El Salvador	ES-12785A	Plagioclase	Hydrothermal	55.82	0.05	42.49	0.00	0.00	0.01	0.16	0.01	0.01	0.05	98.61
El Salvador	ES-12785A	Plagioclase	Hydrothermal	55.73	0.11	42.40	0.02	0.01	0.00	0.17	0.00	0.02	0.04	98.53
El Salvador	ES-12785A	Plagioclase	Hydrothermal	56.02	0.18	42.30	0.02	0.01	0.00	0.16	0.02	0.06	0.05	98.85
El Salvador	ES-12792	Apatite	Magmatic	59.78	0.17	40.55	0.03	0.01	0.00	0.32	0.08	0.04	0.02	101.01
El Salvador	ES-12792	Apatite	Magmatic	59.88	0.16	40.92	0.00	0.01	0.00	0.31	0.07	0.00	0.00	101.36
El Salvador	ES-12792	Apatite	Magmatic	53.63	0.28	42.33	0.01	0.00	0.00	0.31	0.01	0.04	0.04	96.65
El Salvador	ES-12792	Apatite	Magmatic	55.78	0.28	42.64	0.01	0.00	0.00	0.32	0.02	0.02	0.04	99.10
Encuentro	EEP-1	Apatite	Magmatic	56.80	0.20	41.45	0.01	0.00	0.02	0.39	0.04	0.01	0.02	98.95
Encuentro	EEP-1	Apatite	Magmatic	55.88	0.49	42.66	0.00	0.00	0.00	0.22	0.07	0.04	0.08	99.45
Encuentro	EEP-2	Apatite	Magmatic	55.32	0.35	41.55	0.01	0.00	0.02	0.22	0.01	0.05	0.09	97.63
Encuentro	EEP-2	Apatite	Magmatic	55.87	0.19	41.55	0.00	0.00	0.03	0.23	0.01	0.05	0.07	97.99
Encuentro	EEP-2	Apatite	Magmatic	56.50	0.15	41.24	0.05	0.00	0.00	0.23	0.10	0.02	0.04	98.33
Encuentro	EEP-2	Apatite	Magmatic	57.48	0.18	41.84	0.00	0.00	0.03	0.20	0.00	0.03	0.05	99.81
Encuentro	EEP-4	Apatite	Magmatic	55.58	0.18	42.51	0.00	0.00	0.01	0.17	0.04	0.04	0.05	98.57
Encuentro	EEP-4	Apatite	Magmatic	55.21	0.09	41.24	0.01	0.00	0.05	0.15	0.07	0.02	0.04	96.89
Encuentro	EEP-4	Apatite	Magmatic	56.52	0.15	42.32	0.02	0.00	0.00	0.19	0.02	0.04	0.09	99.33
Encuentro	EEP-4	Apatite	Magmatic	55.94	0.08	41.82	0.02	0.00	0.00	0.19	0.01	0.03	0.04	98.13
Encuentro	EEP-4	Apatite	Magmatic	56.97	0.12	42.57	0.00	0.00	0.04	0.16	0.01	0.04	0.12	100.03
Encuentro	EEP-5	Apatite	Magmatic	58.47	0.18	41.12	0.00	0.00	0.02	0.19	0.04	0.05	0.08	100.15
Encuentro	EEP-5	Apatite	Magmatic	57.55	0.23	40.89	0.00	0.00	0.00	0.19	0.06	0.03	0.06	99.02
Encuentro	EEP-5	Apatite	Magmatic	57.00	0.19	41.78	0.02	0.00	0.00	0.20	0.04	0.02	0.04	99.29
Encuentro	EEP-5	Apatite	Magmatic	56.62	0.13	41.81	0.00	0.00	0.00	0.25	0.05	0.05	0.07	98.99
Encuentro	EEP-5	Apatite	Magmatic	56.49	0.14	42.23	0.00	0.01	0.02	0.26	0.01	0.04	0.09	99.29
Encuentro	EEP-5	Apatite	Magmatic	54.17	0.08	40.58	0.02	0.01	0.00	0.29	0.10	0.05	0.06	95.35
Encuentro	EEP-5	Apatite	Magmatic	55.66	0.10	41.81	0.00	0.00	0.00	0.23	0.07	0.04	0.05	97.96
Encuentro	EEP-5	Apatite	Magmatic	56.20	0.08	42.31	0.00	0.00	0.01	0.23	0.04	0.03	0.02	98.92
Encuentro	EEP-5	Apatite	Magmatic	57.29	0.11	41.93	0.05	0.00	0.01	0.21	0.03	0.04	0.05	99.72
Luhr Hill	LH-1	Apatite	Magmatic	59.32	0.57	40.32	0.00	0.03	0.00	0.33	0.02	0.01	0.02	100.62
Luhr Hill	LH-1	Apatite	Magmatic	59.04	0.26	41.48	0.01	0.01	0.00	0.31	0.10	0.02	0.02	101.26
Luhr Hill	LH-1	Apatite	Magmatic	58.64	0.07	42.14	0.00	0.01	0.00	0.35	0.01	0.03	0.04	101.29
Luhr Hill	LH-1	Apatite	Magmatic	57.74	0.09	42.06	0.00	0.00	0.00	0.33	0.00	0.01	0.04	100.28
Luhr Hill	LH-1	Apatite	Magmatic	55.88	2.09	41.73	0.01	0.02	0.00	0.33	0.02	0.02	0.01	100.11
Luhr Hill	LH-1	Plagioclase	Magmatic	58.26	0.02	41.10	0.15	0.05	0.00	0.58	0.00	0.00	0.01	100.19

Table 2.2 Electron microprobe analyses of anhydrite inclusions (Continued)

Location	Sample	Host mineral	Type ¹	SO ₃	P ₂ O ₅	CaO	FeO	SiO ₂	MnO	SrO	BaO	La ₂ O ₃	Ce ₂ O ₃	Total
Luhr Hill	LH-1	Plagioclase	Magmatic	58.31	0.03	40.60	0.12	0.11	0.00	0.59	0.00	0.02	0.00	99.77
Luhr Hill	LH-1	Plagioclase	Magmatic	57.26	0.03	41.11	0.11	0.06	0.02	0.57	0.00	0.00	0.01	99.15
Luhr Hill	LH-1	Quartz	Magmatic	56.56	0.03	41.48	0.25	0.18	0.00	0.60	0.01	0.00	0.00	99.11
Luhr Hill	LH-1	Quartz	Magmatic	58.35	0.02	40.54	0.21	0.22	0.03	0.64	0.02	0.02	0.01	100.06
Luhr Hill	LH-1	Titanite	Magmatic	53.84	0.10	40.02	0.06	0.04	0.00	0.51	0.00	0.00	0.08	94.65
Luhr Hill	LH-1	Titanite	Magmatic	54.48	0.09	42.85	0.09	0.04	0.00	0.48	0.01	0.03	0.07	98.13
Robinson	VET2B	Titanite	Magmatic	56.77	0.08	40.88	0.03	0.04	0.00	0.52	0.49	0.03	0.06	98.91
Robinson	VET-2B	Amphibole	Magmatic	58.57	0.24	40.86	0.65	0.04	0.00	0.51	0.08	0.03	0.03	101.02
Robinson	VET-2B	Apatite	Magmatic	54.66	0.22	42.35	0.01	0.01	0.00	0.54	0.00	0.05	0.06	97.91
Robinson	VET-2B	Apatite	Magmatic	55.13	0.26	41.43	0.00	0.00	0.01	0.53	0.03	0.06	0.04	97.49

All mineral amounts in wt %

¹Origin of anhydrite inclusions is based on observation of host mineral textures in backscattered electron and cathodoluminescence images and element maps extracted from QEMSCAN energy dispersive spectrometry maps

Chapter III. The sulfur content of apatite inclusions from intrusive anhydrite-bearing rocks

3.1 Abstract

Apatite is one of very few common igneous minerals which incorporates sulfur into its structure in measurable quantities, and as such represents a nearly unique opportunity to track the evolution of magmatic sulfur contents. Here we have analyzed apatite phenocrysts and inclusions from a number of anhydrite bearing plutonic rocks, most of which are associated with magmatic-hydrothermal ore deposits (Chapter II, Hutchinson and Dilles, 2019). We show that high-S apatites (>0.3 wt% S, Van Hoose et al. 2013) were present in all samples and that in all cases apatites included in silicate phases contain more sulfur than their phenocrystic counterparts.

Comparing apatite S contents to a range of geochemical parameters including apatite Sr content, apatite volatile content, host mineral type and host mineral chemistry produces little correlation. At a given value for any of these parameters the apatite sulfur content often varies by ~0.5 wt%, almost the entire measured range. Models of silicate melt sulfur content and sulfur partitioning into apatite suggest that this should require a temperature change on the order of ~200°C. Trends may have been obscured by reequilibration of more rapidly diffusing trace elements (Sr, Cl, F) at lower temperature, or by post entrapment exchange with host minerals.

3.2 Introduction

Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$, is by far the most common naturally occurring phosphate and a ubiquitous mineral in igneous rocks (Piccoli and Candela, 2002). For metaluminous melts, apatite solubility is primarily a function of temperature and melt SiO_2 content (Harrison and Watson, 1984), such that apatite typically begins to crystallize during the cooling and evolution of a magma to more silica rich compositions. Using apatite solubility data (Harrison and Watson, 1984), Piccoli and Candela (1994) showed that it was possible to use whole rock composition to estimate the apatite saturation temperature (AST), and applied this to the plinian phase of the Bishop Tuff (AST = 860°C) and Tuolumne Intrusive Suite (generally AST=900-930°C). They also showed that for the Tuolumne rocks, more than half of the apatite crystallizes within ~60°C of the AST.

The apatite crystal structure ($\text{P6}_3/m$) and chemistry allow for extensive substitution with a broad range of trace elements including alkalis, alkali earths, transition metals and rare earth elements (REE). Indeed, strong preference of REE for apatite over silicate melts (e.g. $D_{\text{REE}}^{\text{apatite-}}$

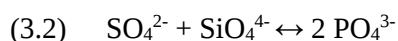
melt – 10-40, granitic melt composition, Watson and Green, 1981) means that the crystallization of apatite commonly exerts a first order control on the igneous REE patterns. Significantly, the apatite structure can also accommodate all major magmatic volatiles, including F, Cl and OH (in the “channel” site) and S and C as SO_4^{2-} and CO_3^{2-} in coupled substitutions involving PO_4^{3-} tetrahedra (Peng et al. 1997, Pan and Fleet, 2002, Marks et al. 2012, Riker et al. 2018) making it possible to use apatite as a tracer of magmatic volatile evolution. In this regard apatite warrants study as an alternative to melt inclusions, which are commonly subject to post entrapment modification (e.g. Esposito et al. 2014).

With regard to tracing magmatic OH, F and Cl contents, a number of methods have been tested. Using secondary ion mass spectrometry (SIMS), Boyce and Hervig (2008) measured the core-rim variation in OH and Cl contents for apatites from the Cerro Galan Ignimbrite, Argentina. They found complex oscillatory zoning in the rims of crystals, implying multiple stages of degassing and “regassing” prior to eruption. Given the fast diffusion of volatile species in apatite (Brenan, 1993, Fig. 3.1), the preservation of this zoning requires less than ~1yr between these events and eruption. Another approach, established by Stock et al. (2016, 2018) has been to analyse apatite trapped as inclusions in a variety of other igneous minerals, with the expectation that these apatite inclusions record the volatile inventory of the magma at the time of crystallization of the host mineral. In this way, a series of apatite inclusions from different minerals should capture the ongoing volatile evolution of the system. Results from a range of eruptive units at Campi Flegrei (Stock et al. 2018) suggest that although all units evolved under dominantly fluid-undersaturated conditions, the initial volatile contents of parental melt may have changed somewhat over time.

While studies like these have demonstrated the utility of apatite as a volatile tracer it is worth noting that apatite composition can only be related quantitatively to melt volatile composition by well characterized exchange reactions including F, OH and Cl. Experimental work has shown that exchange coefficients are a complex function of temperature, pressure and melt and apatite composition and although empirical models for exchange are available, independent estimates of either the F, Cl or H_2O content of the melt are generally still required (e.g. Mathez and Webster 2005; Webster et al. 2009, 2017; Doherty et al. 2014; Li and Hermann 2015, 2017; McCubbin et al. 2015; Potts et al. 2015).

As mentioned above, apatite is able to incorporate SO_4^{2-} into its structure in place of PO_4^{3-} , and igneous apatite may contain several wt% SO_3 . This makes apatite one of very few possible avenues for investigating magmatic sulfur contents, a variable of considerable interest

for many, particularly those studying either volcanic volatile emissions (since volcanic SO_2 is a major climate-forcing agent, e.g. Westrich and Gerlach, 1992, Wallace 2001) or the magmas associated with sulfur rich magmatic-hydrothermal ore deposits (e.g. Gustafson and Hunt, 1975, Dilles et al. 2015). Charge balancing requires that SO_4^{2-} be incorporated into apatite as part of a coupled substitution, generally involving either Na or Si (Eq 1., 2.)



Experimental work (cf. Peng et al. 1997, Parat and Holtz 2004) and studies of natural samples (cf. Streck and Dilles, 1998, Parat et al. 2002, Chelle-Michou and Chiaradia 2017) show that both of these substitutions likely occur, but disagree on which mechanism dominates. Recent S- μ XANES work on apatite (Konecke et al. 2017) confirmed the incorporation of sulfur in apatite as S^{6+} but found that under reduced conditions apatite will also accommodate small amounts of S^{2-} and possibly S^{4+} .

Many previous studies have attempted to use apatite sulfur contents to investigate magmatic sulfur evolution (including Streck and Dilles, 1998, Parat et al. 2002, Imai 2002, Imai 2004, Chambefort et al. 2008, van Hoose et al. 2013, Scott et al. 2015, Chelle-Michou and Chiaradia 2017) but interpreting the results is often challenging. Experimental work by Peng et al. (1997, experiments by Luhr 1990) and Parat and Holtz (2004, 2005) suggest that $D_s^{\text{apatite-melt}}$ is generally ~ 2 -15, but that it varies with temperature, $f\text{O}_2$ and melt composition. While $D_s^{\text{apatite-melt}}$ tends to increase at lower temperature (cf Peng et al. 1997, Parat and Holtz 2004, 2005), this may be offset by falling melt sulfur contents, since sulfate solubility decreases with temperature (e.g. Masotta and Keppler 2015). Superimposed on this general behavior is the effect of changing oxidation state (and accompanied changes to $\text{S}^{6+}/\Sigma\text{S}$), as well as changes related to melt composition, not only because of differences in the ability of different melts to accommodate sulfur, but also because SiO_2 and Na_2O are directly involved in the coupled substitutions detailed above.

Despite the complexity, a number of first order observations can be made regarding apatite sulfur contents. Firstly, high sulfur apatites in magmatic systems (>0.2 - 0.3 wt% SO_3) undeniably require oxidized conditions under which the majority of sulfur in the melt is present as sulfate (i.e. $>\sim\text{NNO}+1$, Carrol and Rutherford, 1987). Indeed experimental apatite measured by Peng et al. (1997) at reducing conditions ($\sim\text{FMQ}$) generally contained <0.05 wt% SO_3 . In almost all of the studies listed above, high-S apatites are accompanied by evidence of high $f\text{O}_2$

conditions, including phenocrysts or inclusions of magmatic anhydrite (Streck and Dilles 1998, Parat et al. 2002, Chambefort et al. 2008, Van Hoose et al. 2013, Hutchinson and Dilles, 2019). Secondly, apatite inclusions in silicate phases are generally more sulfur rich than their phenocrystic counterparts in the same samples (Parat et al. 2002, Imai, 2004, van Hoose et al. 2013). Finally, sulfur zoning in apatite is preserved both in volcanic rocks (e.g. van Hoose et al. 2013) and in plutonic rocks (e.g. Streck and Dilles, 1998), particularly in apatite inclusions, and although zoning can be complex, the most common type involves s-rich cores and s-poor rims. Although there is currently no experimental data on sulfur diffusion in apatite, the presence of sulfur zoning is consistent with relatively slow diffusion expected for a highly charged cation (cf Sr, La diffusion rates, Fig. 3.1). These observations suggest that high-S apatites generally crystallize early, and that the effect of falling melt sulfur contents during cooling (either due to degassing or crystallization of anhydrite) outweighs any increase in $D_s^{\text{apatite-melt}}$, leading to low-S apatite rims and phenocrysts.

In this study, we investigate apatite inclusions and phenocrysts from five intrusive rocks associated with copper porphyry deposits, four of which have been shown to be anhydrite saturated (Hutchinson and Dilles 2019). The aim is to link apatite sulfur contents to apatite and host mineral composition in order to constrain the sulfur evolution of the melt and to estimate the relative timing of anhydrite saturation. Analyzing apatite inclusions hosted in a range of other phases, as well as phenocryst cores and rims should allow us to better understand temporal changes to melt sulfur during magmatic evolution. In particular we hope to determine if sulfur has been added to the system from an external source, either by direct magma mixing or by fluxing of SO_2 from an underplating melt (e.g. Hattori 1993). The sensitivity of apatite composition to changes in melt volatiles, and particularly to degassing make it a powerful tool to assess these sorts of processes. With the exception of the Luhr Hill pluton (LH-1, Dilles 1987) and the El Salvador late latite dike (ES-12792, Lee, 2008, Lee et al., 2017), detailed petrographic and petrologic information is missing from these samples, however it should be possible to test whether or not there are any first order similarities amongst apatites crystallizing from sulfur rich anhydrite saturated magmas.

3.3. Methods

3.3.1 Sample Preparation

The five samples chosen for this study were initially investigated by Hutchinson and Dilles (2019) (Dissertation Chapter II) and sample preparation methods are discussed only

briefly. Whole rock samples were crushed, washed, sieved and phenocrysts were picked by hand using a binocular microscope. Heavy liquid separation using sodium polytungstate solution was also used to separate apatite phenocrysts from a number of samples. Mineral grains were then mounted in epoxy, polished in oil and mapped using Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMScan) at 5 μ m resolution. These maps were used to find apatite inclusions for analysis by electron microprobe (EPMA). Details of samples can be found in table 3.1.

3.3.2 Analytical Methods

In total ~380 apatite analyses, ~80 titanite analyses and ~95 amphibole analyses were performed using a Cameca SX100 electron microprobe at Oregon State University (OSU). Details of analytical conditions can be found in appendix 1, apatite compositions are recorded in appendix 2 and amphibole and titanite compositions are in appendix 3. Conditions for apatite analysis followed recommendations by a number of authors (Stormer et al., 1993; Goldoff et al., 2012; Stock et al., 2015) for minimizing the migration of volatile components during analysis. This meant limiting beam current to 10nA and counting times for F and Cl to 30s. Small apatite inclusions in many samples necessitated a relatively focused 2 μ m beam, and this may increase the uncertainty on volatile measurements compared to a defocused 5-10 μ m beam. Unless otherwise noted, 2 σ uncertainties for apatite measurements are based on repeat analyses (n=10) of Durango apatite standard. No similar standard was available for titanite and amphibole analyses, and in these cases 2 σ analytical uncertainties are calculated based on counting statistics using Cameca software. Stoichiometry was calculated using the method of Ketcham (2015).

Based on repeat analysis of the Durango apatite standard, the reproducibility of fluorine measurements is $\pm \sim 0.37$ wt% (equivalent to ~ 0.2 apfu, or $X_F \sim 10\%$). This is taken to be approximately the precision of the measurements, and is shown in figures 3.4a-e. However, the response of fluorine to the electron beam is complicated and is affected by both the orientation of the apatite crystal, and its bulk composition (Stormer et al., 1993; Goldoff et al., 2012; Stock et al., 2015). In general, apatite grains oriented with their c-axis parallel to the beam, and those with close to end member fluorapatite or chlorapatite compositions are most unreliable. Indeed, a number of apatite grains analyzed in this study have fluorine contents in excess of that expected for pure fluorapatite, up to a maximum of 4.47 wt% F (equivalent to ~ 2.4 apfu, or $X_F \sim 120\%$). In this case, the uncertainty is clearly greater than the figure quoted above, up to ~ 0.65 wt% (~ 0.4

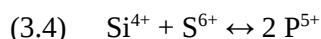
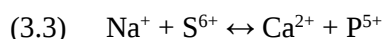
apfu or $X_F \sim 20\%$). However this degree of uncertainty likely only effects analyses of close to pure end member fluorapatites, oriented with the c-axis parallel to the beam.

Apatite inclusions were chosen on the basis that they were fully enclosed by their host grains and were analyzed close to the center in order to avoid a contribution of X-rays from the surrounding host mineral. Growth zoning of host minerals, identified in either BSE images (titanite) or in QEMScan Mg element maps (amphibole) was used to make sure that analysis of the host mineral was performed in an area representing the trapping conditions of the apatite grain (i.e. the same growth zone as the apatite grain was trapped in).

3.4 Results

3.4.1 Heterovalent trace element substitutions

Apatite accommodates a broad range of elements by coupled substitutions, but by far the most abundant are Na^+ , Si^{4+} , S^{6+} and REE^{3+} . Ignoring other elements, and considering the REE together, four possible substitutions are possible:



The concentrations of the substituting elements for each reaction (3-6), expressed as atoms per formula unit (apfu) are plotted in figures 3.2a-d. Of the REE only Ce was regularly above EPMA detection limits however preliminary LA-ICP-MS analyses suggest that $\sum \text{REE}$ can be estimated as $\sim 2 \times \text{Ce}$. The sum of all the reactions is plotted in figure 3.2e, expressed as the total of the less highly charged cations in each couple (i.e. $\text{Na}^+ + \text{Si}^{4+}$) vs the total of the more highly charged cations (i.e. $\sum \text{REE}^{3+} + \text{S}^{6+}$). A close fit to the 1:1 line in figure 3.2e shows that concentrations of these four substituting elements are well explained by some combination of reactions 3-6 above, with no need for any other mechanism. Some deviation in the slope of data in figure 3.2e from the 1:1 line may be related to the calculation of $\sum \text{REE}$. A slightly higher $\sum \text{REE} : \text{Ce}$ ratio might explain the points which fall below the 1:1 line. A close fit of these data to the 1:1 line (Fig 3.2e) also demonstrates that variation in these elements cannot be explained by analytical problems beyond the uncertainties quoted above.

However, while all the data plot consistently in figure 3.2e, there are clear differences in which substitution mechanisms dominate between samples, indicated by scatter in figures 3.2a-d.

Another way to assess these differences is to plot the ratio of less highly charged cations against the ratio of more highly charged cations (i.e. Na/Si vs $\sum\text{REE/S}$) as in figure 3.2f. Points plotting in each quadrant represents a preference for one of the reactions 1-4 and helps to clearly differentiate between samples. In particular it shows that CHR-7 strongly favors reactions involving Na, and to a lesser extent REE, while most samples (LH-1, VET-2B and WF-1) favor reactions involving Si, and to a lesser degree S. Data from ES-12792 appears to form two distinct groups, one which strongly favors S over REE but contains subequal Si and Na, and another which strongly favors Na over Si, but contains subequal proportions of REE and S. While it is tempting to interpret these preferences in terms of melt composition (particularly Na, S and REE concentrations), these exchange reactions will also be affected by temperature, pressure, and apatite composition. Since no comprehensive experimental data exists characterizing these substitution reactions, they can only be interpreted in a qualitative sense.

3.4.2 Comparison of inclusions and phenocrysts

In order to assess differences between apatite phenocrysts and inclusions we have plotted box and whisker plots (Fig. 3.3) showing the mean, median and range of values for S, Ce, Sr, Fe and Cl for each type of apatite from three of the five samples (those with analyses of phenocrysts). These elements were chosen in order to include relatively slowly diffusing, charge coupled elements (S, Ce), more quickly diffusing elements substituting for Ca (Sr, Fe) and a very quickly diffusing element occupying the channel site (Cl) (Fig. 3.1).

Firstly, figure 3.3 clearly shows that apatites hosted in magnetite and other Fe-bearing phases contain significantly more Fe than apatite hosted in other phases or apatite present as phenocrysts. This suggests these apatites have undergone some degree of post entrapment exchange, in which the Fe has diffused into the apatite from the surrounding host mineral. This mechanism has previously been proposed to explain the high Fe contents of anhydrite inclusions hosted in mafic minerals (Chambefort et al. 2008). Another explanation for the apparently high Fe contents is secondary fluorescence within the host mineral during EPMA analysis, although there is no apparent correlation between apatite Fe content and distance from the grain boundary. Further work analyzing couples of Fe-free apatite and Fe-bearing host minerals may help to determine the magnitude of this effect.

Within each sample all apatite inclusion types have broadly similar ranges of Ce, Sr and Cl with only a few exceptions (note that for some apatite types, e.g. plagioclase and magnetite hosted inclusions in VET-2B, only a very small number of apatites were analyzed). The most

obvious exception is magnetite hosted inclusions from LH-1 and ES-12792, which tend to have higher Sr than their counterparts hosted in other minerals or as phenocrysts. Magnetite hosted apatite inclusions from LH-1 also have significantly higher Cl contents than any other apatites from this sample, although they are still low in comparison to other samples. Experimental work by Watson and Green (1981) suggests that $D_{\text{Sr}}^{\text{apatite-melt}}$ is relatively insensitive to changes in either bulk melt composition, temperature or pressure, implying that changes in apatite Sr content are most likely a reflection of melt Sr content. Since melt Sr content is largely controlled by the crystallization of plagioclase ($D_{\text{Sr}}^{\text{plagioclase-melt}} \sim 1-10$, Blundy and Wood, 1991, Bédard 2006) it is likely that in both LH-1 and ES-12792, high-Sr apatite inclusions in magnetite represent the earliest crystallizing apatites, trapped prior to extensive plagioclase crystallization. This is consistent with Dilles (1987) who showed that magnetite, plagioclase and apatite likely began crystallizing close to the liquidus in the Luhr Hill granite, while amphibole and biotite began to crystallize somewhat later. Analyzing apatite grains hosted in early crystallizing An-rich plagioclase may be one way to test this hypothesis. Unfortunately, like apatite Fe contents, this may be complicated by the post entrapment exchange of Sr between plagioclase and apatite.

However, by far the biggest difference between apatite inclusions and phenocrysts is related to their sulfur content. In all three samples apatite inclusions have significantly higher and more varied sulfur contents than their phenocrystic counterparts. Although not shown in figure 3.3, Na and Si contents mirror these trends, since in all cases S is positively correlated with Na and Si (Fig 3.2a-b). Figure 3.3 also shows that there is generally little difference between the core and rim sulfur contents of apatite phenocrysts.

3.4.3 Apatite volatile contents

Apatite volatile contents in this study, expressed as the molar proportion of each in the channel site ($X_{\text{F}} + X_{\text{Cl}} + X_{\text{OH}} = 100$), range from $X_{\text{F}} \sim 30 - 100$, $X_{\text{Cl}} \sim 0 - 25$ and $X_{\text{OH}} \sim 0 - 70$ (Figs 3.4a-e). With the exception of WF-1, the majority of intra-sample variation in apatite volatile contents is related to $X_{\text{F}} - X_{\text{OH}}$ exchange at relatively constant Cl content. However between samples apatite Cl varies considerably. CHR-7 apatites have the highest X_{Cl} ($\sim 15 - 25$), VET-2B apatites have intermediate X_{Cl} (~ 10), ES-12792 apatites have low X_{Cl} (~ 4) while apatites from LH-1 generally have almost no detectable Cl, with the exception of magnetite hosted apatites where $X_{\text{Cl}} \sim 2$. In sample WF-1 amphibole and plagioclase hosted apatite grains generally have very low Cl ($X_{\text{Cl}} \sim 1$) but titanite hosted apatite show a large variation in Cl content ($X_{\text{Cl}} \sim 1 - 15$).

With regards to F and OH, samples LH-1 and VET-2B have the most F-rich apatites, and both show similar ranges with $X_F \sim 80 - 100$ and $X_F \sim 75 - 90$ respectively, with VET-2B apatites offset to higher Cl values. CHR-7 apatites generally have intermediate $X_F \sim 60 - 80$ while ES-12792 apatites are the most varied and most F-poor ($X_F \sim 35 - 70$). Again, WF-1 apatites hosted in plagioclase or amphibole, which are similar in composition to those from LH-1 ($X_F \sim 80 - 95$), are distinctly different from those hosted by titanite, which have lower F ($X_F \sim 65 - 80$). Note that since most of the apatites studied here (and igneous apatites in general) are low Cl (often $X_{Cl} < 10$), the calculated X_{OH} is heavily dependent on the measured X_F . As stated above, EPMA measurement of F in apatite is difficult, and the response of F to the electron beam depends not only on beam conditions but also on apatite orientation and apatite bulk composition (Stock et al. 2015, Fallon, pers. comm). This makes it particularly difficult to estimate the uncertainty on F measurements (and therefore on calculated X_F and X_{OH}), and this may explain some of the spread of data in this direction.

High-S apatites (>0.2 wt % S, >0.5 wt% SO_3) are present in all samples, with the highest S apatites (~ 0.7 wt% S or ~ 1.75 wt% SO_3) present as inclusions in titanite in sample VET-2B. As previously discussed there is generally little difference in the range of sulfur contents recorded by apatite inclusions trapped in different phases, but without exception apatite phenocryst cores and rims all have low sulfur contents (<0.1 wt% S). Sample CHR-7 has the lowest sulfur contents (all <0.3 wt% S) but only biotite hosted inclusions were analyzed.

3.4.4 Host mineral volatile contents

Host amphibole and titanite grains were also analyzed for major elements and volatiles. In amphibole, only Cl and S were detectable (detection limits were ~ 100 ppm and ~ 50 ppm respectively) while in titanite Cl and F were detectable (detection limit for both ~ 50 ppm).

The Cl content of amphiboles ranges from 150-4000 ppm (Figs 3.5a-c) and is generally elevated in higher-Al amphibole (Fig 3.5a). It has been shown that that amphibole chemistry, particularly K content, exerts a first order control on $D_{Cl}^{amphibole-melt}$ (Sato, 2005, Giesting and Filiberto 2014) and it is likely that in this case changes in amphibole K content, rather than changes to melt Cl content during evolution, are responsible for the observed correlation. The exception to this is amphiboles from ES-12792, which appear to have low Cl contents regardless of amphibole major element composition, although only a limited number of analyses were made (Fig 3.5b). S was only routinely above the detection limit in amphiboles from sample VET-2B, and the highest Al amphiboles from ES-12792 (Fig 3.5c). There are currently no data regarding

the effect of amphibole major element composition on sulfur partitioning, but given that high-Al amphiboles in VET-2B and ES-12792 have quite different chemistry (e.g. Fig 3.1b), and both share high sulfur contents it is possible that this reflects high melt-S contents at high T-P conditions.

Titanite F contents range from ~70 - 200 ppm (Fig. 3.6a) but do not vary systematically with titanite Zr content (as a proxy for temperature, Hayden et al. 2008). Puzzlingly, despite the lowest apatite Cl contents of all samples, Cl was only regularly above detection limits (~50 ppm) in titanite from sample LH-1 and ranged from 0-160 ppm (Fig. 3.6b). It is important to note that with the possible exception of Cl in amphibole, the volatile contents of host minerals are significantly lower than those of the apatite inclusions. This means that a contribution of X-rays from secondary fluorescence in the host mineral is unlikely, as is significant exchange between apatite inclusion and host.

3.4.5 Host mineral thermobarometry

Pressure and temperature estimates were made for amphibole hosts using the model of Ridolfi et al. (2010). LH-1 and WF-1 amphiboles yield similarly low temperatures (~ 700 - 800°C, ~ 750 - 820°C respectively) and pressures (~ 50 – 60 MPa, ~ 80 – 130 MPa respectively) while VET-2B amphiboles yield significantly higher temperatures (~ 860 - 920°C) and pressures (~ 250 - 350MPa). Amphiboles from ES-12792 appear to fall into two discreet groups at ~810 – 830 °C, ~150 MPa and 940 – 980 °C, 350-450 MPa (Fig. 3.7). Temperature estimates were also calculated based on titanite host Zr content using the model of Hayden et al. (2008). For this calculation we have used pressures based on amphibole thermobarometry (above, LH-1 ~ 50MPa, WF-1 ~ 100MPa and VET-2B ~ 250MPa), and a reasonable estimate for the activities of SiO₂ and TiO₂ given quartz and rutile undersaturation ($a[\text{SiO}_2] = 0.9$, $a[\text{TiO}_2] = 0.7$) given quartz and rutile undersaturation (Fig. 3.7). LH-1 titanites give the lowest temperatures (~ 660 - 715°C) followed by those from sample VET-2B (~ 710 – 760°C) while the largest range and the highest temperatures were calculated from WF-1 titanite (~670 - 780°C). Varying $a[\text{SiO}_2]$ and $a[\text{TiO}_2]$ up to 1 (implying saturation in quartz and rutile), increases the calculated temperatures by ~50°C. Thermobarometry results are summarized in figure 3.7 and suggest that titanite crystallized at significantly lower temperature than amphibole in VET-2B, slightly lower temperature than amphibole in LH-1 and that both phases were crystallizing at approximately the same temperature in WF-1, with titanite crystallization extending to much lower temperatures.

3.5 Discussion

3.5.1 The evolution of melt volatile content based on apatite composition

In order to put changes in apatite sulfur content in context, it is important to first understand how changes to apatite volatile contents reflect the volatile evolution of the melt. Thermodynamic modelling by Stock et al. (2018) (summarized in Fig. 3.8) provides a framework for understanding the evolution of apatite volatile contents in ternary space, and can be summarized as follows. During fluid-undersaturated crystallization, apatite composition should move away from the F-apex and toward either the Cl or OH apex (depending on the bulk partition coefficients for Cl and OH). In this case F, Cl and OH are all expected to act incompatibly but F the least so due to its incorporation into apatite (Stock et al., 2018 suggest $D_F^{\text{crystal-melt}} \sim 0.99$, is appropriate). Bulk partition coefficients for OH and Cl will depend on the degree of crystallization of amphibole and biotite, both of which can incorporate OH and Cl into their crystal structure, however in an apatite-saturated melt they should be lower than the bulk partition coefficient for F (red arrows, Fig. 3.8). Under fluid saturated conditions the composition of apatite should move rapidly away from the Cl apex, toward the F-OH binary, reflecting high partition coefficients for Cl between fluid and melt (blue arrows, Fig.3.8) . Finally at constant melt F-Cl-OH, cooling and reequilibration should lead to apatite compositions moving away from the OH apex, reflecting a preference for F in the channel site at lower temperature (Piccoli and Candela, 1994, Riker et al. 2018).

ES-12792 apatite compositions (Fig 3.4b) are generally Cl-poor and, given Cl-poor, high-Al amphibole, this likely reflects an initially Cl-poor melt, rather than any significant degassing. High $X_{\text{OH}} / X_{\text{F}}$ ratios are consistent with a deeply sourced, water rich, relatively primitive melt (Lee et al. 2017). Variation in the direction of F-OH exchange could be caused by either ongoing apatite crystallization (moving apatite compositions away from the F-apex), or cooling and reequilibration (moving apatite compositions toward the F-apex). While apatite cores tend to be more F-rich, indicating the former, this is inconsistent with OH-rich apatite being trapped in the earliest crystallizing, high-Al amphibole, which suggests the latter process is responsible.

Apatite from LH-1 (Fig 3.4c) are all extremely poor in Cl, and generally cluster close to the F-apex. As with ES-12792, variation in the direction of F-OH exchange could be explained by different processes, although in this case the range of F contents is much smaller and may be largely explained by analytical uncertainty. Certainly water-undersaturated melt evolution as the controlling process seems unlikely in a hornblende bearing, weakly porphyritic granite, which

was almost certainly fluid-saturated during apatite crystallization. It is possible that in this case almost all the apatite analyzed here crystallized after significant degassing (and associated loss of Cl from the melt). Since the AST calculated for the Luhr Hill granite is $\sim 900\text{--}930^\circ\text{C}$ this would imply that the melt ascended into the upper crust while still relatively hot. The alternative is that initially more Cl rich apatites have reequilibrated, post degassing, at lower P, T and melt Cl concentrations. However, since magnetite hosted apatite inclusions have measurably higher Cl contents, total reequilibration of Cl in apatite inclusions seems unlikely.

VET-2B apatite (Fig. 3.4d) are relatively Cl-rich and cover a similar range of X_F and X_{OH} to those from LH-1. Given temperature estimates for amphibole ($860\text{--}920^\circ\text{C}$) and titanite ($710\text{--}760^\circ\text{C}$), figure 3.4d suggests the evolution of apatite toward higher X_{OH}/X_F as the magma cools. This is consistent with water undersaturated melt evolution, during which OH acts incompatibly while F is taken up by ongoing apatite crystallization. Note that lack of obvious evolution toward more Cl-rich compositions suggests that during this time Cl in the melt was acting less incompatibly than OH (Fig 3.8, from Stock et al. 2018), possibly due to the crystallization of biotite.

A similar interpretation can be applied to apatite from WF-1 (Fig 3.4e), with lower temperature titanite trapping later grown apatite with higher X_{OH}/X_F ratios related to water-under saturated evolution away from the F-apex. Unlike VET-2B, there is also an increase in the Cl content of the most OH rich apatite, indicating that Cl was behaving more incompatibly, consistent with a lack of biotite crystallization (based on hand sample observations no biotite was present in WF-1).

Finally, it is difficult to assess the temporal evolution of CHR-7 apatite composition (Fig 3.4a) because only apatite inclusions in biotite were analyzed. Their high Cl content, however, suggests limited degassing, which should quickly strip Cl from the melt. As with WF-1 and VET-2B it seems likely that most of the variation in apatite volatile composition is related to water undersaturated evolution to lower melt F contents.

3.5.2 Correlating apatite sulfur content with other geochemical parameters

The range of apatite sulfur contents measured in this study is considerable ($\sim 0.05\text{--}0.5$ wt% for most samples). Assuming equilibrium crystallization, a drop in apatite S content from 0.5 to 0.05 wt% requires one of the following:

1 – A ~10 fold decrease in the sulfur content of the melt. This could be related to degassing or, at sulfate saturation, is equivalent to a decrease in temperature from ~950-750°C (Masotta and Keppler, 2015).

2 – A ~10 fold decrease in the partition coefficient for sulfur between apatite and melt. Using the model of Peng et al. (1997) this is equivalent to an increase in temperature from ~800-950°C. Partition coefficients derived by Parat and Holtz (2004), appear to be much less affected by temperature and would imply a much greater temperature increase. Regardless of the partition coefficients used, they should increase with decreasing temperature, diluting the effect of dropping melt sulfur contents.

If we assume that temperature change is the principal control on apatite sulfur content, this implies temperature changes of >>200°C between the highest and lowest sulfur content apatite, which should be accompanied by significant changes in melt composition and therefore apatite trace element concentrations. If we assume that addition of sulfur by fluxing of SO₂ from another source, or removal of sulfur by degassing are the principle controls on apatite sulfur content, we should see changes in sulfur accompanied by changes in apatite volatile concentrations.

Therefore, since the main aim of this study is to use apatite S content as a proxy for changes to melt S content over time, we have tested relationships between apatite S and a number of geochemical proxies for magma evolution. These include temperature estimates from host amphiboles and titanites, apatite Sr content (which should reflect dropping melt Sr content due to plagioclase crystallization), and changes in apatite volatile contents (as discussed in the previous section).

3.5.3 Apatite sulfur vs apatite strontium

As previously noted, magnetite hosted apatite inclusions from LH-1 and ES-12792 generally have higher Sr contents than other apatite types. Figures 3.9a-b show that in both cases, while these apatites also appear to have relatively high sulfur contents, so do amphibole, titanite and biotite hosted inclusions which do not share the high Sr values. One possibility is that plagioclase crystallization, after the trapping of magnetite hosted inclusions, lead to a fall in melt Sr content, without any loss of S (i.e. a sulfur undersaturated melt) and that the onset of anhydrite saturation (or degassing) then lead to a rapid decrease in melt sulfur content, without further plagioclase crystallization. However this explanation is not consistent with the large observed

variability of sulfur contents in high-Sr magnetite hosted inclusions ($\sim 0.1 - 0.3$ wt% and $\sim 0.25 - 0.4$ wt% for LH-1 and ES-12792 respectively).

In sample VET-2B apatite phenocryst cores and inclusions all show uniformly high Sr and inclusions also have elevated S contents. Phenocryst rims generally have lower Sr contents, and low S contents, similar to phenocryst cores. This could be explained if the sulfur content of the melt fell significantly, either due to falling temperature or degassing, before the onset of plagioclase crystallization, which was responsible for the varying Sr content between phenocryst cores and rims.

There was no obvious correlation between apatite S and Sr content in either CHR-7 or WF-1.

3.5.4 Apatite sulfur vs apatite volatile content

Since the majority of variation in apatite volatile content is related to movement toward or away from the F-apex (see Figs. 3.4a-e), we plot apatite sulfur content for each sample as a function of X_F (Figs. 3.10a-e). In general there is little correlation between apatite fluorine content and sulfur content although some very broad comments can be made. Firstly for LH-1, apatite inclusions in magnetite, interpreted as early based on high Sr and S content, generally have low X_F , consistent with the interpretation that in this sample apatite composition evolved toward more F-rich compositions. On the other hand, a number of (presumably) late grown apatite phenocryst rims also have similarly low-F contents. For sample VET-2B low X_F apatites trapped in low temperature titanite have the largest range and the highest S contents, suggesting the latest grown apatites are the most S-rich. Again it is important to note that some very low-S phenocryst cores and rims also have low F contents. The same general pattern is also true for WF-1, where low-F titanite hosted apatite also appear to have relatively high S contents, suggesting that again, these later grown apatites are the most S-rich. In sample CHR-7 the highest X_F apatites, interpreted to be the youngest, generally have very low S contents, suggesting a loss of S by degassing or by falling temperature.

3.5.5. Apatite sulfur vs host mineral thermometry

We also compare apatite S contents to host mineral crystallization temperatures (Fig. 3.11). In this case it is important to remember that lower temperature hosts can trap apatite formed at any time, and given slow reequilibration of S, should trap apatite with a range of sulfur contents. On the other hand higher temperature host minerals should only trap early formed apatite, suggesting a much more limited range of apatite sulfur contents. Figures 3.11a-d don't appear to support this,

and there is little if any correlation between host mineral temperature and apatite S content. In sample VET-2B and WF-1 lower temperature titanite hosted apatite appear to have a slightly larger range of sulfur contents, while in sample LH-1 the opposite appears to be true.

3.5.6 Sulfur in apatite inclusions vs phenocrysts

By far the biggest difference between apatite inclusions and phenocrysts is their sulfur contents, as noted above (Fig. 3.3). There are a number of possible explanations for this:

- 1 – Phenocrystic apatite, not trapped inside a host mineral, has lost sulfur during re-equilibration at lower P-T conditions.
- 2 – All the phenocrystic apatite analyzed represents late growth from a melt with a very low sulfur content, possibly after degassing or the crystallization of anhydrite.
- 3 – Sampling large apatite phenocrysts (generally >300µm compared to inclusions often <10µm) somehow biases analyses toward lower-S contents

Sulfur should diffuse relatively slowly in apatite, since it is highly charged and requires a coupled substitution mechanism (see above). This makes the first explanation unlikely, particularly since any late stage re-equilibration of sulfur must be accompanied by changes in either Na^+ or Si^{4+} content in order to maintain charge balance. Furthermore, experimentally determined diffusion rates (Fig. 3.1) would suggest that re-equilibration of sulfur would be preceded by re-equilibration of fast diffusing volatiles in the channel site. The range of chlorine contents in apatite phenocrysts is generally similar to apatite inclusions for a given sample, suggesting they haven't been affected by this sort of process. This would also be at odds with various observations of sulfur zoning in apatite phenocrysts in other studies (e.g. Streck and Dilles, 1998, van Hoose et al. 2013, Chelle-Michou and Chiaradia 2017).

The second explanation, that all the phenocrystic apatite analyzed here represent the very last apatite growth at low-S conditions, is possible. Apatite phenocrysts were mounted such that basal sections were exposed, and the depth of polishing was approximately 1/4 - 1/3 of the crystal depth, meaning that in general the areas that were analyzed were not “cores” relative to the c axis. It is therefore possible that higher-S cores were missed in these sections. However variability in the concentrations of other elements, even quickly diffusing elements like Cl (e.g. Fig 3.3, Vet-2B), strongly suggests that the analyzed areas of apatite did not all grow under exactly the same conditions, despite homogenous sulfur contents. Sectioning of individual apatite grains relative to both A and C axes, and careful core to rim transects of these sections would help to address this problem.

The final explanation is that by picking only large phenocrysts (generally $>300\mu\text{m}$) some bias has been introduced toward low-S apatite. One possibility is that these large apatite grains are actually xenocrystic and that since their incorporation into the magma they have reequilibrated with respect to most elements, but not with respect to sulfur, due to very slow diffusion. Color cathodoluminescence (CL) images, taken using a cold cathode CITL 8200 Mk 5-1 (University of Geneva), do occasionally show signs of resorption (Fig. 3.12) but in general igneous growth zoning is preserved. Even if all the large apatite grains analyzed were xenocrystic, they might still be expected to feature late overgrowths with sulfur contents similar to those of apatite inclusions and this is not the case.

3.6 Conclusion

Despite large ranges in apatite sulfur content, which necessitate either large ($>>200^\circ\text{C}$) temperature changes, or significant gain or loss of volatiles, there is very little correlation between apatite sulfur content and any other measure of magmatic evolution. One possibility is that ongoing reequilibration of more quickly diffusing elements (e.g. Sr, volatiles) during cooling has obscured any trends that were originally present. However this seems to be at odds with relatively large observed range of volatile contents in all apatite types. Another possibility is that high apatite sulfur contents are not a reflection of equilibrium processes and that apatite sulfur content is more closely related to crystal growth kinetics or interaction with an SO_2 rich fluid phase (e.g. Van Hoose et al. 2013).

Either way this study highlights the need for high quality experimental data on the partitioning of sulfur between apatite and melt at a range of temperatures, pressures and melt compositions. Furthermore, experimental data on the diffusion rate of sulfur in apatite would be useful in determining the likelihood of reequilibration on the timescale of pluton formation.

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3.8 Figures and tables

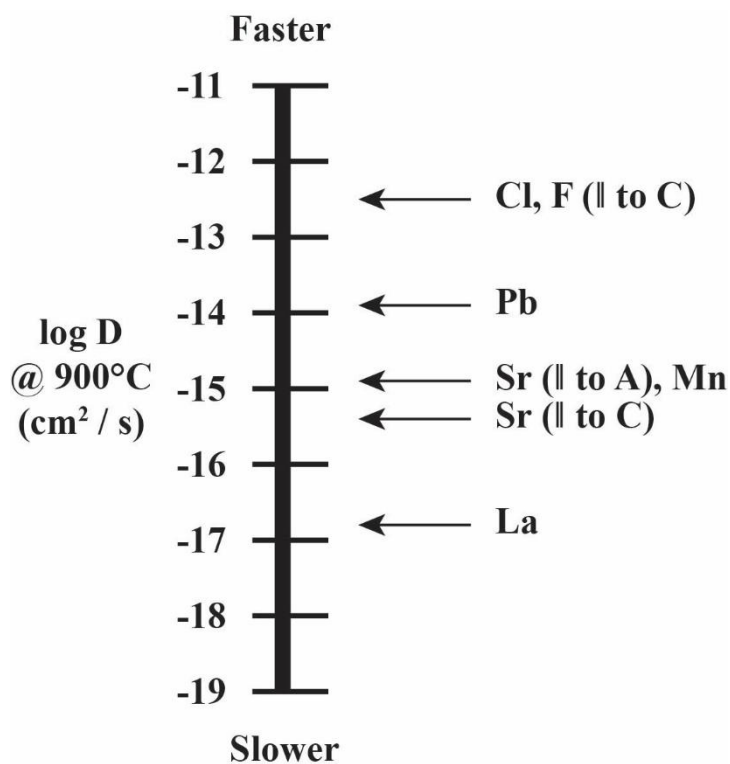


Figure 3.1 Diffusivity of various elements in apatite at 900°C. Where no direction is specified relative to crystal axes, diffusion is assumed to be close to isotropic. Note that Cl and F diffuse several orders of magnitude faster than most 2+ cations, and that La diffuses several orders of magnitude more slowly. Diffusivities are from the following studies: Cl, F (Brenan, 1993), Pb (Cherniak, 1991), Sr (Cherniak and Ryerson, 1993), Mn (Cherniak, 2005), La (Cherniak 2000).

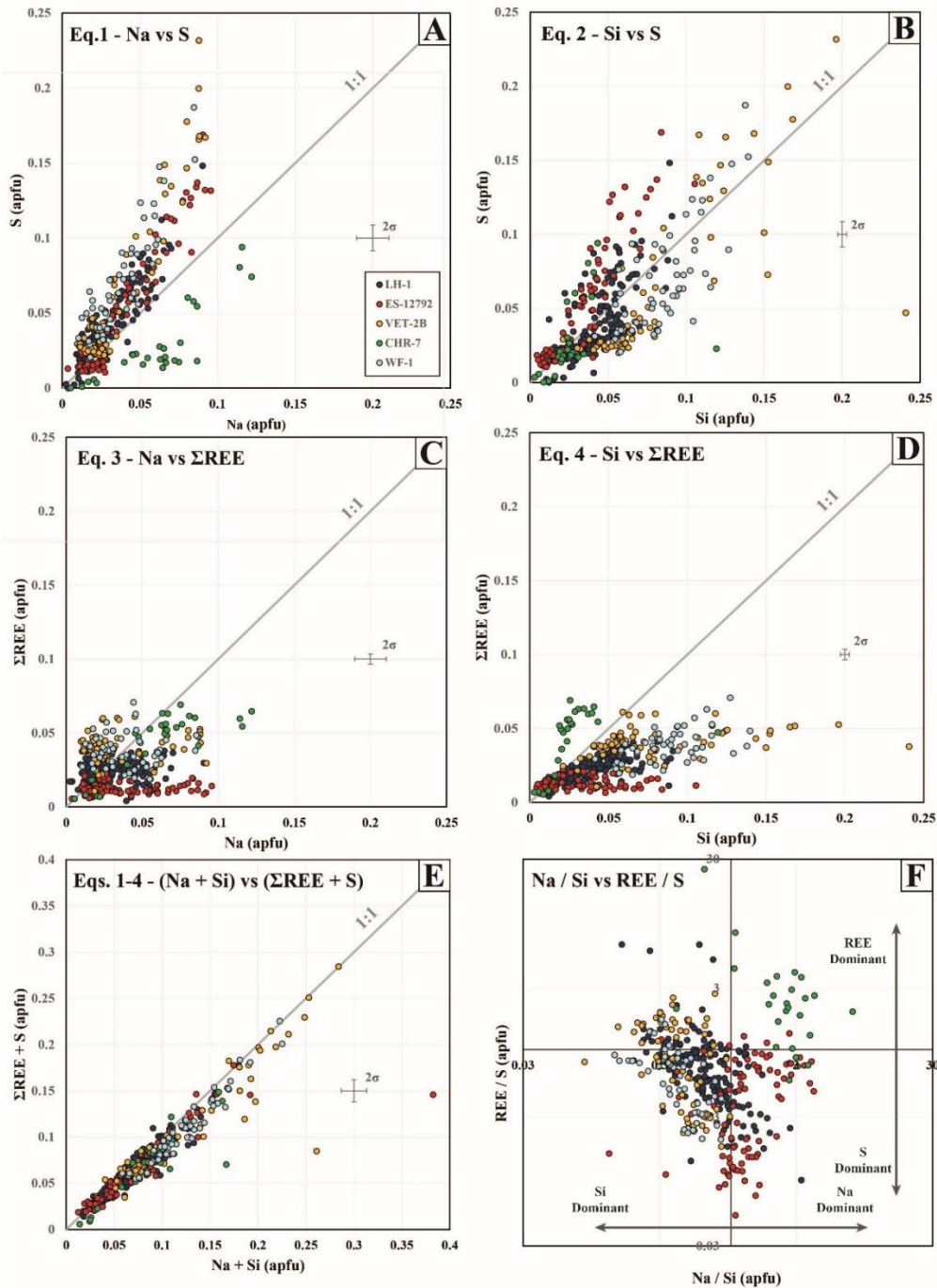


Figure 3.2 Comparison of Na, S, Si and Σ REE trace element concentrations in apatite, expressed as atoms per formula unit (apfu). A close fit to the 1:1 line would imply that concentrations are strongly controlled by the corresponding heterovalent coupled substitution reaction (Eq. 1-4). E: Sum of less highly charged cations (Na + Si) vs the sum of more highly charged cations (Σ REE + S), representing the sum of substitution reactions (Eq.1-4). A close fit to the 1:1 line suggests that these reactions alone are sufficient to explain the variability of trace element concentrations. F: Ratio of less highly charged cations (Na / Si) vs the ratio of more highly charged cations (Σ REE / S).

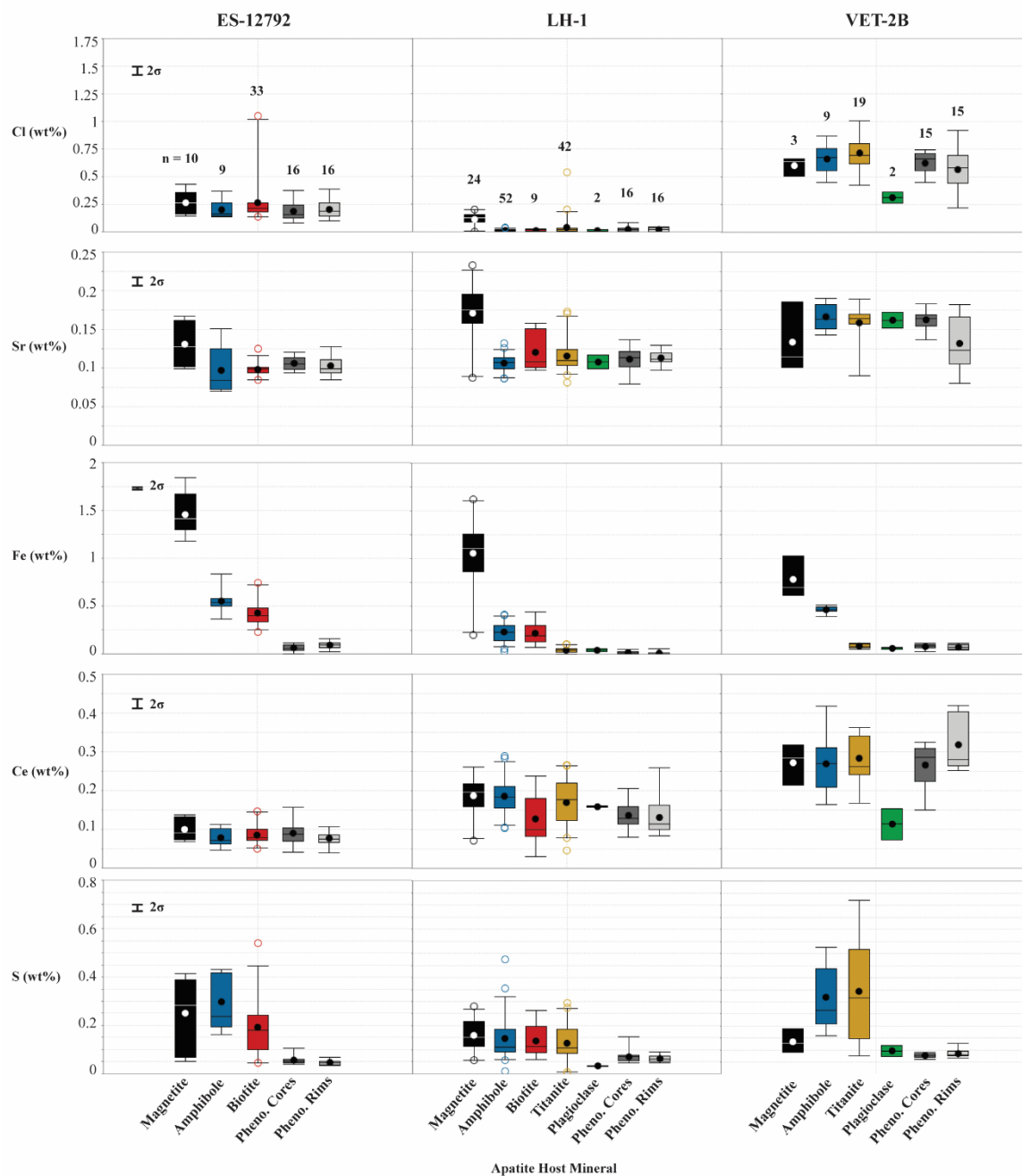


Figure 3.3 Box and whisker plots for Fe, S, Ce, Sr and Cl, comparing trace element concentrations in different apatite types (i.e. inclusions, split up by host mineral, and phenocryst cores and rims). Median values (central line), Q3 and Q1 (top and bottom of the box), the range of values excluding outliers (whiskers) and the mean (black circle) are shown. Outliers (open circles) are defined as points more than $1.5 \times (Q3 - Q1)$ from the box. 2σ uncertainties based on repeat analysis of a standard are shown.

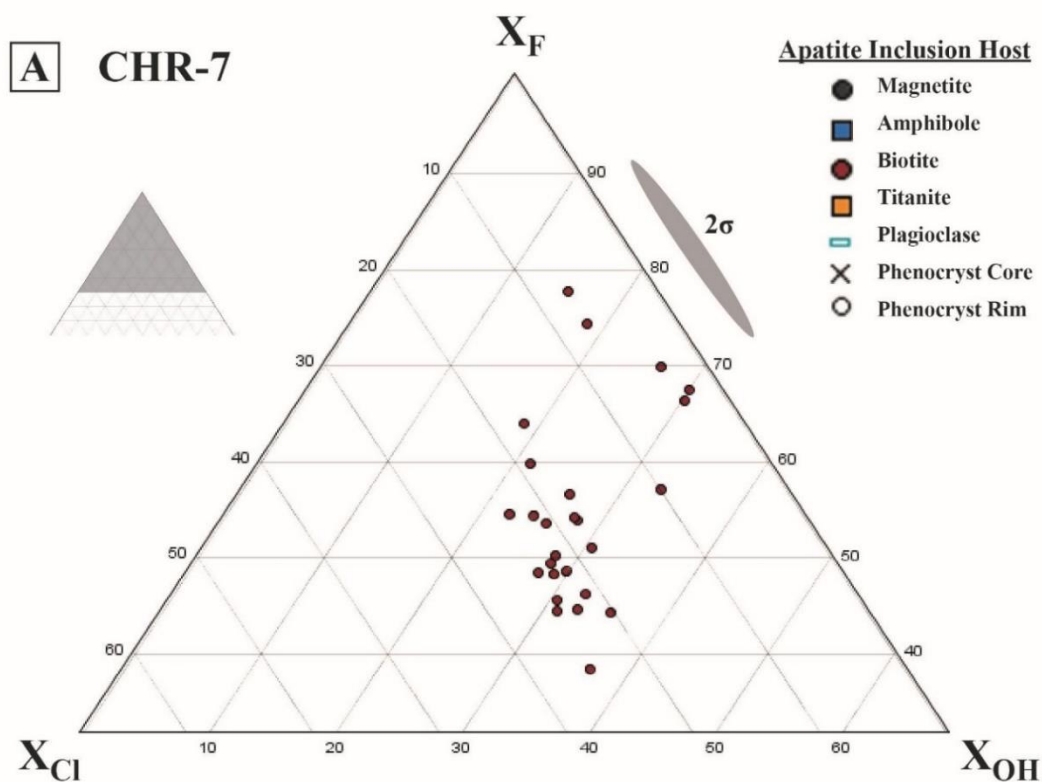


Figure 3.4 Ternary diagrams showing the proportions of F, Cl and OH in the apatite channel site. 2σ uncertainty is based on repeat analyses of the Durango apatite standard. X_{OH} is calculated by difference ($100 - (X_F + X_{Cl})$)

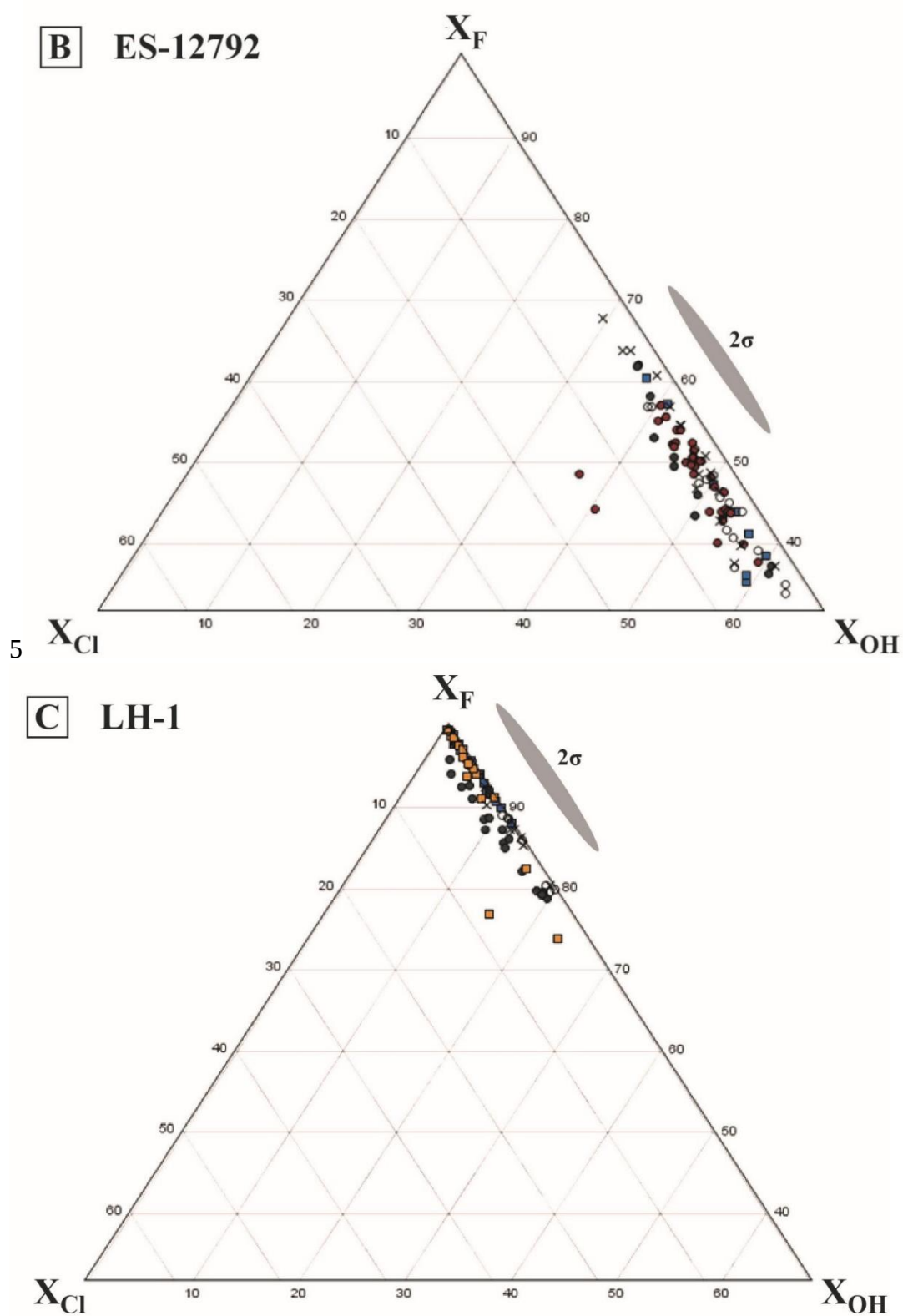


Figure 3.4 Ternary diagrams showing the proportions of F, Cl and OH in apatite (continued)

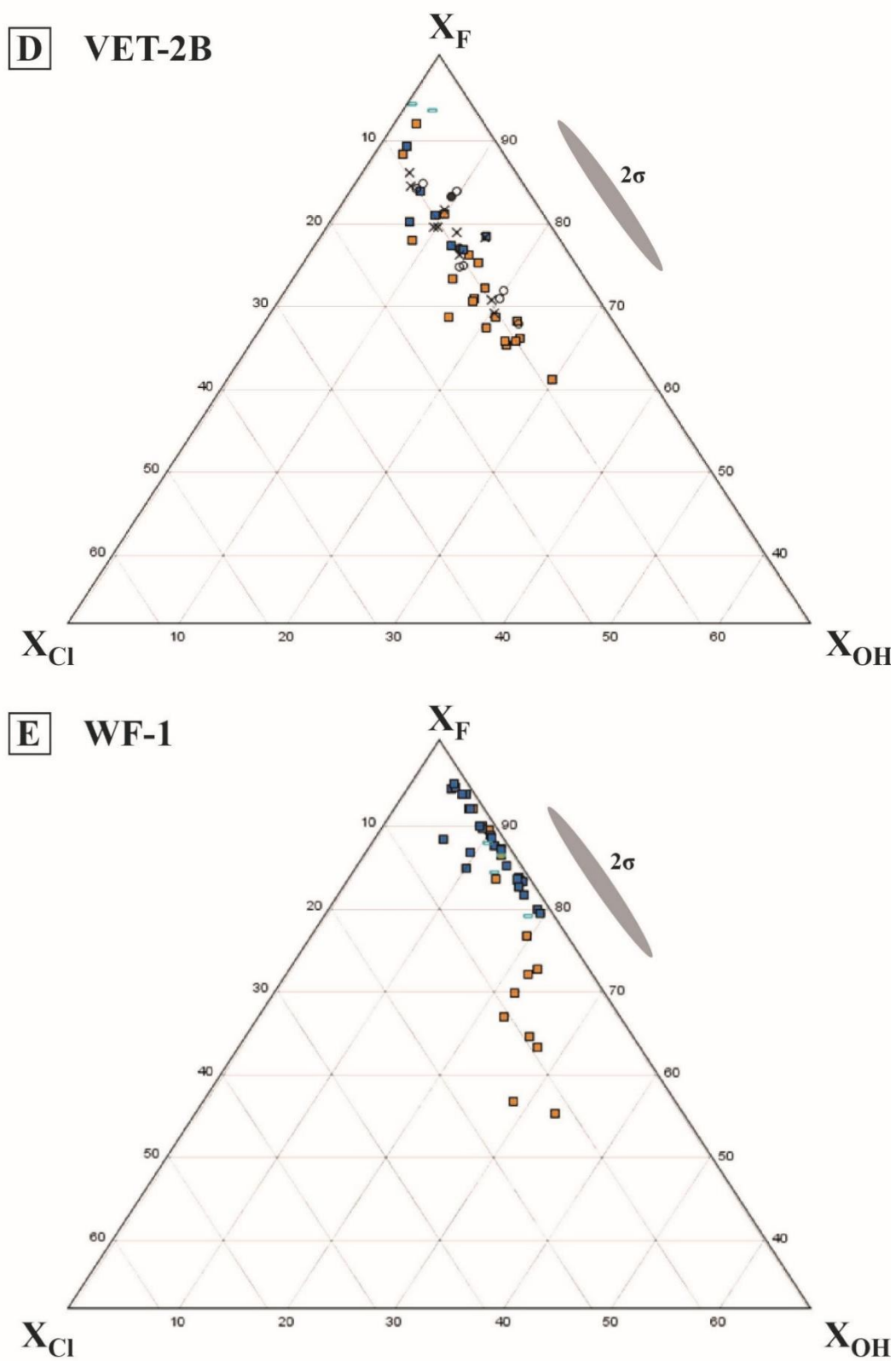


Figure 3.4 Ternary diagrams showing the proportions of F, Cl and OH in apatite (continued)

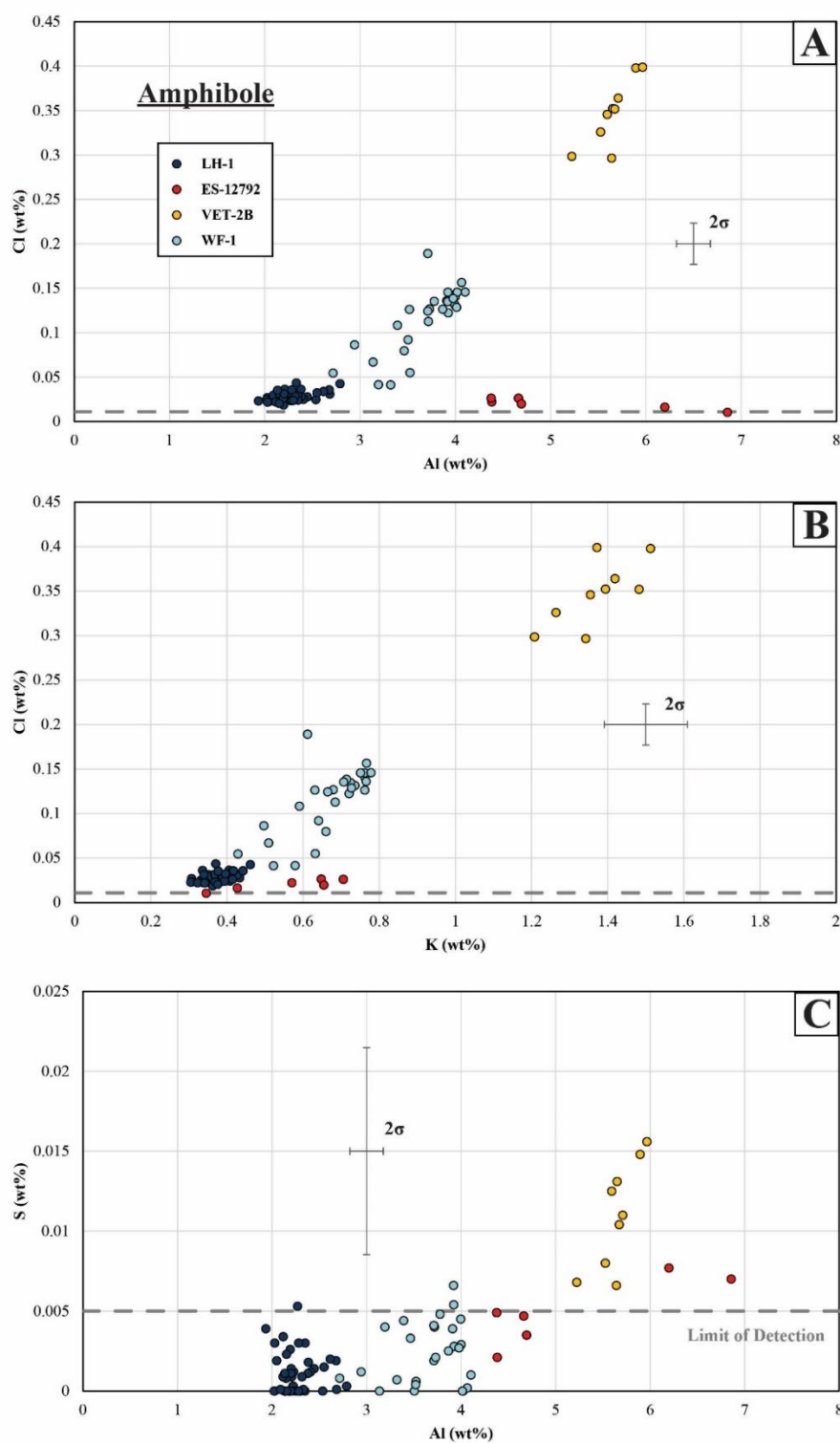


Figure 3.5 Host amphibole Cl and S content vs Al and K content by EPMA. Note 2σ uncertainty is based on counting statistics rather than repeat analysis of a standard. Actual reproducibility is likely significantly better.

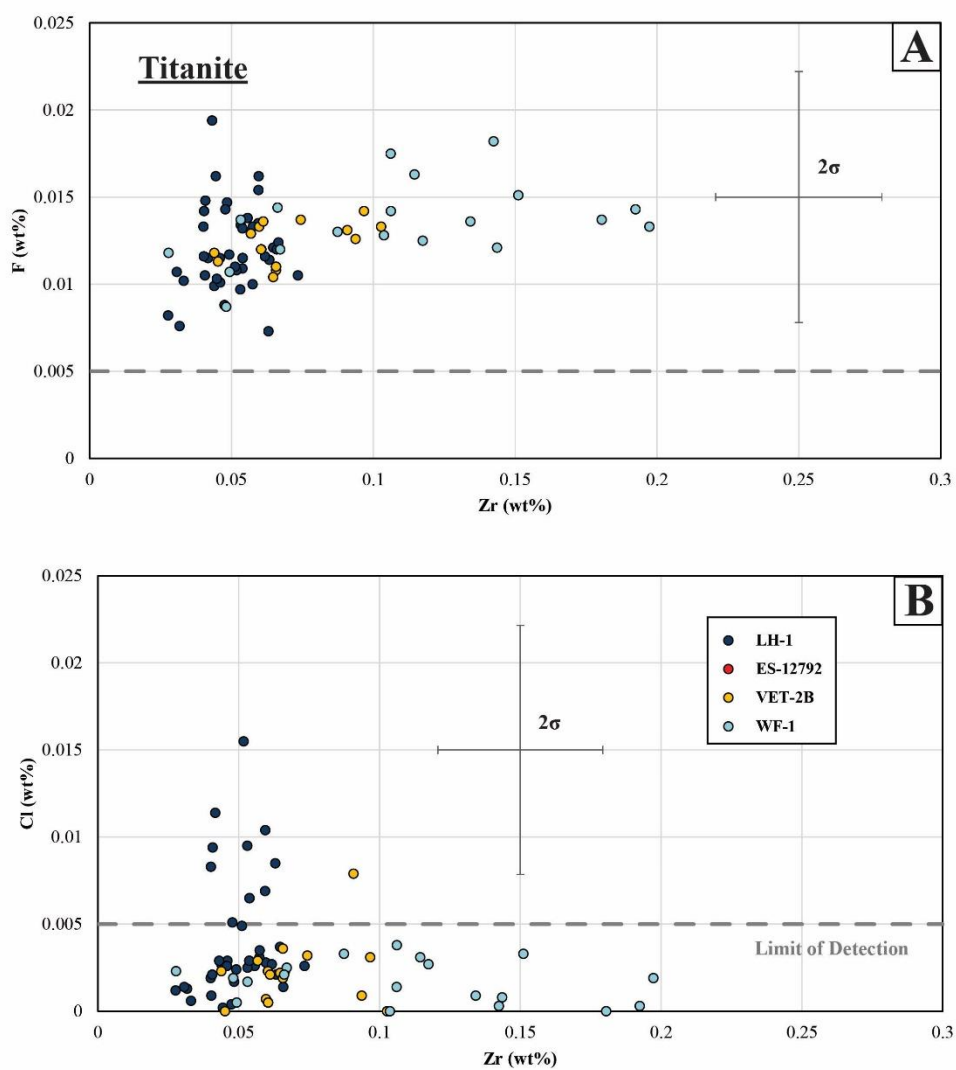


Figure 3.6 Host titanite F and Cl content vs Zr content by EPMA. Note 2σ uncertainty is based on counting statistics rather than the repeat analysis of a standard. Actual reproducibility is likely significantly better.

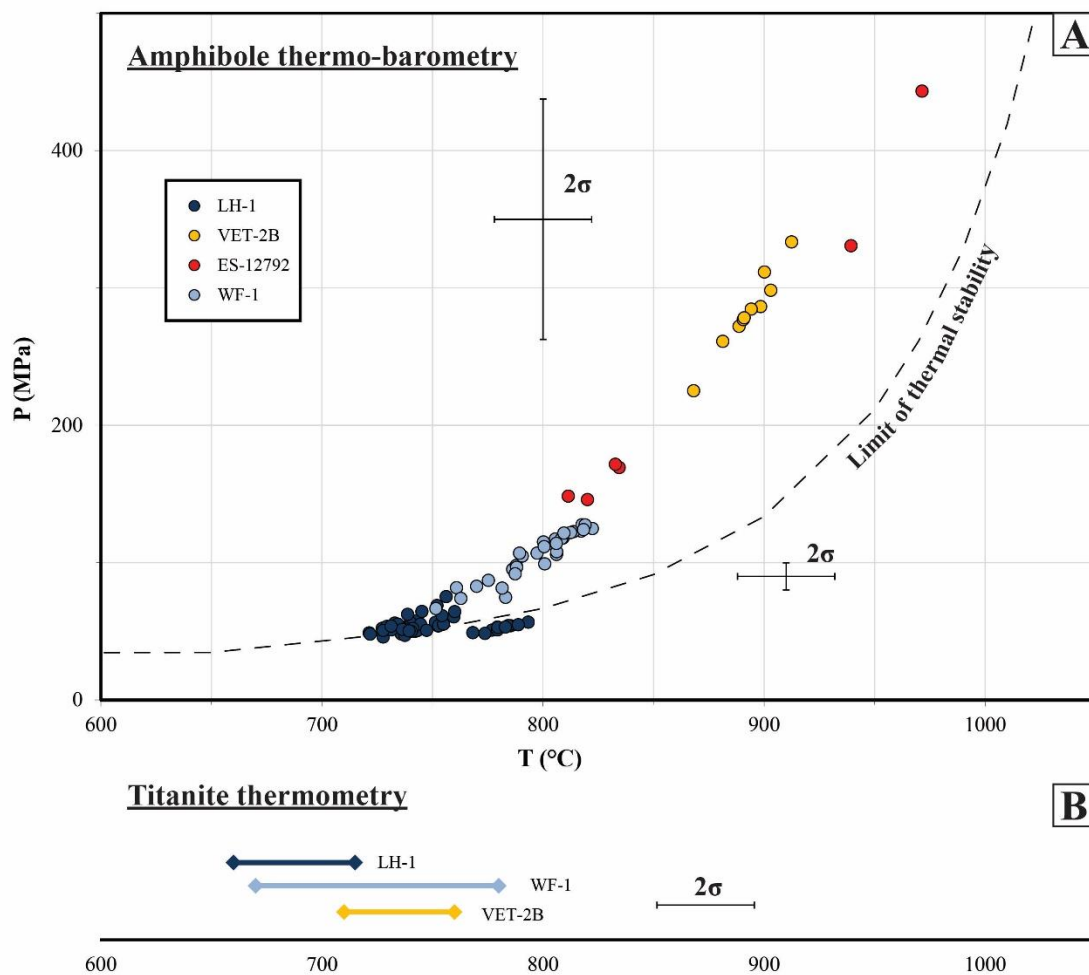


Figure 3.7 Amphibole and titanite thermometry and barometry A) Calculated pressures and temperatures of amphibole crystallization based on Ridolfi et al. (2010). B) Range of calculated titanite crystallization temperatures for each sample based on Hayden et al. (2008).

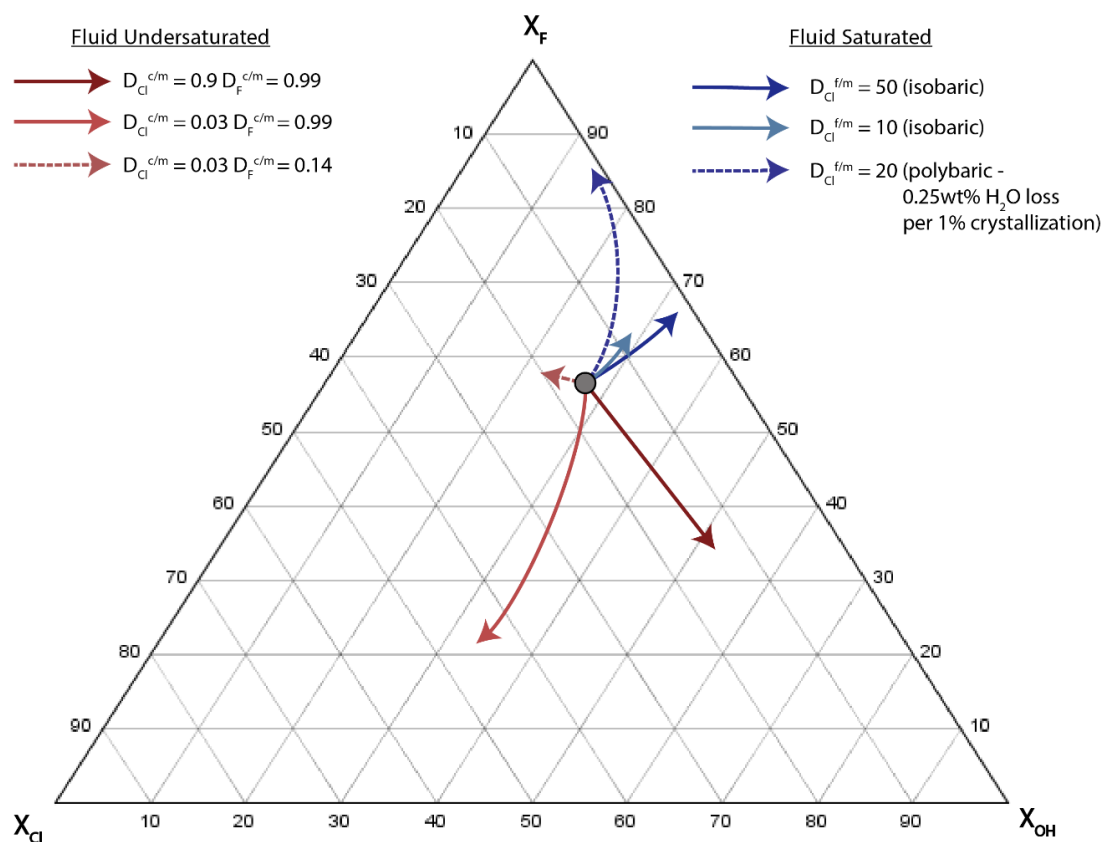


Figure 3.8 Schematic diagram after Stock et al. (2018) showing the modelled evolution of apatite volatile composition during crystallization. Red arrows represent fluid undersaturated conditions, under which apatite compositions generally move away from the X_F . Blue arrows represent fluid saturated conditions, under which apatite compositions generally move toward the $X_F - X_{OH}$ binary due to rapid loss of Cl into a separating fluid phase. Arrows represent 85% crystallization.

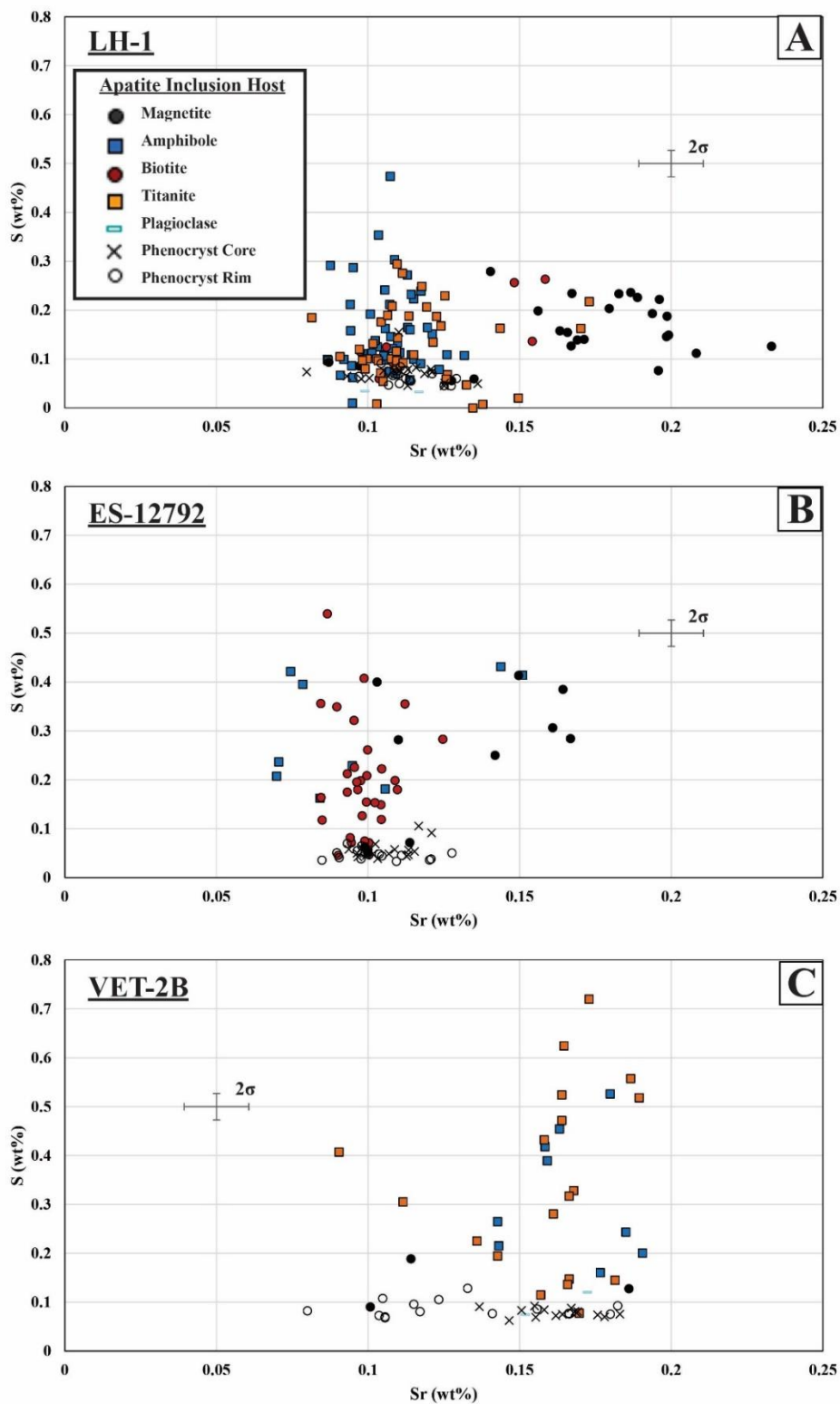


Figure 3.9 Apatite S vs apatite Sr content by EPMA. Average 2σ uncertainties are based on repeat analysis of a standard.

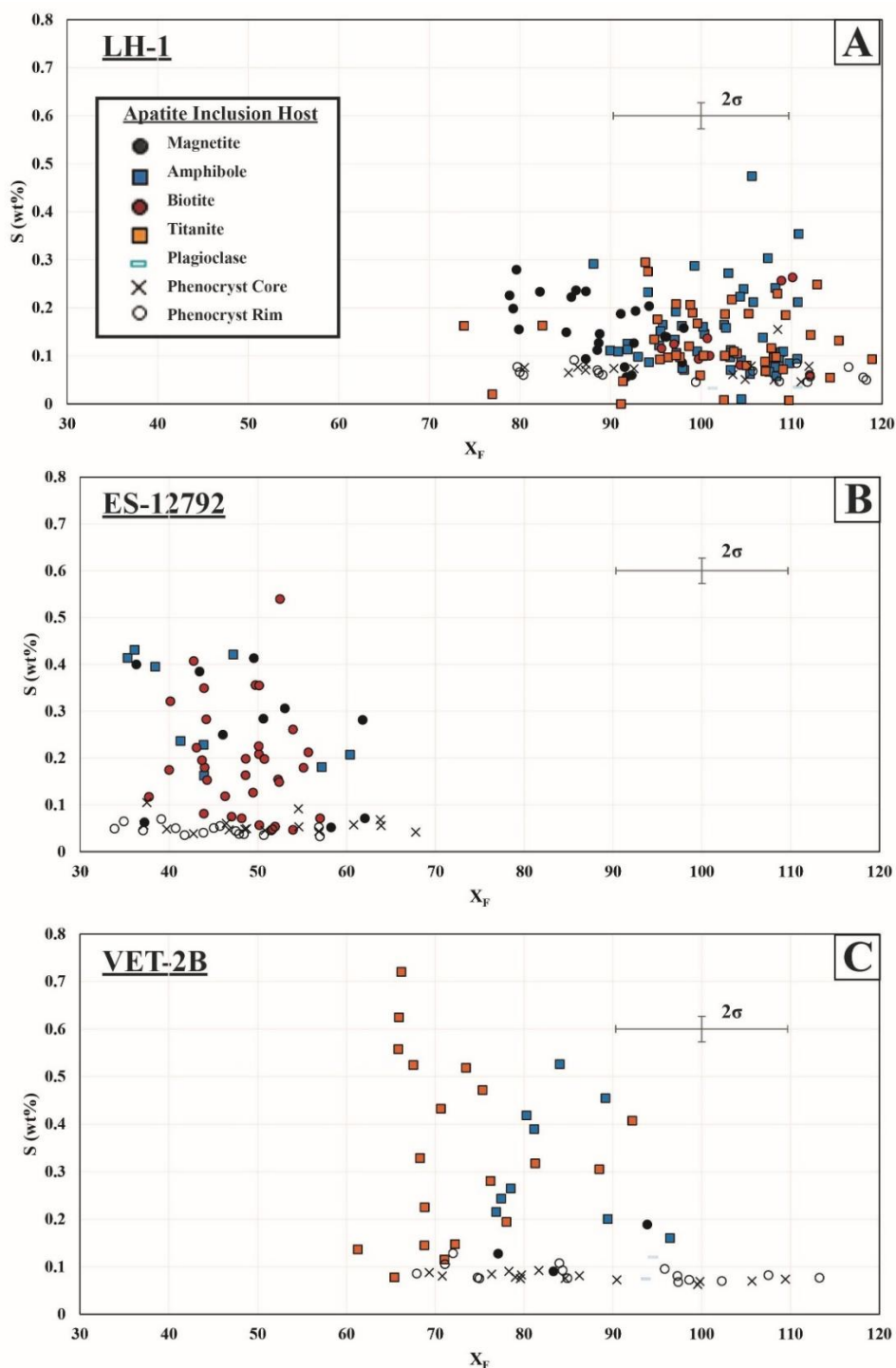


Figure 3.10 Apatite S content vs F content as a proportion of the total channel-site occupancy by EPMA. Uncertainties based on repeat analysis of Durango apatite standard. Note that $X_F > 100$ represents analyses with F content greater than the stoichiometric maximum (~ 3.8 wt%), likely related to beam interaction with apatite of different orientation to the Durango standard. For further details see analytical methods section.

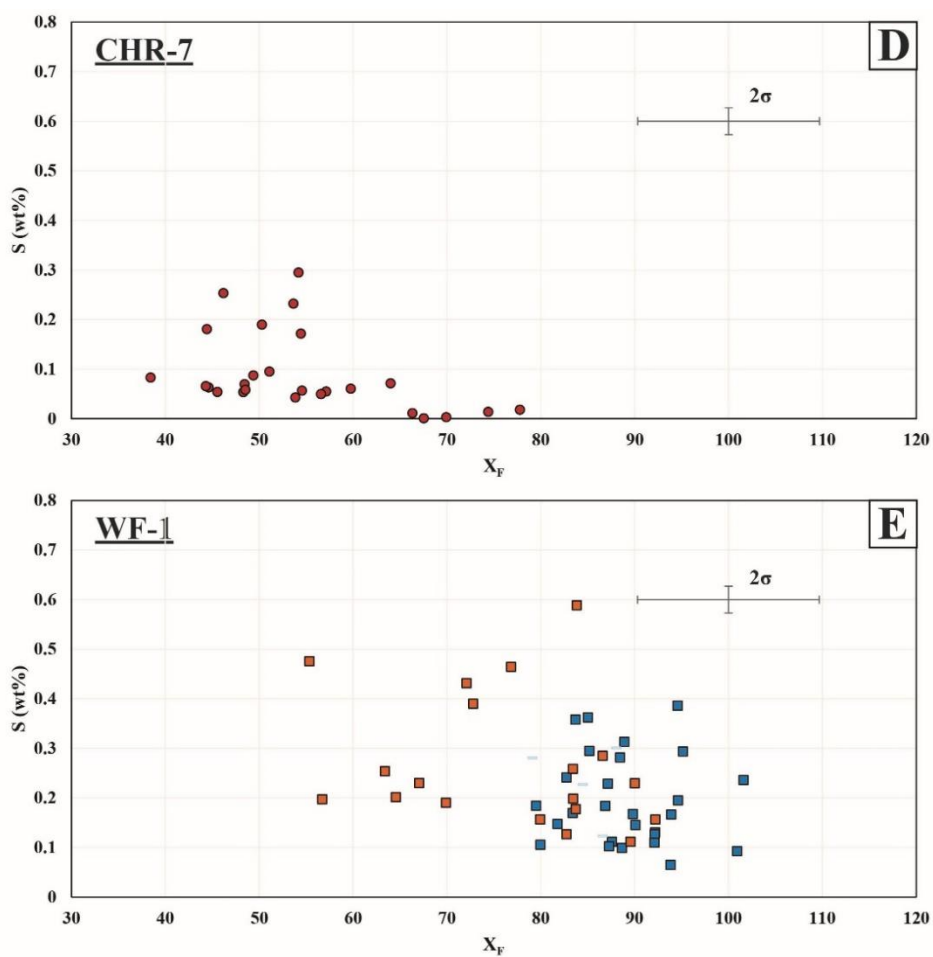


Figure 3.10 Apatite S content vs F content (continued)

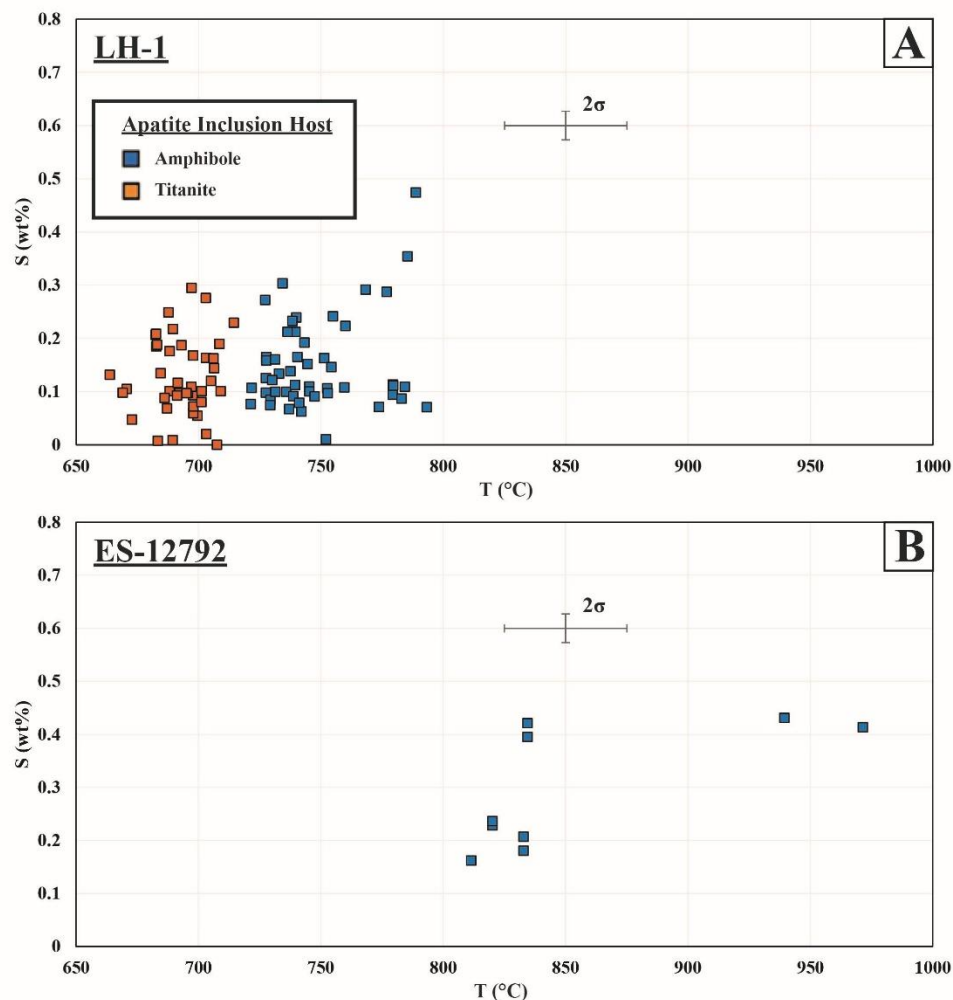


Figure 3.11 Apatite S content vs host mineral crystallization temperature based on EPMA measurements. Growth zoning in host minerals was identified either in element maps (amphibole) or BSE images (titanite) and analyses were made in the same growth zone as the apatite inclusion was trapped. Amphibole crystallization temperatures are calculated using methodology of Ridolfi et al. (2010). Titanite crystallization temperatures are based on Hayden et al. (2008). The 2σ uncertainty in calculated T is shown as $\pm 25^{\circ}\text{C}$ which is slightly larger than both the error on Zr measurements in titanite (see Figure 6) and the uncertainty for amphibole T using Ridolfi et al. (2010) (see Figure 7). Relative uncertainties are likely smaller than that shown for temperature estimates of the same mineral (i.e. comparing titanite temperatures to other titanite temperatures). However uncertainty when comparing titanite to amphibole temperatures may be greater than that shown due to the various assumptions (e.g. pressure of titanite crystallization) involved in the calculation of crystallization temperatures.

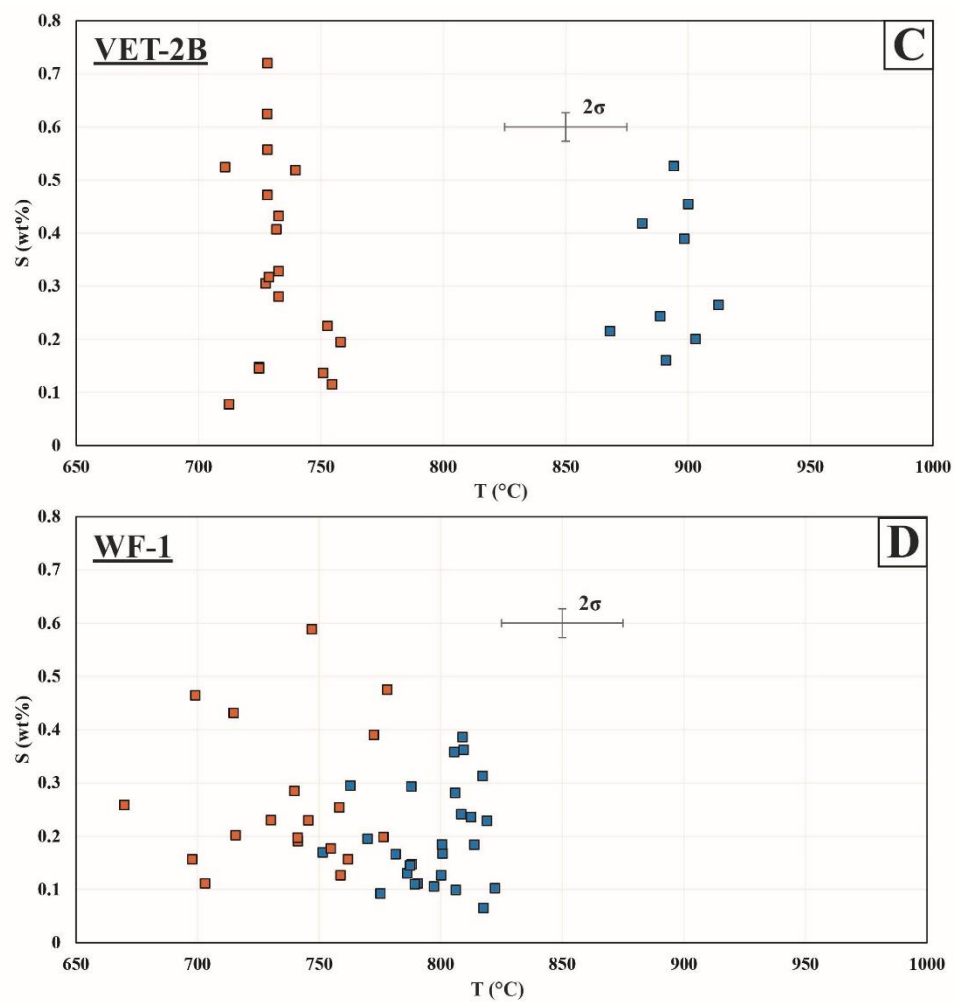


Figure 3.11 Apatite S content vs host mineral crystallization temperature (continued)

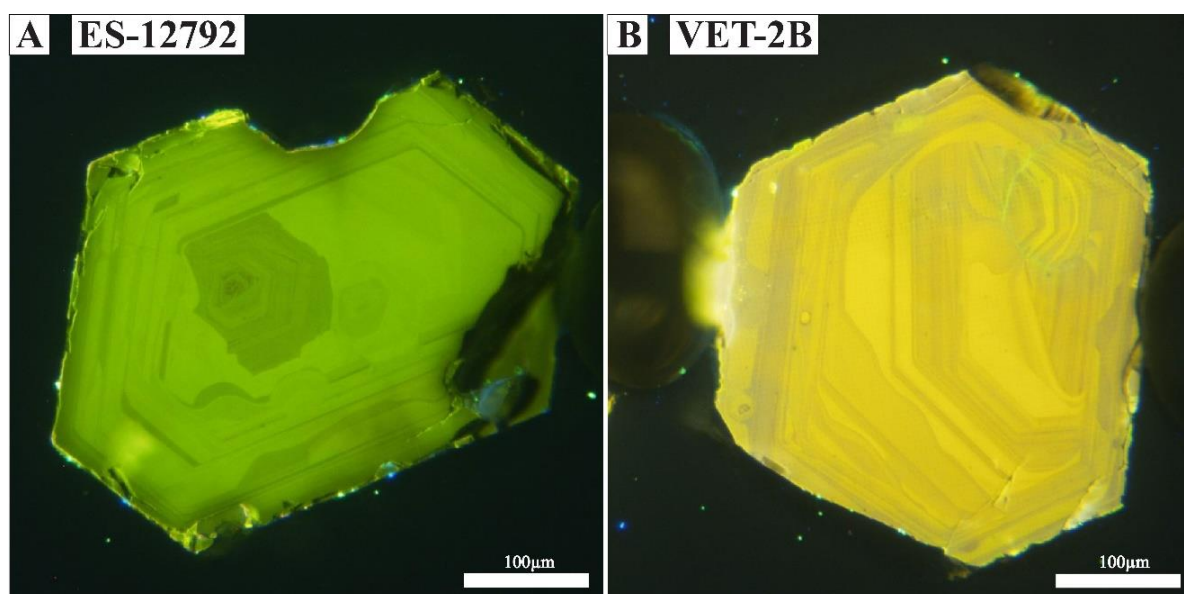


Figure 3.12 Color-CL images of apatite phenocrysts from samples ES-12792 and VET-2B. Both grains exhibit well defined primary growth zoning, as well as irregular boundaries interpreted as resorption of apatite grain and later overgrowth.

Table 3.1 List of samples and apatite types analyzed

Unit, Location	Christmas Pit (AZ)	El Salvador deposit (Chile)	Robinson Mine (NV)	Luhr Hill Pluton, Yerington (NV)	Weary Flat Pluton, Ely (NV)
Sample Number	CHR-7	ES-12792	VET-2B	LH-1	WF-1
Lithology	Porphyritic Dike	Lafite Dike	Porphyritic Dike	Weakly Porphyritic Granite	Quartz Monzonite
Inclusion Hosts	X	X X X	X X	X X	X
Phenocrysts					
Reference		Lee et al. (2017)		Dilles (1987)	Westra (1979)

Chapter IV. The stability and composition of sulfate melts in arc magmas

4.1 Abstract

High temperature-pressure experiments have been conducted with the aim of determining the stability field and the composition of immiscible sulfate melts in equilibrium with arc magmas. Experimental starting materials were trachyandesite and trachydacite in composition, contained 4-7 wt% H₂O, and were doped with 8-10 wt% SO₃ in order to produce analyzable sulfate phases. Experiments were run using piston cylinder and gas pressurized cold seal apparatus at 800-1200°C, 0.2-1GPa and $fO_2 > NNO+2$. The composition of experimental sulfate melts was determined by EPMA and compared to mass balance calculations, based on the composition of the silicate glass. Sulfate melts were dominated by CaO and SO₃, but also contained, in order of abundance, Na₂O, K₂O, MgO, FeO, Cl and P₂O₅. Cl showed particular preference for the sulfate melt, and calculated partition coefficients for Cl between silicate and sulfate melts were 5-13 at 1200°C. Experimental results indicate that sulfate melts should be present in typical arc magmas at temperatures $\geq 1000^\circ\text{C}$, assuming that magmas contain sufficient sulfur. However this minimum temperature estimate may be lower in particularly alkalic or hydrous magmas. At 1000°C silicate melts in our experiments contained 800-2400 ppm S, depending on composition, and the upper end of this range is a reasonable minimum sulfur content for producing sulfate melts in natural systems.

4.2. Introduction

Evidence from the study of ore deposits (e.g. Gustafson and Hunt, 1975), volcanic eruptions (e.g. Varekamp et al. 1984; Andres et al. 1991) and melt inclusions (Wallace and Edmonds 2011, and references therein) suggest that arc magmas commonly have higher sulfur contents than their MORB equivalents. This is in part related to the oxidized nature of arc magmas, since sulfur solubility increases greatly with fO_2 as S⁶⁺ replaces S²⁻ as the dominant sulfur species in solution (Carroll and Rutherford 1987; Luhr 1990). Evidence from the enrichment of $\delta^{34}\text{S}$ in arc lavas (Woodhead et al. 1987, Alt et al. 1993, de Hoog et al. 2001) suggests that the high sulfur content of arc magmas can be attributed to the recycling of subducted seawater sulfate through the mantle wedge.

In oxidized, sulfur-rich magmas, progressive cooling may lead to the precipitation of magmatic anhydrite, first observed in erupted products at El Chichon (Luhr et al. 1984). Although anhydrite is rarely preserved in the geologic record, evidence from a number of other recent

eruptions (e.g. Arculus et al., 1983; Pallister et al., 1992; Matthews et al., 1997, 1999; Dirksen et al., 2006; Larsen et al., 2010), and from anhydrite inclusions in plutonic rocks, suggests that anhydrite saturation may be a common feature of arc magmas (Luhr 2008 and references therein, this study, Chapter II, Hutchinson and Dilles 2019). This is consistent with a number of experimental studies showing that anhydrite is stable under oxidizing conditions at temperatures 800-1000°C (Carroll and Rutherford 1987; Luhr 1990; Clemente et al. 2004; Costa et al. 2004; Huang and Keppler 2015; Masotta and Keppler 2015).

However experiments by Jugo et al. (2004) on oxidized, basaltic starting material showed that at high pressure and temperature (1GPa, 1300°C) an immiscible sulfate melt is stable in place of anhydrite. Difficulties with sample preparation hindered quantitative analysis of sulfate melt blebs but qualitative energy dispersive analyses (EDS) showed that they are dominated by Ca and S and also contain small amounts of Na and Mg. More recent experiments by Veksler et al. (2012), designed to investigate trace element partitioning, produced pairs of immiscible silicate and sulfate melts at lower pressure (0.1GPa) and at temperatures as low as 900°C. However the starting material used for this study was extremely alkaline and deviated significantly from natural systems in that $\text{Na}_2\text{O}+\text{K}_2\text{O} / \text{CaO} \sim 10$ (typical calc-alkaline magma $\text{Na}_2\text{O}+\text{K}_2\text{O} / \text{CaO} < 2$). As a result of this, the experimentally produced silicate glasses generally contained <0.01 wt% CaO and the sulfate melts in equilibrium were dominated by Na_2O (~12-16 wt%) and K_2O (~10-12 wt%), with only minor CaO (~1.5-3 wt%).

Analogous studies have highlighted the role of silicate-carbonate immiscibility in producing carbonatite magmas, including those erupted at Oldoinyo Lengai, Tanzania, and those implicated in the concentration of rare earth elements (REE) at Bayan-Obo, China. Carbonate melts have also been invoked as the source of anomalous, highly conductive regions of mantle Gaillard et al. (2008) and may be genetically linked to diamondiferous kimberlite magmas. (For review see Jones et al. 2013).

Evidence for sulfate melts in nature is understandably sparse, however Chambefort et al. (2008) reported “wormy anhydrite” inclusions in high-Al amphibole from Yanacocha, Peru, texturally distinct from more equant anhydrite inclusions trapped in lower temperature phases. Temperature estimates for these amphiboles (800-1000°C) are significantly lower than that of the Jugo (2004) experiments (1300°C). Wormy anhydrite inclusions also commonly contained a few percent bubbles, interpreted as H_2O derived via exsolution of the sulfate melt upon cooling (Chambefort et al. 2008).

The aim of this study is to determine the principle factors affecting the stability of immiscible sulfate melts at a range of conditions appropriate for arc magmas. Additionally, we aim to determine the major element composition of sulfate melts and to calculate partition coefficients for major elements between sulfate and silicate melts. This information can be used to identify natural magmatic systems which are likely to produce immiscible sulfate melts, and to assess the possible effect of sulfate melts on magmatic evolution. Furthermore, this information will provide context for the discovery of “wormy anhydrite” at Yanacocha (Chambefort et al. 2008) and for any future identification of sulfate melts in natural samples.

4.3 Experimental Methods

4.3.1 Approach

In order to investigate the stability of sulfate melts we have conducted experiments on variably hydrous trachydacitic starting material under oxidized conditions at a range of temperatures (800-1200°C) and pressures (0.2 – 1 GPa) applicable to arc magmas. These conditions were chosen in order to cover the P-T estimates (0.6 – 0.9 GPa, 800-1000°C) for amphibole trapping “wormy anhydrite” inclusions at Yanacocha, Peru (Chambefort et al. 2008) and preliminary 1200°C experiments which contained sulfate melt. A set of experiments were also conducted with a more mafic, trachyandesite starting material in order to assess the effect of bulk composition on sulfate-melt stability. A full list of experimental conditions and run products is provided in table 4.2

4.3.2 Starting materials

Starting materials were prepared by mixing reagent grade oxide and carbonate powders (SiO_2 , Al_2O_3 , TiO_2 , MnO , MgO , CaCO_3 , Na_2CO_3 , K_2CO_3). Prior to weighing, powders were dried overnight at 125°C (1000°C for SiO_2 , Al_2O_3 and MgO) and then mixed, ground under alcohol and decarbonated by slowly heating in a box furnace from 600-1000°C for 24-48 hours. Volatiles were added to the starting mixtures as $\text{Ca}_3(\text{PO}_4)_2$, $\text{Al}(\text{OH})_3$ and NaCl . S was added as a mixture of CaSO_4 , K_2SO_4 and Na_2SO_4 . In order to fix the $\text{Fe}^{3+} / \text{Fe}^{2+}$ ratio of the starting material consistent with $f\text{O}_2 = \text{NNO} + 2.5$ to $+3$ at run conditions, Fe was added as a 50:50 mixture (by weight) of FeO and Fe_2O_3 (Kress and Carmichael, 1991). Finally starting mixtures were doped with 100 ppm of a variety of trace elements as solutions in nitric acid (1000 mg/L ICP standards), and then the nitric acid was allowed to evaporate and the mixtures were re-ground.

In total four starting materials (table 4.1) were prepared based on the compositions of the Luhr Hill porphyritic granite (PG, trachydacite, ~68 wt% SiO_2) and the McLeod Hill quartz

monzodiorite (QMD, trachyandesite ~58 wt% SiO₂) from Yerington, Nevada (Dilles, 1987). Three variations of the trachydacite starting material (D1, D2, D3), with different water contents, and one trachyandesite starting material (A1) were prepared. In all cases the H₂O contents measured in the silicate glass run products were higher than expected, and the bulk H₂O contents listed in table 4.1 are calculated by mass balance using analyses of silicate glasses from 1000°C experiments (see results section). All starting materials were doped with 7-10 wt% SO₃ in order to produce large, analyzable sulfate phases.

4.3.3 Piston cylinder experiments

The majority of experiments were conducted at 0.75 and 1 GPa using end-loaded piston cylinder apparatus at the University of Bristol. Approximately 15 mg of starting material were loaded into 2 mm diameter Au₈₀Pd₂₀ capsules which were welded shut and pressed into cylinders ~5 mm long. These cylinders were then packed into 3mm diameter Au₈₀Pd₂₀ capsules with solid redox buffer (a mixture of MnO and Mn₃O₄ powders) and ~10 µL of deionized H₂O. These capsules were then welded shut, pressed into cylinders ~8mm long and stored overnight in a 200°C oven. Capsules were weighed and those showing loss of H₂O were discarded. This double-capsule configuration (e.g. Eugster, 1957) was employed in order to buffer the sample f_{O_2} by fixing the $f(\text{H}_2)$ in both the inner and outer capsule (discussed further below). Capsules were surrounded in a solid Pyrex sleeve and any space filled with MgO powder. The Pyrex sleeve and the double capsule set-up both serve to minimize the infiltration of carbon into the sample from the graphite furnace (Brooker et al. 1998; Matjuschkin et al. 2015). The capsule and Pyrex sleeve were then loaded into standard 12.7 mm salt-Pyrex assemblies (see McDade et al. 2002, fig 1.d).

For this assembly a pressure correction of 3% is required (McDade et al. 2002) and pressure was controlled automatically to within ±1 psi (<1 MPa) at run conditions. Crushable MgO spacers in the assembly were sized to keep the capsule in the center of the hot spot and temperature was monitored using a type-D W₃Re₉₇-W₂₅Re₇₅ thermocouple, immediately adjacent to the top of the capsule. Temperature measured at the thermocouple was kept to within ±1°C using a Eurotherm controller. Based on numerical modelling and experimental investigation of piston-cylinder thermal gradients (Watson et al., 2002, Schilling and Wunder 2004) we estimate the uncertainty on sample temperature is ±10°C.

For typical experiments the sample was first taken to 1150-1200°C for ~2h in order to ensure melting and homogenization of starting materials. The temperature was then dropped rapidly (~30 seconds) to run temperature, during which time the pressure was manually

controlled to within ~ 20 MPa. Run durations at final temperature were ~ 48 h. Experiments at 1200°C were taken straight to the final run temperature and were run for 4-8h. All experiments were quenched by cutting power to the furnace, and during quench the sample pressure was manually maintained constant to within ~ 20 MPa. The attainment of equilibrium is demonstrated by lack of obvious zoning in solid phases and homogeneity of silicate glass. Major element trends in silicate glasses (see results section, Fig. 20), which vary consistently with temperature, also suggest equilibrium was achieved. This is likely related to experimental design, in which starting materials were first homogenized at super-liquidus temperatures before being brought down to run conditions. No reversal experiments were attempted.

Once unloaded, the outer capsules of the experiments were pierced using a razor blade in order to confirm the presence water. The capsules were then mounted, vacuum-impregnated with epoxy and ground with SiC grits in order to expose the experimental material in the inner capsule. Grinding and diamond-based polishing was done with oil in order to minimize dissolution of sulfate run products. Either methanol or petroleum ether was used in order to clean oil from samples between polishing steps.

4.3.4 TZM experiments

Five experiments were also conducted at lower pressure (0.2 GPa, 900 - 1160°C) using a gas-pressurized TZM (Titanium-Zirconium-Molybdenum) cold seal pressure vessel at the University of Bristol. Single 2mm diameter $\text{Au}_{80}\text{Pd}_{20}$ capsules were loaded with starting material and welded shut. The TZM vessel was pressurized with a H_2 -Ar mix in order to fix the vessel $f\text{H}_2$ and produce oxidized conditions within the experimental capsules. Temperature was measured directly on top of the pressure vessel and the sample temperature was calculated based on calibration using an internal thermocouple. Estimated uncertainty on temperature and pressure are ± 5 MPa and $\pm 5^\circ\text{C}$ (e.g. Stamper et al. 2014).

4.3.5 Control of $f\text{O}_2$

In both cases experimental $f\text{O}_2$ is controlled by fixing $f\text{H}_2$, however, the sample $f\text{O}_2$ is only equal to that of the buffering assemblage if a pure H_2O fluid phase is present in the sample (i.e., activity of water, or $a_{\text{H}_2\text{O}}=1$). With the exception of a small number of experiments run at 0.2 GPa, all of our experimental melts are undersaturated with respect to H_2O (i.e. $a_{\text{H}_2\text{O}} < 1$) and sample $f\text{O}_2$ was fixed at a lower value than the buffering assemblage ($\sim \text{NNO} + 3.5$). In this case the difference may be calculated as $\Delta \log f\text{O}_2 = 2 \log a_{\text{H}_2\text{O}}^{\text{sample}}$, where $a_{\text{H}_2\text{O}}^{\text{sample}}$ can be estimated as the degree of undersaturation of the melt with respect to H_2O . For the most undersaturated

conditions (~ 4 wt% H_2O , 1 GPa) we estimate a minimum $a_{\text{H}_2\text{O}}=0.2$, such that $\Delta \log f\text{O}_2=-1.4$, implying a minimum $f\text{O}_2^{\text{sample}} = \text{NNO}+2$. The predicted range of $f\text{O}_2^{\text{sample}}$ is therefore $\sim \text{NNO}+2$ to $+3.5$ and is dependent on both experimental pressure and water content.

Ilmenite compositions were determined by EPMA in a limited number of experiments which also contained magnetite. Although in all cases magnetite was too small to reliably analyze, magnetite composition (X_{uv}) is relatively insensitive to changes in $f\text{O}_2$ in the range expected for these experiments (i.e. $>\text{NNO}+2$, Ghiorso and Evans, 2008) and the mole fraction of end member ilmenite (calculated using the method of Stormer, 1983) may be used to estimate the experimental $f\text{O}_2$. For high pressure experiments (0.75 – 1 GPa), $X_{\text{ilm}} \sim 0.23 - 0.36$ while in lower pressure TZM experiments (0.2 GPa), $X_{\text{ilm}} \sim 0.12 - 0.14$, suggesting that in all experiments $f\text{O}_2 > \text{NNO}+2.5$ ($X_{\text{ilm}} < 0.35 - 0.4$ at $\text{NNO}+2.5$, Ghiorso and Evans, 2008). Although there is some range in experimental $f\text{O}_2$, this implies that S^{6+} will be the dominant S species in all of the experiments presented here (Carroll and Rutherford, 1988), which is consistent with sulfate phases as run products in all the experiments analyzed.

4.4 Analytical Methods

4.4.1 Electron probe microanalysis (EPMA) and scanning electron microscopy (SEM)

All experimental runs were investigated using FEI QUANTA 600F scanning electron microscope (SEM) at Oregon State University. Back scattered electron (BSE) imaging and energy dispersive spectrometry (EDS) were used to identify the phases present in each run.

The major element compositions of experimental silicate glasses and sulfate melts were determined by EPMA using Cameca SX-100 electron microprobes at the University of Bristol and Oregon State University. Silicate glasses were analyzed using a defocused, 10-15 μm diameter beam with an accelerating voltage of 20kV. Major elements were measured at 4nA after which S and Cl were measured at a second condition of 40nA. K and Na were measured first in order to minimize the effect of alkali migration during analysis.

Sulfate melt blebs were analyzed using an accelerating voltage of 15kV and a beam current of 10nA. To analyze sulfate melts that did not form a sulfate glass but rather quenched to finely intergrown heterogeneous masses of anhydrite and alkali-rich sulfate material (see results section), we tested a number of approaches with beam diameters between 2-30 μm .

4.4.2 Secondary ion mass spectrometry (SIMS)

In addition, the H_2O content of silicate glass from a number of experiments was measured using a Cameca ims-4f at the Edinburgh ion microprobe facility (EIMF). Analyses

were made using a 12-15nA $^{16}\text{O}^+$ mass filtered primary beam of 15 keV net impact energy (10.7 keV primary and 4.5 keV secondary) focused to a 15-25 μm spot. The secondary ion extraction energy was 4.5 keV. Only high energy (120 ± 20 eV) positive secondary ions were measured to reduce the presence of molecular ions. A working curve was made for H_2O based on the H/Si ratio measured in rhyolitic glass standards with known H_2O contents. Because the H ion yield varies with SiO_2 content (Blundy and Cashman, 2005), a single working curve of the form H_2O (wt %) = $1.499 (\pm 0.042) * \text{H/Si}$ was appropriate for glasses with a range of SiO_2 contents. The resulting fully propagated uncertainty on sample H_2O contents was 5-12%.

4.5 Results

4.5.1 Run products

All experimental runs contained silicate glass as well as, either anhydrite, sulfate melt or both, depending on temperature. Experimental run products also included oxide minerals (ilmenite solid solution, Fe-Mg-Al-Cr spinel), silicates (biotite, amphibole) and in a limited number of low pressure runs, also fluid. Representative textures are in figure 4.1 and phase relations in figure 4.3.

Sulfate Phases – Sulfate melt was the only phase present, aside from silicate melt, in almost all runs at 1200°C (Fig. 4.1a,b), and in one lower pressure run at 1160°C, based on BSE imaging. At temperature as low as ~900°C sulfate melt was stable alongside crystalline anhydrite in varying proportions (Fig. 4.1c). Sulfate melts were heterogeneously distributed within capsules, and tended to form blebs wetting capsule walls (Fig 4.1a-c). BSE images (Fig 4.1a-c, Fig 4.2a) and X-ray element maps (Fig 4.2b-f) show that upon quenching the sulfate melt does not form a homogenous glass, but rather separates to form several different phases.

The most abundant quench phase approaches the composition of anhydrite and occurs as elongate, 1-5 μm wide laths of Ca-rich material (Fig. 4.2d), surrounded by more Na-rich material (Fig. 4.2e). Cl concentration appears to be highest in areas that were dark in BSE (i.e. most heavily pitted, Fig. 4.2b), and Mg and Fe form irregular concentrations of different sizes and with different distributions (Figs. 4.2c,f). The different patterns of heterogeneity between elements strongly suggest a number of stages of unmixing, rather than simply separation into anhydrite + sulfate glass. Only weak correlation was observed between X-ray intensities for different elements (appendix 4) suggesting that discrete phases larger than the pixel size (i.e. 1 μm) did not form during quench.

Given these observations, it is important to note that any H₂O present in sulfate melts at experimental conditions would likely form a H₂O rich fluid phase during this unmixing process. In this case, this fluid would then be removed during the polishing process leaving holes, and may in part explain the difficulty in producing a flat surface for analysis.

In a small number of runs halite was also observed as a quench product within sulfate melt blebs (Fig. 4.1c). Halite is somewhat soluble in methanol, and may have been unintentionally removed from other samples during polishing.

Anhydrite was present in all runs $\leq 1100^{\circ}\text{C}$ and showed two distinct habits. In higher temperature runs, anhydrite was often present as large, rounded grains, that are likely pseudomorphs of sulfate melt blebs (Fig. 4.1c,e) which were present during the initial homogenization of experiments at $1150\text{--}1200^{\circ}\text{C}$ (see methods section). In most runs anhydrite was also found as smaller, elongate grains $1\text{--}10\text{ }\mu\text{m}$ wide and $10\text{--}50\text{ }\mu\text{m}$ long (Figs. 4.1d-f).

Silicate Phases – The most common silicate phase in these experiments was biotite (Fig. 4.1e,f), which was present in all high pressure ($0.75\text{--}1\text{ GPa}$) runs at $\leq 900^{\circ}\text{C}$ and in both the andesite (A1) and the least water-rich dacite composition (D1) at $\leq 1000^{\circ}\text{C}$. Additionally, biotite was present in one lower pressure run (0.2 GPa , 900°C) of the moderately hydrous dacite composition (D2) but was replaced by amphibole in the equivalent experiment with the more hydrous dacite composition (D3). Amphibole was also present in experiments with andesite starting material (A1) and with the least hydrous dacite (D1) at 900°C . The presence of biotite rather than amphibole in many experiments may be explained by the peraluminous nature of the coexisting silicate melt, and particularly the loss of CaO from the melt at low temperature due to anhydrite crystallization. Biotite was present as extremely elongate laths, generally $2\text{--}5\text{ }\mu\text{m}$ wide and $10\text{--}100\text{ }\mu\text{m}$ long. Amphibole exhibited characteristic habit and was generally euhedral (Fig 4.1e).

Plagioclase was absent from all experimental runs, likely owing to a combination of high temperatures, high water contents, and relatively low CaO contents in lower temperature runs (related to the crystallization of anhydrite, see below, Fig. 4.4a).

Fe-Ti Oxides – Ilmenite was present in almost all experiments at $\leq 1000^{\circ}\text{C}$ and in more mafic A1 experiments at $\leq 1100^{\circ}\text{C}$. Ilmenite exhibited elongate morphology and was generally $5\text{--}100\text{ }\mu\text{m}$ long (Fig. 4.1f). In a number of runs, primarily low pressure (0.2 GPa) TZM experiments, magnetite was also present and generally formed rounded, equant grains $\sim 1\text{--}10\text{ }\mu\text{m}$ long (Fig. 4.1d). In a small number of higher temperature experiments ($1000\text{--}1100^{\circ}\text{C}$) a Fe-Mg-Al-Cr

spinel was also present although invariably in very low abundance, with only 1-2 grains observed per experiment.

Fluid – No evidence of a water-rich fluid phase was present in any experiments at high pressure (0.75 - 1GPa), consistent with water solubility models for silicate melts (e.g. Burnham, 1975, Ghiorso and Gualda, 2015) and measured water contents in all experiments <9 wt% (see section on silicate glass composition). Two experiments at low pressure (0.2GPa) with the most hydrous starting material (D3) were water-saturated and small (5-20 μ m) vesicles were observed in BSE images of these runs (Fig. 4.1d) although they are difficult to distinguish from small sulfate melt blebs, which were also present.

4.5.2 Silicate glass composition

Silicate glass compositions, calculated on an anhydrous basis ranged from trachydacite – rhyolite (~67-72 wt% SiO₂) in runs with trachydacite starting material, and trachyandesite – trachydacite (59-67 wt% SiO₂) in runs with the trachyandesite starting material. Figure 4.4 shows major element variation with temperature, distinguished by starting composition and pressure. Broadly the same trends are evident in all cases. TiO₂, FeO, MgO and K₂O act compatibly and decrease with temperature at T <1000°C consistent with the crystallization of Fe-Ti oxides, biotite and in some cases amphibole. A drop in the glass P₂O₅ content between 1000-800°C implies the crystallization of small amounts of apatite, although none was observed in BSE images.

As temperature increases above 1000°C there is a decrease in the K₂O, Na₂O, MgO and notably the Cl content of the silicate glass. Since no solid phases were present at 1200°C this decrease must be related to partitioning of these elements into the immiscible sulfate melt at high temperature. This also leads to an increase in the CaO content of the glass since CaO makes up a significantly smaller proportion of sulfate melt than anhydrite. The SO₃ content of the silicate melt increases with temperature and is higher in more mafic runs and in runs with higher H₂O contents, consistent with existing modelling of sulfate solubility in silicate melt (Masotta and Keppler 2015, Zajacz and Tsay, 2019).

4.5.3 The water content of experiments

The H₂O content of a subset of silicate glasses was determined by SIMS and are presented in Figure 4.4i. H₂O contents are 3.5 – 5.5 wt% for experiments with starting material D1, 5 - 7.5 wt% for starting material D2, 6.5 – 9 wt% for starting material D3 and 6.5 – 8 wt% for runs with starting material A1. The water content of the silicate glasses are a function of the water

content of the starting material, the proportion of silicate glass and the partitioning of H_2O between silicate glass and other phases. In lower temperature experiments all the phases present apart from the silicate melt are nominally anhydrous, however at higher temperature some H_2O may partition into sulfate melt. Finally the H_2O content may be effected by the movement of hydrogen into or out of the inner capsule in response to gradients in $f\text{H}_2$. As noted earlier, the water contents of all the experiments in this study were higher than expected and somewhat variable. However with some consideration of these factors it is possible to estimate bulk water content of the experiments.

Firstly, the amount of water that may be produced or lost due to the movement of hydrogen into or out of the capsule can be estimated based on the reduction or oxidation of Fe and S in the system. The large difference in molecular mass between Fe_2O_3 and H_2O means that the reduction of ~ 1 wt% Fe_2O_3 should produce only ~ 0.11 wt% H_2O . Experiments were loaded with equal amounts of Fe_2O_3 and FeO by weight, close to the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio expected at run conditions (Kress and Carmichael, 1991) and there should be little movement of hydrogen related to oxidation or reduction of Fe species. All the sulfur in these experiments was added in the form of sulfates, i.e. S^{6+} , however at run conditions as much as $\sim 5\%$ of the sulfur may be present as sulfide (Matjuschkin et al. 2016) and the reduction of $\sim 5\%$ of the sulfur in these experiments could add as much as 0.4 wt% H_2O .

Secondly, the water content of the starting material may be effected by the uptake of water from the atmosphere, either adsorbed onto the surface of finely ground oxide powders, or structurally bound, for example to produce gypsum from CaSO_4 powder. Starting materials contained $\sim 10 - 13.5$ wt% CaSO_4 and if some or all of this powder was converted to gypsum it is possible that starting materials contained as much as $\sim 2.1 - 2.8$ wt% H_2O more than expected. This may have occurred either during the preparation of the starting material, or when starting materials were taken out of the drying oven in order to load experiments. This is the most plausible explanation of the higher than expected H_2O contents, and may account for some variability between the water content of experiments with the same starting material.

Although the bulk H_2O content of experiments was not as expected it can be calculated based on the measured water contents of silicate glasses at 1000°C , and an estimate of the proportion of silicate melt. In 1000°C experiments the only phases present in a significant proportion were silicate melt and anhydrite, and the proportions of both phases can be determined by mass balance based on the measured S content of the silicate glass and the bulk S content of the starting material. Estimates of bulk H_2O by this method (table 4.1) are subject to uncertainty

related to the measurement of H₂O by SIMS (average 2 s.d. ~0.6 wt% H₂O) and do not account for the possible uptake of H₂O by the starting material between experiments.

4.5.4 Sulfate melt composition – EPMA

In order to get representative average compositions for sulfate melts using EPMA we tested a number of different approaches. Figure 4.5 shows good agreement between the average compositions calculated from analyses using a 1µm beam (n=102), 15µm beam (n=32) and 30µm beam (n=18). As expected, using a larger diameter beam better captures an average composition of heterogeneous quench products (Fig. 4.2a-f), resulting in a smaller standard deviation (Fig. 4.5a,b) for 30µm analyses. Element maps of the area of sulfate melt used for this test are shown in Fig 4.2b-f, which were made following the EPMA analyses. They show faint vertical lines of high CaO content and low Na₂O content corresponding to the location of EPMA analyses, suggesting alkali migration away from the electron beam during analysis. Using a defocused, 30µm beam should minimize this effect, and may explain slightly higher average Na₂O contents for the 30µm analyses compared to 1µm and 15µm analyses.

Using a 30µm beam, ~300 analyses were made of sulfate melt blebs from 12 different experimental runs between 1100 - 1200°C. Totals ranged from 40-100 wt% and are plotted in figure 4.6a-d against major element concentrations, along with a small number of analyses of an anhydrite grain using the same conditions for comparison. Good correlation in figure 4.6a between the analysis total and SO₃ content strongly suggests that low totals are caused by missing material in the area analyzed due to plucking during polishing. As noted above, areas of plucking appear to disproportionately affect Na₂O-rich areas compared to CaO-rich areas (which approach the composition of anhydrite). In figure 4.6b,c this can be seen as a relatively constant CaO content compared to the analysis total, but a sharp drop in the Na₂O content in analyses with the lowest totals. K₂O, figure 4.6d, appears to be less affected than Na₂O. In order to calculate meaningful averages from these data, we have applied a cut-off to the analysis totals of 80% (below which Na₂O contents appear to drop significantly) and analyses have been normalized to a total of 100%.

The alternative, that low totals represent a significant amount of an H₂O in the sulfate melt quench products, is possible but implies a large number of 30µm diameter spots with H₂O contents >20 wt%. As previously noted, if sulfate melts contained significant concentrations of H₂O at run conditions it is likely that a H₂O rich fluid would be produced during quenching, which would then be removed during polishing to leave holes. Since it is not possible to

determine definitively if this is the case from EPMA data, the normalized totals calculated here represent the anhydrous composition of the sulfate melts.

Average sulfate melt compositions were calculated based on EPMA results for 10 experimental runs (table 4.4, Figs. 4.7a-h) at 1100-1200°C. It is important to note here that the uncertainties shown in figures 4.7a-h reflect heterogeneity of the sample rather than purely analytical error and as such, although error bars may overlap, in some cases the mean values are still considered distinct from one another. To illustrate this a Welch's t-test (i.e. a t-test assuming unequal variances between populations) can be used to test the assumption that two mean values were drawn from the same population. Applying this to K₂O concentrations from experiments 69 and 80 (green and blue triangles respectively, Fig. 4.7d, 1100°C) indicates that there is a significant difference between the mean values at a 99% level of confidence.

Despite this, the major element composition of sulfate melts in almost all experiments is similar. Normalized, volatile-free, sulfate melts are dominated by SO₃ (~53-58 wt%) and CaO (~25-31 wt%) and contain significant amounts of Na₂O (~5-8 wt%), K₂O (~1-5 wt%), MgO (~1-2 wt%) and FeO (~0.7-1.5 wt%). EPMA results suggest that with decreasing temperature the CaO and P₂O₅ content of sulfate melts increases slightly, whereas the concentration of alkalis falls.

An exception to this is one experiment at 0.75GPa, 1100°C with starting composition D2 (green triangles). Sulfate melt in this experiment appears to contain less CaO and more MgO and FeO than its higher temperature equivalent, as well as higher alkali contents than sulfate melts from other 1100°C experiments. This may be related to particularly low silicate glass CaO content (~1.4 wt%, Fig. 4.4a) in this experiment. Alternatively, this may be related to difficulties with sample preparation, although as mentioned previously, this should produce the opposite trend (i.e. preferential removal of more alkali rich areas should produce analyses with erroneously low alkali contents).

Chlorine contents measured by EPMA are highly variable (0.04 – 2.06 wt%), and are highest in two experiments in which halite was observed in BSE imaging (0.75GPa, D2, 1100°C - 1200°C). Halite is somewhat soluble in methanol, which was sometimes used during sample preparation, and removal of halite from most samples may explain this discrepancy.

Sulfate melt could only be analyzed in one low pressure experimental run (0.2GPa, 1160°C, D1) but results show that this sulfate melt contained significantly more Na₂O (~16 wt%) and significantly less K₂O, MgO and FeO than sulfate melts in higher pressure experiments.

4.5.5 Sulfate melt composition – mass balance

Since silicate and sulfate melt are the only two phases present in 1160 – 1200°C runs it is also possible to determine the concentration of an element (i) in sulfate melt (X_i^{Sulf}) by mass balance as:

$$(4.1) \quad X_i^{Sulf} = \frac{X_i^{Bulk} - (m^{Sil} X_i^{Sil})}{m^{Sulf}}$$

assuming the proportions (by mass) of silicate and sulfate melt in the experimental charge (m^{Sil} and m^{Sulf} respectively) are known. X_i^{Bulk} is the concentration of an element (i) as part of the anhydrous bulk composition (wt%, table 4.1) and X_i^{Sil} is the concentration of the element in the silicate glass, as determined by EMPA (wt%, table 4.3). The proportion of sulfate melt (table 4.5) present in each experiment was calculated based on both the bulk SO₃ content and the measured SO₃ contents of silicate and sulfate melts (by EPMA, see above) and ranged from 0.13-0.16. Results compare well with EPMA in most cases (Fig. 4.8), although they suggest that EPMA measurements tend to underestimate alkalis and Mg somewhat, and significantly underestimate Cl concentrations. This is consistent with the earlier observation that alkali and Cl-rich areas of the sulfate melt blebs tend to be lost preferentially during sample preparation.

Mass balance estimates for the water content of sulfate melts ranged from 0 – 12 wt% but are subject to a large degree of uncertainty (often >100%) which reflects the uncertainty on the measurement of H₂O in silicate glass (~10%), the uncertainty of the calculation of the bulk H₂O content and the small proportion of sulfate melt relative to silicate melt ($m^{Sulf} = 0.13 - 0.15$). Mass balance estimates put an upper limit on the water content of sulfate melts at ~20 wt% but in almost all cases the water content estimated by this method is not distinguishable from 0. This is consistent with figure 4.4i, which shows that the silicate glass from most experiments at 1200°C, which contain sulfate melt, have indistinguishable water contents from experiments at 1000°C, which contain mostly anhydrite (nominally anhydrous).

4.5.6 Changes to sulfate melt composition with temperature and pressure

Temperature –EPMA data suggest that at 1100°C sulfate melts have slightly higher CaO contents and slightly lower K₂O and Na₂O contents than at 1200°C (Fig. 4.7). However, since anhydrite and sulfate melt are both stable at 1100°C it is difficult to determine if these EPMA analyses provide representative averages of quenched sulfate melts, or if they represent mixtures with some amount of anhydrite that was stable under run conditions. Phase diagrams for binary systems CaSO₄ – MgSO₄, CaSO₄ - K₂SO₄ and CaSO₄ - Na₂SO₄ (Rowe et al. 1967, Du, 2000,

Coursol et al. 2005, Fig 4.9) show that in all cases the composition of sulfate liquids will move away from pure CaSO_4 as temperature falls, and this must also be the case here. However given the large uncertainties associated with EPMA analyses it is likely that such a change is not resolvable here.

Pressure – There is little obvious change in sulfate melt composition with pressure (Fig. 4.10) and in almost all cases the composition calculated at 0.75 GPa is well within uncertainty of the composition calculated at 1 GPa. However, in the one experimental run at 0.2 GPa, the composition of sulfate melt as determined by mass balance differs significantly from that determined by EPMA (Fig. 4.8). Mass balance suggests K_2O (~5.6 wt%) and Na_2O (~5.3 wt%), comparable with the compositions of sulfate melts at higher pressure. EPMA results, however, suggest much higher Na_2O content (~15.4 wt%) and much lower K_2O (~0.7 wt%) than in other samples (Fig. 4.7c,d) as well as low FeO and MgO contents (Fig 4.7e,f). Available data on phase relations for Ca, K, Na and Mg sulfates (summarized by Du, 2000) do not suggest a likely candidate for a discrete Na-Ca rich sulfate phase, and they indicate total solid solution of K_2SO_4 - Na_2SO_4 down to temperatures as low as ~470°C (Du, 2000, data from Akopov and Bergman, 1954).

Another possibility is that rapid quenching of low pressure TZM experiments preserved a sulfate glass in run products rather than the microcrystalline, heterogeneous mass of material produced in higher pressure, more slowly quenched, piston-cylinder experiments (Fig. 4.10a-c). In this case the observed difference in concentration might reflect an extreme reaction of glassy sulfate material in low pressure experiments to the electron beam. Although further work is needed to determine if this is the case, the morphology of sulfate material in the low pressure runs implies that, as in other runs, it was a liquid at run conditions, and mass balance estimates suggest it had a similar composition.

4.6 Discussion

4.6.1 *Factors effecting the stability of sulfate melts*

Since sulfate melt was distributed heterogeneously throughout experimental capsules it is difficult to determine its volume proportion by direct observation (e.g. by point counting). Furthermore in experiments at lower temperature where sulfate melt may only make up a small mass proportion of run products, it may be easily missed. However, since Na is compatible in sulfate melt, but no other run products, it is possible to use silicate glass Na content as a proxy for the presence of sulfate melt. Contours of the “Na-deficit” of silicate glass (i.e. measured –

expected Na_2O content) are plotted in figure 4.3, beginning at -0.5 wt% Na_2O (average 2 s.d. uncertainty on Na_2O measurements is ~ 0.35 wt%). This approach suggests that sulfate melt is present in a number of experiments where it was not observed by BSE imaging, down to temperatures as low as 900°C . Contours of Na-deficit may also be used to qualitatively determine factors favorable for the formation of sulfate melts.

In almost all cases, experiments at 0.2 and 0.75 GPa had a greater Na-deficit than equivalent experiments at 1 GPa (Fig 4.3a,b), suggesting a greater proportion of sulfate melt at lower pressure. The presence of a hydrous fluid phase in low pressure experiments may have affected the melt Na content somewhat, but the magnitude of this effect is likely small. Assuming a molar Cl:Na ratio of $\sim 2:1$ in the fluid phase, the maximum amount of Na that could possibly be removed by a fluid is <0.1 wt% (assuming that all Cl is in this fluid).

Results for starting materials A1 and D3 are broadly comparable, suggesting that bulk SiO_2 content does not have a strong effect on sulfate melt stability. This is consistent with low (generally <1 wt%) solubility of SiO_2 in sulfate melts. By contrast, although the major element composition of starting material D2 is nominally the same as D1 and D3, it appears to have a broader field of sulfate melt stability (Fig 4.3). This is likely due to low silicate melt $\text{CaO} / \text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O}$ ratios in experiments with D2 (~ 0.03 at 900°C compared to ~ 0.13 in similar experiments with starting composition D3), related to slightly higher bulk SO_3 and greater removal of CaO from the melt by anhydrite crystallization.

This observation, that the stability of sulfate melts will be greater in CaO-poor melts is consistent with the experiments of Veksler et al. (2012) in which silicate glasses were nominally CaO-free and run products at 900°C contained only silicate and sulfate melt, with anhydrite absent. Furthermore, phase equilibria projected for the system $\text{CaSO}_4 - \text{Na}_2\text{SO}_4 - \text{K}_2\text{SO}_4$ (Du, 2000) suggest a eutectic at 853°C with a composition of ~ 50 mol% CaSO_4 . By contrast sulfate melt compositions in this study, normalized to $(\text{CaSO}_4 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 = 1)$ were generally >70 mol% CaSO_4 , far more CaSO_4 rich than the minimum melting composition.

Comparing results from starting materials D1 and D3 (Fig. 4.3a,c) shows the effect of H_2O content on the stability of sulfate melt and suggests that a ~ 4 wt% increase in the H_2O content of the silicate glass can extend the stability of sulfate melt by $\sim 50^\circ\text{C}$ to lower temperature.

Contours of Na-defecit can also be used to estimate the solidus and liquidus temperatures for the binary system with anhydrite and a fictive component representing all the non – CaSO_4 components of the sulfate melt. The solidus temperature is equivalent to the minimum

temperature at which sulfate melt is present, while the liquidus is equivalent to the maximum temperature at which anhydrite is present. In almost all cases experiments at 1100°C contained both anhydrite and sulfate melt, while those at 1200°C contained only sulfate melt, meaning that the liquidus in most cases was between 1100 and 1200°C. These estimates are further refined based on contours of Na-defecit and are likely accurate to $\pm 25^\circ\text{C}$. The position of the liquidus for each set of experiments (i.e. for a given composition and pressure) is plotted as a function of the liquidus sulfate melt composition, approximately equivalent to the composition of sulfate melt determined in 1200°C experiments (Fig. 4.9). Liquidus curves for systems $\text{CaSO}_4 - \text{Na}_2\text{SO}_4$, $\text{CaSO}_4 - \text{K}_2\text{SO}_4$ and $\text{CaSO}_4 - \text{MgSO}_4$ at 1 atm (Coursol et al. 2005, Rowe et al. 1967) are also plotted for comparison. In almost all cases, the liquidus temperatures observed are 50-200°C higher than those in the systems $\text{CaSO}_4 - \text{Na}_2\text{SO}_4$ and $\text{CaSO}_4 - \text{K}_2\text{SO}_4$ at equivalent mol fraction CaSO_4 (Coursol et al. 2005, Rowe et al. 1967). This is somewhat surprising, given that Na_2SO_4 and K_2SO_4 make up the majority of the non- CaSO_4 component of the sulfate melt. A predicted liquidus can be calculated for each sulfate melt composition on the basis of mixing between CaSO_4 and components Na_2SO_4 , K_2SO_4 , MgSO_4 , for which the mixing properties are known, and NaCl and FeSO_4 , for which the mixing properties can be estimated as the average of the known components. Taking these extra components into account, the observed liquidus temperatures are still 20-75°C higher than those predicted.

The offset between predicted and observed liquidus temperatures may be explained by the effect of pressure (the binary systems used above are determined at 1 atm), the addition of another component (likely H_2O), or if the mixing properties in the system CaSO_4 - NaCl were very different from those considered above. The effect of pressure must be to increase the liquidus temperature, the effect of the addition of H_2O must be to decrease the liquidus temperature, while the effect of NaCl mixing properties could be in either direction. Large uncertainties on both estimated liquidus temperatures and compositions inhibit the quantitative assessment of these effects.

To summarize, the formation of sulfate melt, as opposed to anhydrite, is favored by lower pressure, higher bulk alkali contents, higher SO_3 and H_2O contents, and by lower CaO contents.

4.6.2 The H_2O content of sulfate melts

Although it is difficult to determine the H_2O content of sulfate melts by either direct measurement (EPMA) or by mass balance, it may be estimated by considering the depression of the sulfate melt – in curve (i.e. the solidus in the system discussed above). Comparing the most water

rich (D3) and water poor (D1) experiments, figure 4.3a,c shows that the minimum temperature at which sulfate melt occurs is $\sim 50^\circ\text{C}$ lower in the more H_2O rich experiments. Phase relations in the system $\text{CaSO}_4 - \text{MgSO}_4 - \text{K}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$ investigated by Du (2000) suggest that the addition of $\sim 3 - 6$ mol % of a second component will depress the melting point of CaSO_4 by $\sim 50^\circ\text{C}$. Assuming similar mixing properties for $\text{CaSO}_4 - \text{H}_2\text{O}$, a depression of 50°C could be achieved by the addition of $\sim 0.4 - 0.85$ wt% H_2O . If the partition coefficient for H_2O in both experiments is the same, this would imply sulfate melt H_2O contents of $0.4 - 0.85$ wt% and $0.8 - 1.7$ wt% respectively, and a partition coefficient for water between sulfate and silicate ($D_{\text{H}_2\text{O}}^{\text{Sulf-Sil}}$) of $\sim 0.11 - 0.22$.

Experimental work on sulfide melting by Wykes and Mavrogenes (2005) came to a similar conclusion, showing that the addition of H_2O could reduce the melting point of $\text{FeS} - \text{PbS} - \text{ZnS}$ mixtures by $\sim 35^\circ\text{C}$, implying limited solubility of H_2O in sulfide melts. However, since sulfide melts in the experiments of Wykes and Mavrogenes (2005) did not quench to glasses, no attempt was made to quantify H_2O solubility.

4.6.3 Major element partitioning

Sulfate melt – Silicate melt partition coefficients have been calculated for experiments at 1200°C using sulfate melt concentrations from mass balance (Ca, Na, K, Fe, Mg, P, Cl) and EPMA data (Mn, Al, Si). They show that aside from major components CaO and SO_3 , Cl and P also heavily favor sulfate melts (Fig. 4.11), and K, Na, Mn and Mg do so moderately. Fe is generally somewhat incompatible in sulfate melt while Al and Si are strongly incompatible.

Broadly these data are consistent with experimental runs of Veksler et al. (2012) at $1000 - 1100^\circ\text{C}$. Despite large differences in the bulk sulfate composition, partition coefficients presented here at higher temperature (1200°C) are somewhat lower for compatible elements K, Na, Ca and Mg and somewhat higher for Si (incompatible), as is expected. The partition coefficient for aluminum presented here is significantly lower than that of Veksler et al. (2012), despite the higher temperature, and can only be a result of the difference in the bulk sulfate composition (i.e. calcium dominated rather than alkali dominated) between the two sets of experiments. Similarly, compositional differences may account for the very large difference in partition coefficients for Mg between the two sets of experiments.

4.6.4 Sulfate melts in arc magmas

These experiments show that immiscible sulfate melts should be expected to form in H_2O -rich magmas at temperatures $\geq 1000^\circ\text{C}$, assuming that enough sulfur is present. The lower

San Jose Ignimbrite, which hosted “wormy-anhydrite” inclusions at Yanacocha (Chambefort et al. 2008) has a molar $\text{CaO} / \text{Na}_2\text{O} + \text{K}_2\text{O}$ (~ 1) and a water content of >6 wt% (based on the presence of amphibole at close to liquidus temperatures, Chambefort et al. 2013), similar to the andesite starting material investigated here. This being the case, these experiments suggest wormy anhydrite trapping temperatures must have been $\geq 1000^\circ\text{C}$, at the upper end of estimates for temperature of amphibole crystallization (Chambefort et al. 2013). A number of experimental studies including Grove et al. (2003) and Krawczynski et al. (2012) show that amphibole is stable in melts with as much as 12 wt% H_2O at pressures up to 800MPa and temperatures up to 1050°C . Under these water rich conditions the predicted lower limit of sulfate melt stability is $900\text{--}950^\circ\text{C}$ and sulfate melts could have been trapped by early crystallizing, high temperature amphibole. In order to saturate in sulfate melt, Yanacocha magmas must have also contained a significant amount of sulfur. At 1000°C the silicate melt in andesite (A1) experiments in this study contained ~ 2400 ppm S (~ 0.6 wt% SO_3 Fig. 4.4h) and this may be considered a reasonable minimum sulfur content needed to produce sulfate melts. Given the abundance of wormy anhydrite inclusions (up to ~ 10 vol% of amphibole hosts, Chambefort et al. 2008) it is likely that Yanacocha magmas had sulfur contents well in excess of this.

Although melt inclusion data suggests that the majority of primitive arc magmas have sulfur contents below this 2400 ppm threshold (commonly $\sim 1000\text{--}2000$ ppm S see fig. 2 in Wallace and Edmonds, 2011), a number of studies have reported significantly higher values. These include olivine hosted melt inclusions from Punalica and Sangay volcanoes in Ecuador (Narvaez, 2018), Augustine and Korovin volcanoes in the Aleutian arc (Zimmer et al. 2010), Mt Shasta, California (Le Voyer et al. 2010) and notably, from the Colima volcanic complex in the western Mexican volcanic belt (Maria and Luhr, 2008, Vigouroux et al. 2008) where basanite and minette melt inclusions contain as much as 10,000 ppm S.

The most primitive melt inclusions at Augustine and Korovin volcanoes, representing parental melts, contain as much as 6000 ppm S and 5-8 wt% H_2O (Zimmer et al. 2010). Based on the sulfur contents of silicate glasses in this study, these melts would have been saturated in sulfate at temperatures as high as 1200°C and would almost certainly have produced sulfate melts rather than anhydrite. During cooling the proportion of sulfate melt should fall, with the CaSO_4 component forming anhydrite and the other major components dissolving back into the silicate melt. This is consistent with the identification of anhydrite phenocrysts in erupted products from the 2006 eruption of Augustine volcano (Larsen et al. 2010).

At the Colima volcanic complex, melt inclusion data suggests that potassic magmas had Cl contents approximately two times higher, and S/Cl ratios up to 5 times higher than nearby calc-alkaline basalts (Vigouroux et al., 2008), despite similar H₂O contents. Authors argued that since large differences in the volatile contents of slab-derived fluids are unlikely, differences in parental melt composition might be attributed to the presence of sulfate phases or apatite in the mantle source region of the minette and basanite magmas. We suggest that the addition of a sulfate melt to the mantle source region could explain both the higher absolute S and Cl contents, as well as higher S/Cl ratios (S/Cl ratio of most sulfate melts in this study were ~10-20). Indeed sulfate melts may well be expected in the mantle wedge above the subducting slab, possibly separating from supercritical fluids during ascent, and would constitute an important S and Cl rich metasomatising agent. However further investigation into the distribution of sulfur between silicate, sulfate and water-rich liquids at high pressure is needed.

4.7 Conclusion

In typical arc magmas sulfate melt is stable, together with anhydrite, at temperatures of 1000-1200°C and pressures up to at least 1 GPa. In particularly water or alkali rich magmas sulfate melt may be present to temperatures as low as 900°C and completely replaces anhydrite as the stable sulfate phase above ~1150-1200°C. The composition of sulfate melts is dominated by CaO and SO₃ but they also contain, in order of relative abundance, Na₂O, K₂O, MgO, FeO, Cl and P₂O₅. Cl has a particular affinity for sulfate melt with $D_{Cl}^{Sulf-Sil} \sim 5-13$ even at high temperature (1200°C).

These results are consistent with the trapping of sulfate melts (“wormy anhydrite”) in high-Al amphibole at Yanacocha, Peru (Chambefort et al. 2008) at ~1000°C and imply that parental melts had high water and sulfur contents, >10 wt% and >2400 ppm respectively. Although there have been currently no other reported occurrences of sulfate melts in nature, this study suggests that they should be present at high temperature in very sulfur rich magmas, for example parental melts beneath Augustine volcano (Zimmer et al. 2010).

Finally, sulfate melts may provide an effective means of transporting and concentrating volatile species (particularly S and Cl) in the mantle wedge and lower crust, and may be instrumental in generating very volatile rich primitive melts.

4.8 References

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4.9 Figures and tables

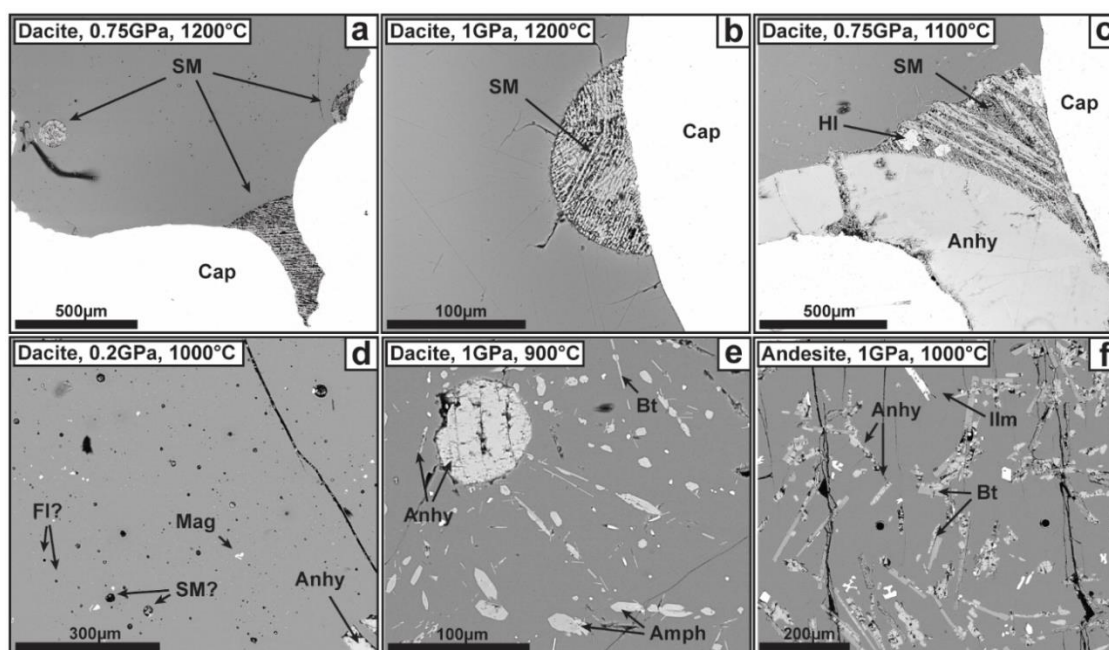


Figure 4.1 BSE images of typical experimental run products. SM – Sulfate Melt, Cap – Au₈₀Pd₂₀ capsule, Anhy – Anhydrite, Hl – Halite, Fl – Vesicles representing H₂O-rich fluid, Ilm – Ilmenite, Mag – Magnetite Bt – Biotite, Amph – Amphibole. A,B – sulfate melt wetting capsule walls in high temperature experiments. C – Sulfate melt quench products (including halite) coexisting with anhydrite, D – Low pressure, fluid saturated run with small vesicles, E,F – Low temperature runs with stable silicate phases, showing two distinct anhydrite habits.

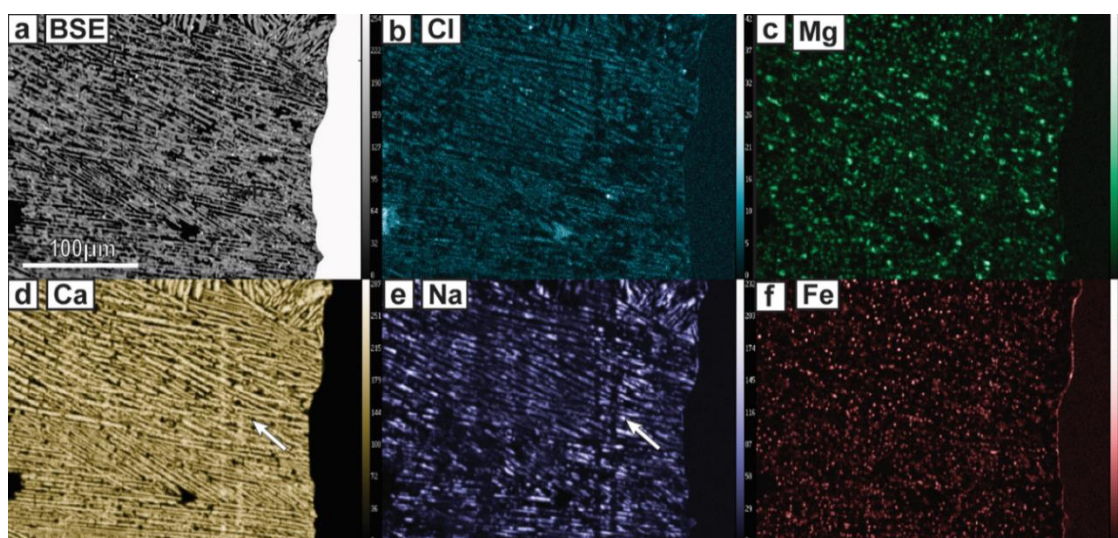


Figure 4.2 BSE image and X-ray element maps of sulfate melt quench products showing differing scales and patterns of heterogeneity for five elements. X-ray maps are scaled in cps, with increased brightness corresponding to increased concentration. Faint vertical linear regions (arrows) of Ca enrichment (d) and Na depletion (e) represent areas previously analyzed using 1µm and 15µm EPMA spots.

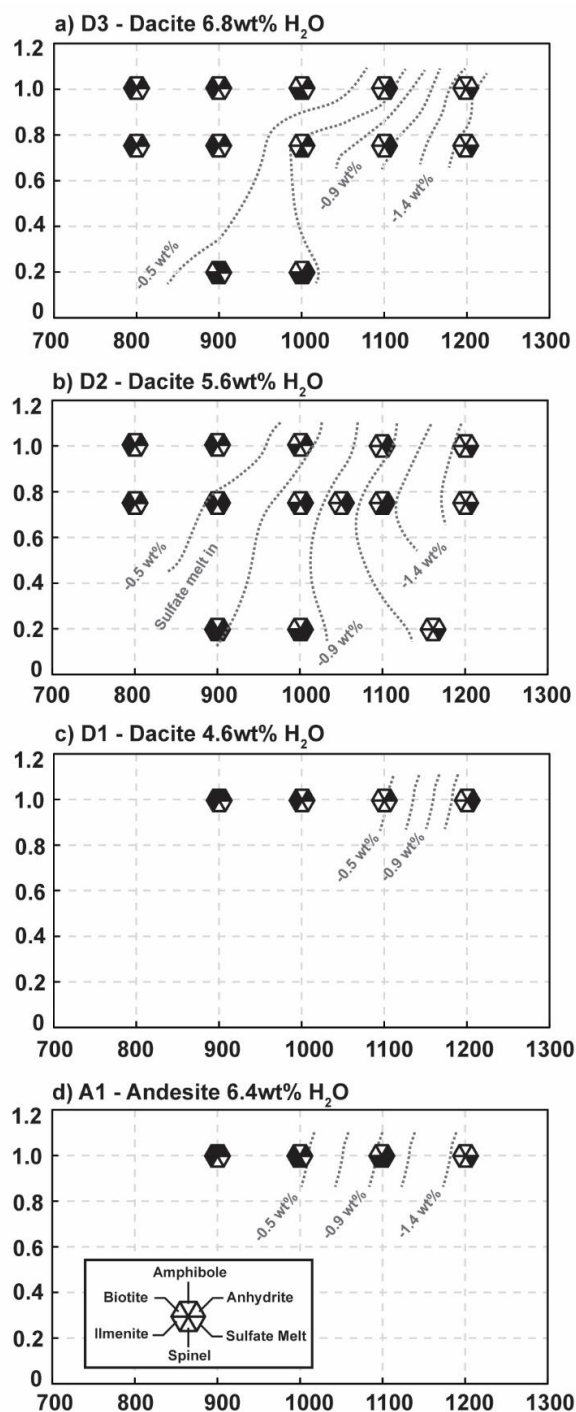


Figure 4.3 Phase relations for experiments with four starting materials as a function of temperature and pressure. Lines of “Na deficit” are calculated based on an expected glass Na content given the crystallization of anhydrite only. “SM-in” is suggested to be at -0.5 wt% Na₂O, given an average 2 s.d. uncertainty on Na₂O measurements of 0.35 wt%. Note broadening of sulfate melt stability field with decreasing pressure, greater bulk H₂O content and with decreasing silicate glass CaO content (see D2 starting material, fig 4.4a). Note that water contents listed are nominal and the actual water contents of experimental runs varies (see text, table 4.3, fig 4.4i)

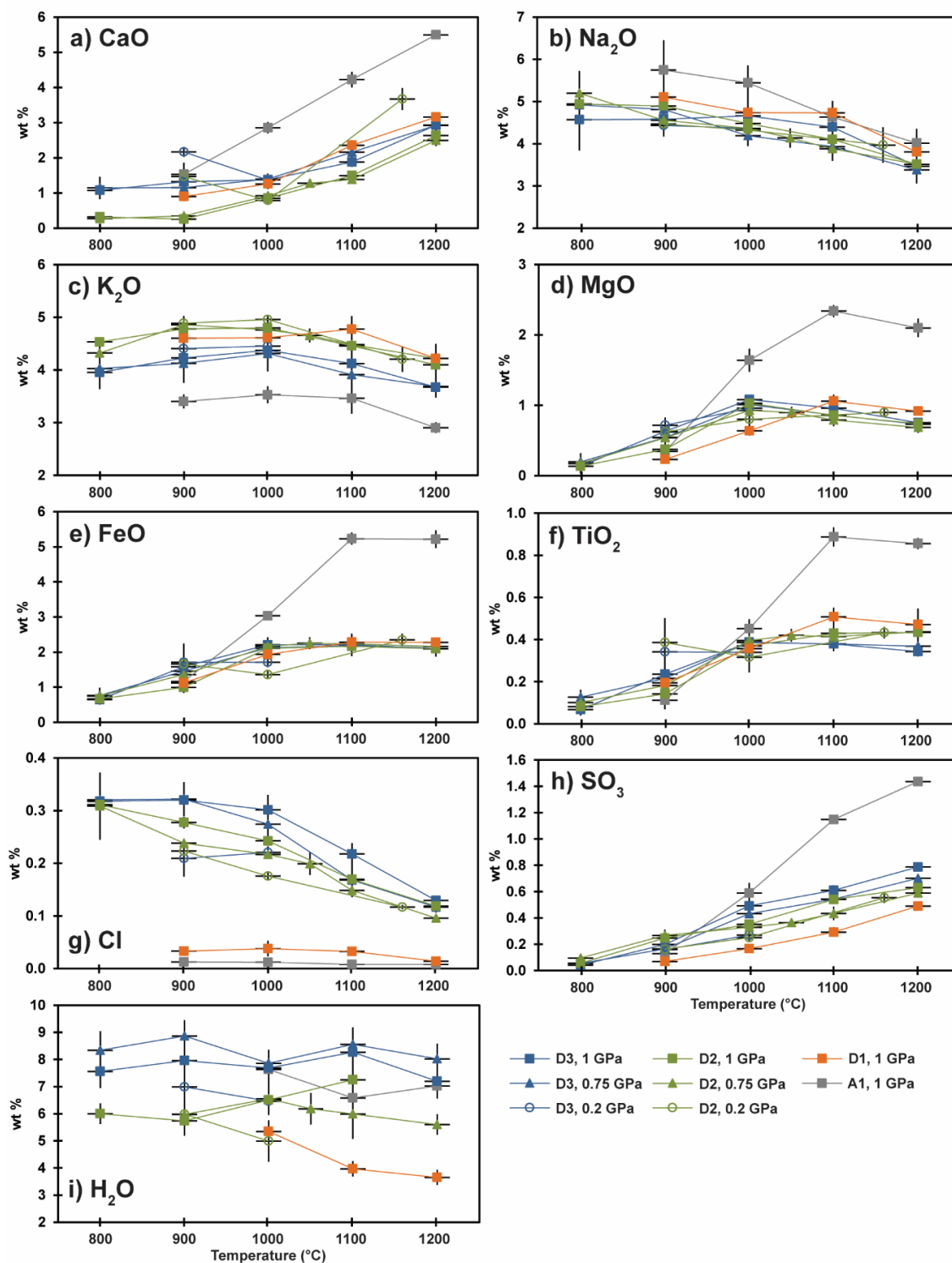


Figure 4.4 Silicate glass major element composition, determined by EPMA and SIMS (H₂O contents). Uncertainties on EPMA measurements are 2 s.d. based on repeat analysis (n=10-12). 2 s.d. uncertainties on SIMS H₂O contents are propagated based on uncertainties calculated for both the working curve and repeat analysis of the silicate glasses (n=2-5).

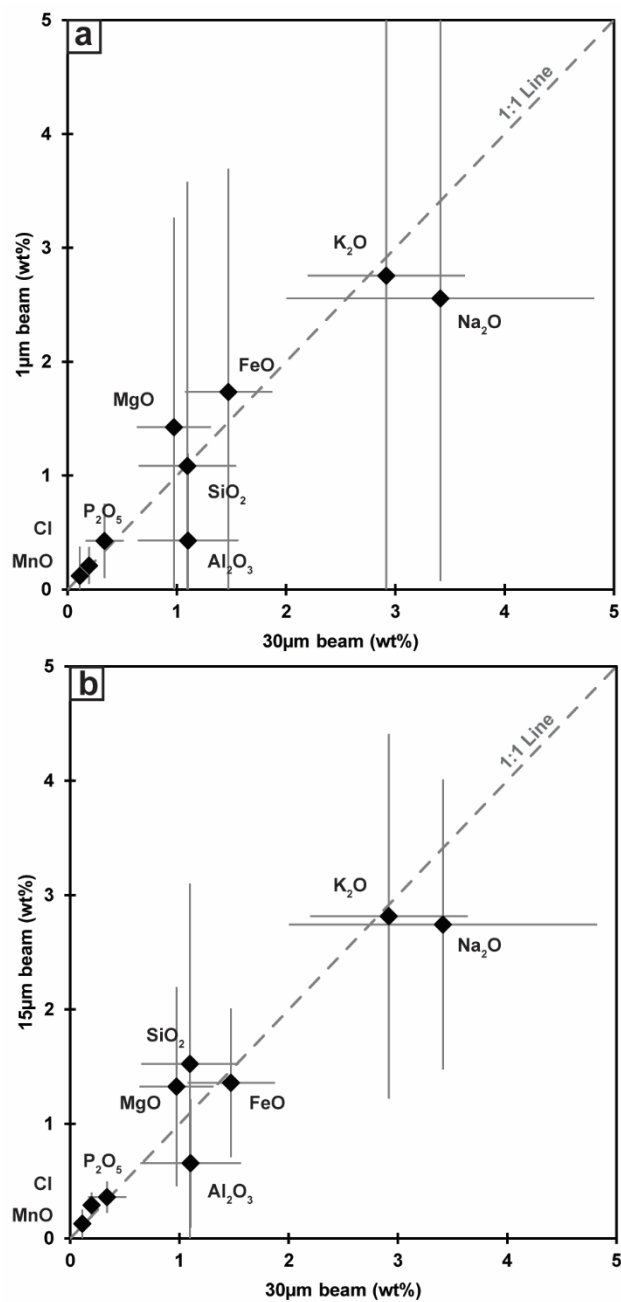


Figure 4.5 Comparison of average sulfate melt composition by EPMA with varying spot size. All analyses were conducted on different parts of one large sulfate melt bleb, shown in figure 4.2. Error bars are 1 s.d. of mean.

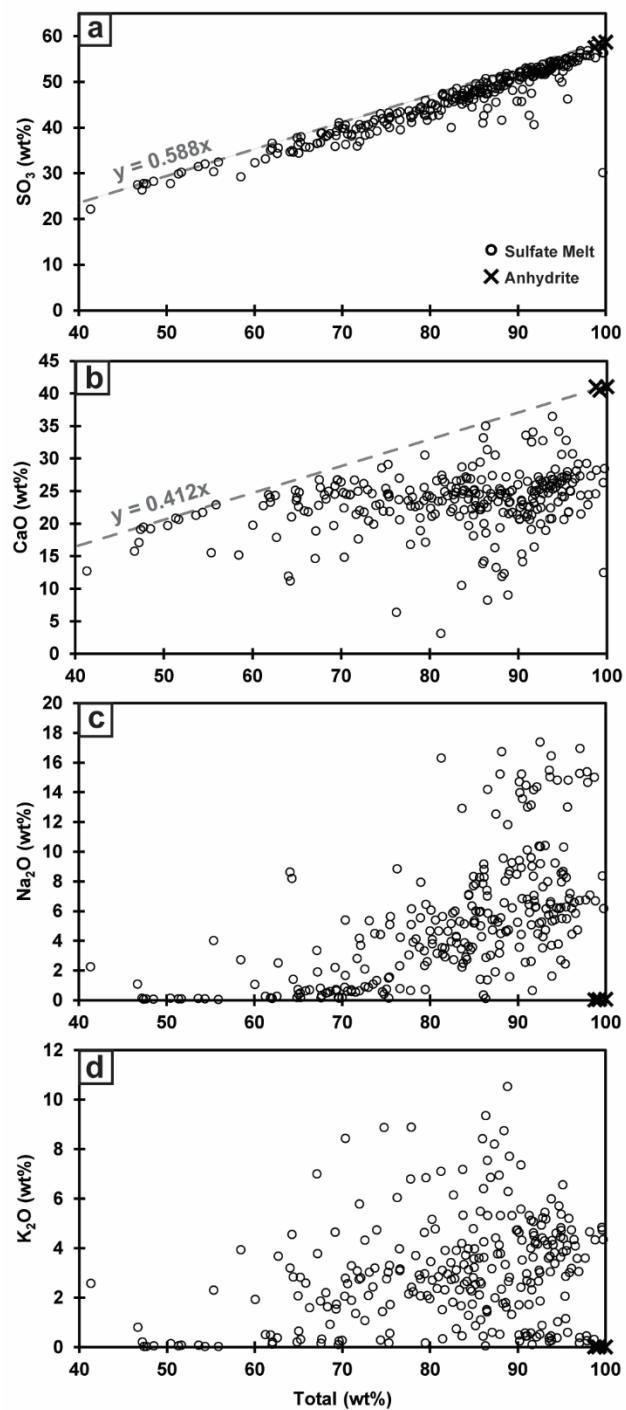


Figure 4.6 All individual 30 μ m EPMA analyses of sulfate melt blebs from 12 different experimental runs. A small number of anhydrite analyses using the same analytical conditions are shown for comparison.

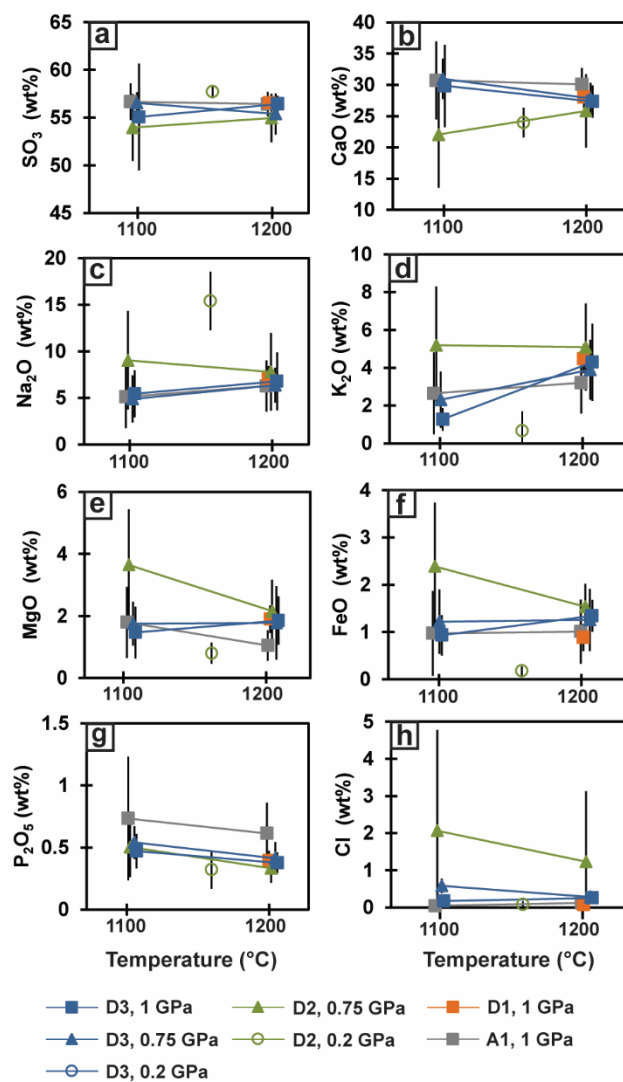


Figure 4.7 Average compositions for sulfate melt blebs based on EPMA analyses. Error bars are 1s.d. of all analyses. Note that error bars reflect heterogeneity of the sample rather than simply instrumental uncertainty.

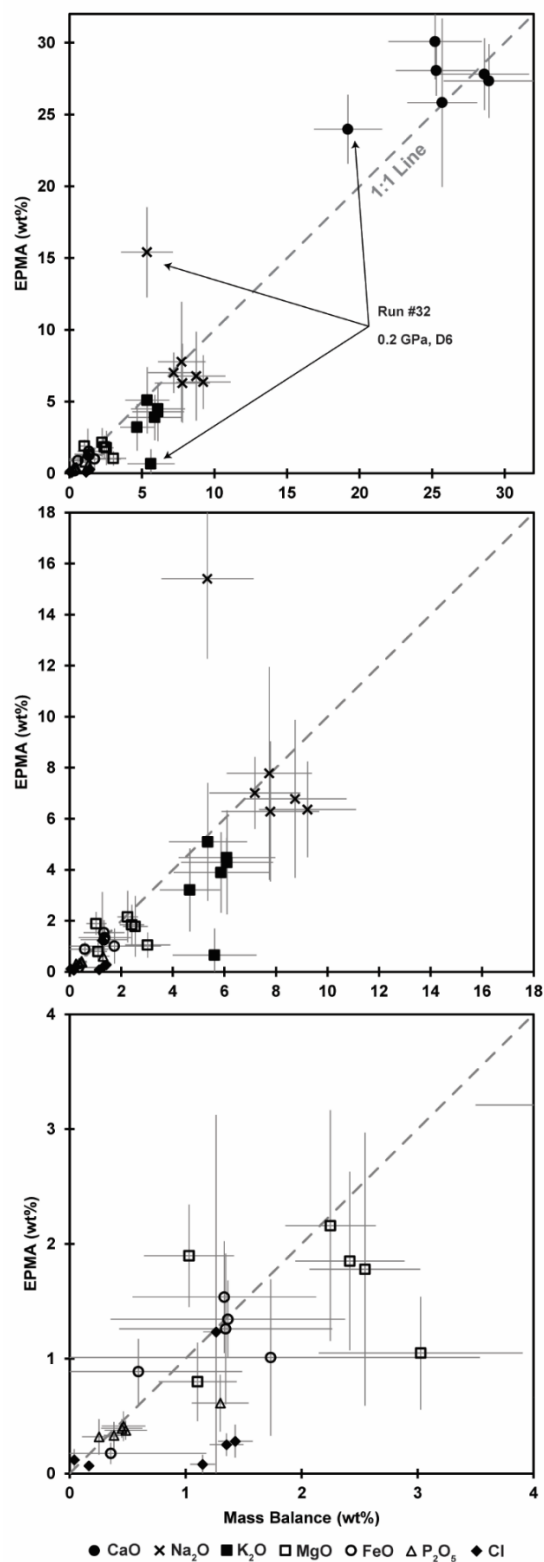


Figure 4.8 Comparison of sulfate melt composition at 1200°C as calculated by mass balance, and from EPMA analyses. Uncertainties shown are 1 s.d.

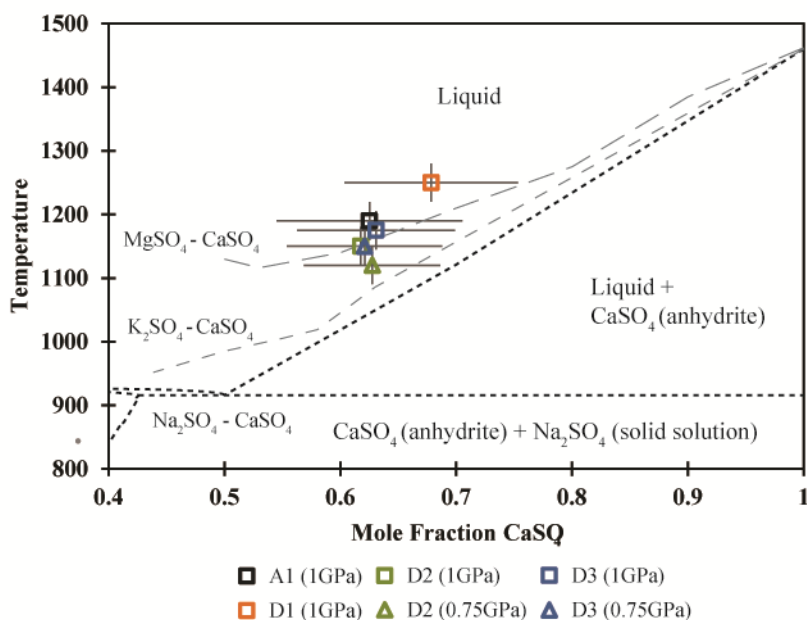


Figure 4.9 Na_2SO_4 - CaSO_4 binary phase diagram at 1 atm with experimental sulfate melt liquidus compositions plotted against estimated liquidus temperatures. Data from Coursol et al. (2005). Short and long dashed lines show the liquidus curves for the systems CaSO_4 - K_2SO_4 and MgSO_4 - CaSO_4 at 1 atm respectively (data from Rowe et al. 1967). Mol fraction CaSO_4 for experimental sulfate melts is normalized based on the sum of components K_2SO_4 - Na_2SO_4 - MgSO_4 - NaCl - FeSO_4 - CaSO_4 .

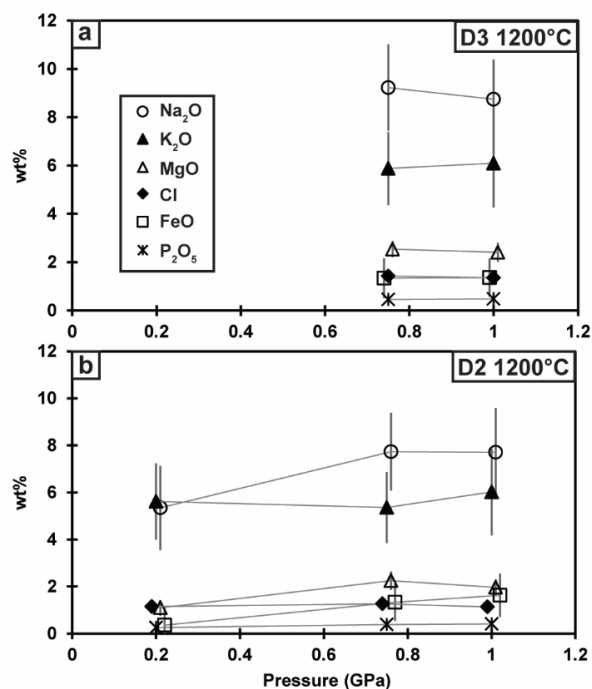


Figure 4.10 Sulfate melt major element composition (from mass balance calculations) as a function of pressure at 1200°C. Note that with the exception of notably lower Na₂O content in the 0.2GPa experiment (cf. Na₂O content of this experiment by EPMA, Fig 7c), there is little systematic change in composition with pressure.

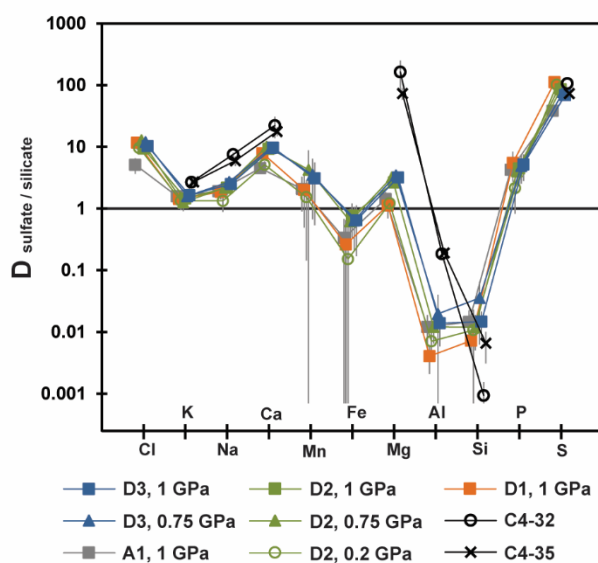


Figure 4.11 Sulfate melt – silicate melt partition coefficients calculated for all 1160-1200°C experimental runs. See text for calculation of sulfate melt composition. Data for experiments C4-32 (0.1GPa, 1000°C) and C4-35 (0.1GPa, 1100°C) are from Veksler et al. (2012). Uncertainties are 1 s.d.

Table 4.1 Composition of starting materials (wt%) on an anhydrous basis

Starting Material	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	FeO	Fe ₂ O ₃	MgO	TiO ₂	MnO	P ₂ O ₅	SO ₃	Cl ¹	Traces	Total	H ₂ O ²
D1	58.92	13.65	6.31	4.43	4.65	1.07	1.07	0.97	0.39	0.04	0.13	8.01	0.02	0.33	100	4.6
D2	57.78	13.43	6.30	4.35	4.60	1.06	1.06	0.97	0.37	0.03	0.14	9.32	0.29	0.30	100	5.6
D3	59.22	13.65	6.43	4.36	4.22	1.07	1.07	1.01	0.37	0.04	0.15	7.80	0.29	0.31	100	6.8
A1	49.38	14.85	8.83	4.82	3.34	2.49	2.49	2.36	0.81	0.08	0.47	9.77	0.01	0.29	100	6.4

1 Lack of Cl in starting materials D1 and A1 was unintentional and bulk Cl content is estimated from analysis of silicate glasses produced in experiments

2 Bulk H₂O contents are based on measured H₂O contents of silicate glasses in 1000°C experiments and are subject to an analytical uncertainty of ± 0.6 wt% (see results section)

Table 4.2 Experimental conditions and run products

Run #	Temperature, °C	Pressure, Gpa	Run Duration, hr	Run Products
<i>"D3" Starting Material</i>				
70	1200	1	4	Si + SM
42	1100	1	48	Si + SM + Anh
26	1000	1	48	Si + Anh + Sp + Ilm
35	900	1	48	Si + Anh + Bt + Ilm
28	800	1	48	Si + Anh + Bt + Ilm
71	1200	0.75	4	Si + SM + Anh
80	1100	0.75	48	Si + SM + Anh
59	1000	0.75	48	Si + SM* + Anh + Sp
40	900	0.75	48	Si + Anh + Bt + Ilm
41	800	0.75	48	Si + Anh + Bt + Ilm
56	1000	0.2	46	Si + SM + Anh + Sp + Ilm
47	900	0.2	46	Si + SM* + Anh + Amph + Sp + Ilm
<i>"D2" Starting Material</i>				
87	1200	1	4.5	Si + SM
81	1100	1	48	Si + SM + Anh
61	1000	1	48	Si + SM* + Anh + Ilm
18	900	1	48	Si + Anh + Bt + Ilm
19	800	1	48	Si + Anh + Bt + Ilm
57	1200	0.75	8	Si + SM
69	1100	0.75	48	Si + SM + Anh + Sp
16	1050	0.75	48	Si + SM + Anh
24	1000	0.75	48	Si + SM + Anh + Ilm
68	900	0.75	96	Si + SM + Anh + Bt + Ilm
85	800	0.75	48	Si + Anh + Bt + Ilm
32	1160	0.2	8	Si + SM
54	1000	0.2	46	Si + SM + Anh + Sp + Ilm
45	900	0.2	46	Si + SM + Anh + Bt + Sp + Ilm
<i>"D1" Starting Material</i>				
62	1200	1	8	Si + SM
63	1100	1	48	Si + Anh
83	1000	1	48	Si + Anh + Bt + Ilm
82	900	1	48	Si + Anh + Bt + Amph + Ilm
<i>"A1" Starting Material</i>				
23	1200	1	24	Si + SM
22	1100	1	48	Si + SM + Anh + Sp + Ilm
21	1000	1	48	Si + Anh + Bt + Sp + Ilm
20	900	1	48	Si + Anh + Bt + Amph + Ilm

Table 4.3 Silicate glass compositions

Run #	Temperature, °C	wt%											2 s.d.											H ₂ O					
		SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	FeO	MgO	TiO ₂	MnO	P ₂ O ₅	SO ₃	Cl	H ₂ O	Total	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	FeO	MgO	TiO ₂		MnO	P ₂ O ₅	SO ₃	Cl	
"D3" Starting Material, 1GPa																													
70	1200	63.73	14.75	2.93	3.47	3.67	2.11	0.75	0.34	0.07	0.09	0.787	0.129	7.20	100.03	0.76	0.26	0.07	0.24	0.14	0.16	0.06	0.02	0.06	0.05	0.015	0.007		0.56
42	1100	63.01	14.70	1.88	4.40	4.12	2.21	0.96	0.38	0.09	0.12	0.611	0.218	8.27	100.95	1.59	0.37	0.13	0.60	0.30	0.32	0.06	0.03	0.09	0.08	0.036	0.020		0.66
26	1000	62.16	14.69	1.38	4.66	4.37	2.21	1.08	0.39	0.07	0.15	0.493	0.301	7.69	99.65	1.24	0.38	0.06	0.64	0.40	0.21	0.05	0.03	0.06	0.06	0.034	0.028		0.52
35	900	63.48	14.73	1.32	4.58	4.23	1.59	0.63	0.24	0.07	0.14	0.198	0.320	7.96	99.48	2.63	0.26	0.10	0.41	0.31	0.25	0.04	0.04	0.07	0.05	0.019	0.005		0.48
28	800	66.17	14.80	1.07	4.57	3.95	0.64	0.13	0.07	0.07	0.06	0.042	0.318	7.56	99.46	2.37	0.56	0.21	0.73	0.32	0.11	0.02	0.03	0.04	0.05	0.012	0.048		0.62
"D3" Starting Material, 0.75GPa																													
71	1200	63.55	14.81	2.92	3.38	3.69	2.10	0.73	0.37	0.07	0.09	0.701	0.117	8.02	100.57	0.55	0.29	0.09	0.16	0.22	0.10	0.06	0.03	0.04	0.05	0.014	0.010		0.56
80	1100	63.81	14.32	2.16	3.93	3.91	2.18	0.86	0.38	0.07	0.11	0.542	0.168	8.56	101.01	2.15	0.28	0.19	0.34	0.31	0.23	0.06	0.03	0.06	0.07	0.018	0.032		0.62
59	1000	62.39	14.12	1.40	4.19	4.31	2.13	1.01	0.39	0.08	0.13	0.432	0.274	7.86	98.71	0.81	0.36	0.16	0.25	0.11	0.16	0.11	0.06	0.09	0.04	0.030	0.034		0.50
40	900	64.62	14.77	1.15	4.82	4.13	1.46	0.54	0.22	0.08	0.16	0.165	0.322	8.87	101.29	1.80	0.27	0.08	0.53	0.37	0.30	0.12	0.08	0.08	0.044	0.032		0.58	
41	800	65.65	15.08	1.15	4.92	4.03	0.77	0.20	0.13	0.07	0.07	0.054	0.321	8.34	100.76	1.47	0.34	0.31	0.55	0.22	0.22	0.05	0.04	0.06	0.06	0.015	0.045		0.70
"D3" Starting Material, 0.2GPa																													
56	1000	64.39	14.63	1.37	4.36	4.45	1.71	0.96	0.34	0.08	0.13	0.269	0.221	6.46	99.37	0.72	0.45	0.11	0.40	0.18	0.14	0.10	0.07	0.04	0.04	0.048	0.012		0.40
47	900	64.19	14.70	2.16	4.43	4.41	1.71	0.72	0.34	0.08	0.07	0.159	0.209	6.99	100.19	0.54	0.58	0.13	0.20	0.09	0.06	0.11	0.09	0.04	0.03	0.021	0.034		0.76
"D2" Starting Material, 1GPa																													
87	1200	65.32	14.78	2.64	3.51	4.10	2.10	0.74	0.43	0.03	0.09	0.631	0.119	5.51*	100.00	1.51	0.28	0.22	0.46	0.40	0.23	0.05	0.11	0.06	0.05	0.032	0.006		1.79
81	1100	64.20	14.67	1.49	4.10	4.46	2.17	0.86	0.43	0.05	0.12	0.541	0.170	7.25	100.51	1.14	0.39	0.12	0.35	0.40	0.12	0.08	0.05	0.07	0.05	0.028	0.016		0.44
61	1000	63.84	15.22	0.85	4.48	4.80	2.11	1.03	0.37	0.05	0.14	0.353	0.242	6.51	99.99	0.65	0.33	0.13	0.25	0.15	0.21	0.04	0.05	0.05	0.04	0.028	0.007		0.48
18	900	67.17	15.29	0.26	4.89	4.78	0.99	0.37	0.14	0.07	0.14	0.248	0.277	5.74	100.37	0.89	0.11	0.06	0.22	0.14	0.16	0.08	0.03	0.07	0.04	0.032	0.011		0.42
19	800	67.41	15.29	0.32	4.94	4.53	0.67	0.13	0.08	0.03	0.11	0.057	0.311	6.00	99.89	0.70	0.17	0.05	0.29	0.08	0.16	0.06	0.03	0.03	0.04	0.011	0.052		0.38
"D2" Starting Material, 0.75GPa																													
57	1200	64.62	14.90	2.49	3.51	4.22	2.16	0.69	0.44	0.03	0.09	0.589	0.096	5.60	99.43	0.76	0.35	0.16	0.31	0.10	0.15	0.08	0.07	0.05	0.03	0.025	0.004		0.38
69	1100	64.91	15.30	1.39	3.88	4.48	2.24	0.79	0.41	0.05	0.12	0.434	0.148	5.99	100.14	0.64	0.19	0.10	0.19	0.14	0.07	0.09	0.05	0.06	0.06	0.050	0.009		0.92
16	1050	64.77	15.10	1.28	4.14	4.65	2.25	0.90	0.42	0.05	0.13	0.365	0.199	6.18	100.43	0.71	0.19	0.08	0.23	0.13	0.17	0.08	0.03	0.07	0.04	0.010	0.021		0.58
24	1000	64.69	15.21	0.92	4.37	4.76	2.16	0.93	0.40	0.04	0.14	0.329	0.217	6.55	100.71	0.71	0.23	0.09	0.29	0.16	0.19	0.06	0.03	0.05	0.03	0.010	0.004		0.60
68	900	66.01	15.53	0.35	4.55	4.86	1.36	0.54	0.18	0.05	0.14	0.268	0.238	5.97	100.05	0.81	0.20	0.04	0.23	0.16	0.16	0.06	0.03	0.05	0.06	0.042	0.006		0.78
85	800	68.54	14.92	0.27	5.20	4.32	0.75	0.17	0.10	0.26	0.12	0.096	0.309	4.95*	100.00	1.20	0.34	0.11	0.52	0.29	0.22	0.15	0.05	0.11	0.10	0.012	0.064		1.45
"D2" Starting Material, 0.2GPa																													
32	1160	63.62	14.91	3.67	3.97	4.20	2.35	0.90	0.43	0.05	0.12	0.553	0.117	5.11*	100.00	1.48	0.30	0.31	0.42	0.24	0.18	0.05	0.03	0.05	0.05	0.041	0.004		1.97
54	1000	65.67	15.24	0.79	4.33	4.96	1.36	0.80	0.32	0.04	0.13	0.252	0.176	4.99	99.04	0.96	0.56	0.08	0.19	0.08	0.12	0.09	0.07	0.04	0.03	0.029	0.008		0.76
45	900	64.76	14.73	1.47	4.47	4.89	1.66	0.62	0.39	0.03	0.11	0.163	0.223	5.98	99.49	1.13	0.33	0.25	0.27	0.06	0.58	0.07	0.12	0.08	0.06	0.047	0.020		0.38
"D1" Starting Material, 1GPa																													
62	1200	64.80	14.80	3.16	3.81	4.22	2.28	0.92	0.47	0.05	0.08	0.491	0.014	3.65	98.74	0.59	0.15	0.13	0.16	0.20	0.13	0.04	0.02	0.06	0.05	0.009	0.005		0.28
63	1100	64.24	14.69	2.35	4.73	4.78	2.29	1.06	0.51	0.02	0.12	0.293	0.033	3.97	99.09	0.48	0.31	0.15	0.28	0.24	0.11	0.09	0.04	0.06	0.05	0.037	0.007		0.28
83	1000	66.87	14.82	1.26	4.74	4.61	1.93	0.64	0.36	0.05	0.14	0.167	0.038	5.35	100.97	1.87	0.48	0.15	0.78	0.38	0.25	0.06	0.06	0.05	0.05	0.025	0.015		0.36
82	900	68.07	14.88	0.90	5.11	4.60	1.12	0.23	0.19	0.14	0.08	0.070	0.033	4.57*	100.00	2.56	0.29	0.14	0.50	0.40	0.18	0.02	0.08	0.10	0.03	0.012	0.008		2.54
"A1" Starting Material, 1GPa																													
23	1200	54.44	16.27	5.49	4.01	2.90	5.21	2.10	0.86	0.11	0.30	1.435	0.008	7.02	100.17	0.86	0.21	0.12	0.34	0.10	0.25	0.13	0.03	0.10	0.06	0.028	0.003		0.46
22	1100	54.62	16.15	4.22	4.63	3.46	5.23	2.34	0.89	0.12	0.36	1.148	0.008	6.58	99.76	1.04	0.31	0.22	0.31	0.29	0.17	0.09	0.05	0.05	0.06	0.033	0.002		0.50
21	1000	57.74	16.93	2.85	5.44	3.53	3.04	1.64	0.45	0.12	0.44	0.590	0.012	7.63	100.41	0.54	0.19	0.17	0.41	0.16	0.12	0.16	0.05	0.07	0.07	0.076	0.002		0.54
20	900	62.125	17.471	1.529	5.743	3.401	1.165	0.345	0.112	0.098	0.161	0.130	0.013	7.71*	100.00	0.95	0.55	0.33	0.71	0.13	0.20	0.07	0.04	0.04	0.04	0.020	0.003		0.89
*H ₂ O contents determined by mass balance																													

*H₂O contents determined by mass balance

Table 4.4 Sulfate melt compositions by EPMA

Run #	Temperature, °C	n	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	FeO	MgO	MnO	P ₂ O ₅	SO ₃	Cl
wt% (1 s.d. uncertainty)													
"D3" Starting Material, 1GPa													
70	1200	24	0.91 (0.41)	0.2 (0.12)	27.34 (2.57)	6.78 (3.10)	4.30 (2.04)	1.34 (0.34)	1.85 (0.78)	0.22 (0.15)	0.38 (0.08)	56.42 (0.85)	0.25 (0.10)
42	1100	4	3.98 (6.86)	1.02 (1.73)	29.85 (6.57)	5.45 (2.52)	1.28 (0.60)	0.93 (0.42)	1.47 (0.83)	0.29 (0.15)	0.47 (0.14)	55.08 (5.60)	0.17 (0.09)
"D3" Starting Material, 0.75GPa													
71	1200	24	2.24 (1.85)	0.29 (0.29)	27.82 (2.49)	6.36 (1.87)	3.9 (1.57)	1.26 (0.66)	1.78 (1.19)	0.27 (0.20)	0.41 (0.13)	55.4 (2.15)	0.28 (0.14)
80	1100	13	0.88 (0.42)	0.16 (0.09)	30.98 (3.23)	4.88 (2.53)	2.31 (1.47)	1.22 (0.68)	1.76 (0.70)	0.15 (0.12)	0.54 (0.13)	56.54 (1.12)	0.58 (0.20)
"D2" Starting Material, 0.75GPa													
57	1200	16	0.75 (0.43)	0.18 (0.08)	25.83 (5.86)	7.78 (4.17)	5.10 (2.31)	1.54 (0.49)	2.16 (1.00)	0.14 (0.10)	0.33 (0.12)	54.96 (2.55)	1.23 (1.89)
69	1100	28	0.81 (0.92)	0.13 (0.09)	22.06 (8.51)	9.03 (5.29)	5.19 (3.11)	2.39 (1.35)	3.64 (1.80)	0.2 (0.12)	0.50 (0.24)	53.97 (3.51)	2.06 (2.72)
"D2" Starting Material, 0.2GPa													
32	1160	18	0.67 (0.76)	0.1 (0.05)	23.98 (2.4)	15.41 (3.15)	0.66 (1.03)	0.18 (0.09)	0.8 (0.34)	0.07 (0.05)	0.32 (0.15)	57.72 (0.69)	0.08 (0.08)
"D1" Starting Material, 1GPa													
62	1200	34	0.46 (0.16)	0.06 (0.03)	28.07 (1.75)	7.02 (1.41)	4.48 (0.76)	0.89 (0.28)	1.9 (0.45)	0.11 (0.05)	0.39 (0.08)	56.55 (0.58)	0.07 (0.04)
"A1" Starting Material, 1GPa													
23	1200	15	0.78 (0.41)	0.19 (0.11)	30.08 (2.63)	6.28 (2.74)	3.21 (1.63)	1.01 (0.68)	1.05 (0.49)	0.23 (0.08)	0.61 (0.25)	56.44 (1.27)	0.12 (0.09)
22	1100	6	1.01 (0.79)	0.16 (0.1)	30.74 (6.24)	5.12 (3.33)	2.65 (2.16)	0.97 (0.90)	1.80 (1.14)	0.12 (0.10)	0.73 (0.50)	56.66 (1.93)	0.04 (0.01)

Table 4.5 Sulfate melt composition by mass balance

Run #	Temperature, °C	Proportion sulfate melt	wt% (1s.d.)						
			CaO	Na ₂ O	K ₂ O	FeO	MgO	P ₂ O ₅	Cl
"D3" Starting Material, 1GPa									
70	1200	0.13	28.88 (3.12)	8.68 (1.99)	6.04 (1.78)	1.33 (1.01)	2.40 (0.47)	0.48 (0.18)	1.35 (0.14)
"D3" Starting Material, 0.75GPa									
71	1200	0.13	28.56 (3.14)	9.17 (3.05)	5.81 (2.00)	1.31 (0.92)	2.53 (0.43)	0.46 (0.20)	1.43 (0.22)
"D2" Starting Material, 1GPa									
87	1200	0.16	24.97 (2.37)	7.71 (1.56)	6.02 (1.54)	1.63 (0.82)	1.96 (0.39)	0.40 (0.12)	1.14 (0.12)
"D2" Starting Material, 0.75GPa									
57	1200	0.16	25.66 (2.37)	7.68 (1.44)	5.30 (1.49)	1.30 (0.68)	2.24 (0.33)	0.38 (0.05)	1.26 (0.11)
"D2" Starting Material, 0.2GPa									
32	1160	0.16	19.14 (2.28)	5.28 (1.85)	5.56 (1.82)	0.32 (0.91)	1.09 (0.33)	0.25 (0.14)	1.14 (0.11)
"D1" Starting Material, 1GPa									
62	1200	0.14	25.28 (2.79)	7.17 (1.76)	6.08 (1.87)	0.59 (0.89)	1.03 (0.39)	0.45 (0.18)	0.16 (0.02)
"A1" Starting Material, 1GPa									
23	1200	0.15	25.15 (3.21)	7.73 (1.89)	4.63 (1.17)	1.67 (1.80)	3.00 (0.88)	1.29 (0.24)	0.04 (0.01)

Table 4.6 Sulfate melt – silicate melt major element partition coefficients

$D_i^{Sulf-Sil}$ (1s. d.)							
Starting Composition	A1	D1	D2	D2	D2	D3	D3
Temperature (°C)	1200	1200	1200	1200	1200	1200	1200
Pressure (GPa)	1	1	0.2	0.75	1	0.75	1
Cl	5.19 (1.50)	12.00 (2.79)	9.81 (0.93)	13.17 (1.20)	9.59 (0.94)	12.25 (1.38)	10.44 (1.15)
K ₂ O	1.61 (0.40)	1.45 (0.44)	1.34 (0.39)	1.27 (0.36)	1.47 (0.45)	1.59 (0.50)	1.66 (0.49)
Na ₂ O	1.94 (0.48)	1.89 (0.46)	1.35 (0.46)	2.20 (0.48)	2.19 (0.56)	2.73 (0.56)	2.52 (0.58)
CaO	4.59 (0.59)	8.01 (0.90)	5.23 (0.68)	10.31 (1.02)	9.48 (1.00)	9.79 (1.06)	9.88 (1.07)
MnO	2.10 (1.20)	2.03 (1.54)	1.55 (1.40)	4.34 (4.57)		3.59 (2.92)	3.11 (2.57)
FeO	0.33 (0.35)	0.26 (0.39)	0.15 (0.35)	0.62 (0.37)	0.78 (0.44)	0.64 (0.44)	0.65 (0.48)
MgO	1.44 (0.42)	1.12 (0.42)	1.23 (0.38)	3.27 (0.60)	2.66 (0.48)	3.49 (0.67)	3.21 (0.64)
Al ₂ O ₃	0.01 (0.01)	0.00 (0.00)	0.01 (0.00)	0.01 (0.01)		0.02 (0.02)	0.01 (0.01)
SiO ₂	0.01 (0.01)	0.01 (0.00)	0.01 (0.01)	0.01 (0.01)		0.04 (0.03)	0.01 (0.01)
P ₂ O ₅	4.32 (0.93)	5.60 (2.86)	2.16 (1.32)	4.08 (1.10)	4.52 (2.10)	4.97 (2.43)	5.26 (2.43)
SO ₃	39.32 (3.03)	115.19 (8.99)	104.38 (8.27)	93.35 (7.17)	87.79 (6.82)	78.98 (6.58)	71.66 (5.92)

Sulfate melt composition by mass balance - Cl, K₂O, Na₂O, CaO, FeO, MgO, P₂O₅Sulfate melt composition by EPMA - SiO₂, Al₂O₃, SO₃, MnO

Chapter V. Trace element partitioning between anhydrite, sulfate melts and silicate melt

5.1 Abstract

Anhydrite has been increasingly appreciated as a primary igneous phase since its discovery in pumices from the 1982 eruption of El Chichon (Luhr, 1984) and in a number of studies since (for review see Luhr et al. 2008). Here we present the most comprehensive data to date on trace element partition coefficients for anhydrite based on SIMS analyses of silicate glass and anhydrite present in experimental runs at 0.2 – 1 GPa, 900 -1100°C and $fO_2 > NNO+2.5$. We also present partition coefficients for elements between immiscible sulfate and silicate melt from the same experiments at temperatures 1100 - 1200°C.

Partition coefficients for +2 and +3 cations between anhydrite and silicate melt can be described in terms of exchange reactions involving the Ca site in anhydrite, and are empirically fit by equations of the form:

$$D_{i(+2)} = e^{\left(\frac{c_1}{T} + c_2\right)} \cdot (CaO_{Sil})^{-1} (wt\%)$$

$$D_{i(+3)} = e^{\left(\frac{c_1}{T} + c_2\right)} \cdot (CaO_{Sil})^{-2} (wt\%)$$

for +2 and +3 cations respectively. The partitioning data are also fit using a lattice – strain approach, and we show that the measured partition coefficients are best described by a “two-site” fit, possibly implying that cations exchange reactions involve two distinct crystal sites with different optimum radii. Variable partition coefficients can be used to model the Sr content crystallizing from a cooling magma. At the Luhr Hill, Yerington, this implies that previously measured anhydrite crystallized at temperatures >930°C.

Sulfate melt – silicate melt partition coefficients are shown to vary consistently with ionic potential (the ratio of nominal charge to ionic radius, Z / r) and show peaks in compatibility close to the ionic potential of Ca and S. Partition coefficients for many elements, particularly REE, are more than an order of magnitude lower than previously published data, likely related differences in silicate melt composition between experiments. Partition coefficients between sulfate melts and natural, high-T primitive silicate melts are therefore likely to be low.

5.2 Introduction

The discovery of primary igneous anhydrite in both erupted products and in intrusive rocks (For review see Luhr et al. 2008, Hutchinson and Dilles 2019, Chapter II, this study) suggests that anhydrite saturation may be a relatively common in arc magmas. The identification

of “wormy anhydrite” inclusions in amphiboles from Yanacocha, Peru (Chambefort et al. 2008) also implies the existence of immiscible sulfate melts at magmatic conditions, similar to those produced in experiments at $>1000^{\circ}\text{C}$ (Jugo et al. 2004, Chapter IV, this study). Since the solubility of oxidized sulfur species (S^{6+}) is significantly greater than reduced species (S^{2-}) (Carroll and Rutherford, 1987), the presence of sulfate phases, particularly of high-temperature sulfate melts, is a good indication of high magmatic sulfur contents.

Sulfate phases are rarely preserved in the geologic record. Phenocrystic anhydrite is easily dissolved by meteoric fluids (Luhr et al. 1984), and may also break down during magmatic degassing, as sulfur is removed from the melt (Chambefort et al. 2008). Sulfate melts are even more difficult to identify in nature, and likely only exist transiently, breaking down to form anhydrite at lower temperature (Chambefort et al. 2008, Chapter IV, this study). Indeed, even in experimental studies the quench products of sulfate melts are easily degraded during sample preparation (Jugo et al. 2004, Chapter IV, this study).

In the absence of preserved sulfate phases, whole rock and mineral geochemistry may help to identify sulfate saturated magmas, if fractionation of sulfate phases leaves a distinctive trace element fingerprint. However, this requires reliable information on trace element partitioning between silicate melt and sulfate phases at a range of magmatic conditions. Partitioning information may also help to interpret anhydrite compositional data in cases where phenocrystic anhydrite can be identified and analyzed.

The only current data on trace element partitioning between anhydrite and silicate melt (Luhr et al. 1984) are based on instrumental neutron activation analysis (INAA) of anhydrite phenocrysts and interstitial silicate glass from the 1982 eruption of El Chichon. This method relies on the analysis of bulk anhydrite separates and is unlikely to represent anhydrite composition in equilibrium with coexisting glass. Analysis of anhydrite in this study was also complicated by apatite inclusions in anhydrite grains, and apatite-corrected anhydrite compositions have correspondingly large uncertainties.

Trace element partitioning between immiscible sulfate and silicate melts was investigated in experiments by Veksler et al. (2012). However the major element composition of sulfate melts in these experiments differed significantly from the CaO-dominated compositions that would be expected in natural arc magmas (i.e. Chapter IV, this study).

Here we present anhydrite – silicate melt and sulfate melt – silicate melt partition coefficients based on analysis of phases produced in experiments on sulfate rich dacite and andesite compositions between $800\text{--}1200^{\circ}\text{C}$ and $0.2\text{--}1\text{ GPa}$.

5.3 Methods

5.3.1 *Experimental methods*

Experimental methods are covered in depth in Chapter IV and are only briefly summarized here. Experiments were conducted at the University of Bristol using both end-loaded piston cylinder apparatus and a gas-pressurized titanium-zirconium molybdenum (TZM) cold seal pressure vessel. Experiments were carried out at oxidized conditions ($fO_2 > \text{NNO}+2.5$) between 0.2-1 GPa and 800-1200°C. Experimental duration was 48hr for experiments $\leq 1100^\circ\text{C}$ and 4-8 hr for experiments at 1200°C. Sulfate melt, anhydrite and silicate glass have been analyzed for trace elements from experiments using three different trachydacite starting materials (table 4.1) with varying water contents (D1, D2 and D3) and one trachyandesite starting material (A1). In order to determine the composition of starting materials for mass balance calculations, aliquots of starting material were fused at $\sim 1500^\circ\text{C}$ for ~ 2 hr at 1 atm and drop quenched in water. For a full list of experimental conditions and run products see table 4.2.

5.3.2 *Analytical methods*

LA-ICP-MS analyses of fused starting materials, experimental silicate glasses, and sulfate melts were carried out at Texas Tech University using a New Wave UP213 Nd:YAG laser coupled with an Argilent 7500cs ICP-MS. Sulfate analyses were obtained with laser conditions of 2-2.5 J/cm², 5Hz and a 40 μm diameter spot. Laser conditions for silicate glass analyses were 4 J/cm², 10Hz and a 30 μm spot size. Basaltic reference glass GSD was used as an external standard, and results were normalized to either ²⁹Si (silicate glass) or ⁴³Ca (sulfate melts) which were measured independently by EPMA (Chapter IV, this study). Experimentally produced anhydrite crystals were in almost all cases too small to be analyzed by LA-ICP-MS, however a number of natural anhydrite standards were analyzed by both LA-ICP-MS and SIMS methods. Based on a comparison of these methods (appendix 5) ion yield corrections have been applied to SIMS measurements of Sr, Y and Ba.

SIMS analyses of experimental silicate glasses, sulfate melts and anhydrite crystals were carried out at the Edinburgh Ion Microprobe facility (EIMF). Most analyses were conducted using a Cameca ims-4f, with a small number of additional analyses using a Cameca ims-1270.

Analyses with the ims-4f used a 12-15nA, ¹⁶O⁻ primary beam with a net impact energy of 15keV and a spot size of 12-25 μm . Only high energy (120 $\pm$ 20 eV) positive secondary ions were measured to reduce the presence of molecular ions. Measurements of rare earth elements (REE) were corrected for the presence of oxides based on REEO / REE ratios for silicate (values from

Hinton et al. 1990) and calcite (for anhydrite and sulfate melt analyses, values from Law et al., 2000). Measured CeO / Ce ratios for anhydrite analyses agreed closely with those predicted. Values for F and Cl in anhydrite and sulfate melts are only approximate as the ion yields for these elements are strongly affected by matrix composition, and no matrix matched standard was available.

Analyses with the ims-1270 used a 3-4nA, $^{16}\text{O}_2^-$ primary beam with a net impact energy of 22.5keV and a spot size of 15-25 μm . Analyses were made at 6000 M/ ΔM mass resolution to remove virtually all molecular ions or doubly charged species. Only moderately high energy (50 ± 20 eV) positive secondary ions were measured to reduce the presence of low energy ions.

In both cases reference glass GSD was used as an external standard, and values were corrected based on Si (silicate glass) or Ca (anhydrite and sulfate melt) concentrations measured by EPMA. Trace element concentrations by both methods are listed for silicate glass in appendix 6, for sulfate melt in appendix 7 and anhydrite in appendix 8.

5.4 Results

5.4.1 Silicate glass trace element composition

The trace element contents of all experimental silicate glasses were measured by LA-ICP-MS. A subset of runs were also analyzed by SIMS and, with the exception of Li and Co, showed good agreement with LA-ICP-MS data (Fig 5.1). Glass trace element concentrations vary systematically with temperature and show a range of behavior related to partitioning between silicate glass and other phases (Fig 5.2). V and Co act similarly, and their concentrations in the silicate glass fall sharply below 1000°C owing to their compatibility in Fe-Ti oxides. Li, Ba, Mo, W, Re and to a lesser extent Rb concentrations in the glass decrease above 1000°C due to their incorporation into sulfate melt. REE, Y, Hf, Nb and Zr concentrations do not change significantly between 800-1200°C indicating that their bulk partition coefficients are relatively constant over this temperature range. The most abundant phase in all experiments, after silicate glass, was sulfate, either anhydrite or sulfate melt. Therefore the similarity of bulk partition coefficients over the entire experimental temperature range implies similar partitioning behavior between silicate melt and both anhydrite and sulfate melt for these elements.

5.4.2 Sulfate melt – silicate melt partition coefficients

Sulfate melt (Sulf) – silicate melt (Sil) partition coefficients ($D_i^{\text{Sulf-Sil}}$) have been calculated based on 10 experiments using both trachyandesite and trachydacite starting compositions at 1100-1200°C and 0.2-1 GPa. Given the nature of sulfate melt quench products

(see chapter IV) and the associated difficulty in obtaining representative analyses, we have measured partition coefficients using LA-ICP-MS (10 experiments, table 5.1) and SIMS (4 experiments, table 5.2) and have calculated partition coefficients for a subset of elements using mass balance (7 experiments, table 5.3). Mass balance calculations are performed on the basis that silicate melt and sulfate melt are the only phases present, and can be used for experiments at $>1160^{\circ}\text{C}$. The proportion of each phase is determined based on the bulk sulfur content (as weighed), the sulfur content of the silicate glass and the sulfate melt as determined by EPMA (Chapter IV). The concentration of each element in the bulk starting material was determined by LA-ICP-MS of starting material fused at 1atm. For further details on mass balance calculations see Chapter IV section 4.5.5.

Comparing $D_i^{\text{Sulf-Sil}}$ as determined by LA-ICP-MS and SIMS (Fig 5.3a) generally shows good agreement, given the large analytical uncertainties (1 s.d. is in many cases a factor of 2-3). The exceptions to this are values for Co, Li, W and Mo which in some experiments (but not all) fall well below the 1:1 line. With the exception of one value for Li, mass balance calculations (for Li, V, Sr, Y, Ba and REE) also show good agreement with LA-ICP-MS data (Fig.5.3b). This Li value, from run #57 is also anomalous compared to SIMS data, and strongly suggests that in the case of disagreement, at least in the case of Li, LA-ICP-MS data likely overestimate the partition coefficient, rather than an underestimate by SIMS. The cause of anomalously high concentrations of Co, Li, W and Mo in some LA-ICP-MS analyses is not clear, although it may be related to the larger volume of material sampled by LA-ICP-MS, for example if a quench phase highly enriched in these elements was present below the surface and was ablated during analysis.

Partition coefficients for 40 elements are presented in figure 5.4. Values for F, Hf, Ta, Th and U are taken from SIMS analyses, Cl, K, Na, Ca, Mg, P and S are taken from EPMA analyses (Chapter IV) and all other elements are based on LA-ICP-MS. Data show that larger +2 cations (Ba, Sr and Ca) are strongly concentrated by the sulfate melt as are light REE, F and Cl, although as noted in the methods section, values for F are only estimates. Some highly charged ions (W, Mo and P) close in size to S are also compatible in the sulfate melt. +1 cations (Cs, Rb, K, Na and Li) appear to increase in compatibility with decreasing ionic radius and vary from moderately incompatible to moderately compatible. Finally high field strength elements (HFSE, Th, U, Zr, Hf, Nb and Ta) tend to be incompatible in sulfate melt.

Although analytical uncertainty accounts for much of the spread in partition coefficient for a given element it is interesting to note that in almost all cases the lowest partition coefficient

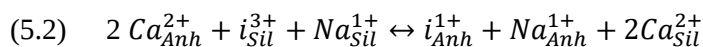
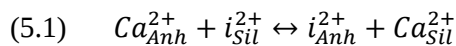
calculated for a particular element belonged to one experiment with the trachyandesite starting material at 1200°C. This is consistent with the general increase in partition coefficients between most phases and silicate melt with increasing silica and hence higher melt polymerization.

5.4.3 Anhydrite – silicate melt partition coefficients

7 sets of anhydrite (Anh) – silicate melt (Sil) partition coefficients ($D_i^{Anh-Sil}$) have been calculated for a variety of trace elements at 900-1100°C, 0.2-1 GPa and for both trachyandesite and tachydacite starting compositions (Table 5.2, Fig. 5.5). As expected +2 and +3 cations, which are close in size to Ca^{2+} (i.e. Sr and light-middle REE), show a preference for anhydrite ($D_{Sr}^{Anh-Sil} \sim 10-40$, $D_{La}^{Anh-Sil} \sim 2-12$, $D_{Gd}^{Anh-Sil} \sim 1.5-14$) whereas smaller 2+ cations (Sc, Mg, Mn) and 1+ cations (Li, Na, K, Ba) strongly favor the silicate melt. Heavier REE (Ho-Lu) are generally somewhat compatible in anhydrite, except in the more mafic trachyandesite experiment. Partition coefficients for elements entering the Ca site are negatively correlated with melt CaO content (shown by decreasing $D_{Ca}^{Anh-Sil}$, Fig 5.5a), consistent with an exchange reaction dependent on the Ca activity in the silicate melt.

The incorporation of +3 cations, principally the REE, into anhydrite requires a coupled substitution mechanism for charge balance. Of the +1 cations measured, only Na and K were present in anhydrite in sufficient concentrations (200-500 ppm and 50-400 ppm, respectively). Figure 5.6 shows that Na alone correlates well with $\sum REE + Y$ and that Na + K does so moderately well. Since the partition coefficient for Na is generally 0.5 – 1 order of magnitude greater than that of K, the contribution of K to exchange reactions involving REE should be relatively small.

Partitioning can therefore be characterized as exchange reactions of the form



For +2 and +3 cations respectively, and equilibrium constants Kd_i can be described by

$$(5.3) \quad Kd_i = \frac{[Ca]_{Sil} [i]_{Anh}}{[Ca]_{Anh} [i]_{Sil}}$$

$$(5.4) \quad Kd_i = \frac{[Ca]_{Sil}^2 [i]_{Anh} [Na]_{Anh}}{[Ca]_{Anh}^2 [i]_{Sil} [Na]_{Sil}}$$

Where $[i]_{Anh}$ and $[i]_{Sil}$ are the activities of an element i in anhydrite and silicate liquid respectively. In all cases anhydrite is close to stoichiometric and mixing is assumed to be ideal, such that $[i]_{Anh} \sim X_{i(Anh)}$ (where $X_{i(Anh)}$ is the molar proportion of element i in the Ca site). The

activity of elements in the silicate melt, $[i]_{\text{Sil}}$, is related to composition by the activity coefficient (γ_i) as $[i]_{\text{Sil}} = X_{i(\text{Sil})} \cdot \gamma_{i(\text{Sil})}$. The term $\frac{[Ca]_{\text{Sil}}}{[i]_{\text{Sil}}}$ in equation 5.3 can therefore be related to the molar composition of the silicate melt by the relationship $\frac{[Ca]_{\text{Sil}}}{[i]_{\text{Sil}}} = \frac{X_{Ca(\text{Sil})} \cdot \gamma_{Ca(\text{Sil})}}{X_{i(\text{Sil})} \cdot \gamma_{i(\text{Sil})}}$.

Although it is difficult to determine the ratio of activity coefficients ($\frac{\gamma_{Ca(\text{Sil})}}{\gamma_{i(\text{Sil})}}$) independently, for experiments with the same nominal composition (i.e. dacite experiments) and the range of temperatures covered (900-1100°C) it should remain close to constant. We can then define a molar equilibrium constant (Kd_i^*) which can be calculated from the molar proportions of elements in anhydrite and silicate melt and which is related to the equilibrium constant (Kd_i) by the ratio of the activity coefficients for Ca and an element in the silicate melt ($\frac{\gamma_{Ca(\text{Sil})}}{\gamma_{i(\text{Sil})}}$). This can be defined for +2 and +3 cations respectively as

$$(5.5) \quad Kd_i \propto Kd_i^* = \frac{X_{Ca(\text{Sil})} X_{i(\text{Anh})}}{X_{Ca(\text{Anh})} X_{i(\text{Sil})}}$$

$$(5.6) \quad Kd_i \propto Kd_i^* = \frac{X_{Ca(\text{Sil})}^2 X_{i(\text{Anh})} X_{Na(\text{Anh})}}{X_{Ca(\text{Anh})}^2 X_{i(\text{Sil})} X_{Na(\text{Sil})}}$$

In order to investigate the effect of temperature and pressure on these exchange reactions, Kd_i^* values are plotted as isobaric (Fig 5.7a,b, 0.75 GPa) and isothermal (Fig 5.7c,d, 1000°C) sections through the data. Kd_i^* values are positively correlated with temperature (Fig 5.7a,b), however pressure seems to have little effect, and calculated Kd_i^* are indistinguishable between 0.2 – 1 GPa, suggesting that the volume change (ΔV) associated with exchange reactions is negligible. Figures 5.7e,f show that, when described in the form of exchange reactions, silicate melt composition (aside from CaO and Na₂O concentration) has a much smaller effect on exchange reactions than might be anticipated base on D values in figures 5.5a,b.

The equilibrium constant Kd_i varies with temperature according to the thermodynamic relationship $RT \ln Kd_i = -\Delta H^0 + T\Delta S - P\Delta V$. As noted above, ΔV of the reaction appears to be small, and the pressure term in this equation can be neglected. We can therefore define the molar equilibrium constant by a relationship of the form:

$$(5.7) \quad \ln Kd_i^* = \frac{C_1}{T} + C_2$$

where C_1 and C_2 are related to the enthalpy and entropy of the exchange. Since Kd_i^* is related to Kd_i by the ratio of activity coefficients discussed above, and since the ratio of activity

coefficients is dependent on bulk composition, the constant C_2 in equation (5.7) is also dependent on bulk composition.

Combining eqs. (5.5) and (5.6) with eq. (5.7) allows for the calculation of molar partition coefficients (D_i^*) as a function of temperature and composition

$$(5.8) \quad D_{i(+2)}^* = \frac{X_{i(Anh)}}{X_{i(Sil)}} = e^{\left(\frac{C_1}{T} + C_2\right)} \cdot \left(\frac{X_{Ca(Anh)}}{X_{Ca(Sil)}}\right)$$

$$(5.9) \quad D_{i(+3)}^* = \frac{X_{i(Anh)}}{X_{i(Sil)}} = e^{\left(\frac{C_1}{T} + C_2\right)} \cdot \left(\frac{X_{Ca(Anh)}}{X_{Ca(Sil)}}\right)^2 \cdot \left(\frac{X_{Na(Sil)}}{X_{Na(Anh)}}\right)$$

where equations (5.8) and (5.9) apply to +2 cations and +3 cations in exchange reactions (5.1) and (5.2) respectively. Although relationships of this form well fit the experimental data, they are somewhat difficult to apply in practice since in most cases anhydrite composition (i.e. $X_{Ca(Anh)}$ and $X_{Na(Anh)}$) is not known independently. A more useful, semi-empirical fit to the data can be produced assuming that anhydrite is close to stoichiometric (i.e. $X_{Ca(Anh)} \sim 1$) and that the effect of changes to the Na partition coefficient in equation (5.7) is negligible compared to the other terms (i.e. $\left(\frac{X_{Na(Sil)}}{X_{Na(Anh)}}\right) \sim \text{constant}$). Since for most geochemical applications Nernst partition coefficients are more useful than those based on molar proportions the equations above are also recast in terms of mass proportions (wt%). The resulting equations, of the form

$$(5.10) \quad D_{i(+2)} = \frac{i_{Anh(wt\%)}}{i_{Sil(wt\%)}} = e^{\left(\frac{C_1}{T} + C_2\right)} \cdot (CaO_{Sil})^{-1}(wt\%)$$

$$(5.11) \quad D_{i(+3)} = \frac{i_{Anh(wt\%)}}{i_{Sil(wt\%)}} = e^{\left(\frac{C_1}{T} + C_2\right)} \cdot (CaO_{Sil})^{-2}(wt\%)$$

have been fit for dacite experimental data for each element (see examples in fig. 5.8) by least-squares regression with values for C_1 and C_2 given in table 5.3. Based on the observed difference between andesite and dacite partition coefficients at 1100°C we have also presented C_2 values which are appropriate for an andesite composition. However since only one andesite experiment was analysed, we use these values with some caution.

5.5 Discussion

5.5.1 Comparison with previous work – Sulfate melt

Representative sulfate melt – silicate melt partition coefficients from the study of Veksler et al. (2012) have been included in figure 5.4 for comparison with this work. Although some general features are similar, for example compatibility of large +2 cations and REE, there are a number of differences. Most noticeably, the partition coefficients for REE, Sr and to some extent

Ba are all significantly higher in the experiments of Veksler et al. (2012) than those calculated here. As previously noted, partition coefficients based on our trachyandesite experiment (silicate glass $\text{SiO}_2 \sim 54$ wt%) are lower than all trachydacite based experiments ($\text{SiO}_2 \sim 64$ -66 wt%). The silicate glass in the Veksler et al. (2012) experiments was in all cases more silica rich ($\text{SiO}_2 \sim 75$ wt%), and increased polymerization of the silicate melt is likely responsible for their higher partition coefficients.

More puzzling is the apparent disagreement between partition coefficients for HFSE elements, for example Veksler et al. (2012) found that Hf and Zr were both compatible in the sulfate melt, whereas in this study they were found to be the least compatible elements. Furthermore they found that pairs of elements that might be expected to act similarly (for example Nb-Ta, W-Mo) often behaved very differently. Elements in figure 5.4 are plotted in order of increasing ionic potential, i.e. the ratio of nominal charge (Z) to ionic radius (r) and this has been shown to be a useful parameter for characterizing the behavior of cations in melts (Hudon and Baker, 2002 and references therein). Our data appears to show peaks in compatibility for elements with ionic potential close to Ca and S, suggesting partitioning is related to the ease with which trace elements are able to replace the major cations in the sulfate melt structure. Particularly, in contrast to previous data, we observe a steady increase in partition coefficient with increasing Z/r between Hf – S.

5.5.2 The effect of sulfate melt saturation on trace element budgets

As noted in Chapter IV, the high temperature required to produce sulfate melts likely restricts their occurrence to very sulfur rich, primitive melts (for example those studied as melt inclusions at Colima and Augustine, Vigouroux et al., 2008, Zimmer et al. 2010) or to the mantle wedge, where they may separate from supercritical fluids. The fractionation of sulfate melt during cooling is unlikely to impart a distinctive trace element signature on the remaining silicate melt because sulfate melt-silicate melt partition coefficients for all elements in more mafic systems. In almost all cases partition coefficients were <10 for our trachyandesite composition. In more primitive melts they may be smaller still, owing to a less polymerized silicate melt structure. The small mass of sulfate melt that may be fractionated also inhibits its ability to alter the trace element composition of the remaining melt. During cooling from 1200°C - 1000°C the sulfur content of our most mafic experiments dropped from $\sim 1.4 - 0.6$ wt% SO_3 (Chapter IV, Fig 4.4h), equivalent to the loss of ~ 1.45 wt% sulfate melt. However over most of this temperature range sulfate melt exists in equilibrium with anhydrite and by 1000°C is almost completely absent from

the melt. As such a reasonable estimate of the quantity of sulfate that could be fractionated from a similar system is <1 wt%.

5.5.3 Comparison with previous work - Anhydrite

Previously published D values for REE, based on instrumental neutron activation (INA) analysis of anhydrite phenocrysts and matrix glass at El Chichon (Luhr 1984), agree well with the experimental values presented here and show greater affinity for light-middle REE than heavy REE in anhydrite (Fig 5.5)

Luhr (1984) values are calculated using matrix glass (~69 wt% SiO₂), and imply equilibrium between anhydrite and melt at low temperature (close to the estimated eruption T ~800°C). However the calculated partition coefficients are more than an order of magnitude lower than those calculated for a similarly low temperature experimental run with a dacite composition melt (green triangles, figure 5.5b). As we have shown, partition coefficients for the REE are a function of the calcium content of the melt ($(\text{CaO}_L)^2$, wt%), temperature (1/T (K)) and bulk composition (dacite vs andesite in these experiments). Accounting for the CaO content of the El Chichon glass, the partition coefficients calculated by Luhr (1984) are actually higher than those calculated for the 900°C experiment in this study and imply a temperature of equilibration slightly greater than 1000°C.

Since INA analyses were used to measure anhydrite trace element concentrations, rather than in-situ measurements of anhydrite rims, they represent an average composition of anhydrite which may have crystallized over a range of temperatures and in equilibrium with different silicate glass compositions. Whole rock data for El Chichon pumices show that the bulk composition is lower in SiO₂ (~59 wt%) and significantly higher in CaO (~7.9 wt%) than matrix glasses. Whereas a more mafic melt composition should increase the partition coefficient for REE somewhat (Fig. 5.8b), higher CaO contents will have the opposite effect and the partition coefficients measured by Luhr likely reflect anhydrite that began to crystallize at >1000°C. Comparing the bulk SO₃ content estimated for El Chichon pumices (1.25 – 2.5 wt%) with the SO₃ content of our andesite experiments (Chapter IV Fig 4.4h) suggest melts would be saturated in anhydrite at temperatures in excess of 1100°C.

5.5.4 Anhydrite lattice strain models

Partition coefficients (D_i) for cations into a crystal site should produce a parabolic distribution on a plot of effective ionic radius (r_i) versus $\log D_i$. Brice (1975) and Blundy and Wood (1994) describe the parabola by the equation:

$$D_i = D_0 \exp \left\{ -\frac{4\pi E_M N_A}{RT} \times \left[\frac{r_0(r_i - r_0)^2}{2} + \frac{(r_i - r_0)^3}{3} \right] \right\}$$

The equation links partition coefficients for various cations to the mechanical strain associated with substituting one cation for another of a different size. In this relationship the center of the parabola (r_0) represents the optimum cation size and the maximum of the parabola represents the partition coefficient for a cation of that size. The curvature of the parabola is related to the Young's modulus (E_M) for the site and to temperature (T). Larger values of E_M imply a “stiffer” site and a tighter parabola. The parabola will also tighten as T decreases. Because for a given experiment $D_i \propto Kd_i^*$, parabolas fit to values of D_i or Kd_i^* will only be different in regard to D_0 , i.e. the maximum of the parabola, and will provide identical estimates of E_M and r_0 .

Figure 5.9a,b shows weighted, non-linear least squares regression fits to Kd values for +2 and +3 cations from one 1000°C experiment (dacite composition, 0.75 GPa). The average Young's moduli calculated for the Ca site using fits to +2 and +3 cation data (Fig.5.9a, b) are 240 ± 25 kbar and 330 ± 22 kbar respectively.

Although the data are fit moderately well by a simple one-site fit to the data, a number of features are not explained. Firstly, all data from this study, as well as the data of Luhr et al. 1984 (Fig 5.5) suggest that $Kd_{La}^{Anh-Sil} > Kd_{Ce}^{Anh-Sil}$, which cannot be explained by simple partitioning of REE into a single site with $r_0 \sim r_{Ca}$ (1.12 Å). Secondly, fits to D values for 2+ cations and 3+ cations suggest significantly different optimum site radii ($r_0 \sim 1.11$ and 1.18 Å respectively). Finally, in all cases a one parabola fit underestimates $D_{Ba}^{Anh-Sil}$ by almost an order of magnitude.

The pattern of +3 cation partitioning behavior may be explained by the presence of two different sites at slightly different optimum radii (Fig. 5.9c,d). The first site (with r_{01} , E_{M1} , Kd_{01}) appears to be well expressed in the partitioning data for +3 cations as a local maximum at $D_{Sm}^{Anh-Sil}$ ($r_{01} \sim 1.08$ Å). Since there are no data for partitioning of +3 cations beyond $r_1 = 1.16$ the size of the second site (r_{02}) is less well determined. Assuming that the Young's modulus of the two sites is approximately equal, i.e. $E_{M1} \sim E_{M2}$, a fit to the data suggests $r_{02} \sim 1.2$ Å. A two-site fit to +2 cation partitioning data, again assuming that $E_{M1} \sim E_{M2}$, better explains observed Kd values for Ba but suggests slightly larger sites with $r_{01} = 1.12$ and $r_{02} = 1.28$.

The observation here that partitioning data are better fit by two individual cation sites is at odds with crystallographic studies of anhydrite (Cheng and Zussman 1963, Hawthorne and Ferguson, 1975) which suggest only one distinct Ca site with four sets of Ca-O bond lengths between ~ 2.32 and 2.56 Å. Differential thermal analysis investigation by Rowe et al. (1967)

suggested a reversible thermal effect at $\sim 1195^{\circ}\text{C}$ attributed to the change from low to high temperature anhydrite (α -anhydrite and β -anhydrite in the notation of Du, 2000), however since it was not possible to quench no details of crystal structure are available. Regardless, since all the partition coefficients reported here are for experimental conditions $< 1200^{\circ}\text{C}$ the formation of high-T, β -anhydrite is unlikely. High P-T studies have suggested a transition for CaSO_4 to monazite or barite structures at pressures between 2 – 21 GPa and temperatures $\sim 1450\text{K}$ (Stephens, 1964, Borg and Smith, 1975, Crichton et al. 2005) but since neither of these crystal structures host two distinct cation sites, the occurrence of these also does little to explain the partitioning data. Clearly further work is required to determine the possible nature of changes to the anhydrite structure in the temperature and pressure ranges employed in this study (i.e. 0.2 – 1 GPa and $900 - 1100^{\circ}\text{C}$).

5.5.5 Modelling anhydrite Sr content

In order to demonstrate the utility of the partitioning information presented here we have modelled the Sr content of anhydrite crystallizing from a cooling magma and compared the results to measured anhydrite Sr contents from Chapter II (Hutchinson and Dilles, 2019). Rhyolite-MELTS was used to model the crystallization of the Luhr Hill batholith and to determine the CaO content of the melt, the extent of plagioclase crystallization and plagioclase composition (mole fraction anorthite, X_{An}) between $1100 - 750^{\circ}\text{C}$. Modelled plagioclase compositions (X_{An} 0.45-0.28) agree well with those measured by Dilles (1987, X_{An} 0.38-0.16).

Plagioclase was assumed to be the only phase having a significant influence on the melt Sr content, based on both the low abundance of all other phases at $> 800^{\circ}\text{C}$ and on low crystal – melt partition coefficients for clinopyroxene, biotite and amphibole (generally < 1). Partition coefficients for Sr between plagioclase and melt were calculated as a function of temperature and X_{An} (Blundy and Wood, 1991) and the bulk Sr content was taken to be 1080 ppm based on whole rock analyses (Dilles 1987). The partition coefficient for Sr between anhydrite and melt was calculated based on equation (5.8).

Figure 5.10 shows the modelled anhydrite Sr content as a function of temperature, along with the range of Sr contents (4000-5500 ppm) measured in silicate hosted anhydrite inclusions from the Luhr Hill. The Sr content of anhydrite decreases close to exponentially above liquidus temperatures, driven by changes to the partition coefficient as described by equation (5.8). At $\sim 900^{\circ}\text{C}$ the onset of clinopyroxene crystallization and an associated decrease in melt CaO content causes the partition coefficient to increase, and buffers the anhydrite Sr content somewhat.

Finally plagioclase crystallization, starting at $\sim 850^{\circ}\text{C}$, quickly strips Sr from the melt resulting in a sharp drop in the Sr content of anhydrite. We assumed no reequilibration of plagioclase with regard to Sr content at lower temperature but the general effect of this would be to decrease the Sr content of the melt more quickly, because $D_{\text{Sr}}^{\text{Plagioclase-Sil}}$ increases with mole fraction albite (X_{Ab} , Blundy and Wood, 1991). For the highest Sr anhydrite inclusions measured (~ 5500 ppm, Chapter II this study), this model suggests an anhydrite crystallization temperature between $930 - 1015^{\circ}\text{C}$ and implies that anhydrite was a liquidus phase. Experiments with a ~ 6 wt% H_2O , dacite composition in Chapter IV had on average ~ 1250 ppm S at 1000°C . Assuming that the water content of the Luhr Hill was similar this implies a minimum bulk sulfur content of ~ 1000 ppm.

5.6 Conclusion

In this study we have measured partition coefficients for a variety of elements between sulfate phases (anhydrite and sulfate melt) and silicate melt at a range of temperatures and pressures relevant to crustal conditions.

Partition coefficients for anhydrite are well described in terms of lattice strain models, although a number of features suggest that Ca may occupy two distinct sites within the anhydrite crystal structure, at odds with low P-T crystallographic studies (Cheng and Zussman 1963, Hawthorne and Ferguson, 1975). For a given composition, partition coefficients (relative to that of Ca) vary predictably, and increase with increasing temperature and can be calculated as a function of melt CaO content and temperature. Using a variable partition coefficient for Sr we have modelled the Sr content of anhydrite crystallizing from the Luhr Hill granite, Yerington and shown that high – Sr anhydrite inclusions, analyzed in Chapter II must have crystallized at temperatures $> 930^{\circ}\text{C}$. This implies that anhydrite was a liquidus phase and that the bulk S content of the magma must have been in excess of ~ 1000 ppm S.

Partition coefficients between sulfate melt and silicate melt (Fig. 5.3) vary somewhat consistently when elements are plotted in order of increasing ionic potential (Z / r) with peaks in compatibility close to Ca and S. We found that partition coefficients for Ca and REE were in most cases almost an order of magnitude lower than those published by Veksler et al. (2012) although this may be related to the high SiO_2 content of their silicate melt phase (~ 75 wt% SiO_2). Differences in the behavior of high field strength elements (HFSE) were also observed, although the cause of this is unclear. Partition coefficients between sulfate melt and our more mafic silicate melt composition (trachyandesite) also tended to be lower than those with more silicic silicate

melt composition (trachydacite), again, probably related to polymerization of the silicate melt. This implies that partition coefficients for all elements between sulfate melt and high-T, primitive magmas are likely to be low (<10) and the fractionation of sulfate melt is unlikely to produce a distinctive trace element signature in this compositional range.

5.7 References

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5.8 Figures and tables

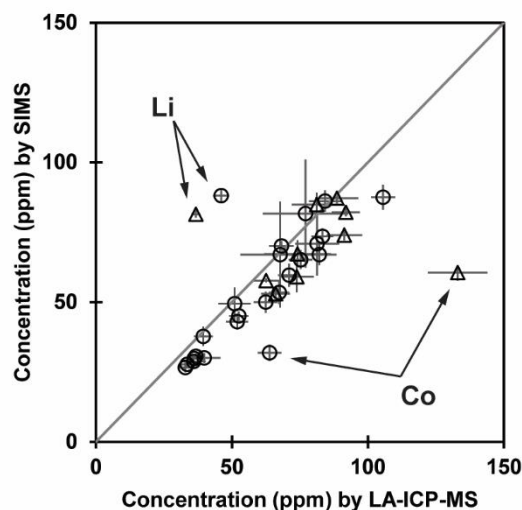


Figure 5.1 Comparison of silicate glass trace element concentrations measured by LA-ICP-MS and SIMS. Uncertainties are 1s.d. based on repeat analyses.

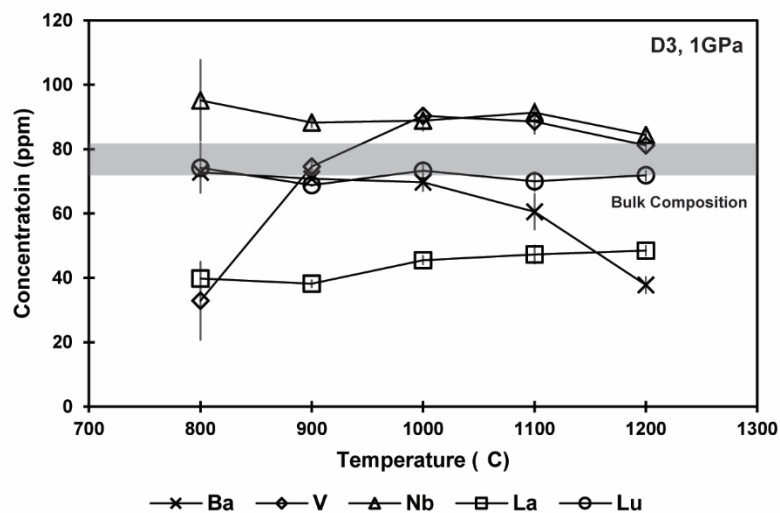


Figure 5.2 Variation in silicate glass trace element concentrations with temperature. Grey bar indicates the concentrations for all the elements shown in the bulk starting material. Depletion in Ba at high temperature reflects its compatibility in sulfate melt which was present in experiments $\geq 1000^\circ\text{C}$. Depletion of La at all temperatures indicates compatibility in both anhydrite and sulfate melt, whereas Lu concentrations approximately equal to the bulk concentration indicate partition coefficients of ~ 1 between both anhydrite and sulfate melt and silicate melt. Uncertainties are 1s.d. based on repeat analysis of glass.

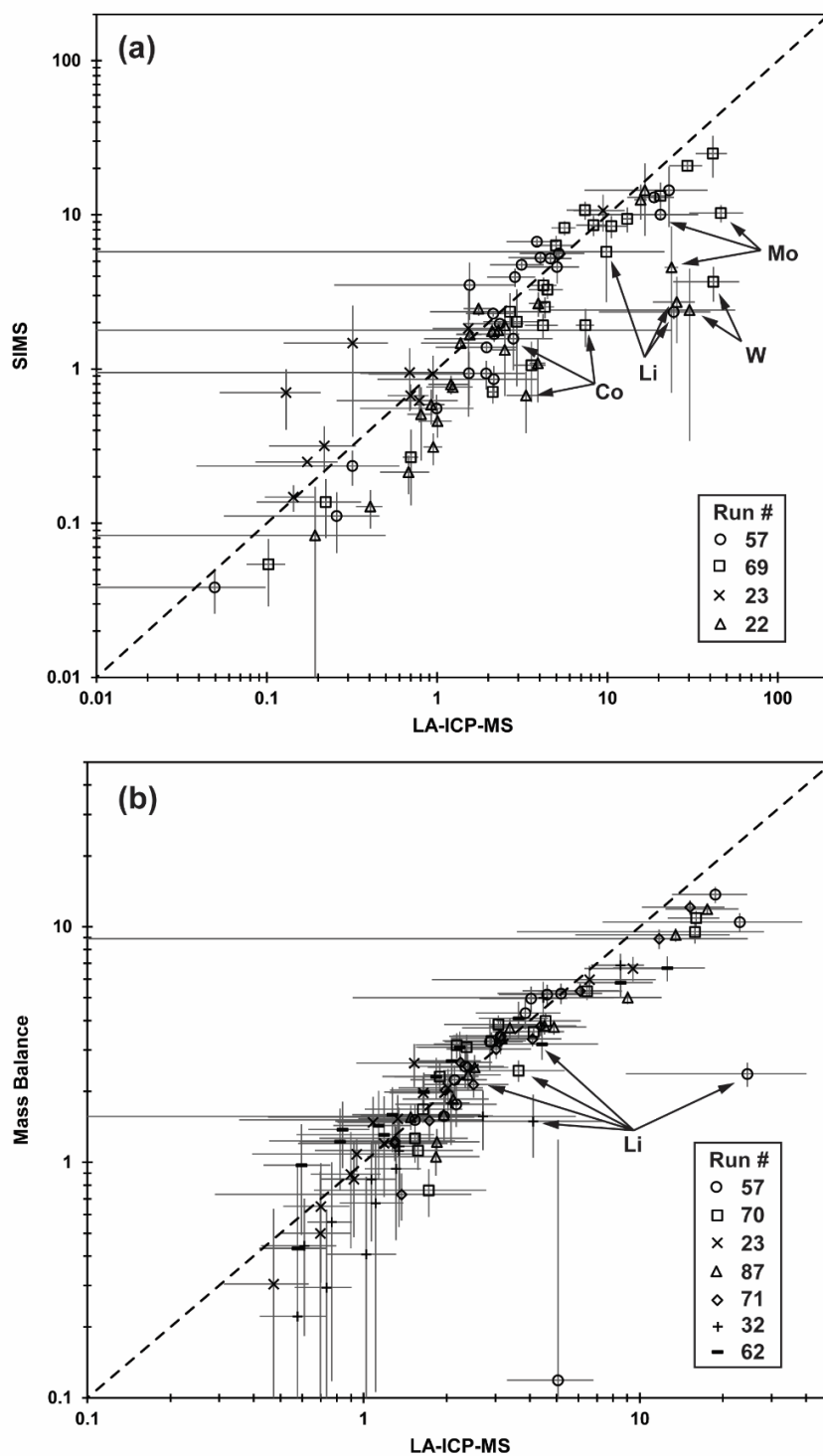


Figure 5.3 Comparison of sulfate melt – silicate melt partition coefficients measured and calculated by different methods. A) LA-ICP-MS vs SIMS partition coefficients. B) LA-ICP-MS vs mass balance calculations. Uncertainties are propagated 1 s.d. based on repeat analysis of silicate melt and sulfate melt.

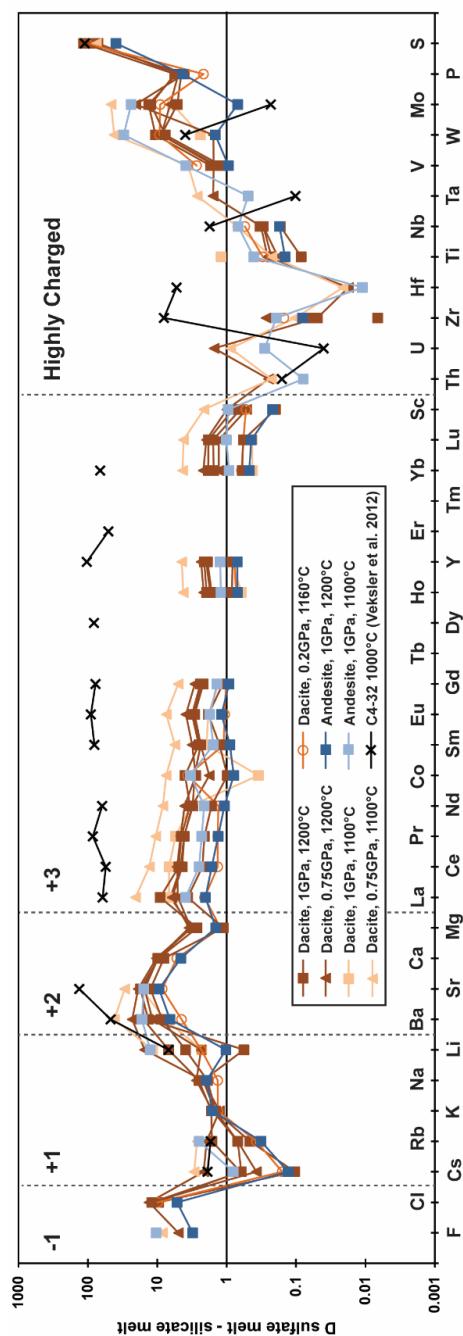


Figure 5.4 Sulfate melt – Silicate melt partition coefficients based on SIMS (F, Hf, Ta, Th, U), EPMA (Cl, K, Na, Ca, Mg, P, S) or LA-ICP-MS (all others). Black crosses indicate data from Veksler et al. 2012. Elements are arranged by ionic potential (Z / r) with r values taken from Shannon 1976 based on a coordination number (CN) of 6. Elements with varying valence state are plotted as Eu^{3+} , Co^{2+} , V^{5+} , W^{6+} , Mo^{6+} .

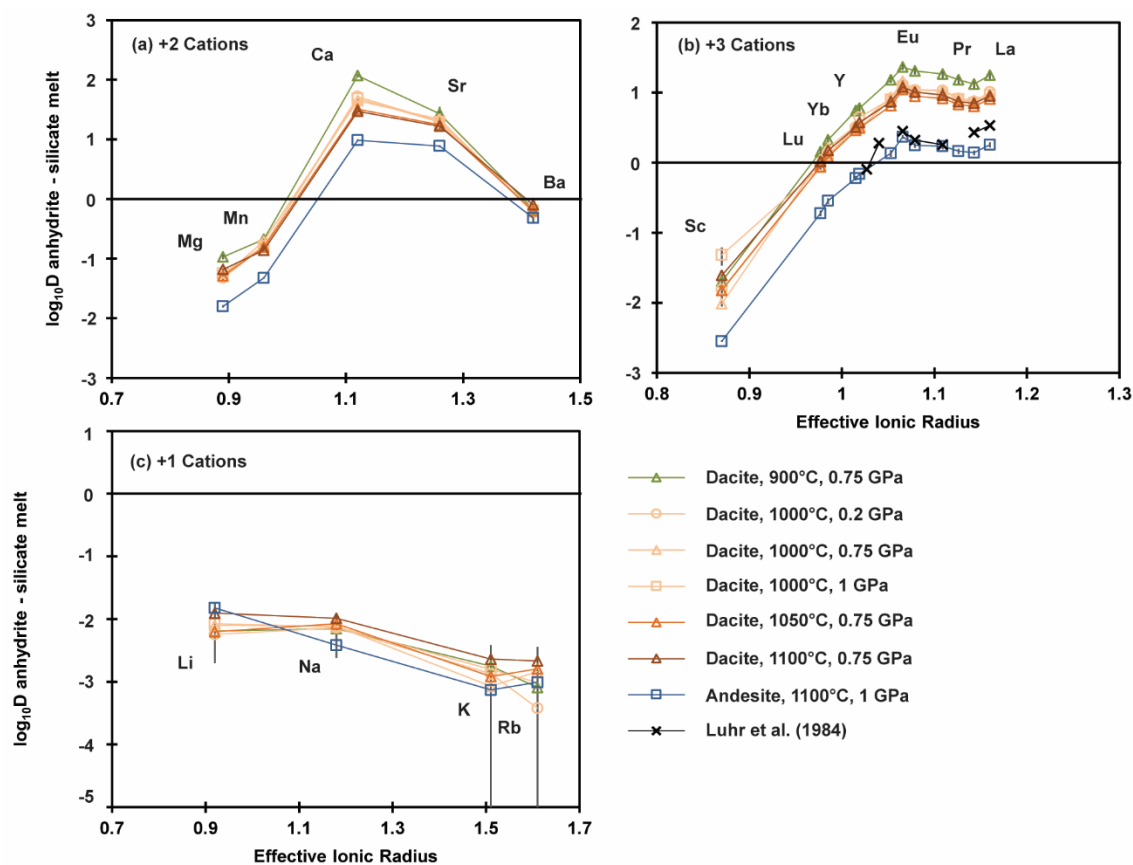


Figure 5.5 Anhydrite – silicate melt partition coefficients for +2 (a), +3 (b) and +1 (c) cations as a function of effective ionic radius. Partition coefficients are based on SIMS analysis of silicate glass and anhydrite, and uncertainties are propagated 1s.d.. Data from Luhr (1984) is based on INA analyses of anhydrite crystals and interstitial glass from the 1982 eruption of El Chichon.

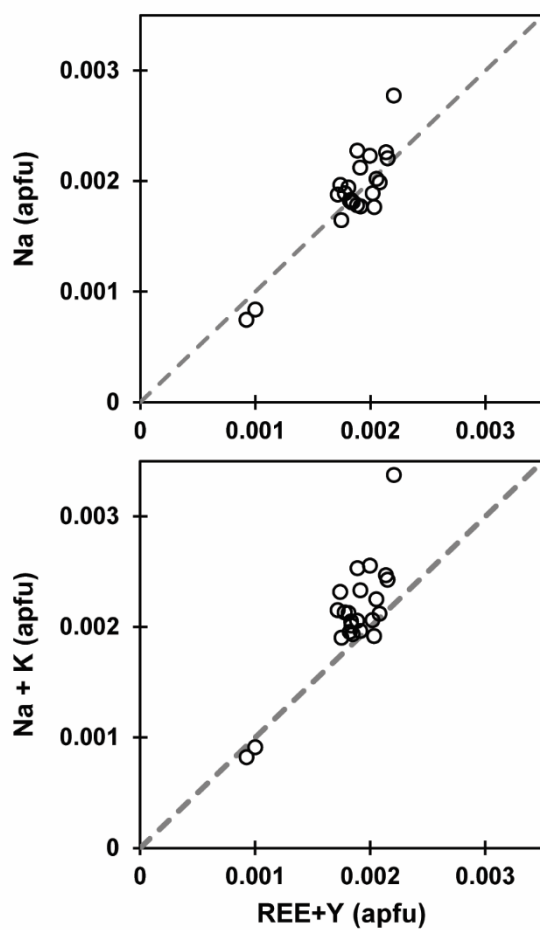


Figure 5.6 Comparison of 3+ and 1+ cation concentrations in anhydrite on the basis of atoms per formula unit (apfu). Close fit to the 1:1 line in (a) suggests that the incorporation of REE and Y into the anhydrite crystal structure is generally charged balanced by Na.

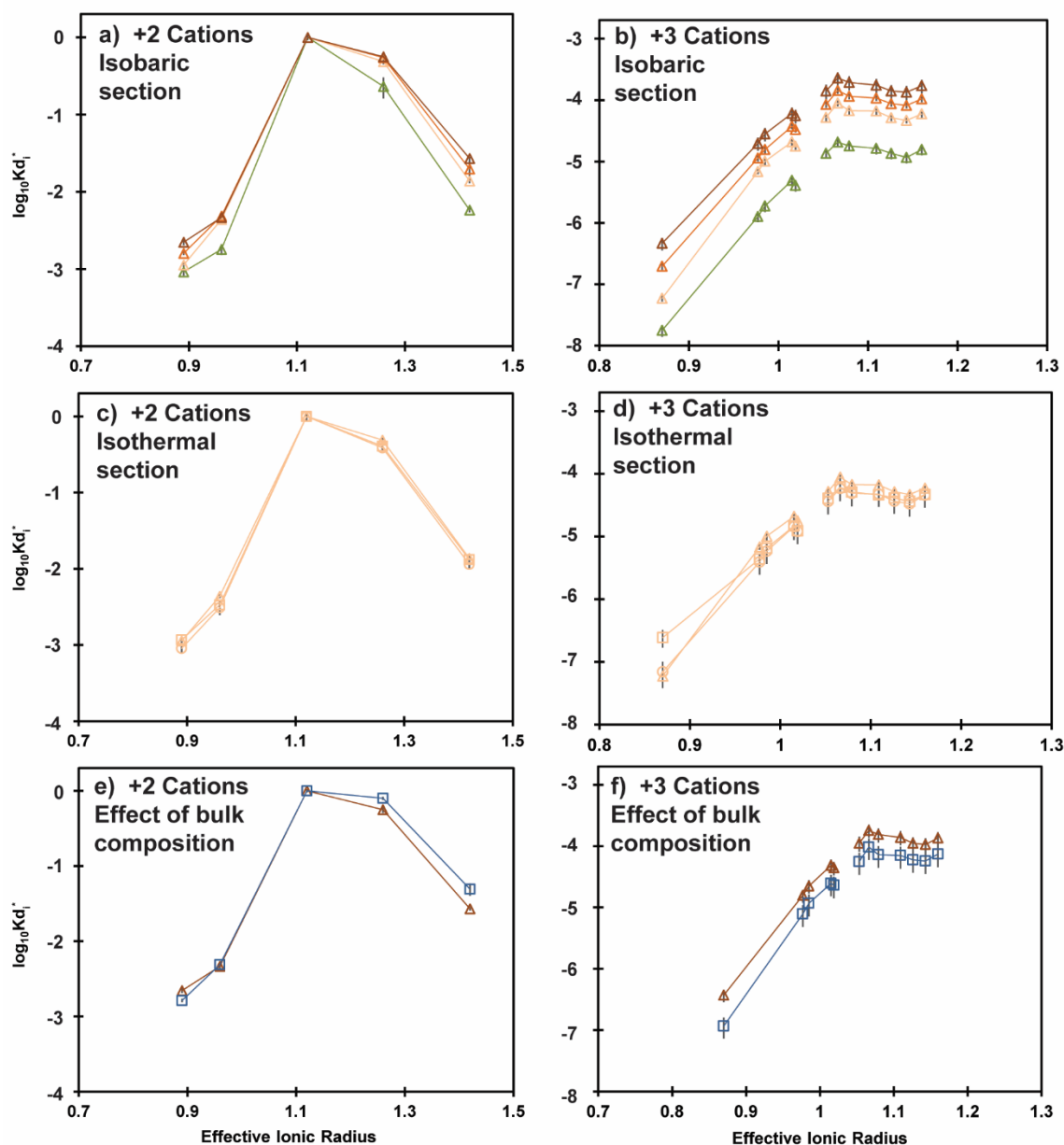


Figure 5.7 Kd_i^* values plotted as a function of effective ionic radius for +2 cations (a,c,e) and +3 cations (b,d,f). Plots show the effect of temperature (a,b) pressure (c,d) and bulk composition (d,e) on the exchange reactions (5.1) and (5.2). Colors and symbols are the same as figure 5.5. Uncertainties are 1s.d. propagated uncertainties based on SIMS measurements of glass and anhydrite.

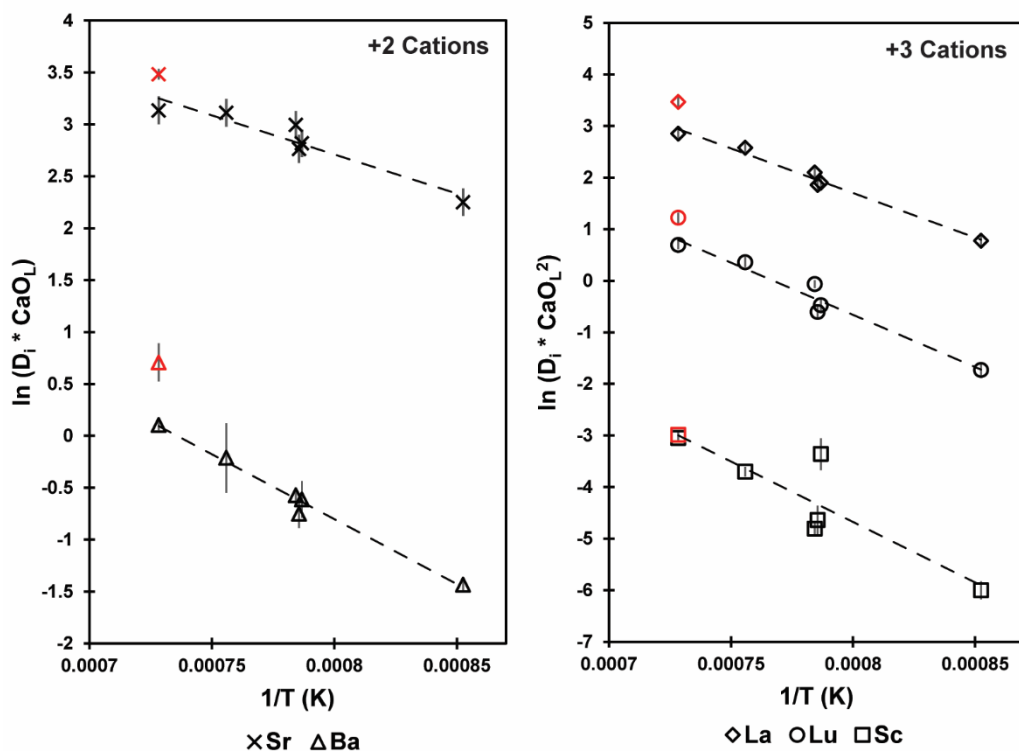


Figure 5.8 $\ln(D_i * \text{CaO})$ as a function of $1/T$ (K) for +2 and +3 cations. Black symbols are data from dacite composition experiments while red symbols are from one andesite composition experiment. Dashed lines indicate least squares regression fits to dacite data used to calculate parameters C_1 and C_2 (table 5.3). Uncertainties are 1s.d..

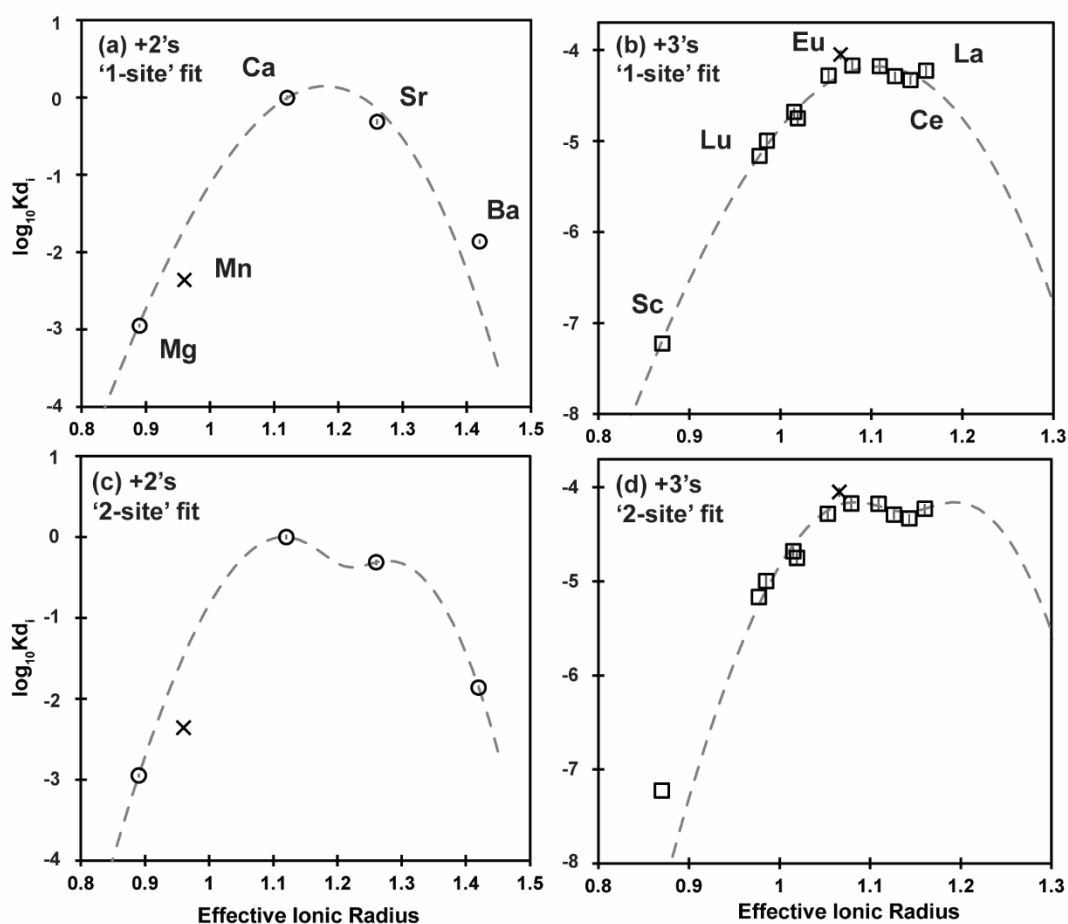


Figure 5.9 Lattice strain models showing “1-site” (a,b) and “2-site” (c,d) fits to partitioning data. Partition coefficients for Mn and Eu were omitted from parabola fitting and are shown as crosses in plots of +2 and +3 cations respectively. Note that “1-site” fits to data underestimate Ba partition coefficients by $\sim$ an order of magnitude and fail to explain the increase in partition coefficient between Ce and La.

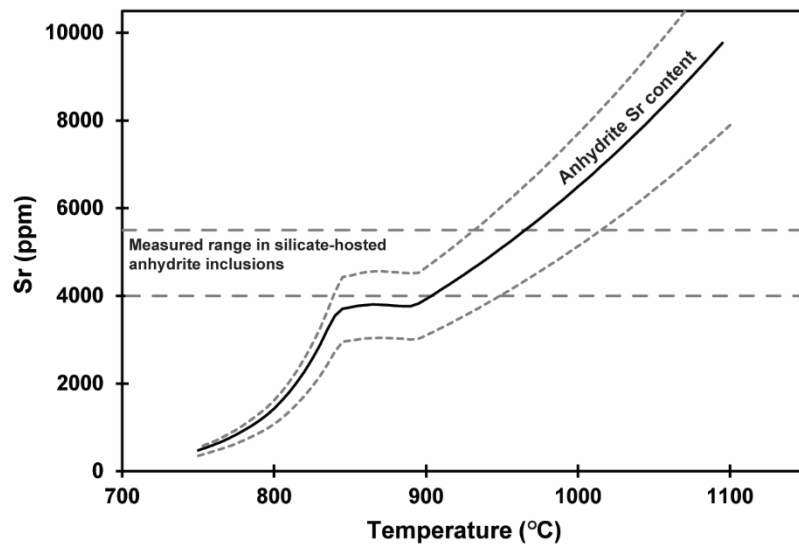


Figure 5.10 Model for the Sr-content of anhydrite crystallizing from a cooling magma based on the composition of the Luhr Hill, Yerington NV. Horizontal dashed lines indicate the range of Sr contents measured in silicate-hosted anhydrite inclusions from this unit (Chapter II, this study). Despite $\sim 20\%$ uncertainty on $D_{Sr}^{Anh-Sil}$ (dotted lines), this indicates that anhydrite was likely a liquidus phase, and may have begun to crystallize at temperatures as high as 930 - 1015°C.

Table 5.1 Sulfate melt – silicate melt partition coefficients by LA-ICP-MS

Run #	Starting Material	$D_{\text{f}}^{\text{sulf-sil}}$ (1s.d.)														22
		70	42	71	87	57	69	32	62	23	23	62	32	62	23	
Pressure (GPa)	Pressure (GPa)	1	1	0.75	1	0.75	0.75	0.2	1	1	1	1	0.2	1	1	A7
Temperature (°C)	Temperature (°C)	1200	1100	1200	1200	1200	1100	1160	1200	1200	1200	1200	1160	1200	1200	1100
Li		6.836 (6.726)	2.284 (2.285)	2.345 (10.970)	0.561 (0.415)	15.166 (11.660)	11.653 (12.757)	2.316 (3.248)	3.917 (1.874)	1.021 (0.643)	1.021 (0.643)	3.917 (1.874)	2.316 (3.248)	3.917 (1.874)	1.021 (0.643)	12.639 (10.302)
Sc		0.632 (0.295)		0.516 (0.541)	0.811 (0.445)	0.994 (0.641)	2.122 (1.140)	0.526 (0.424)	0.198 (0.071)	0.218 (0.115)	0.218 (0.115)	0.198 (0.071)	0.526 (0.424)	0.198 (0.071)	0.218 (0.115)	0.951 (0.506)
Ti		0.226 (0.069)		0.182 (0.067)		0.257 (0.201)	0.222 (0.135)	0.301 (0.103)	0.084 (0.027)	0.143 (0.046)	0.143 (0.046)	0.084 (0.027)	0.301 (0.103)	0.084 (0.027)	0.143 (0.046)	0.406 (0.027)
V		1.721 (1.060)		1.373 (1.084)	1.482 (1.032)	1.536 (1.182)	3.582 (0.744)	2.705 (3.159)	1.186 (0.614)	0.944 (0.549)	0.944 (0.549)	1.186 (0.614)	2.705 (3.159)	1.186 (0.614)	0.944 (0.549)	3.900 (2.030)
Co		2.922 (1.998)	0.349 (0.349)	1.779 (3.081)	3.982 (1.867)	2.798 (1.959)	7.431 (0.905)	3.630 (3.927)	0.978 (0.544)	0.788 (0.531)	0.788 (0.531)	0.978 (0.544)	3.630 (3.927)	0.978 (0.544)	0.788 (0.531)	3.333 (1.982)
Ni		2.562 (2.140)	0.072 (0.072)	1.576 (1.430)	2.360 (1.166)	2.025 (1.503)	6.229 (1.237)	3.291 (2.900)	0.714 (0.427)	0.640 (0.420)	0.640 (0.420)	0.714 (0.427)	3.291 (2.900)	0.714 (0.427)	0.640 (0.420)	2.572 (1.663)
Rb		1.629 (2.099)		0.692 (1.338)	0.461 (0.317)	1.943 (1.335)	2.678 (1.770)	0.371 (0.364)	0.693 (0.234)	0.320 (0.194)	0.320 (0.194)	0.693 (0.234)	2.678 (1.770)	0.371 (0.364)	0.320 (0.194)	2.494 (2.509)
Sr		16.017 (3.394)	17.034 (17.061)	15.216 (5.036)	17.564 (5.206)	18.778 (5.715)	29.501 (6.425)	8.504 (1.829)	12.593 (4.581)	9.448 (3.147)	9.448 (3.147)	12.593 (4.581)	8.504 (1.829)	8.504 (1.829)	9.448 (3.147)	15.684 (9.125)
Y		1.885 (0.718)	0.831 (0.831)	1.977 (0.730)	2.109 (0.726)	2.332 (0.874)	4.451 (1.013)	0.767 (0.140)	0.821 (0.235)	0.701 (0.188)	0.701 (0.188)	0.821 (0.235)	4.451 (1.013)	0.767 (0.140)	0.701 (0.188)	1.240 (0.170)
Zr		0.049 (0.027)		0.270 (0.051)	0.058 (0.054)	0.049 (0.049)	0.102 (0.026)	0.149 (0.120)	0.007 (0.001)	0.080 (0.042)	0.080 (0.042)	0.007 (0.001)	0.149 (0.120)	0.007 (0.001)	0.080 (0.042)	0.193 (0.102)
Nb		0.296 (0.131)		0.296 (0.328)	0.330 (0.179)	0.319 (0.280)	0.702 (0.071)	0.547 (0.526)	0.168 (0.072)	0.173 (0.087)	0.173 (0.087)	0.168 (0.072)	0.547 (0.526)	0.168 (0.072)	0.173 (0.087)	0.681 (0.228)
Mo		13.354 (11.529)	5.988 (6.009)	6.534 (11.819)	5.148 (4.545)	20.483 (13.526)	46.385 (16.135)	9.083 (14.022)	12.351 (6.229)	0.690 (0.724)	0.690 (0.724)	12.351 (6.229)	9.083 (14.022)	0.690 (0.724)	0.690 (0.724)	23.801 (20.147)
Cs		0.634 (0.623)		0.372 (1.602)	0.104 (0.072)	2.147 (1.700)	2.938 (1.070)	0.159 (0.143)	0.616 (0.257)	0.130 (0.077)	0.130 (0.077)	0.616 (0.257)	2.938 (1.070)	0.159 (0.143)	0.130 (0.077)	0.804 (0.800)
Ba		15.861 (12.270)	7.733 (7.767)	11.751 (12.803)	13.493 (7.651)	23.018 (15.689)	41.608 (8.662)	4.475 (3.562)	8.527 (2.610)	6.583 (4.816)	6.583 (4.816)	8.527 (2.610)	41.608 (8.662)	4.475 (3.562)	6.583 (4.816)	16.578 (16.821)
La		6.449 (2.168)	6.798 (6.812)	6.081 (2.318)	9.048 (2.928)	5.051 (1.744)	20.521 (2.984)	2.075 (0.344)	3.639 (1.026)	2.021 (0.681)	2.021 (0.681)	3.639 (1.026)	20.521 (2.984)	2.075 (0.344)	2.021 (0.681)	3.931 (0.438)
Ce		4.563 (1.537)	6.783 (6.793)	4.371 (1.523)	4.888 (1.518)	5.183 (2.125)	13.080 (0.737)	1.344 (0.267)	2.232 (0.656)	1.645 (0.405)	1.645 (0.405)	2.232 (0.656)	13.080 (0.737)	1.344 (0.267)	1.645 (0.405)	2.501 (0.381)
Pr		4.130 (1.193)	5.469 (5.477)	4.086 (1.106)	4.522 (1.351)	4.618 (1.534)	10.553 (2.544)	1.348 (0.211)	2.085 (0.569)	1.328 (0.371)	1.328 (0.371)	2.085 (0.569)	10.553 (2.544)	1.348 (0.211)	1.328 (0.371)	2.289 (0.211)
Nd		3.077 (1.121)	3.297 (3.305)	3.141 (1.034)	3.381 (1.106)	4.042 (1.418)	8.280 (1.714)	1.310 (0.301)	1.654 (0.467)	1.082 (0.279)	1.082 (0.279)	1.654 (0.467)	8.280 (1.714)	1.310 (0.301)	1.082 (0.279)	2.102 (0.449)
Sm		2.362 (0.815)	1.957 (1.961)	2.377 (0.835)	2.523 (0.816)	3.131 (1.089)	5.594 (0.897)	1.106 (0.286)	1.272 (0.362)	0.898 (0.254)	0.898 (0.254)	1.272 (0.362)	5.594 (0.897)	1.106 (0.286)	0.898 (0.254)	1.559 (0.404)
Eu		2.901 (0.967)	1.830 (1.833)	3.016 (1.024)	3.165 (1.101)	3.853 (1.302)	7.384 (1.627)	1.067 (0.235)	1.832 (0.537)	1.187 (0.356)	1.187 (0.356)	1.832 (0.537)	7.384 (1.627)	1.067 (0.235)	1.187 (0.356)	1.754 (0.383)
Gd		2.172 (0.629)	1.318 (1.321)	2.243 (0.668)	2.389 (0.745)	2.867 (0.900)	4.991 (1.286)	1.022 (0.290)	1.134 (0.357)	0.923 (0.219)	0.923 (0.219)	1.134 (0.357)	4.991 (1.286)	1.022 (0.290)	0.923 (0.219)	1.375 (0.426)
Ho		1.641 (0.632)	0.612 (0.612)	1.730 (0.530)	1.950 (0.708)	2.135 (0.658)	4.218 (0.780)	0.734 (0.170)	0.839 (0.209)	0.697 (0.200)	0.697 (0.200)	0.839 (0.209)	4.218 (0.780)	0.734 (0.170)	0.697 (0.200)	1.209 (0.228)
Yb		1.535 (0.843)	0.424 (0.425)	1.296 (0.716)	1.844 (0.779)	2.166 (0.866)	4.299 (0.552)	0.610 (0.184)	0.596 (0.162)	0.472 (0.160)	0.472 (0.160)	0.596 (0.162)	4.299 (0.552)	0.610 (0.184)	0.472 (0.160)	0.923 (0.234)
Lu		1.575 (0.909)	0.428 (0.428)	1.300 (0.845)	1.829 (0.797)	1.956 (0.979)	4.186 (0.915)	0.576 (0.156)	0.577 (0.157)	0.440 (0.135)	0.440 (0.135)	0.577 (0.157)	4.186 (0.915)	0.576 (0.156)	0.440 (0.135)	1.008 (0.301)
W		10.628 (7.627)	2.397 (2.408)	8.747 (9.474)	8.753 (7.550)	1.554 (1.305)	41.824 (17.487)	9.253 (12.694)	7.684 (3.588)	1.457 (2.378)	1.457 (2.378)	7.684 (3.588)	41.824 (17.487)	9.253 (12.694)	1.457 (2.378)	30.367 (18.643)

Table 5.2 Sulfate melt – silicate melt partition coefficients by SIMS

	$D_i^{Sulf-Sil}$ (1s.d.)			
Run #	57	69	23	22
Starting Material	D6	D6	A7	A7
Pressure (GPa)	0.75	0.75	1	1
Temperature (°C)	1200	1100	1200	1100
Li	2.348 (0.246)	5.748 (3.032)	1.836 (1.346)	2.719 (1.243)
B	0.049 (0.015)	0.060 (0.031)	0.503 (0.569)	0.215 (0.186)
F*	4.967 (0.764)	8.455 (1.629)	3.088 (2.075)	10.351 (4.750)
Cl*	32.787 (6.174)	42.360 (27.136)	523.675 (241.111)	58.322 (19.228)
K	1.005 (0.149)	2.455 (0.422)	4.372 (4.117)	2.959 (1.625)
Ca	8.147 (0.172)	11.408 (0.746)	4.690 (0.037)	6.173 (0.066)
Sc	0.555 (0.125)	0.711 (0.112)	0.318 (0.107)	0.311 (0.073)
Ti	0.112 (0.047)	0.137 (0.057)	0.148 (0.029)	0.128 (0.036)
V	0.938 (0.356)	1.058 (0.447)	0.929 (0.288)	1.093 (0.484)
Mn	2.252 (0.288)	2.594 (0.178)	1.610 (1.331)	1.488 (0.275)
Co	1.578 (0.594)	1.924 (0.532)	0.624 (0.173)	0.674 (0.289)
Rb	0.935 (0.195)	2.351 (0.762)	1.473 (1.109)	1.330 (0.661)
Sr	12.997 (0.607)	20.829 (1.742)	10.654 (2.860)	12.531 (3.195)
Y	1.968 (0.057)	3.274 (0.430)	0.672 (0.127)	0.764 (0.059)
Zr	0.038 (0.012)	0.054 (0.025)		0.084 (0.089)
Nb	0.236 (0.060)	0.268 (0.137)	0.250 (0.000)	0.215 (0.060)
Mo	10.030 (0.563)	10.252 (1.313)	0.950 (0.415)	4.566 (3.864)
Cs	0.859 (0.186)	2.033 (1.258)	0.703 (0.299)	0.508 (0.253)
Ba	14.452 (6.076)	25.025 (7.535)		14.448 (7.128)
La	4.597 (1.002)	13.315 (2.889)		2.662 (0.476)
Ce	5.623 (0.526)	9.435 (1.727)		1.917 (0.302)
Pr	5.223 (0.431)	8.448 (1.376)		1.791 (0.240)
Nd	5.287 (0.498)	8.586 (1.285)		1.762 (0.216)
Sm	4.746 (0.243)	8.237 (0.860)		1.671 (0.141)
Eu	6.699 (0.309)	10.743 (1.436)		2.460 (0.232)
Gd	3.949 (0.528)	6.326 (0.991)		1.472 (0.109)
Ho	2.289 (0.097)	3.487 (0.437)		0.796 (0.111)
Yb	1.686 (0.184)	2.528 (0.394)		0.587 (0.150)
Lu	1.385 (0.116)	1.919 (0.357)		0.459 (0.100)
Hf	0.017 (0.011)	0.021 (0.008)		0.011 (0.007)
Ta	1.571 (0.319)	2.659 (0.931)		0.488 (0.135)
W	3.499 (1.408)	3.676 (0.933)		2.416 (2.074)
Th	0.248 (0.057)	0.226 (0.050)		0.079 (0.021)
U	1.508 (0.399)	0.878 (0.243)		0.284 (0.018)

Table 5.3 Sulfate melt – silicate melt partition coefficients by mass balance

	$D_i^{Sulf-Sil}$ (1s.d.)						
Run #	70	71	87	57	32	62	23
Starting Material	D8	D8	D6	D6	D6	D4	A7
Pressure (GPa)	1	0.75	1	0.75	0.2	1	1
Temperature (°C)	1200	1200	1200	1200	1160	1200	1200
Li	2.450 (0.257)	2.140 (0.254)	2.065 (0.343)	2.373 (0.276)	1.495 (0.448)	3.175 (0.450)	2.639 (0.544)
V	0.761 (0.174)	0.731 (0.166)	1.556 (0.186)	1.516 (0.245)	1.570 (0.441)	1.310 (0.596)	1.083 (0.171)
Sr	10.885 (0.802)	12.105 (0.862)	11.893 (0.669)	13.712 (1.070)	6.870 (0.798)	6.680 (0.811)	6.661 (0.784)
Y	2.313 (0.334)	2.025 (0.263)	1.856 (0.188)	2.556 (0.497)	0.559 (0.441)	1.226 (0.464)	0.650 (0.341)
Ba	9.518 (1.025)	8.901 (0.836)	9.246 (0.600)	10.484 (0.920)	4.996 (0.834)	5.797 (0.757)	5.974 (0.844)
La	5.336 (0.455)	5.350 (0.388)	5.014 (0.319)	0.119 (1.130)	1.783 (0.596)	4.094 (0.712)	2.074 (0.421)
Ce	3.988 (0.302)	3.780 (0.347)	3.752 (0.272)	5.217 (0.523)	1.121 (0.589)	3.078 (0.509)	1.976 (0.327)
Pr	3.589 (0.273)	3.343 (0.235)	3.797 (0.296)	5.160 (0.516)	1.169 (0.399)	2.698 (0.487)	1.532 (0.399)
Nd	3.856 (0.352)	3.442 (0.291)	3.723 (0.372)	4.967 (0.611)	0.940 (0.473)	1.988 (0.415)	1.480 (0.417)
Sm	3.087 (0.392)	2.554 (0.340)	2.533 (0.320)	3.437 (0.555)	0.672 (0.566)	1.593 (0.489)	0.889 (0.456)
Eu	3.278 (0.288)	3.028 (0.275)	3.361 (0.264)	4.308 (0.627)	0.848 (0.386)	2.312 (0.463)	1.206 (0.378)
Gd	3.143 (0.384)	2.657 (0.227)	2.351 (0.335)	3.260 (0.798)	0.407 (0.461)	1.432 (0.580)	0.848 (0.367)
Ho	1.681 (0.206)	1.504 (0.269)	1.595 (0.166)	2.243 (0.336)	0.294 (0.337)	1.378 (0.432)	0.499 (0.414)
Yb	1.266 (0.269)	1.202 (0.133)	1.224 (0.162)	1.762 (0.350)	0.442 (0.259)	0.973 (0.481)	0.305 (0.331)
Lu	1.123 (0.194)	1.235 (0.220)	1.056 (0.176)	1.571 (0.333)	0.222 (0.289)	0.431 (0.536)	

Table 5.4 Anhydrite – silicate partition coefficients by SIMS

	$D_i^{Anh-Sil}$ (1s.d.)						
Starting Composition	D2	D2	D2	D2	D2	D2	A1
Temperature	900	1000	1000	1000	1050	1100	1100
Pressure	0.75	0.2	0.75	1	0.75	0.75	1
Li	0.006 (0.001)	0.006 (0.004)	0.008 (0.000)	0.008 (0.000)	0.006 (0.004)	0.013 (0.003)	0.015 (0.003)
Na	0.007 (0.001)	0.007 (0.003)	0.008 (0.000)	0.008 (0.000)	0.008 (0.001)	0.010 (0.002)	0.004 (0.000)
K	0.002 (0.000)	0.001 (0.002)	0.001 (0.000)	0.002 (0.000)	0.001 (0.000)	0.002 (0.002)	0.001 (0.000)
Rb	0.001 (0.001)	0.000 (0.002)	0.001 (0.002)	0.001 (0.000)	0.002 (0.001)	0.002 (0.001)	0.001 (0.001)
Mg	0.107 (0.009)	0.047 (0.007)	0.050 (0.002)	0.057 (0.005)	0.051 (0.002)	0.066 (0.005)	0.016 (0.001)
Mn	0.211 (0.032)	0.161 (0.032)	0.196 (0.004)	0.163 (0.006)	0.155 (0.020)	0.137 (0.011)	0.047 (0.001)
Ca	116.948 (6.967)	51.899 (2.487)	44.624 (2.099)	48.190 (3.609)	32.064 (1.014)	29.580 (1.070)	9.716 (0.254)
Sr	27.059 (8.154)	20.067 (2.566)	21.707 (1.390)	19.682 (2.939)	17.559 (1.562)	16.579 (1.380)	7.714 (0.340)
Ba	0.679 (0.024)	0.596 (0.075)	0.614 (0.024)	0.637 (0.102)	0.632 (0.211)	0.801 (0.027)	0.480 (0.087)
La	17.659 (2.044)	10.272 (0.832)	9.659 (0.920)	9.234 (0.930)	8.087 (0.628)	9.016 (0.880)	1.805 (0.152)
Ce	13.230 (1.710)	7.446 (0.758)	7.621 (0.557)	7.147 (0.678)	6.360 (0.374)	7.093 (0.817)	1.392 (0.108)
Pr	15.298 (1.852)	8.173 (0.617)	8.413 (0.686)	8.027 (0.681)	6.757 (0.401)	7.390 (0.820)	1.462 (0.124)
Nd	18.476 (2.355)	10.598 (0.809)	10.844 (1.368)	9.118 (0.983)	8.318 (0.477)	9.252 (1.154)	1.715 (0.160)
Sm	20.315 (1.970)	10.896 (1.015)	10.954 (1.253)	10.077 (0.880)	8.893 (0.525)	10.280 (1.081)	1.764 (0.134)
Eu	23.345 (2.083)	12.981 (0.733)	14.530 (1.119)	12.019 (0.819)	11.112 (0.864)	12.003 (0.836)	2.347 (0.138)
Gd	15.326 (1.506)	8.101 (0.523)	8.520 (1.222)	7.988 (0.797)	6.515 (0.451)	7.445 (1.044)	1.363 (0.143)
Y	5.995 (1.116)	4.461 (0.245)	3.558 (0.303)	3.117 (0.175)	3.144 (0.141)	3.751 (0.279)	0.692 (0.035)
Ho	5.576 (0.636)	3.209 (0.401)	3.397 (0.286)	2.887 (0.172)	2.907 (0.178)	3.219 (0.242)	0.602 (0.043)
Yb	2.127 (0.286)	1.298 (0.127)	1.640 (0.220)	1.282 (0.139)	1.214 (0.126)	1.489 (0.113)	0.286 (0.026)
Lu	1.442 (0.164)	0.877 (0.077)	1.111 (0.046)	0.859 (0.056)	0.878 (0.077)	1.046 (0.069)	0.190 (0.018)
Sc	0.020 (0.003)	0.016 (0.004)	0.010 (0.001)	0.048 (0.014)	0.015 (0.001)	0.025 (0.001)	0.003 (0.000)
P	0.272 (0.055)	0.306 (0.062)	0.368 (0.032)	0.260 (0.033)	0.393 (0.077)	0.254 (0.057)	0.169 (0.011)

Table 5.5 Calculated best fit parameters for Eq (5.8), (5.9).

Element	C_1	C_2 (Dacite)	C_2 (Andesite)
Sr	-7526 (1237)	8.73 (0.97)	8.96
Ba	-12526 (786)	9.22 (0.62)	9.83
Mg	-7084 (2239)	2.57 (1.75)	2.46
La	-17267 (1175)	15.52 (0.92)	16.04
Ce	-17707 (1440)	15.60 (1.13)	16.10
Pr	-16838 (1445)	15.01 (1.13)	15.52
Nd	-17112 (1522)	15.44 (1.19)	15.88
Sm	-17136 (1307)	15.52 (1.02)	15.92
Eu	-17424 (1829)	15.94 (1.43)	16.42
Gd	-16760 (1425)	14.95 (1.12)	15.39
Y	-18848 (1191)	15.78 (0.93)	16.23
Ho	-18421 (1689)	15.32 (1.32)	15.78
Yb	-19749 (2115)	15.52 (1.66)	16.00
Lu	-20184 (2193)	15.49 (1.72)	15.91
Sc	-23414 (6317)	14.06 (4.95)	14.06

Chapter VI. Synthesis of trace-element doped anhydrite at high temperature in a CaCl_2 flux

6.1 Abstract

Synthetic anhydrite crystals have been grown by precipitation from a molten salt (CaCl_2) flux at temperatures 950 - 550°C using a cooling rate of 2°C/hr. Crystals are well formed, up to 2 mm in length and are generally free of inclusions of flux or other crystalline phases. Anhydrite crystals readily incorporate Sr and P during growth and are homogenous at the level of precision available by electron probe micro analyzer (EPMA). Uptake of rare earths in these experiments was inhibited by lack of a suitable charge balancing cation but with this addition it should also be possible to synthesis rare-earth doped anhydrite crystals, suitable for use as trace element standards.

6.2. Introduction

Anhydrite (CaSO_4) is a mineral common to many geologic environments, most notably in marine evaporites (Warren, 1999; Spencer, 2000) and to sulfur-rich magmatic-hydrothermal environments including sea-floor hydrothermal vents (Shikazono and Kusakabe, 1999) and the deep potassic alteration zone of porphyry copper deposits (Gustafson and Hunt 1975). Anhydrite has also been observed as a primary magmatic mineral (for review see Luhr, 2008) and may be a common, if ephemeral phase in sulfur-rich arc magmas (Chapter II of this study, Hutchinson and Dilles, 2019).

Many previous studies of anhydrite have focused on its sulfur isotopic composition ($\delta^{34}\text{S}$), and measurements of $\delta^{34}\text{S}$ in evaporitic anhydrite are commonly used to track the isotopic composition of past seawater sulfate (Holser, 1977; Claypool et al., 1980; Bottrell and Newton, 2006). $\delta^{34}\text{S}$ can also be measured in-situ in anhydrite using secondary ion mass spectrometry (SIMS) and studies by McKibben et al. (1996) and Luhr and Logan (2002) on magmatic anhydrite from Pinatubo and El Chichon showed significant intra-crystalline heterogeneity. Anhydrite also commonly contains measurable concentrations of trace elements including Na, P, Fe, Sr, Y, Ba and rare earth elements (REE) and these, particularly Sr, have been used to help distinguish hydrothermal from magmatic anhydrite (cf. Chambefort et al. 2008, Xiao et al. 2012 Chapter II of this study). Well characterized, matrix-matched standards are vital for the accurate in-situ measurement of both S isotopic composition and trace element concentrations. This is particularly true for SIMS analyses where mass fractionation during ablation can significantly affects measured ion yields.

Previous attempts at producing synthetic anhydrite have done so by first growing gypsum from aqueous solutions of CaCl_2 and alkali- SO_4 and then dehydrating gypsum at 800-900°C in order to produce anhydrite. Baumer et al. (1997) showed that by adding REE to the aqueous solutions, trace element doped gypsum (and anhydrite) could be produced for use as cathodoluminescence standards. Cody and Hull (1980) showed that using a variety of organic crystallization inhibitors anhydrite could also be grown directly from aqueous solutions at 60°C. However both methods produce crystals far too small ($<2\mu\text{m}$) for practical use as standards for SIMS, LA-ICP-MS or EPMA, which often require areas 5-50 μm for single analyses.

In this study we present a method for producing large (up to 2mm), homogenous, and variably doped anhydrite crystals.

6.3. Methods

6.3.1 *Synthesis of doped anhydrite crystals*

Following a procedure similar to that used to grow chlorapatite (Prener 1967), anhydrite crystals were here prepared by precipitation at high temperature from a molten CaCl_2 flux. Firstly reagent grade CaCl_2 and CaSO_4 were mixed according to a ratio of ~4:1 by weight (~5:1 mol). For trace element-doped experiments, trace element-bearing compounds were also added (Table 6.1) and the mixtures fused at 950°C for several hours in a platinum crucible. Rapid SO_2 loss from the mixture at temperatures $>950^\circ\text{C}$ prohibited fusion at higher temperatures, and necessitated the relatively high $\text{CaCl}_2 : \text{CaSO}_4$ ratio used. Experiments were then slowly cooled at a rate of 2°C/hr to a final temperature of 550°C over the course of ~8 days.

At the end of each experiment the platinum crucible was removed from the furnace and the CaCl_2 flux was leached using boiling water for ~1h in order to separate anhydrite crystals. Whereas anhydrite is soluble in H_2O at atmospheric pressure, its solubility decreases rapidly with increasing temperature between 20-100°C (Kelley et al. 1941) and there was no evidence of significant anhydrite dissolution during this process. Furthermore anhydrite is stable relative to gypsum in aqueous solutions at temperatures $>60^\circ\text{C}$ (Blount and Dickson 1973), such that anhydrite should not become hydrated during leaching of the flux.

6.3.2 *Analytical methods*

Polished anhydrite grains were analyzed for major and trace elements by EPMA using a Cameca SX-100. Beam conditions were 15kV, 30nA and a beam diameter of 1 μm . Counting times and detection limits are given in table 6.2.

Approximately 0.1g of anhydrite crystals from each experimental run were picked, cleaned again with boiling water, and crushed into a fine powder for analysis by powder x-ray diffraction (XRD). XRD analyses were performed using a Philips XRG 3100 x-ray generator with a APD 3520 controller at 27mA and 37kV. X-ray counts were measured at a 2θ angle of 5 - 60° with a 0.01° step length and a counting time of 2s at each step.

6.4 Results

Yield of anhydrite crystals for all experiments was approximately 50-70% of the starting CaSO_4 by mass, suggesting that either some CaSO_4 remained dissolved in the flux at the end of runs or that SO_2 was lost from the system even at the relatively low temperatures used. Anhydrite crystals were grown up to 2mm long and have blocky, equant morphology (Fig. 6.1). Characteristic cleavage is common and crystals are generally free of trapped inclusions of CaCl_2 flux. In experiment SynthAnh3 small light-blue crystals were also present as run products and qualitative energy-dispersive X-ray spectroscopy (EDS) analyses suggest they are F-Al bearing. The source of fluorine to the system is unknown but may be present in trace quantities in other starting materials, for example CaCl_2 .

Powder XRD results (Fig. 6.2) show sharp peaks, closely matching anhydrite reference spectra. No additional peaks were measured, indicating that the anhydrite crystals grown were free of inclusions of any secondary crystalline phases, for example apatite, which may have grown during experiments.

EPMA measurements anhydrite showed that measurable concentrations of P and Sr were present in anhydrite from doped synthesis runs “SynthAnh3” and “SynthAnh5” (Table 6.1, Fig 6.3). No trace elements were above detection limits in anhydrite from run “SynthAnh1”, consistent with a trace-element free starting material. Despite doping starting materials with La_2O_3 , none of the synthetic anhydrite produced in this study contained concentrations of La greater than the EPMA detection limit (320 ppm).

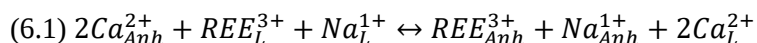
EPMA transects of single anhydrite crystals (Fig. 6.3), show trace element homogeneity relative to the uncertainties associated with EPMA analysis of these elements. This is somewhat surprising given the relatively low temperatures used (synthesis of trace element bearing apatite crystals by this method generally starts at temperatures $>1200^\circ\text{C}$, e.g. Klemme et al. 2013), but may in part be facilitated by the high flux : anhydrite ratio of the starting materials. The uncertainties associated with measuring low-abundance trace elements by EPMA (~10-25%) are relatively large and further investigation by more sensitive techniques, for example laser ablation-

inductively coupled plasmas-mass spectrometry (LA-ICP-MS), is needed to better determine the level of trace element homogeneity.

6.5 Discussion

Figure 6.3 shows that the Sr content of anhydrite is positively correlated with the Sr content of the starting material, and an average partition coefficient between anhydrite and CaCl_2 at 550-950°C can be estimated at ~0.18. P behaves somewhat differently, and despite a ~5 fold difference in the P content of doped synthesis runs, anhydrite P contents are similar. This may be related to contamination of starting materials. If either CaSO_4 or CaCl_2 also contained even a small amount of P the result would be a significant underestimate of the concentration of P in both starting materials. Alternatively, partitioning of P between CaCl_2 and anhydrite may be complicated by the need for a charge balancing cation (since P^{5+} likely replaces S^{6+} in the crystal structure of anhydrite). In this case the P content of anhydrite would be related to both the abundance of P in the starting material and the abundance of possible charge-balancing cations (for example La^{3+}). However in this case the partition coefficient between anhydrite and CaCl_2 should be higher in run “SynthAnh5”, contrary to what was measured. Finally, it is possible that Cl-apatite precipitated during the synthesis runs, effectively buffering the P content of the molten CaCl_2 and fixing the P content of growing anhydrite crystals. However, this is also unlikely, both because no evidence of apatite crystals was found in run products, and because the quantity of $\text{Ca}_3(\text{PO}_4)_2$ added (<1 wt%) should be easily dissolved at $T > 800^\circ\text{C}$ (see Fig.1 in Prener, 1967).

The lack of measurable La in anhydrite may be related to the relatively low abundance in the starting materials. However Chapter V of this study suggested that, as with P^{5+} , the partitioning of REE^{3+} into anhydrite requires a charge balancing cation (for example Na^{1+}) for reactions such as



The lack of a suitable 1+ cation in the starting material may have prohibited the inclusion of La^{3+} in the anhydrite crystal structure, accounting of the lack of measurable La concentrations in synthetic crystals.

6.6 Conclusion

We have shown that using a molten salt (CaCl_2) flux it is possible to synthesize large, homogenous, trace element doped anhydrite crystals at temperatures between 950°C - 550°C . Synthetic anhydrite readily incorporates Sr from the salt flux during growth with a partition coefficient of ~ 0.18 . The uptake of La was likely inhibited by the lack of an appropriate charge-balancing cation, for example Na, and future work should include adding NaCl_2 or similar Na-bearing component to starting materials in order to produce synthetic anhydrite with readily analyzable rare earth contents.

Synthetic anhydrite grow up to $\sim 2\text{mm}$ long and individual crystals are therefore suitable for use as standards for in situ analyses requiring large areas, for example LA-ICP-MS and SIMS. Although no attempt was made to grow anhydrite crystals with varying S-isotope abundances, this should also prove possible using this technique, given the appropriate sulfur source for starting materials.

6.7 References

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6.8 Figures and tables

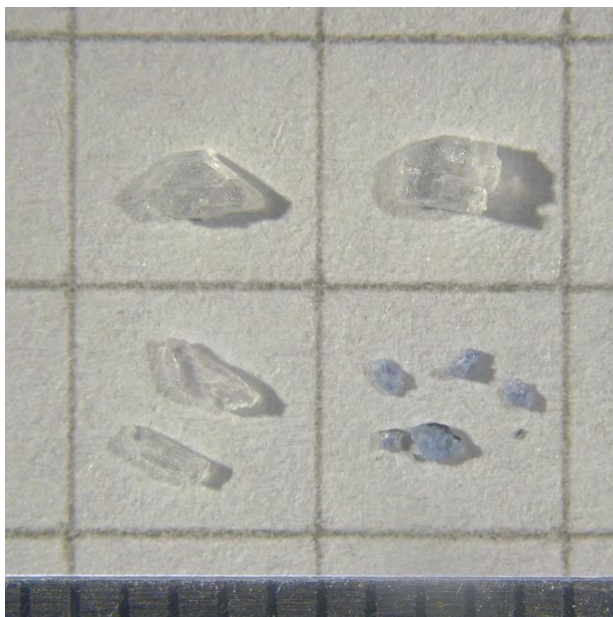


Figure 6.1 Photograph of synthetic anhydrite crystals from run “SynthAnh5”. Blue crystals, present in trace quantities (<1%) are F-Al bearing. Tick marks at bottom of figure are 1 mm.

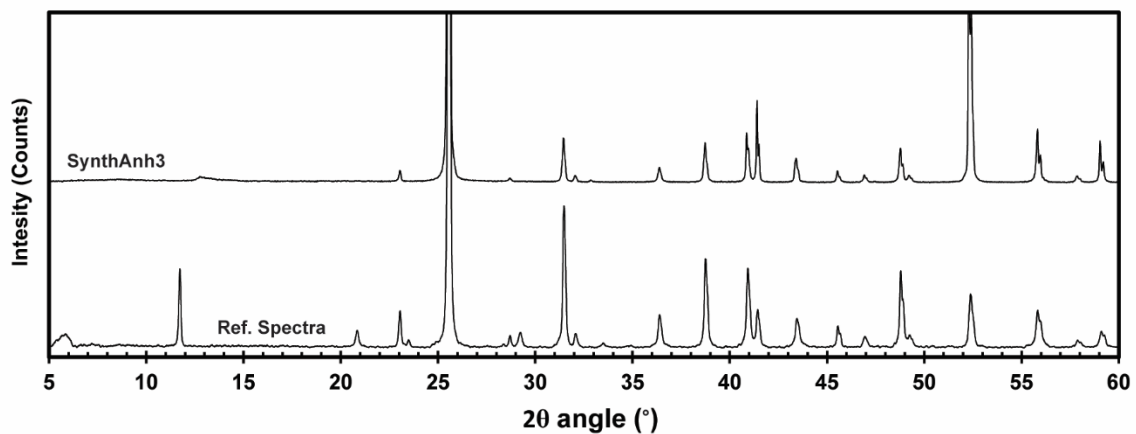


Figure 6.2 Comparison of powder XRD spectra of synthetic anhydrite crystals from run “SynthAnh3” with reference spectra taken from RRUFF database.

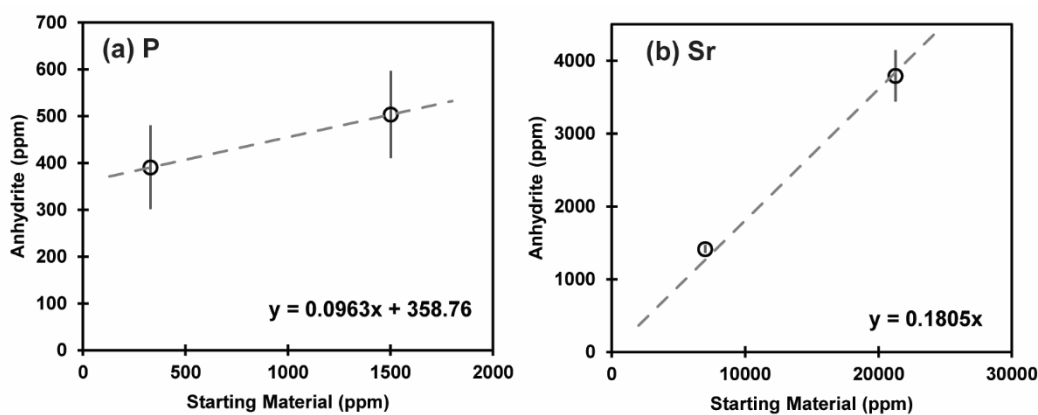


Figure 6.3 a) P and b) Sr abundances measured in synthetic anhydrite (by EMPA) compared to the starting material (weighed). Uncertainties shown are 2s.d. based on repeat analysis of single anhydrite grains (n=15-30).

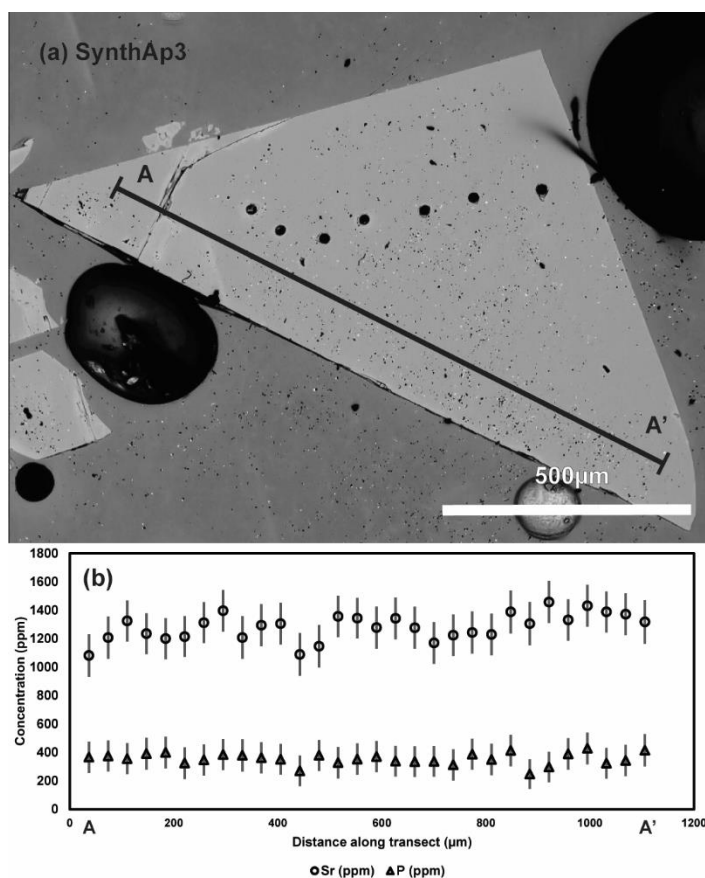


Figure 6.4 Back scattered electron (BSE) image of anhydrite crystal (a) and Sr and P concentrations with distance along transect (b). Position of probe transect A – A' is shown in (a). Uncertainties shown for individual analyses are 2s.d. based on counting statistics.

Table 6.1 Experiment starting materials

Run	weight added (g)				
	CaCl ₂	CaSO ₄	Ca ₃ (PO ₄) ₂	SrCl ₂	La ₂ O ₃
SynthAnh1	5.102	1.016	0.000	0.000	0.000
SynthAnh3	5.056	1.515	0.011	0.087	0.003
SynthAnh5	5.606	1.500	0.063	0.324	0.015

Table 6.2 EPMA analytical conditions

Accelerating Voltage	15kV		
Beam Current	30nA		
Spot Size	1 μ m		
Element	Spectrometer	Peak Time (s)	Det Limit (ppm)
Ca	PET	10	400
S	PET	20	600
P	LPET	40	110
Sr	LTAP, TAP	60	170
La	LPET, PET	40	320

Chapter VII. General Conclusions

This dissertation has been broadly aimed at characterizing the behavior of oxidized sulfur in hydrous, sulfur rich arc magmas which are closely associated with porphyry ore deposits. In particular it has been focused on the saturation of sulfate phases in these magmas, the conditions at which this might happen, and the implications for magmatic evolution, magmatic sulfur budgets and eventually for ore deposit formation.

Evidence presented in chapter II suggests, firstly, that sulfate saturation may be a common feature of ore forming magmas, and may be significantly underreported. By carefully preparing and scanning mineral separates I found small numbers of anhydrite inclusions hosted in plagioclase, titanite, amphibole, and, most commonly, apatite. Many of the samples came from areas that had been previously well studied, but in all cases this was the first report of magmatic anhydrite inclusions at these locations. Indeed at Yerington, anhydrite saturation had previously been proposed based on evidence from apatite sulfur contents (Streck and Dilles, 1998) and here I provide direct evidence, in the form of preserved anhydrite inclusions.

Chapter II also presents anhydrite compositional data, collected by EPMA, and CL images of magmatic zoning in the minerals hosting anhydrite inclusions. These are both useful in distinguishing magmatic anhydrite, precipitated due to sulfate saturation in a magma, from hydrothermal anhydrite, which precipitates from a hydrothermal fluid. Trace element abundances in anhydrite, particularly Sr, can be interpreted based on the partition coefficients presented in Chapter V in order to estimate the conditions at which anhydrite precipitated.

Since anhydrite was most commonly found as an inclusion in apatite, and since apatite incorporates oxidized sulfur into its crystal structure, Chapter III follows by investigating the sulfur content of apatites from the same anhydrite-saturated rocks. Using volcanic rocks, previous studies have shown that it is possible to track the volatile evolution of a system by analyzing apatite inclusions trapped in various silicate phases (Stock et al. 2018). In this chapter I attempted a similar study, and showed that in all cases anhydrite bearing rocks also contained high-sulfur apatite. Unfortunately the sulfur content of apatites produced little in the way of coherent trends when compared to various proxies for the geochemical evolution of the magma. It is likely that during the slow cooling of plutonic rocks such trends might be obscured by low temperature reequilibration and exchange between apatite and host. Although the study of apatite remains a fruitful avenue for investigating the evolution of sulfur in magmatic systems, it is currently hampered by a lack of experimental data on sulfur partitioning between apatite and melt.

The experimental work presented in chapters IV and V had two principal goals – to identify the conditions at which immiscible sulfate melt is likely to be stable in arc magmas, and to characterize the partitioning of trace elements between silicate melt and sulfate phases, both anhydrite and sulfate melt. Results in chapter IV show that sulfate melt is generally present above $\sim 1000^{\circ}\text{C}$ but may be stable to lower temperatures in water or alkali rich magmas. This implies that in order for a typical arc magma to be saturated in sulfate melt, it must be particularly sulfur rich. Sulfate melts contain a significant amount of Cl, and their separation from silicate melts during magmatic evolution in the mid – deep crust may help to concentrate sulfur and chlorine, both critical ore forming ingredients.

Chapter V presents anhydrite – silicate melt and sulfate melt – silicate melt partitioning data for trace elements as measured by SIMS and LA-ICP-MS. Sulfate – silicate melt partition coefficients appear to vary systematically as a function of the ionic potential of elements, with those close to the major cations, i.e. Ca and S, being compatible in the sulfate melt. Partition coefficients for many elements are more than an order of magnitude lower than those previously published, and are lower in experiments with a more mafic, less polymerized, silicate melt. This suggests that partition coefficients between sulfate melt and primitive, high temperature melts are likely to be low for most elements, and the fractionation of small amount of sulfate melt may not impart a detectable trace element signature on the silicate melt.

Partition coefficients for +2 and +3 cations between anhydrite and silicate melt are well modelled as exchange reactions between the cation in the silicate melt and Ca in the anhydrite. As such the CaO content of the silicate melt exerts a first order control on partitioning. Beyond this, partition coefficients are also dependent on temperature and increase exponentially as temperature increases. Using these composition and temperature dependent partition coefficients it is possible to assess the expected trace element content of anhydrite crystallizing from an evolving silicate melt. In order to illustrate this, the crystallization of the Luhr Hill batholith, Yerington, NV has been modelled and the Sr content of anhydrite crystallizing at each temperature calculated. Comparing these results to the Sr content of anhydrite measured from the Luhr Hill indicates that anhydrite crystallized at temperatures between $900 - 1000^{\circ}\text{C}$ but that the Sr content of apatite hosted anhydrite may have reequilibrated at close to eutectic temperatures, as suggested in chapter II.

Finally we have shown that it is possible to grow trace element doped anhydrite crystals at high temperature from a molten salt (CaCl_2) flux. Further work needs to be done to show that anhydrite can be grown with measurable REE contents and with homogenous and varied S

isotopic signatures. If so, synthetic anhydrite crystals should have a broad utility as standards for in-situ trace element and isotope analyses, and possibly also as starting materials for sulfate saturated experiments.

Previous to this study, little was known about the conditions at which sulfate melts are stable in nature, or their major and trace element composition. Although anhydrite was recognized as a primary igneous phase as early as 1982 (at El Chichon, Luhr 1984), only one set of partition coefficients, based on whole crystal INAA measurements, had been published. This study supports the idea that sulfate saturated magmas are relatively common in arc environments and provides a framework for understanding at what conditions sulfate melt might be present in place of anhydrite. Furthermore, characterization of sulfate-silicate partitioning provides context for interpreting anhydrite trace element compositions and for exploring the effect of the fractionation of sulfate phases from an evolving magma.

Significantly, this work also offers tools for estimating the sulfur budgets of low temperature, sulfate saturated magmas. Sulfur solubility is low in silicate melts at low temperature, and the majority of the sulfur in these systems may be present as anhydrite. Because most of this anhydrite is not preserved in the rock record, it is a challenge to reconstruct the total sulfur budgets of these magmas. However if the temperature at which anhydrite began to crystallize is known, this can be used to calculate the sulfur content of the coexisting melt, providing an estimate for the total magmatic sulfur budget. I have shown that using temperature-sensitive trace element partitioning it is possible to determine the approximate temperature of anhydrite crystallization, and to estimate minimum sulfur budgets. A similar approach can be used for “wormy anhydrite” at Yanacocha, calculating a minimum temperature based on the lower temperature limit of sulfate melt stability.

The application of this novel method for estimating sulfur budgets should be broadly applicable and will help to determine if the magmas which generate ore deposits are anomalously sulfur rich. Given the large quantities of sulfur contained in many porphyry and epithermal ore deposits this might be expected, but has never been shown to date. If this is the case, then a high magmatic sulfur budget might play a key role in determining magmatic fertility and could potentially be used as an aid in regional exploration targeting.

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Appendices

Appendix A1 - EPMA analytical conditions for apatite, amphibole and titanite analyses

Table A1.1 EPMA analytical conditions for apatite

Apatite			
Condition 1			
Accelerating Voltage	15kV		
Beam Current	10nA		
Spot Size	2µm		
Element	Spectrometer	Peak Time (s)	Det Limit (ppm)
F	1 - PC0	30	3150
P	2 - LTAP	30	440
Cl	3 - LPET	30	380
Fe	4 - LIF	30	870
Ca	5 - PET	30	440
Condition 2			
Accelerating Voltage	15kV		
Beam Current	20nA		
Spot Size	2µm		
Element	Spectrometer	Peak Time (s)	Det Limit (ppm)
Na	1 - PC0	60	350
Si	2 - LTAP	20	130
Sr	2 - LTAP	40	310
S	3 - LPET	30	120
Ce	3 - LPET	30	470
Fe	4 - LIF	60	870
S	5 - PET	30	120
Ce	5 - PET	30	470

Table A1.2 EPMA analytical conditions for amphibole

Amphibole			
Condition 1			
Accelerating Voltage	15kV		
Beam Current	30nA		
Spot Size	5µm		
Element	Spectrometer	Peak Time (s)	Det Limit (ppm)
Si	1 - TAP	20	370
Al	1 - TAP	20	230
Na	2 - LTAP	30	200
Mg	2 - LTAP	20	160
Cl	3 - LPET	40	110
Ti	3 - LPET	20	180
Mn	4 - LIF	30	490
Fe	4 - LIF	30	310
K	5 - PET	30	240
Ca	5 - PET	30	180
Condition 2			
Accelerating Voltage	15kV		
Beam Current	60nA		
Spot Size	5µm		
Element	Spectrometer	Peak Time (s)	Det Limit (ppm)
F	1 - TAP	120	180
F	2 - LTAP	120	180
S	3 - LPET	120	55
Cr	4 - LIF	120	240
S	5 - PET	120	55

Table A1.3 EPMA analytical conditions for titanite

Titanite			
Condition 1			
Accelerating Voltage	15kV		
Beam Current	100nA		
Spot Size	5µm		
Element	Spectrometer	Peak Time (s)	Det Limit (ppm)
Si	1 - TAP	20	130
Al	1 - TAP	20	120
F	1 - TAP	120	40
Y	2 - LTAP	60	110
F	2 - LTAP	120	40
Cl	3 - LPET	60	50
Nb	3 - LPET	40	210
Zr	3 - LPET	80	160
Mn	4 - LIF	60	210
Fe	4 - LIF	60	250
V	4 - LIF	60	280
Ca	5 - PET	20	130
Ti	5 - PET	20	190
Ce	5 - PET	140	230

Appendix A2 – Apatite major and trace element concentrations

Table A2.1 Apatite major and trace element concentrations

		wt %																	
Sample	Host Mineral	CaO	P ₂ O ₅	F	Cl	SiO ₂	SO ₃	Ce ₂ O ₃	Na ₂ O	FeO	SrO	O = F,Cl	Total	X _F	X _{OH}	X _{Cl}			
LH-1	Phenocryst Core	54.68	40.79	4.03	0.04	0.26	0.39	0.19	0.15	0.03	0.13	-1.706	98.99	108.55	-9.13	0.58			
LH-1	Phenocryst Core	55.24	41.57	3.97	0.02	0.20	0.20	0.24	0.07	0.07	0.14	-1.674	100.03	105.57	-5.87	0.30			
LH-1	Phenocryst Core	55.13	41.66	4.58	0.02	0.13	0.15	0.14	0.09	0.02	0.12	-1.931	100.10	122.12	-22.34	0.22			
LH-1	Phenocryst Core	54.97	41.49	3.19	0.02	0.14	0.16	0.17	0.05	0.01	0.11	-1.347	98.96	85.39	14.35	0.26			
LH-1	Phenocryst Core	54.99	42.08	3.49	0.02	0.14	0.18	0.17	0.05	0.07	0.14	-1.475	99.87	92.63	7.09	0.29			
LH-1	Phenocryst Core	55.09	41.44	3.91	0.00	0.11	0.13	0.13	0.05	0.00	0.15	-1.648	99.37	104.90	-4.90	0.00			
LH-1	Phenocryst Core	54.90	41.18	4.02	0.00	0.14	0.12	0.15	0.05	0.05	0.16	-1.691	99.08	108.09	-8.09	0.00			
LH-1	Phenocryst Core	54.70	41.74	3.24	0.00	0.16	0.19	0.20	0.05	0.03	0.12	-1.363	99.07	86.41	13.59	0.00			
LH-1	Phenocryst Core	55.06	41.86	3.40	0.08	0.12	0.18	0.15	0.05	0.00	0.09	-1.449	99.55	90.40	8.42	1.17			
LH-1	Phenocryst Core	55.34	41.88	3.03	0.01	0.09	0.19	0.09	0.04	0.00	0.13	-1.279	99.53	80.52	19.30	0.18			
LH-1	Phenocryst Core	55.15	40.75	4.56	0.04	0.11	0.11	0.16	0.04	0.03	0.15	-1.931	99.16	123.45	-24.06	0.61			
LH-1	Phenocryst Core	55.49	41.62	4.17	0.01	0.16	0.11	0.17	0.05	0.00	0.13	-1.758	100.16	111.07	-11.22	0.51			
LH-1	Phenocryst Core	55.18	41.74	3.27	0.04	0.11	0.18	0.11	0.03	0.01	0.14	-1.386	99.42	87.26	12.23	0.51			
LH-1	Phenocryst Core	54.46	41.08	4.15	0.02	0.22	0.20	0.21	0.07	0.00	0.13	-1.752	98.80	111.97	-12.26	0.28			
LH-1	Phenocryst Core	54.95	41.40	3.86	0.00	0.12	0.15	0.12	0.07	0.00	0.12	-1.625	99.18	103.54	-3.54	0.00			
LH-1	Phenocryst Core	55.03	41.99	3.29	0.01	0.16	0.21	0.13	0.05	0.03	0.14	-1.387	99.64	87.34	12.54	0.12			
LH-1	Phenocryst Rim	54.67	41.07	4.11	0.04	0.27	0.21	0.30	0.08	0.01	0.13	-1.740	99.15	110.61	-11.15	0.54			
LH-1	Phenocryst Rim	54.28	41.39	3.92	0.04	0.10	0.17	0.11	0.08	0.04	0.13	-1.661	98.61	105.75	-6.32	0.57			
LH-1	Phenocryst Rim	54.70	41.90	4.42	0.02	0.13	0.14	0.14	0.08	0.01	0.14	-1.866	99.81	117.97	-18.21	0.23			
LH-1	Phenocryst Rim	55.08	41.47	3.33	0.03	0.12	0.15	0.15	0.04	0.00	0.13	-1.408	99.11	89.15	10.47	0.38			
LH-1	Phenocryst Rim	54.91	41.73	3.32	0.00	0.09	0.16	0.12	0.06	0.00	0.11	-1.399	99.13	88.73	11.23	0.04			
LH-1	Phenocryst Rim	54.98	41.62	4.06	0.00	0.10	0.12	0.10	0.04	0.00	0.13	-1.709	99.44	108.66	-8.67	0.01			
LH-1	Phenocryst Rim	55.05	41.69	3.72	0.02	0.09	0.11	0.12	0.05	0.00	0.15	-1.571	99.44	99.44	0.32	0.25			
LH-1	Phenocryst Rim	54.91	41.64	3.23	0.00	0.21	0.23	0.22	0.05	0.05	0.12	-1.359	99.29	86.03	13.97	0.00			
LH-1	Phenocryst Rim	55.12	41.41	2.98	0.04	0.18	0.19	0.19	0.05	0.07	0.13	-1.265	99.10	79.72	19.71	0.57			
LH-1	Phenocryst Rim	54.62	41.60	2.99	0.00	0.20	0.17	0.20	0.03	0.01	0.13	-1.258	98.68	79.99	20.01	0.00			
LH-1	Phenocryst Rim	54.55	41.33	4.16	0.03	0.11	0.14	0.13	0.07	0.00	0.13	-1.758	98.90	112.09	-12.50	0.41			
LH-1	Phenocryst Rim	54.94	41.08	4.14	0.02	0.11	0.11	0.12	0.05	0.00	0.15	-1.749	98.98	111.80	-12.02	0.23			
LH-1	Phenocryst Rim	55.06	42.36	3.04	0.04	0.13	0.15	0.12	0.03	0.00	0.15	-1.290	99.80	80.38	18.99	0.63			
LH-1	Phenocryst Rim	54.56	41.44	4.33	0.03	0.14	0.19	0.19	0.09	0.00	0.13	-1.831	99.28	116.33	-16.72	0.39			
LH-1	Phenocryst Rim	54.95	41.68	4.43	0.00	0.11	0.12	0.14	0.07	0.01	0.13	-1.864	99.77	118.30	-18.33	0.02			
LH-1	Phenocryst Rim	55.43	41.59	3.32	0.00	0.13	0.18	0.11	0.06	0.00	0.14	-1.400	99.56	88.59	11.39	0.01			
LH-1	Amphibole	54.68	40.26	4.14	0.02	0.54	0.88	0.28	0.20	0.42	0.12	-1.749	99.80	110.87	-11.13	0.26			
LH-1	Amphibole	54.83	41.43	3.85	0.01	0.35	0.25	0.31	0.04	0.16	0.10	-1.622	99.71	102.65	-2.73	0.08			
LH-1	Amphibole	54.80	41.00	3.96	0.02	0.31	0.53	0.21	0.14	0.29	0.11	-1.674	99.71	105.84	-6.19	0.35			
LH-1	Amphibole	54.67	41.20	3.88	0.01	0.42	0.68	0.19	0.17	0.38	0.13	-1.638	100.10	103.11	-3.30	0.19			
LH-1	Amphibole	54.89	41.86	3.47	0.02	0.31	0.31	0.22	0.06	0.15	0.12	-1.465	99.95	91.90	7.85	0.25			
LH-1	Amphibole	54.84	41.54	3.49	0.01	0.32	0.24	0.23	0.05	0.13	0.13	-1.472	99.51	93.06	6.82	0.13			
LH-1	Amphibole	54.71	41.45	3.45	0.03	0.28	0.28	0.26	0.07	0.26	0.13	-1.457	99.46	91.93	7.67	0.40			
LH-1	Amphibole	55.17	41.93	3.63	0.00	0.17	0.41	0.13	0.15	0.24	0.13	-1.527	100.44	95.81	4.19	0.00			
LH-1	Amphibole	55.29	41.60	3.67	0.02	0.13	0.48	0.12	0.18	0.17	0.12	-1.550	100.23	97.30	2.45	0.26			
LH-1	Amphibole	55.12	41.58	3.67	0.02	0.39	0.27	0.33	0.07	0.27	0.12	-1.550	100.28	97.30	2.40	0.30			
LH-1	Amphibole	55.35	41.28	4.09	0.02	0.31	0.27	0.26	0.08	0.29	0.16	-1.726	100.38	108.85	-9.07	0.22			
LH-1	Amphibole	55.06	41.18	3.94	0.01	0.32	0.60	0.21	0.14	0.34	0.14	-1.663	100.29	104.75	-4.87	0.12			
LH-1	Amphibole	55.00	41.12	3.93	0.01	0.38	0.56	0.23	0.15	0.37	0.14	-1.657	100.22	104.40	-4.57	0.18			
LH-1	Amphibole	55.28	41.39	3.69	0.04	0.29	0.41	0.21	0.09	0.24	0.13	-1.561	100.18	97.91	1.54	0.55			
LH-1	Amphibole	55.01	41.36	3.65	0.03	0.33	0.33	0.22	0.07	0.29	0.13	-1.543	99.87	97.12	2.47	0.41			
LH-1	Amphibole	55.16	41.88	3.98	0.00	0.22	0.16	0.14	0.07	0.42	0.11	-1.676	100.47	105.46	-5.46	0.00			
LH-1	Amphibole	55.04	41.50	3.77	0.01	0.34	0.72	0.19	0.16	0.39	0.11	-1.589	100.64	99.35	0.48	0.18			
LH-1	Amphibole	54.86	41.35	3.55	0.00	0.40	0.58	0.18	0.13	0.36	0.14	-1.496	100.06	94.19	5.81	0.00			
LH-1	Amphibole	55.22	41.50	3.69	0.02	0.28	0.18	0.26	0.04	0.24	0.13	-1.558	100.01	98.16	1.56	0.28			
LH-1	Amphibole	54.56	41.47	4.12	0.01	0.36	0.21	0.32	0.04	0.52	0.13	-1.736	99.99	109.77	-9.89	0.12			
LH-1	Amphibole	54.92	42.37	3.92	0.01	0.11	0.18	0.12	0.06	0.52	0.12	-1.651	100.69	103.29	-3.47	0.18			
LH-1	Amphibole	55.39	41.62	4.18	0.01	0.28	0.23	0.21	0.08	0.31	0.13	-1.761	100.67	110.66	-10.85	0.19			
LH-1	Amphibole	55.11	41.42	4.11	0.00	0.37	0.27	0.24	0.10	0.53	0.12	-1.732	100.55	109.13	-9.16	0.04			
LH-1	Amphibole	55.42	41.33	3.60	0.00	0.26	0.38	0.18	0.12	0.35	0.14	-1.516	100.26	95.56	4.38	0.05			
LH-1	Amphibole	54.76	41.65	4.01	0.02	0.25	0.35	0.17	0.11	0.04	0.12	-1.695	99.77	106.88	-7.16	0.28			
LH-1	Amphibole	55.10	41.66	3.75	0.02	0.21	0.27	0.20	0.07	0.07	0.15	-1.581	99.91	99.61	0.15	0.24			

Table A2.1 Apatite major and trace element concentrations (continued)

LH-1	Amphibole	55.42	41.64	3.88	0.02	0.22	0.25	0.15	0.08	0.11	0.14	-1.640	100.27	103.05	-3.37	0.32
LH-1	Amphibole	55.30	41.32	3.59	0.02	0.35	0.30	0.27	0.06	0.39	0.13	-1.517	100.23	95.39	4.30	0.31
LH-1	Amphibole	55.55	41.87	4.11	0.02	0.24	0.23	0.24	0.07	0.13	0.13	-1.737	100.85	108.66	-8.98	0.32
LH-1	Amphibole	55.00	41.46	3.39	0.01	0.38	0.28	0.24	0.04	0.46	0.12	-1.428	99.94	89.99	9.92	0.09
LH-1	Amphibole	54.92	41.13	3.32	0.00	0.33	0.73	0.16	0.20	0.38	0.10	-1.399	99.87	88.19	11.81	0.00
LH-1	Amphibole	55.13	41.74	4.10	0.02	0.25	0.20	0.22	0.06	0.37	0.15	-1.729	100.50	108.63	-8.88	0.25
LH-1	Amphibole	55.34	41.41	3.54	0.00	0.23	0.22	0.19	0.07	0.20	0.11	-1.490	99.81	94.29	5.71	0.00
LH-1	Amphibole	55.03	40.75	4.01	0.00	0.54	1.18	0.25	0.28	0.43	0.13	-1.689	100.91	105.73	-5.76	0.02
LH-1	Amphibole	55.00	41.99	3.95	0.01	0.28	0.23	0.18	0.06	0.48	0.14	-1.667	100.66	104.46	-4.61	0.15
LH-1	Amphibole	55.16	41.90	3.93	0.02	0.13	0.03	0.17	0.04	0.39	0.11	-1.659	100.21	104.48	-4.74	0.26
LH-1	Amphibole	54.85	41.84	4.07	0.00	0.19	0.19	0.17	0.09	0.28	0.13	-1.714	100.10	108.23	-8.23	0.00
LH-1	Amphibole	55.14	42.21	3.71	0.01	0.16	0.19	0.17	0.06	0.25	0.13	-1.563	100.45	97.96	1.95	0.09
LH-1	Amphibole	54.55	41.05	4.04	0.00	0.43	0.76	0.22	0.21	0.45	0.13	-1.703	100.12	107.47	-7.47	0.00
LH-1	Amphibole	54.95	41.40	3.87	0.00	0.32	0.24	0.28	0.07	0.27	0.10	-1.632	99.89	103.24	-3.30	0.06
LH-1	Amphibole	54.96	41.68	3.78	0.00	0.34	0.25	0.23	0.08	0.37	0.11	-1.591	100.20	100.24	-0.24	0.00
LH-1	Amphibole	54.27	40.80	4.04	0.02	0.47	0.60	0.28	0.15	0.32	0.12	-1.706	99.37	108.27	-8.54	0.27
LH-1	Amphibole	54.83	41.88	3.88	0.00	0.28	0.41	0.20	0.11	0.29	0.14	-1.634	100.40	102.61	-2.61	0.00
LH-1	Amphibole	54.92	41.59	4.03	0.00	0.19	0.17	0.16	0.05	0.26	0.11	-1.697	99.79	107.57	-7.57	0.00
LH-1	Amphibole	55.02	41.54	3.88	0.02	0.36	0.40	0.25	0.12	0.16	0.11	-1.636	100.22	102.80	-3.06	0.26
LH-1	Amphibole	55.45	41.66	4.21	0.01	0.35	0.53	0.24	0.16	0.15	0.13	-1.773	101.11	110.76	-10.89	0.13
LH-1	Amphibole	55.18	41.11	3.88	0.01	0.48	0.28	0.34	0.07	0.48	0.12	-1.637	100.31	103.32	-3.40	0.08
LH-1	Amphibole	54.84	41.61	3.89	0.02	0.34	0.27	0.22	0.06	0.39	0.12	-1.641	100.11	103.30	-3.54	0.24
LH-1	Amphibole	54.54	41.78	3.78	0.01	0.30	0.36	0.21	0.10	0.18	0.13	-1.593	99.79	100.43	-0.52	0.09
LH-1	Amphibole	55.67	41.96	3.47	0.02	0.13	0.14	0.08	0.05	0.26	0.15	-1.466	100.46	91.80	7.89	0.31
LH-1	Amphibole	55.74	41.77	3.49	0.00	0.15	0.15	0.11	0.05	0.38	0.16	-1.469	100.52	92.36	7.64	0.00
LH-1	Amphibole	55.35	41.66	4.07	0.01	0.17	0.14	0.16	0.07	0.18	0.13	-1.718	100.24	108.36	-8.51	0.16
LH-1	Amphibole	55.36	40.98	3.40	0.00	0.31	0.27	0.27	0.04	0.16	0.14	-1.431	99.49	90.86	9.08	0.06
LH-1	Amphibole	54.90	41.47	3.77	0.01	0.30	0.40	0.20	0.12	0.34	0.13	-1.590	100.05	100.28	-0.36	0.08
LH-1	Biotite	55.43	42.23	3.83	0.00	0.07	0.34	0.03	0.12	0.25	0.18	-1.611	100.88	100.75	-0.75	0.00
LH-1	Biotite	55.00	41.39	4.11	0.01	0.35	0.64	0.12	0.17	0.15	0.18	-1.733	100.38	108.95	-9.04	0.09
LH-1	Biotite	54.97	41.30	4.17	0.00	0.53	0.66	0.09	0.14	0.57	0.19	-1.757	100.86	110.18	-10.22	0.04
LH-1	Biotite	54.95	42.05	3.62	0.02	0.24	0.29	0.10	0.04	0.36	0.12	-1.528	100.26	95.66	4.06	0.28
LH-1	Biotite	55.31	41.72	4.22	0.02	0.25	0.15	0.24	0.07	0.27	0.12	-1.783	100.59	112.05	-12.33	0.28
LH-1	Biotite	54.62	41.62	3.78	0.02	0.24	0.25	0.18	0.04	0.09	0.12	-1.597	99.38	100.95	-1.29	0.33
LH-1	Biotite	54.84	41.85	3.76	0.00	0.23	0.23	0.18	0.06	0.24	0.13	-1.581	99.95	99.75	0.25	0.00
LH-1	Biotite	55.10	41.78	3.67	0.01	0.33	0.31	0.28	0.05	0.41	0.13	-1.549	100.53	97.05	2.81	0.14
LH-1	Biotite	55.64	41.80	3.94	0.01	0.15	0.20	0.12	0.06	0.17	0.13	-1.660	100.56	104.35	-4.45	0.10
LH-1	Magnetite	55.07	41.32	3.45	0.16	0.26	0.47	0.24	0.11	1.33	0.23	-1.488	101.15	91.18	6.62	2.20
LH-1	Magnetite	55.02	41.45	2.99	0.09	0.30	0.56	0.25	0.14	0.95	0.22	-1.280	100.70	78.91	19.80	1.29
LH-1	Magnetite	54.53	41.40	3.50	0.11	0.28	0.48	0.19	0.13	0.99	0.23	-1.499	100.36	92.83	5.54	1.62
LH-1	Magnetite	54.24	41.18	3.70	0.17	0.27	0.39	0.21	0.10	2.09	0.19	-1.595	100.95	98.14	-0.56	2.41
LH-1	Magnetite	54.23	40.70	3.60	0.03	0.32	0.35	0.24	0.08	1.97	0.20	-1.522	100.20	96.21	3.31	0.48
LH-1	Magnetite	54.99	41.73	3.47	0.03	0.20	0.19	0.22	0.07	1.55	0.23	-1.468	101.22	91.60	8.00	0.40
LH-1	Magnetite	54.72	40.91	3.55	0.18	0.40	0.51	0.25	0.13	1.40	0.21	-1.537	100.74	94.33	3.06	2.62
LH-1	Magnetite	54.97	41.62	3.70	0.02	0.26	0.21	0.19	0.07	1.30	0.11	-1.563	100.89	97.95	1.79	0.26
LH-1	Magnetite	54.56	41.06	3.32	0.14	0.34	0.32	0.28	0.06	0.91	0.20	-1.429	99.75	88.72	9.33	1.95
LH-1	Magnetite	55.15	41.24	3.62	0.13	0.30	0.35	0.28	0.06	1.09	0.20	-1.555	100.87	96.03	2.09	1.88
LH-1	Magnetite	54.47	40.49	3.21	0.14	0.32	0.56	0.24	0.13	1.63	0.23	-1.381	100.03	85.73	12.32	1.95
LH-1	Magnetite	54.96	41.37	3.34	0.17	0.31	0.28	0.26	0.06	1.27	0.25	-1.445	100.83	88.56	9.09	2.35
LH-1	Magnetite	54.86	41.07	3.21	0.15	0.31	0.37	0.25	0.06	1.46	0.24	-1.383	100.59	85.14	12.76	2.10
LH-1	Magnetite	54.94	41.14	3.30	0.20	0.21	0.59	0.14	0.16	1.59	0.20	-1.435	101.03	87.34	9.81	2.85
LH-1	Magnetite	54.58	41.49	3.36	0.12	0.34	0.36	0.30	0.05	1.27	0.23	-1.441	100.67	88.84	9.39	1.77
LH-1	Magnetite	55.23	41.85	3.32	0.09	0.20	0.23	0.19	0.07	1.69	0.10	-1.419	101.55	87.30	11.44	1.26
LH-1	Magnetite	54.89	41.34	3.02	0.09	0.24	0.70	0.18	0.15	1.51	0.17	-1.294	101.02	79.67	19.03	1.29
LH-1	Magnetite	54.72	41.19	3.49	0.18	0.26	0.32	0.24	0.10	1.49	0.28	-1.508	100.74	92.63	4.85	2.51
LH-1	Magnetite	54.70	41.02	3.25	0.09	0.31	0.59	0.21	0.15	1.45	0.22	-1.389	100.60	86.24	12.54	1.22
LH-1	Magnetite	54.65	41.32	3.12	0.13	0.41	0.58	0.30	0.13	1.19	0.22	-1.342	100.71	82.27	15.83	1.90
LH-1	Magnetite	54.72	41.28	3.02	0.12	0.24	0.39	0.16	0.07	1.99	0.20	-1.299	100.88	79.90	18.37	1.73
LH-1	Magnetite	52.85	40.35	2.93	0.11	0.51	0.50	0.22	0.12	1.90	0.18	-1.260	98.41	79.30	19.09	1.61
LH-1	Plagioclase	55.64	41.71	3.81	0.02	0.15	0.08	0.19	0.03	0.03	0.14	-1.609	100.20	101.30	-1.55	0.25
LH-1	Plagioclase	55.49	41.50	4.15	0.00	0.16	0.09	0.18	0.05	0.07	0.12	-1.747	100.07	110.71	-10.71	0.00

Table A2.1 Apatite major and trace element concentrations (continued)

LH-1	Titanite	55.65	41.72	4.12	0.02	0.06	0.02	0.10	0.02	0.04	0.16	-1.737	100.17	109.72	-9.97	0.25
LH-1	Titanite	55.78	40.84	4.31	0.01	0.28	0.33	0.18	0.12	0.03	0.12	-1.818	100.18	115.27	-15.38	0.11
LH-1	Titanite	55.73	40.88	4.25	0.01	0.34	0.62	0.19	0.17	0.08	0.14	-1.792	100.61	112.91	-13.03	0.13
LH-1	Titanite	55.18	40.85	3.88	0.00	0.31	0.26	0.30	0.06	0.06	0.11	-1.632	99.38	104.02	-4.02	0.00
LH-1	Titanite	55.38	41.14	3.86	0.01	0.29	0.47	0.18	0.14	0.02	0.14	-1.627	99.99	102.70	-2.89	0.18
LH-1	Titanite	55.66	41.39	4.02	0.02	0.20	0.17	0.16	0.05	0.05	0.15	-1.698	100.18	107.15	-7.41	0.27
LH-1	Titanite	55.35	40.73	3.87	0.04	0.25	0.54	0.21	0.18	0.06	0.20	-1.638	99.80	103.48	-4.03	0.55
LH-1	Titanite	55.47	40.83	3.74	0.03	0.31	0.25	0.31	0.08	0.06	0.12	-1.583	99.62	100.31	-0.71	0.40
LH-1	Titanite	55.29	41.01	3.57	0.01	0.32	0.44	0.25	0.15	0.04	0.12	-1.505	99.69	95.25	4.61	0.14
LH-1	Titanite	54.90	41.51	2.88	0.53	0.24	0.05	0.31	0.03	0.10	0.18	-1.332	99.40	76.97	15.37	7.66
LH-1	Titanite	55.30	40.42	3.51	0.03	0.34	0.69	0.17	0.15	0.05	0.13	-1.486	99.31	94.20	5.42	0.38
LH-1	Titanite	55.84	41.63	4.30	0.01	0.12	0.14	0.12	0.05	0.05	0.12	-1.814	100.57	114.29	-14.46	0.17
LH-1	Titanite	55.07	40.73	3.53	0.09	0.40	0.74	0.30	0.21	0.12	0.13	-1.506	99.81	93.94	4.72	1.34
LH-1	Titanite	55.77	41.84	3.43	0.09	0.07	0.00	0.14	0.01	0.01	0.16	-1.464	100.05	91.17	7.55	1.28
LH-1	Titanite	54.99	41.16	3.09	0.10	0.27	0.41	0.26	0.11	0.05	0.17	-1.323	99.28	82.51	16.09	1.39
LH-1	Titanite	55.46	40.86	3.55	0.01	0.32	0.34	0.26	0.11	0.10	0.14	-1.497	99.66	94.89	4.94	0.17
LH-1	Titanite	55.54	42.04	3.77	0.04	0.08	0.15	0.05	0.05	0.03	0.15	-1.597	100.31	99.94	-0.51	0.57
LH-1	Titanite	55.71	41.61	4.11	0.01	0.22	0.18	0.24	0.03	0.06	0.12	-1.734	100.57	109.07	-9.27	0.20
LH-1	Titanite	55.81	41.41	4.48	0.00	0.26	0.23	0.24	0.07	0.00	0.13	-1.887	100.75	118.93	-19.00	0.07
LH-1	Titanite	55.29	41.06	3.60	0.04	0.26	0.24	0.27	0.13	0.00	0.12	-1.524	99.47	96.40	3.09	0.51
LH-1	Titanite	55.45	41.07	3.72	0.00	0.32	0.47	0.21	0.12	0.12	0.13	-1.568	100.05	99.12	0.88	0.00
LH-1	Titanite	55.00	40.85	4.07	0.03	0.39	0.57	0.31	0.20	0.05	0.15	-1.719	99.88	108.53	-8.96	0.43
LH-1	Titanite	55.31	40.90	2.76	0.20	0.29	0.41	0.24	0.10	0.02	0.20	-1.207	99.22	73.86	23.31	2.83
LH-1	Titanite	55.66	40.94	3.84	0.02	0.31	0.25	0.26	0.05	0.14	0.13	-1.623	99.98	102.67	-2.96	0.29
LH-1	Titanite	55.37	40.93	4.03	0.01	0.31	0.29	0.29	0.09	0.00	0.13	-1.699	99.76	107.81	-8.01	0.21
LH-1	Titanite	55.65	41.79	4.05	0.02	0.19	0.22	0.20	0.04	0.03	0.13	-1.708	100.62	107.09	-7.39	0.30
LH-1	Titanite	55.44	42.18	3.87	0.03	0.09	0.02	0.14	0.01	0.07	0.12	-1.636	100.34	102.53	-2.93	0.39
LH-1	Titanite	56.07	41.15	4.12	0.02	0.21	0.46	0.12	0.16	0.05	0.10	-1.741	100.71	109.43	-9.71	0.28
LH-1	Titanite	55.14	41.24	3.73	0.03	0.17	0.42	0.10	0.17	0.04	0.15	-1.577	99.61	99.66	-0.05	0.39
LH-1	Titanite	55.96	41.05	3.73	0.02	0.35	0.52	0.22	0.12	0.09	0.14	-1.576	100.62	98.86	0.84	0.30
LH-1	Titanite	55.54	41.62	3.69	0.01	0.30	0.24	0.22	0.06	0.05	0.13	-1.555	100.30	97.71	2.11	0.18
LH-1	Titanite	55.48	41.47	3.89	0.02	0.16	0.27	0.10	0.10	0.06	0.14	-1.645	100.05	103.67	-4.00	0.32
LH-1	Titanite	55.38	41.07	3.92	0.00	0.24	0.20	0.22	0.05	0.05	0.12	-1.651	99.59	105.06	-5.06	0.00
LH-1	Titanite	55.68	40.95	4.04	0.01	0.22	0.24	0.23	0.06	0.05	0.13	-1.702	99.90	108.05	-8.17	0.12
LH-1	Titanite	55.64	41.54	3.60	0.03	0.28	0.23	0.26	0.05	0.08	0.13	-1.522	100.31	95.47	4.12	0.41
LH-1	Titanite	55.75	41.80	3.45	0.00	0.17	0.12	0.14	0.04	0.08	0.16	-1.452	100.26	91.39	8.58	0.03
LH-1	Titanite	55.46	41.66	3.66	0.00	0.20	0.25	0.16	0.08	0.00	0.12	-1.543	100.05	97.29	2.71	0.00
LH-1	Titanite	55.42	41.12	3.95	0.03	0.24	0.47	0.15	0.17	0.03	0.13	-1.670	100.04	105.33	-5.70	0.37
LH-1	Titanite	55.48	41.32	4.21	0.01	0.15	0.36	0.11	0.14	0.00	0.13	-1.773	100.12	112.18	-12.27	0.09
LH-1	Titanite	55.53	40.97	4.04	0.03	0.22	0.24	0.15	0.06	0.09	0.12	-1.708	99.73	108.31	-8.68	0.36
LH-1	Titanite	55.94	41.37	3.73	0.02	0.42	0.30	0.17	0.09	0.04	0.11	-1.574	100.61	98.72	1.05	0.22
LH-1	Titanite	55.54	41.38	3.67	0.00	0.19	0.52	0.09	0.17	0.03	0.13	-1.545	100.19	97.33	2.64	0.04
ES-12792	Phenocryst Core	54.64	41.55	2.03	0.13	0.06	0.13	0.08	0.04	0.07	0.14	-0.887	97.99	54.64	43.42	1.93
ES-12792	Phenocryst Core	54.47	40.76	1.37	0.12	0.03	0.14	0.08	0.05	0.05	0.13	-0.602	96.59	37.19	61.07	1.75
ES-12792	Phenocryst Core	54.62	41.01	1.47	0.25	0.04	0.12	0.10	0.06	0.12	0.13	-0.675	97.24	39.75	56.60	3.65
ES-12792	Phenocryst Core	54.74	41.59	1.82	0.14	0.06	0.12	0.12	0.06	0.05	0.11	-0.796	98.01	48.74	49.29	1.97
ES-12792	Phenocryst Core	55.09	42.14	1.83	0.23	0.03	0.12	0.06	0.07	0.11	0.12	-0.821	98.98	48.57	48.20	3.23
ES-12792	Phenocryst Core	55.08	40.96	2.51	0.19	0.06	0.10	0.12	0.06	0.12	0.11	-1.100	98.21	67.80	29.46	2.73
ES-12792	Phenocryst Core	55.09	41.90	1.76	0.31	0.05	0.12	0.11	0.05	0.14	0.13	-0.808	98.82	46.78	48.86	4.36
ES-12792	Phenocryst Core	55.16	41.38	2.27	0.08	0.09	0.14	0.11	0.07	0.04	0.11	-0.973	98.48	60.82	38.04	1.14
ES-12792	Phenocryst Core	54.97	41.42	1.73	0.17	0.05	0.15	0.07	0.06	0.09	0.12	-0.767	98.07	46.48	51.13	2.39
ES-12792	Phenocryst Core	54.47	41.39	1.40	0.38	0.12	0.26	0.15	0.08	0.09	0.14	-0.673	97.80	37.54	57.06	5.41
ES-12792	Phenocryst Core	55.21	41.31	2.04	0.14	0.15	0.23	0.17	0.07	0.07	0.14	-0.890	98.64	54.61	43.43	1.96
ES-12792	Phenocryst Core	54.91	41.74	1.60	0.29	0.07	0.10	0.08	0.04	0.15	0.12	-0.739	98.36	42.78	53.07	4.16
ES-12792	Phenocryst Core	55.31	41.58	2.13	0.12	0.04	0.11	0.10	0.07	0.00	0.13	-0.924	98.67	56.91	41.33	1.76
ES-12792	Phenocryst Core	54.77	41.55	1.89	0.10	0.04	0.11	0.05	0.05	0.03	0.12	-0.820	97.89	50.84	47.67	1.50
ES-12792	Phenocryst Core	55.18	41.80	2.40	0.20	0.13	0.14	0.18	0.08	0.07	0.13	-1.055	99.26	63.90	33.31	2.79
ES-12792	Phenocryst Core	55.36	41.58	2.39	0.14	0.12	0.17	0.11	0.08	0.07	0.12	-1.040	99.11	63.82	34.11	2.06
ES-12792	Phenocryst Rim	54.88	41.25	1.67	0.14	0.04	0.13	0.10	0.04	0.06	0.11	-0.736	97.67	45.06	52.87	2.07

Table A2.1 Apatite major and trace element concentrations (continued)

ES-12792	Phenocryst Rim	54.94	41.38	1.30	0.13	0.07	0.16	0.12	0.06	0.02	0.12	-0.576	97.72	34.93	63.25	1.82
ES-12792	Phenocryst Rim	54.66	41.20	1.55	0.28	0.05	0.09	0.09	0.04	0.13	0.14	-0.713	97.50	41.76	54.26	3.98
ES-12792	Phenocryst Rim	54.67	41.16	1.25	0.17	0.04	0.12	0.10	0.06	0.14	0.12	-0.566	97.26	33.88	63.72	2.40
ES-12792	Phenocryst Rim	55.25	41.41	1.71	0.18	0.06	0.14	0.09	0.07	0.11	0.11	-0.760	98.35	45.77	51.62	2.61
ES-12792	Phenocryst Rim	54.73	41.54	2.12	0.27	0.05	0.13	0.09	0.07	0.12	0.12	-0.954	98.27	56.90	39.15	3.95
ES-12792	Phenocryst Rim	55.00	41.12	1.51	0.27	0.04	0.12	0.09	0.05	0.18	0.15	-0.697	97.84	40.76	55.38	3.86
ES-12792	Phenocryst Rim	55.22	41.95	1.80	0.19	0.06	0.10	0.07	0.06	0.09	0.12	-0.802	98.86	47.90	49.32	2.78
ES-12792	Phenocryst Rim	54.53	41.71	1.46	0.16	0.06	0.17	0.10	0.07	0.14	0.11	-0.651	97.86	39.14	58.56	2.30
ES-12792	Phenocryst Rim	54.25	41.39	1.37	0.39	0.07	0.11	0.13	0.03	0.20	0.13	-0.667	97.40	37.10	57.27	5.63
ES-12792	Phenocryst Rim	54.94	41.09	1.88	0.19	0.05	0.09	0.06	0.04	0.16	0.10	-0.834	97.77	50.68	46.55	2.77
ES-12792	Phenocryst Rim	55.06	41.53	1.78	0.26	0.06	0.11	0.09	0.08	0.13	0.12	-0.806	98.41	47.54	48.76	3.70
ES-12792	Phenocryst Rim	54.64	41.22	1.79	0.14	0.04	0.09	0.07	0.07	0.14	0.14	-0.786	97.56	48.45	49.58	1.97
ES-12792	Phenocryst Rim	54.59	41.45	1.63	0.10	0.05	0.10	0.05	0.01	0.08	0.11	-0.709	97.46	43.88	54.63	1.48
ES-12792	Phenocryst Rim	55.00	41.32	2.12	0.24	0.06	0.08	0.11	0.08	0.06	0.13	-0.947	98.27	57.02	39.51	3.47
ES-12792	Phenocryst Rim	55.44	41.62	1.94	0.14	0.03	0.12	0.10	0.06	0.10	0.12	-0.848	98.83	51.68	46.28	2.04
ES-12792	Amphibole	54.72	41.15	1.65	0.15	0.32	0.57	0.07	0.17	0.77	0.11	-0.728	98.94	43.94	53.98	2.07
ES-12792	Amphibole	53.79	40.19	1.76	0.18	0.62	1.05	0.09	0.26	0.69	0.09	-0.782	97.95	47.29	50.14	2.57
ES-12792	Amphibole	55.13	41.60	1.66	0.18	0.20	0.41	0.08	0.11	0.47	0.10	-0.738	99.19	43.97	53.52	2.51
ES-12792	Amphibole	54.74	40.67	2.33	0.16	2.58	0.52	0.08	0.17	1.08	0.08	-1.017	101.39	60.43	37.29	2.27
ES-12792	Amphibole	53.17	39.47	1.32	0.37	1.69	1.03	0.12	0.29	0.67	0.18	-0.639	97.66	35.39	59.29	5.33
ES-12792	Amphibole	53.73	40.40	1.35	0.34	0.48	1.08	0.13	0.26	0.68	0.17	-0.646	97.98	36.18	58.91	4.92
ES-12792	Amphibole	54.28	40.76	1.54	0.15	0.28	0.59	0.08	0.14	0.72	0.08	-0.681	97.95	41.33	56.56	2.11
ES-12792	Amphibole	54.09	40.72	1.44	0.14	0.44	0.99	0.12	0.24	0.69	0.09	-0.638	98.31	38.49	59.57	1.95
ES-12792	Amphibole	54.07	40.93	2.13	0.13	0.28	0.45	0.05	0.13	0.62	0.13	-0.926	98.00	57.24	40.82	1.94
ES-12792	Biotite	54.93	41.20	1.96	0.27	0.24	0.39	0.15	0.13	0.49	0.12	-0.887	98.97	52.32	43.80	3.89
ES-12792	Biotite	55.10	41.96	1.94	0.16	0.10	0.11	0.11	0.03	0.29	0.11	-0.852	99.07	51.53	46.20	2.27
ES-12792	Biotite	55.42	42.18	1.83	0.16	0.08	0.18	0.09	0.05	0.40	0.11	-0.806	99.69	48.21	49.47	2.32
ES-12792	Biotite	55.65	42.25	1.91	0.19	0.10	0.14	0.07	0.05	0.41	0.12	-0.845	100.04	50.18	47.15	2.67
ES-12792	Biotite	54.76	40.72	1.99	0.24	0.50	1.35	0.07	0.28	0.52	0.10	-0.893	99.64	52.57	43.99	3.43
ES-12792	Biotite	55.03	41.64	1.51	0.23	0.21	0.44	0.09	0.11	0.61	0.11	-0.689	99.30	40.04	56.64	3.32
ES-12792	Biotite	54.70	41.71	1.89	0.15	0.23	0.52	0.06	0.13	0.49	0.12	-0.832	99.17	50.16	47.64	2.19
ES-12792	Biotite	54.81	41.55	1.89	0.26	0.25	0.56	0.09	0.19	0.51	0.11	-0.856	99.37	50.15	46.16	3.70
ES-12792	Biotite	54.72	41.50	1.86	0.22	0.16	0.32	0.09	0.09	0.56	0.12	-0.832	98.79	49.50	47.32	3.18
ES-12792	Biotite	53.79	41.11	1.81	1.01	0.24	0.50	0.08	0.11	0.71	0.13	-0.990	98.49	48.68	36.82	14.50
ES-12792	Biotite	54.32	41.83	1.95	0.27	0.24	0.13	0.17	0.04	0.92	0.12	-0.883	99.10	51.98	44.20	3.83
ES-12792	Biotite	54.89	41.64	2.14	0.18	0.18	0.18	0.12	0.04	0.52	0.12	-0.943	99.07	57.02	40.35	2.62
ES-12792	Biotite	54.88	41.27	1.62	0.26	0.25	0.55	0.08	0.13	0.59	0.12	-0.742	99.03	43.13	53.13	3.75
ES-12792	Biotite	54.23	41.60	2.10	0.20	0.28	0.53	0.14	0.13	0.62	0.11	-0.927	99.02	55.72	41.50	2.78
ES-12792	Biotite	54.19	41.67	1.97	0.14	0.36	0.37	0.09	0.10	0.50	0.12	-0.860	98.65	52.43	45.61	1.96
ES-12792	Biotite	54.22	41.45	1.64	0.24	0.20	0.20	0.17	0.04	0.55	0.11	-0.743	98.07	43.94	52.67	3.40
ES-12792	Biotite	54.75	41.75	2.02	0.18	0.07	0.12	0.06	0.04	0.33	0.12	-0.891	98.56	53.97	43.42	2.61
ES-12792	Biotite	54.43	41.53	1.66	0.20	0.14	0.38	0.08	0.10	0.36	0.12	-0.743	98.25	44.32	52.86	2.82
ES-12792	Biotite	54.38	41.30	1.90	0.19	0.19	0.49	0.09	0.13	0.39	0.12	-0.841	98.33	50.77	46.56	2.67
ES-12792	Biotite	53.63	40.26	1.84	0.23	0.41	0.89	0.10	0.20	0.38	0.10	-0.827	97.20	49.80	46.87	3.34
ES-12792	Biotite	54.02	41.20	1.64	0.20	0.19	0.45	0.09	0.13	0.58	0.11	-0.735	97.89	44.04	53.15	2.81
ES-12792	Biotite	53.81	41.03	1.40	0.21	0.23	0.29	0.11	0.09	0.88	0.10	-0.637	97.51	37.76	59.22	3.03
ES-12792	Biotite	54.45	41.25	1.64	0.18	0.23	0.49	0.09	0.12	0.48	0.11	-0.730	98.32	43.75	53.64	2.61
ES-12792	Biotite	53.93	40.58	1.50	0.39	0.39	0.80	0.08	0.18	0.66	0.11	-0.719	97.89	40.18	54.14	5.68
ES-12792	Biotite	54.64	41.18	2.06	0.26	0.20	0.45	0.09	0.17	0.45	0.13	-0.928	98.70	55.19	41.07	3.74
ES-12792	Biotite	54.57	41.18	1.82	0.25	0.19	0.41	0.09	0.08	0.54	0.10	-0.822	98.40	48.65	47.71	3.64
ES-12792	Biotite	53.59	40.30	1.63	1.05	0.28	0.71	0.12	0.18	0.73	0.15	-0.925	97.81	44.23	40.47	15.30
ES-12792	Biotite	53.44	39.97	1.59	0.27	0.45	1.02	0.13	0.24	0.96	0.12	-0.728	97.46	42.84	53.26	3.91
ES-12792	Biotite	53.53	40.46	1.63	0.31	0.34	0.87	0.09	0.22	0.80	0.11	-0.757	97.59	43.98	51.53	4.48
ES-12792	Biotite	54.28	41.17	1.72	0.13	0.25	0.30	0.14	0.11	0.43	0.12	-0.757	97.89	46.35	51.71	1.94
ES-12792	Biotite	54.40	41.41	1.75	0.17	0.14	0.19	0.06	0.04	0.51	0.12	-0.777	98.00	47.06	50.43	2.51
ES-12792	Biotite	54.25	40.50	1.87	0.16	0.34	0.89	0.10	0.21	0.55	0.13	-0.825	98.19	50.20	47.46	2.34
ES-12792	Biotite	54.35	40.95	2.02	0.16	0.26	0.65	0.09	0.16	0.43	0.12	-0.884	98.30	54.01	43.73	2.26
ES-12792	Magnetite	54.72	41.58	2.34	0.15	0.12	0.18	0.15	0.07	1.92	0.13	-1.021	100.36	62.07	35.76	2.16
ES-12792	Magnetite	53.89	39.79	2.28	0.17	0.22	0.70	0.15	0.25	1.51	0.13	-0.998	98.11	61.87	35.69	2.44
ES-12792	Magnetite	52.99	40.59	1.36	0.19	0.31	1.00	0.16	0.25	2.14	0.12	-0.616	98.50	36.36	60.86	2.77

Table A2.1 Apatite major and trace element concentrations (continued)

ES-12792	Magnetite	53.03	40.77	1.89	0.31	0.42	0.71	0.08	0.20	1.74	0.20	-0.866	98.48	50.67	44.81	4.52
ES-12792	Magnetite	54.24	41.57	2.18	0.20	0.09	0.13	0.09	0.06	1.52	0.12	-0.965	99.24	58.27	38.80	2.93
ES-12792	Magnetite	53.72	41.20	1.39	0.14	0.11	0.16	0.15	0.08	1.72	0.12	-0.615	98.17	37.25	60.72	2.03
ES-12792	Magnetite	53.38	40.57	1.63	0.43	0.30	0.96	0.09	0.25	1.85	0.19	-0.782	98.87	43.50	50.35	6.16
ES-12792	Magnetite	52.79	40.09	1.70	0.32	0.26	0.62	0.10	0.18	2.37	0.17	-0.787	97.80	46.11	49.30	4.60
ES-12792	Magnetite	52.78	40.03	1.84	0.35	0.36	1.03	0.08	0.28	2.20	0.18	-0.854	98.26	49.63	45.31	5.06
ES-12792	Magnetite	53.96	41.08	2.00	0.37	0.29	0.76	0.12	0.23	1.79	0.19	-0.926	99.88	53.10	41.64	5.26
VET-2B	Phenocryst Core	54.49	40.93	3.69	0.56	0.33	0.16	0.36	0.06	0.11	0.17	-1.681	99.18	99.57	-7.59	8.02
VET-2B	Phenocryst Core	53.87	40.78	3.12	0.71	0.33	0.19	0.35	0.05	0.06	0.22	-1.474	98.20	84.65	5.02	10.34
VET-2B	Phenocryst Core	54.07	40.06	2.89	0.61	0.34	0.19	0.35	0.06	0.08	0.20	-1.353	97.49	79.04	12.03	8.93
VET-2B	Phenocryst Core	54.36	40.80	2.89	0.45	0.12	0.23	0.20	0.06	0.08	0.16	-1.319	98.04	78.31	15.09	6.60
VET-2B	Phenocryst Core	54.21	40.43	3.88	0.47	0.19	0.17	0.24	0.06	0.14	0.21	-1.738	98.26	105.68	-12.57	6.89
VET-2B	Phenocryst Core	54.04	41.04	3.70	0.45	0.28	0.17	0.30	0.07	0.14	0.18	-1.658	98.72	99.84	-6.39	6.56
VET-2B	Phenocryst Core	54.12	41.39	3.36	0.75	0.18	0.18	0.17	0.06	0.08	0.19	-1.583	98.90	90.48	-1.23	10.75
VET-2B	Phenocryst Core	54.18	40.82	3.02	0.60	0.38	0.23	0.36	0.03	0.07	0.18	-1.408	98.48	81.67	9.68	8.65
VET-2B	Phenocryst Core	54.54	41.28	2.98	0.71	0.32	0.21	0.37	0.08	0.12	0.18	-1.414	99.36	79.73	10.02	10.25
VET-2B	Phenocryst Core	54.48	41.36	2.59	0.71	0.31	0.22	0.37	0.03	0.12	0.20	-1.251	99.14	69.33	20.47	10.20
VET-2B	Phenocryst Core	54.13	40.92	2.82	0.69	0.26	0.21	0.31	0.05	0.12	0.19	-1.344	98.35	76.37	13.65	9.98
VET-2B	Phenocryst Core	54.41	41.09	4.07	0.57	0.29	0.18	0.33	0.05	0.14	0.21	-1.842	99.51	109.45	-17.70	8.25
VET-2B	Phenocryst Core	54.41	40.94	2.62	0.68	0.27	0.20	0.26	0.06	0.03	0.20	-1.258	98.42	70.81	19.36	9.83
VET-2B	Phenocryst Core	54.52	40.55	2.94	0.74	0.34	0.19	0.38	0.05	0.13	0.19	-1.405	98.63	79.61	9.64	10.74
VET-2B	Phenocryst Core	53.88	40.27	3.16	0.66	0.35	0.20	0.33	0.04	0.09	0.20	-1.479	97.72	86.24	4.06	9.70
VET-2B	Phenocryst Rim	54.17	40.26	3.56	0.37	0.24	0.17	0.31	0.08	0.08	0.12	-1.585	97.78	97.40	-2.84	5.45
VET-2B	Phenocryst Rim	53.77	40.34	2.75	0.70	0.33	0.19	0.36	0.05	0.14	0.21	-1.315	97.53	74.98	14.71	10.31
VET-2B	Phenocryst Rim	54.34	40.32	3.94	0.22	0.26	0.21	0.29	0.06	0.06	0.09	-1.711	98.09	107.53	-10.74	3.22
VET-2B	Phenocryst Rim	53.87	40.28	3.08	0.44	0.41	0.27	0.47	0.10	0.06	0.12	-1.399	97.73	84.00	9.53	6.47
VET-2B	Phenocryst Rim	53.96	40.54	3.77	0.44	0.34	0.17	0.49	0.14	0.15	0.12	-1.685	98.43	102.33	-8.68	6.35
VET-2B	Phenocryst Rim	54.21	40.55	4.17	0.45	0.28	0.19	0.31	0.09	0.13	0.17	-1.858	98.70	113.30	-19.89	6.59
VET-2B	Phenocryst Rim	54.30	40.20	3.57	0.92	0.32	0.20	0.31	0.06	0.05	0.14	-1.708	98.36	97.29	-10.72	13.43
VET-2B	Phenocryst Rim	54.56	40.59	2.67	0.55	0.39	0.32	0.39	0.06	0.07	0.16	-1.248	98.50	72.01	19.99	8.01
VET-2B	Phenocryst Rim	54.44	40.93	2.77	0.74	0.32	0.19	0.33	0.05	0.11	0.20	-1.336	98.75	74.78	14.46	10.76
VET-2B	Phenocryst Rim	54.32	41.12	2.65	0.62	0.38	0.26	0.42	0.04	0.08	0.15	-1.254	98.78	71.09	20.03	8.89
VET-2B	Phenocryst Rim	54.37	40.81	3.12	0.69	0.35	0.23	0.33	0.03	0.09	0.22	-1.472	98.78	84.35	5.63	10.01
VET-2B	Phenocryst Rim	53.59	40.70	3.63	0.52	0.37	0.18	0.48	0.07	0.06	0.12	-1.646	98.08	98.61	-6.26	7.65
VET-2B	Phenocryst Rim	54.81	40.69	2.52	0.60	0.26	0.21	0.31	0.04	0.13	0.18	-1.195	98.55	67.91	23.38	8.71
VET-2B	Phenocryst Rim	54.03	40.74	3.13	0.63	0.30	0.19	0.32	0.06	0.09	0.20	-1.459	98.22	84.91	6.01	9.09
VET-2B	Phenocryst Rim	53.74	40.11	3.51	0.58	0.46	0.24	0.48	0.07	0.10	0.14	-1.608	97.81	95.86	-4.36	8.50
VET-2B	Amphibole	54.29	38.96	2.96	0.87	0.64	1.04	0.33	0.21	0.66	0.19	-1.441	98.70	80.35	7.02	12.63
VET-2B	Amphibole	53.98	38.78	3.28	0.80	0.71	1.13	0.38	0.24	0.60	0.19	-1.560	98.53	89.25	-0.88	11.63
VET-2B	Amphibole	53.99	39.23	3.12	0.68	0.84	1.31	0.35	0.27	0.59	0.21	-1.468	99.13	84.10	6.13	9.77
VET-2B	Amphibole	53.52	40.23	3.02	0.68	0.68	0.97	0.32	0.24	0.60	0.19	-1.427	99.01	81.22	9.01	9.77
VET-2B	Amphibole	53.83	41.30	2.90	0.71	0.35	0.61	0.19	0.18	0.63	0.22	-1.384	99.54	77.48	12.34	10.18
VET-2B	Amphibole	53.90	40.51	3.32	0.57	0.47	0.50	0.29	0.15	0.58	0.23	-1.527	98.99	89.48	2.23	8.29
VET-2B	Amphibole	53.96	40.46	2.92	0.45	0.46	0.66	0.24	0.19	0.50	0.17	-1.329	98.67	78.55	15.00	6.45
VET-2B	Amphibole	53.57	40.53	2.86	0.65	0.69	0.54	0.49	0.10	0.59	0.17	-1.351	98.84	76.89	13.72	9.39
VET-2B	Amphibole	54.21	41.04	3.61	0.54	0.45	0.40	0.25	0.11	0.64	0.21	-1.641	99.81	96.46	-4.26	7.79
VET-2B	Magnetite	55.01	40.33	3.09	0.50	0.22	0.23	0.25	0.09	0.79	0.12	-1.413	99.22	83.34	9.37	7.28
VET-2B	Magnetite	54.64	39.73	3.46	0.64	0.42	0.47	0.33	0.10	0.90	0.13	-1.603	99.24	93.91	-3.21	9.30
VET-2B	Magnetite	54.43	39.77	2.84	0.66	0.47	0.32	0.37	0.05	1.33	0.22	-1.346	99.11	77.09	13.33	9.58
VET-2B	Plagioclase	55.22	40.40	3.46	0.26	0.25	0.19	0.09	0.06	0.06	0.18	-1.516	98.65	93.74	2.45	3.82
VET-2B	Plagioclase	54.16	41.34	3.52	0.36	0.37	0.30	0.18	0.07	0.09	0.20	-1.566	99.04	94.54	0.25	5.22
VET-2B	Titanite	54.25	39.61	2.86	0.92	0.55	0.49	0.30	0.14	0.11	0.17	-1.413	98.00	78.06	8.43	13.51
VET-2B	Titanite	55.21	40.32	2.85	0.64	0.50	0.70	0.20	0.13	0.08	0.19	-1.343	99.48	76.26	14.60	9.14
VET-2B	Titanite	54.45	39.89	2.69	0.67	1.42	0.37	0.31	0.06	0.14	0.20	-1.283	98.91	72.24	18.05	9.71
VET-2B	Titanite	54.52	40.41	2.63	0.77	0.45	0.29	0.28	0.08	0.12	0.19	-1.280	98.44	71.05	17.73	11.23
VET-2B	Titanite	54.12	39.34	2.52	1.01	0.88	0.56	0.37	0.10	0.10	0.16	-1.290	97.88	68.84	16.43	14.73
VET-2B	Titanite	53.71	39.91	3.27	0.63	0.68	0.76	0.42	0.20	0.15	0.13	-1.518	98.34	88.54	2.31	9.15
VET-2B	Titanite	54.23	40.99	2.42	0.77	0.31	0.19	0.28	0.07	0.10	0.20	-1.195	98.38	65.42	23.45	11.13
VET-2B	Titanite	53.53	39.83	2.61	0.80	0.62	1.08	0.35	0.19	0.12	0.19	-1.281	98.04	70.68	17.70	11.61
VET-2B	Titanite	53.74	40.27	3.44	0.42	0.73	1.02	0.39	0.20	0.14	0.11	-1.543	98.91	92.25	1.67	6.09

Table A2.1 Apatite major and trace element concentrations (continued)

VET-2B	Titanite	53.57	40.57	2.83	0.61	0.91	1.18	0.40	0.20	0.06	0.19	-1.330	99.20	75.38	15.92	8.70
VET-2B	Titanite	52.70	38.72	2.44	0.66	1.14	1.80	0.42	0.26	0.07	0.20	-1.176	97.24	66.25	24.21	9.54
VET-2B	Titanite	53.49	39.55	2.45	0.69	0.99	1.39	0.42	0.24	0.10	0.22	-1.188	98.36	65.89	24.12	9.99
VET-2B	Titanite	53.97	40.62	2.54	0.72	0.39	0.36	0.31	0.06	0.10	0.21	-1.232	98.06	68.79	20.76	10.44
VET-2B	Titanite	54.03	40.76	2.55	0.60	0.50	0.82	0.20	0.17	0.14	0.20	-1.210	98.77	68.33	23.02	8.65
VET-2B	Titanite	53.50	39.10	2.44	0.76	0.97	1.56	0.41	0.27	0.14	0.19	-1.201	98.14	65.97	22.99	11.04
VET-2B	Titanite	54.21	41.00	2.28	0.62	0.41	0.34	0.30	0.08	0.08	0.20	-1.100	98.42	61.29	29.79	8.93
VET-2B	Titanite	53.31	39.77	2.73	0.84	0.73	1.29	0.40	0.27	0.11	0.22	-1.337	98.33	73.54	14.35	12.11
VET-2B	Titanite	53.21	40.50	3.02	0.62	0.88	0.79	0.30	0.14	0.08	0.20	-1.412	98.34	81.31	9.78	8.92
VET-2B	Titanite	53.71	39.91	2.51	0.83	0.64	1.31	0.24	0.28	0.09	0.19	-1.245	98.46	67.60	20.47	11.93
CHR-7	Biotite	52.94	41.32	1.68	1.65	0.15	0.14	0.56	0.23	0.35	0.10	-1.080	98.03	45.58	30.51	23.91
CHR-7	Biotite	54.44	41.16	1.66	1.58	0.16	0.16	0.43	0.17	0.26	0.11	-1.056	99.06	44.62	32.57	22.81
CHR-7	Biotite	53.51	41.45	2.03	1.60	0.12	0.14	0.38	0.26	0.32	0.12	-1.214	98.73	54.59	22.26	23.14
CHR-7	Biotite	53.36	41.53	2.03	1.48	0.14	0.43	0.34	0.26	0.60	0.11	-1.191	99.09	54.49	24.22	21.29
CHR-7	Biotite	53.23	40.73	1.99	1.43	0.24	0.58	0.52	0.37	0.52	0.08	-1.161	98.54	53.70	25.57	20.73
CHR-7	Biotite	53.44	41.64	2.00	1.26	0.12	0.11	0.40	0.20	0.46	0.11	-1.128	98.60	53.88	27.95	18.17
CHR-7	Biotite	53.74	41.44	1.84	1.56	0.15	0.22	0.45	0.19	0.37	0.11	-1.126	98.93	49.39	28.15	22.47
CHR-7	Biotite	53.63	41.45	1.80	1.58	0.18	0.13	0.51	0.20	0.31	0.11	-1.114	98.80	48.33	28.84	22.83
CHR-7	Biotite	53.36	41.57	1.90	1.28	0.14	0.24	0.46	0.23	0.36	0.08	-1.089	98.53	51.11	30.47	18.42
CHR-7	Biotite	52.77	41.01	2.37	1.20	0.70	0.18	0.38	0.14	0.74	0.07	-1.268	98.30	64.02	18.68	17.30
CHR-7	Biotite	52.99	41.18	1.72	1.48	0.22	0.63	0.49	0.35	0.58	0.10	-1.059	98.67	46.23	32.45	21.32
CHR-7	Biotite	54.71	42.29	2.93	0.48	0.03	0.04	0.06	0.06	0.39	0.10	-1.342	99.76	77.78	15.32	6.90
CHR-7	Biotite	54.53	42.52	2.64	0.25	0.07	0.01	0.07	0.04	0.57	0.10	-1.167	99.61	69.92	26.59	3.49
CHR-7	Biotite	53.65	41.75	1.81	1.67	0.14	0.17	0.41	0.14	0.27	0.09	-1.136	98.96	48.44	27.62	23.94
CHR-7	Biotite	53.41	41.36	1.88	1.51	0.17	0.47	0.50	0.25	0.48	0.11	-1.131	99.01	50.32	27.99	21.69
CHR-7	Biotite	54.33	41.90	2.14	0.70	0.11	0.14	0.23	0.12	0.55	0.10	-1.060	99.26	57.15	32.91	9.93
CHR-7	Biotite	53.30	40.75	1.64	1.69	0.23	0.45	0.49	0.26	0.67	0.09	-1.074	98.50	44.45	31.06	24.49
CHR-7	Biotite	54.00	41.41	2.23	1.32	0.20	0.15	0.52	0.19	0.32	0.11	-1.235	99.20	59.79	21.29	18.91
CHR-7	Biotite	54.03	41.69	1.82	1.52	0.15	0.15	0.44	0.22	0.37	0.11	-1.107	99.39	48.57	29.70	21.73
CHR-7	Biotite	53.07	40.89	2.02	1.27	0.25	0.74	0.44	0.35	0.50	0.12	-1.135	98.51	54.24	27.47	18.29
CHR-7	Biotite	53.54	41.69	1.65	1.41	0.11	0.16	0.42	0.20	0.41	0.11	-1.014	98.70	44.34	35.38	20.28
CHR-7	Biotite	54.72	42.25	2.54	0.18	0.05	0.00	0.05	0.02	0.23	0.10	-1.107	99.02	67.53	29.97	2.50
CHR-7	Biotite	54.08	41.53	2.11	1.21	0.12	0.12	0.29	0.16	0.40	0.10	-1.161	98.97	56.61	25.96	17.42
CHR-7	Biotite	54.07	42.04	2.78	0.49	0.09	0.03	0.15	0.05	0.20	0.10	-1.281	98.73	74.39	18.52	7.09
CHR-7	Biotite	54.88	42.12	2.49	0.24	0.02	0.03	0.06	0.07	0.22	0.12	-1.103	99.14	66.33	30.20	3.47
CHR-7	Biotite	53.13	41.52	1.42	1.72	0.15	0.21	0.46	0.20	0.25	0.11	-0.989	98.18	38.44	36.64	24.92
WF-1	Amphibole	55.40	41.20	3.15	0.04	0.47	0.42	0.30	0.06	0.19	0.12	-1.334	100.01	83.42	15.97	0.61
WF-1	Amphibole	54.56	40.55	3.33	0.06	0.53	0.78	0.32	0.19	0.40	0.11	-1.416	99.42	88.97	10.16	0.87
WF-1	Amphibole	54.06	40.87	3.24	0.26	0.55	0.46	0.42	0.09	0.45	0.14	-1.423	99.13	86.89	9.43	3.68
WF-1	Amphibole	53.41	40.40	3.52	0.12	0.65	0.96	0.23	0.18	0.53	0.11	-1.509	98.60	94.64	3.69	1.67
WF-1	Amphibole	54.81	40.86	3.55	0.08	0.50	0.49	0.25	0.09	0.55	0.12	-1.513	99.80	94.66	4.16	1.19
WF-1	Amphibole	54.76	41.54	3.79	0.07	0.32	0.23	0.21	0.05	0.36	0.12	-1.611	99.84	100.94	-1.93	0.99
WF-1	Amphibole	54.86	41.15	2.99	0.06	0.33	0.26	0.22	0.03	0.68	0.13	-1.275	99.45	79.97	19.11	0.91
WF-1	Amphibole	54.99	41.48	3.33	0.06	0.25	0.25	0.24	0.05	0.14	0.15	-1.413	99.52	88.66	10.55	0.79
WF-1	Amphibole	54.26	41.06	3.35	0.08	0.50	0.42	0.32	0.08	0.19	0.12	-1.430	98.95	89.83	9.05	1.13
WF-1	Amphibole	54.38	40.44	3.13	0.07	0.59	0.89	0.22	0.16	0.26	0.10	-1.334	98.91	83.76	15.23	1.01
WF-1	Amphibole	54.39	40.91	3.45	0.08	0.62	0.33	0.47	0.08	0.35	0.10	-1.469	99.30	92.21	6.67	1.12
WF-1	Amphibole	54.77	40.23	3.54	0.07	0.38	0.73	0.15	0.17	0.31	0.12	-1.506	98.97	95.22	3.77	1.02
WF-1	Amphibole	54.38	41.58	3.29	0.08	0.35	0.28	0.21	0.08	0.45	0.12	-1.402	99.41	87.61	11.28	1.11
WF-1	Amphibole	54.55	41.49	3.51	0.04	0.34	0.16	0.29	0.05	0.21	0.12	-1.487	99.28	93.85	5.59	0.56
WF-1	Amphibole	54.42	41.42	3.28	0.05	0.47	0.26	0.42	0.08	0.33	0.13	-1.390	99.46	87.29	12.05	0.66
WF-1	Amphibole	55.13	40.93	3.11	0.09	0.34	0.60	0.16	0.14	0.36	0.12	-1.330	99.66	82.78	15.89	1.33
WF-1	Amphibole	54.51	40.65	3.05	0.09	0.53	0.37	0.35	0.04	0.52	0.12	-1.302	98.92	81.78	16.96	1.25
WF-1	Amphibole	54.77	40.91	3.44	0.09	0.43	0.32	0.33	0.07	0.28	0.13	-1.468	99.30	92.17	6.60	1.23
WF-1	Amphibole	54.45	41.18	3.45	0.08	0.49	0.27	0.38	0.07	0.52	0.16	-1.471	99.59	92.13	6.73	1.14
WF-1	Amphibole	54.22	40.13	3.76	0.11	0.60	0.59	0.27	0.11	0.43	0.12	-1.610	98.74	101.65	-3.24	1.59
WF-1	Amphibole	54.87	41.12	3.52	0.07	0.32	0.42	0.19	0.13	0.36	0.13	-1.498	99.62	93.94	5.05	1.01
WF-1	Amphibole	54.77	40.58	3.26	0.05	0.58	0.57	0.32	0.10	0.34	0.14	-1.384	99.33	87.18	12.11	0.71
WF-1	Amphibole	54.48	40.88	3.19	0.09	0.47	0.74	0.21	0.14	0.31	0.13	-1.365	99.27	85.23	13.55	1.22
WF-1	Amphibole	54.15	41.21	3.36	0.09	0.36	0.36	0.32	0.09	0.38	0.14	-1.436	99.03	90.12	8.62	1.25

Table A2.1 Apatite major and trace element concentrations (continued)

WF-1	Amphibole	54.25	40.31	3.18	0.35	0.65	0.90	0.31	0.18	0.47	0.17	-1.418	99.35	85.07	9.93	5.01
WF-1	Amphibole	53.98	40.60	3.30	0.38	0.62	0.70	0.36	0.15	0.43	0.16	-1.476	99.20	88.49	6.10	5.41
WF-1	Amphibole	54.68	40.77	2.97	0.06	0.54	0.46	0.38	0.06	0.22	0.13	-1.265	99.00	79.51	19.59	0.90
WF-1	Plagioclase	54.49	40.67	3.22	0.07	0.48	0.31	0.35	0.09	0.06	0.14	-1.370	98.50	86.63	12.35	1.02
WF-1	Plagioclase	54.44	40.39	3.29	0.11	0.62	0.75	0.30	0.18	0.13	0.16	-1.408	98.98	88.09	10.36	1.55
WF-1	Plagioclase	53.79	40.28	2.94	0.16	0.75	0.70	0.58	0.13	0.06	0.16	-1.273	98.26	79.15	18.59	2.26
WF-1	Plagioclase	55.25	40.56	3.16	0.19	0.45	0.57	0.22	0.09	0.04	0.16	-1.372	99.31	84.49	12.78	2.73
WF-1	Titanite	54.53	41.01	3.08	0.09	0.40	0.32	0.27	0.07	0.06	0.10	-1.318	98.62	82.76	15.97	1.27
WF-1	Titanite	54.36	40.49	2.73	0.32	0.61	0.97	0.25	0.15	0.08	0.10	-1.219	98.85	72.84	22.59	4.57
WF-1	Titanite	53.23	39.60	2.05	0.81	0.82	1.19	0.39	0.26	0.27	0.23	-1.044	97.78	55.41	32.92	11.67
WF-1	Titanite	54.74	40.75	3.24	0.07	0.50	0.71	0.18	0.12	0.08	0.11	-1.381	99.11	86.64	12.38	0.98
WF-1	Titanite	54.14	41.53	2.62	0.57	0.34	0.48	0.28	0.14	0.06	0.16	-1.232	99.07	69.93	21.99	8.08
WF-1	Titanite	54.22	40.01	2.87	0.25	0.76	1.16	0.27	0.19	0.06	0.11	-1.264	98.63	76.88	19.53	3.58
WF-1	Titanite	53.97	40.55	2.40	0.65	0.68	0.50	0.43	0.05	0.12	0.16	-1.157	98.37	64.57	26.00	9.43
WF-1	Titanite	53.75	40.36	2.10	1.02	0.57	0.49	0.42	0.14	0.14	0.21	-1.114	98.09	56.74	28.42	14.84
WF-1	Titanite	52.90	40.24	2.67	0.39	0.68	1.08	0.37	0.20	0.17	0.16	-1.214	97.64	72.15	22.14	5.71
WF-1	Titanite	53.44	39.86	3.13	0.06	0.81	1.47	0.31	0.26	0.12	0.15	-1.330	98.27	83.92	15.25	0.82
WF-1	Titanite	54.52	41.08	3.14	0.21	0.46	0.44	0.36	0.15	0.05	0.20	-1.367	99.23	83.77	13.29	2.95
WF-1	Titanite	54.08	40.45	3.09	0.06	0.40	0.65	0.28	0.18	0.05	0.19	-1.316	98.11	83.48	15.63	0.89
WF-1	Titanite	53.27	40.27	2.34	0.63	0.54	0.63	0.41	0.12	0.10	0.25	-1.127	97.45	63.43	27.34	9.23
WF-1	Titanite	53.51	40.62	2.49	0.73	0.66	0.57	0.51	0.14	0.12	0.16	-1.213	98.31	67.08	22.42	10.50
WF-1	Titanite	54.09	40.51	3.09	0.07	0.56	0.50	0.38	0.11	0.05	0.11	-1.319	98.15	83.48	15.48	1.03
WF-1	Titanite	54.32	40.78	2.98	0.07	0.52	0.39	0.33	0.05	0.22	0.12	-1.269	98.52	79.96	19.03	1.01
WF-1	Titanite	54.29	40.79	3.43	0.06	0.46	0.39	0.31	0.08	0.13	0.13	-1.456	98.61	92.23	6.91	0.86
WF-1	Titanite	54.97	41.55	3.37	0.05	0.39	0.28	0.30	0.07	0.03	0.11	-1.430	99.69	89.57	9.74	0.69
WF-1	Titanite	54.63	40.93	3.37	0.07	0.56	0.57	0.29	0.12	0.06	0.10	-1.437	99.26	90.05	8.88	1.06

Appendix A3 – Amphibole and titanite composition by EPMA

Table A3.1 Amphibole composition by EPMA

Sample	Crystal # (Analysis #)	wt %												O = F, Cl	Total
		SiO ₂	MgO	FeO _{tot}	CaO	Al ₂ O ₃	Na ₂ O	TiO ₂	K ₂ O	MnO	SO ₃	Cl	F		
LH-1	1 (1)	50.46	16.44	12.07	11.32	4.19	0.88	0.52	0.46	0.46	0.00	0.03	0.00	-0.007	96.82
LH-1	1 (2)	51.70	16.87	11.57	11.23	3.83	0.93	0.42	0.37	0.47	0.00	0.03	0.00	-0.008	97.42
LH-1	1 (3)	51.57	16.57	11.98	11.31	4.11	0.88	0.47	0.46	0.54	0.00	0.03	0.00	-0.008	97.92
LH-1	2 (1)	52.05	16.48	12.10	11.23	4.20	0.94	0.44	0.41	0.44	0.00	0.02	0.00	-0.006	98.31
LH-1	2 (2)	51.89	16.31	12.40	11.41	4.03	0.78	0.41	0.40	0.51	0.00	0.03	0.00	-0.006	98.17
LH-1	2 (3)	51.32	16.49	12.40	11.39	4.17	0.89	0.37	0.40	0.48	0.00	0.02	0.00	-0.006	97.93
LH-1	2 (4)	52.28	16.59	12.16	11.43	3.65	0.72	0.41	0.37	0.46	0.01	0.02	0.00	-0.005	98.09
LH-1	3 (1)	51.16	16.32	12.29	11.45	4.62	0.92	0.63	0.52	0.48	0.00	0.03	0.00	-0.007	98.42
LH-1	3 (2)	51.58	16.63	12.34	11.31	4.34	0.90	0.60	0.45	0.45	0.00	0.03	0.00	-0.007	98.63
LH-1	3 (3)	50.52	16.31	12.55	11.17	4.79	1.15	0.63	0.48	0.43	0.00	0.02	0.00	-0.007	98.06
LH-1	3 (4)	51.55	16.40	12.45	11.21	4.55	1.05	0.65	0.45	0.43	0.00	0.02	0.00	-0.006	98.75
LH-1	3 (5)	50.58	16.09	12.84	11.22	5.07	1.02	0.69	0.52	0.47	0.00	0.03	0.00	-0.007	98.50
LH-1	4 (1)	49.94	14.95	14.23	11.35	5.69	1.11	0.57	0.60	0.52	0.01	0.04	0.00	-0.011	99.01
LH-1	4 (2)	50.71	15.94	13.04	11.11	4.49	1.03	0.57	0.49	0.53	0.00	0.04	0.00	-0.009	97.94
LH-1	4 (3)	51.89	15.90	13.11	11.35	4.50	0.80	0.37	0.42	0.46	0.00	0.03	0.00	-0.007	98.84
LH-1	5 (1)	52.09	16.89	11.86	11.32	4.03	0.93	0.52	0.42	0.56	0.00	0.03	0.00	-0.007	98.65
LH-1	5 (2)	52.08	16.70	12.40	11.36	4.03	0.88	0.41	0.45	0.52	0.00	0.03	0.00	-0.006	98.84
LH-1	6 (1)	51.62	16.47	12.38	11.40	4.12	0.83	0.38	0.41	0.46	0.00	0.02	0.00	-0.005	98.11
LH-1	7 (1)	50.83	16.47	12.44	11.28	4.43	0.98	0.55	0.49	0.48	0.00	0.03	0.00	-0.007	97.99
LH-1	7 (2)	52.13	16.67	11.98	11.25	4.21	0.97	0.48	0.42	0.50	0.00	0.03	0.01	-0.010	98.62
LH-1	7 (3)	52.09	16.97	11.80	11.30	3.82	0.87	0.39	0.41	0.48	0.00	0.02	0.00	-0.007	98.14
LH-1	8 (1)	51.96	16.46	12.70	11.30	4.07	0.84	0.41	0.44	0.54	0.00	0.02	0.00	-0.006	98.73
LH-1	8 (2)	51.26	16.60	12.41	11.32	4.00	0.85	0.48	0.44	0.44	0.01	0.03	0.00	-0.006	97.82
LH-1	8 (3)	51.46	16.52	12.66	11.37	4.28	0.95	0.43	0.43	0.44	0.00	0.03	0.00	-0.007	98.57
LH-1	8 (4)	51.47	16.28	12.85	11.30	4.44	0.93	0.45	0.49	0.49	0.01	0.02	0.00	-0.007	98.71
LH-1	9 (1)	51.84	16.47	12.53	11.38	4.24	0.88	0.44	0.46	0.43	0.00	0.03	0.00	-0.008	98.71
LH-1	9 (2)	50.71	15.65	13.23	11.21	5.06	1.00	0.58	0.53	0.49	0.00	0.04	0.00	-0.008	98.49
LH-1	9 (3)	51.61	16.41	12.23	11.43	4.11	0.85	0.39	0.43	0.44	0.00	0.03	0.00	-0.006	97.92
LH-1	9 (4)	51.38	15.67	13.15	11.48	4.94	0.89	0.47	0.50	0.53	0.01	0.03	0.00	-0.009	99.05
LH-1	10 (1)	51.36	16.59	12.60	11.41	4.16	0.84	0.33	0.41	0.42	0.00	0.02	0.00	-0.005	98.14
LH-1	10 (2)	52.11	16.80	12.20	11.52	3.87	0.76	0.33	0.37	0.47	0.00	0.02	0.00	-0.007	98.44
LH-1	10 (3)	51.54	16.53	12.27	11.37	4.17	0.90	0.53	0.41	0.41	0.00	0.04	0.00	-0.010	98.14
LH-1	11 (1)	50.88	16.39	12.32	11.34	4.15	0.91	0.51	0.44	0.55	0.00	0.02	0.00	-0.006	97.49
LH-1	11 (2)	52.35	17.00	11.76	11.26	3.77	0.86	0.39	0.43	0.51	0.00	0.02	0.00	-0.006	98.36
LH-1	11 (3)	50.85	16.56	12.29	11.28	4.28	0.89	0.49	0.46	0.50	0.01	0.02	0.00	-0.007	97.65
LH-1	12 (1)	51.59	16.79	11.83	11.38	4.07	0.83	0.48	0.41	0.53	0.00	0.02	0.00	-0.005	97.92
LH-1	13 (1)	49.81	15.44	13.18	11.27	5.27	1.06	0.59	0.56	0.50	0.00	0.04	0.00	-0.010	97.72
LH-1	13 (2)	52.69	16.46	12.22	11.50	3.95	0.81	0.47	0.43	0.50	0.00	0.03	0.00	-0.008	99.07
LH-1	13 (3)	51.96	16.40	12.12	11.40	4.31	0.92	0.54	0.44	0.48	0.01	0.02	0.00	-0.006	98.60
LH-1	13 (4)	50.97	16.18	12.16	11.42	4.37	0.90	0.59	0.47	0.47	0.00	0.03	0.01	-0.009	97.56
LH-1	13 (5)	51.26	16.65	12.07	11.31	4.34	0.90	0.58	0.47	0.44	0.00	0.02	0.00	-0.007	98.05
LH-1	13 (6)	51.38	16.42	11.79	11.44	4.06	0.81	0.52	0.44	0.51	0.00	0.03	0.00	-0.008	97.39
LH-1	13 (7)	51.04	16.51	12.18	11.28	4.40	0.83	0.56	0.45	0.43	0.00	0.04	0.00	-0.011	97.72
LH-1	13 (8)	51.61	16.62	11.97	11.30	4.00	0.86	0.49	0.39	0.50	0.00	0.02	0.00	-0.005	97.76
LH-1	13 (9)	51.66	16.50	12.19	11.30	4.14	0.93	0.50	0.50	0.51	0.01	0.03	0.00	-0.006	98.25
LH-1	13 (10)	52.06	16.58	12.04	11.56	4.07	0.79	0.44	0.45	0.46	0.01	0.02	0.00	-0.006	98.46
LH-1	13 (11)	52.12	16.70	12.23	11.39	4.16	0.88	0.42	0.41	0.49	0.00	0.03	0.00	-0.008	98.82
LH-1	13 (12)	51.60	16.64	11.93	11.41	4.03	0.83	0.46	0.45	0.48	0.00	0.04	0.00	-0.009	97.87
LH-1	14 (1)	52.21	16.69	11.90	11.58	3.83	0.76	0.35	0.41	0.40	0.01	0.02	0.00	-0.006	98.15
LH-1	15 (1)	50.20	15.62	13.41	11.20	4.81	0.95	0.54	0.48	0.47	0.00	0.03	0.00	-0.009	97.71
LH-1	15 (2)	51.57	16.09	12.67	11.29	4.31	0.91	0.54	0.50	0.49	0.00	0.04	0.00	-0.010	98.39
VET-2B	21 (1)	42.74	10.28	18.95	10.82	10.44	1.48	1.57	1.52	0.84	0.02	0.33	0.00	-0.075	98.90
VET-2B	24 (1)	41.62	10.02	19.55	10.81	10.72	1.52	1.57	1.79	0.78	0.03	0.35	0.00	-0.080	98.69
VET-2B	25 (1)	42.97	10.67	18.12	10.90	10.66	1.45	1.78	1.62	0.77	0.02	0.30	0.00	-0.067	99.19
VET-2B	26 (1)	42.69	10.39	18.46	10.89	10.68	1.55	1.63	1.71	0.82	0.02	0.34	0.01	-0.080	99.12
VET-2B	26 (2)	42.28	9.88	18.99	10.87	11.14	1.59	1.72	1.82	0.85	0.04	0.40	0.00	-0.092	99.51
VET-2B	27 (1)	41.79	9.86	19.56	10.73	10.68	1.68	1.55	1.68	0.77	0.03	0.35	0.00	-0.079	98.60
VET-2B	27 (2)	41.22	9.72	19.52	10.81	10.79	1.62	1.64	1.71	0.78	0.03	0.36	0.00	-0.082	98.12

Table A3.1 Amphibole composition by EPMA (continued)

VET-2B	28 (1)	41.34	9.45	19.42	11.03	11.27	1.71	1.73	1.65	0.84	0.04	0.40	0.00	-0.092	98.78
VET-2B	29 (1)	43.52	10.75	18.27	10.86	9.87	1.55	1.56	1.46	0.80	0.02	0.30	0.00	-0.068	98.88
VET-2B	30 (1)	41.98	9.93	19.03	10.76	10.57	1.59	1.68	1.63	0.79	0.03	0.35	0.00	-0.079	98.27
ES-12792	10 (1)	42.05	13.50	13.22	10.78	12.95	2.69	3.08	0.42	0.12	0.02	0.01	0.00	-0.004	98.85
ES-12792	10 (2)	42.78	13.77	13.63	10.75	11.71	2.39	2.59	0.51	0.22	0.02	0.02	0.00	-0.004	98.39
ES-12792	11 (1)	45.85	12.28	17.61	10.85	8.27	1.57	1.07	0.78	0.47	0.01	0.03	0.00	-0.006	98.79
ES-12792	11 (2)	44.96	11.77	18.13	10.89	8.81	1.59	1.02	0.85	0.42	0.01	0.03	0.00	-0.006	98.46
ES-12792	11 (3)	45.77	11.78	17.88	10.70	8.28	1.48	1.00	0.69	0.45	0.01	0.02	0.00	-0.005	98.05
ES-12792	12 (1)	45.10	11.55	18.10	10.90	8.87	1.57	1.17	0.79	0.44	0.01	0.02	0.00	-0.005	98.51
WF-1	18 (1)	49.81	15.22	13.45	11.44	5.13	0.98	0.41	0.52	0.83	0.00	0.05	0.00	-0.014	97.84
WF-1	18 (2)	46.93	14.03	14.38	11.15	6.94	1.36	1.06	0.86	0.77	0.01	0.13	0.00	-0.031	97.59
WF-1	19 (1)	46.47	13.70	14.91	11.04	7.56	1.40	1.09	0.92	0.71	0.01	0.14	0.00	-0.032	97.91
WF-1	20 (1)	46.59	13.49	15.17	11.06	7.55	1.39	1.10	0.89	0.66	0.01	0.13	0.00	-0.030	98.01
WF-1	21 (1)	48.76	15.18	13.66	11.29	5.58	1.10	0.51	0.61	0.84	0.00	0.05	0.01	-0.014	97.57
WF-1	21 (2)	47.02	13.50	15.03	11.15	7.41	1.41	1.02	0.92	0.77	0.01	0.15	0.00	-0.034	98.37
WF-1	21 (3)	48.94	14.82	13.89	11.13	6.03	1.15	0.58	0.70	0.83	0.01	0.04	0.00	-0.010	98.11
WF-1	21 (4)	48.98	14.90	13.93	11.13	6.27	1.23	0.56	0.63	0.85	0.00	0.04	0.00	-0.010	98.53
WF-1	22 (2)	46.77	13.87	14.70	11.15	7.01	1.22	0.96	0.74	0.88	0.00	0.19	0.01	-0.045	97.46
WF-1	22 (1)	47.57	13.97	14.26	11.09	7.02	1.24	0.95	0.82	0.90	0.01	0.11	0.00	-0.027	97.94
WF-1	23 (1)	47.03	14.11	14.45	11.03	6.66	1.28	0.78	0.76	0.91	0.00	0.06	0.00	-0.012	97.05
WF-1	23 (2)	47.23	13.69	14.57	11.06	7.39	1.30	1.04	0.92	0.81	0.01	0.14	0.00	-0.032	98.13
WF-1	23 (3)	47.87	14.25	14.20	11.08	6.54	1.17	0.81	0.80	0.88	0.01	0.08	0.00	-0.020	97.67
WF-1	24 (1)	47.34	13.70	15.02	11.07	6.62	1.18	0.75	0.77	0.97	0.00	0.09	0.00	-0.022	97.50
WF-1	25 (1)	48.58	14.25	14.22	11.04	7.05	1.36	0.98	0.82	0.80	0.01	0.13	0.01	-0.031	99.22
WF-1	25 (2)	46.60	13.60	15.16	10.94	7.75	1.42	1.11	0.94	0.75	0.00	0.15	0.00	-0.033	98.39
WF-1	26 (1)	46.17	13.68	14.83	11.05	7.59	1.46	1.16	0.90	0.69	0.00	0.15	0.00	-0.034	97.67
WF-1	27 (1)	46.95	13.59	15.34	11.15	7.42	1.27	0.96	0.87	0.81	0.01	0.12	0.01	-0.030	98.45
WF-1	28 (1)	48.16	14.38	14.25	11.22	6.65	1.24	0.77	0.76	0.76	0.00	0.13	0.00	-0.029	98.29
WF-1	29 (1)	48.12	13.73	14.73	11.15	7.41	1.42	1.07	0.87	0.82	0.02	0.13	0.00	-0.032	99.44
WF-1	30 (1)	47.69	13.25	15.31	11.10	7.01	1.26	0.97	0.80	0.86	0.01	0.12	0.00	-0.030	98.35
WF-1	30 (2)	48.59	13.86	14.77	11.13	5.91	0.95	0.67	0.63	0.85	0.00	0.08	0.00	-0.021	97.42
WF-1	31 (1)	46.66	13.20	15.21	11.16	7.51	1.37	1.16	0.86	0.88	0.01	0.14	0.00	-0.033	98.12
WF-1	32 (1)	48.36	14.79	14.06	11.14	5.93	1.10	0.48	0.61	0.89	0.00	0.07	0.00	-0.017	97.42
WF-1	33 (1)	46.26	13.29	15.23	11.12	7.68	1.35	1.09	0.92	0.81	0.00	0.16	0.00	-0.036	97.88
WF-1	34 (1)	46.00	13.32	15.06	11.15	7.52	1.31	1.05	0.83	0.82	0.01	0.13	0.00	-0.032	97.18
WF-1	34 (2)	49.22	14.86	14.20	11.25	5.56	0.99	0.51	0.60	0.75	0.00	0.09	0.00	-0.021	98.00
WF-1	35 (1)	47.95	14.68	13.78	11.09	6.41	1.22	0.90	0.71	0.73	0.01	0.11	0.00	-0.026	97.56
WF-1	36 (1)	47.35	13.84	14.65	11.06	7.58	1.40	1.06	0.88	0.67	0.00	0.13	0.00	-0.030	98.60
WF-1	36 (2)	47.28	14.02	14.53	10.99	7.31	1.38	1.02	0.92	0.74	0.01	0.13	0.00	-0.030	98.28
WF-1	36 (3)	46.74	13.32	15.30	10.95	7.14	1.29	1.00	0.85	0.84	0.01	0.14	0.00	-0.033	97.54

Table A3.2 Titanite composition by EPMA

Sample	Crystal # (Analysis #)	wt%													Total
		TiO ₂	SiO ₂	CaO	FeO	Al ₂ O ₃	Ce ₂ O ₃	MnO	Y ₂ O ₃	V ₂ O ₃	Nb ₂ O ₅	ZrO ₂	Cl	F	
LH-1	3 (1)	37.55	30.53	24.79	1.76	1.13	0.63	0.10	0.11	0.20	0.07	0.06	0.01	0.01	96.94
LH-1	4 (1)	38.62	30.72	25.25	1.39	0.95	0.42	0.10	0.04	0.18	0.07	0.04	0.00	0.01	97.79
LH-1	4 (2)	39.03	30.75	25.45	1.22	0.82	0.13	0.10	0.00	0.15	0.02	0.06	0.00	0.02	97.74
LH-1	4 (3)	38.20	30.49	24.94	1.55	0.88	0.52	0.13	0.03	0.17	0.08	0.04	0.00	0.01	97.03
LH-1	4 (4)	37.76	30.37	24.72	1.72	1.03	0.64	0.10	0.13	0.20	0.10	0.07	0.00	0.01	96.84
LH-1	4 (5)	38.28	30.56	25.13	1.65	0.86	0.57	0.11	0.04	0.17	0.08	0.06	0.00	0.01	97.52
LH-1	5 (1)	37.86	30.57	25.30	1.74	1.17	0.40	0.12	0.02	0.20	0.04	0.06	0.00	0.01	97.50
LH-1	5 (2)	37.60	30.27	24.95	1.72	1.06	0.61	0.09	0.12	0.19	0.05	0.10	0.00	0.01	96.76
LH-1	5 (3)	37.63	30.58	25.19	1.84	1.17	0.34	0.11	0.01	0.20	0.04	0.06	0.00	0.01	97.17
LH-1	5 (4)	38.47	30.58	25.15	1.43	0.95	0.50	0.10	0.01	0.18	0.06	0.08	0.00	0.02	97.53
LH-1	5 (5)	38.56	30.41	25.38	1.36	0.91	0.38	0.10	0.01	0.17	0.05	0.09	0.00	0.02	97.45
LH-1	6 (1)	38.30	30.35	24.61	1.44	0.97	0.77	0.12	0.14	0.20	0.08	0.08	0.01	0.01	97.09
LH-1	6 (2)	37.55	30.14	24.81	1.80	1.20	0.74	0.12	0.15	0.21	0.05	0.08	0.00	0.01	96.87
LH-1	6 (3)	38.18	30.81	25.34	1.60	1.21	0.23	0.11	0.00	0.19	0.05	0.07	0.00	0.01	97.79
LH-1	6 (4)	38.09	30.47	24.80	1.61	1.03	0.65	0.09	0.13	0.20	0.07	0.09	0.00	0.01	97.26
LH-1	6 (5)	38.40	30.76	25.16	1.42	0.98	0.42	0.09	0.01	0.19	0.07	0.08	0.01	0.01	97.60
LH-1	6 (6)	38.58	30.54	25.00	1.35	1.00	0.56	0.09	0.06	0.20	0.07	0.06	0.01	0.01	97.53
LH-1	7 (1)	37.80	30.39	24.88	1.65	1.10	0.71	0.09	0.11	0.21	0.07	0.07	0.01	0.01	97.08
LH-1	8 (1)	37.95	30.75	25.21	1.65	1.08	0.30	0.12	0.01	0.17	0.04	0.07	0.00	0.01	97.36
LH-1	8 (2)	38.43	30.33	24.68	1.32	0.90	0.75	0.11	0.10	0.18	0.10	0.08	0.00	0.02	96.98
LH-1	8 (3)	38.22	30.51	25.20	1.43	1.00	0.43	0.10	0.02	0.19	0.05	0.07	0.00	0.01	97.25
LH-1	9 (1)	38.61	30.36	25.01	1.42	0.92	0.51	0.10	0.10	0.16	0.05	0.09	0.00	0.01	97.34
LH-1	9 (2)	38.40	30.39	24.78	1.46	0.90	0.90	0.09	0.20	0.16	0.08	0.10	0.00	0.01	97.47
LH-1	9 (3)	38.47	30.36	25.08	1.35	0.98	0.78	0.08	0.09	0.20	0.05	0.09	0.01	0.01	97.54
LH-1	10 (1)	37.64	30.36	24.89	1.76	1.11	0.53	0.10	0.10	0.20	0.06	0.09	0.00	0.01	96.85
LH-1	11 (1)	38.27	30.52	25.28	1.38	0.99	0.33	0.10	0.03	0.19	0.07	0.06	0.01	0.01	97.25
LH-1	11 (2)	38.88	30.53	25.21	1.15	0.91	0.42	0.09	0.02	0.19	0.06	0.06	0.00	0.02	97.53
LH-1	11 (3)	38.57	30.37	25.08	1.30	0.89	0.49	0.10	0.06	0.17	0.05	0.06	0.00	0.01	97.15
LH-1	25 (1)	38.13	30.37	25.19	1.52	1.06	0.45	0.12	0.06	0.20	0.04	0.05	0.00	0.01	97.20
LH-1	25 (2)	36.76	30.27	24.74	1.94	1.34	0.85	0.10	0.17	0.19	0.09	0.07	0.00	0.01	96.54
LH-1	25 (3)	36.53	30.94	23.74	1.77	1.58	1.02	0.09	0.15	0.20	0.09	0.05	0.00	0.01	96.20
LH-1	25 (4)	36.47	30.09	24.58	2.15	1.39	0.93	0.08	0.20	0.23	0.07	0.07	0.02	0.01	96.28
LH-1	25 (5)	36.72	30.21	24.59	2.09	1.42	0.90	0.10	0.18	0.25	0.07	0.07	0.01	0.01	96.63
LH-1	25 (6)	36.47	30.33	24.43	2.25	1.43	0.98	0.11	0.20	0.21	0.05	0.08	0.00	0.01	96.56
LH-1	25 (7)	36.64	30.18	24.27	2.19	1.38	1.08	0.10	0.23	0.22	0.07	0.07	0.00	0.01	96.44
LH-1	25 (8)	38.19	31.16	24.73	1.36	1.17	0.49	0.10	0.04	0.21	0.07	0.06	0.00	0.01	97.60
LH-1	25 (9)	38.26	30.63	25.08	1.65	0.91	0.52	0.09	0.05	0.21	0.08	0.04	0.00	0.01	97.54
LH-1	25 (10)	38.48	30.47	24.79	1.31	0.87	0.84	0.09	0.16	0.19	0.06	0.08	0.00	0.01	97.36
LH-1	25 (11)	36.70	30.62	24.68	1.99	1.38	0.76	0.11	0.15	0.24	0.06	0.05	0.00	0.01	96.76
LH-1	25 (12)	36.80	30.59	24.79	2.02	1.40	0.77	0.11	0.17	0.20	0.05	0.09	0.00	0.01	97.00
LH-1	25 (13)	38.60	30.86	25.38	1.31	0.94	0.47	0.11	0.03	0.17	0.06	0.04	0.00	0.01	97.99
LH-1	25 (14)	38.55	30.39	25.01	1.43	0.92	0.65	0.10	0.11	0.15	0.07	0.08	0.00	0.01	97.49
LH-1	25 (15)	37.07	30.63	24.79	1.95	1.37	0.79	0.11	0.15	0.20	0.07	0.05	0.01	0.01	97.19
WF-1	1 (1)	36.67	29.97	24.43	1.80	1.68	0.62	0.15	0.29	0.19	0.22	0.19	0.00	0.02	96.23
WF-1	1 (2)	36.56	30.24	24.52	1.89	1.57	0.61	0.13	0.21	0.21	0.17	0.19	0.00	0.01	96.34
WF-1	2 (1)	36.74	30.30	24.49	1.77	1.60	0.62	0.15	0.29	0.24	0.24	0.24	0.00	0.01	96.71
WF-1	2 (2)	36.85	30.09	24.36	1.81	1.58	0.61	0.17	0.34	0.22	0.21	0.27	0.00	0.01	96.54
WF-1	3 (1)	36.83	30.15	23.89	1.74	1.36	0.92	0.19	0.49	0.19	0.34	0.14	0.00	0.01	96.26
WF-1	3 (2)	35.99	30.38	23.49	2.05	1.71	0.89	0.17	0.47	0.17	0.29	0.12	0.01	0.01	95.77
WF-1	3 (3)	36.60	30.20	24.27	1.90	1.43	0.92	0.17	0.30	0.19	0.33	0.14	0.00	0.01	96.48
WF-1	4 (1)	37.41	30.66	25.23	1.68	1.36	0.24	0.17	0.01	0.19	0.10	0.07	0.00	0.01	97.13
WF-1	4 (2)	36.86	30.60	24.56	1.85	1.44	0.71	0.16	0.17	0.19	0.24	0.09	0.00	0.01	96.88
WF-1	5 (1)	36.39	30.32	24.62	1.89	1.84	0.46	0.18	0.15	0.19	0.14	0.14	0.00	0.02	96.34
WF-1	6 (1)	36.50	30.37	24.66	1.66	1.72	0.65	0.21	0.17	0.17	0.21	0.09	0.00	0.01	96.43
WF-1	6 (2)	36.63	30.18	24.34	1.84	1.47	0.84	0.17	0.25	0.17	0.29	0.12	0.01	0.01	96.31
WF-1	7 (1)	36.99	30.28	24.39	1.78	1.50	0.68	0.14	0.38	0.19	0.21	0.16	0.00	0.01	96.71
WF-1	7 (2)	36.80	30.17	24.37	1.78	1.48	0.69	0.17	0.32	0.22	0.24	0.18	0.00	0.01	96.43
WF-1	7 (3)	36.88	30.79	25.03	1.42	1.75	0.08	0.11	0.38	0.17	0.28	0.04	0.00	0.01	96.94

Table A3.2 Titanite composition by EPMA (continued)

WF-1	8 (1)	36.62	30.40	24.20	1.75	1.60	0.69	0.13	0.38	0.21	0.25	0.19	0.00	0.02	96.45
WF-1	8 (2)	35.87	30.47	23.79	2.11	1.72	0.92	0.17	0.60	0.21	0.24	0.12	0.00	0.01	96.24
WF-1	9 (1)	36.96	30.34	24.29	1.71	1.48	0.66	0.13	0.38	0.21	0.26	0.26	0.00	0.01	96.70
WF-1	11 (1)	36.45	30.34	24.20	2.07	1.56	0.67	0.19	0.32	0.19	0.22	0.20	0.00	0.02	96.43
WF-1	11 (2)	37.71	30.53	24.77	1.52	1.15	0.48	0.19	0.20	0.16	0.19	0.07	0.00	0.01	96.98
WF-1	11 (3)	37.80	30.73	25.13	1.44	1.19	0.31	0.17	0.02	0.16	0.12	0.07	0.00	0.01	97.16
WF-1	11 (4)	36.62	30.34	24.47	1.83	1.58	0.64	0.19	0.30	0.17	0.21	0.15	0.00	0.02	96.54
VET-2B	1 (1)	36.31	30.59	24.64	1.79	1.88	0.56	0.23	0.20	0.18	0.25	0.08	0.00	0.01	96.72
VET-2B	2 (1)	36.83	30.25	24.43	1.83	1.50	0.87	0.18	0.25	0.18	0.24	0.09	0.00	0.01	96.65
VET-2B	2 (2)	37.23	30.48	24.78	1.65	1.54	0.61	0.21	0.21	0.17	0.19	0.06	0.00	0.01	97.15
VET-2B	3 (1)	36.86	30.37	24.35	1.84	1.51	0.82	0.17	0.29	0.17	0.27	0.09	0.00	0.01	96.75
VET-2B	4 (1)	36.69	30.44	24.64	1.89	1.76	0.67	0.22	0.26	0.17	0.26	0.08	0.00	0.01	97.08
VET-2B	5 (1)	36.56	30.19	24.25	1.78	1.66	0.75	0.16	0.46	0.18	0.28	0.14	0.00	0.01	96.42
VET-2B	5 (2)	36.02	30.26	24.34	2.20	1.80	0.90	0.22	0.26	0.19	0.26	0.09	0.00	0.01	96.54
VET-2B	6 (1)	36.44	30.43	24.44	1.95	1.85	0.76	0.23	0.29	0.20	0.23	0.08	0.00	0.01	96.91
VET-2B	8 (1)	37.07	30.38	24.75	1.68	1.61	0.56	0.17	0.21	0.19	0.21	0.13	0.00	0.01	96.96
VET-2B	8 (2)	37.24	30.22	24.51	1.61	1.55	0.69	0.19	0.34	0.19	0.26	0.13	0.00	0.01	96.94
VET-2B	9 (1)	36.14	30.51	24.57	1.95	1.82	0.67	0.21	0.23	0.17	0.20	0.08	0.00	0.01	96.57
VET-2B	10 (1)	36.64	30.20	24.37	1.84	1.68	0.79	0.20	0.27	0.19	0.24	0.12	0.01	0.01	96.56
VET-2B	12 (1)	36.50	30.17	24.42	1.88	1.67	0.85	0.19	0.31	0.19	0.24	0.10	0.00	0.01	96.54
VET-2B	13 (1)	36.59	30.40	24.58	1.90	1.77	0.66	0.23	0.25	0.18	0.28	0.08	0.00	0.01	96.93
VET-2B	16 (1)	36.87	30.14	24.34	1.73	1.51	0.89	0.20	0.28	0.18	0.33	0.09	0.00	0.01	96.58
VET-2B	16 (2)	36.68	30.61	24.88	1.71	1.74	0.46	0.21	0.21	0.17	0.30	0.06	0.00	0.01	97.03

Appendix A4 – Comparison of X-ray intensities for pixels in sulfate melt element maps

Element maps for Cl, Fe, Mg, Na and Ca were made over an area of quenched sulfate melt from one piston cylinder experiment (shown in Fig. 4.2). These maps suggest that during quench, sulfate melts do not form a glass but rather unmix rapidly into a number of microlitic solid phases. The most abundant of these forms laths with a composition close to that of anhydrite (i.e. nominally stoichiometric CaSO_4). Element maps show that surrounding these laths are areas which are more Na-rich and that Mg and Fe form irregular concentrations which do not appear to be coincident with each other. Finally Cl appears to be more abundant in areas which are dark in BSE.

In order to better investigate the phases which might be formed on quench, we have produced a matrix of scatter plots, comparing the X-ray intensities for each element at each pixel (Fig. A4.1). Strong correlation between elements would indicate the formation of a phase incorporating both those elements, although it should be noted that the X-ray intensities only qualitatively reflect element concentrations.

Firstly, there is fairly strong negative correlation between Ca and Cl, which is consistent with the formation of anhydrite laths which do not incorporate Cl. Fe, Mg and Na are also low in the most Ca rich pixels, consistent with this interpretation, but their highest values tend to correspond to moderate calcium concentrations. This suggests that these elements may form a glass or solid-solution which involves calcium. Conversely, the highest values for Na are associated with the lowest values for Mg and Fe, suggesting that Na is not mutually compatible with Mg and Fe in any of the phases formed. Comparing Mg and Fe X-ray intensities, there appear to be two positive trends, which may indicate the formation of two Mg and Fe bearing phases with differing Mg:Fe ratios.

Given that the bulk composition of these mixtures is dominated by sulfate, the likely phases to form are sulfate minerals including anhydrite, glaserite, langbeinite and other solid sulfate phases summarized by Du (2000) for the system $\text{K}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-MgSO}_4\text{-CaSO}_4$. Little information is available on naturally occurring Fe-Mg sulfates and it is unclear which phases are responsible for the correlation between these two elements.

Regardless, the trends shown in Fig. A4.1 are diffuse and there appears to be significant mixing of phases at each pixel. Given a nominal pixel size of $\sim 1\mu\text{m}$ this suggests unmixing does not produce large, distinct, analyzable phases and suggests that analysis of large areas of sulfate melt (either by EPMA or LA-ICP-MS) should give reasonable estimates of the bulk composition.

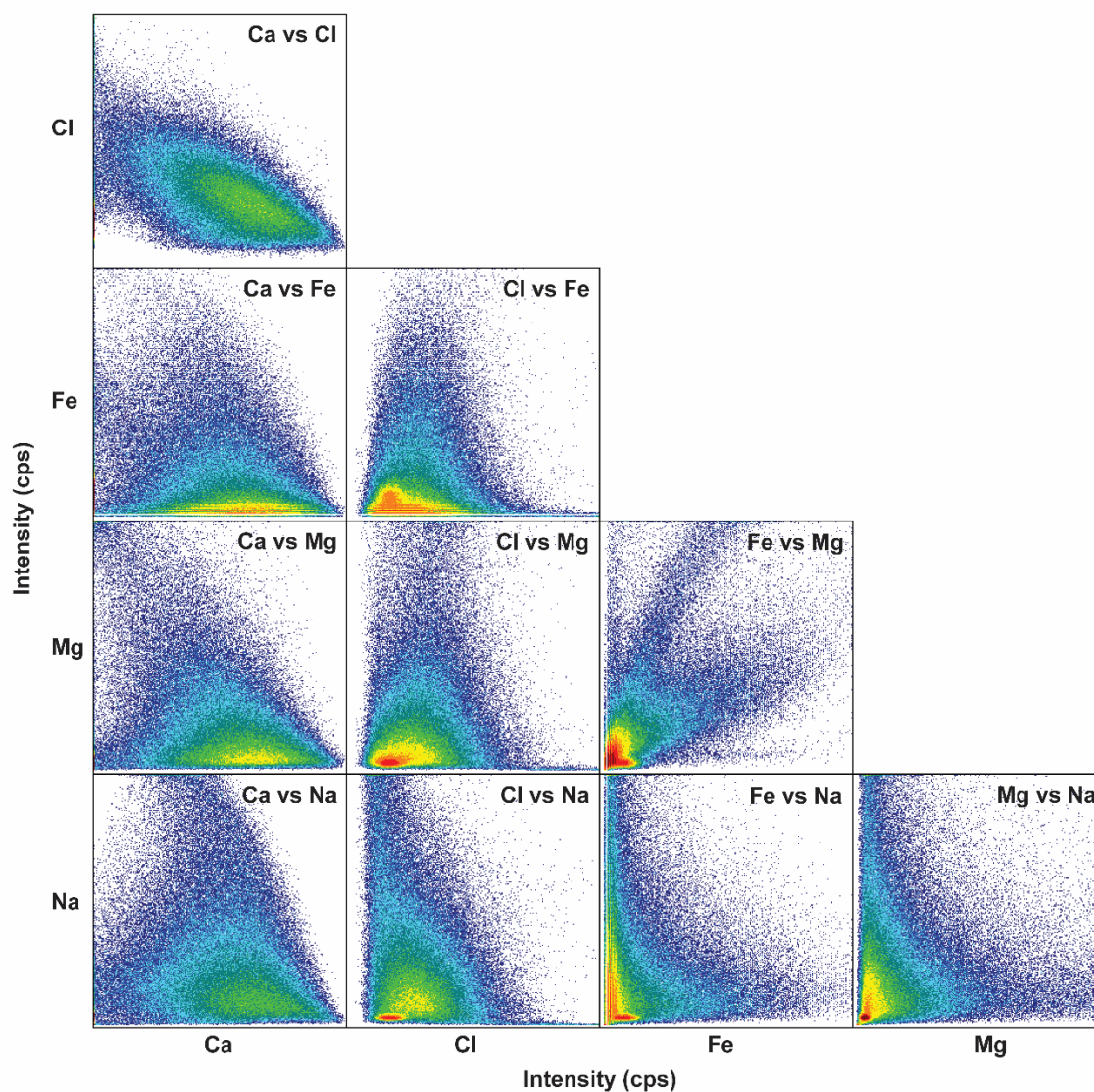


Figure A4.1 Comparison of X-ray intensities for each pixel in figure 4.2. Vertical scales is in counts per second (cps). Color represents the density of points, with warmer colors reflecting a greater number of points at that position.

Appendix A5 – SIMS ion yield corrections

SIMS analyses are sensitive to matrix effects, and ion yields for different elements can vary significantly in different materials. In this study we use SIMS to measure the trace element content of both anhydrite and the heterogeneous quench products of sulfate melts, which are also dominated by sulfate. Although a true matrix-matched standard was not available for all trace elements, we measured Sr, Ba, Y and REE in two natural anhydrite standards, and two synthetic anhydrites, grown from a CaCl_2 flux (see chapter VI). These standards had previously been characterized by LA-ICP-MS which, due to the greater volume of material ablated, is less sensitive to matrix effects. On the basis of this comparison (Fig. A5.1), we have applied small corrections for Sr (*0.83), Ba (*0.75) and Y (*1.24) to concentrations measured by SIMS. Taken together, the concentrations of REE measured fit close to a 1:1 line and so no corrections were applied.

Although unfortunately a matrix matched standard was not available for other trace elements, these comparisons show that the difference in ion yields between anhydrite and the silicate glass standard used during SIMS analyses (GSD basaltic reference glass) are likely <25%.

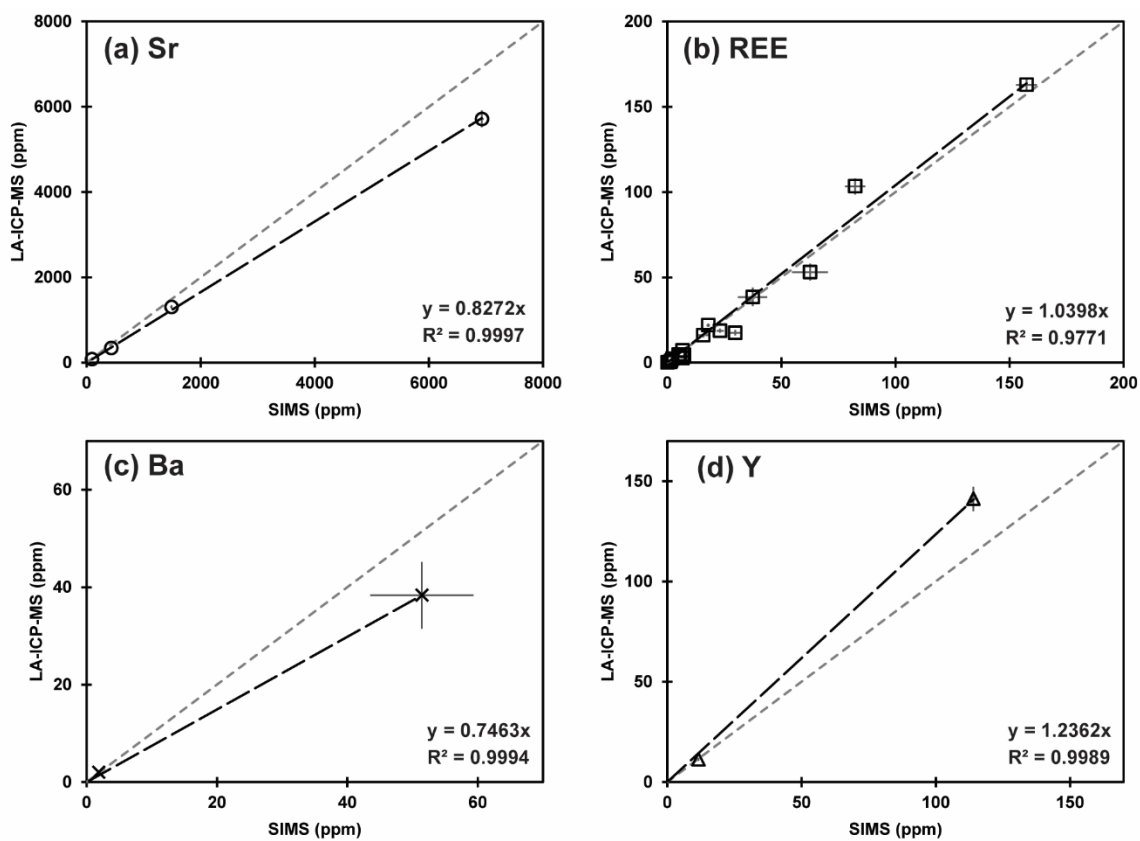


Figure A5.1 Comparison of trace element concentrations in anhydrite standards as measured by SIMS and LA-ICP-MS. Uncertainties are 1 s.d. based on repeat analysis of each standard (n=5).

Appendix A6 – Silicate glass trace element concentrations

Table A6.1 Silicate glass trace element concentrations by SIMS

Run #	Concentration (ppm)			
	57	69	23	22
Starting Composition	D2	D2	A1	A1
Temperature (°C)	1200	1100	1200	1100
Pressure (GPa)	0.75	0.75	1	1
n	5	5	5	4
Li	62 (1.3)	80 (1.5)	51 (0.4)	61 (0.2)
B	11 (0.9)	12 (0.1)	5 (0.2)	6 (0.1)
F	334 (29.9)	474 (35.9)	585 (18.5)	754 (21.2)
Si	302048 (0.0)	303403 (0.0)	254464 (0.0)	255305 (0.0)
P	356 (1.9)	416 (10.7)	1028 (8.7)	1182 (33.5)
Cl	651 (52.9)	1195 (238.1)	55 (13.1)	80 (7.5)
Sc	70 (0.5)	73 (1.0)	92 (0.5)	94 (0.3)
Ti	2426 (2.8)	2484 (35.1)	4760 (26.5)	4808 (15.9)
V	78 (0.3)	87 (1.2)	111 (1.2)	114 (1.2)
Mn	178 (2.9)	270 (7.3)	655 (2.7)	641 (5.0)
Co	56 (1.7)	34 (1.8)	99 (0.6)	106 (2.7)
Rb	52 (1.5)	61 (1.5)	68 (1.8)	80 (0.2)
Y	50 (0.8)	44 (0.6)	84 (1.1)	84 (1.0)
Nb	88 (2.7)	94 (2.4)	95 (1.3)	99 (1.1)
Mo	42 (0.5)	55 (5.0)	53 (2.6)	73 (5.6)
Sn	1 (0.1)	2 (0.2)	1 (0.5)	1 (0.5)
Cs	56 (1.8)	67 (3.4)	100 (1.3)	111 (1.1)
Ti	2427 (97.1)	2461 (146.8)	0 (0.0)	4963 (50.4)
Sr	88 (1.2)	75 (2.3)		131 (5.4)
Y	50 (0.7)	44 (1.3)		86 (3.8)
Zr	71 (1.7)	68 (1.0)		95 (3.7)
Nb	91 (1.8)	93 (1.2)		102 (4.2)
Ba	26 (10.9)	41 (0.8)		78 (6.9)
La	73 (15.1)	25 (1.5)		67 (4.1)
Ce	33 (2.2)	28 (1.6)		114 (5.3)
Pr	31 (2.0)	27 (1.8)		70 (4.4)
Nd	32 (2.9)	28 (2.3)		71 (5.2)
Sm	35 (0.6)	28 (1.5)		70 (3.9)
Eu	36 (1.4)	30 (1.8)		72 (3.4)
Gd	42 (5.3)	35 (4.2)		82 (6.1)
Ho	46 (1.5)	43 (1.9)		80 (3.1)
Yb	50 (2.0)	48 (1.0)		79 (6.3)
Lu	52 (0.7)	53 (0.8)		81 (4.1)
Hf	69 (1.5)	72 (3.5)		90 (4.9)
Ta	3 (0.5)	2 (0.6)		6 (0.8)
W	4881 (1624.0)	65 (7.7)		77 (6.1)
Pb	9 (2.8)	13 (1.3)		8 (1.9)
Th	81 (3.3)	85 (2.3)		107 (5.8)
U	70 (2.4)	81 (1.5)		93 (5.2)

Table A6.2 Silicate glass trace element concentrations by LA-ICP-MS

Run #	Concentration (ppm)								
	70	71	87	57	69	32	62	23	22
Starting Composition	D3	D3	D2	D2	D2	D2	D1	A1	A1
Temperature (°C)	1200	1200	1200	1200	1100	1160	1200	1200	1100
Pressure (GPa)	1	0.75	1	0.75	0.75	0.2	1	1	1
n	10	10	10	10	10	6	10	8	10
Ti	2280 (33.7)	2251 (58.1)	2599 (59.5)	2619 (48.6)	2663 (59.8)	2511 (96.0)	3105 (79.5)	5046 (120.6)	5020 (267.3)
Li	52 (1.4)	54 (1.6)	53 (3.0)	51 (1.6)	62 (1.2)	58 (4.1)	64 (3.1)	48 (1.4)	61 (5.2)
Sc	92 (1.7)	92 (1.2)	78 (1.6)	77 (1.5)	85 (1.6)	85 (2.2)	112 (6.0)	102 (1.9)	93 (6.0)
V	81 (1.8)	82 (1.8)	74 (2.2)	75 (1.6)	81 (1.9)	74 (2.9)	83 (6.7)	107 (0.9)	123 (11.2)
Co	77 (1.4)	79 (2.2)	144 (4.3)	125 (4.4)	68 (1.1)	127 (3.9)	149 (9.7)	148 (2.1)	159 (18.3)
Rb	61 (2.0)	62 (1.5)	65 (2.7)	62 (2.2)	69 (1.6)	65 (2.0)	91 (4.1)	87 (2.7)	99 (5.7)
Sr	100 (3.2)	93 (2.8)	91 (2.0)	83 (3.2)	69 (1.7)	129 (5.4)	150 (4.0)	150 (2.8)	120 (9.8)
Y	68 (2.8)	70 (2.2)	64 (1.8)	58 (2.4)	57 (1.5)	78 (4.6)	94 (6.2)	94 (3.5)	86 (5.9)
Zr	78 (2.9)	79 (2.8)	77 (2.1)	82 (1.9)	85 (2.1)	80 (3.2)	111 (5.5)	101 (3.4)	95 (7.1)
Nb	84 (1.9)	87 (1.5)	101 (2.3)	102 (1.9)	106 (2.6)	101 (2.1)	121 (3.6)	107 (2.4)	112 (9.3)
Mo	52 (2.6)	48 (2.7)	40 (2.1)	42 (1.6)	50 (2.9)	39 (2.5)	49 (4.7)	60 (2.1)	81 (7.2)
Cs	66 (2.5)	67 (1.6)	69 (3.9)	63 (2.3)	70 (1.8)	68 (2.1)	103 (7.5)	121 (1.5)	134 (8.0)
Ba	38 (2.7)	39 (2.2)	35 (1.2)	32 (1.1)	41 (2.3)	49 (1.7)	58 (3.6)	59 (2.3)	75 (5.5)
La	48 (1.7)	48 (1.1)	42 (1.1)	81 (16.9)	31 (0.9)	62 (3.1)	72 (6.0)	73 (2.1)	69 (5.3)
Ce	55 (1.1)	56 (1.8)	47 (1.4)	40 (1.7)	35 (1.3)	66 (2.8)	80 (5.2)	120 (3.9)	119 (11.0)
Pr	51 (0.9)	53 (0.6)	44 (1.5)	38 (2.1)	34 (1.2)	62 (2.2)	79 (4.7)	81 (3.1)	75 (3.8)
Nd	54 (1.7)	56 (1.4)	47 (2.3)	41 (2.7)	36 (1.3)	68 (2.6)	86 (4.5)	86 (2.8)	75 (5.7)
Sm	58 (2.6)	61 (2.5)	53 (2.6)	47 (2.7)	42 (1.6)	69 (4.5)	90 (5.7)	90 (2.1)	76 (6.8)
Eu	55 (1.4)	56 (1.5)	49 (1.5)	44 (1.8)	38 (0.9)	69 (3.1)	80 (4.7)	84 (3.3)	75 (9.3)
Gd	60 (2.6)	63 (1.2)	54 (2.9)	48 (4.4)	43 (1.8)	73 (4.1)	90 (6.9)	88 (3.8)	81 (8.7)
Ho	65 (1.5)	67 (2.4)	59 (1.4)	54 (2.0)	54 (1.7)	73 (1.1)	91 (5.5)	85 (2.8)	80 (5.6)
Yb	71 (2.6)	72 (1.0)	65 (1.7)	60 (2.3)	62 (1.8)	74 (1.2)	95 (6.8)	92 (3.1)	87 (4.4)
Lu	72 (1.8)	71 (2.0)	66 (2.0)	61 (2.8)	67 (1.6)	76 (3.4)	98 (8.2)	95 (1.8)	86 (5.7)
Hf	80 (3.0)	80 (2.2)	78 (3.2)	76 (3.1)	83 (2.1)	84 (3.3)	111 (7.5)	100 (4.3)	94 (7.8)
W	54 (1.9)	46 (4.1)	50 (3.0)	4047 (1652.0)	60 (4.7)	46 (6.6)	83 (28.7)	67 (2.2)	88 (10.0)

Appendix A7 – Sulfate melt trace element concentrations

Table A7.1 Sulfate melt trace element concentrations by SIMS

Run #	Concentration (ppm)			
	57	69	23	22
Starting Composition	D2	D2	A1	A1
Temperature (°C)	1200	1100	1200	1100
Pressure (GPa)	0.75	0.75	1	1
n	3	3	4	3
Li	145 (14.8)	462 (243.3)	93 (68.4)	166 (75.8)
B	1 (0.2)	1 (0.4)	3 (3.0)	1 (1.2)
F	1660 (207.9)	4011 (711.0)	1806 (1212.1)	7804 (3574.8)
Si	1085 (208.1)	1497 (364.1)	5272 (1169.0)	3875 (1347.9)
P	541 (42.2)	484 (67.1)	2284 (1348.0)	2728 (1250.1)
Cl	21335 (3623.7)	50620 (30818.7)	29057 (11481.9)	4645 (1468.4)
Sc	39 (8.8)	52 (8.1)	29 (9.9)	29 (6.9)
Ti	271 (115.0)	340 (141.4)	703 (136.9)	617 (171.6)
V	73 (27.6)	92 (38.8)	104 (32.1)	125 (55.4)
Mn	402 (50.9)	700 (44.1)	1055 (871.8)	954 (176.4)
Co	88 (33.1)	66 (17.9)	62 (17.2)	71 (30.5)
Rb	49 (10.1)	143 (46.1)	100 (75.3)	107 (53.0)
Y	99 (2.4)	144 (18.9)	57 (10.7)	64 (4.9)
Nb	21 (6.6)	25 (11.5)	24 (6.0)	21 (4.8)
Mo	423 (23.1)	566 (51.3)	50 (21.9)	334 (281.9)
Sn	0 (0.1)	2 (0.7)	0 (0.3)	0 (0.4)
Cs	48 (10.3)	135 (83.5)	70 (29.9)	57 (28.2)
Ti	312 (80.6)	382 (117.6)	707 (124.1)	608 (193.2)
Sr	1222 (24.4)	1668 (290.0)	1611 (372.7)	1591 (333.8)
Y	103 (5.5)	145 (19.9)	56 (6.4)	66 (9.8)
Zr	3 (0.9)	4 (1.7)	4 (0.9)	8 (8.5)
Nb	25 (5.4)	29 (12.8)	26 (3.6)	23 (6.0)
Ba	379 (18.4)	1031 (309.6)	956 (710.1)	1132 (549.6)
La	335 (22.8)	327 (68.3)	152 (31.8)	180 (30.3)
Ce	184 (12.0)	264 (46.1)	183 (22.9)	219 (33.0)
Pr	161 (8.3)	227 (33.9)	102 (7.4)	125 (14.8)
Nd	172 (5.8)	237 (29.7)	103 (3.8)	126 (12.4)
Sm	165 (7.9)	232 (20.9)	94 (3.6)	118 (7.4)
Eu	241 (6.3)	327 (38.9)	147 (9.2)	177 (14.4)
Gd	165 (7.0)	222 (22.4)	100 (14.2)	120 (0.6)
Ho	106 (2.9)	150 (17.6)	54 (4.8)	64 (8.5)
Yb	84 (8.6)	122 (18.8)	43 (5.8)	46 (11.3)
Lu	72 (5.9)	102 (18.9)	36 (7.1)	37 (7.9)
Hf	1 (0.8)	2 (0.6)	2 (0.6)	1 (0.7)
Ta	4 (0.3)	5 (0.7)	2 (0.2)	3 (0.7)
W	17079 (3864.7)	240 (53.9)	27 (9.0)	186 (159.0)
Pb	66 (15.3)	69 (38.2)	22 (4.2)	45 (14.3)
Th	20 (4.6)	19 (4.2)	9 (1.3)	8 (2.2)
U	105 (27.6)	71 (19.6)	66 (23.9)	26 (0.8)

Table A7.2 Sulfate melt trace element concentrations by LA-ICP-MS

Run #	Concentration (ppm)								
	70	71	87	57	69	32	62	23	22
Starting Composition	D3	D3	D2	D2	D2	D2	D1	A1	A1
Temperature (°C)	1200	1200	1200	1200	1100	1160	1200	1200	1100
Pressure (GPa)	1	0.75	1	0.75	0.75	0.2	1	1	1
n	10	10	12	8	3	6	10	8	6
Ti	516 (157.9)	409 (150.7)	0 (0.0)	673 (526.7)	591 (359.0)	755 (256.0)	261 (84.7)	724 (232.4)	2038 (84.0)
Li	359 (352.8)	127 (594.6)	30 (22.0)	774 (594.6)	722 (790.7)	133 (186.9)	249 (118.7)	49 (30.6)	766 (620.5)
Sc	58 (27.2)	47 (49.6)	63 (34.7)	77 (49.6)	180 (11.4)	45 (36.1)	22 (7.8)	22 (11.7)	88 (46.6)
V	140 (86.0)	112 (88.4)	110 (76.7)	115 (88.4)	291 (60.1)	201 (234.2)	98 (50.1)	101 (58.7)	481 (246.6)
Co	224 (153.4)	141 (244.0)	572 (267.8)	349 (244.0)	504 (60.8)	461 (498.3)	146 (80.6)	116 (78.4)	528 (308.3)
Rb	99 (127.9)	43 (83.2)	30 (20.7)	121 (83.2)	186 (122.8)	24 (23.5)	63 (21.1)	28 (16.9)	248 (249.1)
Sr	1608 (336.7)	1419 (467.8)	1607 (474.9)	1549 (467.8)	2036 (440.7)	1094 (230.8)	1894 (687.2)	1416 (470.9)	1883 (1084.4)
Y	127 (48.2)	138 (50.7)	135 (46.4)	136 (50.7)	252 (56.9)	60 (10.4)	77 (21.6)	66 (17.5)	107 (12.7)
Zr	4 (2.1)	21 (4.0)	4 (4.1)	4 (4.0)	9 (2.2)	12 (9.6)	1 (0.1)	8 (4.3)	18 (9.6)
Nb	25 (11.0)	26 (28.5)	33 (18.0)	32 (28.5)	74 (7.3)	55 (53.0)	20 (8.7)	19 (9.4)	76 (24.7)
Mo	691 (595.8)	311 (562.4)	204 (179.9)	853 (562.4)	2311 (793.0)	352 (542.2)	610 (302.1)	42 (43.5)	1921 (1617.3)
Cs	42 (41.1)	25 (107.6)	7 (5.0)	136 (107.6)	206 (74.8)	11 (9.7)	63 (26.0)	16 (9.3)	108 (106.9)
Ba	599 (461.6)	459 (499.2)	468 (264.6)	733 (499.2)	1698 (340.7)	218 (173.5)	491 (146.9)	391 (285.7)	1237 (1252.1)
La	313 (104.6)	293 (111.6)	383 (123.7)	407 (111.6)	638 (90.8)	128 (20.2)	263 (71.0)	148 (49.7)	269 (21.6)
Ce	251 (84.4)	244 (84.8)	228 (70.5)	208 (84.8)	452 (18.9)	88 (17.2)	178 (51.1)	197 (48.0)	298 (36.0)
Pr	213 (61.3)	215 (58.1)	200 (59.3)	177 (58.1)	354 (84.5)	84 (12.8)	166 (44.1)	108 (29.9)	172 (13.2)
Nd	166 (60.3)	176 (57.7)	160 (51.6)	167 (57.7)	297 (60.7)	89 (20.2)	142 (39.5)	93 (23.8)	158 (31.6)
Sm	136 (46.7)	145 (50.5)	132 (42.4)	147 (50.5)	235 (36.6)	76 (19.0)	114 (31.8)	81 (22.9)	119 (28.8)
Eu	159 (53.0)	170 (57.4)	156 (54.1)	171 (57.4)	280 (61.4)	74 (16.0)	146 (42.1)	99 (29.5)	131 (23.5)
Gd	130 (37.2)	141 (41.8)	130 (39.9)	139 (41.8)	215 (54.6)	74 (20.6)	102 (31.0)	81 (18.9)	111 (32.3)
Ho	107 (41.2)	115 (35.1)	115 (41.5)	115 (35.1)	227 (41.3)	53 (12.3)	76 (18.3)	59 (16.8)	97 (16.9)
Yb	110 (60.1)	93 (51.5)	119 (50.4)	130 (51.5)	267 (33.4)	45 (13.6)	56 (14.8)	43 (14.6)	80 (19.9)
Lu	113 (65.3)	92 (59.8)	121 (52.7)	120 (59.8)	279 (60.6)	44 (11.7)	57 (14.7)	42 (12.9)	87 (25.3)
W	579 (414.8)	406 (4616.1)	442 (380.0)	6288 (4616.1)	2518 (1034.0)	425 (579.8)	638 (200.2)	98 (159.7)	2687 (1621.5)

Appendix A8 – Anhydrite trace element concentrations

Table A8.1 Anhydrite trace element concentrations by SIMS

Run #	Concentration (ppm)						
	68	54	24	61	16	69	22
Starting Composition	D2	D2	D2	D2	D2	D2	A1
Temperature	900	1000	1000	1000	1050	1100	1100
Pressure	0.75	0.2	0.75	1	0.75	0.75	1
n	5	1	3	3	4	3	2
Li	0.72 (0.15)	0.54 ()	0.77 (0.03)	0.82 (0.03)	0.56 (0.38)	1.01 (0.22)	0.92 ()
Na	324.32 (37.68)	307.66 ()	314.99 (16.72)	312.61 (7.50)	324.44 (24.82)	378.37 (84.46)	133.09 ()
K	81.97 (14.40)	63.04 ()	36.80 (1.42)	68.32 (9.44)	51.25 (6.82)	96.35 (65.04)	21.24 ()
Sc	1.18 (0.18)	1.00 ()	0.69 (0.06)	3.39 (0.98)	1.11 (0.09)	1.80 (0.05)	0.27 ()
V	0.39 (0.05)	0.53 ()	0.29 (0.02)	0.49 (0.05)	0.37 (0.11)	0.35 (0.06)	0.57 ()
Mn	37.82 (3.93)	27.95 ()	41.98 (0.30)	34.81 (1.20)	44.49 (5.29)	37.10 (2.73)	30.46 ()
Co	1.56 (0.12)	1.71 ()	1.57 (0.07)	1.62 (0.20)	1.64 (0.08)	1.34 (0.22)	1.26 ()
Rb	0.05 (0.04)	0.02 ()	0.09 (0.12)	0.06 (0.03)	0.10 (0.07)	0.13 (0.09)	0.08 ()
Y	125.43 (10.87)	139.93 ()	114.50 (8.73)	105.51 (3.82)	114.40 (4.71)	133.28 (9.75)	46.97 ()
Nb	9.08 (1.32)	0.15 ()	5.68 (4.89)	0.00 (0.00)	12.11 (3.97)	0.00 (0.00)	0.00 ()
Si	5.72 (0.52)	5.88 ()	17.76 (8.84)	44.59 (21.88)	16.54 (5.72)	4.49 (1.20)	23.35 ()
Ti	1.45 (0.37)	0.95 ()	1.73 (0.59)	1.35 (0.15)	1.69 (0.31)	1.27 (0.09)	3.13 ()
Sr	1294.28 (89.31)	1459.20 ()	1415.97 (71.01)	1450.30 (205.03)	1489.35 (123.61)	1417.30 (42.99)	1107.50 ()
Y	119.36 (8.61)	104.99 ()	115.24 (7.96)	101.53 (2.53)	115.14 (4.86)	130.02 (12.76)	47.14 ()
Ba	49.28 (1.44)	42.83 ()	44.56 (0.13)	52.83 (7.92)	41.63 (13.65)	43.98 (1.19)	50.20 ()
La	207.40 (14.85)	203.99 ()	207.47 (14.06)	208.60 (12.28)	215.28 (15.28)	221.72 (17.14)	121.73 ()
Ce	177.43 (18.17)	167.57 ()	185.61 (13.05)	179.97 (10.83)	189.87 (11.07)	198.74 (19.97)	158.91 ()
Pr	179.27 (14.99)	172.89 ()	184.26 (14.13)	173.54 (6.66)	187.33 (10.26)	199.02 (17.87)	102.18 ()
Nd	231.73 (21.90)	232.34 ()	233.32 (14.74)	218.10 (6.70)	239.22 (8.21)	255.79 (23.95)	122.22 ()
Sm	255.83 (20.08)	251.01 ()	256.12 (26.21)	244.84 (10.29)	267.03 (13.71)	289.33 (26.36)	124.30 ()
Eu	306.86 (21.33)	335.36 ()	342.07 (21.27)	303.55 (10.21)	339.86 (25.77)	364.83 (12.64)	169.00 ()
Gd	240.17 (13.33)	231.29 ()	232.20 (28.26)	219.65 (3.09)	246.17 (12.62)	260.93 (19.04)	111.48 ()
Ho	127.65 (10.59)	115.17 ()	125.75 (9.03)	108.35 (2.63)	125.08 (6.50)	138.31 (8.42)	48.15 ()
Yb	71.13 (8.05)	58.15 ()	75.30 (2.62)	56.85 (3.08)	60.67 (5.85)	71.82 (5.24)	22.60 ()
Lu	54.60 (5.93)	42.89 ()	54.45 (1.88)	41.20 (1.94)	47.01 (3.68)	55.61 (3.55)	15.37 ()
Hf	0.10 (0.10)	0.25 ()	0.21 (0.17)	0.02 (0.08)	0.03 (0.11)	0.14 (0.17)	0.11 ()
Ta	4.26 (0.55)	4.93 ()	5.28 (1.52)	4.18 (0.85)	5.11 (0.22)	4.33 (1.01)	1.70 ()
W	2.37 (0.42)	4.74 ()	2.77 (0.68)	2.97 (1.42)	2.60 (1.20)	4.20 (1.65)	4.68 ()
Pb	7.30 (0.82)	2.45 ()	2.72 (0.28)	3.10 (0.90)	2.23 (0.67)	5.16 (0.78)	1.56 ()