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Apatite Crystal Populations of the 1991 Mount Pinatubo eruption, Philippines:
Implications for the Generation of High Sulfur Apatite in Silicic Melts

by

Ashley Elizabeth Van Hoose

A thesis submitted in partial fulfillment of the
requirements for the degree of

Master of Science
in
Geology

Thesis Committee:
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ABSTRACT

On June 15, 1991, Mount Pinatubo, Philippines, ejected 20 million tonnes of sulfur dioxide into the atmosphere, significantly impacting global climate and stratospheric ozone. Recharging basaltic magma mixed into the 50 km³ dacitic magma reservoir 6 to 11 km beneath Mount Pinatubo, and triggered the 1991 eruption. The result of the magma mixing was a hybrid andesite with quenched basalt inclusions that erupted as a dome between June 7 and June 12. On June 15, approximately 5 km³ of anhydrite-bearing magma was erupted from the main phenocryst-rich, dacitic reservoir. This study will utilize this extraordinary framework of the 1991 Pinatubo eruption to investigate the systematics of sulfur uptake by apatite in order to further develop apatite as a monitor for magmatic sulfur.

In the dacite and hybrid andesite, apatite occurs as individual phenocrysts (up to ~200 μ m diameter) or included within anhydrite, hornblende, and plagioclase phenocrysts. In the basaltic magmatic inclusions, apatite is found as acicular microphenocrysts. Electron microprobe data collected on apatite yield low- (<0.3 wt.% SO₃), medium- (0.3-0.7 wt.% SO₃), and high-sulfur (>0.7 wt.% SO₃) apatites in all juvenile products, and show that two distinct populations of apatites exist: “silicic” apatites (hosted in dacite and andesite) and basalt apatites. Apatites crystallizing from silicic melt have predominantly low- to medium-sulfur contents, but high-sulfur apatites with as much as 1.2-1.7 wt.% SO₃ occur sporadically as inclusions in plagioclase, hornblende, Fe-Ti oxide, and anhydrite. These concentrations are much

higher than what could be achieved through equilibrium crystal-melt partitioning at pre-eruption conditions ($760\pm 20^{\circ}\text{C}$, 220MPa, NNO+1.7, 77 ppm S in melt inclusions) and a partition coefficient of 13. Apatite in the basalt is always sulfur-rich with compositions forming a continuous array between 0.7 to 2.6 wt.% SO_3 . The population of apatite that crystallized from silicic melt has elevated cerium, fluorine, and chlorine and lower magnesium concentrations (average dacite values in wt.%: 0.21 Ce_2O_3 , 1.4 F, 1.1 Cl, & 0.14 MgO) relative to the population of apatite from the basalt (average basalt values in wt.%: 0.05 Ce_2O_3 , 1.0 F, 0.78 Cl, & 0.22 MgO).

LA-ICP-MS trace element data also show distinct apatite populations between silicic and basalt apatites. Silicic apatites have elevated REE concentrations (La avg. = 750 ppm), lower Sr (avg. = 594 ppm), and a pronounced negative Eu anomaly (avg. $\text{Eu}/\text{Eu}^* = 0.57$) relative to basalt apatites (avg. values: 217 ppm La, 975 ppm Sr, and $\text{Eu}/\text{Eu}^* = 1.16$). The correlation of EMP sulfur data and LA-ICP-MS trace element data show no difference between high-S and low-S silicic apatites. These compositional systematics rule out the possibility that sulfur-rich apatite from dacite are inherited from mafic magma.

Sulfur element maps of apatites show no evidence of S-diffusion from anhydrite hosts. Areas of high-S concentrations show complicated patterns that suggest multiple periods of sulfur enrichment.

High-S silicic apatites are likely the product of “fluid-enhanced crystallization” from early enrichment of a SO_2 -rich fluid phase from the underplating basalt, which occurred prior to or at anhydrite saturation. This fluid phase is the only possible

sufficient source of sulfur for generating high-S apatites in a cool, “wet”, dacitic melt. The dynamics of apatite sulfur enrichment via “fluid-enhanced crystallization” is yet unclear and requires further experimental laboratory investigation.

DEDICATION

For Arron Steiner, your passion for hard rock geology
continues to inspire me.

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INTRODUCTION

On June 15, 1991, Mount Pinatubo, Philippines, erupted 5 km³ dense rock equivalent (DRE) of volcanic material, and, along with it, 20 million tonnes (Mt) of SO₂ into the stratosphere. At the time, it was the highest recorded amount of SO₂ released from a single eruption event recorded by the Total Ozone Mapping Spectrometer (TOMS) on NASA satellite, Nimbus 7 since it began monitoring global SO₂ and ozone in 1978 (Bluth, 1992). The 1991 Pinatubo eruption exceeded the SO₂ erupted from El Chichón in 1982 (~8 Mt) by nearly threefold (Luhr et al., 1984; Bluth, 1992). As a result, global warming trends were reversed for a few years after the eruption with some regional decreases in average temperature of 0.5 degrees Celsius as predicted by Hansen et al., (1992). The eruption was triggered by an injection of basaltic magma into the base of the dacitic magma chamber, which led to magma mixing and a hybrid andesitic scoria and lava. The hybridized material erupted days before the climactic plinian eruption of June 15th (Pallister et al., 1992, 1996; Wolfe and Hobbli, 1996).

High-sulfur eruptions such as the 1991 Pinatubo eruption are being recognized as more common than previously thought. The recognition of magmatic anhydrite crystallizing from these eruptions as a primary phase was first observed in the 1982 El Chichón trachyandesite, and has since been found in the 1991 Pinatubo dacite, Lascár Volcano, Chile (1993 and 26.5 ka), Redoubt Volcano, Alaska (USA) (1989-1990), Nevado del Ruiz, Columbia (1985), Mount Lamington, Papua New Guinea (1951), Sutter Buttes, California (USA) (Pleistocene 1.36-1.59 Ma), El Teniente “Porphyry

A", Central Chile (Late Miocene 5.7 Ma), Julcani, Peru (10.2 to 9.7 Ma), Yanacocha, Peru (14.5 to 8.4 Ma), Eagle Mountain (Oligocene), Santa Rita, New Mexico (USA) (63Ma) Cajon Pass Deep Scientific Drillhole, USA, California (Late Cretaceous (?)), and Cerro Lanza, Mexico, (Williams and Curtis, 1977; Arculus et al., 1983; Luhr et al., 1984; Rye et al., 1984; Drexler and Munoz, 1988; Fournelle, 1990; Luhr, 1990, 2008; Matthews et al., 1994; Bernard et al., 1996; Hattori, 1996; Pallister et al., 1996; Peng et al., 1997; Barth and Dorais, 2000; Parat et al., 2002; Audétat et al., 2004; Stern et al., 2007; Chambefort et al., 2008; Swanson and Kearney, 2008). Subduction zone-related, calc-alkaline, hydrous, highly oxidized volcanism with an excess of sulfur is the perfect environment for magmatic anhydrite to crystallize (Carroll and Rutherford, 1987). In addition to anhydrite, these conditions promote the growth of high-S apatite (>0.7 wt.% SO₃) by exchanging oxidized S⁶⁺ for P⁵⁺ via charge-balancing coupled substitutions with Na⁺, Si⁴⁺, and REE³⁺. It is because of this and apatite's resistance to weathering and ubiquitous nature, that apatite is being developed as a monitor for the changes of magmatic sulfur within a given melt (Peng et al; 1997; Streck and Dilles, 1998; Parat et al., 2002; Broderick, 2008).

The problem lies in the genesis of apatites with such enriched S contents in dacitic to rhyolitic melts (64 to 78 wt. % SiO₂). Sulfur concentrations in a melt are controlled by many interacting intensive parameters that may be in flux, such as temperature, pressure, oxygen fugacity (*f*O₂), and melt composition (i.e. silica content). Generally speaking, a relatively cool (800°C), oxidized, rhyolitic melt within a few kilometers of the surface cannot dissolve as much sulfur as a hot (1100°C),

oxidized, basaltic melt generated at depth. Furthermore, temperature, fO_2 , and S, P, and Ca concentrations of the surrounding melt also affect sulfur partitioning into apatite, complicating the relationship with sulfur further (Peng et al., 1997; Parat and Holtz, 2004, 2005). However, apatites with nearly 2 wt.% SO_3 have been observed in this and other studies (Streck and Dilles, 1998; Parat et al., 2002; Broderick, 2008). These high-S apatites were hosted in magmas that could not have the required sulfur concentration of 1,000 ppm or 615 ppm assuming equilibrium partitioning of sulfur between apatite and melt and a partition coefficient of 8 or 13, respectively (Baker and Rutherford, 1996b; Parat and Holtz, 2004, 2005). This means that such apatites either 1) grew in a melt different from the one they are currently hosted, i.e. they are inherited from a more mafic melt, 2) apatite is gaining sulfur from neighboring anhydrite, or 3) a transient and heterogeneous sulfur-rich fluid was present at times in the silicic melts, providing the required sulfur concentrations for high-S apatite crystallization. The object of this study is to determine which of these three mechanisms is generating high-S apatites in the 1991 Pinatubo system.

To do this, apatites from the three juvenile components of the 1991 Pinatubo eruption (dacitic pumice, hybrid andesite, and basalt inclusions within the andesite) were analyzed for major elements, including SO_3 , using electron microprobe (EMP) analyses, and trace elements, including rare earth elements (REE), using laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Apatites have long been recognized for controlling the REE budget in whole rock, and as such, used to monitor changes within a melt, such as magma mixing. Evidence for this would be expressed

as distinct apatite populations or chemical zonation, which has been shown with back-scattered electron (BSE) and cathodoluminescence (CL) imaging with a scanning electron microscope (SEM) in other studies. REE patterns and zonation in apatites give us many clues about a changing melt environment and are excellent tools for determining inheritance from another melt.

GEOLOGIC SETTING AND DESCRIPTION OF UNITS

Geologic Setting

Mount Pinatubo (1,745 meters above mean sea level; pre-eruption) (Newhall et al., 1996) is the northern-most volcano within a chain of mostly inactive volcanoes that comprise the Bataan segment of the Luzon Arc, which extends from the Philippines to Taiwan (Fig. 1). The 1,200 km arc consists of a chain of late Tertiary and Quaternary stratovolcanoes and volcanic necks of mostly andesitic composition (Defant et al., 1988, 1989, 1991). Mount Pinatubo is located on Luzon Island at latitude 15° 08' N, longitude 120° 22' E, 90 km northwest of Manila and 120 km east of the Manila Trench (Wolfe and Hoblitt, 1996). The Manila Trench and Luzon Arc are the result of the subduction of the South China Sea oceanic crust beneath the Philippine Sea plate that began 15 Ma in the Middle Miocene (Defant et al., 1988, 1989, 1991).

The Central Luzon Arc is divided into three segments. From north to south, these segments are the Bataan arc (BA), the Macolod Corridor (MC), and the Mindoro arc (MA) (Defant et al., 1988, 1989, 1991). The BA has two semi-parallel lineaments: the Western Bataan Lineament (WBL) and the Eastern Bataan Lineament (EBL). The MA is similar to the BA, and has two parallel lineaments: the West Mindoro Lineament (WML) and the East Mindoro Lineament (EML). These arcs are separated by the NE-SW “cross-arc” zone of volcanism, the Macolod Corridor, and may represent rifting (Defant et al., 1988, 1989, 1991). Mount Pinatubo lies north in the tightly spaced, arcuate volcanism of the WBL. The WBL is more depleted in alkalis,

large ion lithophile elements (LILE), and light rare earth elements (LREE) when compared to the MC, EBL, and MA (Defant et al., 1988, 1989, 1991). This is due to different levels of crustal and sediment contamination and degrees of partial melting (Defant et al., 1988, 1989, 1991).

Exposed west and northwest of Mount Pinatubo, the east-dipping Zambales Ophiolite Complex (ZOC) consists of gabbros, pyroxenites, peridotites, and related felsic intrusions. Directly north, the ZOC exposure is primarily basalt (Abranjano et al., 1989; Delfin et al., 1996; Newhall et al., 1996). Subsurface investigations for geothermal resources between August 1988 and November 1989 revealed the plutonic nature of the ZOC as “a chaotic mixture of hornfels and moderately to completely altered microdiorite, micro-quartz monzodiorite, diabase, and gabbroic dikes” (Delfin et al., 1996). The complex is intersected orthogonally by the Iba fracture zone; splitting it into three sections. Mount Pinatubo lies at the intersection of the two significant geologic features (Defant et al., 1988, 1989, 1991; Newhall et al., 1996). The WBL developed on the ZOC beginning about 4 Ma.

The Tarlac Formation consists of marine, non-marine, and volcanoclastic sediments of Miocene to Pliocene age that lie unconformably above the ZOC (Newhall et al., 1996). Exposures of this formation can be found northeast and southeast of Mount Pinatubo (Newhall et al., 1996).

Figure 1: Location map of Mount Pinatubo study area (after Delfin et al., 1996).

Eruptive History of Mount Pinatubo

The eruptive history of Mount Pinatubo can be divided into two main time periods: Ancestral Pinatubo (1Ma to some time prior to 35 ka) and Modern Pinatubo (35 ka to present) (Fig. 2). Relicts of the walls of the caldera of ancestral Pinatubo are embodied as rugged terrain surrounding Modern Pinatubo. Ancestral Pinatubo was an andesite-dacite stratovolcano that was roughly in the same location as Modern Pinatubo. Eruptive materials from ancestral Pinatubo include a two-pyroxene, hornblende andesite interbedded with pyroclastic flows and near-vent fall breccias. No evidence exists in support of large eruptions in ancestral Pinatubo's history, and all activity ceased tens to thousands of years prior to the initial growth and caldera forming eruptions of Modern Pinatubo (Newhall et al., 1996).

Modern Pinatubo's history can be divided into six or as many as a dozen eruptive periods. Due to the indistinct nature between the rock units from each period, classification of stratigraphy of Modern Pinatubo primarily relies upon radiogenic ^{14}C dating techniques performed on charcoal remnants from trees. Uncertainty of the sources of some of the charcoal samples and the potential of a tree fixing the amount of ^{14}C prior to its death from any given eruption prevents good certainty of the exact number of eruptive periods. The eruptive periods are significantly shorter than the periods of respite that can last hundreds to thousands of years (Newhall et al., 1996; Wolfe and Hoblitt, 1996) The main six eruptive periods of Modern Pinatubo are: Inararo period (>35 ka), Sacobia period (17 ka), Pasbul period (9 ka), Maraunot period (3.9 – 2.3 ka), and Buag period (500 a).

Products and eruptive phenomena of past eruptions of Modern Pinatubo are very similar to that of the 1991 eruptions (Newhall et al., 1996; Di Muro et al., 2008). The magma reservoir becomes enriched with volatiles from periodic influxes of basaltic magmas during long periods of respite. Evidence for this is observed in inclusions within products of historic eruptions (Daag et al., 1996b; Newhall et al., 1996; Wolfe and Hobblit, 1996; Di Muro et al., 2008). Andesitic to dacitic lavas erupt and form vent-filling domes, which then erupt explosively, destroying the initial dome. Over time, this has produced a stratigraphy rich in pumiceous pyroclastic flow and pumiceous lahar deposits. Late-stage domes of andesitic to dacitic lavas rebuild Pinatubo to pre-eruptive elevations. The repetitive phenomena, in addition to the unwelded, easily erodible pyroclastic flow materials, prevent Modern Pinatubo from ever growing very large (Newhall et al., 1996).

The main eruptive material from each of the Modern Pinatubo eruptive periods consists of a cummingtonite-hornblende dacite (~64 wt.% SiO₂) that almost always exists in two distinct phases: a white, crystal-rich phase (~47% phenocrysts), and a tan-grey crystal-poor phase (~15% phenocrysts) (Newhall et al., 1996; Pallister et al., 1996; Di Muro et al., 2008). The source of this material is believed to have existed consistently throughout Modern Pinatubo's history as a large, shallow, cool body of magma, and has been repeatedly replenished with volatiles from an underplating basaltic magma source. This is supported by the consistent material and nature of Modern Pinatubo eruptions (Daag et al., 1996b; Newhall et al., 1996). The source for this dacite reservoir is believed to be the fractionation of basalt that is generated by

direct partial melting of primitive mantle wedge material. The basalt melt ponds at the lower-crust/upper-mantle interface, briefly allowing the crystallization of garnet. This material begins fractional crystallization, and the more buoyant dacitic residue rises to shallow crustal levels, where it collects into a large magma reservoir beneath Modern Pinatubo (Prouteau and Scaillet, 2003). Eruptions only occur when there is sufficient saturation of volatiles in the dacite magma reservoir. Repose periods are growing shorter and eruptive volumes appear to be diminishing with time. The 1991 eruption was the smallest in Modern Pinatubo history with the shortest repose period (~500 years) (Newhall et al., 1996).

Figure 2: Geologic map of Ancestral and Modern Pinatubo volcanic deposits (after Newhall et al., 1996). Explanation of units is on the following page.

1991 Eruptions of Mount Pinatubo

The 1991 eruptions ended a 500 year hiatus from activity (Newhall et al., 1996) and produced four distinct juvenile magmatic components: a primary (~85 % volumetric proportion), white, phenocryst-rich dacitic pumice, a secondary (~15 %) tan, phenocryst-poor dacitic pumice, a hybrid-andesite, and an olivine-clinopyroxene quenched basalt that occurs as inclusions of variable size in the hybrid andesite (Bernard et al., 1996; David et al., 1996; Pallister et al., 1996).

Beginning in March 1991, two and a half weeks of local earthquakes announced the re-awakening of Mount Pinatubo. On April 2, the native Aeta people observed several steam eruptions, and numerous volcano-tectonic earthquakes occurred persistently, indicating the injection of a volatile-rich basalt into the dacitic magma reservoir (Pallister et al., 1992, 1996; Wolfe and Hoblitt, 1996). Pallister et al. (1992, 1996) have documented significant petrographic and geochemical evidence of magma mixing between the basaltic and dacitic endmembers to produce the hybrid andesite (Fig. 3). There is no evidence of assimilations of the ZOC (Fournelle et al., 1996; Pallister et al., 1996).

Correlation Spectrometer (COSPEC) measurements of SO₂ emissions from Pinatubo first taken in mid-May showed a rate of 500 tonnes of SO₂/day. This number increased tenfold by late May indicating either 1) magma was rising, or 2) the hydrothermal system beneath Pinatubo that had absorbed a good portion of the SO₂ released was being boiled, allowing more SO₂ to reach the surface (Daag et al., 1996a). From June 1st to 7th, localized, shallow earthquakes resolved a narrow pipe-like zone near the summit. The COSPEC measurement taken on June 5th was only 260 tonnes of SO₂/day, indicating that the conduit for the escaping gas was being plugged (Daag et al., 1996a). Shortly thereafter, a hybrid andesite dome with basaltic inclusions was formed between June 7th and 12th at the head of the Maraunot River canyon, northwest of the pre-eruption summit. A final pre-climactic eruption COSPEC measurement was made on June 10th and gave an SO₂ emission rate of 13,000 tonnes/day (Daag et al., 1996a). Four brief vertical eruptions began at 0851 (local

time) on June 12, destroying part of the andesitic dome, and continued until June 14. Eruptions during this time produced ash and andesitic scoria (Pallister et al., 1996; Wolfe and Hoblitt, 1996). A sequence of 13 surge-producing eruptions began June 14, leading to the final climatic eruption at 1342 on June 15 (Wolfe and Hoblitt, 1996). Peak eruptive conditions lasted for three hours and sent 2 to 10 km³ of eruptive material into the stratosphere at a discharge rate of 4x10⁸ to 2x10⁹ kg per second (Koyaguchi, 1996; Paladio-Melosantos et al., 1996). By 1440, the eruption cloud was 60,000 km² (Koyaguchi, 1996). The climactic plinian eruption covered 2,000 km² with normally graded ash and pumice 10 to 25 cm thick. The eruption spread material over most of Luzon plus 4 million km² of the South China Sea and Southeast Asia and ejected 17 million tons of SO₂ into the stratosphere (Bluth et al., 1992; Lynn et al., 1996).

To make matters worse for the people of Luzon, Typhoon Yunya passed within 75 km of Pinatubo on June 15 at 1100. The copious rainfall mixed with the tephra of the eruption, producing a heavy, sodden mess that caused a great deal of damage. Strong winds from the typhoon spread ash further than it would have traveled without the tropical storm. Post-paroxysmal eruptions and the residual heat near Mount Pinatubo generated moisture condensation and atmospheric instability. The result was increased rainfall, devastating lahars, and secondary phreatic eruptions (Oswalt et al., 1996).

Two pumice-types were produced during the June 12-14 and June 15 climactic eruptions. Each exhibit identical mineralogies and chemical compositions, including

both major and trace elements. It has been suggested that the difference in types is strictly due to a change from a sudden and violent eruptive episode early in the climactic June 15 eruption, to a less violent, more sustained eruption. The violent nature in the early eruption physically shattered any crystals that had grown in the magma reservoir, as evidenced in the abundant and small (<10 micrometers (μm) to <1 μm) crystal fragments observed in the phenocryst-poor type (Bernard et al., 1996; David et al., 1996; Pallister et al., 1996).

Rutherford and Devine (1996) report pre-eruption conditions of $780^{\circ}\pm 10^{\circ}\text{C}$, $f\text{O}_2$ of 3 log units above the nickel-nickel oxygen buffer (NNO+3). However, there is work by Evans and Scaillet (1997) and Scaillet and Evans (1999) that suggests that this is an overestimate due to improper use of the Fe-Ti oxide geothermometer at such high oxygen fugacities and that pre-eruption $f\text{O}_2$ is likely closer to NNO+1.7. Total pressure was 220 ± 50 megapascals (MPa). This pressure is the equivalent of depths of 7.7 ± 1.75 kilometers (km) beneath Mount Pinatubo, and correlates well with the low seismic velocity zone measured at depths of 6 to 11 km (Mori, et al., 1996; Rutherford and Devine, 1996). The dacitic magma reservoir was hydrous and volatile-rich with 5.1 to 6.4 wt.% H_2O . Sulfur concentrations varied between melt inclusions (55 to 77 ± 28 ppm) and matrix glass (36 ppm) (Rutherford and Devine, 1996). Fe-Mg exchange equilibria suggest a basalt magma temperature of 1200°C (Pallister et al., 1996).

Between July and November 1992, a freshly mixed andesite dome grew in the floor of the caldera before it was filled with rainwater. Geochemical evidence showed

that a new batch of basalt had injected into the dacitic reservoir to produce the 1992 andesite dome (Daag et al., 1996b). COSPEC measurements during this period revealed an SO₂ emission rate of only 200 – 600 tonnes/day (Daag et al., 1996a). The dacitic chamber was still degassed or gas-poor and only able to produce effusive lava dome eruptions (Daag et al., 1996a, 1996b).

Figure 3: Magma mixing model for the trigger of the 1991 Mount Pinatubo eruptions. Basalt recharge into the dacitic magma reservoir generated a hybrid andesite that buoyantly rose to the surface, generating a path for the volatile-saturated dacite magma to follow and erupt explosively (after Pallister et al., 1996).

Sample Descriptions

Dr. John S. Pallister graciously donated samples for this study from the collection at the Cascades Volcano Observatory (CVO) United States Geologic Survey (USGS) in Vancouver, WA. The samples are generic representatives of three of the four juvenile magmatic components from the 1991 Pinatubo eruption and were

collected shortly after the climactic eruption. The samples are the phenocryst-rich dacitic pumice, PH12C (64 wt.% SiO₂) collected from the Bucao drainage on the northwest flank of Pinatubo, the hybrid andesite lava, CN6791-d (59 wt.% SiO₂), and the basalt inclusion, P-22892-2a (51 wt.% SiO₂). Both the andesite and basalt samples were collected from the Maraunot River drainage northwest of the current caldera (Fig. 4 and Fig. 5) The phenocryst-poor dacitic pumice has been selectively excluded from the scope of this study due to a lack of sufficiently sized and preserved crystals. Detailed sample descriptions can be found in Appendix A.

Apatite is present in all of the samples. Dacite- and andesite-hosted apatites (silicic apatites) are euhedral to subhedral, range in size from 10 µm to 180 µm, and are found as inclusions in anhydrite, plagioclase, hornblende, and Fe-Ti oxides, or as individual groundmass phenocrysts. Basalt-hosted apatites (mafic apatites) have a strikingly different morphological expression, and are often acicular and skeletal, suggesting rapid growth due to quenching. These apatites are typically much smaller than silicic apatites (~5 µm to 60 µm) and do not occur as inclusions in other host phenocrysts. Due to this morphological difference, apatites in the hybrid andesite were likely inherited solely from the dacite endmember. The objective of this study was to constrain the conditions of the formation of high-S silicic apatites using the well-documented 1991 Pinatubo system as a framework.

Figure 4: Mount Pinatubo sample location map. Basalt (green) and andesite (blue) samples were taken from stratified pyroclastic flow deposits at the top of the Maraunot River drainage. Dacite (red) samples were collected from ash fall deposits in the Bucayo drainage (after Pallister et al., 1996).

Figure 5: Samples and thin sections from the 1991 Mount Pinatubo eruption used in this study. PH12C (red) is a sample of the crystal-rich dacitic pumice from the climactic June 15 plinian eruption. CN6791-d (blue) is a sample of the hybrid andesite lava from the June 7-12 dome. P-22892-2a (green) is a sample of a large, quenched basaltic inclusion from the June 7-12 dome.

ANALYTICAL METHODS

Electron Microprobe (EMP) Analysis

Apatites from thin sections were analyzed for major elements using a five-spectrometer CAMECA SX100 electron microprobe housed at Oregon State University. Analyses were controlled via remote access at Portland State University. Apatite analysis operating conditions were an accelerating voltage of 15kV, a beam current of 20 nA, and a beam size of 2 μm diameter. Apatite analyses and EMP procedures can be found in Appendix B. The main purpose of the EMP analyses was to determine the sulfur content and intra-grain variability across apatite grains using traverse analyses (Fig. 6).

Additionally, several of the smaller apatites that were unsuitable for LA-ICP-MS were selected for element mapping of S, Na, F, Cl, and P to produce a more complete picture of sulfur distribution within a given grain. Apatites selected for element mapping were hosted within primarily anhydrite, but also hornblende and Fe-Ti oxides. Apatite element mapping operating conditions were an accelerating voltage of 15kV, a beam current of 30 nA, and a beam size of 0 μm diameter. All element maps generated in this study can be found in Appendix F.

Figure 6: Illustration of the method used to correlate major element data collected with EMP (green traverse) and trace element data collected with LA-ICP-MS (red circles). Laser spots were selected to overlap the microprobe traverse. Major element values used with trace element data are the average of the EMP spots overlapped by the laser spot. Two examples of apatites: a) apatite cut perpendicular to the c-axis with a single laser spot; b) apatite cut parallel to the c-axis with multiple laser spots.

Laser-Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

Trace elements, including REE, were acquired on apatites, anhydrites, plagioclase, hornblendes, and glass from thin sections using LA-ICP-MS analyses. To ensure data consistency, a large crystal of Durango apatite was also analyzed. These analyses agreed well with published values (Fig. 7). LA-ICP-MS data were acquired

using the 193 nm ArF Excimer Laser coupled with an ELAN 6100 ICP quadrupole mass spectrometer at Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland. Laser settings were 23, 24, 28, and 30 kV and a 10 Hz repetition rate, yielding a fluence of about 12 J/cm² on the ablation site. For apatites, beam sizes of 15, 20, and 40 µm were used.

Figure 7: Durango apatite REE data collected from LA-ICP-MS in this study compared to other reported data. Data collected by Roeder et al., 1987, Young et al., 1969, and Rogers et al., 1984 was converted to ppm from oxide EMP results. Data from Kimura et al., 2000 was collected by LA-ICP-MS and compares well with the data collected during this study.

Apatites selected for LA-ICP-MS analyses had to be large enough for the sizeable laser spots. Dacite-, andesite-, and basalt-hosted apatites were selected with a variable range of SO₃ including low (<0.3 wt.%), medium (0.3-0.7 wt.%), and high (>0.7 wt.%). Locations of EMP traverses were recorded on petrographic microscope images taken of the apatites. Using these images, laser spot positions were selected to overlap the pre-existing traverses (Fig. 6). Some apatites were large enough for up to

four laser spots, but the majority was only large enough for one. Host minerals were analyzed in order to identify and reduce sources of potential contamination (Figs. 8 and 9) during ablation using 15, 20, and 40 μm beam sizes appropriate for individual crystals (See Appendix E for host and glass LA-ICP-MS results).

The MATLAB-based program, SILLs, was used to process all LA-ICP-MS data. SILLs requires both an internal and external standard to quantify element concentrations. NIST 610 was the external standard used at ETH, and the internal standard for apatites was CaO concentration set to 54 wt.%. For further details on the calculation settings used in SILLs for apatites, Durango apatites, host minerals, and glass, refer to Appendix C. Figures 8 and 9 are examples of the user interface window used to select integration intervals for background levels, signal (apatite concentrations), and matrix (host mineral/glass concentrations). Apatite intervals were selected in order to minimize contamination from any surrounding matrix by maximizing P, Ca, and Ce signals, and minimizing signals belonging to matrix, such as Al, K, S, Ba, and Mg. Comparison of measured REE values from this study to previously published Durango apatite REE data normalized to C1 chondrite (Fig. 7) provides confidence in the accuracy of the LA-ICP-MS results from this study.

Figure 8: SILLS user interface window with selected integration intervals for background levels and signal (apatite).

Figure 9: SILLs user interface window. Selected interval for apatite signal was carefully chosen to reduce the effects of matrix contamination from host anhydrite.

Correlation of EMP and LA-ICP-MS

SO₃ and other major element concentrations determined by EMP analyses were correlated with the trace and REE concentrations, such as Sr and La, acquired with LA-ICP-MS by taking the average of the EMP spot values overlapped by the LA-

ICP-MS laser spot (Fig. 6). Concentric growth was assumed for apatites when laser spots did not directly overlap a microprobe traverse, i.e. major element concentrations were assumed to have the same profile from the center to any point along the rim. By overlapping EMP sulfur concentrations and LA-ICP-MS trace element data, we can observe if changing sulfur concentrations correlates with changing trace element and REE concentrations. Ce, S, and Na₂O were collected with both analytical methods, and the comparison of results is provided in Figures 10, 11, and 12. A general trend with some scatter along the 1:1 line provides confidence in the quality of both data sets.

Figure 10: Cerium concentrations of apatites measured by EMP and LA-ICP-MS. Positive trend along the 1:1 line gives confidence in the accuracy of the LA-ICP-MS data. The bars that correspond with the EMP axis represent the range of EMP Ce values overlapped by the laser spot.

Figure 11: Sulfur concentrations of apatites measured by EMP and LA-ICP-MS. Positive trend along the 1:1 line gives confidence in the accuracy of the LA-ICP-MS data. Measuring sulfur concentrations with LA-ICP-MS is a difficult process and some deviation from the 1:1 line is expected. Additionally, laser spots may not correspond perfectly with the area measured by EMP. The bars that correspond with the EMP axis represent the range of EMP S values overlapped by the laser spot.

Figure 12: Sodium concentrations of apatites measured by EMP and LA-ICP-MS. Positive trend along the 1:1 line gives confidence in the accuracy of the LA-ICP-MS data. High Na₂O values measured by LA-ICP-MS reflect some contamination from the matrix. However, these data points showed acceptable trace element concentrations and were kept in the data set. The bars that correspond with the EMP axis represent the range of EMP S values overlapped by the laser spot.

RESULTS

Major Element Apatite Populations

One of the theories behind the generation of high-S apatites in dacitic to rhyolitic melts tested in this study is inheritance of apatites from more mafic melts. To address this and determine if significant populations of apatite exist among those hosted in the dacite, andesite, and basalt based on major element data alone, F- and t- statistical tests were performed using descriptive statistics of the EMP data (Table 1 and Table 2). Confidence levels were set to $\alpha = 0.05$ for all statistical analyses.

The F-test is a comparison of the variances (i.e. the width of the normal distribution curve) between two populations under the assumed null hypothesis (H_0) that the variances are equal (Davis, 2002). The results of the F-test (Table 1, Fig. 13) between the dacite- hosted apatites and the andesite-hosted apatites show that H_0 is rejected for Cl, SO_3 , Ce_2O_3 , FeO, SiO_2 , Na_2O , and MgO, meaning that there is a statistically significant difference between the variances of each of these oxides between dacite- and andesite-hosted apatites. No significant difference could be detected in the variances of CaO, P_2O_5 , F, and MnO. Comparing dacite- and basalt-hosted apatites, there were significant differences in variances of all elements of Table 1 except Cl, and Ce_2O_3 . The andesite- vs. basalt-hosted apatite F-test resulted in differences in variances of all elements except F, Ce_2O_3 , and FeO. In short, the results of the F-tests indicate that the variance of the most abundant oxides within an apatite (CaO and P_2O_5) cannot be distinguished between the dacite- and andesite-hosted

apatites, but can be distinguished when either the dacite- or andesite-hosted apatites are tested against the basalt-hosted apatites. These data support the position of andesite-hosted apatites coming solely from the dacite during magma mixing.

The t-test is a comparison of the means of two populations where H_0 = means of the two populations are the same (Davis, 2002). When comparing the means of the major elements and oxides of the basalt-hosted apatite with the dacite- and andesite-hosted apatites, all of the elements and oxides measured in the EMP analyses reject H_0 . There is a significant difference in the means of all the oxides of dacite-hosted vs. basalt-hosted apatites and andesite-hosted vs. basalt-hosted apatites (Table 2, Fig. 14). The results of the t-test between the dacite- and andesite-hosted apatites show that only CaO and SiO₂ cannot be distinguished at $\alpha=0.05$. Overall, the results of the statistical tests show that there are at least two (dacite/andesite and basalt), maybe three (dacite, andesite, and basalt) statistically significant apatite populations based solely on major element concentrations. Plots of Ce₂O₃ vs. MgO and major elements against SO₃ further confirm these results (Figs. 15, 16, and 17). For purposes of simplicity and clarity, dacite and andesite apatites will be a single group collectively referred to as “silicic apatites”. This term in no way suggests any significantly large amount of SiO₂ within these apatites, such that they should be classified as Ellestadite (Pasero et al., 2010).

One additional statistical test was performed on a particular basalt-hosted apatite (P-22892-2a Ap1). This apatite, unlike all of the other analyzed basalt apatites, is an inclusion hosted in a hornblende that has experienced significant disequilibria

conditions and does not display the typical acicular and skeletal morphologies. Furthermore, EMP analysis of this apatite shows major element concentrations that more closely resemble that found in dacite and andesite apatites. To determine statistically if this apatite is a xenocryst originally from the dacite, a Z-test was performed to compare the mean values of the single microprobe traverse across P-22892-2a Ap1 with the means and standard deviations of dacite, andesite, and basalt apatites. For this test, H_0 = xenocryst is the same as the major group. Rejection of H_0 occurred only when P-22892-2a Ap1 was tested against the basalt apatites (P_2O_5 , Cl, SO_3 , Ce_2O_3 , and MgO). This confirms that P-22892-2a Ap1 is a xenocryst and likely originated from the dacite. This special case will be re-visited in the discussion.

Table 1: Descriptive statistics of the EMP data collected from Pinatubo apatites. Listed are the results of the F-test comparing the means of apatites from the three juvenile components. There are three statistically significant groups between the dacite, andesite and basalt apatites.

		CaO	P ₂ O ₅	F	Cl	SO ₃	Ce ₂ O ₃	FeO	SiO ₂	Na ₂ O	MnO	MgO
Mean	N											
Dacite	401	53.72	41.16	1.40	1.13	0.30	0.21	0.37	0.27	0.13	0.18	0.14
Andesite	70	53.90	41.68	1.20	1.16	0.19	0.21	0.47	0.21	0.12	0.20	0.16
Basalt	145	53.33	39.35	1.00	0.78	1.52	0.05	0.49	1.17	0.34	0.13	0.22
Std Dev												
Dacite		0.97	0.80	0.25	0.18	0.26	0.07	0.18	1.25	0.07	0.06	0.02
Andesite		0.91	0.81	0.22	0.14	0.20	0.06	0.15	0.46	0.06	0.05	0.03
Basalt		1.48	1.22	0.20	0.20	0.53	0.06	0.15	1.71	0.16	0.07	0.03
Xenocryst		53.86	41.79	1.10	1.19	0.16	0.20	0.52	0.12	0.11	0.22	0.13
F-Test												
H ₀ = The variances of the 2 groups are the same												
α = 0.05												
Dacite vs. Andesite												
F-Stat		1.14	1.03	1.36	1.78	1.81	1.60	1.39	7.45	1.67	1.30	1.47
F-Table Value		1.38	1.33	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.33
Reject H₀?		Fail	Fail	Fail	Reject	Reject	Reject	Reject	Reject	Reject	Fail	Reject
Dacite vs. Basalt												
F-Stat		2.32	2.36	1.58	1.22	4.05	1.20	1.49	1.90	4.54	1.79	2.37
F-Table Value		1.25	1.25	1.26	1.25	1.25	1.26	1.26	1.25	1.25	1.25	1.25
Reject H₀?		Reject	Reject	Reject	Fail	Reject	Fail	Reject	Reject	Reject	Reject	Reject
Andesite vs. Basalt												
F-Stat		2.63	2.30	1.16	2.17	7.32	1.33	1.07	14.1	7.61	2.33	1.62
F-Table Value		1.43	1.43	1.39	1.43	1.43	1.43	1.39	1.43	1.43	1.43	1.43
Reject H₀?		Reject	Reject	Fail	Reject	Reject	Fail	Fail	Reject	Reject	Reject	Reject

Table 2: Results of the t-test comparing the means of apatites from the three juvenile components. Z-test results comparing the average EMP values of the xenocryst apatite hosted in basalt to each of the groups confirms it did not grow in the basalt.

	CaO	P ₂ O ₅	F	Cl	SO ₃	Ce ₂ O ₃	FeO	SiO ₂	Na ₂ O	MnO	MgO
t-Test											
H ₀ = The mean values of the 2 groups are the same											
α = 0.05											
Dacite vs. Andesite											
t-Stat	-1.54	-6.34	24.73	-8.72	12.6	-1.98	-26.2	0.33	15.5	-48.5	-176
Two-Tail	1.97	Fail	Reject	Reject	Reject	Reject	Reject	Fail	Reject	Reject	Reject
One-Tail	1.65	Fail	Reject	Reject	Reject	Reject	Reject	Fail	Reject	Reject	Reject
Dacite vs. Basalt											
t-Stat	3.17	21.6	70.1	101	-99.8	353	-43.4	-4.88	-208	150	-1173
Two-Tail	1.96	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject
One-Tail	1.65	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject
Andesite vs. Basalt											
t-Stat	2.26	13.1	31.5	77.7	-44.8	296	-5.79	-3.23	-86.0	111	-432
Two-Tail	1.97	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject
One-Tail	1.65	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject
Z-Test											
H ₀ = Xenocryst is the same as rock sample											
α = 0.05											
Z-Stat											
Dacite	0.14	0.80	-1.18	0.32	-0.54	-0.12	0.83	-0.12	-0.35	0.76	-0.46
Andesite	-0.05	0.14	-0.46	0.17	-0.19	-0.18	0.29	-0.20	-0.27	0.49	-0.82
Basalt	0.36	1.99	0.48	2.00	-2.56	2.37	0.17	-0.62	-1.51	1.29	-2.52
Critical Value	1.96										
Reject H₀?											
Dacite	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail
Andesite	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail
Basalt	Fail	Reject	Fail	Reject	Reject	Reject	Fail	Fail	Fail	Fail	Reject

Figure 13: Descriptive statistics of the EMP data collected from Pinatubo apatites. Results of the F-test comparing the means of the three groups are shown above each oxide/element. Null hypothesis states that the variances of the groups are the same: Reject – reject the null, Fail – fail to reject the null. There are three statistically significant groups between the dacite, andesite and basalt apatites.

Figure 14: Descriptive statistics of the EMP data collected from Pinatubo apatites. Results of the t-test comparing the means of the three groups are shown above each oxide/element. Null hypothesis states that the means of the groups are the same: Reject – reject the null, Fail – fail to reject the null. There are three statistically significant groups between the dacite, andesite and basalt apatites.

Figure 15: EMP apatite data distinguishing populations of apatites. The dacite and andesite-hosted apatites form a population with higher Ce_2O_3 wt.% concentrations and lower MgO wt.% concentrations. Basalt-hosted apatites have lower Ce_2O_3 wt.% concentrations and higher MgO wt.% concentrations.

Figure 16: EMP apatite data. Apatite populations are distinguished by Ce_2O_3 wt.%, Cl wt.%, and F wt.%. FeO wt.% concentrations are comparable between populations. Colors and symbols are as previously defined. Purple dashed lines delineate the boundaries between low- and medium-S apatites (0.3 wt.% SO_3) and medium- and high-S apatites (0.7 wt.% SO_3).

Figure 17: EMP apatite data. Apatite populations are distinguished by MgO wt.% concentrations. MnO wt.% concentrations are comparable between populations. Negative correlation between P_2O_5 wt.% and SO_3 wt.% (c.) shows the replacement of P^{5+} for S^{6+} . Colors and symbols are as previously defined.

Sulfur

EMP results revealed SO_3 concentrations ranging from 0.1 to 2.6 wt.%, with a single basalt apatite analysis reaching as high as 3.5 wt.%. Apatites were divided by their SO_3 concentrations as defined by Broderick (2008): low-S apatites (<0.3 wt.%), medium-S apatites (0.3-0.7 wt.%), and high-S apatites (>0.7 wt.%). Silicic apatites

ranged from 0.1 to 1.7 wt.% SO₃, and 29% of these apatites analyzed had a least one EMP analysis with a high-S value. All basalt apatites analyzed were found to be high-S apatites with only two analysis points falling below 0.7 wt.%. Tables 3 through 6 present representative EMP data of low, medium, high, and variable-S apatites. Refer to Appendix B for complete EMP analyses.

S⁶⁺ was readily available in all three juvenile components due to the high oxidative conditions of the 1991 Pinatubo eruption. This is consistent with the data indicating that most sulfur exists as S⁶⁺ species at or above NNO+1 (Carroll and Rutherford, 1985, 1987, 1988; Nilsson and Peach, 1993; Metrich and Clocchiatti, 1996; Paris et al., 2001; Jugo et al., 2005a, 2005b). Sulfur can only enter the T-site in apatite (Fig. 18) by replacing P⁵⁺ via coupled substitutions as sulfate, S⁶⁺. Sulfide, S²⁻, generated under reducing conditions, is unsuitable as a replacement for P⁵⁺. Several exchange reactions governing the concentration of sulfur in apatite have been proposed:

Table 3: Representative EMP results for low-S (<0.3 wt.% SO₃) apatites from 1991 Pinatubo eruption. Position of analysis on crystal is approximate.

Sample Apatite Position	PH12C-1 ap7 core	PH12C-1 ap7 mid	PH12C-1 ap7 rim	CN6791-d ap2 core	CN6791-d ap2 mid	CN6791-d ap2 rim	P-22892-2a ap1 core	P-22892-2a ap1 mid	P-22892-2a ap1 rim
CaO	53.91	54.12	53.38	54.14	54.55	54.01	54.00	53.69	54.16
P ₂ O ₅	42.15	41.96	41.28	42.19	42.39	42.36	42.29	41.89	41.55
F	1.26	1.08	1.26	1.11	1.12	1.50	1.10	1.08	0.91
Cl	1.14	1.15	1.33	1.26	1.27	1.13	1.12	1.17	1.24
SO₃	0.11	0.10	0.15	0.11	0.12	0.22	0.13	0.09	0.14
Ce ₂ O ₃	0.09	0.14	0.21	0.14	0.18	0.20	0.18	0.19	0.27
FeO	0.43	0.32	0.41	0.30	0.35	0.62	0.53	0.52	0.64
SiO ₂	0.06	0.07	0.13	0.09	0.04	0.14	0.06	0.07	0.08
Na ₂ O	0.12	0.10	0.14	0.09	0.11	0.12	0.09	0.10	0.10
MnO	0.18	0.21	0.20	0.21	0.19	0.11	0.25	0.22	0.30
MgO	0.15	0.15	0.15	0.15	0.15	0.17	0.14	0.13	0.15
Subtotal	99.60	99.40	98.63	99.80	100.46	100.57	99.88	99.14	99.54
-O = F + Cl	0.79	0.71	0.83	0.75	0.76	0.89	0.72	0.72	0.66
Total	98.81	98.69	97.79	99.05	99.71	99.69	99.16	98.42	98.88

Table 4: Representative EMP results for medium-S (0.3-0.7 wt.% SO₃) apatites from 1991 Pinatubo eruption. Position of analysis on crystal is approximate.

Sample Apatite Position	PH12C-7 ap18 core	PH12C-7 ap18 mid	PH12C-7 ap18 mid	PH12C-7 ap18 rim	CN6791-d ap1 core	CN6791-d ap1 rim
CaO	54.05	54.04	54.26	53.90	54.26	54.06
P ₂ O ₅	41.22	40.95	41.01	41.08	42.01	41.56
F	1.95	1.75	1.82	1.99	1.57	1.79
Cl	0.49	0.49	0.51	0.44	1.04	0.88
SO₃	0.46	0.58	0.42	0.35	0.24	0.35
Ce ₂ O ₃	0.09	0.20	0.16	0.17	0.18	0.19
FeO	0.28	0.28	0.26	0.25	0.58	0.57
SiO ₂	0.15	0.19	0.16	0.12	0.12	0.56
Na ₂ O	0.20	0.23	0.17	0.17	0.16	0.19
MnO	0.08	0.23	0.21	0.16	0.21	0.05
MgO	0.13	0.13	0.12	0.11	0.17	0.20
Subtotal	99.11	99.07	99.11	98.73	100.54	100.39
-O = F + Cl	0.93	0.85	0.88	0.94	0.90	0.95
Total	98.17	98.22	98.23	97.79	99.64	99.44

Table 5: Representative EMP results for high-S (>0.7 wt.% SO₃) apatites from 1991 Pinatubo eruption. Position of analysis on crystal is approximate.

Sample Apatite Position	PH12C-7 ap7 core	PH12C-7 ap7 mid	PH12C-7 ap7 rim	CN6791-d ap4 core	CN6791-d ap4 rim	P-22892-2a ap26 core	P-22892-2a ap26 mid	P-22892-2a ap26 rim
CaO	53.57	54.01	54.29	52.45	54.30	53.07	54.32	55.86
P ₂ O ₅	40.40	40.69	41.12	40.29	40.90	39.37	39.09	37.74
F	1.42	1.41	1.33	1.17	1.20	1.37	1.33	0.92
Cl	1.21	1.17	1.16	0.64	0.61	0.58	0.46	0.50
SO₃	1.33	0.76	0.92	1.03	1.14	1.14	1.49	1.47
Ce ₂ O ₃	0.37	0.20	0.17	0.17	0.17	0.16	0.08	0.10
FeO	0.33	0.38	0.31	0.24	0.22	0.39	0.49	0.43
SiO ₂	0.32	0.13	0.10	0.62	0.64	0.67	0.80	0.68
Na ₂ O	0.23	0.15	0.16	0.32	0.36	0.24	0.41	0.34
MnO	0.19	0.26	0.13	0.18	0.14	0.12	0.03	0.07
MgO	0.14	0.15	0.13	0.11	0.12	0.20	0.23	0.23
Subtotal	99.51	99.31	99.83	97.21	99.79	97.31	98.73	98.34
-O = F + Cl	0.87	0.86	0.82	0.64	0.64	0.71	0.66	0.50
Total	98.64	98.45	99.01	96.58	99.15	96.60	98.07	97.84

Table 6: Representative EMP results for 1991 Pinatubo “silicic” apatites with variable SO₃ concentrations. Position of analysis on crystal is approximate.

Sample Apatite Position	PH12C-7 ap16 core	PH12C-7 ap16 core	PH12C-7 ap16 mid	PH12C-7 ap16 mid	PH12C-7 ap16 rim	CN6791-d ap5 core	CN6791-d ap5 mid	CN6791-d ap5 mid	CN6791-d ap5 rim
CaO	53.11	53.84	53.44	54.16	54.38	54.36	53.47	53.96	53.61
P ₂ O ₅	40.50	40.59	40.26	41.52	41.00	42.34	41.30	41.19	41.94
F	1.36	1.35	1.33	1.30	1.26	1.05	1.09	1.01	1.06
Cl	1.33	1.36	1.40	1.27	1.25	1.15	1.25	1.16	1.19
SO₃	0.57	0.67	0.91	0.41	0.15	0.09	0.87	0.42	0.10
Ce ₂ O ₃	0.22	0.21	0.24	0.25	0.06	0.14	0.24	0.25	0.16
FeO	0.59	0.54	0.63	0.62	0.68	0.54	0.55	0.47	0.55
SiO ₂	0.42	0.30	0.38	0.16	0.20	0.08	0.30	0.14	0.15
Na ₂ O	0.20	0.22	0.27	0.15	0.11	0.09	0.31	0.19	0.08
MnO	0.09	0.25	0.26	0.15	0.14	0.21	0.21	0.16	0.20
MgO	0.15	0.16	0.17	0.15	0.14	0.15	0.14	0.15	0.17
Subtotal	98.53	99.49	99.27	100.14	99.37	100.19	99.74	99.09	99.22
-O = F + Cl	0.87	0.87	0.87	0.83	0.81	0.70	0.74	0.69	0.72
Total	97.66	98.61	98.39	99.30	98.56	99.50	99.00	98.41	98.50

Table 6: Continued. Basalt apatite.

Sample	P-22892-2a	P-22892-2a	P-22892-2a
Apatite	ap33	ap33	ap33
Position	core	mid	rim
CaO	54.21	53.75	54.58
P ₂ O ₅	38.11	38.92	40.66
F	1.30	0.89	1.14
Cl	0.54	0.66	0.61
SO₃	0.89	1.31	0.64
Ce ₂ O ₃	0.09	0.10	0.05
FeO	0.33	0.41	0.35
SiO ₂	0.64	0.68	0.44
Na ₂ O	0.19	0.29	0.16
MnO	0.14	0.12	0.06
MgO	0.21	0.20	0.17
Subtotal	96.65	97.33	98.86
-O ≡ F + Cl	0.67	0.53	0.62
Total	95.98	96.80	98.24

Figure 18: Apatite crystal structure and unit cell. S^{6+} replaces P^{5+} in the T site through various coupled substitutions (after Pasero et al., 2010).

The positive linear trend between Na_2O and SO_3 (Fig. 19) suggests that Na^+ is a more significant cation in coupled substitutions when compared to the scatter seen between SiO_2 and SO_3 (Fig. 20). Figures 21 through 25 show the exchange reactions listed above for Pinatubo apatite EMP data. Figure 21 and Figure 22 confirm that Na^+ is preferred over Si^{4+} for coupled substitutions in both silicic and basalt apatites. In fact, the highest correlation coefficients (i.e. the strongest linear trend between two cations or cation pairings) for andesite and basalt apatites are associated with the exchange reaction in Eq 1. However, the basalt apatite data falls poorly on the 1:1 trend line. Exchange reactions that involve Na^+ , Si^{4+} , and REE^{3+} (Ce^{3+}) (Eq 3, 4, and 5) produce good correlation coefficients for all apatites and the data fall nicely on the 1:1 trend line. The highest correlation coefficient for dacite apatites is associated with Eq 3 (Fig. 23), but the data do not pass as well through the origin as it does in Figure

24 (Eq 4). Therefore, the exchange reaction that best matches the data is

Figure 19: EMP apatite data. The strong positive correlation between Na_2O wt.% and SO_3 wt.% suggests that $\text{S}^{6+} + \text{Na}^+ \rightleftharpoons \text{P}^{5+} + \text{Ca}^{2+}$ could be a significant coupled substitution for incorporating S into apatites in all three juvenile products from Pinatubo. Purple dashed lines delineate the boundaries between low- and medium-S apatites (0.3 wt.% SO_3) and medium- and high-S apatites (0.7 wt.% SO_3). r = correlation coefficient.

Figure 20: EMP apatite data. The lack of a strong positive correlation between SiO_2 wt.% and SO_3 wt.% in dacite apatites suggests that $\text{S}^{6+} + \text{Si}^{4+} \rightleftharpoons 2\text{P}^{5+}$ is not a significant coupled substitution. However, there is a strong correlation in andesite- and basalt-hosted apatites. The Si-S coupled substitution has more significance in more primitive magmas. r = correlation coefficient.

Figure 21: EMP apatite data. $\text{S}^{6+} + \text{Na}^+ \rightleftharpoons \text{P}^{5+} + \text{Ca}^{2+}$ coupled substitution. This exchange reaction is associated with the highest correlation coefficients (r) for andesite (b.) and basalt (c.) apatites. However, the basalt data does not fall well on the 1:1 line.

Figure 22: EMP apatite data. $S^{6+} + Si^{4+} \rightleftharpoons 2P^{5+}$ coupled substitution. This exchange reaction is associated with the lowest correlation coefficients (r) for dacite (d.) and basalt (c.) apatites. The scatter produced around the 1:1 line shows that Si^{4+} alone is not the cation used during coupled substitution.

Figure 23: EMP apatite data. $\text{S}^{6+} + \text{Na}^{+} + \text{Si}^{4+} + \text{REE}^{3+} \Leftrightarrow 2\text{P}^{5+} + 2\text{Ca}^{2+}$ coupled substitution. There is good correlation along the 1:1 line for all three juvenile component apatites, yet the data pass just above the origin.

Figure 24: EMP apatite data. $\text{S}^{6+} + \text{Na}^{+} + \text{Si}^{4+} + 2\text{Ce}^{3+} \rightleftharpoons 3\text{P}^{5+} + \text{Ca}^{2+}$ coupled substitution. There is good correlation along the 1:1 line for all three juvenile component apatites, and the data pass through the origin. This exchange reaction is the best fit for Pinatubo apatites.

Figure 25: EMP apatite data. $\text{Si}^{4+} + 2\text{Na}^{+} + 2\text{S}^{6+} + 4\text{REE}^{3+} \rightleftharpoons 4\text{P}^{5+} + 5\text{Ca}^{2+}$ coupled substitution. Basalt apatites (c.) have the best correlation coefficient in this exchange reaction and fall well along the 1:1 line.

Core to rim sulfur profiles of apatites come in four varieties: 1) homogenous SO_3 , 2) rimward increasing SO_3 , 3) rimward decreasing SO_3 , and 4) oscillatory SO_3 (Fig. 26). All four profiles were found in each apatite population. Intra-grain variations in SO_3 concentrations can range from low to high with very abrupt transitions over short distances ($\sim 2\text{-}5\ \mu\text{m}$). High-S silicic apatites occur primarily as inclusions in

anhydrite. However, they also occur as inclusions in plagioclase, hornblende, and Fe-Ti oxides. Large apatites that occur as microphenocrysts in the groundmass never show high-S concentrations. These apatites range in SO_3 from 0.05 wt.% to 0.30 wt.% with an average of 0.13 wt.%. This is consistent with previous studies on Pinatubo apatites (Imai et al., 1993, 1996) and Eagle Mountain Andesite apatites (Parat et al., 2002).

Figure 26: Sulfur profiles found in Pinatubo apatites: a) homogenous sulfur, b) rimward increase in sulfur, c) rimward decrease in sulfur, and d) oscillatory sulfur.

S-element maps (Figs. 27 and 28) of small apatites show that S distributions within a single crystal can be very irregular and correspond with Na distributions. High-S concentrations most commonly appear as globular blobs near to off-center of the grain, sometimes surrounded by a high-S halo that follows the shape of the crystal.

Even more irregular shapes were observed, such as horseshoe shapes or slightly curved lines (Figs. 29 and 30). EMP analyses showed that 29% of silicic apatites analyzed had a high-S concentration. However, this percentage could be grossly underestimated if the selected traverses missed pockets of high-S observed in the element maps, like in Figure 28. It is speculated that high-S silicic apatites are closer to 50%. Refer to Appendix F for all apatite element maps.

PH12C-1 Ap2
0.37 – 0.85 SO₃ wt. %

Figure 27: Backscatter image and element maps of P, S, Na, and F for PH12C-1 Ap2 in contact with anhydrite and glass. The lack of sulfur enrichment at the apatite/anhydrite contact shows that apatite is not leaching sulfur from nearby anhydrite. Sulfur concentrations in this apatite are very complex with two globular concentrations near the center surrounded by a halo of sulfur enrichment. The matching patches of Na-enrichment with S confirm that Na⁺ is an important cation in coupled substitutions with S⁶⁺.

PH12C-6 Ap5
0.27 – 0.66 SO₃ wt. %

Figure 28: Backscatter image and element maps of P, S, Na, and F for PH12C-6 Ap5 hosted in anhydrite. The lack of sulfur enrichment around the rim of the crystal at the apatite/anhydrite contact shows that apatite is not leaching sulfur from nearby anhydrite. Sulfur concentrations in this apatite are very complex with two globular concentrations near the center surrounded by a halo of sulfur enrichment.

PH12C-3b Ap11
0.52 – 0.93 SO₃ wt. %

Figure 29: Backscatter image and element maps of P, S, Na, F, and Cl for PH12C-3b Ap11 hosted in anhydrite. Sulfur enrichment is in the form of a horseshoe shape.

PH12C-7 Ap6
0.23 – 0.90 SO₃ wt. %

Figure 30: Backscatter image and element maps of P, S, Na, F, and Cl for PH12C-7 Ap6. Sulfur enrichment is in the form of an irregular line running from the center of the crystal to the rim. High-S measured at the rim of the crystal is likely due to the interaction volume of the electron beam including anhydrite.

REEs

Apatites have been much studied for their ability to control whole rock REE concentrations and retain REE concentrations representative of the melt from which they grew. Apatite plus sphene have been shown to contain approximately 30% of the total whole rock REE budget. Because of the incompatible nature of REEs, more evolved, silicic melts have higher concentrations of REEs than more primitive, mafic melts. REEs enter apatite through the coupled substitutions listed in the previous section in addition to the following exchange reactions:

We can use this relationship to track the melt environment of apatites. Representative trace element and REE LA-ICP-MS data are presented in Table 7.

Figure 31 shows REE patterns normalized to C1 chondrite of all LA-ICP-MS analyses and the average REE patterns of dacite, andesite, and basalt apatites, respectively. Silicic apatites have overall higher concentrations of REEs than basalt apatites, and display the typical enrichment in LREEs relative to middle and HREEs. For example, La concentrations in dacite apatites range from 320 to 1110 ppm, andesite apatites range from 690 to 890 ppm, and basalt apatites range from 79 to 326 ppm. Average La concentrations for dacite, andesite, and basalt apatites are 750 ppm, 785 ppm, and 217 ppm, respectively.

Europium concentrations create very different patterns between silicic and basalt apatites. When the Eu concentration in a REE pattern is much lower than the

trend developed by the Sm and Gd concentrations on either side, then a negative Eu anomaly ($\text{Eu}/\text{Eu}^* < 1$) is generated. Felsic magmas will generally grow apatites with larger negative Eu anomalies than basaltic magmas (Watson and Green, 1981).

Eu/Eu^* in dacite apatites range from 0.47 to 0.79, andesite apatites range from 0.56 to 0.67, and basalt apatites range from 0.81 to 1.50. Average Eu/Eu^* for dacite, andesite and basalt apatites are 0.57, 0.60, and 1.16, respectively. These results are consistent with the general trend of silicic melts having more negative (< 1) Eu/Eu^* than mafic melts with no or positive Eu/Eu^* (≥ 1), and add further evidence to the hypothesis that the andesite apatites were inherited solely from the dacite.

Figure 31: REE patterns for all apatites analyzed using LA-ICP-MS. All apatites have LREE enrichment over HREE. Dacite and andesite apatites make a distinct population when compared to basalt apatite REE patterns. Basalt apatites have significantly lower total REE, and are lacking the negative Europium anomaly ($\text{Eu}/\text{Eu}^* < 1$) that is seen in dacite and andesite apatites. One apatite hosted in the basalt has a pattern like the more silicic apatites and is likely a xenocryst.

$(\text{La}/\text{Sm})_N$ and $(\text{La}/\text{Yb})_N$ normalized ratios can be used to express the steepness of the LREE pattern and whole REE pattern, respectively. Any differences in these ratios could suggest separate apatite populations. Figure 32 does not show any groupings when comparing these ratios among the silicic and basalt apatites. The average La/Yb for dacite (28.9), andesite (29.5), and basalt (29.4) apatites are almost identical. Regardless of the similarity in REE pattern steepness between populations of apatites, the overall difference in REE concentrations and Eu/Eu* distinguish silicic and basalt apatites.

Figure 32: Plot of La/Sm (steepness of the LREE) versus La/Yb (steepness of all REE). There are no significant groupings between silicic apatites and basalt apatites, which suggests that the slope of the REE patterns do not vary much.

Figure 33 is a simplified version of Figure 31 to better show the variability of REE concentrations among apatite populations represented by the filled regions. In each population, there is one apatite (PH12C-6, CN6791-d Ap6, and P-22892-2a Ap13) that falls below the range of its population enough that it was not included in the main shading. Although the concentrations of the apatites are lower than the general population, the patterns of each represent the population in which they belong, and should not be considered separate populations of $n=1$. Reason for these depleted concentrations could simply reflect heterogeneities of REE concentrations in the melt. Each of these apatites is rather small, $\sim 20\ \mu\text{m}$ in the longest dimension, and the low concentrations of REE could be a consequence of a lower volume of ablated material available for analysis in the mass spectrometer. The low concentrations could also be due to dilution of REE by analyzing low REE of the surrounding material.

Figure 33: Shaded regions represent the range of REE concentrations in a) dacite apatites, b) andesite apatites, and c) basalt apatites. Silicic apatites have a narrower range and a pronounced negative Eu anomaly. Basalt apatites have a broader range of REE concentrations. Each group has one apatite that falls below the range of the group.

Other Trace Elements

In addition to the distinctions made between apatite population based on REE concentrations and patterns, apatites from the 1991 Pinatubo eruptive products also show populations through trace element chemistry, particularly Th, U, and Sr (Fig. 34). Th and U concentrations, on average, are higher in silicic apatites than basalt apatites. These concentrations are a reflection of the levels of differentiation experienced by the dacite and basalt magmas. The more differentiated dacite magma has higher concentrations of the more incompatible elements (Th and U) when compared to the less differentiated basalt magma. Th and U show a negative correlation with Eu/Eu^* . Average U concentrations are 7.7 ppm, 7.6 ppm, and 4.4 ppm in dacite, andesite, and basalt apatites, respectively. Average Th concentrations are 20.0 ppm, 19.7 ppm, and 15.7 ppm in dacite, andesite, and basalt apatites, respectively. Apatites have been shown in many studies to be good proxies for determining the level of differentiation and oxidation state of the melt from which they grew (Puchelt and Emmermann, 1976; Watson and Capobianco, 1981; Sha and Chappell, 1999; Tepper and Kuehner, 1999; Belousova et al., 2002; Dempster et al., 2003; Humphreys et al., 2006; Macdonald et al., 2008; Boyce and Hervig, 2009).

Sr concentrations in apatites also reflect the level of differentiation and silica content of the host melt. Basalt apatites have the highest Sr concentrations (average = 975 ppm), and dacite apatites have the lowest (average = 594 ppm). Andesite apatites show slightly higher Sr concentrations (average = 625) than dacite apatites. This may reflect the effects of magma mixing between dacite and basalt. Sr has a positive

correlation with Eu/Eu^* . Two basalt apatites (P-22892-2a Ap12 and P-22892-2a Ap13) have low Sr concentrations (~ 620 and ~ 450 ppm, respectively). P-22892-2a Ap13 is much smaller than other basalt apatites analyzed with LA-ICP-MS, and the low Sr concentration likely reflects dilution from analysis of the low Sr surrounding material. A second analysis of P-22892-2a Ap12 gave a Sr concentration of $\sim 1,030$ ppm. The other analysis of ~ 620 ppm Sr may also be a result of dilution.

In summary, silicic apatites and basalt apatites fall into distinct populations based upon major element chemistry, REE concentrations and patterns, and other trace element concentrations. Strong morphological differences also exist between silicic apatites and basalt apatites (Fig. 42).

Figure 34: Distinct populations of apatites based upon Th, U, and Sr concentrations. The more differentiated melts produce apatites with higher concentrations of incompatible elements.

Table 7: Representative LA-ICP-MS results for “silicic” apatites from 1991 Pinatubo eruption. SO₃ are averages of EMP data.

Sample Apatite	"Silicic" Apatites of Dacite					"Silicic" Apatites of Hybrid Andesite			
	PH12C-2 ap6	PH12C-7 ap4 pt1	PH12C-7 ap4 pt2	PH12C-7 ap16 pt1	PH12C-7 ap16 pt3	CN6791-d ap5 pt1	CN6791-d ap5 pt2	CN6791-d ap6	CN6791-d ap7
SO ₃	0.32	0.13	0.18	0.63	0.38	0.23	0.65	0.13	0.12
S	932	675	689	1237	926	1701	1355	666	912
Sc	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.30
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	12.3	n.d.	n.d.	n.d.	n.d.
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	4.6	4.2	n.d.	5.8
Zn	2.9	n.d.	n.d.	11	5.3	2.1	2.9	2.5	1.7
Rb	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	518	644	632	673	597	639	629	611	621
Y	293	269	262	325	245	268	263	216	283
Zr	1.4	0.69	0.48	1.6	n.d.	0.68	0.40	0.57	0.60
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	3.9	4.1	5.6	8.52	4.50	4.0	2.8	2.5	4.0
La	795	733	733	830	737	780	805	691	746
Ce	1864	1821	1853	1921	1743	1828	1902	1573	1786
Pr	222	219	218	227	204	211	223	176	214
Nd	888	783	809	894	809	815	833	706	826
Sm	141	119	118	138	115	118	120	98	126
Eu	22	21	20	25	20	21	21	18	20
Gd	108	93	88	108	82	92	91	73	97
Tb	13	9	10	12	11	10	10	8	11
Dy	65	51	52	60	46	53	52	41	57
Ho	11	9	10	10	8	9	11	8	10
Er	30	26	22	27	25	23	26	20	25
Yb	23	19	14	16	13	18	20	13	18
Pb	32	17	3.6	127	259	3.2	14	4.2	3.9
Th	27	17	15	37	20	27	21	16	17
U	9.8	6.3	6.3	11	8.1	9.5	7.8	6.6	6.6

Table 7: Continued. Basalt apatites.

Sample Apatite	Basalt Apatites			
	P-22892-2a ap12 pt1	P-22892-2a ap12 pt2	P-22892-2a ap20	P-22892-2a ap23
SO₃	1.46	1.84	1.21	0.81
S	2532	5510	2829	3566
Sc	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.
Cu	8.7	12	7.4	4.7
Zn	4.0	1.7	4.4	12
Rb	n.d.	n.d.	5.0	15
Sr	621	1027	1011	1066
Y	53	83	76	54
Zr	0.44	5.0	9.5	12
Nb	n.d.	0.15	0.31	0.48
Ba	n.d.	8.2	23	61
La	168	254	217	176
Ce	363	565	491	428
Pr	44	68	63	49
Nd	178	250	228	177
Sm	20	43	33	27
Eu	6	13	12	10
Gd	13	31	24	15
Tb	1	3	3	2
Dy	11	16	16	8
Ho	2	2	3	2
Er	3	8	9	5
Yb	4	7	5	3
Pb	30	2.4	12	4.8
Th	12	18	18	13
U	3.7	5.2	4.4	4.7

DISCUSSION

Sulfur Concentrations in Apatite

Sulfur (S) is a major volatile component of magmatic systems the solubility of which is highly dependent upon pressure, temperature, oxygen fugacity (fO_2), sulfur fugacity (fS_2), and bulk composition of the melt (Carroll and Rutherford, 1985, 1987, 1988; Wallace and Carmichael, 1992; Jugo et al., 2005a). Sulfur exists as S^{2-} in sulfides (FeS-rich melt) under reducing conditions and as S^{6+} in sulfates (e.g. Anhydrite - $CaSO_4$) under oxidizing conditions (Carroll and Rutherford, 1985, 1987, 1988; Nilsson and Peach, 1993; Metrich and Clocchiatti, 1996; Paris et al., 2001; Jugo et al., 2005a, 2005b). S solubility is most significantly affected by fO_2 in both basaltic and silicic magmas (Carroll and Rutherford, 1985, 1988; Clemente et al., 2004; Jugo et al., 2005a, 2005b).

Experiments performed by Buchanan and Nolan (1979) at 1200°C and 1 atm with synthetic tholeiitic melts showed that the amount of dissolved sulfur in these melts increased with increasing sulfur fugacity and decreasing oxygen fugacity. Sulfur saturation was achieved at oxygen fugacity isobars of -log 10.50 and -log 11.50 with corresponding sulfur fugacity values of -log 1.75 and -log 3.75, respectively. In other words, there is a positive correlation between sulfur fugacity and oxygen fugacity at sulfur saturation. Immiscible sulfide phases will only form in sulfur-saturated tholeiitic melts at lower oxygen fugacities. In rhyolitic melts at a given fO_2 , sulfur solubility will increase with increasing fS_2 (Clemente et al., 2004).

Figure 35 from Hattori (1996) shows the behavior of sulfur solubility with increasing oxygen fugacity in a dacitic melt at 900°C. At ~QFM-1.7 the concentration of sulfur as the S^{2-} species dissolved in the melt is about 330 ppm. This value decreases to a minimum of ~130 ppm at ~QFM+0.6. At this point, the main dissolved sulfur species begins to transition from S^{2-} to SO_4^{2-} (S^{6+}), and S dissolved in melt as a function of oxygen fugacity changes from a negative correlation to a positive correlation. At QFM+4, approximately 850 ppm of sulfur as sulfate can be dissolved in a melt (Carroll and Rutherford, 1987, 1988; Hattori, 1996). Rhyolitic melts at 933°C, 2 kbar, and NNO+2.4 can achieve sulfur concentrations of nearly 1,000 ppm (Clemente et al., 2004). This quick transition of sulfur speciation is common in calc-alkaline, dacitic-rhyolitic magmas (Carroll and Rutherford, 1988). Experiments on basaltic melts have shown that changes in fO_2 from sulfide-saturation to sulfate-saturation produced a ten-fold increase in dissolved sulfur (Jugo et al., 2005a). Trachyandesitic melts supersaturated in sulfur at <NNO+1 will begin to precipitate sulfides (i.e. pyrrhotite: Fe-S), and anhydrite will begin to precipitate at NNO+1-1.5 (Carroll and Rutherford, 1987; Luhr, 1990).

Figure 35: Sulfur solubility curve of a dacitic melt at 900°C is strongly dependent upon the oxidation state of the melt. Under reducing conditions (I) S²⁻ is the dominant sulfur species dissolved in the melt and sulfides will precipitate if the sulfur concentrations fall above the curve. Between I and II, the solubility decreases with increasing fO_2 . At II, a solubility minimum is reached and the dominant species shifts from S²⁻ to S⁶⁺, and anhydrite may precipitate with sufficient sulfur present. From there, solubility increases dramatically with increased fO_2 (after Hattori et al., 1996).

Higher temperatures allow more S to be dissolved in the melt (Liu et al., 2007).

MnO-Mn₃O₄ (MNO) buffered experiments utilizing El Chichón trachyandesite have shown glass S concentrations of ~2,000 ppm and ~500 ppm at 985°C and 870°C, respectively at anhydrite saturation (Carroll and Rutherford, 1987). The effect of temperature increase on increasing sulfur solubility is magnified under oxidizing conditions. Sulfide saturated melts only hold 150 ppm less than anhydrite-saturated melts at a temperature of 850°C. In contrast, melts at 1025°C differ by 1750 ppm between MNO (2,200 ppm) and NNO (450 ppm) (Carroll and Rutherford, 1987).

The concentration of FeO in the melt also has a large effect on sulfur solubility for reducing conditions. At 2 kb pressure, sulfide saturated melts have 100 ppm S at 2 wt.% FeO and 700 ppm S at 8.5 wt.% FeO (Carroll and Rutherford, 1987; Wallace and Carmichael, 1992; Carroll and Webster, 1994; Moretti and Ottonello, 2005). This is due to Fe-S complexes (Clemente et al., 2004). Lower sulfur solubilities are associated with SiO₂-rich melts due to higher polymerization (Katsura and Nagashima, 1974; Carroll and Webster, 1994; Moretti and Ottonello, 2005; Liu et al., 2007). Water content does not seem to have a significant effect on sulfur solubility (Luhr, 1990; Wallace and Carmichael, 1994; Liu et al., 2007).

Sulfur solubility has been shown in experimental studies to increase with pressure under fluid-saturated conditions (Fig. 36). Dacitic melts at manganite-hausmanite (MNO) and hematite-magnetite (HM) oxidizing buffer conditions and 1,025°C showed an increase in S concentrations from ~1,400 ppm at 100 MPa to ~3,000 ppm at 300 MPa. Comparatively, quartz-fayalite-magnetite (QFM) reducing buffer conditions at 1,025°C only showed an increase in S concentrations from ~600 ppm at 100 MPa to 1,000 ppm at 200 MPa (Carroll and Rutherford, 1985). Sulfur contents at sulfide saturation (SCSS) in basaltic melts show an opposite trend and decrease with increasing pressure with temperature held constant (Mavrogenes and O'Neill, 1999).

In summary, oxidized, high-temperature, basaltic magmas can dissolve a greater amount of sulfur than their low-temperature, silicic counterparts. This will affect the expected sulfur contents of apatites.

Figure 36: Sulfur solubility is also dependent upon pressure and temperature. Increasing temperature and pressure allows for more sulfur to be dissolved in melts. The shaded region in B represents Pinatubo dacite pre-eruption pressure and temperature conditions (after Fournelle et al., 1996).

Sulfur concentrations in apatite are determined by the concentration of sulfate in the melt and the partition coefficient of sulfur between crystallizing apatite and melt ($D_s^{\text{apatite/melt}}$). Experimental results on anhydrite-undersaturated and anhydrite-saturated haplogranitic melts have shown $D_s^{\text{apatite/melt}}$ to depend strongly upon the sulfate concentration of the melt, and to a lesser extent temperature (T). The partition

coefficient decreases with increasing wt% SO₃ in the melt ($D_s^{\text{apatite/melt}}$: 14.2 to 2.7, at SO₃ wt% in melt: 0.03 to 0.19, respectively), and increases with decreasing temperature ($D_s^{\text{apatite/melt}}$: 4.5 to 14.2, at T=1,100 to 900°C, respectively) (Parat and Holtz, 2004, 2005). $D_s^{\text{apatite/melt}}$ does not seem to be greatly affected by melt composition and is very similar for dacitic and trachyandesitic compositions at similar temperatures and oxygen fugacities (Baker and Rutherford, 1996b; Peng et al., 1997; Parat and Holtz, 2005). Cool, oxidized, sulfate-rich melts should produce a sulfur-rich apatite. However, the correlation between sulfate in melt and sulfur in apatite is not that simple. Both an anhydrite-undersaturated melt (0.04 wt.% SO₃) and an anhydrite-saturated melt (0.2 wt.% SO₃) at 1,000°C can produce an apatite with 0.5 wt.% SO₃ (Parat and Holtz, 2005).

At anhydrite-saturated conditions, Parat and Holtz (2005) showed sulfur concentrations in apatite decreased with increasing P₂O₅ concentrations in the melt, regardless of concomitant increasing sulfur concentrations in melt. Sulfur exchange reactions in Eqs. 1 through 5 are influenced by the activities of P in the melt probably more so than fS_2 (Parat and Holtz, 2005).

Mount Pinatubo dacites show very high bulk sulfur concentrations ranging from 1,470 ppm to 2,210 ppm (Bernard et al., 1996), and melt inclusions with average sulfur concentrations of 55 to 77±29 ppm (Rutherford and Devine, 1996). The majority of the bulk sulfur is in the phase of anhydrite phenocrysts (Gerlach et al., 1996; Pallister et al., 1996; Bernard et al., 1996). Estimated conditions of the ~50 km³ dacitic magma chamber (760±20°C, 220MPa, NNO+1.7, 77 ppm S in melt inclusions)

(Scaillet and Evans, 1999) (Fig. 36b and Fig. 37) could produce apatite with 1,000 ppm S or 0.25 wt% SO₃, using a partition coefficient of 13. This $D_s^{\text{apatite/melt}}$ was determined with Pinatubo dacite crystallization experiments performed by Baker and Rutherford at pre-eruption conditions (1996a).

Figure 37: Pre-eruption fO_2 and temperature for Buag period and 1991 Pinatubo erupted materials. fO_2 of Pinatubo juvenile components during the past 500 years fall consistently 1.7 $\log_{10}$ units above the NNO oxygen buffer (after Di Muro et al., 2008).

In this study, high-sulfur apatites (>0.7 wt% SO₃) in Mount Pinatubo dacites with SO₃ values up to 1.7 wt% were found. Producing an apatite with 1.7 wt% SO₃ via equilibrium partitioning with the surrounding melt would require a concentration of 523 ppm dissolved sulfur assuming a $D_s^{\text{apatite/melt}}$ of 13. This is nearly an order of magnitude higher than the sulfur concentrations measured in Pinatubo dacite glass inclusions. Parat and Holtz (2005) showed that, at NNO+3.6, 200 MPa, and 900°C, producing an apatite with 0.67 wt% SO₃ from a hydrous rhyolite melt would require a

sulfur concentration of 413 ppm in the surrounding melt and a partition coefficient of 6.5. At higher oxygen fugacities and temperatures, more sulfur should dissolve in any given melt. Therefore, it is more likely to produce high-S apatites under the conditions of the experiment of Parat and Holtz (2005) than at Pinatubo dacite pre-eruption conditions, which were cooler and less oxidized. This is not the case. Even the extreme conditions of the Parat and Holtz (2005) experiment could not produce high-S apatites through equilibrium apatite/melt partitioning. It must be the case that high-S apatites are grown under different conditions.

Low-S, groundmass apatites have an average of 0.13 wt.% SO₃ that corresponds to a melt concentration of 40 ppm using a partition coefficient of 13. This corresponds well to the measured values of sulfur in melt inclusions and gives confidence in the value of the partition coefficient for Pinatubo dacite melt and apatites.

In Figure 38, high-S silicic apatites show three sulfur profiles: 1) rimward decrease in SO₃, 2) rimward increase in SO₃, and 3) oscillatory SO₃. Apatites with type 1 profiles may be recording the transition from a sulfur-undersaturated environment to a sulfur-saturated environment with the onset of anhydrite crystallization. Greater partitioning of sulfur into anhydrite would prevent sulfur from entering apatite (Streck and Dilles, 1998; Parat et al., 2002). Also, decreased SO₃ in apatite may be due to a decreasing $D_s^{\text{apatite/melt}}$, or apatite inheritance from a more mafic melt. An inherited apatite should have a high-S core and a low-S rim that reflect the transition in melt composition during magma mixing from a mafic to felsic.

Figure 38: Profiles of high-S silicic apatites. a) rimward decrease, b) rimward increase, and c) oscillatory. Such abrupt transitions between high- and low-S concentrations suggest that interactions of apatites between silicic and mafic magmas are not responsible for generating high-S apatites.

Type 2 sulfur profiles suggest a possible decrease in temperature during ascent that raised the $D_s^{\text{apatite/melt}}$, but would also lower the sulfur solubility in the melt and thus the sulfur content. This scenario seems unlikely due to the rapid ascent of the dacite magma during the climactic eruption. There exists plenty of petrological evidence for the dacite reservoir being in equilibrium at $760 \pm 20^\circ\text{C}$ prior to eruption, and having likely been at a similar temperature throughout Modern Pinatubo history (Newhall et al., 1996; Pallister et al., 1996; Scaillet and Evans, 1999). Another

possible explanation for profile 2 is an increase in the oxygen fugacity of the melt would allow more SO_3 to be dissolved in the melt and increase the sulfur content of the apatite, but it is difficult to say if the concomitant drop in $D_s^{\text{apatite/melt}}$ will affect the apatite SO_3 concentration more or less (Parat and Holtz, 2004, 2005). It is also uncertain if increases in $f\text{O}_2$ above $\sim\text{NNO}+1$ will significantly affect the sulfur solubility in dacitic melts. Data from Clemente et al. (2004) show that at 2 kbar and 800°C , the concentration of sulfur in a rhyolitic melt decreases slightly from 373 ppm to 281 ppm when $f\text{O}_2$ increases from $\text{NNO}+1$ to $\text{NNO}+1.8$. Other experimental runs under these conditions showed no significant increase in sulfur content in the melt with increasing $f\text{O}_2$. It has been argued by Imai et al. (1993) that the dacitic reservoir beneath Pinatubo was already oxidized and volatile-rich prior to phenocryst crystallization.

Rimward increase in sulfur was often observed in apatites hosted in anhydrite. It is quite possible that increasing sulfur concentrations could simply reflect sulfur from anhydrite. The electron beam near the rim of the crystal could have generated an excitation volume that included some of the host anhydrite, thereby increasing the observed sulfur content. Assuming no contamination from anhydrite, the increase in sulfur could also mean that a diffusion profile exists between anhydrite and apatite. Sulfur element maps of apatites hosted in or near anhydrite (Figs. 39a, b, d, and e) show that this is not the case. Sulfur distribution is very complex and not isolated to the rims of apatite grains. Higher sulfur contents are generally localized in discrete globular blobs near-center of the grain, sometimes surrounded by sulfur-rich halos

(Fig. 39b and e). Even sulfur-rich apatites not hosted in anhydrite display similar sulfur distributions (Fig. 39c).

Type 3 sulfur profiles display rapid changes in the SO_3 concentration. To achieve such a profile, sulfur as S^{6+} would have to diffuse quickly in the melt to reach an apatite in order for the change in surrounding sulfur to be recorded in the apatite. Such rapid diffusion of sulfur in a dacitic melt is kinetically impossible. The most mobile sulfur species is S^{2-} , which does not partition into apatite (Baker and Rutherford, 1996b; Freda et al., 2005). Such strongly oscillating sulfur profiles suggest that the interaction between apatite, melt, and sulfur is complicated and not restricted to simple melt/apatite equilibrium partitioning. Kinetic effects during growth or heterogeneities in the melt could possibly generate oscillatory profile (Baker and Rutherford, 1996a). The oscillation may represent multiple regions and periods of sulfur enrichment prior to or during anhydrite saturation in the dacite. The apatites in Figure 39b and e have two high-S cores that may have originally been two separate apatites that grew together. The two spots could represent one period of sulfur enrichment and the halo surrounding them could represent a second enrichment period.

Figure 39: Sulfur distributions in apatites fully or partially hosted by anhydrite (a, b, d, e) do not show diffusion profiles from the contact between apatite and anhydrite. The distribution of sulfur is very complex and suggests multiple periods of sulfur-enrichment during apatite growth prior to anhydrite saturation. Apatites with multiple high-S cores may have originally been multiple crystals that grew together. Apatites hosted in Fe-Ti oxides (c.) show similar sulfur distributions.

Trace Element Concentrations in Apatite

Apatites have long been recognized for the ability to control the majority of the whole-rock REE budget (Watson and Capobianco, 1981). REE and trace element fractionation into apatite is generally governed by Henry's Law behavior (with some exceptions, e.g. Gd), such that the activity and concentration of an infinitely dilute species are linearly related to the concentration of the species multiplied by Henry's Law constant (Pan et al., 2003). REE concentrations of apatite reflect the degree of fractionation and oxidation state of the magma from which they grew (Belousova et al., 2002). As such, the slope of REE patterns when normalized to C1 chondrite varies systematically from ultramafic to mafic/intermediate and to fractionated granitoids (Belousova et al., 2002). Apatites from different rock groups can be distinguished by Sr, Y, Mn, total REE, degree of LREE enrichment, and size of Eu/Eu* (Puchelt and Emmermann, 1976; Sha and Chappell, 1999; Belousova et al., 2002). The Σ REE in apatite from metamorphic rocks were shown to be much lower than that in apatite from igneous rocks (Puchelt and Emmermann, 1976). They are also an excellent indicator of granite petrogenesis (Sha and Chappell, 1999).

Magma mixing and differentiation are also recorded in apatite REE concentrations, and show that these dynamic processes must occur within very short timescales (days to years) to be reflected in very strongly zoned apatites (e.g. intracrystalline La concentrations ranging from 100 ppm to 300 ppm) (Tepper and Kuehner, 1999; Dempster et al., 2003; Humphreys et al., 2006; Macdonald et al., 2008; Boyce and Hervig, 2009). This zonation is observed via back-scattered electron

and cathodoluminescence images (Tepper and Kuehner, 1999; Dempster et al., 2003). Dempster et al. (2003) presented data on the Shap Granite apatites, many of which show evidence of inheritance from other magmas. Cores of these apatites have drastically different chemistries, and were brought into the chamber early while there was still vigorous mixing. For example, one apatite had La concentrations of ~1000 ppm at the core and ~750 ppm at the rim.

Apatites can tell many things about the melt from which they grew. Therefore, we can use this information to determine if high-S apatites found in the dacitic pumice are inherited from the basalt intrusion. Examining the results of REE concentrations of Pinatubo apatites, it was determined that two distinct populations exist: silicic apatites and basalt apatites (Fig. 40). REE profiles from both silicic and basalt apatites have the typical enrichment in LREE over HREE (Puchelt and Emmermann, 1979; Roeder et al., 1987; Hughes et al., 1991) and similar REE slopes, which means that both came from melts that were LREE enriched (Watson and Green, 1981). However, there are two fundamental differences between silicic and basalt apatite REE profiles: 1) silicic apatites have higher concentrations of REE, and 2) silicic apatites have a strong negative Europium anomaly (Fig. 40). These results are consistent with previous studies (Puchelt and Emmermann, 1976; Watson and Green, 1981; Sha and Chappell, 1999; Tepper and Kuehner, 1999; Belousova et al., 2002; Broderick, 2008).

Apatites from more fractionated, enriched melts have higher REE concentrations. Increased REE concentrations may also be explained by larger REE partition coefficients in more felsic melts (Watson and Green, 1981). A $\text{Eu}/\text{Eu}^* < 1$ in

apatite can be generated when the surrounding melt in which it grows is more differentiated and has experienced significant feldspar crystallization, or when the ratio of $\text{Eu}^{2+}/\text{Eu}^{3+}$ is high in the melt. Eu behaves compatibly in feldspars, but Eu^{2+} is preferred as a substitute for Ca^{2+} , Sr^{2+} , and Na^{+} . Apatites prefer Eu^{3+} as a substitute for Ca^{2+} in both M sites (Fig. 18). Pinatubo apatites obtain Eu/Eu^* directly from the surrounding melt, which is why basalt and silicic apatites have $\text{Eu}/\text{Eu}^* \geq 1$ and $\text{Eu}/\text{Eu}^* < 1$, respectively. Sha and Chappell (1999) showed that S-type and felsic I-type (S-sedimentary, I-igneous) granitic magmas are more reduced and peraluminous than mafic I-type magmas, and therefore, have higher $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratios and more negative Eu anomalies. This may only have a minor effect on Pinatubo apatites.

Figure 40: The average REE patterns for silicic and basalt apatites are very different. If high-S apatites were inherited from the basalt, then they should exhibit REE patterns closer to basalt apatites. Instead, the REE patterns for silicic apatites reflect a more differentiated melt environment.

Sr is also a good indicator of melt environment for apatites. The partitioning of Sr follows Henry's Law behavior (Pan et al., 2003) and is not dependent upon melt composition or temperature (Watson and Green, 1981; Pan et al., 2003). Therefore, Sr concentration in an apatite is a direct reflection of the Sr concentration of the surrounding melt. More mafic melts will have higher Sr concentrations, and more felsic melts will have lower Sr concentrations due to the compatible nature of Sr. If high-S apatites are inherited from the basalt, the Sr concentrations of these apatites should be elevated compared to other silicic apatites. In Figure 41, silicic apatites display much lower Sr concentrations than basaltic apatites and much higher La concentrations. There is no group of silicic apatites with high-S that plot with basalt apatites. There is one dacite apatite with a Sr concentration of ~1250 ppm. This apatite is low-S and hosted in anhydrite. It is likely that this elevated Sr concentration may be a result of contamination.

Previous studies showed intracrystalline diffusion of elements that do not require coupled substitutions (e.g. Sr, Mn, Fe) proceed much faster than others that do (e.g. REE), and LREE diffusion will proceed more rapidly than Σ REE (Tepper and Kuehner, 1999). Homogenous intracrystalline Sr concentrations and chondrite normalized La/Sm ratios may indicate diffusion of these elements and not the original concentration at crystallization. Assuming that high-S dacite apatites have cores inherited from the basalt and rims that are in equilibrium with the dacite, if intracrystalline diffusion of Sr had taken place in these crystals, then these apatites would have an intermediate Sr concentration between basalt apatites and low-S,

homogenous silicic apatites. There is no such group in Figure 41. Basalt apatites and silicic apatites are grouped fairly tight with respect to Sr and La with some scatter. This means either 1) intracrystalline diffusion is not occurring, or 2) there are no silicic apatites with cores inherited from the basalt. Since there are no high-S, silicic apatites with high Sr concentrations, scenario 2) is more likely the case.

Overall, the evidence from the REE patterns and Sr concentrations suggest that apatites found in the dacite grew in a dacite melt, regardless of sulfur concentration. The same can be said of basalt apatites.

Figure 41: Silicic apatites plot nowhere near the Sr vs. La field of basalt apatites. These data suggest that silicic apatites, regardless of sulfur concentration, did not grow in the basalt. One dacite apatite has a Sr concentration of ~1250 ppm. This is a low-S apatite and the high Sr concentration is likely due to contamination from the host.

Melt Environment of High-S vs. Low-S Apatites

Major and trace element concentrations of apatites have shown that silicic apatites and basalt apatites are distinct populations and come from different melt environments. High-S, silicic apatites show no difference in chemistry from other silicic apatites except sulfur. Additionally, silicic apatites and basalt apatites have very different morphologies. Basalt apatites are skeletal and often acicular, indicating: 1) rapid growth from quenching (Gardner et al., 1972), and 2) that apatite saturation in the basalt is only achieved at high degrees of crystallinity during quenching. Silicic apatites are euhedral to subhedral with no textural evidence of quenching (Fig. 42). These results are consistent with the findings of high-S apatites from the San Juan Central Caldera Complex (Broderick, 2008; Parat et al., 2002). The origin of these high-S apatites must be of means other than inheritance or S-diffusion from anhydrite.

Figure 42: Reflected light petrographic images of a) skeletal basalt apatite and b) euhedral dacite apatite. These apatites exhibit very different morphologies.

Inheritance of high-S apatite cores from the basalt was not shown to have occurred in this study of 1991 Pinatubo apatites. However, that doesn't mean that inheritance of dacite apatites in the basalt didn't occur. Figure 43 further examines the scenario of the xenocrystic apatite hosted in a xenocrystic hornblende found in the basalt. SO_3 in this apatite ranges from ~0.1 to ~0.3 wt. %, values much lower than the high-S content of basalt apatites, which are generally greater than 1 wt.%. The REE pattern of the xenocrystic apatite also matches patterns of silicic apatites by having elevated REE concentrations relative to basalt apatites and a distinct negative Eu/Eu^* . The REE pattern of the hosting xenocrystic hornblende also matches the pattern of hornblendes from a more silicic source. Furthermore, there are clear disequilibria textures, including a resorption rim on the hornblende host and a reaction rim around a nearby quartz xenocryst. This example shows that our approach to tracking original apatite melt using major and trace element chemistry is valid.

If we examine an apatite (PH12C-7 Ap16) that has strong changes in SO_3 more closely by comparing the SO_3 content with corresponding REE patterns (Fig. 44), we see that there is no significant difference in the REE patterns between laser spots that overlap high-S zones, and laser spots that overlap low-S zones. There is no evidence for an inherited high-S core. Such abrupt changes in SO_3 within this and many other apatites do not suggest interaction with silicic and basaltic melts. PH12C-7 Ap16 is hosted in an Fe-Ti oxide, so there is no possibility that the high-S concentration near the center (~0.9 wt.% SO_3) is an artifact of interaction volume including anhydrite.

Furthermore, low-S apatites and high-S apatites from the dacite and andesite melts do not show any significant difference in REE patterns, Sm, or Eu/Eu* (Figs. 45 and 46), and there is no correlation between Sr and sulfur concentration (Fig. 47). As discussed, Sr and Eu/Eu* are indicators of degrees of magma differentiation, and any correlation of these with SO₃ would suggest that the sulfur content of the apatite is controlled by the degree of differentiation of the surrounding melt. Figure 48 shows no correlation among the silicic apatites between SO₃, Sr, Eu/Eu*. These apatites are clustered very tightly with respect to Sr and Eu/Eu*, away from the distinct region of basalt apatites, regardless of SO₃ being high or low.

Figure 43: The xenocrystic apatite, P-22892-2a Ap1, is located as an inclusion in a xenocrystic hornblende with strong disequilibria textures (a). Sulfur concentrations (b) and REE pattern (c) of this apatite match more closely to silicic apatite. REE patterns of hornblende from each juvenile component show that the xenocrystic hornblende also originated from the dacite (d).

Figure 44: REE patterns from multiple laser spots in an apatite (PH12C-7 Ap16) with SO_3 concentrations ranging from ~0.1 to ~0.9 wt.% show no significant difference. The high-S core does not show an REE pattern that would suggest inheritance from the basalt. The melt environment of this apatite did not change during growth other than the amount sulfate available for exchange.

Figure 45: Comparison of REE patterns between high-S apatites (filled symbols) and low-S apatites (empty symbols) for apatites from each juvenile component. REE patterns do not vary significantly for dacite (a) and andesite (b) apatites and suggest that they grew in the same melt. The difference in REE patterns for the basalt apatites reflects that the only low-S apatite in the basalt was xenocrystic (Fig. 43).

Figure 46: Silicic apatites do not plot with basalt apatites based upon Sm (a) and Eu/Eu* (b), regardless of sulfur concentrations. This shows that high-S silicic apatites grew in a more differentiated melt. The “error bars” represent the minimum and maximum SO_3 concentrations measured by EMP that was overlapped by the laser spot.

Figure 47: Sr concentrations represent the level of differentiation of the melt hosting silicic and basalt apatites. Sr concentrations vary among groups without correlation to SO₃ or Na₂O. In fact, some of the most sulfur-rich silicic apatites have the lowest Sr concentrations. The “error bars” represent the minimum and maximum SO₃ and Na₂O concentrations measured by EMP that was overlapped by the laser spot.

Figure 48: Basalt apatites have Sr concentrations and Eu/Eu* that reflect a less differentiated melt. If high-S silicic apatites were inherited from the basalt, they would plot closer to this field. However, silicic apatites are tightly grouped in a field indicating a more differentiated melt. The size of the data markers is directly correlated to the average SO₃ of the apatites. Low-, medium-, and high-S silicic apatites plot in the same field, and therefore, grew in the same melt.

Fluid-Enhanced Crystallization

Thus far, we have examined three scenarios for generating high-S silicic apatites: equilibrium partitioning, S-diffusion from anhydrite, and mafic inheritance. Each of these mechanisms has failed to explain how these apatites are obtaining such high sulfur concentrations. One remaining scenario to consider is the presence of a sulfur-rich fluid phase as a source for the excess sulfur needed to grow high-S apatites.

Gerlach et al. (1996) studied the S and Cl content of melt inclusions and matrix glass using EMP and found that there was no significant difference in S and Cl concentrations between the two types of glass. From this, they concluded that there was no significant degassing of S or Cl from the melt during ascent and eruption. 20 million tons of SO₂ was injected into the stratosphere during the 1991 Pinatubo

eruption, 17 million tons during the climactic event. This amount of SO₂ is one order of magnitude higher than the amount of sulfur that could have been dissolved in the 5 km³ DRE of melt erupted at the pre-eruption conditions. In order to account for the “excess” sulfur ejected into the atmosphere, an additional source of sulfur is required. Many previous studies, including ones about Pinatubo, have concluded that the likely source of sulfur is a sulfur-rich fluid phase that has significantly accumulated over time within the magma reservoir from injections of underplating basaltic magmas (Luhr et al., 1984; Matthews et al., 1992; Pallister et al., 1992; Westrich and Gerlach, 1992; Wallace and Gerlach, 1994; Gerlach et al., 1996; Pasteris et al., 1996; Kress, 1997; Scaillet et al., 1998; Keppler, 1999; Parat et al., 2002; Broderick, 2008; Chambefort et al., 2008).

Volcanic eruptions that have recorded “excess” sulfur input into the stratosphere commonly have anhydrite as a primary igneous phase, such as the 1982 El Chichón and 1991 Mount Pinatubo eruptions (Luhr et al., 1984; Bernard et al., 1991, 1996; Pallister et al., 1992, 1995, 1996; Hattori, 1993, 1996; Gerlach et al., 1996; Fournelle et al., 1996; Pasteris et al., 1996). Conditions for generating anhydrite-saturated eruptions (Fig. 49) include: high water content (5-6 wt.%), water-bearing phenocryst phases (e.g., hornblende and biotite), high fO_2 , and fluid-saturated at 7-9 km depth (Luhr, 2008). The timing of anhydrite saturation and its close association with apatite is important when considering the melt conditions for crystallizing high-S silicic apatite because anhydrite will become the dominate sulfur phase at sulfur saturation.

Figure 49: Temperature and oxygen fugacity field for anhydrite-bearing eruptions, including the 1991 Pinatubo eruption. The presence of anhydrite can have a significant effect on the sulfur partitioning between apatite, melt, and sulfur-rich fluid. The dotted lines at 10%, 50%, 70%, and 90% represent the amount of sulfur dissolved as S^{6+} (after Luhr, 2008).

I propose the following model for the generation of high-S apatites in the 1991 Pinatubo dacite:

- 1) SO_2 from the hot ($\sim 1200^\circ C$) basaltic intrusion was reduced when it came into contact with the cool ($\sim 780^\circ C$), water-rich dacite magma reservoir approximately 8-9 km below the surface (Matthews et al., 1992; Hattori, 1993, 1996; Pallister et al., 1996). The SO_2 was reduced to H_2S and oxidized the dacite and added more sulfur to the melt (Fig. 50) (Hattori, 1993, 1996).
- 2) Minor amounts of sulfides, including pyrrhotite, were deposited from a separate fluid phase, as indicated by globular inclusions in oxides, plagioclase, and hornblende (Fig. 51) (Hattori, 1993, 1996).

This likely happened when the sulfur saturation curve reached the minimum at $\sim\text{NNO}+0.6$ (Hattori, 1996).

- 3) Prior to or concurrent with anhydrite crystallization, early-crystallizing apatites hosted in other phenocryst phases (e.g., plagioclase, hornblende, and Fe-Ti oxide) acquired medium- and high-S concentrations from the surrounding melt and sulfur-rich fluid phase. It has been speculated that apatite could have precipitated directly from the fluid phase via “magmatic vapor deposition” (Jakubowski et al., 2002), which could account for the high-S and abrupt intracrystalline transitions from high- to low-S. Lack of anhydrite inclusions in plagioclase and quartz phenocrysts suggests that anhydrite saturation occurred later in the crystallization of the dacite magma after fluid saturation, which allowed sulfur to be partitioned into apatite (Pasteris et al., 1996).
- 4) Anhydrite saturation was reached in the dacite at $\text{NNO}+1-1.5$ (Carroll and Rutherford, 1987; Luhr, 1990), and at depth based upon evidence of anhydrite inclusions in deep-forming phenocrysts of hornblende (Fournelle et al., 1996; this study). The relatively constant sulfur concentration among different glass inclusions from Rutherford and Devine (1996) suggests that the melt was at anhydrite saturation prior to eruption (Pasteris et al., 1996).

- 5) Pyrrhotite and other sulfide phases became unstable but were still present at NNO+1.7, the pre-eruption oxygen fugacity of the dacite magma (Scaillet and Evans, 1999). Vapor deposition of small pyramids of anhydrite on pre-existing anhydrite phenocryst faces occurred during this time, pulling sulfur away from late-forming apatite microphenocrysts (Jakubowski et al., 2002). Sulfur concentration for these groundmass apatites achieved equilibrium with the surrounding melt prior to eruption.

Figure 50: Curves of equal concentrations of SO_2 and H_2S under “dry” ($\text{XH}_2\text{O} = 0.001$, X = volume ratio) and “wet” ($\text{XH}_2\text{O} = 1$) conditions. Shaded region is the field of fluids from basalt melts. When water is introduced and temperature and $f\text{O}_2$ is held constant, the ratio of $\text{SO}_2/\text{H}_2\text{S}$ in the fluid drops. To reach a ratio of $\text{SO}_2/\text{H}_2\text{S} = 1$, $f\text{O}_2$ must increase. When S-rich fluids from a hot, “dry” basalt are introduced into a “wet”, cool dacite the $\text{SO}_2/\text{H}_2\text{S}$ ratio must consequently drop (after Hattori, 1996).

Figure 51: Temperature and oxygen fugacity fields of stability for sulfides and sulfates in rhyolitic magmas at ~780°C, ~930°C, and ~1,000°C (after Clemente et al, 2004).

CONCLUSIONS

In this study, apatites from the three juvenile components of the 1991 Mount Pinatubo eruptions were investigated in order to constrain the timing and melt conditions for crystallizing high-S (>0.7 wt.%) apatites hosted in the dacitic pumice. Concentrations of SO₃ in nearly 30% of the apatites analyzed exceeded 0.7 wt.%, which is a much higher concentration than can be achieved through direct apatite/melt equilibrium partitioning. At ~780°C, 220 MPa, NNO+1.7, and 77 ppm S (Scaillet and Evans, 1999), the pre-eruption conditions of the 1991 Pinatubo dacite magma reservoir, a partition coefficient of 13 (Baker and Rutherford, 1996b) would yield apatite with only 0.25 wt.% SO₃.

Direct diffusion from neighboring or hosting anhydrite was also eliminated as a source of high-S apatites. No diffusion profiles were observed in S element maps of apatites hosted in anhydrite. Sulfur concentrated regions were globular or irregularly shaped, near- to off-center of the apatite grain, sometimes surrounded by a sulfur-rich halo. This may suggest multiple events of apatite sulfur enrichment.

All apatites analyzed from the basalt were high-S, which is consistent with sulfur solubility and apatite/melt sulfur partitioning. Major and trace element analysis was used to rule-out the possibility of inheritance of high-S apatite from the basalt into the dacite during magma mixing/mingling. Direct comparison of MgO, Ce₂O₃, Cl, F, Sr, Eu/Eu*, and REE profiles in silicic and basalt apatites show that there are two statistically distinct apatite populations. High-S silicic apatites did not grow under the same melt conditions as the high-S basalt apatites. Melt environments inferred from

trace elements and REE signatures of both low-S and high-S silicic apatites were indistinguishable, meaning there was little change in the dacite melt during apatite growth other than sulfur.

Fluid-enhanced crystallization is proposed to be the mechanism for generating high-S apatites in cool, fluid-saturated, calc-alkaline melts, like the 1991 Pinatubo dacite with the following model. Numerous injections of underplating basalt provided excess sulfur and increased the oxygen fugacity of the dacite reservoir. There is evidence that this has occurred throughout Modern Pinatubo's history (Newhall et al., 1996; Di Muro et al., 2008). Pyrrhotite globules formed early before the dacite reached an oxygen fugacity of $\sim\text{NNO}+1-1.5$ (Carroll and Rutherford, 1987; Luhr 1990; Hattori, 1993, 1996). After the major sulfur species in the fluid phase and melt shifted from S^{2-} to S^{6+} with oxidation of the dacite melt, early medium- and high-S apatite inclusions either 1) directly crystallized from the vapor via vapor phase crystallization or 2) partitioned sulfur from the fluid phase and the surrounding melt via fluid-enhanced crystallization. When anhydrite saturation was achieved later in the crystallization of the dacite reservoir, sulfur was partitioned into crystallizing anhydrite from both the melt and fluid phase (Jakubowski et al., 2002) and was no longer available for late-crystallizing apatite microphenocrysts. Future investigations of apatite crystallization experiments under sulfur-rich fluid saturated conditions at and below anhydrite saturation could be performed to validate this model.

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APPENDIX A: SAMPLES

Sample descriptions

Hybrid Andesite Lava

On June 7, 1991, a small lava dome of approximately 50 to 100 meters in diameter, appeared northwest of the summit in the upper part of the Maraunot River canyon (Wolfe and Hobblit, 1996). The dome continued to grow through June 11. The growth was interrupted June 12-14 when several lateral blasts destroyed the southeastern section of the dome. Lateral expansion of the dome continued despite the destruction, and the dome was reported to be flat topped when it was last seen on June 14. The climatic eruption of June 15 destroyed the remaining dome (Wolfe and Hobblit, 1996).

Samples of the andesitic lava dome were collected from prismatically jointed and scoracious blocks deposited by a series of pyroclastic flows at the base of the Maraunot River on the northwest side of the 2.5 km caldera (Pallister et al., 1996; Wolfe and Hobblit, 1996). The andesite is homogenous. SiO₂ ranges from 59.0 wt.% to 62.4 wt.% with an average of 59.7 wt.% (Pallister et al., 1996). The andesite is phenocryst-rich (52 vol.%) with 3-7 vol.% vesicles, and has the following mineral assemblage (in order of decreasing abundance): plagioclase (31%), hornblende (12%), augite (5%), olivine (2%), Fe-Ti oxides (2%), biotite (1%), quartz xenocrysts (<1%), and trace amounts of: apatite, anhydrite, and sulfides (Pallister et al., 1996; Bernard et

al., 1996). Phenocrysts are set in a pilotaxitic groundmass composed of clinopyroxene, plagioclase, and Fe-Ti microphenocrysts with matrix glass (Pallister et al., 1996; Bernard et al., 1996).

Disequilibria textures are abundant in the form of reaction rims on large plagioclase phenocrysts, and opaque hornblende. Basaltic xenoliths with mineral assemblages of olivine, hornblende, and augite are abundant and can be small (a few mm in diameter) to fairly large (up to ~40 cm) (Pallister et al., 1996). These and other data and have led to the conclusion that the andesite is a result of magma mixing of the dacitic reservoir beneath Pinatubo with a fresh surge of underplating basaltic magma (Pallister et al., 1996; Bernard et al., 1996; Hattori, 1996).

Basalt Inclusion

Basalt inclusions of various sizes (mm to cm) are found in andesite as referenced above. Samples were collected in the same location as the hybrid andesite. SiO₂ ranges from 50.5 wt.% to 52.0 wt.% with an average of 51.2 wt.% (Pallister et al., 1996). The basalt has a quenched, diktytaxitic groundmass texture with abundant elongated hornblende phenocrysts (Pallister et al., 1996; Bernard et al., 1996). The basalt phenocryst assemblage is as follows (in order of decreasing abundance): hornblende (31%), plagioclase (22%), augite (12%), olivine (3%), Fe-Ti oxides, hornblende xenocrysts (1%), quartz xenocrysts (1%), apatite (<1%), and trace amounts of sulfides (Pallister et al., 1996).

A two-stage crystallization event took place. Crystallization began with the anhydrous phases, olivine and augite. As water fugacity and undercooling of the basalt increased as it intruded into the dacite magma reservoir, elongate hornblende, plagioclase, and magnetite began to crystallize, creating the diktytaxitic texture (Pallister et al., 1996).

Phenocryst-rich Dacite Pumice

June 15, 1991 bore witness to the climactic plinian eruption of Mount Pinatubo. Tephra falls from this event are the most voluminous of all of the vertical eruptions that occurred prior to and following this eruption. The climatic eruption produced $3.4 - 4.4 \text{ km}^3$ (DRE) dacite pumice from tephra falls (Paladio-Melosantos et al., 1996) and $\sim 5.5 \text{ km}^3$ (DRE) of pyroclastic flow deposits (Scott et al., 1996). The dacite pumice comes in two varieties with an 80% – 20% distribution: a phenocryst-rich (47 vol.%), white pumice, and a phenocryst-poor (15 vol.%), tan pumice (David et al., 1996). Chemically, there is no difference between the two pumice types (Pallister et al., 1996). Because of this, no samples of the phenocryst-poor pumice were included in this study. Any further reference to “dacite” or “dacite pumice” infers the phenocryst-rich type.

Vesicles are abundant (61 vol.%) and elongated (Pallister et al., 1996). SiO_2 in the dacite is homogenous and ranges from 64.3 wt.% to 65.0 wt.% with an average of 64.6 wt.%. The phenocryst assemblage is as follows (in order of decreasing abundance): plagioclase (31%), hornblende (12%), 1% each cummingtonite, Fe-Ti

oxides, quartz, anhydrite (<1%), and trace amounts of apatite, biotite, olivine, and bronzite (Pallister et al., 1996). Samples for this study were collected from a pyroclastic flow deposit in the Bucao drainage on the northwest flank of Pinatubo.

Apatites

Dacite and Andesite Hosts

Apatites were found primarily as inclusions in anhydrite and to lesser degrees in plagioclase, hornblende, and Fe-Ti oxides. These apatites range in size from very small (~10 µm) to large (~250 µm) and are euhedral to amorphously anhedral (primarily in anhydrite). Microphenocrysts of euhedral apatite are also found in the groundmass with an average diameter of ~130 µm. Apatite samples were prepared in-situ on polished 80 µm thick sections (8 sections of dacite, 1 section of andesite) for EMP and LA-ICP-MS analyses.

Basalt Host

The shapes of apatite in the basalt is significantly different than those found in either the dacite or andesite. All apatites occur as skeletal, acicular microphenocrysts with sizes ranging from ~10 µm to ~90 µm. One polished 80 µm thick section was prepared from the basalt for EMP and LA-ICP-MS analyses.

Sample numbers

Dacite

- PH12C-1
- PH12C-2
- PH12C-3a
- PH12C-3b
- PH12C-4
- PH12C-5
- PH12C-6
- PH12C-7

Andesite

- CN6791-d

Basalt

- P-22892-2a

APPENDIX B: ELECTRON MICROPROBE

EMP data on additional CD

Methods

Major elements of apatites were measured with a CAMECA SX100 electron microprobe (EMP) housed at Oregon State University in Corvallis, OR via remote access at Portland State University in Portland, OR. The EMP operating conditions during apatite analyses were 15 kV, 20 nA, and 2 μm diameter electron beam. Elements selected for analysis were: Ca, P, F, Cl, S, Ce, Fe, Si, Na, Mn, and Mg. Apatite crystals were analyzed using variable point traverses dependant upon crystal length.

Natural mineral standards were analyzed to test the accuracy and precision of the EMP results. Means and standard deviations of standard analyses as unknowns were compared to published data (Tables B-1 through B-3). Three standards were tested prior to apatite analyses: fluorapatite (FLAP; USNM 104021), anhydrite (ANHY), and tugtupite (TUGT).

Table B-1. EMP analysis information for fluorapatite (FLAP) standard USNM 104021 from Durango, Mexico. “n” indicates the number of times this standard was analyzed throughout this study.

Fluorapatite (FLAP) Standard, USNM 104021, Durango, Mexico						
(wt.%)	Mean n = 19	Standard Deviation	Relative Standard Dev.	Published	Detection Limit (ppm)	
SiO ₂	0.37	0.01	2.08	0.34	Si	99
FeO*	0.05	0.02	48.4	0.06	Fe	977
MgO	0.00	0.01	484	0.01	Mg	144
CaO	53.95	0.23	0.43	54.02	Ca	541
Ce ₂ O ₃	0.62	0.06	9.54	0.55	Ce	1590
Na ₂ O	0.27	0.02	7.41	0.23	Na	307
P ₂ O ₅	40.79	0.27	0.66	40.78	P	370
MnO	0.01	0.05	454	0.01	Mn	1171
SO ₃	0.41	0.04	9.92	0.37	S	103
F	3.54	0.48	13.7	3.53	F	1473
Cl	0.41	0.04	10.3	0.41	Cl	277
Total	100.45	0.41	0.40	99.92		

Table B-2. EMP analysis information for anhydrite (ANHY) standard from Cropwell Bishop. “n” indicates the number of times this standard was analyzed throughout this study.

Anhydrite (ANHY) Standard, Cropwell Bishop						
(wt.%)	Mean n = 5	Standard Deviation	Relative Standard Dev.	(ppm)	Published	Detection Limit
SiO ₂	0.00	0.01	284	Si	--	88
FeO*	0.02	0.05	205	Fe	--	958
MgO	-0.01	0.01	-115	Mg	--	131
CaO	42.61	0.65	1.53	Ca	29.38	522
Ce ₂ O ₃	0.02	0.02	96.7	Ce	--	1485
Na ₂ O	0.00	0.01	120	Na	--	281
P ₂ O ₅	0.02	0.01	37.4	P	--	268
MnO	0.01	0.06	651	Mn	--	1079
SO ₃	56.58	1.94	3.43	S	23.55	270
F	0.03	0.03	114	F	--	1101
Cl	0.00	0.01	-671	Cl	--	282
Total	99.34	1.42	1.43			

Table B-3. EMP analysis information for tugtupite (TUGT) standard from SW Greenland. “n” indicates the number of times this standard was analyzed throughout this study.

Tugtupite (TUGT) Standard, SW Greenland				
(wt.%)	Analyzed	Detection		
	n = 1	(ppm)	Limit	Published
SiO ₂	53.17	Si	164	24.02
FeO*	-0.05	Fe	854	--
MgO	-0.01	Mg	131	--
CaO	0.02	Ca	323	--
Ce ₂ O ₃	0.09	Ce	1310	--
Na ₂ O	26.54	Na	661	19.66
P ₂ O ₅	0.03	P	234	--
MnO	-0.06	Mn	1162	--
SO ₃	0.02	S	93	--
F	-0.01	F	917	--
Cl	7.70	Cl	291	7.58
Total	87.57			

Apatite Analysis

Apatites were analyzed in situ from ten polished thick sections (80 µm thickness): eight dacite pumice sections (PH12C-1, PH12C-2, PH12C-3a, PH12C-3b, PH12C-4, PH12C-5, PH12C-6, and PH12C-7), one hybrid andesite section (CN6791-d), and one basalt inclusion section (P-22892-2a). Thick sections were prepared in Germany. The 80 µm thickness was chosen over the standard 30 µm thickness to allow adequate volume for LA-ICP-MS analysis. EMP analyses were performed to constrain the major element chemistry and sulfur content of the apatites. Table B-4 is a summary of apatite analyses and SO₃ wt.% content.

Variable point traverses were used for apatites analysis. The number of points in each traverse was dependent upon the length of the crystal and selected to achieve a point spacing of 3 to 6 µm. Ideally, the selected traverse began at the center of the crystal and ended at the rim. In some smaller crystals, traverses spanned the entire

length of the crystal from rim to rim. Traverses were chosen to avoid any cracks or impurities on the apatite surface.

Table B- 4. Apatite analyses from dacite pumice, hybrid andesite, and basalt inclusion.

Sample	# of crystals analyzed	# of point analyses	(wt.%)	
			Min SO ₃	Max SO ₃
PH12C-1	13	88	0.08	1.09
PH12C-2	9	46	0.13	1.71
PH12C-3a	2	7	0.14	0.81
PH12C-3b	13	58	0.05	0.93
PH12C-4	4	13	0.10	0.49
PH12C-5	3	8	0.15	1.00
PH12C-6	6	24	0.16	0.91
PH12C-7	19	157	0.09	1.53
CN6791-d	10	70	0.08	1.14
P-22892-2a	33	159	0.11 (0.46)*	3.46

* Minimum SO₃ wt.% value of basalt apatites excluding apatite xenocryst from dacite.

EMP results from this study showed that sulfur content of the apatites ranged from low (<0.3 wt.% SO₃) to high (>0.7 wt.% SO₃) in each of the sections analyzed, regardless of host rock type (Fig. B-1). Intra-grain variation of sulfur fell into one of four profiles: 1) rimward increase SO₃, 2) rimward decrease SO₃, 3) oscillatory SO₃, or 4) homogenous SO₃ (Fig. B-2). Each of these sulfur profiles were found within each the dacite, andesite, and basalt samples.

Figure B-1. Histograms showing the distribution of SO_3 wt.% for each rock type. Number of analyses for each unit, “n”, are as follows: dacite n = 401, andesite n = 70, basalt n = 159. The percentage of high-S apatite (>0.7 wt.% SO_3) analyses are reported for each unit: dacite 7%, andesite 4%, and basalt 89%. Purple dashed lines represent the division between low-S and med-S apatites ($x = 0.3$ wt.% SO_3), and med-S and high-S apatites ($x = 0.7$ wt.% SO_3).

Figure B-1. Continued, histograms showing the distribution of SO_3 wt.% for each rock type. The Frequency y-axis has been reduced in the dacite and andesite histograms to zoom-in on the distribution of high-S (>0.7 wt.% SO_3) apatites. The SO_3 wt.% x-axis domain has also been reduced to [0, 2.6].

Figure B-1. Continued. Histograms showing the distribution of the highest SO_3 wt.% value measured in a single apatite grain for each rock type. Number of apatites analyzed for each unit, “n”, are as follows: dacite n = 69, andesite n = 10, basalt n = 33. The percentage of high-S apatite (>0.7 wt.% SO_3) analyses are reported for each unit: dacite 29%, andesite 20%, and basalt 98%.

Figure B-2: EMP SO_3 wt.% center to rim traverses.

Figure B-2: EMP SO_3 wt.% center to rim traverses.

Figure B-2: EMP SO_3 wt.% center to rim traverses.

Figure B-2: EMP SO_3 wt. % center to rim traverses.

Figure B-2: EMP SO_3 wt. % center to rim traverses.

Figure B-2: EMP SO_3 wt. % center to rim traverses.

Figure B-2: EMP SO_3 wt. % center to rim traverses.

Figure B-2: EMP SO₃ wt.% center to rim traverses.

Figure B-2: EMP SO₃ wt.% center to rim traverses.

Figure B-2: EMP SO₃ wt.% center to rim traverses.

Figure B-2: EMP SO_3 wt.% rim to rim traverses.

Figure B-2: EMP SO₃ wt.% rim to rim traverses.

Figure B-2: EMP SO₃ wt.% rim to rim traverses.

APPENDIX C: LA-ICP-MS

ETH

LA-ICP-MS data were acquired at ETH Zurich, Switzerland using a 193nm ArF Excimer laser coupled with an ELAN 6100 ICP quadrupole mass spectrometer. Laser settings were 23, 24, 28, and 30 kV and a 10 Hz repetition rate, yielding a fluence of about 12 J/cm² on the ablation site. Beam size was determined based upon grain size: 15, 20, and 40 µm for apatites, 15-20 µm for anhydrite hosts and matrix glass, and 20 and 40 µm for plagioclase and hornblende hosts.

The MATLAB-based program, SILLS, was used to process all LA-ICP-MS data. SILLS uses a user interface window to select integration intervals of background levels, signal, and matrix. Signal intervals for apatite were chosen to minimize contamination from host minerals, such as anhydrite, hornblende, and plagioclase, or matrix glass. To calibrate these data, both an internal and external standard is used. The internal standard for apatites was CaO = 54 wt.% (derived from EMP data), and the external standard used in this study was NIST 610. If the apatite signal was low, further calibration parameters were entered to further filter the apatite signal from the surrounding matrix. These parameters included a matrix internal standard, and a second apatite parameter. CaO = 42 wt.% was used as the matrix internal standard for anhydrite hosts, and EMP SiO₂ wt.% values presented in Pallister et al., 1996 were used for hornblende and plagioclase hosts. Total oxides were set to 100% for matrix glass. The second calibration parameter for apatite in an anhydrite host was an

equation that defined the ratio of $\text{Ca/P} = 2$. This equation was also used for matrix glass contamination. Apatites in a hornblende or plagioclase host used a matrix-only tracer, such as K or Al, as a second calibration parameter. LA-ICP-MS results are listed in Table C-1. Error summaries and detection limits are listed in Table C-2.

Table C- 1. ETH LA-ICP-MS data reduced using SILLS (major elements in wt.%, trace elements in ppm). CaO = 54 wt.% was used as an internal standard.

	PH12C-1 ap5 pt1	PH12C-1 ap5 pt2	PH12C-1 ap6	PH12C-1 ap7	PH12C-1 ap8 pt1	PH12C-1 ap8 pt2	PH12C-1 ap9
SiO ₂	0.17	0.18	0.14	0.12	0.12	0.09	0.13
TiO ₂	n.d.	n.d.	n.d.	0.00	0.00	n.d.	0.00
Al ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeO*	0.29	0.30	0.30	0.30	0.27	0.28	0.29
MnO	0.18	0.19	0.18	0.19	0.19	0.18	0.21
MgO	0.17	0.16	0.17	0.17	0.16	0.17	0.17
CaO	54	54	54	54	54	54	54
Na ₂ O	0.13	0.14	0.11	0.11	0.11	0.12	0.12
K ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
P ₂ O ₅	38.0	38.7	35.4	33.9	33.4	33.1	34.8
S	908	1224	694	640	684	705	758
Sc	n.d.	n.d.	n.d.	0.26	0.20	0.25	0.24
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.88
Cu	n.d.	n.d.	n.d.	0.22	n.d.	n.d.	n.d.
Zn	3.42	n.d.	2.96	2.14	2.25	2.13	2.33
Rb	n.d.	n.d.	0.06	n.d.	0.03	0.03	n.d.
Sr	605	596	571	593	658	614	589
Y	291	296	245	258	274	237	261
Zr	0.57	0.86	0.53	0.50	0.82	0.65	0.73
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	3.51	4.31	4.46	4.09	4.53	4.34	3.80
Pb	2.94	3.41	3.52	3.00	2.71	2.82	3.81
Th	20.8	20.0	16.9	15.4	18.0	15.5	17.1
U	6.89	7.99	7.02	6.29	7.13	5.81	6.71
La	812	816	696	754	824	722	748
Ce	1912	1939	1747	1743	1898	1683	1785
Pr	221	225	206	205	221	196	215
Nd	868	871	787	813	855	767	845
Sm	128	135	116	123	128	113	126
Eu	21	22	20	20	21	19	20
Gd	102	107	91	93	94	87	100
Tb	11	12	10	11	11	10	11
Dy	60	60	53	53	53	47	53
Ho	10	10	9	9	9	8	10
Er	25	26	22	25	25	24	24
Yb	19	20	18	18	17	16	18

n.d. = not detected

Table C- 1. Continued.

	PH12C-1 ap10	PH12C-1 ap11 pt1	PH12C-1 ap11 pt2	PH12C-1 ap12	PH12C-1 ap13	PH12C-2 ap1 pt1	PH12C-2 ap1 pt2
SiO ₂	0.13	0.12	0.09	0.12	0.15	n.d.	n.d.
TiO ₂	n.d.	n.d.	0.00	n.d.	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	n.d.	n.d.	n.d.	0.00	0.48	2.46
FeO*	0.28	0.28	0.28	0.28	0.24	0.05	0.03
MnO	0.18	0.19	0.19	0.18	0.18	0.16	0.20
MgO	0.17	0.17	0.17	0.16	0.15	0.11	0.14
CaO	54	54	54	54	54	54	54
Na ₂ O	0.12	0.14	0.14	0.14	0.12	0.37	1.62
K ₂ O	0.00	n.d.	n.d.	n.d.	0.00	n.d.	n.d.
P ₂ O ₅	33.8	39.6	39.1	37.9	38.1	44.2	44.2
S	686	1326	773	915	913	n.d.	n.d.
Sc	0.22	n.d.	n.d.	0.57	0.33	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	0.22	n.d.	n.d.	n.d.	0.22	n.d.	246
Zn	2.09	2.69	2.52	1.37	1.68	n.d.	n.d.
Rb	n.d.	n.d.	n.d.	0.12	0.05	0.27	n.d.
Sr	593	584	590	598	424	614	695
Y	262	294	285	274	364	330	392
Zr	0.63	0.67	0.52	1.06	0.45	0.27	0.57
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	n.d.
Ba	4.05	3.38	3.49	4.08	3.68	5.23	28.83
Pb	3.56	3.63	2.95	2.98	3.06	14.03	2.05
Th	15.4	21.0	19.7	21.1	16.5	26.0	32.6
U	6.00	7.48	7.41	8.38	7.44	9.81	13.3
La	776	797	780	790	336	852	988
Ce	1805	1915	1873	1873	1079	2465	2391
Pr	215	226	222	219	150	273	287
Nd	829	873	867	854	648	978	1139
Sm	124	140	133	130	127	159	172
Eu	21	22	22	22	21	23	25
Gd	96	104	103	95	107	115	132
Tb	11	12	11	11	13	14	18
Dy	55	59	58	60	69	69	80
Ho	9	10	10	10	13	13	14
Er	25	28	27	27	34	34	41
Yb	18	20	17	18	27	15	30

n.d. = not detected

Table C- 1. Continued.

	PH12C-2 ap1 pt3	PH12C-2 ap2	PH12C-2 ap6	PH12C-3a ap1 pt1	PH12C-3a ap1 pt2	PH12C-3b ap1 pt2	PH12C-3b ap1 pt1
SiO ₂	n.d.	n.d.	0.19	6.41	n.d.	0.10	0.09
TiO ₂	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	n.d.	0.00	1.01	0.80	0.00	0.00
FeO*	0.12	n.d.	0.28	0.55	n.d.	0.29	0.29
MnO	0.20	0.23	0.17	0.25	0.16	0.23	0.22
MgO	0.10	0.22	0.16	0.39	0.27	0.15	0.16
CaO	54	54	54	55	54	54	54
Na ₂ O	n.d.	n.d.	0.13	0.49	0.24	0.11	0.11
K ₂ O	n.d.	n.d.	0.00	0.24	n.d.	0.00	0.00
P ₂ O ₅	44.2	44.2	35.1	45.0	44.2	39.0	39.8
S	1143	547	932	n.d.	n.d.	655	592
Sc	n.d.	n.d.	n.d.	0.83	n.d.	0.19	0.24
Cr	n.d.	n.d.	n.d.	13.0	n.d.	3.61	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	2.63	9.52	n.d.	34.9	n.d.	0.99	0.19
Zn	n.d.	n.d.	2.90	38.5	n.d.	1.64	2.18
Rb	2.24	4.56	0.10	6.29	6.24	n.d.	0.04
Sr	n.d.	n.d.	518	n.d.	1258	602	593
Y	326	327	293	370	379	215	200
Zr	0.79	4.79	1.39	5.73	25.6	0.33	0.34
Nb	n.d.	0.29	n.d.	0.38	n.d.	n.d.	n.d.
Ba	n.d.	n.d.	3.87	45.7	73.9	3.66	3.48
Pb	n.d.	n.d.	32.4	5576	619	2.98	3.75
Th	26.5	35.7	26.9	28.6	26.9	10.6	10.5
U	10.5	11.8	9.77	11.6	10.3	5.63	5.48
La	824	1012	795	894	1074	644	639
Ce	2094	2500	1864	2225	2441	1706	1730
Pr	244	294	222	271	290	190	194
Nd	985	1116	888	1078	1130	680	683
Sm	157	178	141	168	172	99	101
Eu	23	28	22	26	24	17	18
Gd	112	117	108	132	121	73	76
Tb	15	14	13	15	16	8	8
Dy	74	78	65	81	63	41	41
Ho	14	12	11	14	15	7	7
Er	39	31	30	34	37	20	19
Yb	28	26	23	28	13	13	13

n.d. = not detected

Table C- 1. Continued.

	PH12C-3b ap2	PH12C-3b ap3	PH12C-3b ap5 pt1	PH12C-3b ap7	PH12C-3b ap8	PH12C-3b ap10	PH12C-3b ap13 pt1
SiO ₂	0.10	0.14	7.78	0.12	0.60	0.14	0.13
TiO ₂	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	n.d.	1.12	0.00	0.03	0.00	n.d.
FeO*	0.29	0.29	0.49	0.35	0.33	0.29	0.29
MnO	0.23	0.23	0.25	0.24	0.25	0.18	0.20
MgO	0.16	0.16	0.23	0.20	0.20	0.17	0.17
CaO	54	54	54	54	54	54	54
Na ₂ O	0.11	0.11	0.67	0.21	0.25	0.12	0.13
K ₂ O	n.d.	0.00	0.33	n.d.	0.01	0.00	n.d.
P ₂ O ₅	39.5	38.1	44.2	44.2	44.2	35.9	41.4
S	665	629	n.d.	n.d.	n.d.	630	798
Sc	0.24	0.20	0.39	0.64	0.18	0.23	n.d.
Cr	n.d.	n.d.	4.80	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	1.52	n.d.	11.0	8.46	n.d.	0.46	0.53
Zn	1.83	1.64	7.16	0.63	1.35	2.53	2.80
Rb	0.05	0.03	9.33	0.13	0.52	0.03	n.d.
Sr	597	606	n.d.	n.d.	n.d.	615	589
Y	236	233	308	319	272	269	284
Zr	0.63	0.65	6.34	0.99	0.35	0.61	0.61
Nb	n.d.	n.d.	0.39	n.d.	0.11	n.d.	n.d.
Ba	3.86	3.35	67.4	n.d.	n.d.	4.29	3.46
Pb	2.83	3.42	542	443	17.3	5.23	3.45
Th	15.5	13.8	25.5	20.3	19.4	15.3	19.4
U	6.42	6.15	9.35	9.29	7.86	5.90	7.34
La	692	687	888	866	805	726	741
Ce	1759	1769	2100	2059	1928	1683	1775
Pr	201	200	244	233	222	202	207
Nd	729	723	933	955	863	779	812
Sm	107	110	144	143	126	119	121
Eu	18	18	22	18	23	19	20
Gd	79	83	115	96	105	91	101
Tb	9	9	12	11	10	10	11
Dy	44	45	64	56	53	53	57
Ho	8	8	11	10	11	10	10
Er	19	20	26	27	27	25	26
Yb	15	15	23	32	17	18	17

n.d. = not detected

Table C- 1. Continued.

	PH12C-3b ap13 pt2	PH12C-3b ap13 pt3	PH12C-4 ap1 pt1	PH12C-4 ap1 pt2	PH12C-4 ap2 pt1	PH12C-4 ap2 pt2	PH12C-4 ap2 pt3
SiO ₂	0.17	0.14	10.2	14.3	n.d.	n.d.	n.d.
TiO ₂	n.d.	n.d.	0.01	0.02	n.d.	n.d.	n.d.
Al ₂ O ₃	0.00	n.d.	1.43	2.23	n.d.	n.d.	n.d.
FeO*	0.32	0.29	0.37	0.44	0.14	0.04	0.21
MnO	0.20	0.19	0.17	0.18	0.27	0.27	0.26
MgO	0.17	0.18	0.18	0.19	0.15	0.17	0.18
CaO	54	54	54	54	54	54	54
Na ₂ O	0.16	0.13	0.64	0.94	n.d.	n.d.	n.d.
K ₂ O	0.00	n.d.	0.38	0.66	n.d.	n.d.	n.d.
P ₂ O ₅	40.0	39.9	31.6	31.9	44.2	44.2	44.2
S	1096	689	2989	1066	910	n.d.	1398
Sc	0.29	0.26	n.d.	0.63	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	0.71	n.d.	2.23	2.95	n.d.	24.6	10.2
Zn	2.13	2.06	6.56	14.9	n.d.	n.d.	1.49
Rb	n.d.	n.d.	11.5	20.5	0.20	n.d.	n.d.
Sr	600	596	611	613	n.d.	n.d.	n.d.
Y	288	275	215	223	313	456	345
Zr	0.63	0.68	8.71	8.53	0.70	n.d.	0.62
Nb	n.d.	n.d.	0.47	0.44	n.d.	n.d.	n.d.
Ba	5.05	5.04	94.4	148	n.d.	n.d.	n.d.
Pb	3.82	6.12	192	869	15.7	135	41.3
Th	22.9	19.3	18.3	17.7	19.8	40.3	24.8
U	8.40	7.29	8.13	7.13	7.13	8.47	9.13
La	775	765	665	666	894	1110	890
Ce	1832	1813	1692	1660	2050	2755	2154
Pr	219	210	189	179	238	351	252
Nd	847	820	694	707	1012	1393	1038
Sm	129	129	118	106	124	252	169
Eu	22	20	19	20	23	26	29
Gd	97	98	86	72	118	106	76
Tb	12	11	8	9	10	10	14
Dy	58	56	48	46	58	98	61
Ho	11	10	8	8	10	16	16
Er	26	27	25	21	27	49	34
Yb	20	19	17	13	29	14	12

n.d. = not detected

Table C- 1. Continued.

	PH12C-4 ap3 pt1	PH12C-4 ap3 pt2	PH12C-5 ap3	PH12C-6 ap1	PH12C-7 ap1 pt1	PH12C-7 ap1 pt2	PH12C-7 ap2 pt1
SiO ₂	0.11	0.11	n.d.	3.74	0.12	0.14	n.d.
TiO ₂	0.00	n.d.	n.d.	0.00	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	0.00	n.d.	0.47	0.00	0.00	n.d.
FeO*	0.29	0.29	n.d.	0.20	0.30	0.30	0.29
MnO	0.23	0.23	0.28	0.08	0.24	0.22	0.18
MgO	0.15	0.16	0.18	0.13	0.17	0.17	0.18
CaO	54	54	54	25.0	54	54	54
Na ₂ O	0.11	0.12	n.d.	0.29	0.12	0.13	0.13
K ₂ O	0.00	0.00	n.d.	0.16	0.00	0.00	n.d.
P ₂ O ₅	32.9	33.2	44.2	14.3	33.2	33.0	40.6
S	549	544	1205	16506	604	717	5381
Sc	0.23	0.29	n.d.	0.32	0.26	0.25	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	2.27	n.d.
Ni	1.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	n.d.	n.d.	n.d.	4.00	0.86	0.22	n.d.
Zn	2.45	2.34	n.d.	5.13	2.36	2.18	n.d.
Rb	0.05	0.03	n.d.	4.71	0.03	0.02	n.d.
Sr	604	612	n.d.	363	579	602	646
Y	272	273	305	106	333	333	287
Zr	0.64	0.62	1.82	2.77	0.50	0.82	n.d.
Nb	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	n.d.
Ba	3.97	3.59	n.d.	39.5	4.00	3.82	6.84
Pb	3.89	3.57	n.d.	7.78	3.82	3.87	2.50
Th	16.4	16.9	39.6	8.04	20.0	23.1	14.3
U	6.55	6.45	14.25	3.43	7.53	8.66	6.52
La	767	773	986	321	827	880	489
Ce	1773	1767	2647	784	1983	2072	1374
Pr	208	212	309	91	241	247	173
Nd	809	812	1065	344	942	966	723
Sm	122	124	180	54	143	145	142
Eu	20	21	26	9	23	23	19
Gd	98	95	113	38	107	112	97
Tb	11	11	14	4	12	13	11
Dy	54	54	52	21	65	66	55
Ho	10	10	12	4	12	12	11
Er	25	25	26	9	30	31	35
Yb	18	17	22	7	23	24	19

n.d. = not detected

Table C- 1. Continued.

	PH12C-7 ap2 pt2	PH12C-7 ap3	PH12C-7 ap4 pt1	PH12C-7 ap4 pt2	PH12C-7 ap4 pt3	PH12C-7 ap4 pt4	PH12C-7 ap5
SiO ₂	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TiO ₂	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	0.05	0.00	n.d.	n.d.	0.00	n.d.
FeO*	0.30	0.25	0.29	0.30	0.28	0.24	0.26
MnO	0.19	0.19	0.20	0.20	0.21	0.19	0.23
MgO	0.19	0.19	0.17	0.16	0.17	0.17	0.20
CaO	54	54	54	54	54	54	54
Na ₂ O	0.13	0.15	0.12	0.12	0.12	0.11	0.11
K ₂ O	n.d.	0.01	n.d.	n.d.	n.d.	0.00	n.d.
P ₂ O ₅	41.6	44.2	39.4	39.4	39.9	38.2	44.2
S	930	n.d.	675	689	577	468	n.d.
Sc	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	3.71	10.5	n.d.	n.d.	n.d.	1.59	n.d.
Zn	n.d.	26.8	n.d.	n.d.	n.d.	n.d.	5.78
Rb	n.d.	n.d.	n.d.	n.d.	0.22	n.d.	n.d.
Sr	618	821	644	632	641	616	280
Y	272	233	269	262	268	258	271
Zr	n.d.	n.d.	0.69	0.48	0.59	0.42	1.48
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	5.85	n.d.	4.09	5.59	4.27	4.57	n.d.
Pb	15.6	348	17.5	3.55	6.20	224	28.6
Th	12.2	15.1	17.0	14.6	15.9	17.2	19.0
U	5.63	5.82	6.28	6.30	6.41	5.96	8.79
La	560	613	733	733	790	703	734
Ce	1468	1497	1821	1853	1964	1814	1824
Pr	186	195	219	218	234	215	228
Nd	690	731	783	809	833	771	843
Sm	116	108	119	118	126	113	120
Eu	19	18	21	20	23	19	23
Gd	81	77	93	88	98	84	90
Tb	11	8	9	10	10	11	10
Dy	56	57	51	52	57	54	52
Ho	11	11	9	10	9	8	10
Er	26	21	26	22	26	21	27
Yb	19	17	19	14	19	17	11

n.d. = not detected

Table C- 1. Continued.

	PH12C-7 ap8	PH12C-7 ap11	PH12C-7 ap16 pt1	PH12C-7 ap16 pt2	PH12C-7 ap16 pt3	PH12C-7 ap18 pt1	PH12C-7 ap18 pt2
SiO ₂	1.58	0.16	n.d.	n.d.	n.d.	0.23	n.d.
TiO ₂	0.00	n.d.	0.00	n.d.	n.d.	n.d.	n.d.
Al ₂ O ₃	0.13	0.01	n.d.	n.d.	n.d.	0.01	0.00
FeO*	0.39	0.31	0.32	n.d.	0.23	0.32	0.24
MnO	0.24	0.22	0.18	0.15	0.18	0.20	0.21
MgO	0.24	0.21	0.18	0.09	0.18	0.14	0.14
CaO	54	54	54	54	54	54	54
Na ₂ O	0.22	0.13	0.12	n.d.	0.07	0.20	0.20
K ₂ O	0.05	n.d.	n.d.	n.d.	n.d.	0.00	0.00
P ₂ O ₅	38.8	44.2	32.7	23.6	31.6	36.9	36.3
S	956	n.d.	1237	n.d.	926	1729	1342
Sc	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	12.26	n.d.	n.d.
Cu	2.19	1.39	n.d.	38.5	n.d.	458	21.5
Zn	7.67	4.60	10.9	56.1	5.28	7.21	n.d.
Rb	1.40	n.d.	n.d.	n.d.	n.d.	0.22	n.d.
Sr	633	134	673	550	597	510	530
Y	216	293	325	248	245	395	397
Zr	0.58	1.08	1.64	9.93	n.d.	1.02	1.27
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	9.29	n.d.	8.52	204	4.50	5.34	1.80
Pb	12.8	16.8	127	1186	259	6.31	3.36
Th	9.89	16.0	36.5	25.1	20.5	20.8	18.2
U	5.09	7.88	10.6	2.26	8.05	8.33	9.02
La	681	806	830	566	737	479	512
Ce	1675	2067	1921	1461	1743	1349	1415
Pr	193	243	227	189	204	179	186
Nd	703	911	894	580	809	801	801
Sm	103	136	138	156	115	146	145
Eu	18	21	25	25	20	25	22
Gd	71	106	108	117	82	118	129
Tb	8	12	12	8	11	14	16
Dy	43	52	60	57	46	81	80
Ho	7	10	10	13	8	14	13
Er	21	28	27	29	25	39	42
Yb	17	21	16	9	13	33	26

n.d. = not detected

Table C- 1. Continued.

	PH12C-7 ap18 pt3	PH12C-7 ap19 pt1	PH12C-7 ap19 pt2	CN6791-d ap1	CN6791-d ap2 pt1	CN6791-d ap2 pt2	CN6791-d ap3 pt1
SiO ₂	0.61	n.d.	n.d.	0.12	0.14	0.13	0.08
TiO ₂	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	n.d.	0.00	0.00	0.00	n.d.	n.d.
FeO*	0.26	0.28	0.23	0.31	0.28	0.30	0.28
MnO	0.21	0.27	0.27	0.20	0.18	0.19	0.19
MgO	0.15	0.14	0.13	0.18	0.17	0.17	0.16
CaO	54	54	54	54	54	54	54
Na ₂ O	0.15	0.11	0.11	0.13	0.11	0.12	0.12
K ₂ O	0.00	n.d.	n.d.	0.00	0.00	0.00	n.d.
P ₂ O ₅	37.5	34.3	33.6	39.5	34.9	35.1	37.9
S	1052	488	414	978	831	847	769
Sc	n.d.	n.d.	n.d.	0.43	0.33	0.27	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	3.16	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	3.00	n.d.	n.d.	9.12	0.73	0.50	0.45
Zn	12.7	n.d.	n.d.	2.60	2.10	1.76	1.72
Rb	n.d.	n.d.	n.d.	0.15	n.d.	0.04	n.d.
Sr	568	547	559	627	627	623	627
Y	357	300	303	281	273	251	288
Zr	0.79	1.31	0.30	0.63	0.88	0.72	0.66
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	3.08	2.23	3.81	3.60	4.99	4.14	4.96
Pb	9.31	5.05	5.48	3.01	2.98	2.94	3.86
Th	14.6	17.3	16.1	18.4	21.8	18.8	19.4
U	7.94	7.89	6.28	6.87	7.79	7.23	7.51
La	497	752	734	775	825	784	849
Ce	1295	1859	1845	1812	1907	1787	1972
Pr	184	223	217	213	221	208	227
Nd	784	869	846	819	852	801	885
Sm	140	136	127	121	127	117	135
Eu	24	22	19	22	22	20	23
Gd	108	102	91	98	100	91	99
Tb	14	10	11	11	11	10	11
Dy	72	60	59	56	56	51	56
Ho	13	10	10	10	10	9	10
Er	33	29	29	25	24	23	28
Yb	19	21	17	18	18	17	19

n.d. = not detected

Table C- 1. Continued.

	CN6791-d ap3 pt2	CN6791-d ap5 pt1	CN6791-d ap5 pt2	CN6791-d ap6	CN6791-d ap7	CN6791-d ap8	CN6791-d ap9
SiO ₂	0.12	0.17	0.17	0.16	0.12	3.07	0.15
TiO ₂	n.d.	n.d.	n.d.	0.00	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	0.00	0.00	0.01	0.00	0.76	n.d.
FeO*	0.27	0.31	0.33	0.28	0.32	0.26	0.31
MnO	0.19	0.23	0.24	0.21	0.22	0.22	0.20
MgO	0.16	0.17	0.18	0.16	0.18	0.14	0.17
CaO	54	54	54	54	54	54	54
Na ₂ O	0.12	0.18	0.17	0.11	0.13	0.50	0.12
K ₂ O	n.d.	n.d.	0.00	0.00	0.00	0.02	n.d.
P ₂ O ₅	37.7	36.8	40.3	35.6	35.2	37.2	36.7
S	823	1701	1355	666	912	1024	788
Sc	0.29	n.d.	n.d.	n.d.	0.30	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	0.48	4.61	4.17	n.d.	5.82	10.2	1.79
Zn	1.48	2.07	2.94	2.51	1.75	3.50	1.74
Rb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	636	639	629	611	621	630	593
Y	300	268	263	216	283	275	267
Zr	0.70	0.68	0.40	0.57	0.60	0.55	1.02
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	4.82	4.00	2.85	2.52	4.02	12.7	3.11
Pb	3.56	3.15	13.5	4.22	3.86	5.23	2.82
Th	21.4	26.5	20.5	16.0	17.0	15.8	17.4
U	8.51	9.49	7.84	6.63	6.56	7.43	6.48
La	891	780	805	691	746	773	744
Ce	2035	1828	1902	1573	1786	1911	1767
Pr	238	211	223	176	214	231	208
Nd	919	815	833	706	826	870	808
Sm	134	118	120	98	126	128	126
Eu	23	21	21	18	20	20	20
Gd	104	92	91	73	97	88	96
Tb	12	10	10	8	11	10	10
Dy	61	53	52	41	57	57	52
Ho	10	9	11	8	10	10	10
Er	27	23	26	20	25	25	26
Yb	21	18	20	13	18	20	18

n.d. = not detected

Table C- 1. Continued.

	CN6791-d	CN6791-d	P-22892- 2a	P-22892- 2a	P-22892- 2a	P-22892- 2a	P-22892- 2a
	ap10 pt1	ap10 pt2	ap1	ap12 pt1	ap12 pt2	ap13	ap19 pt3
SiO ₂	0.15	n.d.	0.12	n.d.	0.70	0.55	0.30
TiO ₂	0.00	n.d.	n.d.	n.d.	0.00	0.00	0.00
Al ₂ O ₃	0.00	0.00	0.00	0.02	0.02	0.14	n.d.
FeO*	0.26	0.29	0.28	0.16	0.34	0.15	0.26
MnO	0.18	0.20	0.23	0.09	0.16	0.04	0.12
MgO	0.17	0.17	0.14	0.13	0.24	0.06	0.24
CaO	54	54	54	24.4	54	24.4	54
Na ₂ O	0.15	0.21	0.11	0.15	0.36	0.07	0.37
K ₂ O	n.d.	0.00	n.d.	n.d.	0.00	n.d.	n.d.
P ₂ O ₅	35.6	36.2	36.1	11.0	27.1	13.0	33.9
S	2199	5818	777	2532	5510	2142	4910
Sc	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	36.7
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20.1
Cu	22.8	53.2	1.92	8.66	11.7	42.6	n.d.
Zn	3.27	3.32	1.35	4.01	1.69	5.07	8.58
Rb	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	0.80
Sr	615	652	588	621	1027	449	968
Y	262	298	267	53	83	32	91
Zr	1.06	1.72	0.43	0.44	5.01	1.82	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	0.97
Ba	3.53	5.44	3.47	n.d.	8.21	n.d.	n.d.
Pb	5.61	21.1	4.06	30.2	2.41	5.41	11.6
Th	17.3	25.0	15.7	12.5	18.3	6.98	14.7
U	7.02	9.63	5.81	3.74	5.23	1.89	3.71
La	735	805	741	168	254	79	195
Ce	1713	1902	1679	363	565	162	495
Pr	203	224	198	44	68	22	64
Nd	795	887	764	178	250	83	257
Sm	121	127	123	20	43	13	55
Eu	20	21	18	6	13	5	12
Gd	93	100	88	13	31	13	38
Tb	10	11	10	1	3	2	3
Dy	49	59	54	11	16	6	17
Ho	9	11	8	2	2	1	4
Er	23	29	25	3	8	4	12
Yb	18	20	15	4	7	2	1

n.d. = not detected

Table C- 1. Continued.

	P-22892- 2a ap20	P-22892- 2a ap21	P-22892- 2a ap22	P-22892- 2a ap23	P-22892- 2a ap25	P-22892- 2a ap26	P-22892- 2a ap27
SiO ₂	2.16	0.77	n.d.	4.90	n.d.	3.79	0.38
TiO ₂	0.01	0.00	n.d.	0.01	n.d.	0.01	0.01
Al ₂ O ₃	0.27	0.00	n.d.	0.79	n.d.	0.52	0.09
FeO*	0.29	0.23	0.14	0.35	n.d.	0.36	0.24
MnO	0.10	0.11	0.10	0.13	n.d.	0.13	0.15
MgO	0.24	0.23	0.17	0.26	n.d.	0.25	0.25
CaO	54	54	54	54	54	54	54
Na ₂ O	0.27	0.33	0.07	0.54	n.d.	0.57	0.35
K ₂ O	0.11	n.d.	n.d.	0.38	n.d.	0.24	n.d.
P ₂ O ₅	33.2	37.3	36.0	38.2	44.2	32.9	29.4
S	2829	4221	3126	3566	1413	5109	4236
Sc	n.d.	n.d.	0.76	n.d.	6.33	n.d.	1.89
Cr	n.d.	n.d.	20.5	n.d.	205	n.d.	21.8
Ni	n.d.	11.4	n.d.	n.d.	93.0	n.d.	n.d.
Cu	7.43	n.d.	150	4.70	n.d.	10.4	9.26
Zn	4.43	5.15	18.1	11.9	n.d.	7.88	9.97
Rb	4.96	0.29	2.45	15.2	n.d.	10.6	4.28
Sr	1011	1121	1030	1066	n.d.	1010	969
Y	76.1	66.0	84.9	53.7	110	81.3	74.7
Zr	9.50	4.32	n.d.	12.2	n.d.	9.24	3.85
Nb	0.31	0.12	n.d.	0.48	n.d.	n.d.	n.d.
Ba	23.1	3.15	6.68	61.3	n.d.	37.7	7.20
Pb	11.6	2.55	8.71	4.77	n.d.	27.5	44.6
Th	18.5	10.7	15.4	13.0	n.d.	14.4	17.4
U	4.40	4.96	4.41	4.66	n.d.	2.85	5.33
La	217	178	209	176	323	196	221
Ce	491	435	540	428	871	465	476
Pr	63	52	71	49	106	58	61
Nd	228	201	243	177	407	244	212
Sm	33	29	38	27	70	42	38
Eu	12	12	13	10	17	12	12
Gd	24	25	19	15	55	28	25
Tb	3	2	3	2	5	4	3
Dy	16	13	17	8	28	18	15
Ho	3	3	3	2	4	3	4
Er	9	8	6	5	18	7	11
Yb	5	5	3	3	6	5	7

n.d. = not detected

Table C- 1. Continued.

	P-22892- 2a ap30	P-22892- 2a ap32	P-22892- 2a ap33
SiO ₂	15.2	14.0	n.d.
TiO ₂	0.03	0.03	0.00
Al ₂ O ₃	3.20	2.63	n.d.
FeO*	0.57	0.59	0.41
MnO	0.16	0.21	0.20
MgO	0.30	0.33	0.46
CaO	54	54	54
Na ₂ O	1.26	1.09	n.d.
K ₂ O	1.12	1.04	n.d.
P ₂ O ₅	34.7	27.1	52.6
S	4232	3674	5710
Sc	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	58.7
Ni	n.d.	n.d.	n.d.
Cu	n.d.	29.5	28.7
Zn	n.d.	11.2	36.6
Rb	41.3	42.1	n.d.
Sr	1059	953	1390
Y	54.7	124	161
Zr	37.3	40.5	17.4
Nb	2.04	0.87	n.d.
Ba	192	158	n.d.
Pb	193	10.4	3450
Th	10.8	24.9	26.3
U	3.18	5.30	7.03
La	179	327	323
Ce	457	776	589
Pr	51	100	77
Nd	184	394	371
Sm	33	60	71
Eu	12	16	21
Gd	18	51	61
Tb	3	5	5
Dy	14	29	32
Ho	3	5	6
Er	7	15	9
Yb	3	10	10

n.d. = not detected

Table C- 2. ETH LA-ICP-MS error summary (1 σ) and detection limits (ppm).

ETH - August 3, 2010						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	3.07	0.01	0.19	1451	41.9	356
TiO ₂	0.003	0.00003	0.001	8.43	0.26	2.19
Al ₂ O ₃	0.76	0.00002	0.06	143	0.16	11.4
FeO*	0.33	0.003	0.11	100	4.05	39.3
MnO	0.24	0.0003	0.07	11.6	0.21	3.32
MgO	0.18	0.001	0.06	35.0	0.29	9.06
CaO	54	0.06	18.7	2081	39.6	635
Na ₂ O	0.50	0.0003	0.07	67.1	0.36	7.13
K ₂ O	0.02	0.00005	0.002	21.2	0.54	5.44
P ₂ O ₅	40.3	0.02	12.7	358	2.56	92.8
S	5818	7.18	542	364	12.9	88.7
Sc	0.43	0.03	0.16	1.25	0.05	0.32
Cr	3.16	0.65	1.90	33.5	0.86	8.75
Ni	1.11	0.54	0.83	16.2	0.84	5.21
Cu	53.2	0.08	6.05	3.61	0.10	0.79
Zn	7.61	0.22	1.67	2.69	0.14	0.88
Rb	1.53	0.01	0.23	0.32	0.01	0.09
Sr	652	1.10	235	5.56	0.01	1.46
Y	300	0.75	95.5	3.55	0.01	0.84
Zr	2.27	0.05	0.51	0.38	0.02	0.14
Nb	0.23	0.09	0.18	0.23	0.01	0.07
Ba	12.7	0.23	2.61	4.52	0.07	0.70
Pb	42.9	0.12	4.20	3.35	0.02	0.31
Th	26.5	0.19	7.40	0.88	0.01	0.25
U	9.63	0.11	3.00	0.58	0.01	0.16
La	891	0.89	273	5.64	0.01	1.35
Ce	2035	1.62	637	8.96	0.01	2.08
Pr	238	0.54	75.5	2.75	0.01	0.64
n.d.	919	2.66	294	13.0	0.04	3.07
Sm	135	1.12	45.7	5.36	0.05	1.38
Eu	23.2	0.25	8.00	1.16	0.02	0.32
Gd	104	1.03	35.4	4.62	0.05	1.26
Tb	12.0	0.13	3.96	0.58	0.01	0.16
Dy	61.1	0.59	20.3	2.85	0.03	0.74
Ho	11.1	0.13	3.76	0.60	0.01	0.16
Er	29.1	0.43	9.88	2.01	0.04	0.58
Yb	21.0	0.44	7.59	2.17	0.05	0.64

n = 38

Table C-2. Continued.

ETH - August 4, 2010						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.74	0.01	0.11	1051	86	324
TiO ₂	0.002	0.0004	0.001	5.46	0.34	1.80
Al ₂ O ₃	0.11	0.00002	0.03	185	0.24	22.8
FeO*	0.05	0.003	0.02	53.5	5.03	18.1
MnO	0.04	0.0004	0.01	1.91	0.24	0.79
MgO	0.04	0.001	0.01	4.52	0.31	1.37
CaO	5.47	0.07	0.97	596	48.0	220
Na ₂ O	0.06	0.0003	0.01	77.5	0.38	10.6
K ₂ O	0.03	0.0001	0.005	14.4	1.23	4.86
P ₂ O ₅	6.64	0.02	1.76	25.8	3.05	9.33
S	294	8.97	79.5	377	24.9	102
Sc	0.38	0.04	0.13	0.84	0.04	0.24
Cr	4.84	0.98	3.47	12.8	1.88	5.46
Ni	0	0	0	7.64	1.37	3.58
Cu	14.0	0.08	2.69	1.52	0.11	0.46
Zn	4.50	0.28	0.98	2.28	0.26	0.76
Rb	2.25	0.01	0.53	0.22	0.01	0.06
Sr	193	1.32	18.8	3.87	0.01	0.69
Y	58.0	0.74	13.9	0.13	0.01	0.05
Zr	5.02	0.04	0.69	0.16	0.02	0.07
Nb	0.47	0.04	0.20	0.10	0.01	0.04
Ba	15.4	0.26	2.79	3.94	0.08	0.71
Pb	349	0.13	33.5	0.41	0.03	0.11
Th	4.26	0.17	1.61	0.08	0.01	0.04
U	2.16	0.12	0.85	0.08	0.01	0.03
La	165	1.24	33.6	0.35	0.01	0.10
Ce	376	2.08	81.8	0.47	0.01	0.13
Pr	44.6	0.61	10.4	0.14	0.01	0.05
n.d.	173	2.80	42.4	0.62	0.05	0.24
Sm	26.6	1.16	9.07	0.43	0.06	0.20
Eu	4.16	0.26	1.68	0.16	0.02	0.06
Gd	20.7	1.04	7.41	0.46	0.06	0.20
Tb	2.56	0.13	0.93	0.07	0.01	0.03
Dy	11.2	0.58	4.32	0.29	0.03	0.12
Ho	2.57	0.13	0.91	0.07	0.01	0.03
Er	7.84	0.43	2.86	0.34	0.04	0.13
Yb	13.2	0.43	3.29	0.71	0.06	0.22

n = 20

Table C-2. Continued.

ETH - March 16, 2011						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.73	0.06	0.31	2547	368	976
TiO ₂	0.01	0.001	0.003	23.7	1.80	7.21
Al ₂ O ₃	0.14	0.0003	0.02	172	3.13	15.7
FeO*	0.11	0.01	0.03	182	21.9	57.9
MnO	0.08	0.001	0.01	9.78	1.59	3.89
MgO	0.09	0.01	0.02	32.1	1.94	6.56
CaO	5.31	0.25	0.77	1321	201	533
Na ₂ O	0.09	0.001	0.02	71.3	1.64	6.88
K ₂ O	0.01	0.0004	0.003	40.0	4.54	12.1
P ₂ O ₅	19.0	0.07	1.09	138	14.9	38.3
S	982	43.3	117	479	64.1	178
Sc	3.80	0.76	1.87	4.41	0.38	1.36
Cr	235	21.9	69.6	96.4	17.9	38.2
Ni	195	11.6	63.6	49.6	6.09	17.6
Cu	32.9	1.09	7.39	6.67	0.99	2.54
Zn	35.0	2.00	6.71	13.1	0.97	4.20
Rb	3.33	0.13	1.49	1.49	0.08	0.34
Sr	515	5.13	41.3	3.80	0.12	0.74
Y	86.0	1.52	9.60	1.22	0.10	0.26
Zr	25.8	0.18	2.41	1.81	0.19	0.47
Nb	0.77	0.15	0.39	0.55	0.08	0.23
Ba	141	0.75	10.4	8.12	0.42	1.44
Pb	139	0.54	11.6	3.73	0.11	0.47
Th	10.1	0.64	1.95	0.60	0.08	0.18
U	4.90	0.40	1.02	0.41	0.06	0.15
La	160	2.33	15.8	1.81	0.07	0.31
Ce	465	3.59	36.8	2.78	0.08	0.41
Pr	66.1	1.04	6.55	0.80	0.04	0.15
n.d.	241	4.76	27.3	3.85	0.24	0.80
Sm	38.2	2.00	8.19	1.71	0.23	0.62
Eu	6.73	0.64	1.85	0.42	0.06	0.17
Gd	29.5	1.63	7.31	1.68	0.25	0.67
Tb	3.57	0.21	0.90	0.25	0.03	0.09
Dy	23.3	0.86	4.32	0.88	0.14	0.37
Ho	4.54	0.22	0.94	0.23	0.04	0.10
Er	11.3	0.74	2.98	1.01	0.16	0.43
Yb	13.4	0.76	3.05	2.05	0.24	0.64

n = 29

APPENDIX D: CORRELATION OF EMP AND LA-ICP-MS

To correlate the LA-ICP-MS data with the EMP data (e.g. Sr and SO₃ wt.%), laser spots were ideally placed over the previous EMP point traverses (Fig. D-1). The much larger laser spot size overlapped multiple EMP spots, therefore, the average of the overlapped EMP spots were used in conjunction with LA-ICP-MS data. Data from some laser spots illustrated in Figure D-1 were not used in the final data analysis due to significant contamination from the matrix.

Figure D-1: EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μ m.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO_3 wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO_3 wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μ m.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO_3 wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm .

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 μm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

Figure D-1: Continued, EMP (green line and circles) and LA-ICP-MS (red circle) data correlation. EMP SO₃ wt.% values are shown beside the EMP spots. Laser spot size is represented by scale bar, EMP spot size is 2 µm.

APPENDIX E: HOST/MATRIX LA-ICP-MS

Table E- 1. ETH LA-ICP-MS data of Durango Apatite reduced using SILLs (major elements in wt.%, trace elements in ppm). CaO = 55 wt.% was used as an internal standard.

	Durango 1	Durango 2	Durango 3	Durango 4	Durango 5	Durango 6	Durango 7
SiO ₂	0.29	0.24	0.37	0.37	0.26	0.31	0.37
TiO ₂	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	n.d.	0.0001	n.d.	n.d.	n.d.	n.d.
FeO*	0.05	0.05	0.04	0.04	0.05	0.05	0.04
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.03	0.03	0.02	0.02	0.03	0.03	0.02
CaO	55	55	55	55	55	55	55
Na ₂ O	0.24	0.25	0.19	0.20	0.23	0.24	0.20
K ₂ O	0.0003	0.0002	0.0003	0.0003	0.0002	0.0003	n.d.
P ₂ O ₅	36.4	33.4	35.1	32.4	35.1	35.6	34.0
S	1735	1200	1318	1099	1287	1346	1264
Sc	n.d.	0.12	0.13	0.20	0.15	0.19	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	1.56	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	0.39	0.37	0.49	n.d.	0.23	0.26	0.17
Zn	0.34	n.d.	0.96	n.d.	0.32	0.61	0.39
Rb	0.06	0.03	0.07	n.d.	0.04	0.03	0.06
Sr	489	482	499	492	480	486	476
Y	432	423	561	568	408	432	527
Zr	0.55	0.49	0.66	0.70	0.51	0.64	0.63
Nb	0.02	n.d.	0.02	0.02	n.d.	n.d.	0.01
Ba	1.20	1.58	1.51	1.46	1.79	1.33	1.56
Pb	0.64	0.54	1.01	0.88	0.62	0.78	0.96
Th	197	169	267	272	168	193	272
U	9.51	8.35	13.2	12.9	8.08	9.61	14.1
La	3081	2904	3330	3401	2871	3175	3464
Ce	4032	3878	4144	4142	3769	4051	4499
Pr	325	318	329	329	308	326	323
n.d.	1039	1020	1041	1044	978	1022	1019
Sm	128	131	145	148	125	124	140
Eu	16	16	16	17	16	16	15
Gd	115	112	131	132	108	107	131
Tb	13	13	16	17	13	13	16
Dy	72	70	93	93	68	73	91
Ho	14	14	18	18	13	14	18
Er	39	37	49	51	37	37	50
Yb	27	26	36	35	26	27	34

n.d. = not detected

Table E- 1. Continued.

	Durango 8	Durango 9	Durango 10	Durango 11	Durango 12	Durango 13	Durango 14
SiO ₂	0.38	0.35	0.38	0.39	0.42	0.380	0.364
TiO ₂	n.d.	0.0001	n.d.	n.d.	n.d.	n.d.	0.0001
Al ₂ O ₃	n.d.	n.d.	n.d.	n.d.	0.00	n.d.	n.d.
FeO*	0.05	0.04	0.04	0.04	0.04	0.04	0.04
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.02	0.02	0.02	0.02	0.02	0.02	0.02
CaO	55	55	55	55	55	55	55
Na ₂ O	0.20	0.19	0.19	0.20	0.20	0.20	0.20
K ₂ O	0.00	0.0002	0.0003	0.0002	0.00	n.d.	0.0006
P ₂ O ₅	34.1	32.6	33.0	35.5	35.6	33.4	32.6
S	1232	1303	1169	1209	1183	1264	1139
Sc	0.10	0.08	0.15	0.12	n.d.	0.11	0.11
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	1.52	n.d.	n.d.	n.d.
Cu	0.28	n.d.	1.36	1.47	0.87	n.d.	0.22
Zn	n.d.	n.d.	0.92	0.66	0.77	n.d.	0.35
Rb	0.04	0.06	0.05	0.04	0.06	0.03	0.07
Sr	483	490	482	486	493	485	487
Y	554	547	546	537	541	548	553
Zr	0.72	0.52	0.52	0.52	0.55	0.57	0.61
Nb	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.02
Ba	1.45	1.51	1.49	1.65	1.72	1.56	1.60
Pb	1.00	0.74	1.20	1.20	1.14	0.85	0.82
Th	290	265	281	269	281	286	271
U	14.7	13.6	14.2	13.7	14.4	14.3	13.4
La	3485	3667	3294	3322	3326	3317	3526
Ce	4552	4560	4242	4137	4166	4075	4559
Pr	330	321	323	329	333	323	327
n.d.	1039	1024	1027	1053	1056	1024	1033
Sm	143	139	142	146	144	139	143
Eu	15	15	15	17	15	15	15
Gd	132	132	128	132	132	128	126
Tb	16	16	16	16	16	16	16
Dy	93	90	90	91	89	94	92
Ho	18	18	17	18	17	18	18
Er	50	48	48	49	48	51	50
Yb	35	33	33	34	33	35	34

n.d. = not detected

Table E- 1. Continued.

	Durango 15	Durango 16	Durango 17	Durango 18	Durango 19	Durango 20
SiO ₂	0.36	0.38	0.38	0.39	0.40	0.39
TiO ₂	n.d.	0.00	0.00	n.d.	n.d.	n.d.
Al ₂ O ₃	n.d.	n.d.	n.d.	0.00003	n.d.	n.d.
FeO*	0.04	0.04	0.04	0.04	0.04	0.04
MnO	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.02	0.02	0.02	0.02	0.02	0.02
CaO	55	55	55	55	55	55
Na ₂ O	0.18	0.19	0.20	0.19	0.20	0.21
K ₂ O	0.0002	0.0003	0.0003	0.0002	0.0003	0.0003
P ₂ O ₅	33.8	33.6	33.6	32.9	33.3	32.6
S	1209	1097	1190	1064	1475	1292
Sc	0.09	0.09	0.10	0.11	0.17	0.12
Cr	n.d.	2.01	n.d.	1.42	n.d.	2.30
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	n.d.	0.24	0.26	0.17	0.39	0.30
Zn	0.20	n.d.	0.40	n.d.	0.42	0.34
Rb	0.03	0.05	0.06	0.05	0.09	0.04
Sr	485	488	492	485	491	492
Y	541	548	555	559	553	551
Zr	0.49	0.64	0.59	0.64	0.65	0.52
Nb	0.01	n.d.	n.d.	n.d.	0.04	0.02
Ba	1.57	1.56	1.49	1.71	1.69	1.24
Pb	0.79	0.86	1.03	0.92	1.10	1.01
Th	261	270	276	271	273	280
U	13.3	13.5	14.2	13.9	14.2	14.3
La	3668	3358	3309	3350	3319	3309
Ce	4571	4456	4262	4396	4053	4025
Pr	320	319	326	325	323	321
n.d.	1012	1028	1030	1010	1034	1023
Sm	138	141	140	144	143	140
Eu	16	15	16	15	16	15
Gd	129	129	132	130	130	128
Tb	16	16	16	17	16	16
Dy	90	91	90	90	90	89
Ho	18	18	18	18	18	17
Er	48	50	49	49	50	48
Yb	33	33	34	34	34	34

n.d. = not detected

Table E- 2. ETH LA-ICP-MS data of anhydrite reduced using SILLS (major elements in wt.%, trace elements in ppm). CaO = 42 wt.% was used as an internal standard.

	CN6791-d anhy of ap10	CN6791-d anh1 pt1	CN6791-d anh1 pt2	PH12C-1 anh of ap4	PH12C-2 anh of ap3	PH12C-2 anh of ap4	PH12C-2 anh of ap5&6
SiO ₂	n.d.	n.d.	0.03	12.26	n.d.	n.d.	n.d.
TiO ₂	0.001	0.001	0.001	0.01	0.001	0.002	n.d.
Al ₂ O ₃	0.000	0.002	0.003	0.23	n.d.	0.002	n.d.
FeO*	0.01	0.01	0.01	0.09	0.01	0.01	0.01
MnO	0.0005	0.003	0.002	0.04	0.002	0.002	0.002
MgO	0.002	0.003	0.003	0.71	0.002	0.003	0.001
CaO	42	42	42	42	42	42	42
Na ₂ O	0.0004	0.0005	0.001	2.32	0.002	0.01	0.005
K ₂ O	n.d.	n.d.	n.d.	0.21	n.d.	0.002	n.d.
P ₂ O ₅	0.08	0.02	0.03	7.70	0.07	0.07	0.09
S	163744	140965	150168	126830	161162	167540	152031
Sc	n.d.	n.d.	n.d.	0.26	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	9.62	n.d.	n.d.	n.d.
Cu	20.3	n.d.	n.d.	61.9	n.d.	1.25	n.d.
Zn	n.d.	0.48	0.37	5.87	n.d.	n.d.	n.d.
Rb	n.d.	n.d.	n.d.	6.03	n.d.	n.d.	n.d.
Sr	2230	1482	989	1436	2029	1938	1903
Y	23.1	8.08	9.88	74.8	26.7	25.9	29.8
Zr	n.d.	n.d.	n.d.	18.91	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.
Ba	48.7	49.3	49.2	65.6	43.8	41.0	47.2
Pb	16.7	4.40	27.5	262	11.3	591	3.92
Th	0.51	n.d.	n.d.	3.65	0.47	0.44	0.34
U	n.d.	n.d.	n.d.	1.24	n.d.	n.d.	n.d.
La	204	3	6	306	241	227	248
Ce	363	9	17	653	428	382	444
Pr	37	1	3	73	45	41	45
n.d.	128	7	14	270	162	149	166
Sm	16	2	4	34	19	14	22
Eu	4	0.5	1	8	3	3	4
Gd	11	2	4	26	13	8	14
Tb	1	0.3	0.4	3	1	1	1
Dy	4	1	2	14	5	7	8
Ho	0.4	0.3	0.2	2	1	1	1
Er	1	0.3	1	6	2	1	2
Yb	1	1	0.3	5	1	0.3	1

n.d. = not detected

Table E-2. Continued.

	PH12C-2	PH12C-3a	PH12C-3b	PH12C-3b	PH12C-4	PH12C-5	PH12C-5
	anh of ap8	anh of ap1	anh of ap5&6	anh of ap7-9	anh of ap4	anh of ap1	anh of ap2
SiO ₂	n.d.	n.d.	n.d.	n.d.	5.44	n.d.	0.13
TiO ₂	0.001	0.001	0.001	0.001	0.003	0.001	0.001
Al ₂ O ₃	0.0001	n.d.	n.d.	n.d.	0.07	0.003	0.003
FeO*	0.01	0.01	0.01	0.01	0.04	0.01	0.01
MnO	0.002	0.002	0.002	0.002	0.004	0.003	0.002
MgO	0.002	0.002	0.001	0.001	0.13	0.002	0.003
CaO	42	42	42	42	42	42	42
Na ₂ O	0.002	0.002	0.000	0.002	0.53	0.01	0.01
K ₂ O	n.d.	n.d.	n.d.	0.001	0.07	n.d.	0.004
P ₂ O ₅	0.07	0.07	0.10	0.07	0.09	0.23	0.06
S	155949	157176	144879	145250	200894	176417	158284
Sc	n.d.	n.d.	n.d.	n.d.	0.33	0.76	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	9.12	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	2.13	n.d.	n.d.
Cu	n.d.	0.41	n.d.	n.d.	62.17	2.22	n.d.
Zn	n.d.	n.d.	n.d.	n.d.	19.56	5.81	1.59
Rb	n.d.	n.d.	n.d.	n.d.	2.01	0.46	0.83
Sr	2095	2118	2273	2081	1968	1999	2145
Y	33.1	32.2	7.4	27.6	32.1	32.0	27.1
Zr	n.d.	n.d.	n.d.	n.d.	17.04	0.15	0.13
Nb	n.d.	n.d.	n.d.	n.d.	0.59	0.09	n.d.
Ba	44.7	43.3	15.5	36.1	50.4	41.7	39.1
Pb	1.04	0.68	0.59	1.63	586	400	49.9
Th	0.43	0.41	n.d.	0.46	0.64	0.71	0.13
U	n.d.	n.d.	n.d.	n.d.	0.15	0.37	n.d.
La	254	297	20	218	291	273	271
Ce	465	502	39	393	561	465	446
Pr	50	52	4	41	49	47	44
n.d.	187	180	24	150	182	183	165
Sm	20	19	4	19	22	20	18
Eu	4	4	2	4	4	3	4
Gd	15	12	2	10	16	11	14
Tb	1	2	0.2	1	2	1	1
Dy	7	7	1	5	7	5	4
Ho	1	1	0.1	1	1	1	1
Er	3	2	1	2	2	3	3
Yb	1	1	0.2	1	1	1	0.3

n.d. = not detected

Table E-2. Continued.

	PH12C-6 anh of ap1	PH12C-7 anh of ap2 ctr	PH12C-7 anh of ap2 middle
SiO ₂	n.d.	n.d.	n.d.
TiO ₂	0.001	0.002	n.d.
Al ₂ O ₃	0.001	0.003	n.d.
FeO*	0.01	n.d.	n.d.
MnO	0.002	0.002	0.002
MgO	0.002	0.001	n.d.
CaO	42	42	42
Na ₂ O	0.003	0.004	0.002
K ₂ O	0.001	n.d.	n.d.
P ₂ O ₅	0.07	0.07	0.05
S	144856	192470	194527
Sc	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.
Cu	0.74	n.d.	n.d.
Zn	n.d.	n.d.	n.d.
Rb	n.d.	n.d.	n.d.
Sr	2177	2216	2196
Y	29.5	36.1	32.0
Zr	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.
Ba	51.4	52.1	57.9
Pb	1.33	4.08	3.12
Th	0.37	0.30	0.37
U	n.d.	n.d.	n.d.
La	241	195	168
Ce	422	376	306
Pr	45	42	36
n.d.	146	151	135
Sm	21	22	18
Eu	4	4	4
Gd	13	14	10
Tb	1	1	1
Dy	7	7	7
Ho	1	1	1
Er	2	3	2
Yb	1	n.d.	2

n.d. = not detected

Table E- 3. ETH LA-ICP-MS data of plagioclase reduced using SILLS (major elements in wt.%, trace elements in ppm). SiO₂ = 58 or 59 wt.%, and total oxides = 100% were used as an internal standard dependent on material.

	CN6791-d	CN6791-d	CN6791-d	P-22892- 2a	P-22892- 2a	PH12C-1	PH12C-1
	plag1	plag2	plag3	plag xls1	plag xls2	plag1 pt1	plag1 pt2
SiO ₂	58	58	58	61.19	63.72	59	59
TiO ₂	0.004	0.004	0.004	0.12	0.17	0.004	0.004
Al ₂ O ₃	20.7	22.3	21.0	18.9	20.1	22.4	22.4
FeO*	0.13	0.13	0.13	1.20	1.42	0.12	0.14
MnO	0.002	0.003	0.003	0.09	0.10	0.003	0.004
MgO	0.01	0.01	0.01	0.28	0.34	0.01	0.01
CaO	5.60	6.48	5.56	8.59	5.94	6.40	6.73
Na ₂ O	6.71	6.76	6.82	5.06	5.07	6.71	6.74
K ₂ O	0.31	0.30	0.35	2.51	2.84	0.31	0.31
P ₂ O ₅	0.01	0.01	0.01	2.08	0.29	0.01	0.01
S	578	382	421	946	492	439	357
Sc	0.37	0.54	0.50	1.03	1.73	0.96	0.70
Cr	n.d.	n.d.	n.d.	11.6	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	4.02	6.81	9.51	44.5	27.2	0.62	0.59
Zn	3.48	5.06	3.50	46.2	57.5	3.41	3.19
Rb	0.34	0.29	0.28	89.8	107	0.29	0.47
Sr	884	983	927	1074	984	1046	1020
Y	0.05	0.09	0.08	14.7	11.5	0.12	0.07
Zr	n.d.	n.d.	n.d.	92.8	124	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	3.03	3.97	n.d.	n.d.
Ba	200	182	197	575	678	190	204
Pb	8.54	9.17	8.94	21.6	39.4	9.23	8.83
Th	n.d.	n.d.	n.d.	10.7	13.2	n.d.	n.d.
U	n.d.	n.d.	n.d.	3.70	3.48	n.d.	n.d.
La	5	6	6	50	40	7	7
Ce	6	7	8	103	75	8	9
Pr	0.5	1	1	12	7	1	1
n.d.	2	1	1	41	26	2	1
Sm	0.2	n.d.	n.d.	7	5	0.2	n.d.
Eu	1	1	1	2	1	1	1
Gd	n.d.	n.d.	n.d.	5	3	n.d.	n.d.
Tb	n.d.	n.d.	n.d.	0.4	1	n.d.	n.d.
Dy	n.d.	n.d.	n.d.	2	2	n.d.	n.d.
Ho	n.d.	n.d.	n.d.	0.5	0.4	n.d.	n.d.
Er	n.d.	n.d.	n.d.	1	2	n.d.	n.d.
Yb	n.d.	n.d.	n.d.	1	1	n.d.	n.d.

n.d. = not detected

Table E-3. Continued.

	PH12C-2 plag of ap1	PH12C-2 plag of ap1	PH12C-2 plag of ap2	PH12C-4 plag of ap2	PH12C-5 plag of ap3	PH12C-7 plag1	PH12C-7 plag2
SiO ₂	59	59	59	59	59	59	59
TiO ₂	0.005	0.003	0.01	0.004	0.01	0.01	0.005
Al ₂ O ₃	22.8	23.5	25.1	22.2	23.0	23.1	22.3
FeO*	0.12	0.12	0.15	0.13	0.15	0.13	0.13
MnO	0.003	0.003	0.003	0.003	0.003	0.003	0.003
MgO	0.004	0.01	0.01	0.01	0.01	0.01	0.01
CaO	5.86	6.28	7.10	6.21	6.82	6.45	5.95
Na ₂ O	8.15	7.69	7.63	6.87	6.89	6.89	7.08
K ₂ O	0.36	0.37	0.32	0.31	0.29	0.31	0.31
P ₂ O ₅	n.d.	0.12	0.01	0.03	0.01	0.01	0.01
S	462	305	440	236	294	444	340
Sc	n.d.	0.97	1.04	0.29	0.69	0.47	0.55
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	1.74	0.74	0.74	1.16	1.01	1.90	1.02
Zn	4.27	3.10	2.37	3.17	3.46	4.02	2.74
Rb	0.25	0.28	0.36	0.41	0.21	0.46	0.40
Sr	872	858	1054	990	1052	1111	975
Y	n.d.	0.11	0.05	0.08	n.d.	0.08	0.12
Zr	n.d.	n.d.	n.d.	n.d.	0.13	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	184	215	223	188	189	212	195
Pb	8.51	10.9	8.08	9.13	6.84	8.38	8.73
Th	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
U	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
La	6	7	7	7	5	7	6
Ce	7	14	8	9	7	9	8
Pr	1	1	1	1	0.5	1	1
n.d.	1	2	1	2	1	2	1
Sm	n.d.	0.2	n.d.	n.d.	n.d.	0.2	n.d.
Eu	0.3	1	1	1	1	1	0.5
Gd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dy	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ho	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Er	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Yb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

Table E-3. Continued.

	PH12C-7 plag ctr	PH12C-7 plag rim	PH12C-7 host of ap19	PH12C-7 F2 pt1	PH12C-7 F2 pt2
SiO ₂	59	59	59	59	59
TiO ₂	0.004	0.01	0.01	0.01	0.004
Al ₂ O ₃	23.1	22.8	23.8	24.3	22.7
FeO*	0.12	0.14	0.12	0.12	0.12
MnO	0.003	0.003	0.004	0.003	0.003
MgO	0.005	0.01	0.01	0.01	0.01
CaO	5.95	5.91	5.81	5.92	5.48
Na ₂ O	6.78	6.84	7.08	7.08	7.11
K ₂ O	0.27	0.28	0.25	0.26	0.27
P ₂ O ₅	0.01	0.01	0.01	0.01	0.01
S	230	227	299	226	459
Sc	0.82	0.88	0.44	0.43	0.46
Cr	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	n.d.	n.d.	2.19	0.87	1.00
Zn	3.49	3.32	2.98	2.54	2.97
Rb	0.34	0.24	0.22	0.31	0.29
Sr	876	967	1008	1093	1054
Y	0.09	0.10	0.11	0.08	0.09
Zr	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	158	205	183	233	213
Pb	7.78	6.61	7.32	6.51	6.43
Th	n.d.	n.d.	n.d.	n.d.	n.d.
U	n.d.	n.d.	n.d.	n.d.	n.d.
La	5	5	6	7	5
Ce	7	7	8	9	7
Pr	1	0.5	1	1	0.5
n.d.	1	1	1	2	2
Sm	n.d.	n.d.	n.d.	n.d.	n.d.
Eu	0.5	1	1	1	0.5
Gd	n.d.	n.d.	n.d.	n.d.	n.d.
Tb	n.d.	n.d.	n.d.	n.d.	n.d.
Dy	n.d.	n.d.	n.d.	n.d.	n.d.
Ho	n.d.	n.d.	n.d.	n.d.	n.d.
Er	n.d.	n.d.	n.d.	n.d.	n.d.
Yb	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

Table E- 4. ETH LA-ICP-MS data of hornblende reduced using SILLS (major elements in wt.%, trace elements in ppm). SiO₂ = 41, 42, 44, or 48 wt.% were used as an internal standard dependent on material.

	CN6791-d	CN6791-d	CN6791-d	P-22892- 2a	P-22892- 2a	P-22892- 2a	P-22892- 2a
	hb1	hb of ap5&6	hb2	hb1	hb2	hb of ap1	hb of ap11
SiO ₂	42	44	42	41	41	44	44
TiO ₂	1.62	0.79	0.59	1.06	1.53	0.88	1.07
Al ₂ O ₃	11.4	7.10	5.64	9.51	11.3	7.82	10.9
FeO*	9.92	11.2	9.95	8.78	9.95	8.67	9.62
MnO	0.13	0.47	0.45	0.14	0.13	0.24	0.16
MgO	13.1	12.2	12.0	12.7	12.8	13.2	14.0
CaO	10.4	9.39	8.06	11.8	10.6	12.6	11.1
Na ₂ O	2.42	1.60	1.18	1.89	2.35	1.80	2.44
K ₂ O	0.93	0.35	0.21	0.64	0.91	0.66	0.82
P ₂ O ₅	0.02	0.01	0.01	0.02	0.03	0.02	0.04
S	428	247	227	257	344	337	334
Sc	53.1	71.0	45.7	44.5	62.5	63.6	42.7
Cr	116	83.4	44.0	221	111	94.8	52.3
Ni	148	56.8	76.7	199	158	117	205
Cu	12.0	6.76	18.1	12.4	2.78	31.2	12.9
Zn	59.5	244	207	53.1	65.7	77.0	61.1
Rb	5.09	0.88	0.52	3.25	5.56	7.89	4.85
Sr	271	29.5	25.1	223	309	166	263
Y	19.1	68.8	50.6	18.1	19.5	41.9	19.1
Zr	38.9	26.3	33.8	37.9	40.4	27.8	53.5
Nb	1.19	4.42	3.10	0.95	1.49	1.96	1.46
Ba	105	19.2	15.3	72.8	118	77.7	94.4
Pb	1.68	1.63	1.52	1.13	1.43	2.30	3.37
Th	0.16	0.14	0.15	0.19	0.13	0.43	0.28
U	0.02	0.04	0.05	0.03	0.02	0.11	0.06
La	5	11	8	5	5	6	6
Ce	19	55	37	18	20	24	22
Pr	3	10	7	3	3	5	4
n.d.	20	52	37	20	21	28	19
Sm	6	13	10	6	6	8	6
Eu	2	3	2	2	2	2	2
Gd	6	14	9	5	6	9	6
Tb	1	2	1	1	1	1	1
Dy	4	13	10	4	4	8	4
Ho	1	3	2	1	1	2	1
Er	2	8	5	2	2	4	2
Yb	1	5	5	1	1	4	2

Table E-4. Continued.

	P-22892- 2a	PH12C-1	PH12C-2	PH12C-7	PH12C-7
	hb3	hb1	hb1	hb1	ap8 host hb
SiO ₂	41	48	48	48	48
TiO ₂	1.64	0.76	0.81	0.77	0.63
Al ₂ O ₃	11.9	6.33	7.21	7.50	6.00
FeO*	10.5	11.1	12.0	12.4	10.5
MnO	0.13	0.40	0.47	0.58	0.49
MgO	12.2	14.1	14.1	12.9	13.2
CaO	10.5	9.73	10.3	10.0	8.67
Na ₂ O	2.36	1.36	1.35	1.57	1.19
K ₂ O	0.95	0.23	0.29	0.38	0.20
P ₂ O ₅	0.03	0.01	0.01	0.01	0.01
S	260	182	287	231	261
Sc	50.1	60.1	60.2	70.4	45.3
Cr	11.1	66.0	101	116	118
Ni	104	111	89.4	74.0	59.2
Cu	2.27	1.57	0.90	1.19	6.08
Zn	61.2	225	257	256	236
Rb	4.98	0.52	1.10	0.94	0.44
Sr	298	28.3	31.8	30.0	23.4
Y	19.8	63.4	62.2	75.5	55.5
Zr	44.5	31.0	35.4	28.6	24.5
Nb	1.15	3.92	3.81	4.73	3.34
Ba	122	19.6	25.5	24.2	14.4
Pb	1.41	1.09	5.13	1.82	1.22
Th	0.13	0.12	0.13	0.20	n.d.
U	n.d.	0.04	0.04	0.03	n.d.
La	5	9	10	14	9
Ce	20	44	45	60	43
Pr	4	8	9	11	8
n.d.	21	45	44	57	41
Sm	6	13	15	16	13
Eu	2	3	3	3	2
Gd	6	12	13	15	11
Tb	1	2	2	2	2
Dy	4	12	11	15	11
Ho	1	2	2	3	2
Er	2	7	7	8	5
Yb	2	6	7	8	6

Table E- 5. ETH LA-ICP-MS data of matrix glass reduced using SILLS (major elements in wt.%, trace elements in ppm). Total oxides = 100 wt.% was used as an internal standard.

	CN6791-d	CN6791-d	CN6791-d	P-22892- 2a	PH12C-3b	PH12C-6	PH12C-7
	matrix glass1	matrix glass2	matrix glass3	matrix glass1	glass near ap13	glass near apl	matrix glass1
SiO ₂	60.1	67.9	65.0	72.5	74.4	72.4	78.1
TiO ₂	0.96	0.33	0.27	0.17	0.04	0.06	0.10
Al ₂ O ₃	14.4	15.6	18.7	14.3	5.76	2.85	12.4
FeO*	5.74	2.66	2.11	1.69	0.26	0.73	0.70
MnO	0.11	0.09	0.07	0.16	0.01	0.04	0.03
MgO	6.20	1.89	1.57	0.41	2.60	4.02	0.26
CaO	6.69	4.54	5.34	0.83	4.45	6.47	1.22
Na ₂ O	3.69	4.29	4.54	4.25	10.7	12.20	4.13
K ₂ O	1.95	2.48	2.29	5.61	1.71	1.19	3.01
P ₂ O ₅	0.17	0.19	0.14	0.09	0.03	0.02	0.03
S	381	319	376	n.d.	1038	5150	439
Sc	28.4	6.70	5.05	2.53	n.d.	3.86	1.30
Cr	20.3	8.02	8.54	n.d.	39.5	5.50	7.59
Ni	66.0	5.51	5.01	n.d.	n.d.	5.63	n.d.
Cu	23.0	29.0	19.2	6.01	90.3	34.0	54.6
Zn	64.9	58.9	42.5	96.4	7.55	14.4	39.6
Rb	56.8	81.9	73.6	223	52.2	35.3	94.5
Sr	437	507	728	63.0	108	76.9	178
Y	16.7	11.5	9.70	9.55	2.13	5.30	4.30
Zr	83.0	95.2	92.5	181	92.3	99.9	55.2
Nb	3.29	3.85	3.54	6.43	1.54	0.81	3.89
Ba	493	594	585	821	370	253	730
Pb	11.8	15.8	13.8	24.6	134	94.4	4184
Th	6.07	9.03	8.03	16.9	2.23	1.11	8.22
U	1.81	2.73	2.30	7.49	1.13	0.55	2.62
La	18	24	21	39	5	6	15
Ce	39	47	41	80	10	13	24
Pr	5	5	4	7	1	1	2
n.d.	22	19	16	21	4	6	8
Sm	5	4	4	3	n.d.	1	1
Eu	1	1	1	1	1	0.3	0.2
Gd	4	3	2	2	n.d.	1	1
Tb	1	0.4	0.3	n.d.	n.d.	0.1	0.1
Dy	3	2	2	1	1	1	1
Ho	1	0.4	0.3	0.4	n.d.	0.2	0.1
Er	2	1	1	1	n.d.	1	0.3
Yb	2	1	1	n.d.	n.d.	1	1

n.d. = not detected

Table E-5. Continued.

	PH12C-7 matrix glass
SiO ₂	77.1
TiO ₂	0.10
Al ₂ O ₃	13.4
FeO*	0.72
MnO	0.04
MgO	0.35
CaO	1.20
Na ₂ O	4.33
K ₂ O	2.71
P ₂ O ₅	0.03
S	n.d.
Sc	n.d.
Cr	n.d.
Ni	n.d.
Cu	44.4
Zn	37.4
Rb	93.6
Sr	185
Y	4.07
Zr	63.1
Nb	2.90
Ba	811
Pb	9011
Th	5.53
U	2.82
La	17
Ce	24
Pr	3
n.d.	10
Sm	3
Eu	n.d.
Gd	n.d.
Tb	0.3
Dy	n.d.
Ho	n.d.
Er	n.d.
Yb	n.d.

n.d. = not detected

Table E-6. ETH LA-ICP-MS Durango Apatite error summary (1 σ) and detection limits (ppm).

ETH - August 3, 2010 - Durango						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.01	0.01	0.01	131	80.9	106
TiO ₂	0.00003	0.00003	0.00003	0.83	0.23	0.53
Al ₂ O ₃	0.00003	0.00003	0.00003	0.53	0.21	0.35
FeO*	0.002	0.001	0.001	6.68	4.27	5.56
MnO	0.0001	0.0001	0.0001	0.32	0.19	0.28
MgO	0.001	0.0004	0.001	0.52	0.26	0.37
CaO	0.09	0.061	0.1	81.4	40.4	59.6
Na ₂ O	0.0005	0.0003	0.0004	0.60	0.36	0.46
K ₂ O	0.0001	0.00004	0.0001	2.04	0.84	1.52
P ₂ O ₅	0.023	0.02	0.02	4.11	2.37	3.31
S	13.5	7.04	10.8	40.2	18.0	29.4
Sc	0.05	0.02	0.03	0.12	0.04	0.08
Cr	0.76	0.76	0.76	2.95	1.43	2.13
Ni	0.70	0.70	0.70	1.72	0.91	1.21
Cu	0.12	0.09	0.11	0.29	0.12	0.17
Zn	0.17	0.10	0.13	0.34	0.13	0.22
Rb	0.02	0.01	0.02	0.03	0.01	0.02
Sr	1.47	1.00	1.21	0.03	0.01	0.02
Y	1.51	1.02	1.2	0.01	0.01	0.01
Zr	0.07	0.05	0.06	0.06	0.02	0.03
Nb	0.01	0.01	0.01	0.02	0.01	0.02
Ba	0.21	0.15	0.17	0.10	0.06	0.09
Pb	0.08	0.05	0.06	0.04	0.02	0.03
Th	1.11	0.66	0.83	0.01	0.01	0.01
U	0.24	0.14	0.18	0.02	0.01	0.01
La	3.55	2.50	2.87	0.02	0.01	0.01
Ce	3.95	2.88	3.25	0.01	0.01	0.01
Pr	0.98	0.67	0.81	0.01	0.01	0.01
n.d.	4.24	2.91	3.49	0.06	0.0	0.05
Sm	1.69	1.17	1.38	0.12	0.05	0.07
Eu	0.30	0.21	0.25	0.03	0.01	0.02
Gd	1.67	1.14	1.34	0.08	0.05	0.07
Tb	0.23	0.15	0.18	0.01	0.01	0.01
Dy	1.11	0.75	0.86	0.04	0.03	0.04
Ho	0.24	0.17	0.19	0.01	0.01	0.01
Er	0.87	0.59	0.67	0.05	0.03	0.05
Yb	0.87	0.59	0.68	0.09	0.05	0.07

n = 10

Table E-6. Continued

ETH - August 4, 2010 - Durango						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.01	0.01	0.01	95.9	66.1	79.1
TiO ₂	0.00003	0.00002	0.00003	0.69	0.19	0.44
Al ₂ O ₃	0.00002	0.00001	0.00002	0.34	0.18	0.25
FeO*	0.001	0.001	0.001	6.91	3.51	4.73
MnO	0.0001	0.0001	0.0001	0.32	0.16	0.24
MgO	0.001	0.0004	0.0005	0.39	0.22	0.31
CaO	0.08	0.06	0.07	69.0	36.0	50.4
Na ₂ O	0.0004	0.0003	0.0004	0.50	0.26	0.37
K ₂ O	0.0001	0.00004	0.0001	1.62	0.82	1.18
P ₂ O ₅	0.02	0.01	0.02	3.42	1.73	2.64
S	11.6	6.65	8.88	33.7	15.5	24.3
Sc	0.04	0.02	0.03	0.14	0.04	0.07
Cr	0.59	0.58	0.58	2.60	1.29	1.67
Ni	0.67	0.67	0.67	1.98	0.65	1.13
Cu	0.21	0.06	0.12	0.20	0.08	0.12
Zn	0.19	0.08	0.14	0.35	0.15	0.24
Rb	0.02	0.01	0.01	0.03	0.01	0.02
Sr	1.29	0.95	1.09	0.03	0.01	0.02
Y	1.29	0.98	1.12	0.02	0.01	0.01
Zr	0.06	0.04	0.05	0.03	0.02	0.02
Nb	0.01	0.01	0.01	0.02	0.01	0.01
Ba	0.20	0.14	0.16	0.09	0.05	0.07
Pb	0.08	0.05	0.06	0.03	0.01	0.02
Th	0.9	0.69	0.81	0.01	0.01	0.01
U	0.21	0.15	0.18	0.01	0.01	0.01
La	3.06	2.41	2.68	0.01	0.01	0.01
Ce	3.48	2.75	3.07	0.02	0.01	0.01
Pr	0.87	0.64	0.74	0.01	0.01	0.01
n.d.	3.76	2.75	3.19	0.08	0.03	0.05
Sm	1.50	1.09	1.28	0.11	0.04	0.06
Eu	0.26	0.20	0.23	0.02	0.01	0.02
Gd	1.48	1.10	1.27	0.07	0.04	0.06
Tb	0.19	0.15	0.17	0.02	0.01	0.01
Dy	0.93	0.70	0.81	0.06	0.02	0.04
Ho	0.21	0.16	0.18	0.01	0.01	0.01
Er	0.74	0.55	0.65	0.05	0.03	0.04
Yb	0.74	0.55	0.64	0.07	0.04	0.06

n = 10

Table E-7. ETH LA-ICP-MS anhydrite error summary (1 σ) and detection limits (ppm).

ETH - August 3, 2010 - Anhydrite						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.11	0.01	0.07	350	148	212
TiO ₂	0.001	0.0002	0.0004	2.53	0.43	1.30
Al ₂ O ₃	0.002	0.00011	0.001	0.88	0.34	0.60
FeO*	0.01	0.001	0.003	19.5	6.02	10.5
MnO	0.0005	0.0001	0.0002	0.98	0.29	0.55
MgO	0.01	0.0003	0.003	1.21	0.48	0.68
CaO	0.23	0.10	0.16	192	66.2	123
Na ₂ O	0.004	0.00005	0.001	1.89	0.66	1.04
K ₂ O	0.001	0.0007	0.001	5.01	1.70	2.97
P ₂ O ₅	0.03	0.001	0.01	9.92	4.37	6.22
S	236	93.9	163	105	32.3	58.7
Sc	0.12	0.11	0.11	0.24	0.09	0.16
Cr	2.74	2.74	2.7	6.37	2.76	4.29
Ni	4.50	2.27	3.39	3.88	1.55	2.60
Cu	3.95	2.81	3.50	0.45	0.19	0.32
Zn	2.17	0.20	0.93	0.74	0.26	0.38
Rb	0.41	0.24	0.33	0.09	0.02	0.05
Sr	9.5	3.13	5.79	0.05	0.02	0.04
Y	1.31	0.24	0.73	0.07	0.02	0.03
Zr	0.95	0.92	0.93	0.09	0.04	0.05
Nb	0.13	0.06	0.10	0.06	0.02	0.03
Ba	3.57	1.54	2.59	0.43	0.12	0.22
Pb	4.90	0.23	2.01	0.08	0.03	0.05
Th	0.29	0.12	0.19	0.05	0.02	0.03
U	0.17	0.06	0.11	0.04	0.02	0.03
La	2.62	0.13	1.59	0.05	0.02	0.03
Ce	3.70	0.24	2.26	0.06	0.02	0.03
Pr	1.09	0.08	0.65	0.05	0.01	0.02
n.d.	5.12	0.46	3.02	0.19	0.07	0.10
Sm	1.97	0.24	1.19	0.21	0.09	0.13
Eu	0.50	0.07	0.29	0.06	0.02	0.03
Gd	1.79	0.24	1.06	0.23	0.09	0.14
Tb	0.24	0.04	0.13	0.03	0.01	0.02
Dy	1.00	0.18	0.56	0.14	0.05	0.08
Ho	0.20	0.04	0.10	0.03	0.01	0.02
Er	0.73	0.09	0.37	0.16	0.06	0.09
Yb	0.77	0.13	0.35	0.23	0.09	0.14

n = 5

Table E-7. Continued.

ETH - August 4, 2010 - Anhydrite						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.04	0.04	0.04	598	235	371
TiO ₂	0.001	0.0002	0.0004	3.30	0.86	1.82
Al ₂ O ₃	0.0005	0.0001	0.0003	1.44	0.61	1.00
FeO*	0.003	0.001	0.002	33.4	11.1	18.1
MnO	0.0002	0.0001	0.0001	1.58	0.59	1.06
MgO	0.001	0.0003	0.001	1.77	0.72	1.21
CaO	0.33	0.11	0.22	383	149	216
Na ₂ O	0.001	0.0001	0.0002	2.56	0.89	1.61
K ₂ O	0.0004	0.0002	0.0003	7.56	3.59	5.18
P ₂ O ₅	0.01	0.002	0.003	15.6	5.95	11.2
S	345	114	217	157	65.6	103
Sc	0.30	0.30	0.30	0.40	0.16	0.27
Cr	n.d.	n.d.	n.d.	9.89	4.03	7.32
Ni	n.d.	n.d.	n.d.	6.02	1.91	4.01
Cu	1.35	0.29	0.72	1.14	0.31	0.59
Zn	2.23	1.11	1.67	1.99	0.44	0.94
Rb	0.25	0.21	0.23	0.11	0.05	0.08
Sr	12.9	4.40	8.48	0.10	0.03	0.05
Y	1.57	0.38	0.93	0.06	0.02	0.05
Zr	0.16	0.13	0.15	0.20	0.05	0.10
Nb	0.10	0.10	0.10	0.08	0.03	0.05
Ba	4.70	1.46	3.03	0.62	0.18	0.35
Pb	7.28	0.13	1.90	0.11	0.05	0.08
Th	0.24	0.06	0.12	0.07	0.03	0.04
U	0.16	0.16	0.16	0.06	0.02	0.04
La	4.34	0.59	2.57	0.08	0.02	0.04
Ce	5.73	0.84	3.44	0.06	0.02	0.04
Pr	1.62	0.24	0.98	0.07	0.02	0.03
n.d.	7.75	1.41	4.59	0.27	0.11	0.20
Sm	2.75	0.62	1.70	0.32	0.13	0.22
Eu	0.59	0.22	0.41	0.09	0.04	0.06
Gd	2.14	0.49	1.38	0.34	0.14	0.24
Tb	0.26	0.06	0.16	0.07	0.02	0.04
Dy	1.23	0.26	0.76	0.20	0.09	0.14
Ho	0.23	0.04	0.15	0.06	0.02	0.04
Er	0.97	0.23	0.49	0.23	0.10	0.16
Yb	0.70	0.15	0.37	0.34	0.15	0.23

n = 10

n.d. = not detected

Table E-7. Continued.

ETH - March 16, 2011 - Anhydrite						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	n.d.	n.d.	n.d.	2519	1795	2157
TiO ₂	0.001	0.0008	0.0008	12.8	6.96	9.86
Al ₂ O ₃	0.001	0.001	0.001	14.3	12.2	13.2
FeO*	n.d.	n.d.	n.d.	113	97.6	106
MnO	0.0004	0.0003	0.0003	6.54	6.26	6.40
MgO	0.001	0.0008	0.001	7.26	6.82	7.04
CaO	0.32	0.31	0.31	986	655	820
Na ₂ O	0.0003	0.0003	0.0003	4.70	4.34	4.52
K ₂ O	n.d.	n.d.	n.d.	18.7	17.7	18.2
P ₂ O ₅	0.01	0.006	0.006	67.5	59.79	63.6
S	352	341	347	416	344.6	380
Sc	n.d.	n.d.	n.d.	3.79	3.13	3.46
Cr	n.d.	n.d.	n.d.	65.98	57.95	61.97
Ni	n.d.	n.d.	n.d.	31.78	24.06	27.92
Cu	n.d.	n.d.	n.d.	5.03	3.40	4.22
Zn	n.d.	n.d.	n.d.	5.97	5.23	5.60
Rb	n.d.	n.d.	n.d.	0.45	0.42	0.44
Sr	14.4	13.9	14.1	0.48	0.37	0.43
Y	1.77	1.74	1.75	0.28	0.27	0.27
Zr	n.d.	n.d.	n.d.	0.60	0.56	0.58
Nb	n.d.	n.d.	n.d.	0.46	0.35	0.40
Ba	5.21	4.73	4.97	1.40	1.31	1.36
Pb	0.73	0.67	0.70	0.65	0.62	0.63
Th	0.19	0.16	0.17	0.25	0.23	0.24
U	n.d.	n.d.	n.d.	0.22	0.21	0.21
La	3.37	3.28	3.33	0.19	0.18	0.19
Ce	4.61	4.35	4.48	0.26	0.17	0.22
Pr	1.36	1.32	1.34	0.14	0.13	0.14
n.d.	6.13	6.07	6.10	0.82	0.77	0.79
Sm	2.53	2.40	2.46	0.95	0.89	0.92
Eu	0.60	0.58	0.59	0.27	0.25	0.26
Gd	2.11	1.89	2.00	1.03	0.97	1.00
Tb	0.22	0.21	0.21	0.14	0.13	0.14
Dy	1.17	1.14	1.15	0.60	0.56	0.58
Ho	0.24	0.21	0.22	0.15	0.14	0.15
Er	0.78	0.74	0.76	0.69	0.65	0.67
Yb	0.80	0.80	0.80	1.03	0.97	1.00

n = 2

n.d. = not detected

Table E-8. ETH LA-ICP-MS plagioclase error summary (1 σ) and detection limits (ppm).

ETH - August 3, 2010 - Plagioclase						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.24	0.12	0.16	348	196	288
TiO ₂	0.004	0.0003	0.001	3.23	0.81	1.69
Al ₂ O ₃	0.02	0.01	0.01	1.19	0.48	0.81
FeO*	0.02	0.003	0.006	19.6	10.9	14.6
MnO	0.0007	0.0001	0.0002	1.11	0.49	0.75
MgO	0.006	0.0004	0.001	1.25	0.75	0.92
CaO	0.07	0.04	0.05	200	113	144
Na ₂ O	0.006	0.003	0.004	1.70	1.00	1.32
K ₂ O	0.004	0.0007	0.001	4.58	2.54	3.49
P ₂ O ₅	0.01	0.001	0.002	11.7	6.48	8.29
S	37.2	18.4	23.9	119	50.3	72.8
Sc	0.23	0.08	0.12	0.27	0.13	0.19
Cr	3.26	3.26	3.26	8.22	4.23	5.71
Ni	n.d.	n.d.	n.d.	4.33	2.46	3.37
Cu	2.70	0.24	0.90	0.68	0.28	0.46
Zn	3.62	0.45	1.08	0.78	0.40	0.52
Rb	1.69	0.05	0.35	0.09	0.03	0.06
Sr	4.76	2.50	3.18	0.07	0.03	0.04
Y	0.50	0.02	0.12	0.06	0.03	0.04
Zr	2.37	1.75	2.06	0.10	0.06	0.07
Nb	0.33	0.25	0.29	0.06	0.03	0.05
Ba	9.92	2.71	4.35	0.32	0.19	0.23
Pb	1.24	0.30	0.48	0.09	0.05	0.07
Th	0.54	0.42	0.48	0.05	0.03	0.04
U	0.27	0.24	0.25	0.04	0.03	0.03
La	0.87	0.18	0.34	0.05	0.02	0.03
Ce	1.20	0.20	0.43	0.05	0.02	0.03
Pr	0.37	0.05	0.12	0.06	0.02	0.03
n.d.	1.62	0.18	0.49	0.19	0.11	0.15
Sm	0.75	0.08	0.34	0.23	0.13	0.16
Eu	0.23	0.07	0.11	0.07	0.04	0.05
Gd	0.65	0.53	0.59	0.24	0.14	0.17
Tb	0.09	0.07	0.08	0.03	0.02	0.03
Dy	0.38	0.32	0.35	0.19	0.08	0.12
Ho	0.08	0.08	0.08	0.04	0.02	0.03
Er	0.35	0.27	0.31	0.16	0.10	0.12
Yb	0.35	0.27	0.31	0.24	0.14	0.17

n = 10

Table E-8. Continued.

ETH - August 4, 2010 - Plagioclase						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.28	0.20	0.24	892	315	481
TiO ₂	0.0008	0.001	0.001	4.36	1.67	2.47
Al ₂ O ₃	0.02	0.02	0.02	3.41	0.86	1.61
FeO*	0.007	0.01	0.006	50.9	17.7	28.0
MnO	0.0002	0.0001	0.0001	2.02	0.88	1.22
MgO	0.0009	0.001	0.001	2.43	1.02	1.60
CaO	0.09	0.06	0.07	638	199	330
Na ₂ O	0.009	0.006	0.007	2.42	1.28	1.74
K ₂ O	0.0020	0.001	0.002	14.5	4.82	8.12
P ₂ O ₅	0.004	0.00	0.002	25.3	9.01	14.5
S	91.1	29.1	48.7	284	84.3	153.0
Sc	0.23	0.16	0.19	1.09	0.20	0.51
Cr	n.d.	n.d.	n.d.	15.72	5.95	8.58
Ni	n.d.	n.d.	n.d.	5.93	2.66	3.90
Cu	0.67	0.38	0.50	0.80	0.50	0.65
Zn	1.19	0.68	0.91	1.58	0.78	1.09
Rb	0.11	0.07	0.09	0.16	0.04	0.09
Sr	5.06	4.07	4.63	0.08	0.04	0.05
Y	0.05	0.03	0.04	0.13	0.03	0.07
Zr	0.08	0.08	0.08	0.16	0.07	0.10
Nb	n.d.	n.d.	n.d.	0.09	0.04	0.06
Ba	6.29	5.00	5.65	0.83	0.25	0.42
Pb	0.72	0.49	0.60	0.16	0.08	0.10
Th	n.d.	n.d.	n.d.	0.08	0.04	0.05
U	n.d.	n.d.	n.d.	0.08	0.03	0.05
La	0.39	0.30	0.35	0.07	0.03	0.05
Ce	0.56	0.34	0.43	0.13	0.03	0.07
Pr	0.14	0.08	0.11	0.06	0.03	0.04
n.d.	0.51	0.28	0.39	0.54	0.16	0.27
Sm	0.19	0.19	0.19	0.46	0.19	0.27
Eu	0.19	0.12	0.15	0.14	0.06	0.08
Gd	n.d.	n.d.	n.d.	0.49	0.20	0.29
Tb	n.d.	n.d.	n.d.	0.07	0.03	0.04
Dy	n.d.	n.d.	n.d.	0.31	0.13	0.18
Ho	n.d.	n.d.	n.d.	0.08	0.03	0.05
Er	n.d.	n.d.	n.d.	0.36	0.15	0.21
Yb	n.d.	n.d.	n.d.	0.53	0.22	0.31

n = 4

n.d. = not detected

Table E-8. Continued.

ETH - March 16, 2011 - Plagioclase						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.20	0.12	0.15	379	182	292
TiO ₂	0.0007	0.0004	0.0005	2.33	0.82	1.80
Al ₂ O ₃	0.02	0.01	0.01	2.91	0.89	2.07
FeO*	0.005	0.003	0.004	23.4	9.26	17.0
MnO	0.0001	0.0001	0.0001	1.58	0.68	1.11
MgO	0.0006	0.0004	0.001	1.91	0.86	1.45
CaO	0.05	0.03	0.04	196	92.2	156
Na ₂ O	0.005	0.003	0.004	1.17	0.55	0.81
K ₂ O	0.0009	0.001	0.001	4.95	1.69	3.21
P ₂ O ₅	0.002	0.001	0.001	15.2	7.33	11.5
S	31.6	14.2	21.4	94.3	44.4	68.4
Sc	0.25	0.10	0.18	0.71	0.22	0.45
Cr	n.d.	n.d.	n.d.	19.0	7.14	12.4
Ni	n.d.	n.d.	n.d.	6.26	2.81	4.49
Cu	0.69	0.30	0.47	1.30	0.59	0.92
Zn	0.79	0.49	0.63	1.35	0.97	1.10
Rb	0.08	0.05	0.07	0.16	0.04	0.09
Sr	4.10	2.63	3.22	0.08	0.03	0.06
Y	0.05	0.02	0.03	0.08	0.03	0.05
Zr	n.d.	n.d.	n.d.	0.16	0.07	0.11
Nb	n.d.	n.d.	n.d.	0.09	0.04	0.06
Ba	3.88	2.68	3.15	0.52	0.17	0.27
Pb	0.40	0.23	0.31	0.17	0.07	0.10
Th	n.d.	n.d.	n.d.	0.06	0.03	0.04
U	n.d.	n.d.	n.d.	0.06	0.03	0.04
La	0.26	0.17	0.20	0.05	0.02	0.04
Ce	0.28	0.19	0.22	0.05	0.02	0.03
Pr	0.07	0.04	0.05	0.04	0.02	0.03
n.d.	0.22	0.18	0.20	0.21	0.10	0.14
Sm	n.d.	n.d.	n.d.	0.25	0.11	0.17
Eu	0.09	0.06	0.07	0.07	0.03	0.05
Gd	n.d.	n.d.	n.d.	0.27	0.12	0.18
Tb	n.d.	n.d.	n.d.	0.04	0.02	0.02
Dy	n.d.	n.d.	n.d.	0.16	0.07	0.10
Ho	n.d.	n.d.	n.d.	0.04	0.02	0.03
Er	n.d.	n.d.	n.d.	0.18	0.08	0.12
Yb	n.d.	n.d.	n.d.	0.27	0.12	0.18

n = 5

n.d. = not detected

Table E-9. ETH LA-ICP-MS hornblende error summary (1 σ) and detection limits (ppm).

ETH - August 3, 2010 - Hornblende						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.15	0.08	0.10	223	133	174
TiO ₂	0.006	0.003	0.005	1.13	0.44	0.80
Al ₂ O ₃	0.01	0.00	0.01	0.69	0.40	0.53
FeO*	0.04	0.02	0.03	14.0	7.69	9.2
MnO	0.001	0.0004	0.0006	0.65	0.36	0.47
MgO	0.03	0.01	0.02	0.86	0.43	0.59
CaO	0.06	0.03	0.05	100	70.3	87.9
Na ₂ O	0.002	0.001	0.002	1.16	0.59	0.82
K ₂ O	0.001	0.000	0.001	3.02	1.96	2.34
P ₂ O ₅	0.001	0.000	0.001	6.19	4.21	5.21
S	16.0	10.8	13.5	48.1	27.9	40.3
Sc	1.06	0.50	0.66	0.17	0.10	0.12
Cr	6.34	1.86	3.98	4.74	2.47	3.60
Ni	11.0	5.54	7.79	3.17	1.61	2.41
Cu	1.60	0.22	0.73	0.65	0.15	0.27
Zn	5.29	1.71	2.60	0.63	0.22	0.36
Rb	0.27	0.04	0.14	0.06	0.02	0.04
Sr	1.35	0.30	0.90	0.03	0.02	0.02
Y	0.89	0.30	0.46	0.03	0.02	0.02
Zr	0.86	0.44	0.65	0.05	0.03	0.04
Nb	0.25	0.08	0.13	0.06	0.02	0.03
Ba	2.05	0.64	1.51	0.18	0.10	0.14
Pb	0.20	0.08	0.13	0.05	0.03	0.04
Th	0.06	0.02	0.03	0.04	0.02	0.02
U	0.03	0.01	0.02	0.02	0.01	0.02
La	0.33	0.14	0.19	0.03	0.01	0.02
Ce	0.76	0.28	0.40	0.02	0.01	0.02
Pr	0.29	0.11	0.15	0.02	0.01	0.02
n.d.	1.59	0.63	0.85	0.11	0.06	0.09
Sm	0.86	0.37	0.49	0.18	0.07	0.11
Eu	0.23	0.10	0.13	0.04	0.02	0.03
Gd	0.92	0.37	0.50	0.13	0.08	0.11
Tb	0.13	0.05	0.07	0.02	0.01	0.02
Dy	0.67	0.25	0.36	0.08	0.05	0.06
Ho	0.15	0.05	0.08	0.02	0.01	0.02
Er	0.56	0.19	0.28	0.10	0.05	0.08
Yb	0.56	0.19	0.31	0.13	0.08	0.11

n = 10

Table E-9. Continued.

ETH - August 4, 2010 - Hornblende						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.15	0.15	0.15	141	141	141
TiO ₂	0.006	0.006	0.006	0.90	0.90	0.90
Al ₂ O ₃	0.01	0.01	0.01	0.53	0.53	0.53
FeO*	0.04	0.04	0.04	14.1	14.1	14.1
MnO	0.001	0.001	0.001	0.52	0.52	0.52
MgO	0.03	0.03	0.03	0.53	0.53	0.53
CaO	0.06	0.06	0.06	103	103	103
Na ₂ O	0.002	0.002	0.002	0.53	0.53	0.53
K ₂ O	0.001	0.001	0.001	2.46	2.46	2.46
P ₂ O ₅	0.001	0.001	0.001	4.16	4.16	4.16
S	14.7	14.7	14.7	47.9	47.9	47.9
Sc	0.96	0.96	0.96	0.11	0.11	0.11
Cr	5.74	5.74	5.74	3.12	3.12	3.12
Ni	9.2	9.22	9.22	1.62	1.62	1.62
Cu	0.33	0.33	0.33	0.32	0.32	0.32
Zn	5.33	5.33	5.33	0.26	0.26	0.26
Rb	0.12	0.12	0.12	0.04	0.04	0.04
Sr	0.61	0.61	0.61	0.03	0.03	0.03
Y	0.83	0.83	0.83	0.02	0.02	0.02
Zr	0.90	0.90	0.90	0.04	0.04	0.04
Nb	0.23	0.23	0.23	0.02	0.02	0.02
Ba	1.40	1.40	1.40	0.13	0.13	0.13
Pb	0.32	0.32	0.32	0.03	0.03	0.03
Th	0.04	0.04	0.04	0.02	0.02	0.02
U	0.02	0.02	0.02	0.02	0.02	0.02
La	0.31	0.31	0.31	0.02	0.02	0.02
Ce	0.68	0.68	0.68	0.02	0.02	0.02
Pr	0.26	0.26	0.26	0.01	0.01	0.01
n.d.	1.44	1.44	1.44	0.14	0.14	0.14
Sm	0.91	0.91	0.91	0.09	0.09	0.09
Eu	0.21	0.21	0.21	0.03	0.03	0.03
Gd	0.87	0.87	0.87	0.10	0.10	0.10
Tb	0.14	0.14	0.14	0.01	0.01	0.01
Dy	0.62	0.62	0.62	0.06	0.06	0.06
Ho	0.14	0.14	0.14	0.02	0.02	0.02
Er	0.54	0.54	0.54	0.07	0.07	0.07
Yb	0.66	0.66	0.66	0.10	0.10	0.10

n = 1

Table E-9. Continued.

ETH - March 16, 2011 - Hornblende						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.22	0.22	0.22	744	744	744
TiO ₂	0.008	0.008	0.008	6.57	6.57	6.57
Al ₂ O ₃	0.01	0.01	0.01	3.94	3.94	3.94
FeO*	0.05	0.05	0.05	32.2	32.2	32.2
MnO	0.002	0.002	0.002	2.64	2.64	2.64
MgO	0.04	0.04	0.04	2.86	2.86	2.86
CaO	0.08	0.08	0.08	319	319	319
Na ₂ O	0.003	0.003	0.003	1.61	1.61	1.61
K ₂ O	0.001	0.001	0.001	9.37	9.37	9.37
P ₂ O ₅	0.002	0.002	0.002	23.2	23.2	23.2
S	40.3	40.3	40.3	107	107	107
Sc	1.36	1.36	1.36	1.02	1.02	1.02
Cr	13.2	13.2	13.2	27.4	27.4	27.4
Ni	12.1	12.1	12.1	9.77	9.77	9.77
Cu	1.53	1.53	1.53	2.65	2.65	2.65
Zn	7.20	7.20	7.20	2.35	2.35	2.35
Rb	0.12	0.12	0.12	0.13	0.13	0.13
Sr	0.77	0.77	0.77	0.11	0.11	0.11
Y	1.19	1.19	1.19	0.15	0.15	0.15
Zr	1.15	1.15	1.15	0.23	0.23	0.23
Nb	0.33	0.33	0.33	0.14	0.14	0.14
Ba	1.36	1.36	1.36	0.54	0.54	0.54
Pb	0.23	0.23	0.23	0.22	0.22	0.22
Th	n.d.	n.d.	n.d.	0.10	0.10	0.10
U	n.d.	n.d.	n.d.	0.09	0.09	0.09
La	0.40	0.40	0.40	0.08	0.08	0.08
Ce	0.85	0.85	0.85	0.07	0.07	0.07
Pr	0.32	0.32	0.32	0.06	0.06	0.06
n.d.	1.76	1.76	1.76	0.32	0.32	0.32
Sm	1.06	1.06	1.06	0.37	0.37	0.37
Eu	0.24	0.24	0.24	0.10	0.10	0.10
Gd	1.02	1.02	1.02	0.41	0.41	0.41
Tb	0.16	0.16	0.16	0.06	0.06	0.06
Dy	0.76	0.76	0.76	0.23	0.23	0.23
Ho	0.18	0.18	0.18	0.06	0.06	0.06
Er	0.55	0.55	0.55	0.27	0.27	0.27
Yb	0.75	0.75	0.75	0.41	0.41	0.41

n = 1

n.d. = not detected

Table E-10. ETH LA-ICP-MS matrix glass error summary (1 σ) and detection limits (ppm).

ETH - August 3, 2010 - Matrix Glass						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.24	0.24	0.24	253	253	253
TiO ₂	0.003	0.003	0.003	1.16	1.16	1.16
Al ₂ O ₃	0.01	0.01	0.01	0.83	0.83	0.83
FeO*	0.01	0.01	0.01	15.5	15.5	15.5
MnO	0.0004	0.0004	0.0004	0.72	0.72	0.72
MgO	0.004	0.004	0.004	0.94	0.94	0.94
CaO	0.03	0.03	0.03	160	160	160
Na ₂ O	0.004	0.004	0.004	1.22	1.22	1.22
K ₂ O	0.004	0.004	0.004	3.70	3.70	3.70
P ₂ O ₅	0.002	0.002	0.002	7.94	7.94	7.94
S	22.5	22.5	22.5	62.0	62.0	62.0
Sc	0.18	0.18	0.18	0.15	0.15	0.15
Cr	2.6	2.6	2.6	5.17	5.17	5.17
Ni	n.d.	n.d.	n.d.	4.35	4.35	4.35
Cu	3.08	3.08	3.08	0.36	0.36	0.36
Zn	2.57	2.57	2.57	0.35	0.35	0.35
Rb	1.37	1.37	1.37	0.06	0.06	0.06
Sr	1.76	1.76	1.76	0.04	0.04	0.04
Y	0.27	0.27	0.27	0.03	0.03	0.03
Zr	1.37	1.37	1.37	0.07	0.07	0.07
Nb	0.28	0.28	0.28	0.04	0.04	0.04
Ba	9.02	9.02	9.02	0.23	0.23	0.23
Pb	11.0	11.0	11.0	0.06	0.06	0.06
Th	0.37	0.37	0.37	0.04	0.04	0.04
U	0.20	0.20	0.20	0.03	0.03	0.03
La	0.46	0.46	0.46	0.03	0.03	0.03
Ce	0.60	0.60	0.60	0.03	0.03	0.03
Pr	0.17	0.17	0.17	0.02	0.02	0.02
n.d.	0.72	0.72	0.72	0.14	0.14	0.14
Sm	0.30	0.30	0.30	0.17	0.17	0.17
Eu	0.07	0.07	0.07	0.07	0.07	0.07
Gd	0.24	0.24	0.24	0.18	0.18	0.18
Tb	0.04	0.04	0.04	0.03	0.03	0.03
Dy	0.18	0.18	0.18	0.10	0.10	0.10
Ho	0.03	0.03	0.03	0.03	0.03	0.03
Er	0.13	0.13	0.13	0.12	0.12	0.12
Yb	0.24	0.24	0.24	0.25	0.25	0.25

n = 1

n.d. = not detected

Table E-10. Continued.

ETH - August 4, 2010 - Matrix Glass						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.34	0.12	0.17	1075	115	349
TiO ₂	0.005	0.001	0.003	3.33	0.58	1.27
Al ₂ O ₃	0.01	0.003	0.01	2.51	0.40	0.96
FeO*	0.02	0.01	0.01	63.9	6.19	20.5
MnO	0.0004	0.0002	0.0003	2.87	0.40	1.00
MgO	0.021	0.006	0.011	4.04	0.49	1.33
CaO	0.08	0.03	0.04	584	68.8	192
Na ₂ O	0.01	0.002	0.005	6.54	0.73	1.95
K ₂ O	0.004	0.001	0.002	18.5	2.09	5.63
P ₂ O ₅	0.003	0.001	0.002	39.1	4.68	12.1
S	85.4	15.3	29.7	252	35.3	86.6
Sc	0.48	0.16	0.27	0.76	0.08	0.23
Cr	8.71	1.38	3.18	18.6	3.26	6.69
Ni	5.88	1.55	2.80	21.6	1.58	6.20
Cu	5.79	1.08	2.14	1.46	0.18	0.49
Zn	1.95	0.83	1.63	3.39	0.19	1.00
Rb	1.50	0.44	0.82	0.29	0.02	0.09
Sr	2.12	0.61	1.65	0.15	0.02	0.05
Y	0.31	0.16	0.25	0.14	0.02	0.05
Zr	2.57	0.97	1.34	0.28	0.05	0.10
Nb	0.27	0.07	0.17	0.24	0.02	0.08
Ba	9.46	2.81	5.32	0.96	0.17	0.33
Pb	2.87	0.35	0.97	0.24	0.03	0.08
Th	0.28	0.07	0.20	0.14	0.02	0.05
U	0.20	0.05	0.12	0.13	0.02	0.04
La	0.42	0.16	0.31	0.12	0.02	0.04
Ce	0.58	0.23	0.45	0.13	0.02	0.05
Pr	0.17	0.07	0.13	0.10	0.02	0.03
n.d.	0.74	0.32	0.62	0.59	0.07	0.21
Sm	0.39	0.17	0.31	0.68	0.09	0.23
Eu	0.18	0.05	0.10	0.20	0.03	0.07
Gd	0.37	0.16	0.28	0.73	0.09	0.25
Tb	0.05	0.02	0.04	0.10	0.01	0.04
Dy	0.28	0.12	0.20	0.43	0.06	0.15
Ho	0.06	0.03	0.04	0.16	0.01	0.05
Er	0.19	0.11	0.16	0.50	0.06	0.17
Yb	0.22	0.12	0.18	0.72	0.09	0.24

n = 5

Table E-10. Continued.

ETH - March 16, 2011 - Matrix Glass						
	Error Summary (1 σ)			Detection Limits (ppm)		
	high	low	average	high	low	average
SiO ₂	0.78	0.56	0.67	1925	1377	1651
TiO ₂	0.009	0.009	0.009	10.5	8.23	9.36
Al ₂ O ₃	0.05	0.037	0.04	8.61	6.69	7.65
FeO*	0.05	0.04	0.04	120	97.3	109
MnO	0.002	0.001	0.002	8.48	7.79	8.13
MgO	0.02	0.01	0.02	11.0	8.00	9.51
CaO	0.09	0.07	0.08	950	897	924
Na ₂ O	0.01	0.01	0.01	7.76	5.72	6.74
K ₂ O	0.01	0.01	0.01	20.6	18.0	19.3
P ₂ O ₅	0.008	0.007	0.008	82.4	59.5	71.0
S	n.d.	n.d.	n.d.	430	352	391
Sc	0.92	0.92	0.92	2.64	1.94	2.29
Cr	n.d.	n.d.	n.d.	75.2	69.9	72.6
Ni	n.d.	n.d.	n.d.	51.2	36.1	43.6
Cu	9.03	3.12	6.07	5.41	4.61	5.01
Zn	10.1	8.10	9.08	6.11	5.36	5.74
Rb	5.38	4.58	4.98	0.49	0.35	0.42
Sr	6.06	2.64	4.35	0.61	0.30	0.45
Y	1.04	0.91	0.97	0.43	0.30	0.37
Zr	6.59	5.13	5.86	0.92	0.65	0.78
Nb	0.96	0.84	0.90	0.53	0.38	0.46
Ba	28.1	21.7	24.9	2.13	1.55	1.84
Pb	48.5	2.15	25.3	0.57	0.50	0.54
Th	1.41	0.96	1.19	0.37	0.32	0.34
U	0.88	0.65	0.76	0.33	0.28	0.30
La	1.77	1.49	1.63	0.29	0.22	0.25
Ce	2.51	1.76	2.13	0.28	0.21	0.25
Pr	0.62	0.52	0.57	0.22	0.22	0.22
n.d.	2.66	2.41	2.53	1.24	0.90	1.07
Sm	1.35	1.03	1.19	1.46	1.03	1.24
Eu	0.38	0.38	0.38	0.41	0.29	0.35
Gd	1.01	1.01	1.01	1.55	1.19	1.37
Tb	0.18	0.18	0.18	0.22	0.16	0.19
Dy	0.57	0.57	0.57	0.90	0.67	0.79
Ho	0.17	0.17	0.17	0.23	0.17	0.20
Er	0.60	0.60	0.60	1.05	0.78	0.92
Yb	n.d.	n.d.	n.d.	1.56	1.19	1.38

n = 2

n.d. = not detected

APPENDIX F: ELEMENT MAPS

Methods

Element maps of selected apatites were generated with a CAMECA SX100 electron microprobe (EMP) housed at Oregon State University in Corvallis, OR via remote access at Portland State University in Portland, OR. The EMP operating conditions during apatite analyses were 15 kV, 30 nA, and 0 μm diameter electron beam. Elements selected for mapping and the analyzing crystals were: P (PET), F (PCO), Cl (PET), S (LPET), and Na (LTAP). A backscattered electron (BSE) image was also collected for each apatite crystal mapped.

Apatite Analysis

EMP element maps from this study (Fig. F-1) showed that high-sulfur areas within apatites are typically expressed as small globular clusters (1 to 3 spots) located near- to off-center of the apatite profile. In some cases, high-S rings or semi-rings are expressed in addition to or in lieu of the cluster shape. These shapes are nearly identical in the Na element map and further confirm that Na^+ is important in the coupled substitution with S^{6+} . This physical distribution of high-S content was true regardless of the host mineral of the apatite, (e.g. anhydrite, magnetite, or hornblende). Based upon this and the fact that high-S concentrations are not expressed at the apatite/anhydrite interface as a complete rim, diffusion of S down a concentration gradient from anhydrite to apatite can be ruled-out as a mechanism for generating high-S concentrations in apatite.

Figure F-1: BSE image and element maps (P, S, Na, and F) of apatite. Green circles represent EMP spot traverse analyses and the numbers indicated the SO₃ wt.% at each spot. High-S numbers correlated with the bright spots in the S map. Host is anhydrite.

PH12C-2 Ap9
1.1 – 1.7 SO₃ wt. %

Figure F-1: Continued, BSE image and element maps (P, S, Na, F, and Cl) of apatite. Green circles represent EMP spot traverse analyses and the numbers indicated the SO₃ wt.% at each spot. High-S numbers correlated with the bright spots in the S map. Host is anhydrite.

PH12C-3b Ap9
0.19 – 0.25 SO₃ wt. %

Figure F-1: Continued. Host is anhydrite.

PH12C-3b Ap11
0.52 – 0.93 SO₃ wt. %

Figure F-1: Continued. Host is anhydrite.

Figure F-1: Continued. Host is anhydrite.

PH12C-6 Ap2
0.55 SO₃ wt.%

Figure F-1: Continued. Host is anhydrite.

PH12C-6 Ap3
0.52 – 0.62 SO₃ wt. %

Figure F-1: Continued. Host is anhydrite.

PH12C-6 Ap5
0.27 – 0.66 SO₃ wt. %

Figure F-1: Continued. Host is anhydrite.

PH12C-6 Ap6
0.50 – 0.91 SO₃ wt. %

Figure F-1: Continued. Host is anhydrite.

PH12C-7 Ap6
0.23 – 0.90 SO₃ wt. %

Figure F-1: Continued. Host is anhydrite.

PH12C-7 Ap7
0.76 – 1.3 SO₃ wt.%

Figure F-1: Continued. Host is anhydrite.

PH12C-7 Ap9
0.32 – 0.46 SO₃ wt. %

Figure F-1: Continued. Host is hornblende.

PH12C-7 Ap12
0.85 – 1.5 SO₃ wt. %

Figure F-1: Continued. Host is anhydrite.

Figure F-1: Continued. Host is magnetite.

Figure F-1: Continued. Host is magnetite.

PH12C-7 Ap15
0.32 – 0.68 SO₃ wt. %

Figure F-1: Continued. Host is anhydrite.

Figure F-1: Continued. Host is anhydrite.