Chemical Constraints on the Origin of the Frailes Volcanic Complex in the Central
Andean Altiplano Plateau, Bolivia

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Abstract

The Frailes volcanic complex of the Bolivian Altiplano plateau is the largest and most prominent ignimbrite of the Andean Central Volcanic Zone. With 2000 km³ of exposed volcanic deposits dating from 25 Ma to the present, the complex provides insight into the processes of large-volume silicic melt formation in a back-arc setting. However, the voluminous 0-10 Ma main body of the Frailes complex remains poorly studied, as the majority of the literature focuses on a small region of 12-14 Ma Sn-Ag mineralization at Cerro Rico – the world's largest silver deposit. Here, we present geochemical analyses of 25 representative samples from our fieldwork on the Frailes ignimbrite. Whole-rock major element analysis by X-ray fluorescence spectroscopy showed the ~ 7 Ma samples to be highly peraluminous, potassic (>5% K₂O) andesitic to rhyodacitic welded volcanic tuffs with an Al-rich, chemically reduced mineral assemblage including biotite, calcic feldspar, magmatic cordierite, and ilmenite. Trace element analysis by instrumental neutron activation revealed steep rare earth patterns with Sm/Yb > 5.0, requiring the presence of garnet in a deep-crustal, high-pressure restitic assemblage. In contrast, the presence of cordierite indicates crystallization at low pressure (< 450 MPa), at depths of less than 14 km. In addition, geochemical analyses combined with the geochronological work of Barke et al. (2007) support a recent (~2 Ma) age for the ignimbrites of the main Frailes Meseta. These ignimbrites are consequently best explained by mixing of a mantle-derived melt with a reduced, lower crustal component at great depths to produce hybrid

magmas that ascended and evolved to form shallow crustal (<14 km) magma bodies before erupting in catastrophic, caldera-forming events at ~2 Ma.

Introduction

The 2000 km³ (Schneider, 1985) of andesitic to rhyodacitic ignimbrites contained in the Miocene-age Frailes complex provide a key window into the processes of large-volume silicic-to-intermediate melt production in a back-arc setting. Situated in the high Altiplano plateau of the central Andes (Figure 1) above ~65 km thick crust (Beck et al., 1996), the Frailes complex sits on the edge of one of the largest volcanic provinces on earth: the Altiplano-Puna Volcanic Zone (see e.g. Kay and Coira, 2009), which has erupted at least 12000 km³ of intermediate to silicic magma in the last 10 Ma alone (DeSilva and Gosnold, 2007; Kay et al., *submitted*). As seen in Figure 2, the Frailes complex is one of the largest of all of the Altiplano-Puna ignimbrites, with approximately 2000 cubic kilometers of 0-15 Ma ignimbrite flows exposed over an area of more than 8500 km² (Schneider, 1985). Despite the prominence of the Frailes complex among Andean ignimbrites, there has been little geochemical study of the Frailes volcanics less than 12 Ma in age; with the exception of Jimenez et al. (1997) and Luedke et al (1997), existing work in the area has focused primarily on the associated metallogenic ore deposits (e.g. Schneider, 1985; Rice et al., 2005) or on the wider tectonics of the region (e.g. Kennan et al., 1995; Barke, et al., 2007). Presented here are the results of new mineral and whole-rock major and trace element analysis of 25 samples from the Frailes complex as determined by electron probe microanalysis, neutron activation analysis, X-ray fluorescence spectroscopy and optical microscopy. These analyses complement existing chemical data from the work of Schneider (1985), Jimenez

Left: Figure 1: Location of the Frailes complex in the Central Andes. Regions at elevation above 3700 meters are depicted in pink; thin-skinned fold and thrust belts in green; and thick-skinned thrust belts in gray. Figure adapted from Kay and Coira (2009). Contours of the subducting slab at 50 km intervals adapted from Cahill and Isacks (1992).

Right: Figure 2: Relation of the Frailes ignimbrite complex in relation to other major ignimbrites of the Altiplano-Puna plateau (Kay et al., submitted).

et al. (1997) and Luedke et al. (1997). The data presented here helps to bridge the current gap in understanding of the Frailes ignimbrites and provide a basis for a revised geological and geochemical interpretation of the complex.

Geologic Setting

The Frailes ignimbrite complex stretches between 19 and 20 degrees S at the boundary between the Eastern Cordillera to the east and the Bolivian Altiplano to the west (Figures 1 and 2). The peraluminous andesitic to rhyodacitic (Schneider, 1985; Jimenez et al., 1997) ashflow tuffs of the Frailes complex unconformably overlie the sedimentary sequences of the Eastern Cordillera fold and thrust belt, which is comprised of Ordovician shales and Cretaceous syn-rift sandstones, as well as younger continental redbeds and interbedded volcanics of the Tertiary Mondragon Formation (e.g. Schneider and Halls, 1985; Kennan et al., 1995). As shown in Figures 2 and 3, the Frailes complex extends over 110 km north-south and nearly 100 km east-west, centered on the massive main Frailes Meseta. While the volume of volcanic ejecta contained in the Frailes complex is not well constrained, Schneider and Halls (1985) estimated a total volume 2000 km³ for the 1 to 25 Ma volcanics in the complex. In addition, the Frailes ignimbrite complex is notable for the magnitude of its associated mineralization. Polymetallic sulfide mineralization of variable degree is widespread throughout the vicinity of the Frailes complex, especially at Potosí and Porco on the southeastern edge of the main Frailes ignimbrite. Metallogenic deposits of the region are characterized by Sn-Ag mineralization – suggesting a reduced chemistry – along with additional Zn, Pb, Sb, Bi, As, and W mineralization (Schneider, 1987; Rice et al., 2005; Risse et al., 2008). Most

Figure 3. Thematic Mapper satellite image of the Frailes complex showing sample locations; samples in red collected in 2009, those in white collected in 2010.

notably, Cerro Rico, an extensively altered Miocene rhyodacite dome above the city of Potosí, has been cited as the largest silver deposit on earth (see Schneider, 1985).

Data from seismic surveys of the Altiplano-Puna plateau indicate the presence of pronounced crustal and mantle low velocity anomalies in close alignment with the large Frailes ignimbrite complex. The lithospheric-scale cross-section of Beck and Zandt (2002) in Figure 4 illustrates the dramatic upper-mantle low velocity zone identified by Myers et al. (1998) at the boundary between the Altiplano and the Eastern Cordillera, directly beneath the Frailes complex. This zone of low seismic V_p and V_s is suggestive of high temperatures, and has been interpreted as a region of missing or profoundly modified

Figure 4: Composite lithospheric cross section from Beck and Zandt (2002) showing the location of the Frailes complex with respect to the crustal Altiplano Low Velocity Zone (see Yuan et al. 2002) and the mantle low velocity zone (Myers et al., 1998) attributed to removal of lithosphere. Extent of <3.5 Ma volcanics in Frailes region is based on Barke et al. (2007). Stars show location of seismic stations (see discussion in Beck and Zandt, 2002). Figure is as modified by Kay and Coira (2009).

mantle lithosphere (Beck and Zandt, 2002). These observations are in accordance with the understanding of Los Frailes as a large, recently active volcanic center, and the high temperature and missing mantle lithosphere suggest the possibility of delamination and delamination-induced magmatism, as reviewed by Kay and Coira (2009). The presence of thick crust (~65 km), but absence of a thick lower-crustal high-velocity region under Los Frailes is similarly consistent with crustal delamination (Beck et al., 1996; Beck and Zandt, 2002) of the style suggested by Kay et al. (1994). Furthermore, receiver function studies by Beck and Zandt (2002) noted a small, shallow, low velocity–high L_g attenuation–high V_p/V_s region between 14 and 20 km depth (pink region in mid-crust in Figure 4), also directly beneath Los Frailes. This region, to the east of the similar but larger Altiplano low-velocity zone (ALVZ) of Yuan et al., (2001) may be interpreted as a

crustal zone of partial melt – indicating recent, if not contemporary, surficial magmatic activity at Los Frailes.

At or since the time of volcanism, the main eruptive centers of the Frailes complex have been obscured, with no obvious caldera immediately visible. However, the Frailes eruptives may be separated into broad mesetas each with distinct source regions. As seen in Figure 3, the Livichuco and Condor Nasa Mesetas are located to the north and northeast of the main Frailes Meseta, respectively, while the remnants of the Karikari Caldera and associated ignimbrites are situated to the southeast. A working chronology of

Figure 5: Distribution of ages in the Frailes ignimbrite complex, adapted from Schneider, 1987. Dates prefixed 'E' are K-Ar ages from Evernden et al., 1977; dates prefixed 'BF' are K-Ar ages from Baker and Francis, 1978; light blue dates are K-Ar ages from Schneider and Halls, 1985; dates prefixed 'K' are K-Ar ages from Kennan et al., 1995; dates highlighted yellow are Ar-Ar ages from Barke et al., 2007. All ages on biotite.

the Frailes mesetas may be deduced from existing geochronological studies, a summary of which is shown in Figure 5.

According to Schneider and Halls (1985), the Frailes volcanic zone is marked by five discrete magmatic episodes. The first episode, at about 25 Ma, produced little volume, with only the small Kumurana granodiorite pluton in the southeast of the Frailes complex and the ignimbrite deposits at Azanaques in the northwest thought to have originated at this time. During the second episode, around 20 Ma, activity escalated – most notably including the formation of the Karikari caldera (inset at lower right of Figure 5), as well as some eruptive activity in the north of the Frailes complex near the town of Cruce Ventilla and in the east near Agua Dulce. The Azanaques granite, the second and final intrusive after the Kumurana granodiorite, was also emplaced during the second stage. From 10-17 Ma - the third episode - volcanism occurred throughout the central region of the Frailes complex, producing the widespread upper and lower Cebadillas ashflow deposits. Based on ages available at the time (shown in blue in Figure 5), Schneider and Halls (1985) placed the main Frailes ignimbrite in a fourth episode, from 5-8 Ma. The final "post-Frailes" fifth episode was argued to have formed the resurgent Cerro Torro and Viacollo domes (center of Figure 5) from 4-1 Ma. However, recent dating by Barke et al. (2007) suggests that the main Frailes ignimbrite (fourth stage) may be significantly younger than the 5-8 Ma reported by Schneider and Halls (1985). As shown in Figure 5, the recent biotite Ar-Ar ages of Barke et al. (2007) from the northeastern and southeastern margins of the main Frailes Meseta (highlighted yellow in Figure 5) show dates of 2.24 and 1.86 $\pm$ 0.09 Ma, respectively, suggesting a much

younger age for the main Frailes Meseta – closer in timing to the dome emplacement of the fifth stage. This possibility is consistent with the geophysical data, as the presence of the significant upper-mantle low-velocity zone beneath Los frailes is most consistent with massive recent volcanism.

Prior geochemical work on the bulk of the Frailes ignimbrite has been limited, with only three studies reporting data from the main (non-metallogenic) volume of the complex: the PhD thesis of Schneider (1985), containing data from across the plateau; Jimenez et al. (1997) on the Livichuco Meseta; and Luedke et al. (1997) on the southern part of the complex. Of these, Luedke et al. (1997) and Jimenez et al. (1997) approach Los Frailes from a generally local standpoint and provide relatively little regional or lithospheric-scale interpretation, while Schneider (1985) uses the data mainly to provide context for the associated mineralization. Other volcanic units of interest in the region that have been the subject of some prior study include the Morococala ignimbrite ~75 km to the north and the mafic lavas to the west e.g. Davidson and de Silva (2005) and Hoke and Lamb (2008)(Figure 2). Morgan et al. (1998) present a study of the highly peraluminous rocks of the Morococala ignimbrite, noting an exotic (for an ignimbrite) mineral assemblage including andalusite and cordierite. Given the close geographical location and similar peraluminous composition, some similarities may be expected between the Frailes and Morococala ignimbrites; Ar-Ar isochron ages from Morococala record dates of 6.4 to 8.4 Ma (Koeppen et al., 1987) within the time period during which the Frailes complex was active, and in line with the original estimates for the age of the eruption of the main Frailes Meseta (Schneider and Halls, 1987). Other nearby units

include outcrops of shoshonites and basaltic andesites to the west (Figures 2 and 3), which Hoke and Lamb (2007) model as originating from partial melt of an enriched MORB source at depths between 65 and 95 km.

Experimental Methodology

Ignimbrite samples (Table 1) were collected during two field expeditions to the Frailes complex – in 2009 during a reconnaissance trip by S.M. Kay and B.L. Coira, and in March 2010 as part of this study. Sample locations for the 25 pumice and welded tuff samples are illustrated in Figure 3, with coordinates given in Table 1. Samples were selected and trimmed in the field to minimize the effect of weathering. Petrological, mineralogical, and geochemical data were collected on the ignimbrite samples using electron probe microanalysis, instrumental neutron activation analysis (INAA), and X-ray fluorescence spectroscopy (XRF). In order to avoid contamination and minimize systematic error between techniques in the chemical analyses, all whole-rock analyses were conducted on the same bulk-rock powders mechanically pulverized in an alumina shatter-box.

Whole-rock major element and Rb, Nb, Y, and Zr chemistries were determined by X-ray fluorescence at the University of Jujuy in Argentina, following analytical methodology as discussed by Caffee et al. (2002). Whole-rock trace element analyses by INAA were conducted at Cornell University after sample irradiation at the North Carolina State University PULSTAR research reactor. Prior to neutron irradiation, samples and standards were prepared by sealing bulk rock powder of known mass (~0.5 g) in high-purity silica glass ampoules. Following irradiation, ampoules were individually placed in an ORTEC GEM-20170-S solid-state γ -ray spectrometer and counted for 3-10 hours each

Table 1: Samples and locations.

Sample	Region	Type	Latitude	Longitude	Altitude	~Age
PO-1	Condor Nasa	Ashflow tuff	S 19.3637	W 65.9355	3600 m	7-10 Ma
PO-2	Condor Nasa	Ashflow tuff	S 19.3637	W 65.9355	3600 m	7-10 Ma
PO-3	Condor Nasa	Ashflow tuff	S 19.3687	W 65.9637	3819 m	7-10 Ma
PO-4	Condor Nasa	Ashflow tuff	S 19.3687	W 65.9637	3819 m	7-10 Ma
PO-5	Huari	Ashflow tuff	S 19.1733	W 66.7811	3721 m	1-4 Ma
PO-6	Huari	Ashflow tuff	S 19.1733	W 66.7811	3721 m	1-4 Ma
PT-1	Porco	Ashflow tuff	S 19.71020	W 65.87138	3916 m	12-14 Ma
PT-2	Porco	Ashflow tuff	S 19.71020	W 65.87138	3916 m	12-14 Ma
PT-3	Porco	Intrac. tuff	S 19.80210	W 65.97706	4080 m	12-14 Ma
PT-4	Kumurana	Intrusive	S 19.77537	W 65.67075	4586 m	25 Ma
PT-5	Karikari	Ashflow tuff	S 19.36375	W 65.70851	4361 m	20 Ma
PT-6	Condor Nasa	Ashflow tuff	S 19.36858	W 66.00847	4042 m	7-10 Ma
PT-7	Condor Nasa	Ashflow tuff	S 19.35165	W 66.04090	3890 m	7-10 Ma
PT-8	Los Frailes	Ashflow tuff	S 19.44460	W 66.11150	3943 m	~2 Ma
PT-9	Los Frailes	Ashflow tuff	S 19.38651	W 66.07663	3889 m	~2 Ma
PT-9p	Los Frailes	Pumice	S 19.38651	W 66.07663	3889 m	~2 Ma
PT-10	Los Frailes	Pumice	S 19.38712	W 66.07063	3824 m	2.24 Ma
PT-11	Los Frailes	Ashflow tuff	S 19.38523	W 66.06510	3720 m	2.24 Ma
PT-11p	Los Frailes	Pumice	S 19.38523	W 66.06510	3720 m	2.24 Ma
PT-12	Condor Nasa	Ashflow tuff	S 19.35593	W 66.04590	3762 m	7-10 Ma
PT-13	Livichuco	Ashflow tuff	S 19.02840	W 66.16620	4077 m	7-10 Ma
PT-14	Livichuco	Ashflow tuff	S 19.13400	W 66.37816	4107 m	7-10 Ma
PT-15	Condor Nasa	Ashflow tuff	S 19.34906	W 65.91299	3757 m	7.13 Ma
PT-16	Los Frailes	Ashflow tuff	S 19.60108	W 65.89838	3589 m	~2 Ma
PT-16b	Los Frailes	Silicic lava	S 19.60108	W 65.89838	3589 m	~2 Ma

to determine each sample's emission spectrum, which was then interpreted by comparison to three in-house standards, correcting for decay and interferences (standard analyses shown in Appendix I for reference). In order to obtain a more complete set of analyses of elements with both short- and long-half-life radioisotopes, samples were counted twice: first for ~3 hours each, beginning seven days after irradiation; and second for ~10 hours each, starting 30 days after irradiation.

Electron probe microanalysis and optical microscopy were conducted at Cornell using standard polished petrographic thin sections. Mineral chemistry was determined via wavelength-dispersive spectroscopy using a JEOL 8900 electron microprobe at the Cornell Center for Materials Research. Analyses were conducted with an accelerating voltage of 15 kV, a beam current of 25 nA, a beam diameter of 10 microns, and conductive carbon-coating of approximately 20 nm thickness. The probe standards used were polished, carbon-coated mineral standards from the Smithsonian institution; standard analyses are given in Appendix II.

The samples best characterized to date are samples PO-1 through PO-6, collected in the north of the Frailes complex at coordinates listed in Table 1. As can be seen in Figure 3, these samples originate from two distinct regions: PO-1 through PO-4 are from the Condor Nasa massif in the east, and PO-5 through PO-6 were collected south of the town of Santiago de Huari in the west (see Figure 3). The remaining PT- series samples, collected from locations throughout the Frailes complex in March of 2010, have thus far been only analyzed for trace elements by instrumental neutron activation analysis.

Mineralogy and Petrography

As discussed above, the mineral and whole-rock chemistry of samples PO-1 to PO-6 from the Frailes complex were studied using electron probe microanalysis, optical microscopy, and X-ray fluorescence. Whole-rock major element chemical analyses, as determined by X-ray fluorescence, are summarized in Tables 2-3; results of electron microprobe analysis are summarized in Tables 4-8. Not unlike ignimbrite samples from other large Andean ignimbritic volcanic complexes (e.g. Coira et al., 1993; de Silva and Gosnold, 2007), samples PO-1 to PO-6 were found to be compositionally intermediate-to-silicic welded ashfall tuffs containing 60-70% silica (Table 2). All analyzed samples are highly peraluminous, as indicated by their high Al/(Ca+Na+K) atomic ratios (Figure 6) and their corundum-normative character (Table 3).

In thin section, the samples exhibit textures typical of a welded tuff, with abundant phenocrysts in a glassy groundmass displaying eutaxitic texture, preferential

Table 2: Whole-Rock Major Element Analyses of samples PO-1 to PO-6 (weight %).

	PO-1	PO-2	PO-3	PO-4	PO-5	PO-6
SiO ₂	58.98	60.29	61.11	62.82	71.97	65.76
TiO ₂	1.27	1.30	1.30	1.01	0.34	0.78
Al ₂ O ₃	18.39	18.19	18.24	17.82	14.84	16.82
FeO	5.90	5.30	5.40	3.19	1.92	3.41
MnO	0.08	0.06	0.06	0.03	0.02	0.04
MgO	2.46	2.43	2.36	1.26	0.64	1.12
CaO	4.00	4.23	4.18	2.49	1.69	3.22
Na ₂ O	1.69	2.02	2.36	2.31	2.66	2.94
K ₂ O	4.04	4.37	4.50	5.75	4.82	4.93
P ₂ O ₅	0.50	0.51	0.51	0.45	0.21	0.39
LOI	2.91	1.50	0.68	3.13	1.31	0.86
Total	100.2	100.2	100.7	100.3	100.4	100.3

Table 3: CIPW Normative Mineralogy of samples PO-1 through PO-6 (weight %).

	PO-1	PO-2	PO-3	PO-4	PO-5	PO-6
quartz	19.58	17.79	16.24	19.92	32.95	20.49
orthoclase	23.88	25.80	26.59	34.00	28.46	29.12
albite	14.33	17.09	19.99	19.55	22.52	24.86
anorthite	16.58	17.66	17.41	9.42	7.05	13.47
corundum	5.15	3.67	3.10	4.34	2.67	1.71
apatite	1.25	1.27	1.27	1.13	0.52	0.97
ilmenite	2.41	2.47	2.46	1.91	0.64	1.49
magnetite	1.02	0.92	0.93	0.55	0.33	0.59
hypersthene	13.27	12.20	12.18	6.43	4.03	6.83
Total	97.46	98.86	100.17	97.25	99.17	99.52

Figure 6: Molar $Al_2O_3/(CaO+Na_2O+K_2O)$ versus SiO_2 weight percent for representative ignimbrite samples from the Livichuco and Los Frailes complexes.

orientation of elongate phenocrysts, and occasional axiolitic texture (a type of fibrous intergrowth that is linear in macroscopic form) from devitrification. The samples contain

a phenocryst assemblage including many minerals common to other large Andean ignimbrites, such as biotite, quartz, tridymite, sanidine, plagioclase, and orthopyroxene (e.g. Coira et al., 1993), as well as more atypical constituents such as cordierite and calcic plagioclase (to AN 80; Table 4). Although lateral and stratigraphic variations in composition and mineralogy within each region are not well constrained, the differences between the two sample groups are clear: samples PO-1,3, and 4 from the Condor Nasa Meseta were categorized as moderately crystal-rich (35-50% phenocrysts) biotite andesite ignimbrite (58-63% SiO₂; Table 2), with phenocryst proportions of up to 45% each of biotite and calcic plagioclase, as well as 0-20% quartz and tridymite, 0-6% hypersthene, and 0-2% cordierite. In contrast, samples PO-5 and PO-6 from south of Santiago de Huari (Referred to as Huari samples below; Figure 3) are highly crystal-rich (60-65% phenocrysts by volume), significantly more silicic rhyodacites (65-70% SiO₂; Table 2), containing roughly 20% sanidine and 40% quartz + tridymite, along with approximately 30% plagioclase, 10-15% biotite and no orthopyroxene or cordierite. Accessory (< 1% of phenocrysts by volume) minerals zircon, ilmenite, and apatite were found throughout all samples. With the exception of PO-4, the samples display little evidence of weathering or alteration.

In the Condor Nasa samples, textural relations indicate that plagioclase may have been the first major silicate phase to crystallize, as it lacks inclusions of any other major silicate mineral. Biotite, the other main phase in the Condor Nasa samples contains abundant inclusions of plagioclase and other silicates. In contrast, the Huari samples exhibit the inverse relationship, with many phenocrysts of biotite included in larger

plagioclase grains. Biotite phenocrysts are generally rectilinear due to cleavage, and often bent, reflecting strain incurred during eruption. Further, biotite is frequently associated with opaque Fe-Ti oxides, and many phenocrysts were found to have ragged (embayed), corroded margins. Plagioclase in all samples displays clear oscillatory zoning. Feldspar phenocrysts are frequently fractured and anhedral, but do not display any corrosion or resorption at their margins. In contrast, quartz and tridymite phenocrysts are consistently rounded and embayed, and exhibit clear conchoidal fracture internally. Texturally, quartz and tridymite in the Frailes samples are identical, with tridymite identified by its biaxial optical character and slightly higher birefringence. In all six samples, quartz and tridymite phenocrysts contain inclusions of both plagioclase and biotite, suggesting later crystallization. Sanidine, which is present in samples PO-5 and 6, is pseudouniaxial, with a 2V of zero, and contains inclusions of plagioclase and biotite. In addition, small crystals of apatite, zircon, and ilmenite were found as inclusions and occasionally as free crystals in the glassy groundmass. Zircon and ilmenite were found to be texturally very early, present as inclusions even in the first of the major silicate phases to crystallize.

Notably, sample PO-2 from Condor Nasa contains phenocrysts of the aluminosilicate mineral cordierite. PO-2 is also distinct from the other samples analyzed in that it lacks quartz and tridymite, and contains approximately 6% hypersthene by phenocryst volume.

Figure 7: Photomicrograph of cordierite in sample PO-2 in cross-polarized illumination.

In plane-polarized light, the cordierite displays characteristic violet-to-colorless pleochroism, suggesting moderate to high iron content. As shown in Figure 7, cordierite is texturally associated with the orthopyroxene, and contains inclusions of biotite and

Table 4: Representative microprobe analyses of plagioclase and sanidine.

	po1-5 plag 1	po2-5 plag 1	po2-5 plag 2	po3-2 plag 1	po5-1 plag 2
An%	58.70	70.11	79.08	44.55	26.19
Ab%	39.23	28.41	20.17	51.69	69.79
Or%	2.07	1.48	0.75	3.77	4.02
SiO ₂	53.33	50.52	48.20	56.90	61.30
TiO ₂	0.01	0.04	0.03	0.01	0.02
Al ₂ O ₃	28.83	31.31	32.71	26.67	23.49
FeO	0.07	0.32	0.20	0.06	0.00
MnO	0.02	0.00	0.03	0.03	0.02
MgO	0.02	0.02	0.01	0.00	0.01
CaO	11.85	14.30	16.05	9.08	5.36
Na ₂ O	4.38	3.20	2.26	5.82	7.89
K ₂ O	0.35	0.25	0.13	0.65	0.69
Total	98.86	99.97	99.62	99.22	98.78
	po6-1 plag 1	po5-2 ksp 1	po5-2 ksp 2	po6-4 ksp 1	po6-4 ksp 2
An%	38.95	0.49	0.48	0.67	0.82
Ab%	56.89	21.65	23.01	17.92	19.16
Or%	4.16	77.87	76.51	81.41	80.01
SiO ₂	57.97	64.63	64.45	64.61	64.74
TiO ₂	0.01	0.01	0.00	0.02	0.02
Al ₂ O ₃	25.95	18.52	18.76	18.40	17.89
FeO	0.09	0.00	0.03	0.04	0.01
MnO	0.00	0.01	0.00	0.00	0.00
MgO	0.00	0.02	0.02	0.00	0.01
CaO	8.01	0.10	0.10	0.14	0.16
Na ₂ O	6.46	2.44	2.58	2.02	2.09
K ₂ O	0.72	13.37	13.03	13.96	13.28
Total	99.21	99.09	98.97	99.18	98.20

plagioclase. These inclusions suggest a primary magmatic origin for the cordierite, and indicate later crystallization. Cordierite phenocrysts range from euhedral to anhedral, but consistently show corroded, slightly embayed rims.

Mineral Chemistry:

Plagioclase:

Plagioclase in samples from the Condor Nasa and Huari localities display clear distinctions in composition:

phenocrysts in the Condor Nasa andesite

samples (PO1-4) range from AN 50 – AB 48 – OR 2 to AN 79 – AB 20 – OR 1, whereas those in the more felsic Huari samples range from AN 26 – AB 70 – OR 4 to AN 40 – AB 56 – OR 4 (Figure 8, Table 4). As seen in Figure 8, plagioclase from Condor Nasa plots near that of samples from the adjacent Livichuco Meseta as analyzed by Jimenez et al. (1997), whereas feldspars from the Morococala ignimbrite farther north (Morgan et al, 1997) were found to be significantly more albitic, in accordance with the more felsic nature of the rhyolitic ignimbrites at Morococala.

Biotite:

As shown in Table 5 and Figure 9, biotite from the Frailes complex is highly aluminous and does not plot on the annite-phlogopite solid solution line of Figure 9, as it contains significant components of eastonite ($K_2[Mg_5Al][Si_5Al_3]O_{20}(OH,F)_4$) and siderophyllite ($K_2[Fe^{2+}_5Al][Si_5Al_3]O_{20}(OH,F)_4$). Biotite from the Condor Nasa andesite plots nearly in the center of the diagram, with roughly equal atomic proportions of Fe and Mg. The much less abundant biotite from the Huari rhyodacite is slightly more Fe-rich

Figure 8: Plagioclase composition diagram.

Figure 9: Biotite composition diagram.

Table 5: Representative microprobe analyses of high- and low-Fe biotite.

	PO1-1 bt 2	PO1-1 bt 5	PO1-4 bt 1	PO2-1 bt 1	PO2-1 bt 4	PO2-8 bt 3
Mg #	46.79	47.38	46.94	48.21	48.42	48.39
SiO ₂	33.99	35.77	35.83	36.47	35.75	35.73
TiO ₂	5.30	5.28	5.27	5.22	5.46	5.38
Al ₂ O ₃	16.44	16.30	16.35	16.02	15.91	16.15
FeO	20.21	20.55	21.09	20.22	20.70	20.75
MnO	0.15	0.15	0.14	0.09	0.08	0.09
MgO	9.97	10.38	10.47	10.56	10.91	10.91
CaO	0.03	0.05	0.00	0.09	0.01	0.00
Na ₂ O	0.29	0.42	0.44	0.49	0.55	0.50
K ₂ O	8.67	8.89	9.09	8.85	8.94	9.03
Total	95.04	97.80	98.67	98.00	98.32	98.53
	PO3-3 bt 2	PO4-2 bt 3	PO5-e bt 1	PO5-e bt 2	PO6-3 bt 2	PO6-3 bt 1
Mg #	46.77	46.78	36.06	37.77	43.66	43.59
SiO ₂	35.77	34.98	35.11	35.13	35.75	36.02
TiO ₂	5.26	4.91	3.84	3.95	4.53	4.67
Al ₂ O ₃	16.23	15.60	18.97	19.03	16.34	16.58
FeO	20.97	20.65	23.88	23.37	21.79	21.70
MnO	0.13	0.14	0.19	0.17	0.15	0.19
MgO	10.34	10.18	7.56	7.96	9.47	9.41
CaO	0.00	0.00	0.03	0.00	0.08	0.00
Na ₂ O	0.45	0.45	0.49	0.47	0.33	0.28
K ₂ O	9.30	9.19	9.34	9.46	9.38	9.65
Total	98.44	96.10	99.41	99.54	97.82	98.48

and much less homogeneous, with a clear subpopulation of much more Al-rich micas.

Additionally, the biotite was found to be Ti-rich, containing between 3.5 and 4.5% TiO₂, with more Ti in the more mafic Condor Nasa samples.

Orthopyroxene:

Orthopyroxene, which was found as a minor phase in samples PO-2 and PO-3, consists of hypersthene with negligible calcium content, as shown in Figure 10 and Table 6. The majority of the orthopyroxene contains near equal amounts of Fe and Mg, with a composition of ~ EN 49 – FS 49 – WO

Figure 10: Pyroxene quadrilateral showing composition of pyroxenes from PO-2 and

2. However, some orthopyroxene phenocrysts display strong compositional zoning, with Mg-rich interiors up to 80% En (Table 6). As illustrated in Figure 11, which shows a high-contrast backscattered electron image of an orthopyroxene phenocryst, the Mg - Fe

Table 6: Representative microprobe analyses of high- and low-Fe orthopyroxene.

	po2-1 opx 3	po2-1 opx 4	po2-8 opx 2	po2-4 opx 2	po2-4 opx 4
En%	52.05	50.78	50.72	76.68	77.86
SiO ₂	50.05	50.95	49.52	51.52	52.36
TiO ₂	0.17	0.10	0.20	0.41	0.38
Al ₂ O ₃	2.63	1.25	3.10	5.00	4.24
FeO	28.97	29.89	29.58	14.55	13.90
MnO	0.65	0.77	0.73	0.21	0.17
MgO	17.64	17.30	17.08	26.84	27.43
CaO	0.22	0.26	0.24	1.18	1.14
Na ₂ O	0.01	0.02	0.02	0.03	0.02
K ₂ O	0.00	0.00	0.00	0.00	0.00
Total	100.36	100.53	100.47	99.73	99.64

Figure 11: High-contrast backscattered electron image of orthopyroxene showing Mg-Fe zoning. Zoning is visible due to the difference in average atomic number (Z) and thus nuclear cross-section of the elements present: Light areas contain high-Z Fe; dark areas of the orthopyroxene contain lower-Z Mg. Corrosion of the mineral borders is clearly visible.

zoning of the orthopyroxene is irregular in pattern, not a clear core-rim overgrowth relationship, suggesting formation by melt infiltration and back-reaction.

Cordierite:

Cordierite, which was found only in sample PO-2, consists of a solid solution of Mg-cordierite and Fe-cordierite, with the samples analyzed here falling between 65% and 69% Mg-cordierite ($\text{Mg}/(\text{Mg}+\text{Fe})$: Mg number). Cordierite was spatially associated with pyroxene in PO-2, and was observed to be in textural equilibrium with the Fe-rich population of orthopyroxene. Although it is difficult to rule out a xenocrystic origin for

Table 7: Representative microprobe analyses of cordierite.

	po2-1 cord 1	po2-1 cord 2	po2-1 cord 3	po2-1 cord 4	po2-2 cord 1
Mg #	67.16	67.42	67.09	67.48	68.54
SiO ₂	49.27	49.15	49.4	49.42	49.42
TiO ₂	0.01	0.01	0.01	0.05	0.00
Al ₂ O ₃	33.50	33.62	33.37	33.06	33.28
FeO	8.03	7.98	8.08	8.12	7.76
MnO	0.16	0.14	0.17	0.16	0.13
MgO	9.21	9.27	9.24	9.45	9.49
CaO	0.07	0.02	0.04	0.02	0.02
Na ₂ O	0.10	0.05	0.06	0.02	0.05
K ₂ O	0.15	0.11	0.11	0.11	0.13
Total	100.49	100.36	100.47	100.40	100.28

cordierite in the sample, it appears most likely to be a liquidus phase. On a first-order basis, crystallization of primary cordierite is consistent with the peraluminous bulk rock chemistry of sample PO-2. In addition, the presence of plagioclase and biotite inclusions in cordierite that are compositionally equivalent to the free phenocrysts of plagioclase and biotite in the sample provides evidence for an autochthonous origin, as does the presence of some euhedral phenocrysts.

Sanidine:

Alkali-feldspar phenocrysts analyzed to date were observed to be K-rich, with compositions of AN 0.5 – OR 76-80 – AB 18-23, as shown in Table 4 and Figure 8. Compositional zoning of sanidine, if present, was not clearly visible in optical or backscattered electron images.

Additional Phases:

Quartz and tridymite phenocrysts

occurring in samples PO1-6 are nearly pure

silica as might be expected (Table 8).

Accessory phases zircon, apatite, and

ilmenite were not extensively studied by

microprobe analysis. However, the presence

of ilmenite (Table 8) and iron in the Fe(II)

oxidation state is consistent with a

chemically reduced nature of the samples, in

Table 8: Microprobe analyses of additional phases.

	po1-8 qtz 1	po1-4 ilm 1
SiO ₂	99.00	0.01
TiO ₂	0.02	50.90
Al ₂ O ₃	0.07	0.21
FeO	0.00	48.08
MnO	0.01	0.78
MgO	0.00	1.55
CaO	0.01	0.00
Na ₂ O	0.02	0.00
K ₂ O	0.00	0.00
Total	99.14	101.54

line with known characteristics of the region (see Bolivian tin belt, e.g. Lehmann et al., 1990).

Geothermometry & geobarometry:

Zircon saturation thermometry (Watson and Harrison, 1983) of samples PO-1 through PO-6 yielded whole-rock zircon saturation temperatures between $\sim 810^{\circ}$ and $\sim 875^{\circ}$ C, as summarized in Table 9. Given the presence of zircon both as inclusions and as free grains in the groundmass, along with zircon's texturally early crystallization, it is plausible that the majority of crystallization occurred below these saturation temperatures. Two-feldspar thermometry of samples PO-5 and PO-6 calculated using the SOLV CALC program (Wen and Nekvasil, 1994; with the thermodynamic models of Nekvasil and Burnham, 1987) at a pressure of 400 MPa produced temperatures of 675° and 720° C, respectively. These temperatures are generally consistent with the crystallization of feldspar later than that of zircon in these samples, consistent with textural relations in the samples. The results of two-feldspar geothermometry were fairly insensitive to changes in pressure, increasing or decreasing by only $\sim 20^{\circ}$ C for pressures of 200 and 600 MPa, respectively. In addition, all samples except PO-2 contain tridymite, which is stable only above $\sim 800^{\circ}$ C with the mineral assemblages found in samples PO-1 to 6 (Figure 12).

Pressures at the time of crystallization are not well determined by geobarometry except in sample PO-2. However, general constraints can be placed on the samples based on the mineral assemblage. As shown in Figure 12, cordierite in sample PO-2 is required

<i>Table 9: Whole-rock zircon saturation temperatures.</i>						
Sample	PO-1	PO-2	PO-3	PO-4	PO-5	PO-6
Temperature (°C)	874	871	837	848	813	832

Figure 12: Pressure and temperature constraints on the mineral assemblage of sample PO-2. P-T phase diagram for bulk rock composition of PO-2 calculated using THERIAK-DOMINO software (de Capitani, 1994) with the thermodynamic database of Holland and Powell (1988); phase equilibria for the system annite-phlogopite-cordierite-hypersthene (red lines) as well as the quartz-tridymite transition (blue line) plotted with winTWQ (Berman, 2007) using the thermodynamic data of Berman (1988); green line illustrates zircon saturation temperature for sample PO-2. Additional reactions listed in Appendix III.

to have formed below 450 MPa, corresponding to depths of ~14 km or less. Although equilibrium compositions in figure 12 readily shift laterally with variations in water content and bulk composition, the upper limit for cordierite stability is compositionally insensitive, supporting this 450 MPa limit. Equilibrium assemblage calculations on the system biotite + cordierite + hypersthene using the winTWQ software package (Berman, 2007, with thermodynamic data from Berman, 1988) yielded a rough pressure estimate of

~400 MPa (Figure 12), as well as a temperature for the assemblage of 780 °C in PO-2.

Trace Element Geochemistry

The results of bulk-rock trace element geochemical analysis by X-ray fluorescence and INAA are shown in Table 10. The data reveal typical arc signatures and extremely steep rare earth patterns, with Sm/Yb ratios consistently over 6 and La/Yb ratios consistently over 30 (Table 10; Figures 13-16), necessitating the presence of garnet in a high pressure crustal restitic assemblage. Compared to other large-volume Altiplano-Puna ignimbrites in Figure 13, the Frailes volcanics define a field of light rare earth enrichment and extreme heavy rare earth depletion unpopulated by other major

Figure 13: La/Sm versus Sm/Yb ratios of large-volume units of the Frailes complex and Morococala ignimbrite in comparison to those of other major Altiplano-Puna ignimbrites (see Figure 2) as compiled in Kay et al, submitted.

Table 10a: New trace element data from the Porco ignimbrite and comparison to literature values.

	Porco (this study)			Porco (Luedke et al., 1997)		
	PT-1	PT-2	PT-3	P15	T7	T8
La	63.1	73.6	93.2	98	75.2	82.0
Ce	126.7	143.2	184.8	174	130	147.8
Nd	41.4	50.1	65.4	64.7	49.0	54.3
Sm	7.3	8.1	11.3	11.1	8.7	9.8
Eu	1.29	1.40	1.85	1.78	1.57	1.77
Tb	0.55	0.49	0.61	0.70	0.59	0.67
Yb	0.82	0.73	1.07	0.95	0.95	1.18
Lu	0.11	0.10	0.18	0.12	0.11	0.14
Y						
Rb				248	256	251
Sr	466	533	638	670	549	610
Ba	788	1006	1279	930	1110	928
Cs	8.7	11.3	23.5	6.7	50.2	21.1
U	5.5	4.8	8.4	6.1	5.3	6.3
Th	19.2	21	26.6	25.8	21.4	22.8
Hf	3.7	4.9	6.9	6.4	5.1	6
Zr				240	205	230
Nb					19	22
Ta	1.29	1.47	1.74	2.34	1.48	1.68
Sc	3.9	4.6	5.4	4.5	4.4	5.9
Cr	11	12	15	8	12	17
Ni						
Co	4	4	5			

Table 10b: New trace element data from the Frailes ignimbrite and comparison to literature values.

	Frailes (this study)										Frailes (Luedke et al., 1997)			
	PT-8	PT-9	PT-9p	PT-10	PT-11	PT-11p	PT-16	B82.28	B82.33B	T1	T3	T5		
La	68.0	40.5	64.5	92	65	63.4	66.6	25.4	73.4	67.4	68.6	68.6		
Ce	138.7	76.8	122	192.6	138.6	134.4	146.3	44.6	135.0	128.3	130.9	130.2		
Nd	56.6	30.5	48.2	80.0	55.5	53.9	58.0	19	60.0	52.1	55.3	51.1		
Sm	10.5	6.0	9.4	14.9	10.2	9.7	10.5	4.1	10.2	10.1	10.2	10.3		
Eu	1.63	0.97	1.38	2.05	1.79	1.51	1.67	0.6	1.62	1.77	1.77	1.84		
Tb	0.57	0.50	0.72	1.07	0.85	0.79	0.70	0.65		0.78	0.75	0.81		
Yb	1.29	0.86	1.34	2.03	1.38	1.21	1.27	0.66	0.84	1.29	1.24	1.29		
Lu	0.16	0.11	0.17	0.26	0.18	0.17	0.16	0.08	0.18	0.16	0.14	0.16		
Y										17	18	15		
Rb								347	246	260	247	205		
Sr	502	350	431	615	558	460	501			582	596	550		
Ba	1114	684	982	1141	1223	898	1098	509	774	1100	1150	1140		
Cs	2.4	4.8	7.7	12.8	5.4	8.1	8.7	38.4	8.8	13.3	8.1	8.3		
U	5.4	3.9	7.0	12.8	8.3	8.9	7.9	21.3	6.6	6.1	5.7	4.9		
Th	22.8	13.4	21.6	31.8	22.3	22.1	23.7	10.5	25.1	23.5	24	23.7		
Hf	6.2	3.4	6.1	8.1	6.7	5.7	6.1	2.5	6.3	6.2	6.1	5.8		
Zr								61	238	225	225	235		
Nb								21	21	14	16	16		
Ta	1.43	1.1	1.6	2.46	1.58	1.49	1.66	3.33	2.03	1.72	1.65	1.76		
Sc	2.4	3.9	6.4	9.8	6.9	6.1	6.7	2.3	6.7	6.5	6.4	6.5		
Cr	9	6	9	14	10	9	10	1	8	8	8	9		
Ni														
Co	3	2	3	5	4	3	3							

Table 10c: New trace element data from the Condor Nasa ignimbrite.

	Condor Nasa									
	PO-1	PO-2	PO-3	PO-4	PT-6	PT-7	PT-12	PT-15		
La	80.1	74.9	75	65.2	54.9	56.5	59.8	97.6		
Ce	173.3	163.1	158.7	137.6	116.2	121.6	124.1	198.8		
Nd	72.3	65.4	67.6	59.9	46.8	48.7	52.9	74.3		
Sm	13.2	11.7	12.4	10.9	9.1	8.6	9.8	14.3		
Eu	2.74	2.77	2.67	2.22	1.72	1.38	1.99	2.55		
Tb	1.25	1.16	1.15	1.01	0.84	0.60	0.87	1.18		
Yb	2.47	1.99	2.14	1.74	1.57	1.08	1.67	3.00		
Lu	0.31	0.26	0.27	0.22	0.21	0.14	0.21	0.38		
Y	28	27	23	17						
Rb	233	169	147	247						
Sr	614	644	649	438	425	416	563	565		
Ba	1140	1160	1258	1102	909	869	1071	1291		
Cs	23.2	7.8	5.5	11.1	5.6	8.0	3.1	14.5		
U	5.7	3.8	4.4	5.4	4.3	6.1	3.4	7.7		
Th	19.8	18.1	18	16.7	14.2	19.8	14.4	30		
Hf	8.2	7.4	8.0	7.0	5.7	5.1	6.3	10.1		
Zr	342	358	254	227						
Nb	33	33	30	29						
Ta	2.34	2.08	2.23	2.35	1.81	1.37	1.77	2.50		
Sc	13.9	13.8	14.1	9.5	9.9	5.3	11.5	8.9		
Cr	23	24	23	14	18	8	21	25		
Ni	8	18	19	11						
Co	8	8	9	3	6	3	8	7		

Table 10d: New trace element data from Livichuco ignimbrite and comparison to literature values

	Livichuco (this study)						Livichuco (Jimenez et al., 1997)					
	PT-13	PT-14	PO190	PU1	PU7	PU27	PU29					
La	45.8	90.2	58.9	61.8	76.3	60.9	65.4					
Ce	96.5	109.5	118.9	126.0	157.7	122.0	128.4					
Nd	43.3	68.8	49.6	58.1	69.9	54.9	60.3					
Sm	8.3	13.4	9.5	11.7	12.8	10.2	11.0					
Eu	1.69	1.83	1.92	2.85	2.89	2.39	2.33					
Tb	0.74	0.84	0.88	1.31	1.24	1.05	1.08					
Yb	1.40	1.75	1.60	2.31	2.09	1.69	1.94					
Lu	0.19	0.22	0.36	0.46	0.34	0.24	0.29					
Y			15	27	27	25	26					
Rb			239	133	176	204	204					
Sr	371	391	403	621	477	453	494					
Ba	916	1114	888	1156	1307	1156	1041					
Cs	3.9	5.5										
U	5	11	7.2	3.6	4.7	6.1	5.9					
Th	12.1	13.6	21.9	15.4	21.3	17.0	21.1					
Hf	5	5.2										
Zr			205	251	306	235	251					
Nb			18	27	26	22	28					
Ta	1.47	1.55	1.29	1.89	1.84	1.59	1.96					
Sc	10.1	11.3	5.0	10.3	9.3	8.3	10.1					
Cr	15	16	87	55	60	41	79					
Ni			5	6	7	4	5					
Co	5	6	3	6	5	4	6					

Table 10e: Additional new trace element data.

	Kumurm.		Karikari		Huari	
	PT-4	PT-5	PO-5	PO-6		
La	107.8	97.6	38.7	67.9		
Ce	211.4	198.8	84.5	146.8		
Nd	78.5	74.3	32.8	59.9		
Sm	15.1	14.3	6.8	10.8		
Eu	2.56	2.55	1.04	2.07		
Tb	1.39	1.18	0.62	0.74		
Yb	3.41	3.00	1.34	1.54		
Lu	0.44	0.38	0.17	0.19		
Y			10	15		
Rb			272	212		
Sr	593	565	272	475		
Ba	1254	1291	761	1259		
Cs	23.4	14.5	9.5	12.4		
U	5.2	7.7	7.0	7.6		
Th	32.7	30	15.4	20.0		
Hf	10.7	10.1	3.8	6.2		
Zr			140	221		
Nb			14	20		
Ta	2.94	2.50	1.65	1.93		
Sc	9.7	8.9	4.8	7.2		
Cr	26	25	10	8		
Ni			4	6		
Co	7	7	3	5

Figure 14: *La/Sm versus Sm/Yb ratios of small-volume units of the Frailes complex and Morococala ignimbrite in comparison to those of other minor Altiplano-Puna ignimbrites (see Figure 2) as compiled in Kay et al., submitted.*

ignimbrite complexes. As Figure 13 illustrates, the main units of the Frailes complex have La/Sm ratios of 5 to 9, and Sm/Yb ratios of 5 to 12.5 – values traditionally associated with small ignimbrites derived from low-percentage partial melts. However, at the Frailes complex, the large-volume ($\sim 60 \text{ km} \times \sim 60 \text{ km} \times \sim 300 \text{ m} \approx 1000 \text{ km}^3$) main Frailes Meseta falls within this range. Small-volume eruptives at Los Frailes (e.g. Porco) display yet steeper rare earth patterns, with La/Sm of 7 to 10 and Sm/Yb of 7 to 12 (Figure 14), and La/Yb greater than 100 in some samples from the 14-12 Ma Porco ignimbrite (Table 10).

In addition to steep rare earth fractionation, chondrite- and mantle-normalized multielement diagrams (Figures 15 and 16) illustrate signatures typical of an arc setting,

Figure 15: Chondrite-normalized multi-element diagram of selected trace and rare earth element concentrations in samples PO-1 to PO-6.

Figure 16: Primitive mantle normalized multi-element diagram of trace element concentrations in samples PO-1 to PO-6.

with depletion of minor-phase compatible high field strength (HFS) elements and enrichment of large-ion lithophile (LIL) elements such as barium relative to the light rare-earth elements, conventionally suggesting the influence of arc fluids. Although the Frailes ignimbrites display significant depletion of HFS elements, they exhibit less corresponding enrichment of LIL elements. Europium anomalies are moderate and negative ($\text{Eu}/\text{Eu}^* 0.9\text{--}0.6$), indicating some fractionation of plagioclase from the melt.

Other, spatially adjacent ignimbrites display similarly steep rare-earth profiles, most notably Morococala ~100 km to the north (see Figure 2). As determined by Morgan et al. (1998) the Morococala ignimbrite exhibits La/Sm ratios near 6 and Sm/Yb ratios of 5 to 10 (Figure 13), and plots with the Frailes ignimbrites on multielement diagrams

Figure 17: Chondrite-normalized multielement diagram of selected trace and rare earth element concentrations in major units of the Frailes and Morococala ignimbrites.

Figure 18: Primitive mantle normalized multielement diagram of trace element concentrations in major units of the Frailes and Morococala ignimbrites.

(Figures 17 and 18). The degree of high field strength element depletion and LIL enrichment are roughly equivalent in samples from Los Frailes and Morococala (Figure 18), reflecting the similarities in the setting of the two ignimbrites.

The peraluminous nature of rocks from the Frailes complex is reflected in Figure 6, with molar $\text{Al}_2\text{O}_3/(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$ (Al/CNK) greater than one for all samples, and significantly greater in some silicic samples (for instance 1.28 in sample PO-1). Samples from the Condor Nasa and Livichuco mesetas, while comparatively low in silica, were nevertheless high in Al/CNK (1.1–1.3; Figure 6). As seen in Figure 19, potassium contents in samples from Los Frailes are also high, approaching shoshonitic values, and rising slightly with increasing percent silica. Such potassium content is not unexpected

Figure 19: K_2O versus SiO_2 weight percent for representative ignimbrite samples from the Livichuco and Los Frailes ignimbrite complexes.

Figure 20: La/Yb ratio versus FeO weight percent for representative ignimbrite samples from the Livichuco and Los Frailes ignimbrite complexes.

for the back-arc region, given the well-known though simplistic K-h relationship sometimes seen with arc to backarc magmatism (see Kuno, 1959). Notably, La/Yb ratios (Figure 20) are highest for FeO contents of approximately 3%, showing that high La/Yb in samples from the Frailes complex reflects their crustal evolution as well as the mantle influence.

Ba/Ta and La/Ta ratios, shown in Figure 21, tend to plot with Ba/La slopes between 10 and 20, lower than values seen in a main arc setting but in line with those expected for back-arc volcanism and seen in other Puna-Altiplano backarc ignimbrites (Coira et al., 1993; Kay et al., 1999; Kay et al., *submitted*). Samples from the Frailes and Morococala complexes that plot with low absolute Ba and La contents are those with

Figure 21: Ba/Ta versus La/Ta ratios of representative ignimbrite samples from the Livichuco and Los Frailes ignimbrite complexes. Diagonal lines represent Ba/La ratios of 5, 10, 20, and 30.

Figure 22: La/Ta ratio versus SiO₂ weight percent for representative ignimbrite samples from the Livichuco and Los Frailes ignimbrite complexes.

Figure 23: Ba/La versus U/La ratios of representative ignimbrite samples from the Livichuco and Los Frailes ignimbrite complexes.

high silica and low La/Ta ratios in Figure 22; the presence of Ta- and Ba-bearing phases at higher percent silica may be responsible for this trend. As seen in Figure 23, most samples fall near a U/La ratio of 0.1; however, outliers with much higher uranium content are present. In general, samples with anomalously high uranium content tend to be rich in barium as well, reflecting the similar solubilities of the ions under reduced conditions.

Discussion

The mineralogical and geochemical data from Los Frailes recount a clear history of melt creation and evolution, from production of melt at the base of the crust through transport, fractionation, and eruption at the surface. Extreme depletion of heavy rare earth elements demonstrates the presence of garnet in the restitic assemblage, whereas enrichment of light rare earths records melt evolution and fractionation. As is well known, the stability field of garnet in the crust necessitates that for garnet to be present in the restitic assemblage, fractionation must occur at high pressures, corresponding to the lower levels of a thick crust. Crustal thicknesses beneath the Frailes region are considered to be ~65 km based on seismological imaging (Beck et al., 1996; Yuan et al., 2002; McGlashan et al., 2008) beneath the Frailes complex. At the same time, the mineral assemblage of the Frailes samples, including plagioclase and cordierite, records low pressures – less than 450 MPa for cordierite-bearing samples, corresponding to depths in the less than 14 km in the mid to upper crust (Figure 24). Consequently, it can be reasonably concluded that the Frailes magmas underwent two periods of ponding or storage at distinct depths: first, at the base of the crust, as mantle-derived melts ponded at the base of the crust, fractionating a garnet-bearing restitic assemblage; and second, at

Figure 24: Lithospheric-scale diagrammatic cross-section of the Frailes region.
Adapted from Kay et al., submitted.

mid to upper crustal depths, as the ascending magma accumulated and further fractionated in crustal magma chambers.

Geochemical data also indirectly shed light on the age of the central Frailes Meseta. Sample PT-11 was collected from the same location as Barke et al. (2007) sample G1, dated by Ar-Ar techniques on biotite at 2.24 ± 0.09 Ma (See Figure 5). As seen in Table 11, INAA data show that the samples from the dated locality falls within the range of compositions seen in Luedke's (1997) samples from the south of the main ignimbrite ~40 km away (Figure 3), consistent with the interpretation that this age is representative of the whole of the Frailes Meseta ignimbrite. This, combined with a yet younger biotite Ar/Ar age of 1.86 ± 0.09 Ma recorded by Barke et al. (2007) on sample YURb approximately 60 km to the south (Figure 5), is strong evidence for an ~2 Ma age for the central Frailes volcanics. Due to the size of the Frailes meseta, a reassessment of the age of this massif significantly changes the eruptive history of the complex: with the

main meseta covering an area of roughly 3600 km², it makes up roughly half of the Frailes complex and involves the eruption of a massive amount of volcanic material in a short time span, requiring a very large input of heat to the crust at this time.

If the central Frailes Meseta of the ignimbrite complex is indeed of ~2 Ma provenance, a more coherent picture of volcanism at the Frailes complex begins to take form. Recent volcanism, the current-day presence of crustal and mantle low-velocity anomalies, and steep rare-earth fractionation from a high-pressure resititic assemblage are all consistent with a history of delamination-induced magmatism. This process, as detailed in the context of the Altiplano-Puna plateau by Kay et al. (1994) and Kay and Coira (2009), is triggered by foundering of high-density material from the base of orogenically thickened crust. Influx of hot asthenospheric mantle to fill the place of the foundered mass creates the mantle low-velocity anomaly observed in the geophysical images of Myers et al. (1998) and Beck and Zandt (2002) (Figure 4); decompression melting of the asthenosphere produces mantle-derived basalt, which ponds at the base of the crust, producing the garnet fractionation seen in the rare earth element ratios; and the large volume further of basalt produced by such a process provides way to produce the huge volumes of magma erupted at the surface, after further evolution of the melt and interaction with the crust (Figure 24).

Conclusion

The Frailes ignimbrite complex fills a gap in the understanding of large-volume ignimbrites of the Altiplano-Puna plateau. As the largest and most prominent ignimbrite of the Andean Central Volcanic Zone, the complex supplies insight into the processes of large-volume silicic melt formation in a back-arc setting. Trace element analyses

demonstrate the presence of garnet in a deep-crustal, high-pressure restitic assemblage, while the presence of cordierite in the phenocryst assemblage indicates crystallization at low pressure. The geochemical data from the complex suggest a history of melt formation at depth in the upper mantle, the formation of residual garnet at the base of the crust, and evolution and crystallization of the melt at upper crustal levels. In a back-arc setting, these characteristics along with the large volume of the Frailes ignimbrite and geochemical and geochronological data are most compatible with recent delamination and delamination-induced magmatism.

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Appendix

<i>Appendix I: Standards used for neutron activation analysis.</i>						
	Known values			This study (run 1)		
	WBD	PAL	SIT	WBD	PAL	SIT
FeO	9.59	10.15	4.34	9.59	10.15	4.34
Na₂O	0.11	2.07	5.30	0.1	2.06	5.30
La	82.9	10.5	14.6	82.9	10.2	13.7
Ce	158.0	23.6	33.8	158.0	23.9	33.2
Nd	58.0	13.0	18.3	58.0	12.8	18.7
Sm	8.23	3.42	4.68	8.23	39.55	4.69
Eu	2.14	1.07	1.09	2.14	1.11	1.03
Tb	0.620	0.67	0.760	0.617	0.67	0.732
Yb	0.610	2.18	3.42	0.673	2.18	3.48
Lu	0.085	0.3	0.500	0.085	0.3	0.501
Sr		183	255	478	202	255
Ba	1280	185	935	1159	182	935
Cs	1.81	2.19	1.25	1.81	2.06	1.43
U	2.35	0.497	2.58	2.35	0.479	2.52
Th	11.00	2.07	5.26	11.00	1.99	5.11
Hf	3.92	2.56	4.61	3.92	2.66	4.7
Ta	8.30	0.65	0.54	8.30	0.65	0.61
Sc	20.2	37.5	9.25	20.2	39.5	9.6
Cr	1910	314	2	1910	309	1
Ni	991	89	2	991	89	6
Co	88	53	36	88	53	26

<i>Appendix II: standards used in electron probe microanalysis.</i>					
Known Values					
	Px1	S-15	A 99	JdF	Kak
SiO₂	53.94	39.69	50.94	50.81	40.37
TiO₂	0.26	4.27	4.06	1.85	4.72
Al₂O₃	0.66	14.37	12.49	14.06	14.90
FeO	2.93	10.74	13.32	11.83	10.92
MnO	0.07	0.09	0.19	0.22	0.09
MgO	16.93	13.28	5.08	6.71	12.80
CaO	24.55	11.58	9.30	11.12	10.30
Na₂O	0.24	2.12	2.66	2.62	2.60
K₂O	0.01	1.96	0.82	0.19	2.05
Total	99.59	98.10	98.86	99.41	98.75
This study					
	Px1	S-15	A 99	JdF	Kak
SiO₂	54.55	40.05	51.1	50.36	40.24
TiO₂	0.23	4.41	4.06	1.85	4.85
Al₂O₃	0.66	14.56	12.45	14.07	14.24
FeO	2.87	9.92	13.43	11.76	10.79
MnO	0.07	0.08	0.18	0.19	0.09
MgO	16.99	13.53	5.06	6.87	12.64
CaO	24.92	11.55	9.26	11.02	10.15
Na₂O	0.22	2.37	2.91	2.85	2.65
K₂O	0	2.1	0.84	0.19	2.09
Total	100.51	98.56	99.31	99.17	97.73

Appendix III: Key to reactions shown in Figure 12.

- 1): (2)FSP OPX CORD q H₂O = (2)FSP OPX CORD trd H₂O
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- 27): (2)FSP GARNET OPX CORD LIQt_c q = (2)FSP OPX CORD LIQt_c q
- 28): (2)FSP GARNET BIO q H₂O = (2)FSP GARNET OPX BIO q H₂O
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- 41): FSP LIQt_c = FSP LIQt_c H₂O
- 42): FSP LIQt_c H₂O = LIQt_c H₂O
- 43): LIQt_c = LIQt_c H₂O
- 44): (2)FSP GARNET OPX CORD LIQt_c q H₂O = (2)FSP OPX CORD LIQt_c q H₂O
- 45): (2)FSP GARNET BIO q H₂O = (2)FSP GARNET OPX BIO CORD q H₂O
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- 47): (2)FSP OPX CORD LIQt_c q H₂O = (2)FSP OPX CORD LIQt_c trd H₂O
- 48): (2)FSP GARNET OPX CORD q H₂O = (2)FSP OPX CORD LIQt_c q H₂O
- 49): (2)FSP OPX CORD LIQt_c q H₂O = FSP OPX CORD LIQt_c q