Petrology and Oxygen Isotope Geochemistry of the Pucón Ignimbrite - Southern Andean Volcanic Zone, Chile: Implications for Genesis of Mafic Ignimbrites

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Introduction: Although mafic components of dominantly intermediate to silicic ignimbrites are rather common, voluminous, dominantly mafic ignimbrites are rare (e.g., Smith, 1979; cf. Freundt and Schmincke, 1995). Volcán Villarrica, the most active composite volcano in South America, located in the Southern Andean Volcanic Zone (SAVZ, López-Escobar and Moreno, 1994*a*), has produced two such ignimbrites, respectively the Licán and Pucón Ignimbrites, in the last 14,000 years (Clavero, 1996). The two ignimbrites are low-Si andesite and basaltic-andesite to low-Si andesite, respectively, the former about twice as voluminous as the later (10 and 5 km^3). Eruption of the ignimbrites produced calderas respectively 5 and 2 km in diameter (Moreno, 1995; Clavero, 1996). In addition to its mafic bulk composition, the Pucón Ignimbrite (PI) is also distinguished by numerous xenolithic fragments among and also within magmatic pyroclasts. Many of these are fragments of granitoid rocks. Volcán Villarrica has also produced numerous smaller mafic ignimbrites and pyroclastic surge deposits, as well as dominantly basaltic fallout and lava flows (López-Escobar and Moreno, 1994; Moreno, 1995; Clavero, 1996; Hickey-Vargas et al., 1989; Tormey et al., 1991).

Reasons for the unusual style of mafic explosive activity at Volcán Villarrica are unclear. Clavero (1996), based upon an exemplary thesis-study of the physical volcanology and petrology of the PI, suggests it formed in response to a sequence of events beginning with injection of a shallow basaltic andesite magma chamber by hotter basaltic magma. In his model mixing and heat transfer between the two magmas initiated a violent Strombolian eruption that destabilized the chamber causing infiltration of large amounts of meteoric-water saturated country rocks. The Pucón Ignimbrite formed in response to subsequent phreatomagmatic interactions. In contrast, López-Escobar and Moreno (1994) infer on geochemical grounds that volatiles leading to the explosive eruptions were originally dissolved within in the pre-PI magma. They document an important repeating pattern between chemically evolved compositions and explosive eruptions at Volcán Villarrica that is particularly prominent in the cases of the two largest ignimbrite-forming eruptions. They infer that the precursor magma chamber became compositionally stratified through time, with the most evolved, volatile rich magma accumulating towards the top of the chambers, and culminating in voluminous mafic ignimbrite eruptions.

In this study we characterize petrologic, geochemical and oxygen isotope characteristics of magmatic pyroclasts from the Pucón Ignimbrite, and one accidental granitoid lithic, extending on the previous work by Clavero (1996) and López-Escobar and Moreno (1995). We critically evaluate previous models, and combine ours and previous data to constrain and develop an alternate petrogenetic model of magmatic evolution of the pre-PI magma chamber, focusing on possible sources of volatiles derived from country rocks and from processes operating within the original magma chamber. We also document the occurrence of a previously unidentified, dacitic, magmatic enclave component of the ignimbrite.

Petrology and Geochemistry: Magmatic pyroclasts are dominantly black, moderately to weakly porphyritic (~10%, calculated vesicle-free), highly vesicular bread-crust bombs and more massive, dense bombs and angular blocks of basaltic andesite to low-Si andesite (BA) (53.0 to 57.5% SiO_2). Rare samples are compositionally bimodal, consisting of a dominant basaltic-andesite component and a proportionately minor dacitic “magmatic enclave” component (DAC).

BA pyroclasts are seriate porphyritic, consisting of euhedral to subhedral phenocrysts of plagioclase (An_{52-92}, mostly An_{70-90}) > clinopyroxene ($Wo_{39-44}En_{42-48}Fs_{12-18}$), olivine ($Fo_{80-72}$, Fa_{16-28}, La_3), and trace Mg-Al-chromite in a black, tachyllitic matrix. Most plagioclase phenocrysts are moderately normal and oscillatory zoned, but some have prominent reversely zoned rims, as previously noted by Clavero (1996). Rare plagioclase grains contain inclusions of chromite. Pyroxenes are aluminian magnesium-rich augite where Al_2O_3 is dominantly in the form of CaTs component (3.6 - 7.2%) and also exhibit normal and reverse types of zoning. They rarely contain inclusions of plagioclase. Olivine grains exhibit little or no systematic zoning or mineral inclusions. All phenocryst types contain tachyllitic glass inclusions.

DAC occurs as dark gray, wispy to irregular pod-like enclaves up to a few centimeters across in a matrix of black basaltic-andesite. Microphenocrysts of plagioclase (An_{57-69}), clinopyroxene ($Wo_{34-41}En_{44-48}Fs_{15-21}$), olivine ($Fo_{72-68}Fa_{24-31}La_{3-6}$), and magnetite-ulvospinel$_{ss}$ ($Mt_{44}Usp_{44}Sp_{12}$), and xenocrysts of BA-type-plagioclase, occur in a brown (in thin section) hypohaline matrix. Interestingly, one large euhedral plagioclase xenocryst has the most calcic average composition, and is also slightly reversely zoned (from An_{90} to An_{92}).

Plagioclase micophenocrysts in DAC are slightly more sodic and potassic than in BAS, plotting along a smooth extension of the trend defined by BAS feldspars in the system Ab-An-Or. Olivine is enriched in Fa-component and Ni relative to BAS. Pyroxenes in DAC are less calcic than in BAS, and also moderately aluminous, containing 2.8 to 3.5% Al_2O_3, again dominantly in the form of CaTs component. The microphenocrysts exhibit little or no zoning.

EMP analyses of nonvolatile constituents of the tachyllitic matrix of BA pyroclasts overlap bulk rock compositions, albeit shifted towards more evolved compositions (56.5 to 59.0% SiO_2). Analyses of crystallite-clouded “glass” inclusions in phenocrysts are similar for nonvolatile constituents. BAS chlorine contents vary from 300 to 1800 ppm, increase systematically with silica content, and are about 700 ppm higher in glass inclusions than in matrix. DAC chlorine content is roughly constant at 1000 ppm. EMP totals are essentially identical for matrix and inclusion analyses, suggesting that the H_2O content of the inclusions was low (probably less than 1%). These data are preliminary and we hope to make direct analyses of H_2O in homogenized inclusions in the future.

BA has trace-element characteristics that overlap those of Volcán Villarrica in general, overlap with other mafic composite volcanoes of the SAVZ (e.g., Tormey et al., 1991), and that distinguish volcanic rocks at Volcán Villarrica from more eastern parts of the Villarrica-Lanín chain (e.g., Hickey-Vargas et al., 1989). For example the rocks have high Ba/La (28-31), low La/Lu (2.3 to 3.5), no Eu-anomaly, low Sr (430-460) and Sc (29-33). Some elements which normally express incompatible behavior with respect to pl + cpx + ol (e.g., Ba and LREE) correlate positively with silica and negatively with Mg#, whereas compatible elements (e.g., Cr and Sr) correlate in the reverse manner. However, others exhibit no significant covariation (e.g., Zr, Sc, Cs, Co).

Many magmatic pyroclasts contain xenoliths of accessory phyric and aphyric basalt and, more prominently, medium grained, equigranular granodiorite-granite, and rare gneiss. Such fragments are also common in the matrix of the pyroclastic flow, however the high abundance of such fragments, and their associated xenocrysts, within magmatic pyroclasts is unusual. We have not systematically analyzed the abundance of xenoliths. However they are present in almost all pyroclasts, and often make up from 1 to 10% of the volume of the magmatic fragments.

Granitic xenoliths commonly exhibit evidence of partial melting, such as finger-print textured feldspars, minor intergranular glass, and in some cases they are ductilly-sheared and partially dissaggregated. Many partially melted granodiorite xenoliths are surrounded by envelopes of highly vesiculated scoria. More strongly partially melted samples are partially fragmented by expansion of vesicles within glassy components of their interiors.

We have analyzed one characteristic sample of granitoid rock from the ignimbrite for major and trace elements and $\delta^{18}O$. It is a medium grained, equigranular granodiorite containing 73% SiO_2 and overlaps compositionally with the most evolved parts of the northern Patagonian Batholith.

Oxygen Isotopes: We analyzed separates of microcrystalline to tachyllitic matrix material from two BA pyroclasts, one containing a weakly palagonitized rind and abundant, partially melted granitoid material (sample number 3240001C), and another (3240001B) which exhibits no evidence of palagonitization and only minor amounts of xenoliths. We also analyzed quartz separates from a representative granodiorite lithic (4280002).

Two discrete volumes from the buff-colored, weakly palagonitized rind of the sample 3240001C yield $\delta^{18}O$ values of +6.4 and +5.9‰. Samples of microcrystalline, black matrix material from the interior of the xenolith-rich scoria yield $\delta^{18}O$ of +5.8 and +5.2‰. Tachyllitic matrix from the nonpalagonitized sample 3240001B yield $\delta^{18}O$ of about +5.2‰. We infer an original magma (liquid component) $\delta^{18}O$ of between +5.2 and +5.8‰. Higher values are attributed to palagonitization (Cuadros et al., 1999). Quartz from the granite (4280002) yields a $\delta^{18}O$ of +6.1‰ corresponding to an estimated bulk-rock $\delta^{18}O$ of +5.7‰ (fractionation factors from Zheng, 1993).

These preliminary oxygen isotope data suggest limited meteoric water interaction with the pre-PI magma. Assuming an initial magma $\delta^{18}O$ of +5.8‰ - the highest end of the range for isotopically primitive effusive mafic rocks in the Villarrica area (Déruelle et al., 1983; Hickey-Vargas et al., 1989), then the amount of meteoric water needed to shift the composition down to +5.2‰ (the lowest observed value in our samples) is 4.0 to 2.4%, assuming meteoric water $\delta^{18}O$ values of -10 and -20‰, respectively - the probable range for meteoric water at Volcán Villarrica, corrected for an elevation of 1-2 km (IAEA, 2001). Thus, at a maximum, we calculate 4% meteoric water could have been present in the pre-PI magma.

Water derived by dehydration of granitic xenoliths comparable to sample 4280002 would have a value of ~ +5‰. Assuming that our quartz results from granite are representative of wall rock xenoliths, little effect on the parent magma $\delta^{18}O$ would occur by granite xenolith assimilation, and derivation of nearly all water in pre-PI magma from these xenoliths is permissable from our results. Other sources of water allowed by the oxygen isotope data include those associated with intra-magma chamber diffusion or differentiation, or by volatiles transferred during mixing with additional hydrous magmas.

Summary and Discussion:

Salient features of the unusually voluminous mafic Pucón Ignimbrite include: 1. a chemically evolved basaltic andesite (BA) composition; 2. two populations of phenocrysts; 3. dacitic (DAC) magmatic enclaves; 4. abundant partially melted granitoid xenoliths; 5. $\delta^{18}O$ that is comparable to or perhaps slightly lighter than primitive magmas.

Clavero (1996) inferred that bimodal plagioclase compositions resulted from injection of a dominantly BA magma chamber by basalt. However there is no direct evidence for basalt mixing with the BA (i.e. basaltic enclaves); in contrast some BA pyroclasts contain rare dacitic magmatic enclaves. High An-contents were more likely the product of variable water content in the source magma (Sisson and Grove, 1993; Sisson and Layne, 1993), rather than differences in bulk magma composition. López-Escobar and Moreno (1994) also argued for higher water contents based upon high Al_2O_3/CaO of the magma (and its effect upon pyroxene stability).

Additionally, Clavero argues that ingestion of large volumes of meteoric water into the top of the magma chamber initiated a phreatomagmatic process leading to formation of pyroclastic flows. Phreatomagmatic interaction of the large magnitude suggested by Clavero (1996) seems physically implausible to us, and if it had occurred we would expect an even larger proportion of accessory (as opposed to accidental) xenoliths, particularly in stratigraphically lower parts of the ignimbrite.

López-Escobar and Moreno (1994) argue that high Metal-Oxide/MgO and Al_2O_3/CaO ratios originated from hydrous fractional crystallization within the pre-PI magma chamber. Systematic declines in these ratios, for explosively erupted magmas occurred for a period of several hundred years after the PI-forming eruption are inferred to reflect an original vertical zonation of the source chamber. Volatiles, independent of their source, were probably concentrated towards the top of the chamber.

Our mass-balance calculations, based upon observed phenocryst compositions and bulk rock chemistries, support the plausibility of fractional crystallization over the range of 53 to 57% SiO2 (~25% fractional crystallization of pl > ol > cpx). In contrast we could not obtain acceptable models for production of DAC. Major element characteristics of the dacite also exclude formation by assimilation of Patagonian-Batholith-type country rocks into plausible BA or basaltic parent magma. DAC enclaves apparently originated from another parent rock type, or possibly from a similar parent at deeper crustal levels.

Assuming that the pre-PI magma chamber was initially vertically zoned, as suggested by López-Escobar and Moreno (1994), what inhibited convective mixing, and from where and how did the volatiles originate? We speculate that most of the original chamber was convecting, but that upper portions of the chamber became density-stabilized and stagnant because of buoyancy originating from increases in dissolved water content of up to 6 wt.%. We propose that significant sources of water were from dehydration of stoped wall-rock fragments (including connate and possibly also meteoric water), and also from diffusive transfer from deeper convecting magma. Eruption of the ignimbrite may have occurred when P_{H2O} exceeded $P_{Lithostatic}$, or when dacitic magma was injected into the chamber.

Acknowledgments:

McCurry acknowledges funding from ISU FRC Grant #812. Isotopic work was conducted at the University of Southern California Stable Isotope Lab, under direction of Jean Morrison. We thank Lisa Calder (OVDAS), Jeff Witter (Univ. Washington), and Marcelo San Martín (PolyTour) for logistical help and for many stimulating discussions about the evolution of Volcán Villarrica. Jose Luis Palma (U. de Chile) helped with the collection of some samples. McCurry also thanks geology students, faculty, and administrative staff at Universidad de Chile, Santiago, for their kind hospitality, support for the project, and many useful interactions.

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