

## Chemical stratigraphy of lavas from the Casitas Shield, Descabezado Grande-cerro Azul volcanic complex, Chilean Andes

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The Descabezado Grande-Cerro Azul (DGCA) volcanic complex is located at approximately 35.4 degrees S in the Chilean Andes. The complex is characterized by two large latest Pliocene to early Holocene volcanic edifices and many smaller vents rising above a plateau comprising lavas of the Casitas Shield. This plateau has been deeply encised, revealing stacks of lava flows exposed along the valley walls. More than 100 lava flows were sampled from eight vertical stratigraphic sections and have been analyzed for complete major and trace element abundances. These were compiled in a composite chemical stratigraphy, with at least twelve eruptive episodes identified by field observations and confirmed by nine  $^{40}\text{Ar}/^{39}\text{Ar}$  dates. The second lowest flow in the composite section yielded an age of  $0.51 \pm 0.05$  Ma, and the majority of flows in the composite section erupted in the range .47-.43 Ma. These flows are primarily basalts/basaltic andesites characterized by generally high incompatible element abundances, particularly Sr (800-1080 ppm), and rather low Ni and Cr. The composite chemical stratigraphy shows changes in lava compositions reflecting different parental magmas and the secular dominance of different petrogenetic processes. In general, lavas become more evolved through episodes 1-5 during periods of low eruptive rates. Lavas are more compositionally similar during episodes 6-8, and sparsely olivine-phyric basalts erupted during episode 9 (0.2 Ma younger), including lavas that are among the most primitive in the SVZ with high Cr (254-267 ppm) and MgO (8-8.3%), and low LILE,  $\text{P}^{2}\text{O}^5$ ,  $\text{Al}^{2}\text{O}^3$ ,  $\text{Na}^2\text{O}$ , and  $\text{K}^2\text{O}$ . Lavas erupted during episodes 10 and 11 become progressively more evolved. The shield is capped by aphanitic basalts, with the youngest age of  $0.10 \pm 0.09$  Ma.

Strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) ratios increase from 0.703578 near the bottom of the composite section to 0.704033 in the upper flows, generally mirroring a trend towards decreasing Sr abundances with time. Nd and Pb isotope data are less systematic in variation, with  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios ranging from 0.512762-0.512811 in a generally negative correlation with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Several cross-cutting basaltic dikes are characterized by high MgO (11.7%), Ni (226 ppm) and Cr (776 ppm) contents, very low Nb, Zr, Y, Rb, and Ba, and the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.703533).

## Solubility of andradite in $\text{H}_2\text{O}$ -NaCl at 800°C, 1 GPa, and the origin of grandite in high-grade calc-silicates

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The solubility of andradite garnet was determined at 800°C and 10 kbar in a solution of 10 mol% NaCl and 90 mol%  $\text{H}_2\text{O}$ . Experiments were carried out with pure natural wollastonite and reagent hematite or natural specular hematite (~1 wt %  $\text{TiO}_2$ ). All experiments were performed with  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  or  $\text{Mn}_2\text{O}_3$ - $\text{Mn}_3\text{O}_4$   $f\text{O}_2$  buffers in a piston-cylinder apparatus with NaCl-graphite furnaces and 1-3 day run times [1-4]. Andradite solubility was determined by bracketing the fluid composition at garnet saturation. Andradite dissolves incongruently to hematite and fluid with  $\text{CaSiO}_3$  molality ( $m_{\text{CS}}$ ) of  $0.0838 \pm 0.0015$  (1 $\sigma$ ) for the reagent hematite and both buffers. Slightly higher  $m_{\text{CS}}$  of  $0.0895 \pm 0.0005$  for the natural hematite and Mn-oxide  $f\text{O}_2$  buffer is likely due to incomplete equilibration and/or ~9 mol% Ti in run-product andradite. Approximate Fe molality is at least ten times lower than  $m_{\text{CS}}$ . Quenched fluids had pH=11-12.  $\text{Fe}_2\text{O}_3$  solubility in andradite-saturated  $\text{H}_2\text{O}_{90}$ -NaCl<sub>10</sub> is lower than that of  $\text{Al}_2\text{O}_3$  at grossular saturation at the same  $P$ ,  $T$  and fluid composition [5]. The results test a model of  $\text{CaSiO}_3$  dissolution in NaCl solutions to three dominant aqueous species:  $\text{CaCl}^+$ ,  $\text{OH}^-$  and  $\text{H}_3\text{NaSiO}_4$ . Combination of the  $\text{CaSiO}_3$  molality at andradite saturation with wollastonite solubility at the same conditions ( $0.1253 \pm 0.0047$  molal [4]) leads to  $\Delta G$ , for  $3\text{wo}+\text{hem}=\text{and}$  of  $-32.21 \pm 2.45$  kJ at 800°C, 1 GPa. The good agreement between this value and that derived from previous studies supports the dissolution model of  $\text{CaSiO}_3$  in NaCl solutions. The low solubility of the  $\text{Fe}_2\text{O}_3$  component of andradite contrasts with the high solubility of magnetite and of Fe in pelitic and granitic mineral assemblages measured in acidic chloride solutions by previous workers at lower  $P$  and  $T$ . The results imply that  $\text{Fe}_2\text{O}_3$  is conserved during metasomatic processes affecting calc-silicates at high metamorphic grades.

[1] Manning & Boettcher (1994) *Am. Min.* **79**, 1153-1158.

[2] Manning (1994) *GCA* **58**, 4831-4839. [3] Newton & Manning (2005) *J. Pet.* **46**, 701-716. [4] Newton & Manning (2006) *GCA* **70**, 5571-558. [5] Newton & Manning (2007) *GCA* **71**, 5191-5202.