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Melt inclusions in silicate lavas and iron-oxide tephra of the El Laco volcano, Chile.

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Introduction

The El Laco volcano of northern Chile is widely known for its controversial iron ore deposits, which some researchers regard as examples of iron oxide eruptions but others regard as hydrothermal deposits replacing pre-existing silicate volcanic rocks [1, 2, 3, 4, 5]. Lava flows and pyroclastic deposits with textures and structures typical of ordinary silicate eruption products are composed almost entirely of magnetite and hematite. Field relations and geochemistry provide convincing evidence that the bulk of the El Laco ores formed from the eruption and shallow intrusion of iron-rich magmas as was originally proposed when they were first described [6]. Given that the melting temperature of the iron-oxide ores in their present state is in excess of 1500°C, the original magma must have contained additional components that were lost during or after eruption. The composition of the magma responsible for the El Laco iron-oxide eruptions is unknown, but judging from the vesicular texture of the ore lavas, and the abundant pyroclastic ore, volatiles were probably an important component.



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Melt inclusions in El Laco silicate lavas

Although famous for unusual Fe-oxide lavas, the El Laco volcano is dominated by silicate lavas that predate, postdate, and are interbedded with the Fe-ore lavas. Although extensive hydrothermal alteration is common at El Laco, many of the silicate lavas, including some in contact with the iron ore, are very fresh. The surface lavas comprise two-pyroxene, biotite-bearing andesites and dacites. Plagioclase and pyroxene phenocrysts within these lavas contain multi-phase inclusions in which rounded iron-oxide blebs with abundant apatite crystals are contained within silica-rich glass. The iron-oxide blebs consist of a felted intergrowth of submicron crystals with a bulk composition dominated by Fe_2O_3 , FeO, and TiO_2 with minor Mg, Al, P, and K. The composition of the iron-oxide blebs is distinct from that of magnetite microphenocrysts in the host lava with lower Fe and Al, and higher Ti, Mg, K, and P in the blebs. The silicate host glass has the composition of a high-Si, high-K rhyolite, but contains less P than the iron-oxide blebs. Apatite crystals associated with the inclusions have compositions similar to the apatite found associated with the El Laco Fe-ores. The variable Fe-bleb/Si-glass host ratios suggest that separation into two phases occurred prior to trapping the inclusions.

Melt inclusions in El Laco Fe-oxide tephra

Associated with the El Laco Fe-oxide lavas are bedded, size-sorted, and in most places, completely unconsolidated layers of Fe-oxide ash and lapilli. The ash component of the tephra is composed of magnetite and hematite crystals and polycrystalline aggregates with morphologies that include euhedral Fe-oxide crystals and crystal fragments as well as irregularly shaped polycrystalline Fe-oxide aggregates. Within the layers are a number of blocks and bombs some of which appear to sit in bomb sags. Also common are spheroidal nodules or lumps of orange, crystallized (largely amorphous) diadochite [$\text{Fe}^{3+}_2(\text{PO}_4)(\text{SO}_4)(\text{OH})\cdot 6(\text{H}_2\text{O})$]. The lumps have rounded upper surfaces and lower surfaces that conform to the fragmental layer on which they lie, suggesting that if they were deposited during eruption, they were still deformable (molten?) when they landed. Examination of Fe-oxide ash, lapilli, and bombs in polished mounts prepared in oil to prevent loss of water-soluble minerals reveals two melt compositions in apparent textural equilibrium, with Fe-oxide. Many of the fragments contain what appear to be Fe-P-S-rich melt inclusions. Most oxide crystals and aggregates display fenestral textures and locally highly convoluted margins. Scanning electron microscopy (SEM) supplemented by energy dispersive X-ray spectrometry (EDS) of the grain mounts show that the re-entrant cavities along grain margins are partially or completely filled by aggregates of Fe-phosphate, Fe-oxide, silica, and monazite. Ovoid cavities within some of the oxide ash particles are wholly or partially occupied by the same polymineralic assemblage, but also include domains interpreted to be finely crystallized melt with large voids interpreted to be trapped gas bubbles. EDS analysis of domains interpreted as quenched melt contain, in



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approximately descending order of abundance, Fe, P, Si, S, K, and Cl, with subsidiary and variable contents of Ti, Al, Ca, Mg, and light rare earths. A polished section through a Fe-oxide bomb contains a second liquid composition in apparent equilibrium with crystalline Fe-oxide. Interstitial areas and thin coatings on oxide-grain boundaries consist of K-rich, ferro-basaltic, silicate glass with high P and S. This glass represents a much earlier fractionation stage than the rhyolite glass trapped in silicate phenocrysts described above, but both glasses have unusually high K/Na.

Discussion

The multi-phase inclusions trapped in phenocrysts in andesitic and dacitic El Laco lavas appear to represent an immiscible liquid pair in which an apatite-rich, nelsonitic liquid is in equilibrium with high-silica rhyolite. This late stage immiscibility is unlikely to be the source of the El Laco Fe-oxide lavas. The immiscibility occurs too late in the differentiation history ($\text{SiO}_2 = 80\%$) to allow effective two-liquid physical separation, and is unlikely to produce the volume of Fe-rich liquids observed in the El Laco deposit. In addition, the El Laco ores contain less than 1% Ti and P, in comparison to the trapped Fe-rich blebs with $>20\%$ Ti and abundant apatite. This late stage immiscibility, however, suggests that the El Laco silicate fractionation trend is differentiating towards a two-liquid immiscibility field. Early-stage immiscibility in the magmatic system, triggered by the assimilation of S-rich, altered crust could have resulted in Ti-poor, Fe-rich liquids in equilibrium with alkali-rich silicate magma much earlier in the differentiation history ($\text{SiO}_2 = 46\%$) which would allow for effective physical separation of the iron-rich melt. Previous studies have demonstrated that Fe-rich immiscible liquids with significant S contents will be very low in Ti [7]. Experimental studies suggest that a Fe- PO_4 - SO_4 liquid is immiscible with a silicate liquid at 900°C , 1.4 kbars, in P- and S-saturated andesite [8] and in experimental K-Fe-Si-Al-O liquids doped with P, F, Cl, S, and H_2O over a range of temperatures [9]. We suggest that the magma from which the El Laco magnetite and hematite ores crystallized was an iron phosphate melt with important amounts of SiO_2 , K_2O , P_2O_5 and several weight % sulfate, as well as other dissolved volatiles. Fe-phosphate melts have received much attention in recent years as matrices for nuclear waste storage due to their tremendous capacity to dissolve other oxide components (including Fe_2O_3) while remaining liquid to relatively low temperatures.

Conclusions

The Fe-oxide lavas and Fe-oxide tephra at El Laco appear to have crystallized in equilibrium with two distinct liquid compositions, one liquid similar to that of the Fe-P-S-O melt inclusions trapped in the tephra, and a second K-rich, silicate liquid similar to that observed interstitially in magnetite volcanic bombs. Early-stage immiscibility in the magmatic system, triggered by the assimilation of S-rich rocks resulted in Ti-poor, Fe-P-



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S-rich liquids in equilibrium with alkali-rich silicate magma. Eruptive volatile loss left an assemblage dominated by magnetite and hematite. There is very little phosphorous or sulfur left in the massive lava flows, despite their abundance in the tephra deposits, suggesting that some process during slow cooling of the lavas must have efficiently removed these components.

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