

Origin of Magnetite “Lava Flows” at El Laco Volcano, Chile

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Introduction:

Iron ore bodies at El Laco volcano have the appearance of dikes, lava flows, scoria, ash, and other pyroclastics and are composed of almost pure magnetite. Although an origin as Fe-oxide magmas has been proposed by many investigators [1], others have suggested an origin as hydrothermal or metasomatic replacement deposits [2, 3].

Magnetite Composition:

Excluding samples with obvious minor pyroxene or apatite, magnetite ore samples are 95 to 97% iron oxide with: 0.6-1.5% SiO₂; 0.01-0.03% TiO₂; 0.15-0.69% Al₂O₃; 0.002-0.039% MnO; 0.09-1.20% MgO; 0.18-1.18% CaO; 0.03-0.38% Na₂O; 0.05-0.21% K₂O; and 0.8-2.5% P₂O₅. Trace element abundances in the ore average: 90 ppm Ba; 96 ppm Co; 26 ppm Cr; 212 ppm Ni; 9 ppm Sc; 147 ppm Sr; 793 ppm V; 105 ppm Zn; 5 ppm Zr; and 24 ppm Y. Relative to associated unaltered andesites, the ores are enriched (ores/andesites) in Ni (7.7), P (7.3), V (5.3), Cu (2.6), and Zn (1.6), and depleted in Cr (0.7), Sc (0.6), Sr (0.3), Ba (0.2), Mn (0.1), Zr (0.03), and Ti (0.02). The ores are enriched in REEs (La 150X and Yb 14X chondritic) with steep LREE slopes ($L_{a_N}/Sm_N = 8.1$), relatively flat HREE slopes ($Sm_N/Yb_N = 1.7$), middle REE depletions ($Sm/Sm^* = 0.23$), and negative Eu anomalies ($Eu/Eu^* = 0.5$). In contrast, associated unaltered andesites have similar abundances (La 145X and Yb 12X chondritic) but less steep LREE ($L_{a_N}/Sm_N = 4.6$), steeper HREE ($Sm_N/Yb_N = 2.7$), less middle REE depletion ($Sm/Sm^* = 0.39$), and less Eu depletion ($Eu/Eu^* = 0.65$). Fe isotopes in the ores ($\delta^{56} = 0.52-0.90\text{‰}$) are elevated relative to fumarolic and vein deposits ($\delta^{56} = 0.23-0.29\text{‰}$) or andesites ($\delta^{56} = 0.49\text{‰}$) at El Laco. In a single ore sample measured, Re = 460 ppt, Os = 23 ppt, $^{187}\text{Os}/^{188}\text{Os}_{\text{measured}} = 0.52$, $^{187}\text{Re}/^{188}\text{Os}_{\text{measured}} = 2$, and $^{187}\text{Os}/^{188}\text{Os}_{\text{initial}} = 0.51$ indicates that there is a large contribution of Os from the continental crust.

Conclusions:

The high abundance of some relatively immobile elements (V, Ni, Y, and REEs) and the low abundance of other immobile elements (Zr, Ti, Cr, and Sc) is inconsistent with a hydrothermal or replacement origin for the ores. $\delta^{56}\text{Fe}$ in the ores is systematically higher than $\delta^{56}\text{Fe}$ in hydrothermal magnetite. Immiscibility between silicate magma and volatile-rich Fe-P-S-O magma, possibly initiated by crustal contamination, is compatible with all of the data.

[1] Naslund et al. (2002) *Hydrothermal iron-oxide copper-gold & related deposits* **Volume 2**, 207-226. [2] Rhodes et al. (1999) *Soc. of Econ. Geol. Spec. Pub.* **Volume 7**, 299-351. [3] Sillitoe & Burrows (2002) *Economic Geology* **Volume 97**, 1101-1109.

Mudstone pore networks: characterization and flow modeling

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In geochemically active systems the pore network is arguably the most important physical characteristic of a rock because it provides pathways for reactive fluid flow and solute transport. The pore network is defined by an interface that advances and retreats with mineral precipitation and dissolution. These geochemical reactions can change important physical rock properties, such as interfacial roughness and area, and pore volume and connectivity, that in turn influence rates and mechanisms of future geochemical reactions and fluid flow. Despite their importance on geochemical behaviour of rocks, pore networks and their evolution with geochemical reaction are poorly understood. However, characterizing pore networks is not straightforward due to their dynamic nature and features at different length scales (nm to mm).

Problems associated with the characterization of pore networks are compounded in fine-grained rocks such as shales and mudstones that have a high percentage of nm scale pores. However, these rock types are increasingly important due to the role they play in unconventional natural gas production and geologic CO₂ storage. Small angle neutron scattering (SANS) is an ideal tool to study structural heterogeneities in porous materials on nanometer to micron length scales and complements other traditional techniques such as sorption, mercury intrusion porosimetry (MIP), or microscopy.

In this study we characterized the nm to mm scale pore network in samples from three different mudstone formations using SANS, MIP, BET gas adsorption techniques and focused ion beam scanning electron microscopy imaging. These formations all serve as seals for containment of CO₂ in prospective geologic storage sites. Porosity and surface area in pores < 700 nm diameter was measured with small angle neutron scattering. According to this data pores < 10 nm radius contribute 20-50% of the total porosity and > 80% of the total surface area of these mudstones. The total pore volume determined from small angle neutron scattering is higher than porosity determined from mercury intrusion porosity for most of the samples. The discrepancy between these measured porosities may be related to low pore connectivity or the inability of MIP to fully access the pore network due to pressure limitations of the method. A comparison of cumulative pore fractions determined from SANS and MIP suggests that < 30% of the total porosity is accessible through pore throats < 1 nm radius. At these length scales Fickian diffusion of solutes and Knudsen diffusion of gas become the dominant transport mechanisms.

These data demonstrate the importance of very small pores to the overall pore structure of the mudstones. To really understand pore scale processes we need to not only develop a fully realized view of what the pore network looks like at multiple length scales but also understand how different techniques provide windows into that view. Results from flow simulation using pore networks created from FIB-SEM data will be presented. These simulations will help determine the contribution of different types of flow mechanisms and will form the basis for reactive transport models of geochemical processes.

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