Chlorine Partitioning: The behavior of Cl in the presence of sulfide - silicate melts and aqueous fluid

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Can sulfide melts exsolve halogen rich fluids? Several ore deposits around the world (eg. Broken Hill, Stillwater, Sudbury and Bushveld) have occurrences of halogen-rich minerals in association with the ore. To help better understand these occurrences, piston cylinder experiments were performed to investigate the partitioning behavior of Cl between coexisting haplogranite and Pb-Fe-Zn-sulfide melts at 0.5 GPa pressure and 810ºC temperature.

In water undersaturated experiments where a Cl doped haplogranite glass was used as the silicate starting material, the Cl was found to partition strongly into the sulfide melt. Here Cl may be acting as a flux within the sulfide melt resulting in lowering its eutectic temperature. Not only is Cl dissolved in the sulfide melt, but as the sulfides crystallize the residual sulfide melt progressively enriches in Cl. In water saturated experiments where Cl was doped into the sulfides, Cl was noticeably absent from both quenched sulfide melt and silicate glass, suggesting strong partitioning into the coexisting aqueous fluid. The results indicate that the partitioning preference of Cl, when in equilibrium with sulfide-silicate melts and aqueous fluid, decreases in the order aqueous fluid - sulfide melt - silicate melt.

These experimental results can be applied to understand the cooling of sulphur- and chlorine-bearing magmatic systems. Initially, Cl will partition into a sulfide melt that coexists with a hydrous silicate melt. Once an aqueous fluid exsolves from the silicate melt – due to decompression or crystallization at the solidus – Cl will partition into the newly formed fluid causing the sulfides to freeze and crystallize rapidly. The escaping Cl-rich fluid might lead to extensive halogen alteration in the country rocks of the intrusion. The concepts investigated in this study may have significant implications for understanding the evolution of magmas giving rise to copper porphyry deposits and aid in our understanding of halogen-alteration and halogen-rich minerals in major sulfide deposits.

Planktonic foraminifera: Calcifying microenvironments, diffusive boundary layers and a peek at the event horizon

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The planktonic foraminifera, *Orbulina universa*, should be considered the proverbial white rat for researchers studying biomineralization in the marine realm. This protozoan produces a spherical test in a single brief (several hours) calcifying event, that involves organic matrix secretion, rapid calcite precipitation and spine elongation. Chamber thickening in subsequent days is intimately linked to diurnal physiological oscillations related to symbiont photosynthesis and host assemblage respiration which controls large shifts in microenvironment pH (7.8 – 8.8) and [O_2] (~80-220% air saturation) (Rink, *et al.*, 1998). Interestingly, microelectrode measurements of Ca^{2+} at the chamber surface show concentrations that are 10% higher than ambient seawater, while [CO_2] measurements on *O. universa* under dark and light conditions suggest ΣCO_2 varies between ambient (~2 mMol/kg) and ~5 mMol/kg respectively in the boundary layer near the calcifying shell (Köhler-Rink and Kühl, 2005). Together these data point to an active calcium and carbon concentrating mechanism in this species, and may help explain how *O. universa* can calcify in seawater at pH between 7.4 and 8.8 (Bijma, *et al.*, 1999).

Laboratory experiments and stable isotope and trace/minor elemental analyses of *O. universa* demonstrate that shell geochemistry is influenced by physiologically-controlled boundary layer chemistry. Elemental ratio banding, possibly related to the diurnal cycle, as well as observations of non-equilibrium calcite precipitation, provide insight into aspects of calcification that were previously poorly constrained. Together, these observations may provide clues for novel applications of foraminifera geochemistry for paleoenvironmental reconstructions.

References

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