Heterogeneous melt inclusions from heterogeneous mantle: An example from Baffin Island, Canada

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Melt inclusions can be used to probe the compositional diversity present within magmatic systems, although the use of melt inclusions to study mantle heterogeneity in primitive basalts has been subordinate to studies of mantle melting. This study presents major and trace element compositions of olivine-hosted melt inclusions from picritic pillow basalts from Baffin Island Canada. Host lavas have trace element and isotopic compositions derive from two distinct mantle sources – depleted MORB mantle and an enriched composition, possibly recycled metasomatized oceanic lithosphere [1]. The influences of crustal or lithospheric contamination appear negligible and melt inclusions provide a means to study a primitive basaltic magmatic system that is demonstrably sampling two different mantle-derived components.

Melt inclusions show a large range of incompatible trace element compositions, with indices of incompatible element enrichment such as K/Ti and La/Sm_N in melt inclusions from individual samples varying to greater extents than evident in the entire suite of host lavas. Trace element variations rule out crustal contamination or incomplete aggregation of a polybaric melting column as the source of incompatible trace element variations. Furthermore, arrays defined by trace element compositions of melt inclusions directly overlie and extend those defined by host lavas, and strongly imply that melt inclusion compositions reflect mixtures of melts derived from the same two mantle endmembers sampled by the host lavas. This is supported by (1) near-normal distributions of K/Ti that can be reproduced by models of continued mixing and (2) the similarity of average K/Ti for melt inclusions to that of their host lava. The larger variations evident in melt inclusions are consistent with sampling mixtures at a smaller scale, but similarities between inclusions and hosts demonstrates that the compositions of melts trapped within inclusions have not had their trace element abundances further fractionated by diffusional exchange during mixing or by equilibration between inclusion and host or external melt subsequent to trapping. Projected compositions of mantle endmembers from mixing arrays suggests melts derived from DMM and EM1-like mantle can reproduce the observed compositional arrays.

[1] Kent *et al.* (2004) *Geochemistry Geophysics Geosystems* **5**, Q11004, doi: 10.1029/2004GC000743.

Electron-transfer reactions at water- and cytochrome-iron oxide interfaces

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Redox reactions that take place at the mineral-water interface play a major role in many geochemical and biogeochemical processes such as metal contaminant mobility and microbial iron respiration.

For example, dissimilatory iron-reducing bacteria are capable of electron transfer to iron oxide minerals as part of their anaerobic respiration process. Although there is evidence that multiheme outer-membrane cytochromes are involved in direct electron transfer to iron oxide surfaces, the molecular-level mechanisms of this process are still unclear. In this paper, molecular computational techniques are used in the framework of Marcus theory to compute elementary electron-transfer rates from a well-defined cytochrome model to surfaces of hematite (α-Fe_2O_3). These simulations show for the first time that interfacial electron transfer distances of 10 Å or less can be achieved for the purpose of oxide reduction. In addition, we computed rates of interfacial electron transfer in good agreement with recent experimental data on comparable systems and concluded that the interfacial electron transfer step is feasible but is a potential kinetic bottleneck in the bioreduction process [1].

Another critical issue is the fate of electrons injected in the iron oxide, whether as a result of biotic or abiotic reactions. Indeed, the rate at which electrons diffuse away from the injection site is a key factor in determining the turnover of electron accepting sites at the interface and has implications in the possible formation of new phases. In this paper, we use atomistic and quantum mechanical calculations to investigate the kinetic and thermodynamic properties of electron transfer reactions between adsorbed iron(II) and hematite surfaces and at two water-hematite interfaces. Our findings indicate that diffusion of small electron polarons occurs through the lattice at an appreciable rate and that, in the case of the basal (001) plane, lateral diffusion is significantly faster than diffusion into the bulk [2, 3].

[1] Kerisit S., Rosso K.M., Dupuis M., & Valiev M. (2007) *J. Phys. Chem. C* **111**, 11363-11375 [2] Kerisit S. & Rosso K.M. (2007) *J. Chem. Phys.* **127**, 124706 [3] Kerisit S. & Rosso K.M. (2006) *Geochim. Cosmochim. Acta* **70**, 1888-1903.