The sometimes ignoble behavior of noble gases in minerals

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The noble gases continue to hold the interest of solid-Earth geochemists and cosmochemists because of their potential to shed additional light on planetary outgassing, thermal histories and early solar system processes. Despite this interest, many questions remain surrounding the behavior of noble gases in planetary solid-liquid systems, some of which stem from seemingly paradoxial observations of natural systems, others from contradictory experimental characterizations of noble-gas partitioning and diffusion. Recently we have shown in laboratory experiments that Ar is taken up by orthopyroxene and olivine (among other minerals) at the ~1000-2000 ppm level in crystals heated in an Ar atmosphere [1]. These results suggest, contrary to expectation, that Ar may behave as a compatible element during mantle melting, favoring residence in point defects in minerals over ‘escape’ to the melt. Diffusivities extracted from the same experiments indicate that Ar is probably distributed uniformly among the minerals of a subsolidus mantle and equilibrates with melt during partial melting.

Emerging results from similar experiments aimed at Ne and He reveal disparate behaviors of these two elements. Neon mimics Ar in that exposure of minerals to a Ne atmosphere results in diffusive uptake of Ne at a level on the order of 1000 ppm. Perhaps not surprisingly, however, Ne diffuses 1 to 2 orders of magnitude faster than Ar. The similarity in behavior of Ar and Ne does not extend to He, which (for a given noble-gas pressure) is incorporated into minerals at substantially lower concentrations, suggesting Henrian behavior that is not seen in Ar. Helium also diffuses much faster than Ar and Ne: our preliminary Arrhenius line for olivine, obtained over a temperature range of 300-500°C, extends to intersect the line of Hart [2], but our activation energy is ~1/3 his value.

At this juncture there is reason to conclude that the noble gases are not a coherent group in terms of their partitioning and diffusion behavior; indeed, there may be a fundamental ‘discontinuity’ in geochemical behavior between He and Ne.

[1] Thomas J.B. *et al.* (2008, in review) *Chem. Geol.* [2] Hart S.R. (1984) *Earth Planet. Sci. Lett.* **70**, 297-302.

Water structure on mineral surfaces: Comparisons between quartz, corundum and goethite

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Water structure near mineral-water interfaces is of prime interest for an understanding of near surface binding of solutes, and especially for elucidation of so-called “outer sphere” complexation. Basic electrical double layer (EDL) theory neglects molecular structure in the water, and hence water organization would be expected to alter EDL formulations as now developed. Water structuring near interfaces has consequences for the geometry of sorption and can affect pka values and other interface properties, notably the local dielectric coefficient.

For the past several years we have been developing a phase sensitive sum frequency vibrational spectroscopy technique (PS-SFVS) that allows extraction of the imaginary part of the non-linear optic response for water at mineral surfaces. Using this method we have been able to obtain the net dipole orientations and constrain the types of water hydrogen binding for water at fused silica, quartz and corundum surfaces. Most recent work has also addressed the observed ZPC variation on corundum surfaces as a function of particle size.

In a completely different approach, we have been able to identify three-dimensionally ordered water structure at the surface of goethite using surface x-ray diffraction methodology (See also Ghose *et al.* abstract this meeting)

We expect that ordering of near surface water can set up a molecular competition where water at the surface must adapt to the local electrostatic field variations with a periodicity near that of the lattice, but gradually change into a fully tetrahedral network farther from the surface. In this presentation the differences in results from the various surfaces and techniques will be described, with suggestions about the possibilities for a holistic understanding of interface water structure and its consequences.