Geochemical reactions in nanopores and nanotubes

YIFENG WANG[1, 2], HUIFANG XU[2], CHARLES BRYAN[1], HUIZHEN GAO[1, 2], AND TIANHU CHEN[2]

[1] Sandia National Laboratories, New Mexico, USA (ywang@sandia.gov)
[2] Department of Earth and Planetary Sciences, The University of New Mexico, New Mexico, USA (hfxu@unm.edu)

Nanopores are ubiquitous in porous geologic media and may account for >90% of total mineral surface areas. Surface chemistry, ion sorption, and the related geochemical reactions within nanopores can be significantly modified by a nanometer-scale space confinement. As the pore size is reduced to a few nanometers, the difference between surface acidity constants ($\Delta pK = pK_2 - pK_1$) decreases, giving rise to a higher surface charge density on a nanopore surface than that on an unconfined mineral-water interface (Figure 1).

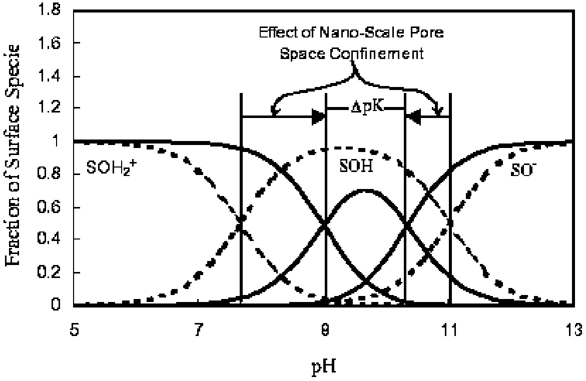

Figure 1: Surface speciation on nanoporous alumina (solid lines) and activated alumina particles (dashed lines). The separation between the two acidity constants becomes significantly narrowed for the nanoporous alumina as compared to that for the alumina particles.

The change in surface acidity constants results in a shift of ion sorption edges and enhances ion sorption on nanopore surfaces. Also, the water activity in a nanopore is greatly reduced, thus increasing the tendency for inner sphere complexation and mineral precipitation. Replacement of nanoporous calcite by Mg-bearing calcite occur at room temperature in Mg-bearing solution because of reduced hydration of Mg cation in nanopores. Activity of outside surface of a nanotube is higher than that of inner surface. All these effects combine to preferentially enrich trace elements in nanopores, as observed in both field and laboratory studies. The work reported here sheds new light on such fundamental geochemical issues as the irreversibility of ion sorption and desorption, the bioavailability of subsurface contaminants, the enrichment of trace metals in ore deposits, and mineral replacement reactions, as well as the kinetics of mineral dissolution/precipitation. This research is supported by NSF (EAR02-10820) and LDRD program of DOE.

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New insight into the origin of the low $\delta^{18}O$ magmas in Iceland

ZHENGRONG WANG, JOHN EILER AND NAMI KITCHEN

Division of geological and Planetary Sciences, Caltech, Pasadena, CA 91125, USA,(wzhr@gps.caltech.edu)

Iceland contains abundant low $\delta^{18}O$ volcanic rocks, reflecting ^{18}O-depleted sources and/or crustal contamination by assimilation and/or mixing with crustal melts. Previous attempts to distinguish among these mechanisms have been based principally on oxygen isotope measurements of whole-rocks, glasses, or mixed populations of phenocrysts. Here we add further constraints from micro-analyses of individual phenocrysts and xenocrysts.

Oxygen isotope data for phenocryst populations and glass from Icelandic basalts [1,2,3,4] show that olivine, pyroxene and plagioclase are anomalously low and highly variable in $\delta^{18}O$ compared to n-MORBs (olivine: +5.0 ~ +5.2‰). Ranges are: +3 ~ +5.4‰ for olivines; +4.4 ~ +5.3‰ for clinopyroxenes; +4.0 ~ +5.4‰ for plagioclases from the northern volcanic zone; and +4.4 ~ +5.1‰ for plagioclase from ultraphyric lavas in the southern volcanic zone. Variation up to ±0.3‰, 1σ –many times analytical uncertainty - occur within individual hand specimens.

We report new analyses of the oxygen isotope compositions of minerals from Theistareykir lavas and nodules contained therein, made by either infra-red laser fluorination of mineral separates, or by UV-laser fluorination of portions of single crystals, made *in situ*. We find significant intra-crystaline oxygen isotope variability within plagioclase, olivine and clinopyroxene, and frequent non-equilibrium (even reversed) differences in $\delta^{18}O$ between co-existing phases. Similar (though less extreme) phenomena are observed in previous measurements of mixed phenocryst populations [1-4], and were recently found to be typical of low-$\delta^{18}O$ Hawiian basalts [5]. These fine-scale, disequilibrium isotopic distributions reflect one or more of: mixing between low-$\delta^{18}O$ and higher-$\delta^{18}O$ magmas over the course of crystallization/differentiation; AFC processes; and/or incorporation of aqueously altered mineral grains into Icelandic magmas from surrounding rocks. We will discuss evidence for and against these alternatives. Finally, Intra- and inter-crystalline oxygen isotope disequilibrium cannot be preserved at magmatic temperatures (eg. 1160ºC) for long times, limiting the time-scale between mixing of these components and eruption to at most ca. 3 kyrs.

References

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