Site-specific, size-dependent reactivity of Al-oxide nanoparticle surfaces

JAMES R. RUSTAD[1], JIANWEI WANG[1]
AND WILLIAM H. CASEY[1,2]

[1]Department of Geology, University of California, Davis, One Shields Avenue, Davis, CA 95616

[2]Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, CA 95616

We use molecular dynamics calculations to estimate water-exchange rates for a series of aluminum (oxy)hydroxide compounds. These include the $Al(H_2O)_6^{3+}$ monomer; the ε-Keggin ion $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+/8+}$ (Al_{13}); the $[Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ (Al_{30}) aqueous polyoxocation; the surfaces of Al-oxyhydroxide minerals boehmite (AlOOH) and gibbsite ($Al(OH)_3$); and the aluminosilicate mineral kaolinite ($Al_2Si_2O_5(OH)_4$). X-ray structural data can be used in conjunction with rate data from ^{17}O NMR studies[2] to test predictions of reactivity trends at a site-specific level. The molecular dynamics calculations here tie these structurally diverse systems together into a simple structure-reactivity trend based on Al-water bond lengths, and highlight the role of the Al_{13} and Al_{30} ions in systematically bridging the structural gap between the hexaaquo ion and the oxide surfaces.

Water-exchange rates were calculated for each species using the reactive-flux method. The rate constant is taken as $k=\kappa k_{TST}$ where k_{TST} is the transition state rate constant and κ is the transmission coefficient. κ is highly variable across the spectrum of reactive sites, ranging from 0.1 to 0.001.

Overall, the estimates of τ^{298} for the aluminous minerals are surprisingly short, falling within the range of $\sim 10^{-8}$-10^{-10} s, close to those for alkali and alkaline-earth metal ions. Waters bound at the edges of the minerals will exchange rapidly with bulk waters and with other ligands. The fast rates for these surface sites are consistent with the long Al-water bond lengths and also follow the general trend that rates increase, and $\Delta H^{\ddagger}$ values decrease, with increasing size and decreasing charge/Al ion of the complex.

This framework provides, for the first time, a means for estimating kinetic parameters for individual sites at aqueous polynuclear ions and oxyhydroxide surfaces. This result is enormously important for environmental chemistry where treatment of reactions at the aqueous-mineral interface is a long-standing problem. The structure-reactivity relation presented here places the ligand-exchange properties of extended interfacial systems on a new site-specific, quantitative footing.

References
(1) Casey, W. H (2006) *Chem. Rev.*, **106**, 1-16.
(2) C. H. Bennett, in *Diffusion in Solids: Recent Developments*, edited by A. S. Nowick and J. J. Burton (Academic, New York, 1975)

Potential temperature and volatile contents in mantle plume of Siberian trap province

I.D. RYABCHIKOV

Institute for Geology of Ore Deposits, Russian Academy of Sciences, 119017, Moscow, Russia, (iryab@igem.ru)

Magmatism in the Siberian CFB province is mainly represented by the voluminous lava flows of tholeiitic plateau basalts and subordinate amounts of highly magnesian volcanics and dyke rocks These highly magnesian rocks are strongly enriched in incompatible trace elements and are characterized by high LREE/HREE ratios. It suggests that their primary magmas were near solidus melts formed at high pressures. P-T conditions of the generation of these hi-Mg melts must be nearly identical with the P-T parameters characterizing magma-generating mantle plume.

To assess the formation conditions of hi-Mg Siberian magmas we investigated melt and fluid inclusions in the phenocrysts of these rocks, which were analyzed for major and trace elements (EMPA and SIMS methods). High Ti/Na ratios and high normative olivine contents in the melt compositions recalculated to the condition of equilibrium with mantle peridotites imply, that initial pressure of magma-generation is in the range of 7–9 GPa.

Ion microprobe data for reheated melt inclusions in phenocrysts from Siberian rocks show low concentrations of volatile and fluid-mobile components. H_2O/Ce ratios in melt inclusions from picrobasalts and meimechites are significantly lower than from MORBs and many OIBs. This implies that the source of Siberian magmas was even poorer in water by comparison with the depleted mantle. The same relations are observed for the ratios of a number of other volatile and fluid-mobile components to their non-volatile geochemical analogues, like B/Ce, Pb/Nd etc.

Low levels of volatiles contents imply that the estimates of near-solidus temperature based on comparison with volatile-free systems would not be changed significantly. Comparison of the estimated from melt inclusion data pressures with experimental data shows that the temperature of rising plume material was ca 400°C higher by comparison with convecting upper mantle at the same depth. This proves that plume material arrived from deep levels in the mantle.