Alkali metal and H_2O dynamics at clay-water interfaces: Lessons from NMR

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Many geochemical processes are highly dependent on the fundamental molecular-scale structure and dynamics of ions and H_2O at solid-water interfaces. We present here a detailed description of the behavior of alkali metal cations and H_2O in the interlayers and on external surfaces of smectite/H_2O pastes based on variable temperature nuclear magnetic resonance (VT NMR) spectroscopy.

Our new and previously published data show that alkali metal cations occupy multiple distinct binding environments in natural hectorite and that dynamic averaging of these sites is intimately linked to the dynamics of free and confined H_2O from -80°C to 50°C. For hectorite, K^+ and Cs^+ occupy two cation sites (likely 12-coordinate and 9-coordinate interlayer environments) that undergo rapid exchange above -20°C and -50°C, respectively [1, 2]. Companion ^{2}H NMR shows that exchange between K^+ environments is linked to the onset of diffusional exchange among confined and free H_2O populations [1]. Recent variable temperature ^{23}Na NMR data at 9.4 T and 21.1 T reveal two Na^+ sites in hectorite with distinct quadrupolar couplings. These two sites experience distinct dynamic behaviors (and no evidence of direct two-site exchange) that appear more strongly linked with the dynamics of specifically free H_2O. The dynamics of confined H_2O in the Na- and K-hectorites appear to be quite similar at temperatures < -20°C and reflect a combination of fast C2 symmetry jumps and exchange among positions in the ion hydration shell. Above -20°C there is diffusional exchange between confined and free H_2O populations for the Na- and K-hectorites. Differences in the residual ^{2}H quadrupolar splitting at these temperatures are likely due to differences in cation hydration energies and whether the cations prefer inner- or outer-sphere interactions with the clay surface.

[1] Bowers, Bish, and Kirkpatrick (2008), *J. Phys. Chem. C*, **112**, 6430-6438. [2] Weiss, Kirkpatrick, and Altaner (1990), *Geochim. Cosmochim. Acta*, **54**, 1655-1669.

Isotopically-zoned zircons: Records of fluid/melt flow in the lower crust, Kapuskasing Uplift

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Ion microprobe (SHRIMP and CAMECA 1280) analyses document primary isotopic (Pb, O) and trace element zoning in zircon from lower crustal paragneiss in the granulite zone of the Kapuskasing Uplift, Archean Superior Province. Older and low-δ^{18}O (5.1 to 7.1‰) igneous cores are overgrown by metamorphic zircon rims (2.66±0.01 to 2.58±0.01 Ga in age) which have significantly higher but variable δ^{18}O values (8.4 to 10.4‰). Several individual rims are zoned, with δ^{18}O decreasing outward from >10‰ to values as low as 8.4‰ at rim edges. Rims fall into two geochemically distinct groups: Type 1 rims have lower δ^{18}O (8.4 to 9.4‰), higher Th/U (0.1 ave.) and lower U/Yb (6.9 ave.). Type 2 rims have higher δ^{18}O (9.4 to 10.4‰), lower Th/U (0.025 ave) and higher U/Yb (20 ave.). Garnets separated from leucosome and melanosome in this paragneiss have significantly different δ^{18}O values of 9.2 and 9.9‰ (laser fluorination), respectively. These δ^{18}O values are similar to the average δ^{18}O values of the type 1 and 2 zircon rims; this similarity suggests that type 1 and type 2 rims are equilibrated with the leucosome and melanosome domains, respectively. The δ^{18}O data indicate that the leucosome domain is not in isotopic equilibrium with the rock matrix, which supports leucosome formation by infiltration of lower δ^{18}O fluid/melt rather than by *in situ* partial melting.

In mafic gneiss adjacent to this paragneiss, metamorphic zircons (2.67±0.01 to 2.56±0.01 Ga) have variable δ^{18}O values from 7.6 to 11.3‰. A number of zircon rims are markedly zoned, with δ^{18}O values ranging from 11.1‰ down to values as low as 7.6‰ at rim edges. These variations in δ^{18}O(Zrc), coupled with some cases of disquilibium fractionation between zircon and garnet (up to 1.1‰), record multiple fluid/melt infiltration events involved in the geochemical evolution of this section of the deep crust.