Structure and Energetics of Smectite Interlayer Hydration: Molecular Dynamics Investigations of Na- and Ca-Hectorite

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Molecular-scale interactions present at mineral-water interfaces and in clay interlayer galleries control numerous environmental processes, including chemical interactions in soils and transport of nutrients and pollutants through them.[1-4] Understanding these processes requires accurate knowledge of the structure, energetics, and dynamics of the interaction among the mineral substrate, ions, and water molecules.[5, 6] Challenges to this objective include experimental difficulties in probing these interfaces and interlayers at the molecular scale; fully characterizing the mineral substrate; and identifying how the mineral surface, ions, and water molecules each contribute to the overall structure, energetics, and dynamics of these systems.[6] Linked computational molecular dynamics (MD) simulations and experimental nuclear magnetic resonance (NMR) studies are particularly effective in addressing these issues.[7-9]

Here we focus on MD studies of Na- and Ca-smectite (hectorite) interlayer galleries to provide a molecular-scale picture of the structure and dynamics of their hydration[9, 10] and to complement our earlier NMR investigations of these systems.[7-9] Classical MD simulations were undertaken in the *NPT* and *NVT* ensembles to determine the structural and energetic changes with increasing hydration with focus on the single- and double-layer hydrates. The results show substantial changes in the hydration of the interlayer cations, the orientations of the water molecules, the hydrogen bond network involving the water molecules and basal oxygen atoms, and the resulting potential energies as the interlayer gallery expands.

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Reconstructing a young martian history with igneous microbaddeleyite rimmed by metamorphic zircon

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A current paradox in martian geochronology is that basaltic shergottites yield whole rock and unradiogenic mineral isotopic Pb-Pb compositions consistent with a primary Noachian (>4 Ga) age for crystallization whereas mineral isotopic analyses consistently return 'young' post-Amazonian (<0.6 Ga) dates. To assess the significance of the mineral dates, we have combined single-grain isotopic SIMS U-Pb microbaddeleyite dating with chemical and deformation microstructure data obtained with electron nanobeam techniques (e.g. CL, EBSD) to resolve baddeleyite paragenesis and potential for isotopic disturbance by shock processes. We have focused on microbaddeleyites from shergottite NWA 5298, an enriched basaltic shergottite exhibiting a primary phaneritic igneous texture which has similarities to other basaltic shergottites. The baddeleyites are generally subhedral to euhedral blocky to bladed grains, 2 to 20 μm long, at the boundaries of larger main phase minerals. SE and BSE imaging of grain interiors showed that grains are often composed of equant microdomains that give the appearance of a granular texture. Grains are often surrounded by discontinuous rims of zircon a few microns wide identified by EDS and EBSD. CL zoning types in baddeleyite include simple bright, narrow rims of variable thickness surrounding dark cores, and patchy to diffuse and mottled CL domains at the margins of grains or in areas of crystal disruption and apparent granular texture. A subset of grains exhibits oscillatory planar growth banding similar to that which we have observed in terrestrial igneous baddeleyite. Our EBSD mapping indicates clearly that the baddeleyite is now quasi-amorphous and is hosted by amorphous maskelyinite, whereas zircon is crystalline and apparently unshocked, although an investigation at higher resolution for the high pressure polymorph, reidite, is ongoing. SIMS analysis of 12 grains yielded $^{206}Pb/^{238}U$ dates ranging from 209 ± 22 Ma (2σ) to 26 ± 2 Ma. An unforced discordia line has an upper intercept with concordia at 0.9 +1.2/-0.7 Ga and a zero age lower intercept. Our SIMS data together with microtextural data for the baddeleyites are consistent with U-Pb disturbance of primary, post-Noachian igneous crystals during shock, recent shock heating, and zircon growth. A scenario is favoured wherein bulk melting of ancient 4 Ga parent material produced the NWA 5298 source magma through volcanic or impact melting. This would reconcile 'young' mineral dates and isochrons with the unradiogenic and whole rock Pb-Pb age data from basaltic shergottites.