

Atomistic simulations of zeolite surfaces and water-zeolite interface

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We describe recent atomistic simulations which are based on the Born model of solids to study surface structure, growth and dissolution of silicate minerals. We have initially focused on the surfaces of microporous zeolites; sodalite (SOD) zeolite A (LTA) and L (LTL), which contain pores and channels that are accessible to the ions in solution.

The approach is first to use static lattice simulation techniques to identify possible surface structures and then immerse the minerals in water by performing a series of molecular dynamics simulations where we vary the solution conditions, particularly the ionic strength and pH.

The results of the static simulations on the silicious forms predict that the most stable surfaces of sodalite are {001} and is terminated with complete β -cage. In case of LTA 2 distinct surfaces were the most stable: {100} terminated with complete β -cage and {111} terminated with double four-rings. For LTL the most stable surfaces were {100} terminated with CAN cage. The predicted equilibrium morphologies in absence of solvent are in good agreement with the experiment for LTL and SOD, but were poor for LTA. Simulations of LTA in contact with different solutions using molecular dynamics in the NVT ensemble at 300K and zero pressure for 1ns showed clear ordering of water at the interface. The distribution of density revealed layering near the surface and spotting inside the cages. Furthermore, we found that ordering of water significantly affects the diffusivity. Similar simulations were performed for solutions at extremes of pH, with $\text{pH} \approx 0$ and $\text{pH} \approx 14$. The low pH simulations showed layers of H_3O^+ ions strongly adsorbed on the surfaces. Finally, we investigated the beginnings of growth by evaluating the free energy profiles of the $\text{Si}(\text{OH})_4$ and $\text{SiO}(\text{OH})_3^-$ monomers approaching the LTA surface in various conditions of pH and surface charge. These calculations showed significant differences in free energy profiles for different conditions suggesting, perhaps unsurprisingly, that in this system kinetic factors will play a crucial role.

In summary, the simulations show that we can begin to model transport at the silicate-solution interface at the atomic level, thereby providing a useful complement to experiment.

Chopinite-sarcopside in meteorite GRA95209

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Chopinite, $(\text{Mg,Fe})_3(\text{PO}_4)_2$, is the Mg-dominant analogue of sarcopside [1] and a high-pressure polymorph of the meteorite mineral farringtonite [2]. $(\text{Mg,Fe})_3(\text{PO}_4)_2$ with $X_{\text{Mg}} = \text{Mg}/(\text{Mg}+\text{Fe})$ ranging 0.01–0.87, is a minor constituent in Graves Nunatak 95209, a lodranite containing Fe-Ni metal masses and forsterite-orthopyroxene aggregates [3, 4]. New analyses of $(\text{Mg,Fe})_3(\text{PO}_4)_2$ –johnsomervilleite-chladniite $[\text{CaNa}_8(\text{Ca}_4\text{Na}_4)(\text{Mg,Fe})_{43}(\text{PO}_4)_{36}]$ pairs give two trends, one consistent with terrestrial sarcopside-johnsomervilleite (Fig. 1); Mn-Fe distribution is also consistent. Electron backscatter diffraction patterns confirm identification of chopinite and farringtonite. Regular Mg-Fe distribution and restriction of farringtonite to Mg-rich compositions imply approach to equilibrium. Isoleths calculated for chopinite $X_{\text{Mg}} = 0.65$ at 500–1050°C as in [1], but with $K_D = 2.10$, give 4–7 kbar, pressures far too high for a meteorite. We suggest that Fe-rich sarcopside initially formed by oxidation and replacement of P-rich metal; subsequent exchange with Mg-rich silicates resulted in Mg-rich compositions that failed to transform into farringtonite, leaving chopinite as a metastable phase as the meteorite cooled.

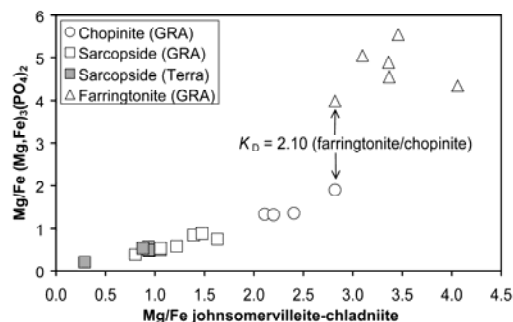


Figure 1: Mg/Fe ratio of coexisting phosphates in GRA95209 and terrestrial rocks [1].

[1] Grew *et al.* (2007) *Eur. J. Mineral.* **19**, 229-245. [2] Brunet & Vielzeuf (1996) *Eur. J. Mineral.* **8**, 349-354 [3] Floss (1999) *Am. Mineral.* **84**, 1354-1359. [4] McCoy *et al.* (2006) *GCA* **70**, 516-531.