

## 2.1.12

### Molecule-mineral inner surface interactions in nanoporous silicates: A Raman spectroscopic investigation

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We have undertaken single-crystal Raman measurements of zeolites (bikitaite, natrolite), SiO<sub>2</sub>-clathrates (melanophlogite) and other silicate structure types with small nanopores (beryl, cordierite, hemimorphite) at different temperatures. The goal is to investigate the nature of inner surface molecule-crystal interactions and the role of hydrogen bonding in minerals. The angular dependencies of the OH-mode scattering intensities in single-crystal measurements, made at low and ambient temperatures, permits the direction of the molecular bonds and the main molecular polarizabilities for different O-H bonds to be obtained.

In bikitaite, H<sub>2</sub>O molecules occur in infinite [010] channel ways and build a hydrogen-bonded H<sub>2</sub>O chain termed 'one-dimensional ice'. The molecules are ordered, whereby one H atom per molecule is unbonded and the other is hydrogen-bonded to a neighboring H<sub>2</sub>O molecule. They show little interaction with the framework. The hydrogen-bonded O-H stretching bands in the Raman spectra show little line broadening, which is not typical for many hydrogen-bonded systems. With increasing temperature, the hydrogen bonding weakens continuously until the chain 'breaks' and isolated H<sub>2</sub>O molecules are present.

The Raman spectrum of melanophlogite shows the presence of quasi-free N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>, but no H<sub>2</sub>O molecules. Most of the CH<sub>4</sub> is partitioned into the smaller nearly spherical [5<sup>12</sup>] cage, while CO<sub>2</sub> and N<sub>2</sub> appear to prefer the larger more oblate [5<sup>12</sup>6<sup>2</sup>] cage. The difference in wavenumber for their stretching modes between room temperature and 4 K is minimal. The molecules are orientationally disordered in the cavities and they have only weak dispersion interactions with the SiO<sub>2</sub>-crystal framework. However the incorporation of molecules is necessary to allow the SiO<sub>2</sub> framework to condense.

Cordierite and beryl contain quasi-free CO<sub>2</sub> molecules, as well as H<sub>2</sub>O in small cavities. The CO<sub>2</sub> molecules are orientated parallel to the crystallographic *x*-axis. The H<sub>2</sub>O molecules have their H-H vector parallel to the *z*-axis in alkali-free crystals and are dynamically disordered about the *z*-axis. They show little hydrogen bonding with their frameworks.

It is noteworthy that the polar H<sub>2</sub>O molecule can be found these two 'zeolite-like phases', but not in melanophlogite. Melanophlogite is hydrophobic, while nearly all other nanoporous silicates are hydrophilic. The incorporation of the polar H<sub>2</sub>O molecule may be related to the nature of the electronic charge distribution within the crystal framework.

## 2.1.13

### A geochemical model for dissolution, nucleation and growth of minerals in aqueous solutions

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Most geochemical codes accounting for static water-rock interactions focus on the thermodynamic equilibria between the mineral phases and the solution, and on the growth and dissolution of particles in the solution, but treat the nucleation step in an ad-hoc manner (Fritz et al, this issue). It is generally assumed that, as soon as saturation exceeds a critical value, particles nucleate all of a sudden, with a pre-defined size, more or less taken from experimental knowledge. Moreover, subsequent growth or dissolution is usually described by a rate which is independent of the size of the particles, thus excluding important effects such as Ostwald ripening.

In a way reminiscent of Steefel and Van Cappellen's approach [1], we have introduced in the KINDIS code [2] an account of the first stages of particle precipitation, based on the classical theory of nucleation, which explicitly expresses the critical radius of the nuclei as a function of temperature (*T*), surface energy ( $\sigma$ ) and saturation index (*I*). Depending upon the evolution of *I* with time, these particles may grow or re-dissolve. Making a microscopic description of the exchange of matter at the particle/solution interface, we derive an algebraic expression for the growth rate, which explicitly depends upon the particle radius *R*, *T* and *I*, and yields the usual expression in the macroscopic limit (*R* going to infinity).

On a simple example, we show that this improved description of water-rock interactions is a predictive tool, able to account for various precipitation behaviours, due to the highly non-linear character of the equations, with a limited number of parameters.

#### References

- [1] Steefel C. I. and Van Cappellen Ph. (1990) *GCA* **54**, 2657-2677.  
[2] Madé B., Clément A. and Fritz B. (1994) *Computers and Geosciences* **20** (9), 1347-1363.