

## Internal fractionation of oxygen in hydrous minerals: Reconciling thermal dehydroxylation and partial fluorination through theoretical predictions

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Phyllosilicates contain two types of oxygen: structural oxygen (Os), strongly bonded and thus expected to have high  $^{18}\text{O}/^{16}\text{O}$ , and hydroxyl oxygen (OH), expected to have lower  $^{18}\text{O}/^{16}\text{O}$ . Selective extraction and isotopic measurement of those two oxygen types should provide an internal geothermometer. This approach is thus similar to clumped-isotope methods, that have raised much interest in recent years. Attempts to separate the two oxygen types for analysis have followed two pathways: partial fluorination (PF) [1] and thermal dehydroxylation (TD) [2]. However, the two methods gave contradictory results.

Recently, we have developed a calibration method based on first-principles electronic structure calculations, which succeeds in reproducing experimentally measured oxygen fractionations between minerals [3]. Fractionation properties of individual crystal sites, and thus internal fractionation properties, can be computed just as easily and presumably with comparable accuracy.

Our calculations suggest that  $^{18}\text{O}/^{16}\text{O}$  ratios in OH sites are different from those in Os sites, and also different between themselves. In kaolinite, inner OH is predicted to be 10 permil lighter than interlayer OH at 25°C. This clearly is of some importance if one cannot extract all the OH, since incomplete extraction could preferentially sample one type of site. This is the case with TD, which is known to extract only half of the OH. If, as expected, inner OH are extracted first in TD, we find that TD and PF methods actually both give results consistent with the theoretical calibration. A similar argument can explain the results of rapid TD of gibbsite [2], without invoking any kinetic effects.

Calculations on lizardite, muscovite, phlogopite and clinocllore have also been realized, and will be discussed.

[1] Hamza and Epstein (1980) *Geochim. Cosmochim. Acta* **44**, 173-182. [2] Girard and Savin (1996) *Geochim. Cosmochim. Acta* **60**, 469-487. [3] Meheut *et al.* (2007) *Geochim. Cosmochim. Acta* **71**, 3170-3181

## Microcosm studies on microbial sulfate-reduction and secondary mineral formation at low pH

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Fe and S cycling are closely linked through the formation of iron sulfide minerals which occur in low-temperature environments primarily as the result of microbial sulfate reduction. Besides the production of hydrogen sulfide, microbial sulfate reduction generates alkalinity which causes lighter metals, such as Al, to hydrolyze and precipitate as hydroxides. Both processes of secondary mineral formation are of interest when it comes to the remediation of acid mine drainage contaminated sites. However, little is known on how mineral precipitation may affect cell activity. Sediments of an acidic mine pit lake were chosen as a model system. Sulfate-reducing microorganisms constituted only a small proportion of the indigenous microbial community, therefore, selective enrichments in artificial pore water with elevated concentrations of Fe(II) and Al were studied. Microbial community fingerprinting revealed the dominance of *Desulfosporosinus* spp. in enrichments at pH 5 – 6 while *Thermodesulfobium* spp. predominated at pH 3 – 4. Electron microscopy showed amorphous Al-rich precipitates closely associated to the cell surfaces. Occasionally cells were completely enclosed and compact aggregates of cells and Al-rich precipitates were observed. Iron sulfides precipitated as crystalline, monosulfidic particles away from bacterial cells in the bulk phase. When investigating the effect of dissolved Fe(II) and Al separately, it became clear that Fe(II) had a positive effect by acting as a H<sub>2</sub>S scavenger. Quite contrary to the expected negative effect of Al due to its increased toxicity at low pH, cells appeared to be tolerant to higher concentrations of free sulfide in the presence of Al than in its absence. Al-rich coatings enclosing single or several cells may function as a protective layer. Mineral precipitation did not affect sulfate-reducing activities. Although our enrichments cultures might not truly represent the conditions prevailing in acidic lakes, our study on mineral formation provides some insights on how these processes may affect microbial activity and, hence, element cycling.