

New analyses of dissolution processes: Application to gypsum crystal surfaces

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Understanding the surface behaviour of minerals during dissolution and crystallisation processes is of key importance in many areas. This poster presentation is concerned specifically with studies of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), but the measurement techniques developed should be generally applicable. Although the dissolution and crystallisation of gypsum has been studied by several approaches, ranging from kinetic measurements in particulate systems [1-2] to high resolution studies with atomic force microscopy (AFM) [3] there is considerable discrepancy as to what processes (diffusion/surface reactions) control the rates of dissolution.

Using natural single crystals as a model, we have found that dissolution occurs via the formation of etch pits which grow with time. We seek to address the question of whether the pit size and morphology can be used to extract quantitative dissolution kinetics in a simple way. Full etch pit characterisation has been conducted using atomic force microscopy (AFM) which reveals the time-dependent etch pit morphology. This is analysed quantitatively via a MATLAB program. A finite element model of the diffusion-reaction process is developed which mimics the experiment. In this way, one can obtain information in spatially resolved dissolution fluxes and surface concentration which provide considerable quantitative information on reaction rates.

- [1] H. Singh and M. S. Bajwa (1990) *Aust. J. Soil. Res* **28**, 947. [2] S.-T. Liu *et al.* (1971) *J. Inorg. Nucl. Chem* **33**, 2311. [3] G. Jordan *et al.* (2001) *Geochim et Cosmochim Acta* **65**, 4257.

Abiotic Fe isotope fractionation during sulfide mediated reductive dissolution of Fe oxide minerals

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Sulfide-mediated reductive dissolution of Fe(III) oxide minerals is a major process occurring during anoxic diagenesis and in the water column of anoxic marine basins. Abiotic redox cycling of Fe by this process has potential for significant fractionation of Fe isotopes due to changes in oxidation state between Fe(III) and Fe(II). Previous studies of biological processes, such as dissimilatory Fe reduction, regard the isotopic fractionation observed between the original Fe substrate and dissolved Fe(II) ($\delta^{56}\text{Fe} = -1.3\%$; [1]) as an unambiguous geochemical tracer of microbial activity in both modern marine environments and in relation to the rock record. However, these conclusions do not consider the effect of key abiotic reactions such as reductive dissolution, due to lack of fundamental knowledge of the isotopic fractionation effects of such reactions.

This experimental investigation has traced the isotopic composition of Fe produced via both the reductive step and subsequent dissolution step during the sulfidation of synthetic 2-line ferrihydrite over a range of pH conditions. Experiments were carefully controlled and Fe isotope compositions were measured by MC-ICP-MS. A significant isotopic fractionation is observed ($\Delta^{56}\text{Fe}_{(\text{Fe(II)}_{\text{diss}}-\text{Fe(II)}_{\text{sur}})} = 0.45\%$) under acidic conditions where dissolved Fe^{2+} from the original ferrihydrite surface is fully released into solution.

Similar experiments have been conducted with a variety of other Fe oxide minerals, including lepidocrocite, goethite and hematite. All minerals produce an isotopic fractionation, but to differing degrees. This presentation will discuss the extent of the Fe isotope fractionation during reductive dissolution of these different minerals and will consider the controlling factors on the extent of fractionation for individual minerals.

- [1] Beard *et al.*, (1999) Iron isotope biosignatures, *Science* **288**, 1889-1892