

## Macroscopic and infrared spectroscopic investigation of the synergistic effect between small organic ligands and desferrioxamine-B on the dissolution of goethite

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In several recent papers, Kraemer *et al.* [e.g. 1-2] have suggested that the dissolution of goethite by desferrioxamine-B (des-B) is enhanced in the presence of small organic ligands such as oxalate that actively shuttle iron from the goethite surface to bulk solution. The goal of the present study was to further an understanding of this phenomenon in both the oxalate- and malonate-goethite-des-B systems using macroscopic and spectroscopic methods. All experiments were performed at 25 °C in the absence of visible and ultraviolet light. The amount of oxalate and malonate adsorbed and the concentration of Fe(III) dissolved were studied after a reaction time of one week at total ligand concentrations between 0 and 5  $\mu\text{mol}/\text{m}^2$  and covering the pH range 3 to 9.5. Several different types of *in situ* infrared spectroscopic experiments were performed at constant pH values of both 4 and 6, total oxalate and malonate concentrations of 1  $\mu\text{mol}/\text{m}^2$ , and des-B concentrations of between 0.1  $\mu\text{mol}/\text{m}^2$  and 1  $\mu\text{mol}/\text{m}^2$ . First, spectra were collected to monitor the adsorption and surface speciation of oxalate and malonate on the goethite surface in the absence of des-B as a function of time, and the desorption of these ligands was followed spectroscopically to clarify the relative stabilities of the different types surface complexes. Second, spectra were collected as a function of time after the simultaneous addition of 1  $\mu\text{mol}/\text{m}^2$  concentrations of both oxalate or malonate and des-B to identify the complexes present at the goethite surface. Third, oxalate and malonate were reacted with goethite in the absence of des-B, and then spectra were collected as a function of time after repeated 0.1  $\mu\text{mol}/\text{m}^2$  additions of des-B every 24 hours. These experiments have revealed the type of surface complex responsible for the synergistic effect between these small organic ligands and des-B on the dissolution of goethite. The results are also discussed with respect to their broader implications toward mechanisms for ligand-promoted mineral dissolution.

### References

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## Variable Calcium isotopic fractionation factor in natural carbonated water

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Carbonates precipitated inorganically under laboratory conditions are fractionated relative to the coexisting solution by up to about -1‰ in their  $^{44}\text{Ca}/^{42}\text{Ca}$  ratio [1,2]. Such Ca isotopic fractionation ( $^{44/42}\alpha_{\text{carb}}$ ) is dependent upon the rate of carbonate precipitation with a temperature dependency as a knock-on effect [2] and has been attributed to kinetic effects. The mechanism by which Ca gets enriched in the light isotope in carbonate is rather controversial [1,2] but the experimental approach can be reconciled with the data obtained for biomineralisation. Evidence for a kinetic effect behind the preferential incorporation of light isotopes in inorganic carbonate is more elusive since studies at catchment scale [3-5] are complicated by the role of the vegetation and the incorporation or release of Ca by the biomass.

Here we report  $\delta^{44/42}\text{Ca}$  for paired dripping water and speleothems previously studied for Mg isotopic fractionation [6]. The  $^{44/42}\alpha_{\text{carb}}$  ranges from 0.9998 to 0.9988 while the  $\delta^{44/42}\text{Ca}$  of the dripping water are either indistinguishable from the values of the country rock or enriched toward heavier values by up to 0.22‰. The largest  $^{44/42}\alpha_{\text{carb}}$  is found in a slow dripping speleothem while fast dripping stalagmites precipitate carbonate weakly fractionated. Qualitatively, our data support Lemarchand *et al.* [2] model but with a much greater  $^{44/42}\alpha_{\text{carb}}$  value for very low rate of carbonate precipitation. While this data is not direct evidence for an equilibrium fractionation of Ca isotopes, it is worth noticing that the incorporation of O and Mg isotopes in all of these speleothems occurs at equilibrium [6] and clearly suggests that the mechanisms responsible for Mg and O isotopic fractionations are distinct from those responsible for Ca isotopic fractionation.

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