Macroscopic and infrared spectroscopic investigation of the dissolution of goethite in the presence of desferrioxamine-B

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Siderophore-promoted dissolution has been well studied macroscopically, but there is a lack of understanding of this dissolution process at the microscopic level. Here, we focused on the dissolution of goethite in the presence of desferrioxamine-B (DFO-B). Based on macroscopic results and the structural properties of goethite, it has previously been proposed that DFO-B adsorbs to the goethite surface inner-spherically via one or two hydroxamate groups, leading to dissolution via a ligand-promoted process [1-2]. To date, there has been no spectroscopic study that confirms or refutes this proposed mechanism.

The goal of the present study was to investigate adsorption and dissolution in the goethite-DFO-B system using a combination of macroscopic and infrared spectroscopic methods. All experiments were performed at a total ligand concentration of 0.25 μmol/m^2, in 0.1 M NaCl ionic medium, and in the absence of light. The pH was held at 6 using pH STAT methods. Samples were collected as a function of time, and concentrations of DFO-B that were adsorbed, uncomplexed, and complexed to Fe(III) in solution were determined using UV-VIS spectroscopy. The concentration of adsorbed DFO-B increases by a factor of two over the four day time span of the experiment. The change in adsorbed DFO-B with time mirrors the release of dissolved Fe(III). Dissolved Fe(III) and adsorbed DFO-B concentrations plateau when the concentration of uncomplexed DFO-B goes to zero. Infrared spectra of DFO-B adsorbed at the goethite surface were also measured as a function of time, and we observed the growth of infrared bands at about 1410 and 1555 cm^{-1} as the mineral dissolved. These spectra were interpreted by comparison with the spectra of the different protonation states of DFO-B and the FeHDFO-B$^+$ complex in solution.

[1] Cocozza et al. (2002) Geochim. Cosmochim. Acta **66**, 431-438. [2] Holmen and Casey (1996) Geochim. Cosmochim. Acta **60**, 4403-4416.

The misuse of Nernst-type D's: A case study with R factors

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Nernst-type partition coefficients (i.e., $D_i^{a,b} = C_i^a / C_i^b$) are used extensively by the geologic community to model the mass transfer of one element between coexisting phases; e.g., the partitioning of the platinum group elements (PGE) between silicate melt and sulfide melt. Geochemical models almost exclusively assume that D values are static entities and, thus, overlook the fact that D values may change as a function of dynamic properties affecting the system being studied. Hence, there may rarely be a unique D value that remains unchanged during the evolution of magmatic or magmatic-hydrothermal systems. One powerful use of D's is found in the formulation of "R" factors which estimate the metal enrichment of a sulfide melt coexisting with silicate melt. The R factor equation is written as:

$$[i]_{sulfide} = D_i * [i]_{silicate}^o * (R+1)/(R+D_i)$$

where $[i]_{sulfide}$ is the final concentration of element i in a sulfide melt, $[i]_{silicate}^o$ is the initial concentration of element i in the silicate melt (prior to sulfide saturation) and R is the mass ratio of silicate to sulfide. Most applications of the R factor to modeling the evolution of ore forming systems assume a unique value for D. We show in this study that this seemingly ubiquitous assumption may lead to considerable error in the model predictions because D may vary significantly with changes in intensive variables, particularly fO$_2$ and fS$_2$. For example, the partitioning of Cu between pyrrhotite and silicate melt may be written as:

$$CuO_{0.5}^m + FeS^{po} + 0.5S_2 = CuFeS_2^{po} + 0.25O_2.$$
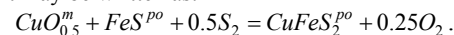
We quantified experimentally the effect of varying fO$_2$ and fS$_2$ on $D_{Cu}^{po/m}$. The data indicate that $D_{Cu}^{po/m}$ can vary by several orders of magnitude over the range of fO$_2$ and fS$_2$ values found in magmatic-hydrothermal systems. Calculations of the effect of variable D values and R factors on metal enrichment in sulfide phase show that at low R values the effect of variable D can be neglected, but that at high R factors, variations in D values determine the metal enrichment in the sulfide phase. Therefore, any effort to model ore forming processes wherein intensive variables such as fO$_2$ and fS$_2$ are not constant should carefully evaluate potential variations in D values and how these may effect the model results.