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Reactions of copper and cadmium ions in aqueous solution with goethite, lepidocrocite, mackinawite, and pyrite

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Abstract

The uptake of Cu and Cd in aqueous solution by interaction with the surfaces of carefully synthesized finely sized particles of goethite, lepidocrocite, mackinawite, and pyrite was measured as a function of initial metal concentration in solution. The results show how reactions between metal ions in solution and mineral surfaces depend in a subtle way on the nature of the surfaces and, in certain cases, on the initial concentration of metal in solution. The uptake curves fall into two groups; type I in which the efficiency of uptake decreases with increasing concentration (Cu and Cd on goethite and lepidocrocite, Cd on pyrite), and type II in which it remains constant (Cu on mackinawite and pyrite, Cd on mackinawite). The total uptake is an order of magnitude greater for the latter group.

X-ray absorption spectroscopies (XANES and EXAFS) were used to define the local environments of the metals taken up at the mineral surfaces. All examples showing the type I behavior yield information on local environments consistent with their being bound to the surfaces by an inner sphere complex formation mechanism. Thus, Cu on goethite appeared to form a Jahn-Teller distorted octahedral complex (four O atoms at 1.94 Å; two O atoms at 2.41 Å) but with evidence for interaction with two further Fe (or Cu) at 2.92 Å. On lepidocrocite, the first coordination sphere was essentially identical to that on goethite but with a second Cu or Fe shell at 3.04 Å and, for the highest Cu loadings, a third shell (2 Cu or Fe) at 3.67 Å. The Cd on goethite showed best fits for sixfold coordination to O (at 2.26 Å) but with evidence for a second shell of Fe atoms at 3.75 Å. On lepidocrocite, the first shell was essentially the same as for goethite, but a second shell of Fe atoms appeared to occur at the shorter distance of 3.31 Å. For Cd-loaded pyrite, best fits were given by a single shell of six O atoms at 2.27 to 2.28 Å and with no evidence for a second shell of metal atoms. The systems exhibiting the type II behavior yielded spectra consistent with the formation of new phases on the surfaces, either by precipitation or replacement reactions. In the case of Cu interaction with mackinawite, a chalcopyrite phase appeared to form, whereas interaction with pyrite seemed to produce binary Cu sulfides—covellite at lower loadings and chalcocite at higher loadings. Cd interaction with mackinawite seemed to produce a CdS phase.