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XAFS study of Cu model compounds and Cu^{2+} sorption products on amorphous SiO_2, γ-Al_2O_3, and anatase

SING-FOONG CHEAH,[1,*] GORDON E. BROWN JR.,[1,2] AND GEORGE A. PARKS[1]

[1]Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.
[2]Stanford Synchrotron Radiation Laboratory, Stanford, California 94309, U.S.A.

ABSTRACT

The primary objective of this study is to determine the effect of substrate type on the coordination environments of Cu^{2+} adsorbed on amorphous SiO_2, γ-Al_2O_3, and anatase at a surface coverage of approximately 1 μmol/m^2. We also collected X-ray absorption fine structure (XAFS) data for several Cu^{2+}-containing model compounds, including tenorite (^{VI}CuO), spertiniite [$^{VI}Cu(OH)_2$], dioptase ($^{VI}CuSiO_2\cdot H_2O$), shattuckite [$^{VI}Cu_5(SiO_3)_4(OH)_2$], chrysocolla [$^{VI}(Cu,Al)_2H_2Si_2O_5(OH)_4\cdot nH_2O$], and Cu^{2+} acetate monohydrate [$^{VI}Cu(CH_3CO_2)_2\cdot H_2O$], for comparison with the sorption sample data. Detailed analysis of these model compounds indicates that the bonding of second neighbors surrounding a central Cu absorber determines whether these second neighbors can be detected by XAFS. The XAFS results of Cu^{2+} sorption samples are consistent with the presence of Jahn-Teller distorted $Cu^{2+}(O,OH)_6$ octahedra, with four equatorial Cu-O bonds (1.95 Å) and two longer axial bonds; the axial Cu-O bonds are difficult to characterize quantitatively by XAFS spectroscopy. Cu^{2+} sorbed on amorphous SiO_2 was found to have Cu second and third neighbors at 2.95 Å, 3.30 Å, and 5.72 Å, but no Cu-Si correlation was detected for these sorption products associated with amorphous SiO_2. Based on XAFS and wet chemical results, it seems likely that a $Cu(OH)_2$ precipitate has formed in the Cu^{2+}/amorphous SiO_2 system. Cu^{2+} sorbed on γ-Al_2O_3 is present as a mixture of monomeric, dimeric, and perhaps a small number of oligomeric hydroxo-bridged $Cu(O,OH)_6$ species with a Cu-Cu distance of approximately 2.95 Å. Sorbed Cu^{2+} on anatase is present predominantly as hydroxo-bridged Cu dimers. At similar sorption densities, Cu^{2+} cluster sizes on amorphous SiO_2 are significantly larger than those on γ-Al_2O_3 or anatase, indicating that the substrate has an important effect on the type of Cu^{2+} sorption complex or precipitates formed.