

Experimental study of germanium adsorption on goethite and germanium coprecipitation with iron hydroxide: X-ray Absorption Fine Structure and macroscopic characterization.

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**Abstract**

Adsorption of germanium on goethite was studied at 25°C in batch reactors as a function of pH (1 to 12), germanium concentration in solution ( $10^{-7}$  to 0.002 M) and solid/solution ratio (1.8 – 17 g/L). The maximal surface site density determined via Ge adsorption experiments at pH from 6 to 10 is equal to  $2.5 \pm 0.1 \mu\text{mol/m}^2$ . The percentage of adsorbed Ge increases with pH at  $\text{pH} < 9$ , reaches a maximum at  $\text{pH} \sim 9$  and slightly decreases when pH is further increased to 11. These results allowed generation of a 2-pK Surface Complexation Model (SCM) which implies a constant capacitance of the electric double layer and postulates the presence of two Ge complexes,  $>\text{FeO-Ge}(\text{OH})_3^\circ$  and  $>\text{FeO-GeO}(\text{OH})_2^-$ , at the goethite solution interface. Coprecipitation of Ge with iron oxy(hydr)oxides formed during Fe(II) oxidation by atmospheric oxygen or by Fe(III) hydrolysis in neutral solutions led to high Ge incorporations in solid with maximal Ge/Fe molar ratio close to 0.5. The molar Ge/Fe ratio in precipitated solid is proportional to that in the initial solution according to the equation  $(\text{Ge/Fe})_{\text{solid}} = k \times (\text{Ge/Fe})_{\text{solution}}$  with  $0.7 \leq k \leq 1.0$ .

The structure of adsorbed and coprecipitated Ge complexes was further characterized using XAFS spectroscopy. In agreement with previous data on oxyanions adsorption on goethite, bi-dentate bi-nuclear surface complexes composed of tetrahedrally coordinated Ge attached to the corners of two adjacent Fe octahedra represent the dominant contribution to the EXAFS signal. Coprecipitated samples with Ge/Fe molar ratios  $>0.1$ , and samples not aged in solution ( $< 1$  day) having intermediate Ge/Fe ratios (0.01-0.1) show  $4 \pm 0.3$  oxygen atoms at  $1.76 \pm 0.01 \text{ \AA}$  around Ge. Samples less concentrated in Ge ( $0.001 < \text{Ge/Fe} < 0.10$ ) and aged longer times in solution (up to 280 days) exhibit a splitting of the first atomic shell with Ge in both tetrahedral ( $R = 1.77 \pm 0.02 \text{ \AA}$ ) and octahedral ( $R = 1.92 \pm 0.03 \text{ \AA}$ ) coordination with oxygen. In these samples, octahedrally coordinated Ge accounts for up to  $\sim 20\%$  of the total Ge. For the least concentrated samples ( $\text{Ge/Fe} < 0.001$ -0.0001) containing lepidocrocite, 30 to 50% of total co-precipitated germanium substitutes for Fe in octahedral sites with the next-nearest environment dominated by edge-sharing  $\text{GeO}_6$ - $\text{FeO}_6$  linkages ( $R_{\text{Ge-Fe}} \sim 3.06 \text{ \AA}$ ). It follows from the results of our study that the largest structural change of Ge (from tetrahedral to octahedral environment) occurs during its coprecipitation with Fe hydroxide at Ge/Fe molar ratio  $\leq 0.0001$ . These conditions are likely to be met in many superficial aquatic environments at the contact of anoxic groundwaters with surficial oxygenated solutions. Adsorption and coprecipitation of Ge with solid Fe oxy(hydr)oxides and organo-mineral colloids and its consequence for Ge/Si fractionation and Ge geochemical cycle are discussed.