

Trace element and contaminant fate during Fe(II)-catalyzed iron oxide surface transformations

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The biogeochemical cycling of iron involves primarily the alternation of iron between oxidized and reduced forms. Recent work has shown that when microorganisms initiate such cycling a cascade of secondary abiotic processes occur through reaction of aqueous Fe(II) and solid Fe(II) oxide minerals. These reactions involve oxidative Fe(II) adsorption, electron transfer into or through the mineral solid, and atom exchange between dissolved Fe(II) and solid Fe(III) [1-3]. This results in mineral recrystallization that proceeds through a surface growth and dissolution mechanism [4]. The resulting dynamic surface transformations may affect the fate of iron oxide-associated trace elements and contaminants.

We have investigated the effect of dissolved Fe(II) on the repartitioning of elements adsorbed on or incorporated in goethite and hematite. Adsorbed As(V), which is structurally incompatible with iron oxides, is unaffected by the presence of Fe(II). In contrast, adsorbed Ni(II) and Zn(II) incorporate into iron oxide mineral structures in the presence of Fe(II). Fe(II) also induces the release of incorporated Ni and Zn back into solution; this is inhibited when insoluble elements co-substitute into goethite or hematite. Redox-active substituting elements, such as Cu(II), Co(III), and Mn(III/IV), undergo coupled reduction and repartitioning upon introduction of aqueous Fe(II). Preliminary stable isotope measurements show that Zn repartitioning during Fe(II)-catalyzed iron oxide recrystallization produces a fractionation distinct from that produced by Zn adsorption and that differs between goethite and hematite. These studies show that the effect of Fe(II) on the fate of trace elements and contaminants is dependent on the compatibility of these elements with the iron oxide structure. The observed element repartitioning demonstrates new pathways for contaminant entrapment and micronutrient release and suggests that iron oxides may not be reliable recorders of trace elements in the rock record.

[1] William & Scherer (2004) *ES&T* **38**, 4782. [2] Yanina & Rosso (2008) *Science* **320**, 218. [3] Handler *et al.* (2009) *ES&T* **43**, 1102. [4] Catalano *et al.* (2010) *GCA* **74**, 1498.

Hydrothermal alteration of the products of transformation of cement-asbestos

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In some European countries the transformation products of cement-asbestos (CATP) can be recycled to produce stoneware tile mixtures, bricks, and concrete incorporated into mortars or to provide both refractoriness and reinforcement to other materials (e.g., road beds) [1]. Not recycled CATP materials must be moved in controlled landfill. An interesting study deals with the fate of the CATP placed in the landfill where solutions could percolate. Can the growth of fibers, perhaps asbestos, occur over a long period of time? The present work studies the experimental conditions involved in the transformation of the CATP and the resulting products. For two sets of reactions, two different deeply characterized CATP mixtures (KC2S; KA) were used. KC2S contained ferrite, periclase, ternesite Ca(OH)₂, merwinite, wollastonite, yeelimite; KA contained akermanite, amorphous, merwinite, bredigite, wollastonite, quartz, calcite, magnetite. The CATP, after addition of H₂O as reactant, was hydrothermally altered in the following range conditions: temperature from 300 to 360 °C; pressure between 15 and 200 MPa; time from 168 to 504 h. Samples have been characterized in detail through XRPD, SEM-EDS and TEM-AEM. Some altered samples showed a large amount of Ca-inosilicate fibrous phases as hillebrandite, foshagite. Other products (i.e. Ca-garnet, brucite, monticellite) were also detected together with low amount of starting material relicts.

[1] Gualtieri, Giacobbe, Sardisco, Saraceno, Lassinantti Gualtieri, Lusvardi & Cavenati Zanatto, (2011) *Waste Manag.* **31**, 91–100.