

Role of Al - Fe (hydr)oxides on mobility and bioavailability of contaminants. Part 1: mechanism of arsenic fixation.

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A mechanism responsible for long-term As fixation in the environment is described here for the first time. Arsenic (1.6 ± 0.5 wt%) was unambiguously identified in mesocrystals of Al-hematite with an As/Fe molar ratio of 0.026 ± 0.006 in environmental samples. The As-bearing Al-hematite is interpreted as a secondary phase formed from iron (hydr)oxides. Experimental evidence supports a mechanism whereby arsenic adsorption onto Al-ferrihydrate nanoparticles (NPs) is followed by Al-ferrihydrate aggregation in a process of self-assembly oriented attachment (OA) to produce nanosized Al-hematite mesocrystals, with goethite as a possible intermediate phase. Arsenic species are incorporated and thus irreversibly trapped in the aggregates. Structural Al was identified in all the As-bearing iron (hydr)oxides.

The key role of iron or aluminum (hydr)oxides on the mobility and bioavailability of As in the environment is well established. However, the detailed ageing/recrystallization mechanisms taking place following the initial adsorption/coprecipitation of As, and the role of Al in these processes remain to be fully understood.

The structural characterization of As-bearing phases in environmental samples is not trivial due to particles heterogeneity, small grain size and low concentrations. Synchrotron-based analytical techniques combined with theoretical molecular modeling or with other spectroscopic techniques have been increasingly applied to investigate As distribution, speciation, and bonding characteristics. The spatial resolution limit of the aforementioned techniques, however, can be overcome by transmission electron microscopy (TEM). This method allows the characterization of

solid phases at the nanoscale, with better spatial resolution than any other technique.

The combined spectroscopy and X-ray diffraction (for bulk analysis) with high resolution TEM (for phase characterization at nanoscale) were applied to investigate As-bearing phases in environmental samples (Freitas *et al.*, 2015). New insights into the mechanism of As incorporation in the structure of Al-Fe-(hydr)oxides such as Al-substituted goethite and hematite are provided.

Arsenic fixation in enriched Al and Fe oxisols

Enriched Fe-Al-enriched oxisols exposed to As-sulfide tailings from hydrometallurgical processing plant in a gold mine in Minas Gerais State were investigated. After more than a decade of disposal the impoundments were removed and the oxisol liner samples were recovered for analyses. A sample from the local oxisol, representing the material before exposure to the As-sulfide tailings, was also investigated. The main constituents of the samples were identified as quartz, kaolinite, muscovite, siderite, albite, gibbsite, hematite and goethite by XRD analysis (Freitas *et al.* 2015).

The As content was 12 ± 7 mg.kg⁻¹ in the natural oxisol (NOX) and ranged from 1,886 mg.kg⁻¹ to 6,375 mg.kg⁻¹ in the oxisol liners (OXL). TEM analysis showed the presence of ferrihydrate, goethite and hematite. Most arsenic (60-69 wt%) in the OXL samples was found in association with crystalline nanoparticle aggregates of Fe-Al-(hydr)oxides. Structural Al was identified in all As-bearing phases by EDS analysis. Arsenic was homogeneously distributed in the structure of nanocrystals of Al-substituted hematite (α -(Fe,Al)₂O₃) (Figure 1) and goethite (α -(Fe,Al)OOH). The arsenic content found in Al-hematite ranged

from 0.90 to 3.23 wt%, (e.g. from 9,000 to 32,300 mg.kg⁻¹). In Al-goethite, the As content ranged from 1.20 to 2.40 wt% (12,000 to 24,000 mg.kg⁻¹). As hematite and goethite are the most stable phases among Fe-(hydr)oxides, the large amount of As incorporated in crystal structure of such phases is therefore less mobile in the environment.

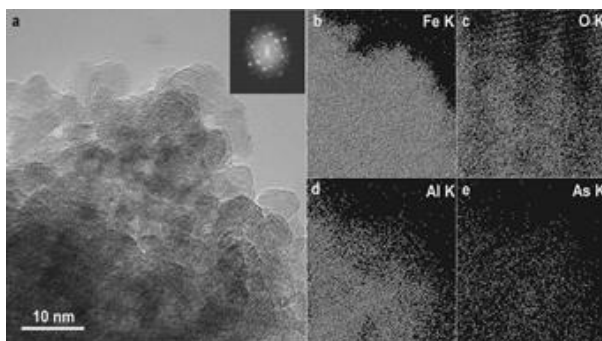


Figure 1: (a) HRTEM image of an aggregate of crystalline hematite NPs. The inset shows the fast Fourier Transform of the aggregate; (b-e) EDS maps of Fe, O, Al and As of the aggregate shown in (a).

A mechanism is proposed for the incorporation of As into hematite in which Al-ferrihydrate nanoparticles (NPs) act as a template. According to this mechanism (Figure 2), As is adsorbed onto existing or newly-formed Al-ferrihydrate, thus modifying its surface properties. The Al-ferrihydrate NPs then aggregate through a self-assembling oriented attachment (OA) process, ultimately resulting in hematite mesocrystals by ageing. The formation of goethite in an intermediate step cannot be excluded. It is known that Al in the system increases the surface area of ferrihydrate, thus improving its adsorption capacity, slowing down phase transformation into hematite, and giving more stability to these phases (Schwertmann et al., 1979; Violante et al., 2009; Adra et al., 2015).

The presence of Al might have hindered the growth of the newly formed Fe-(hydr)oxides NPs so that the OA-based crystal growth was favoured, and therefore the amount of As immobilized in the OA upon attachment of the Al-Fe-(hydr)oxide nanoparticles. Then, arsenic primarily sorbed on the NPs is irreversibly incorporated in the Al-hematite phase.

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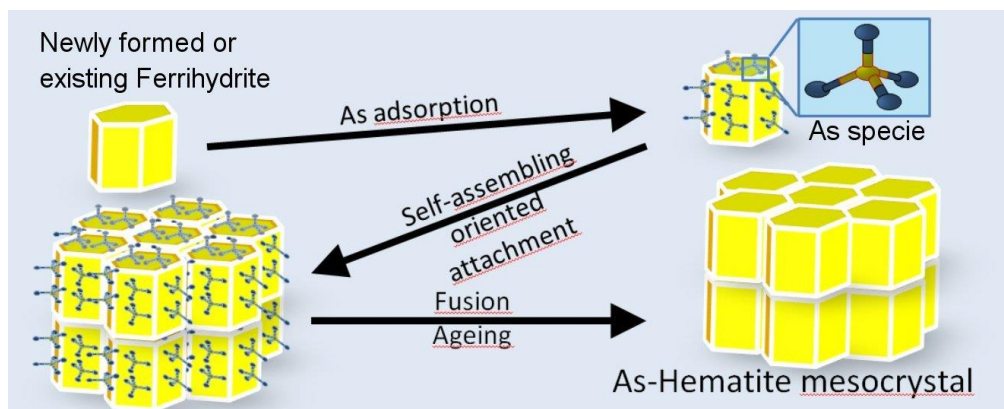


Figure 2. Schematic model illustrating the formation of mesocrystals of hematite and the process of As incorporation in its structure.