



Arsenic entrapment by nanocrystals of Al-magnetite: The role of Al in crystal growth and As retention



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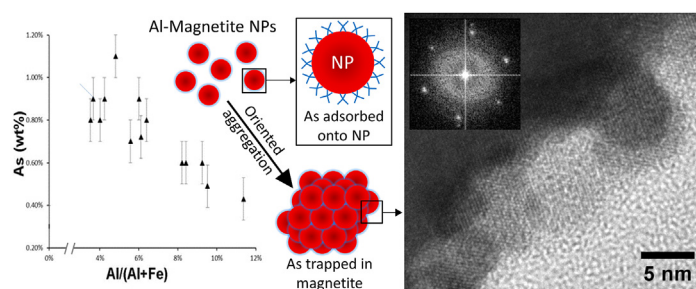
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HIGHLIGHTS

- Oriented attachment crystal growth of magnetite and goethite favoured by the presence of aluminium.
- Increased capacity for As retention by nanostructured Al-magnetite relative to Al-free magnetite.
- Negative correlation between Al and As in magnetite for Al/(Al + Fe) higher than 3–5%.
- Arsenic trapped into Al-magnetite mesocrystals growing by oriented aggregation.
- Trace amounts of As detected in As-Al-Fe co-precipitates by high-resolution electron microscopy techniques.

GRAPHICAL ABSTRACT



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ABSTRACT

The nature of As-Al-Fe co-precipitates aged for 120 days are investigated in detail by High Resolution Transmission Electron Microscopy (HRTEM), Scanning TEM (STEM), electron diffraction, Energy Dispersive X-Ray Spectroscopy (EDS), Electron Energy-Loss Spectroscopy (EELS), and Energy Filtered Transmission Electron Microscopy (EFTEM). The Al present in magnetite is shown to favour As incorporation (up to 1.10 wt%) relative to Al-free magnetite and Al-goethite, but As uptake by Al-magnetite decreases with increasing Al substitution (3.53–11.37 mol% Al). Arsenic-bearing magnetite and goethite mesocrystals (MCs) are formed by oriented aggregation (OA) of primary nanoparticles (NPs). Well-crystalline magnetite likely formed by Ostwald ripening was predominant in the Al-free system. The As content in Al-goethite MCs (having approximately 13% substituted Al) was close to the EDS detection limit (0.1 wt% As), but was below detection in Al-goethites with 23.00–32.19 mol% Al. Our

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As partitioning
As speciation
Al magnetite

results show for the first time the capacity of Al-magnetite to incorporate more As than Al-free magnetite, and the role of Al in favouring OA-based crystal growth under the experimental conditions, and therefore As retention in the formed MCs. The proposed mechanism of As incorporation involves adsorption of As onto the newly formed NPs. Arsenic is then trapped in the MCs as they grow by self-assembly OA upon attachment of the NPs. We conclude that Al may diffuse to the crystal faces with high surface energy to reduce the total energy of the system during the attachment events, thus favouring the oriented aggregation.

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1. Introduction

The immobilization of As released by geogenic and anthropogenic sources is a major environmental concern due to the toxicity of this metalloid, which depends on the As species and their bioavailability in different matrices (Smedley and Kinniburgh, 2002; Smith et al., 2008, 1998). Recent studies have investigated the processes of immobilization of this metalloid in iron and/or aluminium (hydr)oxides (Bolanz et al., 2013; Das et al., 2014; Doerfelf et al., 2015; Duarte et al., 2012; Guo et al., 2013; Ladeira and Ciminelli, 2004; Morin et al., 2009, 2008; Ona-Nguema et al., 2010, 2005; Violante et al., 2007, 2006; Wang et al., 2015) or in mixed Al-Fe-(hydr)oxides (Adra et al., 2015, 2013; Freitas et al., 2015; Masue et al., 2007; Silva et al., 2010; Violante et al., 2009). Mixed Al-Fe-(hydr)oxides have been identified as successful candidates for long-term As immobilization due to the effects of Al-for-Fe substitution in these phases. Aluminium-bearing Fe-(hydr)oxides are ubiquitous in rocks, soils and acid mine drainage (AMD) water, and are also known to favour stable alpha-over gamma-phases (Taylor and Schwertmann, 1978). Up to a certain concentration, Al gives more stability to Al-substituted Fe-(hydr)oxides such as ferrihydrite, goethite, hematite, and magnetite (Cornell and Schwertmann, 2003), slowing down further phase transformation. The properties of mixed Al-Fe-(hydr)oxides have been explored in recent investigations on As immobilization and in water treatment. In a study of co-precipitation of As, Al and Fe from Fe and Al nitrates at 20 °C, with initial Fe:Al molar ratio of 1, Violante et al. (2009) reported that As(V) is mainly incorporated in short-range ordered precipitates such as ferrihydrite, whose transformation is retarded due to the presence of Al. The decrease in As(V) concentration at the surface of co-precipitated products is followed by an increase in pH and ageing (Violante et al., 2009), which the authors attributed to a decrease of the solids' surface area as they evolved to a more ordered structure. Investigations on As adsorption onto Al-substituted goethite were undertaken by Silva et al. (2010). The results showed the high loading capacity of Al-goethite with respect to As(V) relative to pure goethite and hematite. Masue et al. (2007) and Adra et al. (2015) carried out similar investigations on As sorption onto Al-substituted ferrihydrite. Both groups reported a decreasing sorption of As(III) with increasing Al:Fe molar ratio (up to 20 mol%) in Al-containing ferrihydrite at nearly neutral pH. However, Masue et al. (2007) observed no change in the adsorption of As(V) on Al-substituted ferrihydrite for increasing Al:Fe molar ratios, whilst Adra et al. (2015) reported an increase in As(V) adsorption. More recently, magnetite sorbents have become a topic of much interest due to their various applications, such as the removal of trace contaminants from aqueous systems. Despite these recent advances, there is relatively little information on As-bearing Al-magnetite compared to other iron oxides. Al-free magnetite NPs have been shown to have high As adsorption capacity (Akin et al., 2012; Farrell et al., 2014; Liu et al., 2015; Morin et al., 2009; Ona-Nguema et al., 2010; Türk and Alp, 2014) and

are commonly used for the treatment of polluted water. Al-bearing magnetite-based materials have been proposed as new types of adsorbents for As removal from contaminated water (Moradlou et al., 2016; Zhang et al., 2012). In general, the increased loading capacity onto mixed Al and Fe (hydr)oxides has been ascribed to increased surface area due to the presence of Al (Silva et al., 2010). The effect of increasing amounts of Al over As sorption, however, is still debated. Arsenic adsorbed onto metal (hydr)oxide nanoparticles (NPs) can be incorporated into the crystal structure as these phases evolve to more ordered phases, as shown by ageing As-bearing ferrihydrite (Bolanz et al., 2013; Das et al., 2014; Violante et al., 2007), and As-bearing Al-substituted ferrihydrite (Violante et al., 2009). Nevertheless, very few studies have investigated the mechanisms of structural As incorporation in Fe-(hydr)oxides. The pioneering work of Waychunas et al. (2005) suggested that oriented aggregation (OA)-based crystal growth could play a major role in metal contaminant scavenging from polluted waters. Nevertheless, to the Authors' knowledge there is no experimental evidence in the literature showing the role of OA-based crystal growth on the mechanism of As fixation in Al-containing Fe-(hydr)oxides. In our previous work (Freitas et al., 2015) we proposed that As immobilization in tailings impoundments in a gold mine occurred mainly by the incorporation of As(V) in natural nanostructured Al-hematite upon OA of primarily As-adsorbed Al-ferrihydrite NPs, which ultimately formed Al-hematite by ageing. However, the role of Al in the process of As immobilization in such mixed phases is yet to be fully understood.

In this study, As-bearing, synthetic As-Al-Fe co-precipitates aged for 120 days were investigated using High Resolution Transmission Electron Microscopy (HRTEM), Scanning TEM (STEM), Selected Area Electron Diffraction (SAED), Energy Dispersive X-ray Spectroscopy (EDS), Electron Energy-loss Spectroscopy (EELS), and Energy Filtered Transmission Electron Microscopy (EFTEM). The aim of this investigation was to understand (1) the nature of As-bearing phases; (2) the role of Al in the formation of these As-bearing phases; and (3) the mechanisms of As incorporation in magnetite. The effects of Al on As incorporation in co-precipitated Al-magnetite are shown here for the first time. Our results provide evidence for As scavenging by Al-magnetite whose magnetic properties can be utilized for its recovery from treated water.

2. Materials and methods

For the purpose of this study synthetic samples were prepared according to a modified version (Silva et al., 2010) of the procedure described by Schwertmann and Cornell (2000). Synthetic Al-Fe-(hydr)oxides were prepared by co-precipitating Fe and Al from ferrous and Al sulphates in the presence and absence of As, under reducing conditions (Eh of app. - 400 mV), at pH 11.7 and ambient temperature, using three different initial Fe:Al molar ratios (R = 1:0, 1:0.3, and 1:0.7) and different As concentrations in the initial solution (C = 1 and 5 mg.L⁻¹). The co-precipitated samples

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