Interactions of arsenic with calcite surfaces revealed by in situ nanoscale imaging

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Abstract

Arsenic dissolved in water represents a key environmental and health challenge because several million people are under the threat of contamination. In calcareous environments calcite may play an important role in arsenic solubility and transfer in water. Arsenic–calcite interactions remain controversial, especially for As$^{(III)}$ which was proposed to be either incorporated as such, or as As$^{(V)}$ after oxidation. Here, we provide the first time-lapse in situ study of the evolution of the (10–14) calcite cleavage surface morphology during dissolution and growth in the presence of solutions with various amounts of As$^{(III)}$ or As$^{(V)}$ at room temperature and pH range 6–11 using a flow-through cell connected to an atomic force microscope (AFM). Reaction products were then characterized by Raman spectroscopy. In parallel, co-precipitation experiments with either As$^{(III)}$ or As$^{(V)}$ were performed in batch reactors, and the speciation of arsenic in the resulting solids was studied by X-ray absorption spectroscopy (XAS). For As$^{(V)}$, AFM results showed that it interacts strongly with the calcite surface, and XAS results showed that As$^{(V)}$ was mostly incorporated in the calcite structure. For As$^{(III)}$, AFM results showed much less impact on calcite growth and dissolution and less incorporation was observed. This was confirmed by XAS results that indicate that As$^{(III)}$ was partly oxidized into As$^{(V)}$ before being incorporated into calcite and the resulting calcite contained 36% As$^{(III)}$ and 64% As$^{(V)}$. All these experimental results confirm that As$^{(V)}$ has a much stronger interaction with calcite than As$^{(III)}$ and that calcite may represent an important reservoir for arsenic in various geological environments.
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1. INTRODUCTION

Calcium carbonate, a major constituent of the rocks in the Earth's upper crust, has the ability to trap several kinds of ions in its structure. Among them, cations (Paquette and Reeder, 1995; Rimstidt et al., 1998; Davis et al., 2000; Stipp et al., 2006), and anions (Dove and Hochella, 1993; Alexandratos et al., 2007; Montes-Hernandez et al., 2009) could be incorporated or interact with mineral surfaces, making calcite a potential sink for these elements at the global scale. Several studies have characterized how arsenic, phosphorous or selenium oxyanions could be incorporated during the growth of calcite crystals at near surface conditions (Montes-Hernandez et al., 2009, 2011; Aurelio et al., 2010). Here, we report on time-lapse in situ observations

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of the interactions between arsenic oxyanions with calcite surfaces during growth, dissolution, and co-precipitation.

Arsenic exists in nature in four oxidation states. $As^{(-I)}$ in arsenian pyrite (Simon et al., 1999) and $As^{(-III)}$ (as arsenide) are mainly found in native minerals and metallic alloys containing arsenic, and $As^{(III)}$ (arsenite compounds) and $As^{(V)}$ (arsenate compounds) are present as constituents of various minerals and organic compounds or as oxyanions dissolved in groundwater (arsenite AsO_3^{3-} and arsenate AsO_4^{3-} anions, respectively) in which they can be transported. $As^{(III)}$ species are more soluble and toxic than $As^{(V)}$ species (Cullen and Reimer, 1989). $As^{(V)}$ is the dominant species under oxidized conditions, whereas $As^{(III)}$ is stable at intermediate to low redox potentials.

Arsenic has both toxic and carcinogenic effects on animals and humans and has accumulated to phytotoxic levels in some soils and groundwaters because of both human activity (e.g. use of pesticides in agriculture, mining activities, industry) and natural processes (e.g. rock– and mineral–fluid interaction such as during weathering). It represents a key environmental health problem in many countries (Christen, 2001; Rodrìguez-Lado et al., 2013), especially when it affects drinking water. The drinking guideline of 10 micrograms per liter (10 ppb) is recommended by the World Health Organization and used as the maximum contaminant level by the European Union and the USA. Hazard assessment associated with natural arsenic enrichment in soils and groundwaters depends heavily on the ability to understand and predict the mobility of arsenic and its transport between various reservoirs. In addition, there is growing interest in characterizing the effects of potential leakage of carbon dioxide repositories into freshwater aquifers, and the risk of toxic element release due to pH decrease and the dissolution of some minerals or the desorption of some species (Montes-Hernandez et al., 2013) during dissolution–precipitation processes (Putnis, 2009; Ruiz-Agudo et al., 2012).

Because of the importance of arsenic in various natural environments, we first describe in the following sections various hydrological systems with arsenic contaminations. Then, we report on various environmental systems where arsenic and calcite have been shown to interact. Finally, we present several mechanisms of arsenic–calcite interactions that have been proposed in the literature.

1.1. Arsenic in groundwaters and its origin

Various studies have pointed to contamination of groundwater by arsenic, well above the drinking guidelines and have demonstrated widespread dissolved arsenic concentrations in the range 0.05–3 ppm, and above 100 ppm in some localized contaminated sites. Usually arsenic has a geogenic origin, coming from the weathering of bedrock. In several mining areas, associated mine and drainage waters are contaminated. Mine tailings are leached by rain and arsenic has been transported to nearby groundwater reservoirs contaminating the soils in agricultural fields, leading to serious health problems (Carillo and Drever, 1998; Romero et al., 2004).

Up to 0.05 ppm was measured in the freshwaters in eastern New England, USA with more than 200,000 people using this water (Ayotte et al., 2003), up to 3 ppm in Vietnam (Christen, 2001), up to 1.3 ppm in Bangladesh (Zheng et al., 2004), above 0.05 ppm in the San Antonio-El Triunfo mining area in southern Baja California peninsula, Mexico (Carillo and Drever, 1998), and up to 0.65 ppm in the mining area of the Zimápan valley, Mexico (Romero et al. 2004; Song et al., 2006). In the calcareous environment of the Matehuala-Cerrito Blanco area, northern Mexico, Martínez-Villegas et al. (2013) reported concentrations in groundwaters as high as 158 ppm, with average values in the range 5–10 ppm. There, the dissolved arsenic is proposed to originate from the leaching of the abandoned wastes of mines. In an industrial area contaminated with by-products of arsenic ore exploitation, the mineral wastes were drained by meteoritic water and concentrations of dissolved arsenic as high as 235 ppm were measured (Julliot et al., 1999), in water with a pH down to 2.1. Bowell and Parshley (2005) have shown that the experimental leaching of rocks in a pit-lake could release up to 165 ppm dissolved arsenic.

In many environments, the distribution of arsenic concentrations in the water table of a given area is heterogeneous, with patches of high concentrations (Charlet et al., 2007). Arsenic concentrations above 50 ppb, the permissible current drinking level in Bangladesh, are found in over 30% of the wells of this country (Zheng et al., 2004) and more than 19.6 million inhabitants in China are living in areas where a risk of geogenic arsenic contamination has been estimated (Rodrìguez-Lado et al., 2013). In the aquifers of the southwest Songnen basin, China, residents are exposed to drinking water with more than 0.34 ppm of total arsenic (60–80% $As^{(III)}$, 20–40% $As^{(V)}$), with deeper groundwater showing on average higher arsenic concentrations (Guo et al., 2014). The sediments hosting the aquifer there contain between 2 and 102 ppm arsenic, which is bound to carbonates, iron oxides and clays and some arsenic is incorporated into siderite and calcite (Guo et al., 2014). In the Ganges delta, the concentration of arsenic in groundwater is very heterogeneous. Arsenic is present in carbonates and iron-oxide rich sediments, with associated concentrations in groundwater up to 0.5 ppm. There, the proportion of $As^{(III)}$ and $As^{(V)}$ are 42% and 58%, respectively (Charlet et al., 2007). In these sediments, the total concentration of arsenic is close to 3 ppm and major carriers are the amorphous iron oxides, sulfides and/or carbonates that liberate arsenic when they dissolve. The leaching of arsenic in the Marshall sandstone (Michigan) into the groundwater was attributed to the reaction between dissolved bicarbonate and arsenic-rich sulphide minerals initially present in the rock (Kim et al., 2000). As a result, the groundwater contains concentrations of arsenic in the range 0.2–0.3 ppm, mostly in the form of $As^{(III)}$. In the groundwater of the Chalkidiki area, Northern Greece, the concentration of arsenic in groundwaters reaches 3.7 ppm, mainly in the form of $As^{(V)}$, and some travertines have precipitated with concentrations up to 913 ppm $As^{(V)}$ trapped into the carbonate (Winkel et al., 2013). In this natural system, where the concentration of iron oxides is low and geothermal degasing of CO_2 is active, carbonates represent the main sink for arsenic uptake.