Arsenic in hydrothermal apatite: Oxidation state, mechanism of uptake, and comparison between experiments and nature

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Abstract

Element substitution that occurs during fluid–rock interaction permits assessment of fluid composition and interaction conditions in ancient geological systems, and provides a way to fix contaminants from aqueous solutions. We conducted a series of hydrothermal mineral replacement experiments to determine whether a relationship can be established between arsenic (As) distribution in apatite and fluid chemistry. Calcite crystals were reacted with phosphate solutions spiked with As(V), As(III), and mixed As(III)/As(V) species at 250 °C and water-saturated pressure. Arsenic-bearing apatite rims formed in several hours, and within 48 h the calcite grains were fully replaced. X-ray Absorption Near-edge Spectroscopy (XANES) data show that As retained the trivalent oxidation state in the fully-reacted apatite grown from solutions containing only As (III). Extended X-ray Fine Spectroscopy (EXAFS) data reveal that these As(III) ions are surrounded by about three oxygen atoms at an As─O bond length close to that of an arsenate group (AsO_4^{3-}), indicating that they occupy tetrahedral phosphate sites. The three-coordinated As(III)–O_3 structure, with three oxygen atoms and one lone electron pair around As(III), was confirmed by geometry optimization using *ab initio* molecular simulations.

The micro-XANES imaging data show that apatite formed from solutions spiked with mixed As(III) and As(V) retained only As(V) after completion of the replacement reaction; in contrast, partially reacted samples revealed a complex distribution of As(V)/As(III) ratios, with As(V) concentrated in the center of the grain and As(III) towards the rim. Most natural apatites from the Ernest Henry iron oxide copper gold deposit, Australia, show predominantly As(V), but two grains retained some As (III) in their core. The As-anomalous amphibolite-facies gneiss from Binntal, Switzerland, only revealed As(V), despite the fact that these apatites in both cases formed under conditions where As(III) is expected to be the dominant As form in hydrothermal fluids.

These results show that incorporation of As in apatite is a complicated process, and sensitive to the local fluid composition during crystallization, and that some of the complexity in As zoning in partially reacted apatite may be due to local fluctuations of As(V)/As(III) ratios in the fluid and to kinetic effects during the mineral replacement reaction. Our study shows for the first time that As(III) can be incorporated into the apatite structure, although not as efficiently as As(V). Uptake of As(III) is probably highly dependent on the reaction mechanism. As(III)O_3^{3-} moieties replace phosphate groups, but cause a high strain on the lattice; as a result, As(III) is easily exchanged (or oxidized) for As(V) during hydrothermal recrystallization, and the fully reacted grains only record the preferred oxidation state (i.e., As(V)) from mixed-oxidation state solutions.

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Overall this study shows that the observed oxidation state of As in apatite may not reflect the original As(III)/As(V) ratio of the parent fluid, due to the complex nature of As(III) uptake and possible *in situ* oxidation during recrystallization.

1. INTRODUCTION

The apatite group, with its general formula of $A_{10}(XO_4)_6(F, OH, Cl)_2$; A = Ca, Sr, Ba, Pb, ±Na, REE on two different crystallographic sites; $X = P^{5+}$, As^{5+}, V^{5+}, Si^{4+} on a rigid tetrahedral site; and F, Cl, OH^- (so-called 'column anions') located within channels down the *c*-axis; plays an important role in various geological, industrial, and biological processes (e.g. Pan and Fleet, 2002; Pasero et al., 2010; Hughes and Rakovan, 2015). Apatite-group minerals are widespread accessory minerals in many rock types, accounting for a large part of P mass balance, but also hosting significant amounts of other key petrologically and environmentally significant elements such as F, Sr, As, U, or REE. The ability of apatite to scavenge toxic metals such as As or U forms the basis of its use in environmental remediation and waste disposal, and apatite is probably the most important biomineral of relevance for human health.

Trace element substitutions in apatite can be used to investigate the nature of geological fluids from which the apatite precipitates or by which the apatite has been altered (e.g., Harlov, 2015). Tracing the origin of the observed zonation and interpreting it in terms of fluid–rock interaction is fundamental to understanding how metals are transported and deposited. In particular, the trace element zonation observed in hydrothermal apatite may be used to track fluid chemistry (Bath et al., 2013), and help mineral exploration (Mao et al., 2016).

Studies of As incorporation in apatite also have applications for As mobility and treatment in environmental and industrial systems. Arsenic can be released into an aqueous phase from As-bearing minerals during various processes such as weathering and mining (Jamieson et al., 2011; Alam et al., 2014). Many approaches have been developed to remove As from water, including chemical reactions to form As-bearing minerals, adsorption of As onto mineral surfaces, and co-precipitation of As into mineral structures (Choong et al., 2007; Renard et al., 2015). For example, lime has been used to immobilize As in wastewater due to the formation of arsenate apatite instead of calcium arsenate (Bothe and Brown, 1999).

Arsenic has eight oxidation states from −3 to +5, and As(III) and As(V) are the main species in aqueous solutions depending on oxygen fugacity, pH and temperature (Testemale et al., 2004; James-Smith et al., 2010; Qian et al., 2013; Renard et al., 2015). Arsenic(V) exists mainly as charged tetrahedral arsenate complexes (e.g., $H_2AsO_4^-$ and $HAsO_4^{2-}$) in natural waters, whereas due to a stereochemically active lone electron pair, As(III) exists mainly as a neutral trigonal pyramidal $As(OH)_3(aq)$ complex, with three oxygen on the basal plane and As on the apex

(Testemale et al., 2004). As the arsenate (AsO_4^{3-}, As—O distance ~1.69 Å) and phosphate (PO_4^{3-}; P—O distance ~1.53 Å) moieties share a similar tetrahedral geometry, phosphate groups in solids can be substituted by arsenate groups, despite large differences in ionic radii of the P^{5+} (0.17 Å) and As^{5+} (0.34 Å) cations.

Several studies have investigated As(V) incorporation in apatite; most are characterization of As-bearing apatite synthesized from stoichiometric reactions of chemical compounds (e.g., Lee et al., 2009; Zhu et al., 2009; Zhang et al., 2011). They found that a complete solid solution series can be formed between hydroxylapatite ($Ca_5(PO_4)_3OH$) and johnbaumite ($Ca_5(AsO_4)_3OH$). A recent study investigated the process of As substitution during the calcite – apatite replacement reaction under hydrothermal conditions (Borg et al., 2014). This study showed that arsenate (AsO_4^{3-}) moieties from the solution are rapidly (within an hour) taken up by apatite, initially resulting in a complex zoning pattern of As within the apatite structure. Within two days the zoning disappears and a homogeneous As-bearing hydroxylapatite forms as the final product. Borg et al. (2014) show that the uptake of As and the chemical zoning in apatite formed via calcite replacement are controlled by the local fluid-mineral equilibrium (see Putnis, 2009; Altree-Williams et al., 2015). So far to the authors' knowledge there is no report on As(III) substitution in apatite-group minerals.

The aim of this paper is to investigate the uptake of As in hydroxylapatite from solutions containing both As(III) and As(V), and the effects of the different As oxidation states in solution on the zoning and composition of the resulting hydroxylapatite (we will use 'apatite' for the 'hydroxylapatite' for the rest of the paper). Both As(III) and As(V) were incorporated in apatite formed via hydrothermal replacement of calcite at 250 °C. We used synchrotron micro-XANES, bulk XAS and SEM techniques to determine and map element distribution and the oxidation state of As in the hydrothermally synthesized As-bearing apatite, as well as in natural hydrothermal apatite from the Ernest Henry iron oxide copper gold deposit, Queensland, Australia, and from an As-anomalous amphibolite-facies gneiss from Binntal, Switzerland. *Ab initio* molecular simulations were used to help constrain the coordination structure of As(III) and As(V) in apatite, and the substitution mechanism of different oxidation states of As in apatite.

2. MATERIAL AND METHODS

2.1. Hydrothermal synthesis of As-bearing apatite

Arsenic-bearing apatite grains were synthesized by reacting calcite crystals with As(III)- and As(V)-bearing