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 hours 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. 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.

**Keywords**: apatite, arsenic, oxidation state, mineral replacement reaction, XANES spectroscopy, molecular simulations, trace element partitioning.

**Highlights**

- As(III) and As(V) both can be incorporated in hydroxylapatite during dynamic coupled dissolution/reprecipitation reactions.
- As(III) moieties replace phosphate groups with a high local strain compared to As(V).
- Upon recrystallization, As(V) replaces the As(III) in the hydroxylapatite structure.
- Most studied natural apatites retain mainly As(V), even though they formed from solutions that mainly contained As(III).
- Reaction pathway and kinetics exert a major controls on As(III) uptake in apatite.

**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;
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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 (Alam et al. 2014; Jamieson et al. 2011). 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 coprecipitation 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., H2AsO4- and HAsO42-) 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 (AsO43-, As-O distance ~1.69 Å) and phosphate (PO43-; 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 P5+ (0.17 Å) and As5+ (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 \( \text{Ca}_5(\text{PO}_4)_3\text{OH} \) and johnbaumite \( \text{Ca}_5(\text{AsO}_4)_3\text{OH} \). 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 \( (\text{AsO}_4^{3-}) \) 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. \textit{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 phosphate solutions at 250 °C in a titanium cell that had been preheated to 380 °C to form a thin inert TiO$_2$ layer on the surface. Three series of experiments were conducted aiming to incorporate As(V), As(III) and mixture of As(V) and As(III) into apatite (Table 1): in Series V the starting solutions are a mixture of sodium arsenate and phosphate solutions with 0.12 m As(V) concentration (Borg et al., 2014); in Series III the starting solutions are phosphate
solutions spiked with 0.03-0.14 m As$_2$O$_3$; and in Series M the starting solutions contain mixtures of different concentrations of As$_2$O$_3$ and sodium arsenate to get variable As(III)/As(V) ratios. The solution pH$_{250\text{°C}}$ ~5.6, calculated based on geochemical modelling package HCh and default thermodynamic database (Shvarov, 2008).

For each experiment, the solutions were purged with N$_2$ gas before sealing the Ti cell to remove the air; during the experiments the solution was only in contact with the inner wall of the Ti cell. For each series, a few short runs of 3-5 hours were conducted to achieve partial replacement of calcite by apatite, and longer runs of 48 hours to obtain complete replacement, as indicated in Borg et al. (2014).

2.2. Natural hydrothermal apatite from Ernest Henry IOCG deposits, NT, Australia

The Ernest Henry Fe-oxide-Cu-Au (IOCG) deposit is located in the Eastern Succession of the Mount Isa Inlier, Queensland, Australia. The deposit is a mineralised breccia hosted in volcanics within the Mary Kathleen Group. The mineralisation comprises chalcopyrite, pyrite, electrum and magnetite associated with calcite and apatite and the ore-zone is surrounded by a 100 m-scale zone of K-metasomatism that overprints earlier regional Na-Ca alteration. Ore-minerals are located between clasts of K-feldspar-altered volcanics. Fluid inclusion studies indicate the presence of hyper-saline brines with a distinct magmatic component (Mark et al. 2005) that provide an effective transport medium for large amounts of K and metals. Reactive transport modelling indicates that whilst many of the alteration assemblages observed at Ernest Henry can be produced by fluid-rock reaction with a hypersaline brine, mixing of a second fluid is required to reproduce the voluminous calcite-bearing assemblages (Cleverley and Oliver 2005).

Apatite from Ernest Henry is enriched in fluorine and As (Rusk et al. 2010) compared to other IOCG deposits. Individual grains are zoned with respect to As and S and contain up to 5 and 0.5 wt% respectively (Cleverley 2006). The sample analysed in this study comes from the upper ore zone of the Ernest Henry mine. It contains pyrite, apatite, hematite, and quartz with minor magnetite and calcite. The apatite is irregularly zoned in As, with As-poor cores and a series of variably well-developed As-bearing rims with up to several percent of As concentrations.

2.3. Apatite from As-anomalous amphibolite-facies gneiss from Binntal, Switzerland

The Binntal Valley (Central Alps, Switzerland) is a hot spot of mineral diversity, being the type locality for forty-three new mineral species, many of which contain As. Gneisses (including
meta-rhyolites) from the Monte Leone Nappe (Brianconnais Domain) are a likely As source for
the numerous small-scale hydrothermal and metamorphic-hydrothermal As-bearing
mineralization occurrences in the Valley (e.g., Lengenbach metamorphosed sedimentary
exhalative deposit, and the As-REE-Ti-rich minerals in the alpine vugs of Monte Cervandone;
Knill, 1996). The studied sample is a quartz-K-feldspar-muscovite±biotite gneiss from Ritterpass
(Cuchet et al. 2014). The Monte Leone Nappe has experienced Barrovian style, medium
temperature and pressure amphibolite facies metamorphism during the Neoalpine period
(≤ 30 Ma). Apatite in this sample occurs within the main schistosity, which formed at peak
temperatures 450-580°C (Carrupt, 2003; Gregory, 2012). The sample also contains a folded quartz-
K-feldspar vein with a cm-sized As-Nb-REE-bearing titanite (Cuchet et al. 2014).

2.4. Synchrotron bulk XAS measurement

Arsenic K-edge X-ray absorption spectroscopic (XAS) measurements of bulk samples
were conducted at the XAS beamline of the Australian Synchrotron (AS). The AS storage ring
operated in top-up mode with beam current of 200 mA. The XAS beamline has a 1.9 T wiggler
source, and a Si(111) monochromator was used for As K-edge measurement with an energy
resolution of 1.5 ×10⁻⁴ at 10 keV. The size of the X-ray beam on the sample was 0.5 mm (V) x
1 mm (H). The samples were ground to powder and sealed with Kapton tape, and XANES and
EXAFS data were collected under ambient conditions in fluorescence mode with a Canberra 100-
element Ge detector.

2.5. Synchrotron µ-XRF and µ-XANES imaging

Elemental mapping and As K-edge XANES imaging (Etschmann et al. 2010; 2014) was
performed for the partially reacted apatite samples and natural apatite from Ernest Henry and
Binntal. The synthesized apatite grains (0.5- 3 mm diameter) were mounted on a quartz slide and
polished to ~30 µm thickness for optimal Synchrotron µ-XRF measurement. The ore samples
from Ernest Henry and Binntal were also prepared into 30 µm thin sections on quartz slides.

Elemental maps and XANES stacks were measured at the X-ray fluorescence microscopy
(XFM) beamline (Paterson et al., 2011) at Australia Synchrotron. Details of the measurement
procedure and data reduction are found in Li et al. (2016) and Etschmann et al. (2014). The Si(111)
monochromator delivers an energy resolution ΔE/E of ~2.8 × 10⁻⁴, and the beam was focused to a
~2 µm spot size using Kirkpatrick-Baez mirrors. Fluorescence data were collected using the Maia
model C 384 detector array, which has an energy resolution of 240 eV and can detect elements down to atomic number 15 (phosphorous) (Ryan et al. 2014; Kirkham et al., 2010). Samples were mapped using different scanning speeds (1.024 to 2.048 mm/s), corresponding to dwell times of 2 to 12 ms/pixel. The MSXRF data were analyzed with the GeoPIXE software package (Ryan et al., 1990, 2010b), using standard foils (Pt, Mn, Fe) as external standards as well as Ca as an internal standard (from calcite starting material) to constrain the quantification parameters (detector geometry and efficiency; calibration of ion chamber to measure photon flux). The method uses the Dynamic Analysis (DA) method (Ryan et al., 1993, 2000, 2010a) to deconvolute the spectral components due to As and other elements from elastic and inelastic scattering. A separate DA matrix is used for each beam energy stack to track the changing energy of the scatter peaks. The result is a 3D data cube providing As XANES spectrum at each pixel position.

SXRF maps were collected at eighty-seven irregularly spaced monochromator energies that spanned the As-K edge, averaging 1 eV per step, with 0.5 eV steps across the edge. The As concentrations at each pixel in the SXRF map, at each monochromator energy, were extracted and used to construct XANES spectra at each pixel. These XANES spectra were normalized and smoothed using box-car smoothing over 2x2 pixels and then the resulting XANES spectra were fitted using a linear combination of As$_2$O$_3$ and Na$_2$HAsO$_4$$\cdot$7H$_2$O. The resulting linear fitting components were normalized to one and As(III)/As maps were generated (Etschmann et al. 2010; 2014). An overview map of each sample was performed covering areas of about 130 mm$^2$ at 4 µm pixel pitch (typically 4500 x 1700 pixels) with a transit time of 1 ms per pixel. Regions of interest were selected from these overviews for detailed XANES mapping. These XANES stacks comprised image frames (typically 250 x 150 pixels) at 10 µm pitch and 4.9 ms transit per pixel, repeated over a sequence of 181 energies spanning the K absorption edge of As. The data was analyzed as described above.

A detailed XANES data cube on one sample was also acquired at the P06 beamline at the PETRA III synchrotron at DESY (Schroer et al., 2010). This experiment also used a Maia model C detector, but benefitted from a finer beam resolution (~0.4 µm), a monochromator energy resolution $\Delta E/E$ of $\sim$1.4 x $10^{-4}$ and scanning of the energy axis as the fast axis to provide uniformly fine energy steps (0.5 eV at 1 ms/step).
2.6. Assessment of beam damage and As oxidation due to sample preparation

Arsenic is known to be susceptible to synchrotron X-ray beam damage, depending on sample type, concentration, type of the X-ray source, and photon flux density (Smith et al., 2005). For example, As(III) in solution may be oxidized to As(V) due to beam damage (e.g., James-Smith et al., 2010). Time-dependent measurements show that for bulk XAS analyses conducted at room temperature, no beam damage is observed for the arsenolite (As$_2$O$_3$) standard and all As(V) samples. For the As(III) apatite samples, there is slight beam damage (1.1% oxidized to As(V) based on linear combination fit) among repeated scans lasting 35 minutes. For the micro-XANES measurement, it is more difficult to assess the extent of the beam damage and oxidation of As during the preparation of thin sections; however it is suggested that this is not a significant issue, as pure As(III) and mixed As(III)/As(V) spectra were retrieved from the XANES maps for mixed As(III)/As(V) samples, and only qualitative interpretations are made from the measured spectra. Significant beam damage is unlikely for micro-XANES measurement, because the dwell time is very low (12 ms).

2.7. Ab initio molecular simulations

Structure optimizations of arsenolite, hydroxylapatite and hydroxylapatite substituted with As(V) and As(III) were carried out using density functional theory (DFT) within the CPMD code (version 3.17.1, Car and Parrinello, 1985). The DFT-based ab initio simulations have been successfully used to simulate the structure of hydroxylapatite (Slepko and Demkov, 2011), and cations substitution in hydroxylapatite (e.g., Terra et al., 2009; Zeglinski et al., 2012).

The CPMD method implements DFT using plane-wave basis sets and pseudopotentials to simulate the presence of the core electrons and the nucleus. In this study, the BLYP (Becke, Lee, Yang and Parr) exchange correlation-functional was employed (Lee et al., 1988; Becke, 1988) together with Martins–Troullier pseudo-potentials (plane-wave cutoffs of 80 Ry) from the CPMD package (Troullier and Martins, 1991). In each calculation, wavefunction optimization was conducted initially and then followed by geometry optimization. Convergence criteria of $10^{-5}$ and $10^{-3}$ were applied for wavefunction and geometry optimization, respectively. All calculations were conducted using periodic boundary conditions.

Geometry optimization of arsenolite (As$_2$O$_3$) was performed with a single unit cell containing 80 atoms (crystal structure refinement of Ballirano and Maras, 2002). Calculations with up to 12 super-cells of hydroxylapatite (crystal data from Wilson 1999; 44 atoms per unit cell;
[Ca₅(PO₄)₃OH], Z = 2) were conducted to test the effect of super-cell size. The cells were aligned in the order of 1-1-1, 1-1-2, 1-1-3, 2-2-2 and 2-2-3 along a-b-c dimension; where 1-1-1 is defined to be the unit cell, 1-1-2 is defined to consist of the unit cell plus a second unit cell along the c axis, 2-2-3 consists of 2 unit cells along a, 2 unit cells along b and 3 unit cells along c, etc. The unit cell size was kept constant for all calculations, which is consistent with the low concentration of As substituted into the apatite (≤2.5 wt% As). As the geometrical properties of the 1-1-3 super-cell (132 atoms) and 2-2-3 (528 atoms) gave a similar agreement between the optimized bond distances and the measured values of Wilson (1999), the super-cell 1-1-3 was chosen for geometry optimization of As-substituted hydroxylapatite. Series of calculations were performed with As substitution in different oxidation states: i) As(V)-substituted hydroxylapatite (132 atoms in a 1-1-3 super-cell with one AsO₄³⁻ replacing one PO₄³⁻, corresponding to 2.45 wt% As; and ii) As(III)-substituted hydroxylapatite (131 atoms in a 1-1-3 super-cell with one AsO₃³⁻ moiety replacing one PO₄³⁻ group). Four different possibilities of replacing PO₄³⁻ by AsO₃³⁻ were calculated by removing each of the four oxygen atoms in the PO₄³⁻ site.

3. Results

3.1. Arsenic oxidation state in apatite as a function of reaction progress and As(III)/As(V) ratio in the mother solution

All the short (3-5 hour) experimental runs resulted in calcite grains with an As-bearing apatite rim, and the 48 hour runs ended up with complete replacement of calcite by As-bearing apatite. Micro-XANES maps were measured for the partially reacted samples from the mixed As(III)/As(V) solutions, and bulk XANES and EXAFS data were collected for the fully reacted (no calcite left) samples (Table 1).

**As(V)-only experiment.** Calcite crystals were reacted in the presence of solutions that contained only As(V) (Sample V-2-8). The XANES spectrum (Fig. 1) shows only the spectral features characteristic of As(V), consistent with substitution of As(V) for P(V) in the tetrahedral PO₄³⁻ sites.

**As(III)-only experiments.** The bulk XANES spectra for the fully replaced samples from solutions that contained only As(III) (1.3 m (NH₄)₂HPO₄ and variable amounts of dissolved As₂O₃) show only the As(III) features (samples III-13-5 and III-13-6, Fig. 1), suggesting substitution of As(III) in the apatite structure. There is a linear trend between the As concentrations
in the solid and the initial As concentrations in the fluid (Fig. 2) for both As(V) and As(III) experiments, with the As$_\text{solid}$/As$_\text{solution}$ ratio lower in the case of the As(III) solutions (ratio around 0.1) than in the case of As(V) (~0.2; Borg et al., 2014), indicating that As(III) incorporation in apatite is less effective than As(V) incorporation.

**Mixed As(III)/As(V) experiments.** For the *fully reacted samples* made from solutions that contained both As(III) and As(V) (samples M-5 – M-8, Table 1), the bulk XANES spectra show only the presence of As(V) in all three samples (Fig. 1), despite the fact that these samples have different As(III)/As(V) ratios in the initial solutions (M-5, M-6 and M-8, Table 1). Micro-XANES spectra for one of these samples (M-6, solution As(III)/As(V) ratio = 1) also shows predominantly As(V) (Fig. 3).

In contrast, the micro-XANES maps show heterogeneous distribution of As(III) and As(V) for *partially reacted* samples formed under the same conditions from solutions containing both As(III) and As(V) (samples M-7 and M-9; Table 1; Fig. 4-5). For example, As(V) is concentrated in the inner part, and As(III) is more abundant on the outer part of the reaction rim of sample M-7 (solution As(III)/As(V) ratio = 1, Fig. 4). The M-9 sample, which has the highest ratio of As(III) among the mixed oxidation state solutions (As(III)/As(V) = 10.5), also has the highest level of As(III) (Fig. 5). Similar to M-7, As(III) in M-9 is enriched preferentially around the edge, and As(V) is concentrated towards the center of grain (Fig. 5b, c). The micro-XANES imaging on the smaller area in the M-9 sample, performed at PETRA beamline P06, is consistent with the results collected at the Australian Synchrotron, although the As(III) and As(V) peaks are better resolved as a result of the finer energy resolution of the beamline (Fig. 5e, f).

### 3.2. Nature of arsenic in apatite formed via calcite replacement

Bulk EXAFS were recorded for the fully reacted samples, as well as the As(III) and As(V) compounds that were used in the preparation of the solutions (hydrated sodium arsenate Na$_2$HAsO$_4$(H$_2$O)$_7$ and arsenolite As$_2$O$_3$). The EXAFS fitting results conducted in both R and K space are similar within the quoted errors, and fit parameters from R space fitting are compiled in Table 2, and the fitted EXAFS spectra and their Fourier Transform are plotted in Fig. 6a-b. Fitting the EXAFS spectrum of the sodium arsenate with 4 oxygens yields an As-O bond length of 1.697(7) Å, similar to previously reported crystallographic values (average 1.688(4) Å, Ferraris and Chiari 1970). The fitted As-O distance for arsenolite (As$_2$O$_3$) is much longer at 1.805(4) Å than in the arsenate (Table 3); this value is similar to the literature values of 1.786(2) Å from the
single crystal X-ray crystal structure refinement (Ballirano and Maras 2002). Both fits gave a similar value of 0.88 for the scale factor $S_o^2$, which is used in the subsequent refinement of the samples described below.

Results of fitting the Fourier transform of the EXAFS data are given in Table 2. There are a number of interesting points to note. The As(III)-bearing samples (R13-5 and R9-6) can be fitted with approximately three oxygen atoms at a bond length of 1.69(1) (R13-5) and 1.70(1) (R9-6) Å. Calcium can be fitted at 3.19(4) and 3.21(3) Å; Attempts to fit As-O multiple scatterings did not improve the fit, as there are some multiple scattering interactions but they do not contribute enough intensity.

These distances are similar to the published As(V)-O bond length values of 1.68(1) Å for As(V) solid solutions in apatite (Lee et al., 2009), and to the As-O distances (average 1.685 Å) in the calcium arsenates measured by Catti and Ivaldi (1983). The XANES spectra clearly show that the predominant oxidation state of this sample is As(III); however the fitted bond length is much shorter than the measured As(III)-O bond distance of 1.805(4) Å in arsenolite (Table 2), and 1.786(2) Å from the single crystal X-ray crystal structure refinement (Ballirano and Maras 2002). These differences, combined with the fact that an As-Ca bond length can be fitted, clearly indicate that the As(III) observed in these samples is not hosted in arsenolite inclusions (arsenolite was used to prepare the starting solutions).

For the fully reacted samples from the mixed As(III)/As(V) solutions, for which the XANES spectra show only As(V) feature (Fig. 1), the EXAFS fits for both end-member samples (M-5 and M-8, Table 1) result in ~4 oxygens at an As-O distance of 1.68(1) Å, as expected for As-O bonds in As(V)-bearing apatite (1.68(1) Å, Lee et al., 2009). As-Ca distances could be refined at 3.27(2) and 3.67(5) Å. The As(V)-Ca distance is longer than the As(III)-Ca, 3.27 vs 3.20 Å.

3.3. Ab initio molecular simulations of As(III/V) in the apatite structure

We performed DFT geometry optimization on arsenolite and hydroxylapatite (model benchmarking) and hydroxylapatite substituted by both As(V) and As(III). The optimized structures are shown in Fig. 7-9 and bond distances are listed in Table 3.

The optimized geometry of arsenolite gives an average As(III)-O distance of 1.815 Å, longer than the distance of 1.786(2) Å from x-ray crystallography (Ballirano and Maras, 2002), and our EXAFS measurement of 1.805(4) Å (Table 2). Geometry optimization of hydroxylapatite
predicted a P(V)-O distances of 1.55-1.56 Å, slightly longer than the crystallographic distance of 1.542 Å (Wilson et al., 1999). In arsenolite there are three coordinated O around As(III), resulting in a pyramidal structure with lone electron pair on top of As(III) (opposite the O3 position; Fig. 7a). In contrast, the fourfold PO$_4^{3-}$ structure in hydroxylapatite gives evenly distributed electrons in a tetrahedral arrangement. In As-substituted hydroxylapatite crystals, the As-O bond distances are longer that the P-O distances for both As(III) and As(V) (Table 3). The P-O distances are 1.55-1.56 Å in all the hydroxylapatite structures calculated in this study (Fig. 8b). In the As(V)-substituted hydroxylapatite, the calculation gave As(V)-O distances of 1.68-1.69 Å (Fig. 8b), which are consistent with the value of 1.68(1) Å obtained from the EXAFS data fitting. In the structure where one out of every 18 P(V) atoms was replaced by an As(V) ion, the topology and electron distribution are similar to hydroxylapatite, despite the longer As(V)-O distance (Figs. 8a,b), and also very similar to the configuration found in johnbaumite (Fig. 8c).

Arsenic(III)-substituted hydroxylapatite shows slightly longer As-O distances (1.74-1.76 Å) than As(V)-substituted hydroxylapatite (Fig. 9). Similar to the case for arsenolite, this distance is longer than the distance retrieved from EXAFS fitting (1.69-1.70 Å, Table 2), and As(III) forms pseudo-tetrahedral AsO$_3^{3-}$ moieties, where the missing fourth oxygen is occupied by the lone electron pair (Fig. 7a,b). When replacing one tetrahedral PO$_4^{3-}$ by one AsO$_3^{3-}$ moiety, the lone pair can replace one of four different oxygen atoms, and therefore we calculated four different configurations for the substitution of AsO$_3^{3-}$ in hydroxylapatite. These four configurations are shown in Figure 9, illustrating the different types of distortion imposed on the rings surrounding the columnar anion channels using the preferred topological representation of White and Dong (2003). Configurations (b-d) are topologically similar to apatite, but the coordination of one of the neighboring Ca1 ions is reduced from 6 to 5 due to the oxygen vacancy. Configuration (a) shows the largest distortion of the ring.

3.4. Arsenic speciation in natural apatite

The natural apatites investigated in this study both show zoning with respect to As, in general displaying a relatively As-poor core and a relatively As-rich rim (Figs. 10-13). This zoning is visible in backscattered electron images for the Ernst Henry samples (As concentration ranges from 0.2 to 3.5 %), but only on the µ-XRF maps for the Binntal sample, where the highest As concentrations are ~0.23%.
The µ-XANES measurements for the Binntal sample and most of the grains (20 of 22 grains measured) in EH-4 and EH545 from Ernest Henry show only As(V) (e.g., Fig. 10-11), but two grains in the EH-545 sample from Ernest Henry show an As(III) component (Fig. 12-13). In particular, one grain shows clear zonation of As(III) and As(V), with an As(III)-rich core and an As(V)-rich rim (Fig. 13).

4. Discussion

4.1. As(V) incorporation by apatite

Incorporation of As(V) in natural apatite is well established (e.g., Brugger and Gieré, 1999; Bath et al. 2013), with the tetrahedral AsO$_4^{3+}$ arsenate group substituting for the tetrahedral PO$_4^{3-}$ phosphate group (Pan and Fleet, 2002; Lee et al., 2009, Zhu et al. 2009) as a result of similar tetrahedral moiety and charge, in spite of its larger size: the ionic radius of As$^{5+}$ is twice as large as that of P$^{5+}$ (0.34 vs 0.17 Å; Shannon, 1976). Lee et al. (2009) showed that the structure of apatite can accommodate the large size of the tetrahedral site simply with an increase in unit cell volume, with little affect on the sizes of Ca polyhedral, resulting in a complete solid solution with johnbaumite. The incorporation of minor amounts of As changes the physical properties of apatite; for example the solubility of As(V)-bearing apatite is higher than that of As-free apatite (Zhang et al., 2011). In our earlier study (Borg et al., 2014), we reacted calcite crystals with As(V)-bearing phosphate solutions at 250 ºC. These results demonstrated a two-stage replacement mechanism, and showed that an ultra-local equilibrium can form complex chemical zoning patterns in the partially reacted apatite, even when the overall system is highly fluid-buffered.

4.2. As(III) incorporation by apatite

Apatite synthesized from solutions spiked only with As(III) contained only As(III), with lower As concentrations than in the As(V)-bearing apatite for similar aqueous As concentrations (Fig. 2). EXAFS data indicate an arsenite-like structure (three-coordinated AsO$_3^{3-}$ moiety with a stereochemically active electron lone pair), but with As-O bond distances of ~1.68-1.70 Å that are similar to As-O distances in the rigid arsenate group (~1.68 Å) but shorter than typical As(III)-O distances in crystals (1.77(3) Å; Ramirez-Solís et al. 2004) or in aqueous complexes (1.75-1.77(1) Å, Testemale et al. 2004). The short As(III)-O bond distances in our apatite indicate strong over-
bonding, i.e. 3.72 to 4.02 bond valence charges according to the parameters of Brown and Altermatt (1985).

The threefold AsO$_3^{3-}$ structure in apatite has been confirmed by *ab initio* molecular simulations, which show the trigonal pyramidal geometry with the lone electron pair on top of As(III) (Fig. 7b). For As(III) in apatite, the optimized distances are 1.74-1.76 Å, which are ~0.04 Å longer than the distances determined from EXAFS fitting (1.69-1.70 Å). Slightly longer bond distances from DFT-based simulations than experimental values are considered within typical accuracy of such simulations (see Bühl and Kabrede (2006) for a discussion of the accuracy of DFT calculations). For instances, the bond distance by DFT calculations are up to 0.05 and 0.07 Å longer than the experimental values for Mn-O and Pd-O distances (Tian et al., 2014; Mei et al., 2015). Hence, the *ab initio* molecular simulations and the EXAFS data support the substitution of arsenite moieties for phosphate groups in the apatite structure, although the short As-O bonds indicate a strong local strain around the substituted positions. Considering the predominant species in the experimental solutions at 250°C (As(OH)$_3$(aq), H$_3$PO$_4$(aq), and H$_2$CO$_3$(aq), calculated using HCh package), the replacement of calcite by As-bearing apatite in the presence of As(III)-bearing solutions can be expressed as:

$$
10\text{CaCO}_3(s) + (6-x)\text{H}_3\text{PO}_4(aq) + x\text{As(OH)}_3(aq) + 2\text{H}_2\text{O} = \\
\text{Ca}_{10}\text{(PO}_4\text{)}_{6-x}\text{(AsO}_3\text{)}_x\text{(OH)}_2(s) + 10\text{H}_2\text{CO}_3(aq)
$$

(1)

where $x$ refers the moles of AsO$_3$ moiety in the reaction product.

### 4.3. Dynamic uptake of As(III) and As(V)

For the mixed As(III)/As(V) experiments, both As(III) and As(V) can be substituted into the apatite structure, and a complex distribution of As oxidation state was observed in the partially reacted samples (Figs. 4, 5). We show that (i) the local equilibrium determines the heterogeneity of the As(III)/As(V) distribution in the partially-reacted samples: As(V) reaches further to the reaction front and center of the grain, whereas As(III) is more concentrated on the rim of the grain; and (ii) As(III) in apatite is easily replaced by As(V) during progressive recrystallization of apatite.

As shown by the higher $\text{As}_{\text{solid}}/\text{As}_{\text{solution}}$ ratio for As(V) versus As(III) solutions (Fig. 2) and the highly overbonded state of As(III) substituting for phosphate in the apatite structure (EXAFS & DFT), it is easier for As(V)O$_4^{3-}$ to substitute for a phosphate group than As(III)O$_3^{3-}$. The low affinity of the apatite crystal structure for As(III) is easily explained by the longer As(III)-O
distance compared to P-O, as well as by a stereochemical component (symmetrical tetrahedron versus trigonal pyramid + lone pair).

Preferential uptake of As(V) versus As(III) results in a rapidly increasing As(III)/As(V) ratio in the solution near the reaction front, assuming that apatite formation is faster than As(III)/As(V) diffusion from the bulk of the solution to the reaction front. At the initiation of the replacement reaction, aqueous phosphate, arsenate, and arsinite groups are in contact with the calcite grains; as the reaction progresses, these moieties need to diffuse through an increasingly thick layer of arsenian apatite to reach the reaction front. Phosphate and arsenate will diffuse at similar rates (similar charges and geometries; \( H_2AsO_4^- \) versus \( H_2PO_4^- \) at 250 °C and near-neutral pH; James-Smith et al. 2010; Shock and Helgeson 1988), whereas As(III) (as the neutral As(OH)_3(aq) complex; Testemale et al. 2004) differs by both its coordination geometry and its neutral charge. One explanation for the observed zoning in the partially reacted samples is that initially, there is a strong depletion of the As(V) in the fluid at the calcite surface/near the replacement front, due to preferential uptake of As(V). This results in As(III) uptake into the apatite structure. Somehow as reaction progresses, less As(III) is incorporated into the newly formed apatite, which can reflect different transport properties of As(V)/As(III) in the porous apatite, or a change in reaction mechanism that favors preferential formation of the lower energy form of As-apatite.

In the fully replaced grains, after 48 hours all arsinite (AsO_3^{3-}) has been replaced by arsenate (AsO_4^{3-}). This suggests that some extent of dynamic recrystallization took place in the grains, that overprints the original As zoning. A similar two-steps reaction mechanism was described by Borg et al. (2014) for the As(V) system, whereby a highly inhomogeneous and locally As-rich apatite quickly recrystallized into a homogenous As-bearing apatite. In the As(V) only case, recrystallization was driven by chemical gradients and the metastability of high-As apatite with respect to the local solution compositions. In the case of apatite in mixed As(III)/(V) solutions, recrystallization is probably driven by the high energy state (high strain) of the crystal lattice around the As(III) ions. This process obliterates the dynamic uptake of As(III), provided that As(V) ions are available in solution, and results in a final product that contains predominantly As(V). Our experimental results show that although the existence of As(III) make the replacement reaction less effective than As(V) system, indicated by total arsenic concentration (Fig. 2), eventually As(V) is the predominant oxidation state in most As-rich apatite which has also been seen in natural samples.
These results are consistent with recent studies on As(V) and As(III) incorporation into calcite, despite that apatite structure is a better than calcite for incorporating both As(V) and (III) due to similarity among PO$_4^{3-}$, AsO$_4^{3-}$ and AsO$_3^{3-}$ moieties. For example, for the natural calcite from As-bearing travertines in Italy, Benedetto et al. (2006) suggested that As(III) is present in the calcite structure via a CO$_3^{2-} \leftrightarrow$ AsO$_3^{3-}$ substitution, Bardelli et al. (2011) found mixed As(III) and As(V), and Costagliola et al. (2013) suggested 80% As(V) and 20% As(III) incorporation in these calcite. Yokoyama et al. (2012) showed experimentally that As(III) is incorporated into calcite only at high pH (pH$_{25}$\(\geq\)9.3), where anionic form As(III) species such as H$_2$AsO$_3^-$ predominate, and are able to interact with the calcite surface, contrary to the neutral As(OH)$_3$(aq). In Yokoyama et al. (2012)’s experiments, calcite incorporated only As(V) even in the systems spiked with As(III) at circum-neutral pH. They showed that As(III) was oxidized to As(V) as a result of the stabilization of As(V) in the presence of the Ca$^{2+}$ ion, via the formation of thermodynamically stable complexes of As(V) with the Ca$^{2+}$ ion in the calcite-supersaturated water. Renard et al. (2015) found As(III) is less incorporated in calcite than As(V), and partial oxidation of As(III) to As(V), with 36% As(III) and 64% As(V) in the reaction product. They confirmed the relatively small effect of As(OH)$_3$(aq) on calcite dissolution/growth by in-situ AFM, compared to charged complexes such as H$_2$AsO$_4^-$.

4.4. Consequences for trace element tracers

The natural As-bearing apatite from the Binntal gneiss and most As-bearing apatite from the Ernest Henry IOCG hydrothermal deposit contain predominantly As(V). We used the thermodynamic modeling package HCh (Shvarov, 2008) to estimate the oxidation state of As in the fluids from the observed mineral assemblages. For the Ernest Henry samples, the HCh calculations based on the assemblage of K-feldspar, muscovite, biotite, magnetite, and apatite (200-450 °C, 500-2500 bar, Cleverley and Oliver, 2005) shows that As(III) is the only oxidation state (e.g., 92% As(OH)$_3$(aq) and 8% As$_2$SO$_3^-$ at 300°C). For Binntal, the calculations assumed equilibrium with a metamorphic fluid, and similarly show that, even under oxidizing, hematite–magnetite buffered conditions, As(III) species are predominant (>99.9%, mainly as As(OH)$_3$(aq)) in the fluid at the T, P condition relevant to the formation of the apatite (~500 °C, 5,000 bar; note that pressure is limited by the equation of state used in HCh); therefore, it is unlikely that As(V) existed in the fluids from which these two apatites precipitated. Because As(III) uptake is controlled by dynamic processes (dependent on reaction mechanism) rather than equilibrium partitioning in apatite, apatite is not a reliable tracer for the fluid composition. However – and
rather surprisingly given the easy oxidation of As(III)-in-apatite during dynamic recrystallization observed in our experiments – As(III) can be retained in apatite over geological times. The As(V)-rich rim in Fig. 13 probably formed via replacement following a coupled-dissolution-reprecipitation mechanism of As(III) apatite; the As(V) apatite displays typical features for this type of reaction, including abundant micro-porosity, inclusions along the reaction front, and a sharp reaction front (Altree-Williams et al., 2015). Hence, the preservation of the As(III) in the core may be the result of armoring by an As(V) apatite in this particular grain.

In general, three possible processes may contribute to the scarcity of As(III) in most natural apatite samples, and selective incorporation of As(V).

1) Traces amounts of As(V) may have been present in the fluid, despite the suggestion from the thermodynamic modeling;

2) Apatite may have originally taken up As(III) from hydrothermal fluids, but this As(III) has since been oxidized to As(V), e.g. during recrystallization. This would mean that apatite intrinsically is not a good vehicle for preserving the original signature from the hydrothermal fluid. We note that XANES studies have demonstrated preservation of Eu$^{2+}$ and Eu$^{3+}$ in hydrothermal apatite (Rakovan et al. 2001; Takahashi et al. 2005). Together with the As(III) preserved in some Ernest Henry apatites, this shows that in some cases apatite can preserve oxidation state signatures over geological times;

3) Surface enhanced oxidation. The process of oxidation of As(III) via formation of stable As(V)-Ca complexes in the Ca-rich fluid layer near a dissolving calcite surface has been demonstrated at room-temperature by Yokoyama et al. (2012). A similar process could explain the uptake of As(V) from As(III)-dominated fluids by the measured natural apatites. Although such an effect was not observed in our As(III)-only experiments, it may happen under different conditions. Qian et al. (2013) observed a similar surface effect during the uptake of As by pyrite forming via the sulfidation of magnetite; no matter the oxidation state of the As-source, pyrite formed via this process contained predominantly As in an As(II)-like oxidation state.

Irrespective of the cause, As in apatite may not be able to record the original ratios of As oxidation states in the fluid, nor to preserve it during post-crystallization fluid-rock reactions. This example illustrates that one needs to exercise caution when interpreting chemical zonations in hydrothermal minerals (van Hinsberg et al. 2010). Overall, our experiments illustrate the role of local processes in the incorporation not only of trace elements in hydrothermal minerals, but also
their oxidation state. Brugger et al. (2008) found a complex zoning in Eu$^{2+}$/Eu$^{3+}$ ratios preserved in hydrothermal scheelite, and interpreted it in terms of various degrees of fluid-rock reaction. In this case, an external control is supported by variation in Sr isotopic signature, which cannot be explained by chemical fractionation alone (Brugger et al. 2000, 2002). This illustrates the power and necessity of combining various approaches, e.g., trace element, oxidation state mapping, and isotopic studies to decipher the origin and significance of trace elements in minerals formed in the presence of fluids.

Our experimental and molecular simulation results indicate that As(III) can be substituted into PO$_4^{3-}$ in terms of AsO$_3^{3-}$, which is similar to As(V) and As(III) incorporation into calcite structure shown in recent studies (e.g., Bardelli et al., 2011; Renard et al. 2015). Thus hydrothermal synthesis of apatite may provide a way to fix As(III), as well as As(V) from As-bearing aqueous fluids. However, the uptake and preservation of the As(III) in apatite are both controlled by kinetic processes (e.g., reaction pathway), and it is of paramount importance to take these aspects into consideration while designing geochemical barriers based on Ca-minerals for As(III/V) immobilization.

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5. References


Arsenic in apatite


Catti, M. and Ivaldi, G. (1983) On the topotactic dehydration Ca₃(AsO₄)₂·11H₂O (phaunouxite) -→ Ca₃(AsO₄)₂·10H₂O (rauenthalite), and the structures of both minerals. Acta Crystallographica Section B 39, 4-10.


Table 1. Sample information for the experiments of calcite to apatite hydrothermal replacement at 250 °C. As(III)/As(V) is molar ratio.

<table>
<thead>
<tr>
<th>Series name</th>
<th>Sample name</th>
<th>Starting composition</th>
<th>As(III)/As(V) content in initial solution</th>
<th>Reaction time (hours)</th>
<th>XAS measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series V</td>
<td>V-2-8</td>
<td>Calcite + 1.4 m (NH₄)₂HPO₄ and 0.12 m Na₂HAsO₄ solutions</td>
<td>As(V) = 0.12 m</td>
<td>20</td>
<td>Bulk</td>
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<tr>
<td>Series III</td>
<td>III-9-6</td>
<td>Calcite + 1.3 m (NH₄)₂HPO₄ and 0.01 - 0.14 m As₂O₃</td>
<td>As(III) = 0.14 m</td>
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<td></td>
<td>III-13-5</td>
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<td>As(III) = 0.03 m</td>
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<td>Bulk</td>
</tr>
<tr>
<td></td>
<td>III-13-8</td>
<td></td>
<td>As(III) = 0.14 m</td>
<td>48</td>
<td>Bulk</td>
</tr>
<tr>
<td>Series M</td>
<td>M-5</td>
<td>Calcite + mixture of (NH₄)₂HPO₄, Na₂HAsO₄ and As₂O₃ solutions</td>
<td>As(III)/As(V) = 0.2</td>
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<td>Bulk</td>
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<td>M-6</td>
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<td>As(III)/As(V) = 1.0</td>
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<td>Bulk</td>
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<td>M-7</td>
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<td>As(III)/As(V) = 1.0</td>
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<tr>
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<td>M-8</td>
<td></td>
<td>As(III)/As(V) = 10.5</td>
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<td>Bulk</td>
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<tr>
<td></td>
<td>M-9</td>
<td></td>
<td>As(III)/As(V) = 10.5</td>
<td>3</td>
<td>micro</td>
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</table>

Table 2. Results of EXAFS refinement for As₂O₃, Na₂HAsO₄ and AS-bearing apatite, fitted using both k² and k⁴ weighting; S₀²=0.88

<table>
<thead>
<tr>
<th>Sample</th>
<th>XANES results</th>
<th>N</th>
<th>R₀ [Å]</th>
<th>σ² [Å²]</th>
<th>ΔE (eV)</th>
<th>Reduced χ²</th>
<th>R factor</th>
<th>R range [Å]</th>
<th>K range [Å⁻¹]</th>
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<tbody>
<tr>
<td>As₂O₃</td>
<td>(fixed)</td>
<td>3</td>
<td>1.805(4)</td>
<td>0.003</td>
<td>10.62</td>
<td>99</td>
<td>0.019</td>
<td>R1-5</td>
<td>2-14</td>
</tr>
<tr>
<td>Na₂HAsO₄</td>
<td>(fixed)</td>
<td>4</td>
<td>1.697(7)</td>
<td>0.004</td>
<td>6.24</td>
<td>119</td>
<td>0.03</td>
<td>R1-3</td>
<td>2-13.5</td>
</tr>
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<td>III-13-5</td>
<td>As(III)</td>
<td></td>
<td>2.6(2)</td>
<td>1.69(1)</td>
<td>0.006</td>
<td>9(1)</td>
<td>0.01</td>
<td>0.8-3.8</td>
<td>2.5-10</td>
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<tr>
<td></td>
<td>O Casms</td>
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<td>1 (fix)</td>
<td>3.19(4)</td>
<td>0.003</td>
<td>9(1)</td>
<td>0.01</td>
<td>0.8-3.8</td>
<td>2.5-10</td>
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<tr>
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<td>3.28(1)</td>
<td>0.006</td>
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<td>III-9-6</td>
<td>As(III)</td>
<td></td>
<td>2.4(2)</td>
<td>1.70(1)</td>
<td>0.0058</td>
<td>11(1)</td>
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<td>0.8-3.8</td>
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<td>O Casms</td>
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<td>0.01</td>
<td>0.8-3.8</td>
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<td>3.32(8)</td>
<td>0.0058</td>
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<td>M-5</td>
<td>As(Ⅴ)</td>
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<td>3.7(3)</td>
<td>1.68(1)</td>
<td>0.0017</td>
<td>10(1)</td>
<td>0.03</td>
<td>0.8-3.8</td>
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<td></td>
<td>O Ca</td>
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<td>0.03</td>
<td>0.8-3.8</td>
<td>2.5-13</td>
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<tr>
<td></td>
<td>Ca</td>
<td></td>
<td>3.67(5)</td>
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<tr>
<td>M-8</td>
<td>As(Ⅴ)</td>
<td></td>
<td>3.5(2)</td>
<td>1.68(1)</td>
<td>0.001</td>
<td>10(1)</td>
<td>0.02</td>
<td>0.8-3.8</td>
<td>2.5-10</td>
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<td></td>
<td>O Ca</td>
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<td>1 (fix)</td>
<td>3.27(2)</td>
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<td>0.02</td>
<td>0.8-3.8</td>
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<td></td>
<td>Ca</td>
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<td>3.66(5)</td>
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</table>
Table 3 Results of geometry optimization of As in apatite using ab initio molecular simulation, and comparison of P-O and As-O bond lengths with some standard compound.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Super-cell Formula</th>
<th>Calculated bond length [Å]</th>
<th>Experimental bond length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenolite</td>
<td>As$<em>{32}$O$</em>{48}$</td>
<td>1.815</td>
<td>1.786$^{[1]}$, 1.805(4)*</td>
</tr>
<tr>
<td>hydroxylapatite</td>
<td>Ca$_{30}$(PO$<em>4$)$</em>{18}$(OH)$_6$</td>
<td>1.55-1.56</td>
<td>1.542$^{[2]}$</td>
</tr>
<tr>
<td>As(V)-hydroxylapatite</td>
<td>Ca$_{30}$(PO$<em>4$)$</em>{17}$(AsO$_4$)(OH)$_6$</td>
<td>1.55-1.56</td>
<td>1.68-1.69</td>
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<tr>
<td>As(III)-hydroxylapatite</td>
<td>Ca$_{30}$(PO$<em>4$)$</em>{17}$(AsO$_3$)(OH)$_6$</td>
<td>1.55-1.56</td>
<td>1.74-1.76</td>
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<tr>
<td>Calcium-arsenate</td>
<td>As(OH)$_3$(aq)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure Captions:

Fig. 1. As K-edge XANES spectra of bulk measurement of two standards (As$_2$O$_3$ for As(III) and sodium arsenate for As(V)), one sample from As(V) solution (V-2-8), two samples from As (III) solutions (III-13-5 and III-13-8), and partially reacted apatite from mixed As(III)/As(V) solutions (M-5: As(III)/As(V) = 0.01; M-6: ratio = 1; M-8: Ratio = 10).

Fig. 2. Arsenic concentration in final hydroxylapatite product measured by inductively coupled plasma–optical emission spectrometry (ICP-OES) as function of initial arsenic content in hydrothermal solutions. The reaction time is 48 hours, the As(III) data are from this study and the As(V) data are from Borg et al. (2014).

Fig. 3. As k-edge XANES spectra (a) and X-ray fluorescence map (b) for Sample M-6 (48 hours, As(III)/As(V) ratio = 1. The XANES spectra are extracted from areas highlighted in the box in (a).

Fig. 4. As k-edge XANES spectra (a) and X-ray fluorescence map (b) for sample M-7 (3 hours, As(III)/As(V) = 1 in fluid). The XANES spectra are extracted from areas highlighted in the box in (a).

Fig. 5. Arsenic distribution and oxidation state in the reaction rim of sample M-9 (3 hours, As(III)/As(V) in fluid = 10). Sub plots a-d are data collected at the XFM beamline of the Australian Synchrotron: As k-edge XANES spectra (a), As(III)/As$_{total}$ ratio (b) and X-ray fluorescence map (c). The mapped area is located at the top corner of the partially reacted calcite grain shown in (d); subplots (e) and (f) are data collected at P06 beamline of the PETRA synchrotron. The XANES spectra are extracted from the areas highlighted in the boxes in (a) and (d).

Fig. 6. Measured and fitted As K-edge EXAFS spectra (a) and Fourier transforms (b) for As(V) and As(III)-bearing apatites, and two standard compound of As$_2$O$_3$ and Na$_2$HAsO$_4$(H$_2$O)$_7$.

Figure 7. Optimized geometry and local electron density of (a) arsenolite (As$_2$O$_3$), showing lone electron pair near As(III); and (b) As(III) in replacing phosphate in apatite (configuration (a) in Figure 10.

Figure 8. Results from first-principle geometry optimisation for apatite (a) and As(V)-bearing apatite (b), compared to crystal structure of johnbaumite (c) measured by Lee et al. (2009).
Figure 9. Optimized geometry of As(III)-hydroxylapatite in four possible configurations for the oxygen vacancy.

Figure 10. Apatite from amphibolite facies quartz-K-feldspar-muscovite-biotite gneiss, Binntal Valley, Switzerland. (a) Extracted XANES spectrum; (b) X-ray fluorescence map. The XANES spectra are extracted from the area highlighted in the box of (a).

Figure 11. As-bearing apatite grain (EH4-9) from the Ernest Henry IOCG deposit, Queensland, Australia. (a) XANES spectra and (b) backscattered electron image and (c) X-ray fluorescence map of an apatite grain. The XANES spectra are extracted from the area numbered in (c).

Figure 12. As-bearing apatite from the Ernest Henry IOCG deposit, Queensland, Australia. The figure illustrates As distribution and speciation for a cluster of apatite grains. (a) XANES spectra and (b) backscattered electron image and (c) X-ray fluorescence map of a cluster of grain EH545. The XANES spectra are extracted from the area highlighted in the box of (a), showing that only one grain has As(III) feature in the core.

Figure 13. As-bearing apatite (EH5452-6) from the Ernest Henry IOCG deposit, Queensland, Australia. (a) XANES spectra and (b) SEM image (BSE mode) and (c) X-ray fluorescence map of grain EH545. The XANES spectra are extracted from the area highlighted in the box of (a).
Figure 1

**Normalized Fluorescence vs. Energy (eV)**

- **As(III)_std**
- **As(V)_std**
- **V-2-8**
- **III-13-5**
- **III-13-8**
- **M-5**
- **M-6**
- **M-8**

**Legend:**
- Dashed line: As(III)_std
- Solid line: As(V)_std
- Thin dotted line: V-2-8
- Thin dot-dashed line: III-13-5
- Thin dotted line: III-13-8
- Red line: M-5
- Red dotted line: M-6
- Red dash-dot line: M-8
Figure 2

The graph shows the relationship between the mole ratio of As/(As+P) in solids and the mole ratio of As/(As+P) in initial solutions. The graph includes two sets of data points:

- **As(V)**: The line equation is $y = 0.207x$ with $R = 0.9988$.
- **As(III)**: The line equation is $y = 0.097x$ with $R = 0.8560$.

The x-axis represents the mole ratio of As/(As+P) in initial solutions, ranging from 0.02 to 0.14. The y-axis represents the mole ratio in solids, ranging from 0.005 to 0.030.
Figure 3

(a) Plotted data with normalized fluorescence on the y-axis and energy (eV) on the x-axis. The graph highlights two peaks labeled As(III) and As(V).

(b) Image showing a color-coded area with a scale bar indicating 300 μm. The color gradient ranges from 0 to 4.9% As.
Figure 4

(a) Normalised fluorescence vs. Energy (eV)

(b) As(III)/As_{total}

(c) As_{total}

Fig 4
Figure 6

FIGURE 6

(a)

\( \chi(k) \) vs \( k(\text{Å}^{-1}) \)

(1) As\(_2\)O\(_3\)
(2) Na\(_2\)HAsO\(_4\)
(3) M-5: As(III)/As(V) = 0.2
(4) M-8: As(III)/As(V) = 10
(5) III-3-5: As(III)
(6) III-9-6: As(III)

(b)

\( |\chi(R)| \) vs \( R \) (Å)

- Measured
- Fitted

(1) As\(_2\)O\(_3\)
(2) Na\(_2\)HAsO\(_4\)
(3) M-5: As(III)/As(V) = 0.2
(4) M-8: As(III)/As(V) = 10
(5) III-3-5: As(III)
(6) III-9-6: As(III)
a. Apatite

- \( \text{Ca}(1) = 1.534 \text{Å} \)
- \( \text{Ca}(2) = 1.534 \text{Å} \)
- \( \text{O}(1) = 1.534 \text{Å} \)
- \( \text{O}(2) = 1.534 \text{Å} \)
- \( \text{O}(3) = 1.534 \text{Å} \)

b. As(V)-bearing

- \( \text{Ca}(1) = 1.684 \text{Å} \)
- \( \text{Ca}(2) = 1.683 \text{Å} \)
- \( \text{O}(1) = 1.684 \text{Å} \)
- \( \text{O}(2) = 1.684 \text{Å} \)
- \( \text{O}(3) = 1.689 \text{Å} \)
- \( \text{O}(4) = 1.686 \text{Å} \)

Johnbaumite

- \( \text{Ca}(1) = 1.714 \text{Å} \)
- \( \text{Ca}(2) = 1.684 \text{Å} \)
- \( \text{O}(1) = 1.684 \text{Å} \)
- \( \text{O}(2) = 1.677 \text{Å} \)

Fig 8
a. As(III)-bearing

b. 

c. 

d. 

Fig 9
Figure 10

(a) XANES

(b) XFM As

Fig. 10
Fig. 11

(a) XANES

(b) BSE

(c) XFM As
Figure 12

(a) XANES

(b) BSE

(c) XFM As

Fig 12
Figure 13

(a) XANES

(b) BSE

(c) XFM As

Fig. 13