A qualitative and quantitative investigation of partitioning and local structure of arsenate in barite lattice during co-precipitation of barium, sulfate and arsenate

XU MA\textsuperscript{1,2}, ZIDAN YUAN\textsuperscript{1}, MARIO A. GOMEZ\textsuperscript{3,4}, XIN WANG\textsuperscript{1}, SHAOFENG WANG\textsuperscript{1,*}, SHUHUA YAO\textsuperscript{3}, AND YONGFENG JIA\textsuperscript{1,3,*}

\textsuperscript{1}Key Laboratory of Pollution Ecology and Environmental Engineering, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, China, 110016, China

\textsuperscript{2}University of Chinese Academy of Sciences, Beijing, China 100049, China

\textsuperscript{3}Institute of Environmental Protection, Shenyang University of Chemical Technology, Shenyang, China, 110142, China

\textsuperscript{4}Department of Mining and Materials Engineering, McGill University, 3610 University Street, Montreal, Canada

The corresponding author: Dr. Shaofeng Wang, Email: wangshaofeng@iae.ac.cn; Telephone: +86 24 83970502; Fax: +86 24 83970503, Prof. Yongfeng Jia, Email: yongfeng.jia@iae.ac.cn; Telephone: +86 24 83970503; Fax: +86 24 83970503
Arsenic (As), barium (Ba), and sulfate (SO$_4^{2-}$), co-existing in natural and mining impacted environments, possibly lead to As-barite co-precipitation. This work investigated the co-precipitation of Ba$^{2+}$, SO$_4^{2-}$ and AsO$_4^{3-}$ (As(V)) and the incorporation of As(V) into the barite structure. The As(V) content in the coprecipitates increased with pH and the initial aqueous As(V) concentration. At pH ≤ 5, As(V) was dominantly fixed through isomorphic substitution for SO$_4^{2-}$ in the barite structure (< 0.32 wt. %). At pH > 5, barium (hydrogen) arsenate constituted an appreciable fraction of As(V)-bearing species in addition to the incorporated As(V). FTIR spectroscopy indicated that As(V) in the coprecipitate occurred as mixed phases and the As(V) species incorporated into the barite structure was dominated by HAsO$_4^{2-}$ species. EXAFS analysis gave As-O and As-OH bond lengths of 1.67 Å and 1.75 Å for HAsO$_4^{2-}$ in barite structure, respectively. The FPMS structural refinement reproduced well the As K-edge XANES spectrum and gave bond lengths of As-O at 1.63, 1.64, 1.68, and 1.75 Å with an average bond length of 1.68 ± 0.05 Å in HAsO$_4^{2-}$ doped barite structure. The findings are of significance for understanding the geochemical cycle of As in As(V), Ba$^{2+}$, SO$_4^{2-}$ co-existing systems.

**Keywords:** Arsenate, barite, co-precipitation, incorporation, local structure, XANES/EXAFS, FTIR, DFT calculation
INTRODUCTION

Given the toxicity of arsenic (As), a wide range of studies have been undertaken on its transformation, mobilization, and fixation in various environments. Besides As sorption/desorption on the surface of metal oxide/clay minerals and precipitation/dissolution of As-containing minerals (Das et al. 1996; Nickson et al. 1998; Acharyya et al. 1999; Sherman and Randall 2003), incorporation of As into minerals is also one of the most important processes/mechanisms influencing As mobility in natural and mining environments (Savage et al. 2005; Dutrizac and Jambor 2007; Fernández-Martínez et al. 2008; Lee et al. 2009; Gomez et al. 2010, 2011, 2013a, 2013b; Kendall et al. 2013; Lin et al. 2013a, 2013b; Sunyer et al. 2013; Zhang et al. 2015; Wang et al., 2017). It has been found that isomorphic substitution of arsenate (As(V)) for sulfate, phosphate and vanadate positions in mineral structures is widely occurring in hydrometallurgical tailings, As-rich mine waters and natural sediments, which can potentially influence the mobility, bioavailability, and transformation of As(V) (Sunyer et al. 2013; Zhang et al. 2015; Muehe et al. 2016).

Barite could form in some geological environments (e.g. deep-sea, groundwater, river, hot spring water, and crust deposits) and mining related areas that contain considerable amounts of As (Goodarzi 2002; McBeth et al. 2003; Pone et al. 2007; Arik and Sgem 2008; Romero et al. 2010; Liu and Hendry 2011; Gomez et al. 2013a). For instance, barite precipitated from hot spring water and mining areas where As(III) was oxidized as As(V) in the thermal and aerobic environment (Villanueva et al. 2013; Tokunaga et al. 2016). Barite is used as a solubility control of $^{226}$Ra in the
neutralization of acidic As containing sulfate rich hydrometallurgical raffinate solutions in Canada’s uranium industry (Liu and Hendry 2011). These processes may lead to the formation of an As(V)-barite coprecipitate and incorporation of As(V) into the crystal lattice of barite. Tokunaga et al. reported that the concentration of As incorporated into natural barite could reach up to 24.3 mg·kg⁻¹ in an Okinawa hydrothermal vent and was in the range of 5.25 – 438 mg·kg⁻¹ in the laboratory coprecipitates (Tokunaga et al. 2016). In their work, they focused on the influence of As oxidation state in natural barite on its immobilization and the ratio of As(III)/As(V) as an indicator for sub-oxic/anoxic redox conditions. However, the dominant As(V) species (e.g. protonated or not), which strongly influence the amount of As fixed by barite, the local atomic structure of As(V) in the barite crystal lattice, and the possible barium arsenate phases formed are still unclear.

The objectives of the present work were to qualitatively and quantitatively study the amount and species of the As(V) in solid phase and its structure in barite during the co-precipitation of As(V), Ba, and SO₄²⁻ at various pH’s and initial As(V) concentrations.

MATERIALS AND METHODS

All chemicals used in this work were of analytical grade and used without further purification. De-ionized (DI) water was used for all experiments.

Synthesis of standard materials

As(V)-free barite was precipitated by mixing a CO₂-free 0.2 mol L⁻¹ barium solution (from BaCl₂·2H₂O) and a 0.2 mol L⁻¹ sulfate solution (from Na₂SO₄) at a pH
of 7.0 using 0.01 M NaOH as a base. Barium hydrogen arsenate (BaHAsO₄·H₂O) and barium arsenate (Ba₃(AsO₄)₂) were synthesized by adding 20 mL and 30 mL of 0.2 mol L⁻¹ CO₂-free barium solution (from BaCl₂·2H₂O) into a 20 mL of 0.2 mol L⁻¹ of As(V) solution (from As₂O₅·12H₂O) at pH 6 and 12 using 0.01 and 0.1 M NaOH (Zhu et al. 2005). After stabilization at room temperature for 1 h, white precipitates of the three standard materials were separated by filtration, washed with water and ethanol, dried in a vacuum drier at 40 °C overnight, and stored in a desiccator for further analysis.

Co-precipitation of As(V) with barite

The co-precipitation experiments were performed by titrating CO₂-free BaCl₂·2H₂O solution into the mixture of CO₂-free Na₂SO₄ solution and As₂O₅·12H₂O solution (Tokunaga et al., 2016). Briefly, 30 mL of 0.2 mol L⁻¹ sulfate solution (pH 3, 4, 5, 6, 7, 8, 9, 10) and same pH 30 mL of As solution with different concentrations were mixed in a beaker, the pH was adjusted to the desired values (pH 3, 4, 5 6, 7, 8, 9, 10) using 0.01 and 0.1 M NaOH as a base, followed by addition of 30 mL of 0.2 mol L⁻¹ barium solution (i.e. equimolar Ba²⁺ and SO₄²⁻ ions) with magnetic stirring. The mixtures were allowed to stabilize for 24 h with the pH controlled at a constant value. The As(V) concentration in the system (i.e. 50, 500, 2000 mg L⁻¹) based on the final volume is reported. After stabilization, the solids were rinsed 5 times with DI water and separated by centrifugation, dried in a vacuum oven at 40 °C overnight, and stored in a desiccator at room temperature for further analysis.
To obtain the As(V)-doped barite, an aliquot of each As(V)-barite coprecipitate was repeatedly treated with 1 M H$_2$SO$_4$ solution for 5 times in order to remove BaHAsO$_4$·H$_2$O and/or Ba$_3$(AsO$_4$)$_2$ phases that could precipitate during the co-precipitation process (Bluteau and Demopoulos 2007). This procedure was applied because barium arsenate phases are very soluble in acids. Then the acid treated solid was rinsed with DI water for 3 times and dried for further analysis. The acid-treated and non-acid treated coprecipitated samples are designated with a prefix AT and UT hereafter in the manuscript, respectively.

**Determination of As concentrations in the solid phases**

The As concentrations in the UT and AT samples were measured using XRF (Thermo Fisher Niton XL2) (Ene et al., 2010) equipped with X-ray source and an energy-resolving detector. The X-ray was produced by an X-ray source of Ag target run at a voltage of 40 kV with 80 µA current and the ray was collimated with slits collimators. The sample flat discs were prepared prior to XRF analyses, as suggested by the user manual (Thermo Fisher Niton XL2). The samples were placed on the sample stage to make sure that the investigated area of samples is in the optical focus (Jiang et al. 2015). Each sample was measured in triplicates and the mean value is reported. The detection limit of the instrument is approximately 10 µg g$^{-1}$. Standard solid reference material (CCRMP TILL-4, soil) was analyzed to assure the accuracy of the total As concentration. The measured As concentration of standard material was 107 ± 9.7 µg g$^{-1}$, which was highly consistent with the certified value of 111 µg g$^{-1}$. 
**Geochemical modelling**

The Phreeplot software coupled with a batch version PHREEQC was employed to calculate the equilibrium phases and speciation of As in the As(V)-Ba-SO$_4$ co-precipitation systems as a function of pH and initial As(V) concentrations (Kinniburgh and Cooper 2011). The modelling was performed in a 0.1 M NaCl media at 25 °C. The thermodynamic database of wateq4f supplied with the software was modified to include the thermodynamic data of BaHAsO$_4$·H$_2$O (logK$_{sp}$ = -5.6) and Ba$_3$(AsO$_4$)$_2$ (logK$_{sp}$ = -23.53) (Zhu et al. 2005; Nordstrom et al. 2014).

**XRD characterization**

The mineralogical characteristics of the synthetic barite and the AT samples precipitated at pH 4, 7, and 10 with the aqueous As concentration of 2000 mg L$^{-1}$ were characterized by using a Rigaku D/max 2400 X-ray diffractometer (Rigaku Corporation, Japan) equipped with a copper target (Cu K$_\alpha_1$ radiation, $\lambda$=1.5418Å), a crystal graphite monochromator and a scintillation detector. The equipment was run at 56 kV and 182 mA by step scanning from 10° to 80° 20 with increments of 0.02° 20. For the refinements of the arsenate incorporated barite structures, the sulfur position was assumed to be shared with the arsenic atom and the occupancy was calculated from the concentration of arsenate in the AT samples.

**SEM characterization**

The morphologies of the solid samples were analyzed on a FEI Quanta 250 scanning electron microscope. The samples were mounted on pin stubs by use of double-sided carbon tape and sputter-coated with gold, and imaged at 30 kV and a
magnification factor of 5000 and 20000.

FTIR measurement

The infrared spectra of the powdered samples were collected on a Thermo Nicolet 6700 Fourier transform infrared spectrometer. The KBr sample discs were prepared by mixing 0.5% of finely ground samples in high-purity KBr and pressed using a hydraulic press. Then each sample was scanned 200 times in the mid-IR range (400-4000 cm\(^{-1}\)) with a resolution of 4 cm\(^{-1}\) in transmission mode and the averaged spectrum was reported.

XAFS measurement and data processing

The As K-edge XAFS spectra of the AT samples coprecipitated at the initial As(V) concentration of 2000 mg L\(^{-1}\) and pH 3, 7, and 10 as well as the reference materials (BaHAsO\(_4\)·H\(_2\)O and Ba\(_3\)(AsO\(_4\))\(_2\)) were collected on the XAFS beamline (1W1B) at Beijing Synchrotron Radiation Facility (BSRF). To avoid As(V) photoreduction under the beam, all spectra were recorded at 77 K using a homemade cryostat (Mercier-Bion et al., 2011). The BSRF storage ring was run at 2.5 G eV in full-energy injection mode and 250 mA beam current. The monochromator on beamline was a fixed exit double crystal monochromator with Si (111) crystals. The absolute position of the monochromator was calibrated by an Au L\(_3\)-edge spectrum. The scan steps for the XANES and EXAFS regions were set to 0.7 eV and 3 eV, respectively. The spectra of reference materials were collected in transmission mode using an ionization chamber and the As(V)-doped barites were measured in fluorescence mode.
Data normalization was performed by using Athena in the Demeter package (version 0.9.25) (Ravel and Newville 2005). The spectra were background subtracted and normalized to the atomic absorption. The pre-edge of all spectra was fitted with a straight line in the range of 150 – 50 eV before the absorption edge. The post-edge absorption background was subtracted by fitting a cubic polynomial spline to the data in the energy range of 150 – 750 eV after the absorption edge. The EXAFS spectra were Fourier transformed from $k$ to $R$ space using Kaiser-Bessel apodization windows with $R_{bkg}$ value of 0.9 Å. The $k$-space range was set to $3 – 13.5 \, \text{Å}^{-1}$ to obtain the radial structural functions (RSFs). Final fitting of the spectra was done on Fourier transformed $k^3$ weighted spectra in $R$ space. For data fitting and modeling, scattering paths were calculated with ATOMS and FEFF using crystallographic data of BaHAsO$_4$·H$_2$O (Jimenez et al. 2004), Ba$_3$(AsO$_4$)$_2$ (Park and Bluhm 1996) and DFT optimized structure as model structures.

**DFT modeling**

The structures of As(V)-doped barite ($2\times2\times2$ supercell) were optimized with DFT calculations using pw.x code available in QUANTUM ESPRESSO package (Version 6.0) (Giannozzi et al. 2009). The content of As(V) in the As-doped barite supercell is approximately 10 mg g$^{-1}$, which is comparable to the highest As content in the AT sample (~8.9 mg g$^{-1}$). The program uses plane waves and pseudopotentials to solve the Kohn-Sham equations. The geometric optimization was performed in a periodic system using the generalized gradient approximation, the Perdew–Burke–Ernzerhof (GGA-PBE) function (Giacomazzi and Scandolo 2010), and the
semi-empirical dispersion correction at D2 level (DFT-D2) (Grimme 2006). The	norm-conserving pseudopotentials were used for all calculations. Calculations for
supercells with dimension of 14.31×17.76×10.91 Å³ (containing 193 atoms) were
carried out at the Γ-point of the Brillouin zone to save the computation cost, but for
bulk barite and BaHAsO₄·H₂O, denser k-mesh of 4 × 4 × 4 was used. The plane-wave
kinetic energy cut-off for wave functions (charge density and potential) was set to 80
Ry (320 Ry). Tests showed that these parameters could give satisfactory convergence
of total energy (< 0.2 mRy/atom).

XANES analysis

The XANES data in the range of -20 to 150 eV below and above the absorption
edge was analyzed by the full potential multiple scattering theory using the recently
developed FPMXAN code (Benfatto et al. 2001a, 2001b; Hayakawa et al. 2007;
Hatada et al. 2007, 2009, 2010), which has been used to investigate the local structure
of hydrous ferric arsenate and the detail method have been described elsewhere
(Wang et al. 2016). FPMXAN uses the full potential multiple scattering theory to
approximate the shape of the potential based on the local density approximation of the
self-energy of the excited photoelectron. The self-energy is calculated using the real
part of the Hedin-Lundqvist potential. The fitting quality was evaluated using the
square residue function (S²) as following equation (Benfatto et al. 2001a, 2001b):

\[ S^2 = \alpha \left( \sum_{i=1}^{n} \omega_i \left( \psi_i^\text{calc} - \psi_i^\text{exp} \right)^2 \right) \]

(1)

where \( n \) represents the number of independent parameters, \( m \): represents the number
of data points, $y_i^{th}$ and $y_i^{exp}$ represent the theoretical and experimental values, respectively, $\varepsilon_i$ is the error in each point of the experimental data set, and $w_i$ is a statistical weight.

RESULTS AND DISCUSSION

As concentrations in the solid phases

Arsenic content in the coprecipitated solids showed clear increasing tendency as the pH values and the initial aqueous As concentrations increased (Fig. 1). The As(V) contents in the UT samples increased with increasing pH and were in the range of 0.12 – 2.8 mg g$^{-1}$, 0.72 – 11.5 mg g$^{-1}$, and 2.3 – 20.2 mg g$^{-1}$ for the initial aqueous As(V) concentration of 50, 500, and 2000 mg L$^{-1}$, respectively. Accordingly, the content of As(V) in the AT samples was in the range of 0.12 – 2.5 mg g$^{-1}$, 0.72 – 4.9 mg g$^{-1}$, and 2.28 – 8.9 mg g$^{-1}$ increasing with pH. The content of As in the AT samples were almost equal to those of corresponding UT samples at lower pH (i.e. pH 3 – 5) for each initial As(V) concentrations. This meant that As(V) was unable to be extracted from the solids by 1 M H$_2$SO$_4$, indicating that the As(V) was dominantly fixed by incorporation into the barite structure at pH 3 - 5. The increasing As content in the AT samples from pH 3-10 indicated that more As(V) was incorporated into barite structure at higher pH. It is worth to note that the acid treatment by 1 M H$_2$SO$_4$ resulted in a significant difference in As(V) concentrations in the UT and AT samples at pH > 5. The latter fact meant that the formation of acid soluble phases during co-precipitation occurred (Zhu et al. 2005; Weil 2016).

The saturation state with respect to barium (hydrogen) arsenate in the
As(V)-barite co-precipitation systems at different pH and initial arsenic concentrations were calculated (Zhu et al. 2005; Nordstrom et al. 2014). The results (Fig. 2) show that BaHAsO$_4$·H$_2$O precipitates in weak acidic to neutral pH conditions while Ba$_3$(AsO$_4$)$_2$ precipitates at the pH greater than neutral conditions, in agreement with previous experimental and modelling work (Zhu et al. 2005). This suggests that the coprecipitated solids at weak acidic to neutral conditions were probably the mixtures of BaSO$_4$, BaHAsO$_4$·H$_2$O, and Ba$_3$(AsO$_4$)$_2$, while the coprecipitates formed at neutral to alkaline conditions likely contain both BaSO$_4$ and Ba$_3$(AsO$_4$)$_2$. Therefore, the UT samples could be mixtures of As(V)-doped barite and barium arsenate phases, while the AT samples represent only As(V)-doped barite because acid treatment removed the barium arsenate phases that could have formed during co-precipitation.

**Morphology of the precipitated solids**

The SEM images of the As(V)-barite coprecipitates formed at pH 6, 9 and 10 and the initial As(V) concentration of 2000 mg L$^{-1}$ are compared with As(V)-free barite, BaHAsO$_4$·H$_2$O, and Ba$_3$(AsO$_4$)$_2$ standard materials in Figure 3. As(V)-free barite crystals occurred as rice-shaped particles, while BaHAsO$_4$·H$_2$O and Ba$_3$(AsO$_4$)$_2$ appear as irregular plates and irregular particles, in agreement with previous works (Essington, 1988; Zhu et al., 2005). Compared with As(V)-free barite and BaHAsO$_4$·H$_2$O, the morphologies of UT and AT As(V)-barite coprecipitates were remarkably modified (Fig. 2D-I). The morphology of the pH 6 UT and AT samples changed to spherical particles as well as some irregular plates. At pH 9 and 10, the morphologies of the UT and AT precipitates appeared to be the aggregation of small
particles and the particle size significantly decreased (Fig. 3E, F, H, I). The aggregation of small particles and decrease in particle size maybe due to the hindering effect of the formation of \( \text{BaHAsO}_4\cdot\text{H}_2\text{O} \) and/or \( \text{Ba}_3(\text{AsO}_4)_2 \) phases and the higher amount of As(V) incorporated into barite structure which inhibits the growth of barite particles.

**Mineralogical results**

The mineralogical characteristics of the AT As(V)-barite coprecipitates synthesized at initial As(V) concentration of 2000 mg L\(^{-1}\) and pH 4, 7, and 10 were analyzed by XRD (Fig. 4). Barite was the only XRD identifiable crystalline phase in all samples (Jacobsen 1998; Hartman and Strom 1989) and no identifiable diffraction lines of crystalline \( \text{BaHAsO}_4\cdot\text{H}_2\text{O} \) and \( \text{Ba}_3(\text{AsO}_4)_2 \) were observed. Incorporation of As(V) slightly altered the X-ray diffraction features of barite. In the case of the As(V)-free barite, the strongest diffraction peak was the (210) plane located at ~26°, but in the As(V) incorporated samples, the strongest diffraction peak shifted to the (211) plane located at ~28°. This effect may be ascribed to the change in the preferred orientation induced by the incorporation of As(V). The Rietveld refinements showed that the incorporation of As(V) into the structure of barite induced the volume expansion of its unit cell (Table S3), possibly resulting from the larger size of AsO\(_4\) tetrahedron than SO\(_4\).

**FTIR spectroscopy**

The UT and AT samples were characterized using FTIR spectroscopy (Fig. 5). Since barite does not contain water molecules, only the frequency region of interest
(400-1300 cm\(^{-1}\)) is displayed where the stretching and bending vibrations of As-O and S-O bonds show characteristic infrared active bands (Omori 1968; Myneni et al. 1998; Jia et al. 2007).

The As(V)-free barite showed typical bands of the \(\nu_1(A1)\), \(\nu_2(E)\), \(\nu_3(F2)\) and \(\nu_4(F2)\) at 938, 418, [1074, 1110, 1203], and [609, 642] cm\(^{-1}\) (Fig. 5), in agreement with reference literature (Omori 1968). The FTIR spectrum of \(\text{Ba}_3(\text{AsO}_4)_2\) shows a very broad band peaking at 813 cm\(^{-1}\), which was reasonably assigned to a combination of \(\nu_3(F2)\) and \(\nu_1(A1)\) arsenate ions. In the case of \(\text{BaHAsO}_4\cdot\text{H}_2\text{O}\), the weak band at 692 cm\(^{-1}\) was attributed to the \(\nu_s\) of the As-OH bond and the strong bands at 860 and 877 cm\(^{-1}\) arose from the \(\nu_s\) and \(\nu_{as}\) of the As-O bond in the \(\text{HAsO}_4^{2-}\) group.

All the As(V)-free barite and As(V)-barite coprecipitates showed the S-O stretching and bending vibrations at nearly the same frequencies (Fig. 5A). Moreover, the degeneracy of the SO\(_4\) vibrational modes does not change from the As(V)-free barite to the As(V) coprecipitates, indicating that the majority of the symmetry and bonding environment in the SO\(_4\) groups of the barite structure remains almost unchanged due to the low concentration of As(V) incorporated into the barite structure (< 1.0 wt. %). The weak band at 982 cm\(^{-1}\) and three strong bands at 1000 – 1300 cm\(^{-1}\) on the FTIR spectra were assigned to the \(\nu_1\) symmetric and the \(\nu_3\) antisymmetric stretching vibration of SO\(_4^{2-}\). The \(\nu_2\) symmetric and \(\nu_4\) antisymmetric bending of SO\(_4^{2-}\) tetrahedral appeared at 418 and [609, 640] cm\(^{-1}\), respectively (Omori 1968; Shen et al. 2007; Bahl et al. 2014).
Some small features emerged in the range of 700 – 900 cm⁻¹ on the FTIR spectra of the As(V)-barite coprecipitates (Fig. 5B) which are attributed to the As-O stretching vibrations. Because the UT coprecipitated samples could contain various arsenate species (i.e. As(V)-doped barite, BaHAsO₄·H₂O and Ba₃(AsO₄)₂), the As-O stretching vibration bands are likely composites of the arsenate vibrational modes from these phases. The FTIR spectra of UT-pH 7 and 9 samples showed broad bands overlapped with four to five bands at 814, 837, 854, 878, and 892 cm⁻¹. The band at 814 cm⁻¹ on the UT-pH 9 spectrum disappeared after acid treatment (AT-pH 9) to remove barium arsenate phases. Hence the band at 814 cm⁻¹ coincides with the broad band observed in Ba₃(AsO₄)₂, which is estimated to be the barium arsenate phase at pH 9 based on the geochemical modelling (Fig. 2). These results are in agreement with previous studies, Rodríguez-Blanco et al (2007, 2008) states that at pH 7 the dominant As species is HAsO₄²⁻ and the arsenate precipitating is pharmacolite (CaHAsO₄·H₂O) and two As species (HAsO₄²⁻ and AsO₄³⁻) are incorporated in the crystal structure of precipitates obtained at pH 9. The FTIR spectrum of the UT-pH 5 sample does not show the 814 cm⁻¹ band of Ba₃(AsO₄)₂, in agreement with the geochemical modelling results that Ba₃(AsO₄)₂ phase is less likely to form at pH < 6.

The FTIR spectra of acid-treated coprecipitate samples displayed three As-O stretching vibration bands at 892, 878 and 854 cm⁻¹ with the band intensity increasing with pH, which is consistent with the relative contents of arsenic in the AT samples. The FTIR spectra of all AT samples also showed very weak bands at 837 and 708 cm⁻¹ due to the very low arsenic content. Because the AT samples were treated with
an acid repeatedly to remove the BaHAsO$_4$·H$_2$O and/or Ba$_3$(AsO$_4$)$_2$ phases that may have formed, these FTIR bands can be attributed to the As(V) incorporated into barite. The weak band at 708 cm$^{-1}$ is attributed to As-OH stretching vibration (Myneni et al. 1998). Therefore, the arsenate species incorporated into barite structure is most likely HAsO$_4^{2-}$.

**EXAFS analysis**

The EXAFS data of the AT samples as well as our standard BaHAsO$_4$·H$_2$O and Ba$_3$(AsO$_4$)$_2$ were fitted using the crystallographic data of Ba$_3$(AsO$_4$)$_2$ (Park and Bluhm 1996), BaHAsO$_4$·H$_2$O (Jimenez et al. 2004) and DFT optimized structure as the initial models for comparison (Fig. S1 and Table 1).

In the case of the standard BaHAsO$_4$·H$_2$O, the EXAFS fitting gave an As-O and As-OH bonds with an interatomic distance of 1.68 Å with CN of 3 and 1.76 with CN of 1 for first shell, an As-Ba interatomic distance of 3.6-4.2 Å for second shell with CN of 5 shell, in agreement with reported crystallographic data (Park and Bluhm 1996). For the standard Ba$_3$(AsO$_4$)$_2$, an As-O bond at 1.70 Å with a CN of 4 for first shell and an As-Ba interatomic distance of 3.4-3.8 Å for second shell with CN of 6 was determined, again in agreement with previous published crystallographic data (Jimenez et al. 2004). For the AT samples at the three selected pH conditions, the EXAFS fitting using BaHAsO$_4$·H$_2$O model for first shell (R+$\Delta R = 0.9 – 2.0$ Å) showed that the first-neighbor contributions were fitted with 3 oxygen (O) atoms at 1.67 Å from As-O and 1 O atom at approximately 1.75 Å from As-OH, with an average of 1.69 Å (Fig. 6 and Table 1). The second shell (R+$\Delta R = 2.0 – 3.8$ Å) was
used the DFT optimized structure (Fig S1) as the initial model. The crystallographic
data of DFT optimized structure as the initial model fitted the EXAFS data with 6
As-Ba paths at an interatomic distance of approximately 3.5-3.8 Å with CN of 6
(Table 1). In the case of crystallographic data of Ba₃(AsO₄)₂ as the initial model fitted
the EXAFS data showed 4 As-O paths at an interatomic distance of approximately
1.69 Å (Table S4). The second shell (2.0-3.6 Å) gave an As-Ba interatomic distance
of 3.0-3.6 Å with CN of 4 when used the DFT optimized structure as the initial model
(Table S4). The comparison between two models (BaHAsO₄·H₂O and
Ba₃(AsO₄)₂/DFT optimized structure) showed that the BaHAsO₄·H₂O resulted in
smaller goodness-of-fit, the $R$-factor and reduced $\chi^2$ in comparison to the Ba₃(AsO₄)₂
model for all AT samples. This may imply that the BaHAsO₄·H₂O produced a better
fit than the Ba₃(AsO₄)₂ model, possibly due to the fact that the As(V) species
incorporated into the barite structure was more likely in the form of HAsO₄²⁻, in
agreement with FTIR results.

**DFT and XANES analysis**

The FTIR and EXAFS results showed that HAsO₄²⁻ is more likely to be
dominant species in barite structure. However, FTIR spectroscopy and EXAFS
analysis can not give the detail local structure of HAsO₄²⁻. Since the oscillation in the
near edge part (XANES) of XAFS spectra is much stronger than that in the extended
part (EXAFS), XANES features are more sensitive to the atomic positions and have
been used to probe the interatomic distances and angles based on the muffin-tin
approximation (Benfatto et al. 2001a, 2001b; Hayakawa et al. 2007) and FPMS
method (Hatada et al. 2007, 2009, 2010). Therefore, we used DFT calculation to construct the initial model and refined the local structure using FPMS theory.

The DFT optimized local structure are shown in Figure S1 and Table S5. The optimized S-O bond lengths were averaged at 1.48 ± 0.011 Å for As(V)-doped configuration, in good agreement with the As-free barite (1.48 ± 0.011 Å) and the crystallographic data (1.48 ± 0.017 Å) reported by Jacobsen et al. (1998) (Jacobsen et al. 1998), implying that the influence of the incorporation of small amount of As(V) in barite structure on SO₄ groups was very limited. The As-O bond lengths were 1.660, 1.651, and 1.663 Å, with the As-OH bond length of 1.766 Å.

All As K-edge XANES spectra of the As(V)-doped barite samples showed a well resolved near edge white line peak at an energy of 11,875.0 eV which was similar to that of the reference materials (BaHAsO₄·H₂O and Ba₂(AsO₄)₃) indicating that the As incorporated into the barite structure occurred as As(V). The difference among the XANES spectra of the AT samples precipitated at different pH values was negligible except minor difference near the energy position of the white line peak (Fig. 7B). This meant that the As(V) incorporated into the barite structure of our As(V) coprecipitates had a similar electronic environment and geometric structure.

In order to probe the local structure of As(V) incorporated into barite lattice, ab initio FPMS simulations of XANES spectra were performed. The As K-edge XANES spectra of the AT sample precipitated at pH 7 was used as a representative due to high similarity among different AT samples (Fig. 7B). The DFT optimized structure as the initial model (cluster radius = 6 Å and 67 atoms) was used to calculate the theoretical
XANES spectrum. The comparison between unbroadened theoretical and experimental spectra showed that all the XANES features have been reproduced (Fig. 7C). After refinement of the non-structural parameters, a satisfactory goodness of fit ($S^2 = 2.9$) was obtained. This result indicated that the species of As(V) incorporated in barite mainly occurred as HAsO$_4^{2-}$, consistent with our FTIR and EXAFS results.

Then the interatomic distances and angles in the DFT model were refined shell-by-shell to probe the local structure of HAsO$_4^{2-}$ in the barite structure. During the structural refinement, the SO$_4^{2-}$ ions were regarded as groups and moved together. The refinement gave good consistency between the theoretical XANES spectra and the experimental data with a goodness of fit of $S^2 = 1.6$ (Fig. 7D). From the refinement, it was determined that the bond lengths of As-O/H in the arsenate tetrahedral were 1.63, 1.64, 1.68, and 1.75 Å with an average of 1.68 ± 0.05 Å (Fig. 7E), in good agreement with the EXAFS and DFT results.

**SUMMARY**

The species of As(V) in solid phase during the co-precipitation of As(V), Ba, and SO$_4^{2-}$ at various pH’s (3 – 10) and initial aqueous As(V) concentrations (50, 500 and 2000 mg L$^{-1}$) was investigated in this work. The As(V) in the coprecipitates was dominantly present as incorporated species in the barite structure at pH ≤ 5, while at higher pH, BaHAsO$_4$·H$_2$O/Ba$_2$(AsO$_4$)$_3$ could form under our experimental conditions. The content of As(V) incorporated in the barite lattice increased up to 8.9 mg g$^{-1}$ (0.89 wt. %) as the pH and initial As(V) concentration increased. FTIR, DFT, and XAFS
data suggested that the As species in the crystal lattice of barite was dominantly presented as HAsO$_4^{2-}$. The FPMS structural refinement delivered the As-O interatomic distance of 1.63, 1.64, 1.68, and 1.75 Å with an average of 1.68 ± 0.05 Å, in good agreement with the EXAFS and DFT results.

The previous studies have stated that the arsenite molecule (AsO$_3^{3-}$) substituted by CO$_3^{2-}$ in the calcite structure results in a nonbalanced local charge (Benedetto et al., 2006). In the same way, other authors hypothesize that the charge balance of uranyl ions incorporated in calcite through a nonlocal mechanism by which Na$^+$ cation would be compensating the charge (Kelly et al., 2003). Our results suggested that the As(V) species in the crystal lattice of barite was dominantly presented as HAsO$_4^{2-}$, having same charge with SO$_4^{2-}$, via a solid solution mechanism. Hence, charge balance is a strict requirement for the As(V) substitution of SO$_4$ that may occur in ion exchange processes.

**IMPLICATIONS**

Incorporation of arsenate into mineral lattices (e.g. vivianite, rhombooclase, hematite, gypsum, hydroxylapatite, jarosite) (Fernández-Martínez et al. 2008; Lee et al. 2009; Kendall et al. 2013; Bolanz et al. 2013, 2016; Muehe et al. 2016) is an important process influencing the mobility and transformation processes of arsenate in nature and mining related environments. In hot spring water (Tokunaga et al. 2016), some mining related areas and other geological environments (e.g. deep-sea, groundwater, river, and crust deposits) (Goodarzi 2002; McBeth et al. 2003; Pone et al. 2007; Arik and Sgem 2008; Romero et al. 2010; Liu and Hendry 2011; Gomez et
al. 2013) that contain considerable amounts of As, it can co-exist with \( \text{Ba}^{2+} \) and \( \text{SO}_4^{2-} \) leading to the formation of arsenate-barite. The structural incorporation of arsenate into barite represents a sink for arsenic that can impact its mobility and transformation in the environment. To date, there exists limited examples in the literature (Goodarzi 2002; McBeth et al. 2003; Pone et al. 2007; Arik and Sgem 2008; Romero et al. 2010; Tokunaga et al. 2016) on the incorporation of arsenate into barite, how it affects arsenic mobility and transformation in the environment. Moreover, the state of arsenate (protonated or not) incorporated into the barite structure is definitively not well understood, this latter fact is important to know as it may affect some of the chemical properties of the arsenate incorporated barite such as arsenic stability as seen for other mining-geological related phases (Gomez et al. 2011). For example, Tokunaga et al (2006) focused on the influence of As oxidation state in natural barite and its immobilization as well as the ratio of As(III)/As(V) as an indicator for sub-oxic/anoxic redox conditions. In this work, the authors did not consider the coprecipitation of arsenate with barium at neutral conditions, how this may lead to multiple arsenate species, the amount of arsenate in the barite lattice as a function of pH and the arsenate speciation in the barite structure. In the present work, we studied the amount of arsenate in barite, the possible barium arsenate phases, the dominant arsenate species in the barite structure and local atomic structure of As(V) in the barite crystal lattice formed at various pH. The latter facts are of significance for understanding the speciation and formation of \( \text{Ba}^{2+}, \text{SO}_4^{2-} \) minerals in the presence of arsenate as well as the aqueous arsenic fixation and mobility in some natural and
mining-impacted environments with $\text{Ba}^{2+}$ and $\text{SO}_4^{2-}$. In natural systems, the presence of $\text{CO}_3^{2-}$ may induce the formation of $\text{BaCO}_3$ (i.e. witherite, $\log K_{sp} = -8.562$), which may also incorporate arsenic. However, $\text{BaCO}_3$ will transform to barite in the presence of $\text{SO}_4^{2-}$ due to its relatively higher solubility. Therefore, our findings can reflect the effect of barite precipitation on the mobility of As in natural environment.

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REFERENCES


Bolanz, R.M, Gottlicher, J., Steininger, R., and Wieczorek, A. (2016) Structural...
incorporation of $\text{As}^{5+}$ into rhomboclase $(\text{H}_5\text{O}_2)\text{Fe}^{3+}\text{(SO}_4\text{(2)}\text{center dot 2H}_2\text{O)}$ and $(\text{H}_3\text{O})\text{Fe(SO}_4\text{(2)}$. Chemosphere, 146, 338-345.


Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli,


Gomez, M.A., Assaaoudi, H., Becze, L., Cutler, J.N., and Demopoulos, G.P. (2010) Vibrational spectroscopy study of hydrothermally produced scorodite (FeAsO$_4$$\cdot$2H$_2$O), ferric arsenate sub-hydrate (FAsH; FeAsO$_4$$\cdot$0.75H$_2$O) and basic ferric arsenate sulfate (BFAS; Fe$\cdot$(AsO$_4$)$_{(1-x)}$(SO$_4$)$_{(x)}$(OH)$_{(x)}$$\cdot$wH$_2$O). Journal of Raman Spectroscopy, 41, 212-221.


Gomez, M.A., Ventruti, G., Celikin, M., Assaaoudi, H., Putz, H., Becze, L., Lee, K.E., and Demopoulos, G.P. (2013b) The nature of synthetic basic ferric arsenate sulfate (Fe(AsO$_4$)$_{(1-x)}$(SO$_4$)$_{(x)}$(OH)$_{(x)}$) and basic ferric sulfate (FeOH$\cdot$SO$_4$): their crystallographic, molecular and electronic structure with applications in the
environment and energy. Rsc Advances, 3, 16840-16849.


Liu, D.J., and Hendry, M.J. (2011) Controls on (226)Ra during raffinate neutralization at the Key Lake uranium mill, Saskatchewan, Canada. Applied Geochemistry, 26, 2113-2120. 


Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., and Rahman,


Tokunaga, K., Uruga, T., Nitta, K., Terada, Y., Sekizawa O., Kawagucci, S., and


LIST OF FIGURE CAPTIONS

FIGURE 1. As content in the UT (solid symbol) and AT (open symbol) As(V)-barite coprecipitates as a function of precipitation pH and initial As(V) concentrations (50, 500, 2000 mg·L⁻¹). AT and UT mean acid treated and untreated samples, respectively. The error bar represents one standard deviation of three individual experiments.

FIGURE 2. Geochemical modeling of the saturation states with respect to barium arsenate in the As(V)-barite co-precipitation systems at pH 2-12 and initial arsenate concentrations of 50 (●), 500 (○), 2000 (■) mg L⁻¹, respectively.

FIGURE 3. SEM images of As(V)-free barite (A), BaHAsO₄·H₂O (B), Ba₃(AsO₄)₂ (C), and As(V)-barite coprecipitates formed at pH 6, pH 9, pH 10 and an initial As(V) concentration of 2000 mg L⁻¹ with (D-F) and without (G-I) acid treatment.

FIGURE 4. XRD patterns of the AT As(V)-barite coprecipitates formed at pH 4, 7, 10 and an initial As(V) concentration of 2000 mg L⁻¹. Black points and red lines represent the experimental data and the Rietveld best fits, respectively.

FIGURE 5. FTIR spectra of the As(V)-free barite, Ba₃(AsO₄)₂, BaHAsO₄·H₂O standards and the AT and UT As(V)-barite coprecipitates formed at various pHs (pH 3, 5, 7, and 9) and an initial As(V) concentration of 2000 mg L⁻¹.
FIGURE 6. The $k^3$-weighted $\chi$ functions (A), Fourier transformed (FTs)$\chi$ functions (B), and real part of Fourier transformed EXAFS spectra (C) of the reference materials and the As(V) doped-barite samples at pH 3, 7, and 10 with initial arsenate concentration 2000 mg·L$^{-1}$. The BaHAsO$_4$·H$_2$O (for first shell 0.9 - 2.0 Å) and DFT optimized structure (Fig. S1) (for second shell 2 – 3.9 Å) were used as the model for EXAFS fitting of the AT samples. The black dots and red lines represent the experimental data and the best fits, respectively.

FIGURE 7. (A) Normalized As K-edge XANES spectra of reference materials (BaHAsO$_4$·H$_2$O and Ba$_3$(AsO$_4$)$_2$) and AT As(V)-barite coprecipitated at pH 3, 7, 10, respectively. (B) The difference of XANES spectra among AT-pH3, AT-pH7, and AT-pH10 samples. (C) Comparison between experimental As K-edge XANES spectra of the AT-pH 7 sample (black circle-line), unbroadened (dash line), and broadened theoretical (red lines) based on the DFT optimized structure. (D) Comparison between structural refined (red line) and experimental As K-edge XANES spectra (black circle-line) of AT-pH 7 sample. (E) The FPMS refined cluster of HAsO$_4^{2-}$ doped barite.
### TABLE 1. The shell-fit results for the As K-edge EXAFS of the reference materials and the As(V)-doped barite. CN refers to the coordination number. $R_{\text{path}}$ is the interatomic distance. $\sigma^2$ is the Debye-Waller parameter. $\Delta E$ is the energy-shift parameter and $\chi^2_{\text{red}}$ is the reduced chi-square. $R$-factor is the mean-square misfit between the measured and the modeled data. The fitted $k$ was set to $3 - 13.5 \, \text{Å}^{-1}$.

Accordingly, the number of independent points ($N_{\text{idp}}$) and variables ($N_{\text{var}}$) were 19.75 and 7, respectively. $S_0^2$ was set 0.95.

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<th>CN</th>
<th>$R_{\text{path}}$ (Å)</th>
<th>$\sigma^2$ (Å²)</th>
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<th>$\chi^2_{\text{red}}$</th>
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Fig 2
Fig 6