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Alejandro Fernandez-Martinez, Gabriel J. Cuello, Gabriela Roman-Ross, Mark R. Johnson, Fabrizio Bardelli, Xavier Turrillas, Laurent Charlet

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Arsenic uptake by gypsum and calcite: Modeling and probing by neutron and x-ray scattering

A. Fernández-Martínez [a] G. Román-Ross [b] G. J. Cuello [a,*] X. Turrillas [c] L. Charlet [d]
M. R. Johnson [a] F. Bardelli [e]

[a] *Institut Laue-Langevin, B.P. 156, 38042 - Grenoble Cedex 9 (France)*
[b] *Universidad de Girona, Campus de Montilivi, 17071 - Girona (Spain)*
[c] *ICC Eduardo Torroja, CSIC, Serrano Galvache s/n, 28033 - Madrid (Spain)*
[d] *LGIT-IRIGM, Univ. de Grenoble I, B.P. 53, 38041 - Grenoble Cedex 9 (France)*
[e] *INFM-GILDA c/o ESRF, B.P. 220, 38043 - Grenoble Cedex 9 (France)*

Abstract

Uptaking of contaminants by solid phases is relevant to many issues in environmental science as this process can remove them from solutions and retard their transport into the hydrosphere. Here we report on two structural studies performed on As-doped gypsum ($CaSO_4$ $2H_2O$) and calcite ($CaCO_3$), using neutron (D20-ILL) and x-ray (ID11-ESRF) diffraction data and EXAFS (BM8-ESRF). The aim of this study is to determine whether As gets into the bulk of gypsum and calcite structures or is simply adsorbed on the surface. Different mechanisms of substitution are used as hypotheses. The combined Rietveld analysis of neutron and x-ray diffraction data shows an expansion of the unit cell volume proportional to the As concentration within the samples. DFT-based simulations confirm the increase of the unit cell volume proportional to the amount of carbonate or sulphate groups substituted. Interpolation of the experimental Rietveld data allows us to distinguish As substituted within the structure from that adsorbed on the surface of both minerals. Results obtained by EXAFS analysis from calcite samples show good agreement with the hypothesis of replacement of As into the C crystallographic site.

Key words:
arsenic, minerals, simulation, diffraction, EXAFS

1. Introduction

Arsenic is recognized as a dangerous pollutant of the environment [1]. Arsenic present in groundwaters may be trapped in the solid phase of minerals like calcite or gypsum, either by adsorption or by co-precipitation. When a contaminant is incorporated in the bulk rather than simply adsorbed at the surface, it is less available and it can be considered "immobilized" in the environment at least until the host phase dissolution. The aim of this study is to elucidate whether the incorporation of As(III) and As(V) into the bulk of calcite and gypsum, respectively, occurs or not, and to what extent.

Surface-sensitive X-ray Standing Wave (XSW) studies by Cheng *et al.* [2] show that the As atom replaces the C atom in the carbonate molecules of calcite. The geometry of the carbonate group is not preserved, showing a displacement of the As atom of 0.76 Å in the [001] direction. Density Functional Theory (DFT) based simulations have proved that this replacement drives to a similar displacement of the As atom when C atoms are replaced by As atoms in the bulk of calcite (see below). This fact leads us to keep the same hypothesis of arsenite/carbonate replacement in our

* Corresponding Author: Institut Laue-Langevin, B.P. 156, Grenoble Cedex 9, 38042 France. Phone: (0033) 4 76 20 76 97 Fax: (0033) 4 76 20 76 48, Email: cuello@ill.fr

study of As incorporation into the bulk.

The stability diagram of aqueous solutions of $H_nAsO_4^{n-3}$ shows that the arsenate (AsO_4^{3-}) is the most stable specie under oxidizing conditions. This anion is a tetrahedron with the As atom at the centre, surrounded by four O atoms. The fact that both, arsenate and sulphate groups have the same geometry supports the hypothesis of a possible replacement of sulphate by arsenate groups when gypsum is precipitated in presence of As(V). The charge is compensated by bonding to an extra proton.

2. Materials and methods

In order to test the possible mechanisms for As immobilization by calcite and gypsum, samples of both minerals were synthesized in the presence of As(III) and As(V), respectively. Calcite precipitation was conducted at pH = 7.5 by addition of $CaCl_2$ and Na_2CO_3 solutions. Gypsum was precipitated from Na_2SO_4 and $CaCl_2$ solutions at three different pH values: 4, 7.5 and 9. Arsenic concentrations incorporated in the solids range between 30 mM/kg and 1200 mM/kg for calcite and 100 mM/kg to 1000 mM/kg for gypsum.

Powder samples were analysed by neutron diffraction at the high flux powder diffractometer D20 (ILL). Experiments were carried out using a Cu(200) monochromator which gives a wavelength of $\lambda = 1.30$ Å and at ambient conditions of pressure and temperature [4]. Diffraction patterns were taken for the samples in their container and for the empty cell, in the range of $10°$ to $130°$. Also powder diffraction experiments were performed with x-ray at ID11 (ESRF), reproducing the same experimental conditions but using a wavelength of $\lambda = 0.5$ Å. Both diffraction data sets were analysed using Fullprof [5].

Geometrical optimisations of the unit cell and the supercells of pure and As-doped calcite and gypsum were done with the Vienna Ab-initio Simulation Package (VASP) [6]. The PBE functional and PAW pseudopotentials were used. The goal was to reproduce the expansion of the unit cell produced by the incorporation of As atoms into the structure of both minerals. Unit cells of pure calcite and gypsum obtained from Rietveld refinements were used as starting point for all the models. Geometrical optimizations of single unit cells and of supercells of gypsum were done replacing the sulphate molecules SO_4^{2-} by arsenates AsO_4^{3-}. Similar simulations were performed with supercells of calcite replacing C by As atoms [4].

EXAFS data were collected on a diffraction and absorption beamline (GILDA-BM8) at the ESRF of Grenoble and extracted using standard procedures [7]. The theoretical photoelectron paths were generated
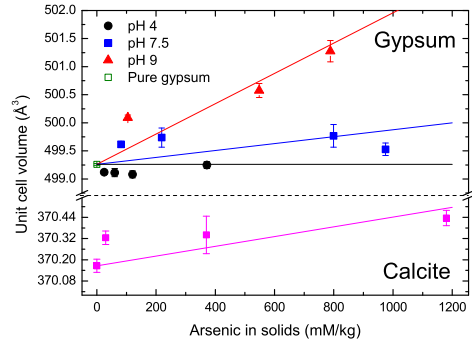

Fig. 1. Experimental unit cell volume of As-doped calcite and gypsum samples in function of As concentration.

using the FEFF8 [8] code and the fit performed using the MINUIT library from CERN [9]. A monochromator of Si(311) was used to set the incident energy at the K-edge of As (11867 eV).

3. Results and discussion

Our diffraction data show an expansion of the unit cell due to As incorporation into calcite crystallites (Fig. 1). By modelling, As concentration in the bulk of the samples can be extrapolated by comparison of the relative volume changes between the experimental and simulated data. Calcite unit cell and two supercells (2x2x1 and 3x2x1) were geometrically optimised replacing one and two units of AsO_3^{3-} (150 mM/kg and 290 mM/kg) by CO_3^{2-} units. The simulations showed a volume expansion linearly dependent on the replacement of As, as expected by Vegard's law (Fig. 2). This augmentation is due to the lattice expansion along the a axis as As concentration in solids increases. The observed As ion displacement of 0.57 Å over the O base along the (0001) is compatible with Cheng's results [2]. The lower value of this displacement (0.57 Å *vs.* 0.76 Å) can be due to the fact that atoms near the surface are less attached to the solid and can move more freely.

The experimental value of the unit cell volume was interpolated using the linear fit of the simulated volume expansion, giving values of 9, 10 and 16 mM/kg of As in calcite for the three synthesised samples. Simulations of 3x2x1 supercells with one CO_3^{2-} unit replaced by one AsO_3^{3-} unit were done to check whether the replacement is more likely in sites at the same or at different crystallographic planes. The higher enthalpy of formation ($\Delta H = 211.36$ meV) for the calcite structure with two As atoms lying on the same plane shows that replacement is more likely to happen in different planes, leading to a more stable structure.
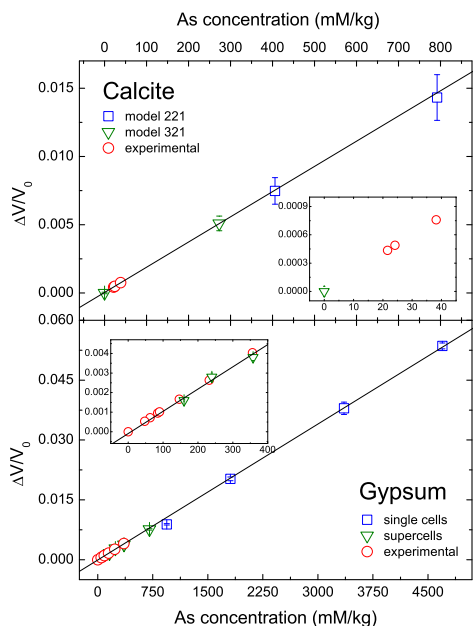
2

Fig. 2. Simulated relative expansion of unit cell volume of gypsum and calcite. The insets show a detail of the interpolation of the experimental data using the simulated expansion.

We found from EXAFS data analysis a nearest neighbour distance of $\approx 1.77(3)$ Å corresponding to the As-O bond distance. This value lies in between the reported one [10] for the arsenite molecule ($d_{As-O}^{L} = 1.84$ Å) and that obtained from the simulations ($d_{As-O}^{sims} = 1.75$ Å). The coordination number was kept fixed to its theoretical value ($N = 3$) in order to reduce the correlation between free parameters in the fitting procedure. This result supports the hypothesis of the incorporation of the As atoms into the C crystallographic sites.

Figure 1 shows the gypsum unit cell volume obtained from combined refinements of neutron and x-ray data. The expansion of the unit cell is proportional to the As concentration in solids and strongly dependent on the pH value: the biggest expansion is found in samples synthesized at pH 9. This result is in good agreement with the hypothesis of replacement of sulphate (SO_4^{2-}) by arsenate groups (AsO_4^{3-}). This replacement is more likely at higher pH values, according to available thermodynamical data regarding speciation of As [3]. The expansion of the unit cell parameters is due to the different lengths for As-O (≈ 1.70 Å) [12] and S-O (≈ 1.50 Å) [11] bonds.

Simulations show an increasing of the unit cell volume proportional to the number of atoms of S replaced by As (Fig. 2). Four single cells (with 940, 1809, 3357 and 4696 mM/kg of As) and four supercells were simu-

lated: two 2x1x2 supercells with one and two As atoms, a 2x1x3 and a 3x1x3 with one As atom each, giving As concentrations of 358, 705, 240 and 160 mM/kg, respectively. The simulations allow us to extrapolate the As concentration in the bulk of the samples by comparing the relative volume variations between the experimental and simulated data (Table 1).

Initial %As	pH 4	pH 7	pH 9
(M)	%As (mM/kg)	%As (mM/kg)	%As (mM/kg)
0.01	0	62	145
0.04	0	84	232
0.06	0	46	355
0.09	0	89	-

Table 1
Extrapolated values of the As concentration in samples of gypsum. The result for pH 4 is due to the near zero relative expansion of the unit cell.

Our results support the hypothesis of As immobilisation by incorporation into the bulk of these minerals. This improves the knowledge on the long term stability of contaminated sludges and it has important consequences for site remediation actions. This work is an example of a direct link between fundamental research and environmental issues. The understanding of the As compounds behaviour in sedimentary environments is essential to estimate and predict possible consequences of forecast or accidental events.

References

[1] J. Nriagu (1984). *Arsenic in the Environment.* Wiley Interscience.

[2] L. Cheng *et al.*, Geochim. Cosmochim. Acta **63** (1999) 3153-3157.

[3] M. Pourbaix (1974). *Atlas of Electrochemical Equilibria in Aqueous Solutions.* Pergamon Press.

[4] G. Román-Ross *et al.*, Geochim. Cosmochim. Acta (2005) (*submitted*).

[5] J. Rodríguez-Carvajal (1990). *Collected Abstracts of Powder Diffraction Meeting.* Ed. by J. Galy. Toulouse, France.

[6] G. Kresse, J. Furthmüller, Software VASP, Vienna (1999); G. Kresse, Phys. Rev. B **54** 11 (1996) 169.

[7] P. A. Lee *et al.*, Rev. Mod. Phys. **53** (1981) 769.

[8] A. I. Ankudinov *et al.*, Phys. Rev. B, **58** (1998) 7565.

[9] F. James, CERN Program Library, **506** (1994).

[10] A. Loewenschuss, Y. Marcus, J. Phys. Chem. Ref. Data **25** (1996) 1495-1507.

[11] S. M. Loureiro *et al.*, J. Sol. Stat. Chem. **121** (1996) 66-73.

[12] U. Kolitsch, P. Bartu, Acta Cryst. C **60** (2004) i94-i96.