Structural Study of Selenium and Arsenic Substitution in Calcite

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INTRODUCTION.

The behaviour of toxic heavy metals in soils has become a subject of great interest in the last years. The release of these contaminants to the environment has increased steadily due to industry and agriculture, but now a great effort is being made to understand the properties and mechanisms involved in environmental pollution in order to prevent and control the bioavailability of these elements (Cuello *et al.*, 2008).

The release and transport of contaminants in the environment may be slowed down by different mechanisms: ion exchange, sorption, or precipitation processes which are in turn affected by variables such as pH, temperature, pressure and composition of soils. In particular, we focus on carbonates which are present in many near-surface environments. More specifically, calcite is a very abundant mineral and so its fundamental importance in many fields, related to immobilization of both inorganic and organic species. In this context, co-precipitation is the most important mechanism by which an ion can get trapped into the bulk of a mineral, retarding its transport and subsequent availability to the environment.

Arsenic is a highly toxic contaminant, present in many industrial sites where mineral ores are smelted (Juillot *et al.*, 1999), releasing high quantities of arsenite - As(III) - or arsenate - As(V) (Charlet *et al.*, 2001). Co-precipitation of As-free minerals in the presence of arsenic may lead to long term immobilization of the contaminant, until the host phase is dissolved.

Selenium is another interesting contaminant to consider. On the one hand, Se is a dangerous pollutant of the environment, leading to a high incidence of deformity and mortality associated with its high concentration in water (McLean & Biedsoe, 1992). On the other hand, because Se is present in nuclear waste in the form of ^{79}Se coming from fission. One possible solution for nuclear waste management is to dispose the wastes in geological formations, which makes essential to identify and characterize the interaction and mechanisms of migration of the radionuclides in soils (Pitteloud *et al.*, 2003). As calcite is a very common mineral in sedimentary environments, it is of great importance to environmental scientists to gain direct information on the incorporation of Se in calcite, in particular, on the sites and mechanisms of incorporation of selenite Se(IV) and selenate Se(VI) species.

The species under study in the present work, i.e., As(III), As(V), Se(IV) and Se(VI) bear some similarities. They all are molecular ions, with a three-dimensional structure, and therefore their incorporation to mineral surfaces or bulk needs to take into account not only charge balance but also the atomic-scale structure of the contaminant molecules. Se(IV) and As(III) assume a pyramidal trigonal shape, whereas Se(VI) and As(V) assume a tetrahedral shape.

In this work we present the results of a crystallographic study of synthetic calcite co-precipitated with arsenic and selenium at different concentrations and pH values. Our aim is to study by different theoretical and experimental methods whether Se(IV,VI) and As(III,V) can be incorporated to bulk calcite by substitution.

EXPERIMENTAL.

We have performed neutron diffraction (ND) and X-ray diffraction (XRD) experiments, extended X-ray absorption fine structure spectroscopy (EXAFS) with synchrotron radiation and a theoretical modelling of the crystallographic structure using ab-initio simulations based on the density functional theory (DFT).

Powder samples were studied by ND at the D20 diffractometer of the Institut Laue-Langevin (ILL) in Grenoble, France. Neutrons are known to be essential to gain information on the bulk properties and investigate the incorporation of contaminant traces into the calcite structure (Fernández Martínez *et al.*, 2006, 2008), while X-rays probe mostly the surface of the samples. However, we took advantage of both techniques and performed simultaneous Rietveld refinements of the crystallographic structure combining conventional XRD and ND.
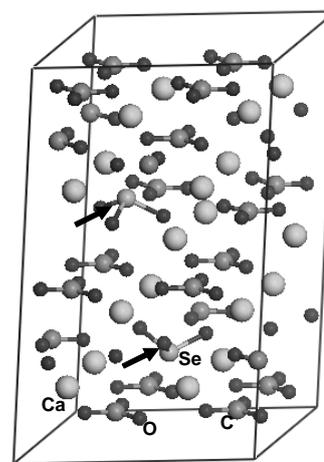
fig 1. Simulated incorporation of selenite molecules SeO$_3^{2-}$ in the calcite unit cell. The arrows show the two Se atoms which were placed at a carbon site in the initial stages of the simulation and evolved to adopt a pyramidal configuration.

In addition, we have collected EXAFS spectra of calcite-Se(IV) samples on the BM30 beam line at the synchrotron facilities in Grenoble, France (ESRF). The data were analysed on the basis of a theoretical model for the local environment of the Se atom in the calcite bulk structure. Such model was obtained from a geometrical optimization of calcite performed with a DFT–based simulation package (VASP) (Kresse & Furthmüller, 1996), as shown in Fig. 1.

We also performed simulations of the
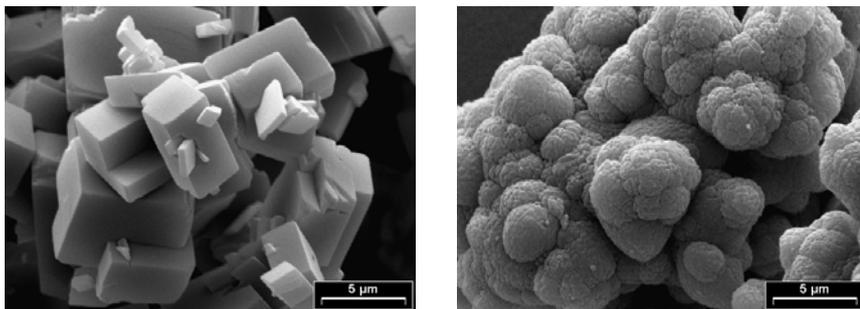
fig 2. *Scanning electron micrographs showing a well-crystallized calcite sample (left) and a vaterite sample (right), synthesized by coprecipitation with Se(VI) and Se(IV), respectively.*

calcite unit cell as well as of bigger supercells in order to study the possible cell expansion as a function of Se concentration. These results were compared against diffraction experiments.

RESULTS.

Samples of calcite coprecipitated with different Se and As concentrations in solution were synthesized as in previous works (Fernández Martínez *et al.*, 2006). Scanning electron microscopy as well as XRD and ND data reveal that under certain conditions the precipitation of calcite is suppressed and other polymorphs of $CaCO_3$ may crystallize, as is the case of vaterite shown in fig.2.

In fig. 3 we present, as an example, the Rietveld refinements of the XRD and ND data for the parent calcite sample (left panels) and for a sample with a nominal content of 0.8 at.% Se which crystallized completely in the calcite structure. We observe a volume expansion of the calcite cell in agreement with the VASP simulations.

EXAFS data on this sample reveal that there is a first neighbors shell around Se atoms in this sample, corresponding to the Se-O distance in a pyramidal configuration, as well as a second shell of neighbors which is indicative of the substitution of Se for Ca in the bulk of calcite. The fits to these data are still under way.

CONCLUSIONS.

We have studied the possibility of two contaminants, Se and As, to substitute for carbonate in the bulk of calcite. To this end, we have performed neutron and X-ray diffraction to test the volume expansion of the calcite unit cell as an indicative of the contaminant incorporation. Furthermore, we have modeled several crystallographic arrangements to evaluate the substitution of Se in the

bulk of calcite for different supercells (concentrations) and used these models to analyze and fit spectra coming from EXAFS experiments, in which the local environment of the contaminant atom is selectively probed. These studies confirm the possibility of Se(IV) substituting for carbon in the calcite structure. More experiments are under way to complete the series Se(VI) and As(V), which we have only studied with diffraction methods.

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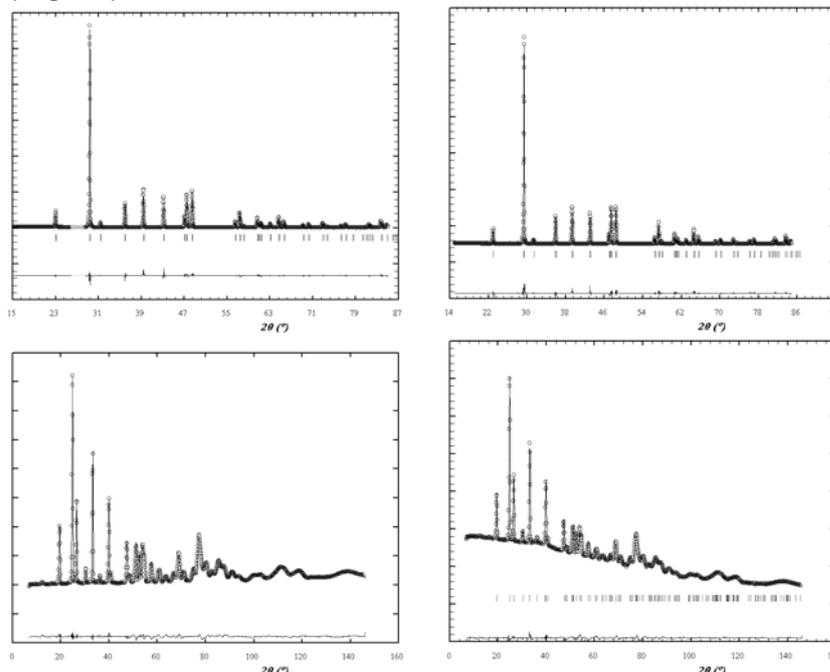
fig 3 *Rietveld refinements of XRD data (upper panels) and ND data (bottom panels) of pure calcite (left) and Se-substituted calcite (0.8% nominal Se content). Simultaneous refinements show an increase in the lattice parameters due to Se incorporation to the calcite structure. Symbols represent experimental data; solid lines correspond to the fit. Vertical bars are the Bragg reflections of the calcite structure and the line at the bottom of the graphs represents the difference between the fit and the data.*