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Report:

In this work [1] we present the results of a crystallographic study of synthetic calcite co-precipitated with selenium. We investigated both at a macroscopic and nanoscopic level, whether Se(IV) can be incorporated to bulk calcite by substitution at carbon sites. Neutron diffraction experiments, EXAFS spectroscopy and a theoretical modelling of the crystallographic structure using VASP are reported. We have found that the calcite unit cell volume obtained from the VASP simulations increases linearly with Se content in the structure. This allows estimating the Se content effectively incorporated into calcite based on volume measurements. Diffraction results are combined with VASP modelling to estimate a concentration of Se(IV) co-precipitated with calcite of 30–75mmol/kg solid. EXAFS spectroscopy, in combination with our theoretical model of the local structure surrounding the Se atom, confirms the possibility of selenite ion substituting for carbonate anion in the calcite structure.

EXAFS spectra were collected using the fluorescence mode at the BM30 [2], using a Si(220) double-crystal monochromator. Multiple scans were taken over the Se K-edge (12658 eV). The sample was held at near 20 K using a liquid He cryostat, which improved the signal/noise ratio. Absorption spectra for the Se-doped calcite sample were obtained using a Ge 30-element detector.

Data analysis proceeded by subtraction of a linear pre-edge background, a second-order polynomial post-edge background, normalization, and conversion to k -space, followed by μ_0 fitting using a cubic spline. The $\chi(k)$ function was Fourier transformed using k^2 weighting. All data processing was performed using the Athena software [3]. The quantitative analyses of EXAFS data were performed using the Artemis software [3] based on IFEFFIT. Fits were conducted in the R -space using as input the theoretical model for the selenium local structure obtained from the VASP calculations. The FEFF program in Artemis calculates a theoretical EXAFS spectrum, which is composed of individual backscattering paths. Fitting was performed by minimizing the difference between the raw data and our model for $\text{FT}[\chi(k)]$ from $R = 0.8$ to 3.8 \AA , being $\text{FT}[\chi(k)]$ the Fourier transform of the EXAFS function $\chi(k)$ between $k = 2.8$ and 13.5 \AA^{-1} . The minimization proceeded by refining the parameters for each individual path.

X-ray absorption spectroscopy at the Se K-edge has been used to characterize the local structure and coordination of selenium co-precipitated with calcite starting from room temperature aqueous solutions containing Se(IV). The XANES spectra provide information on the actual oxidation state of Se in the solid.

In addition EXAFS reveals the short-range order around the selenium atom. The obtained spectra for our calcite sample is consistent in shape and position with the XANES of an aqueous SeO_3^{2-} solution [4], confirming that in these samples Se is present as Se(IV).

After extracting the EXAFS signal from the spectrum, fits were conducted in the R -space using as input the theoretical model for the local structure around Se obtained from our VASP calculations. Four scattering paths were considered in the fits, corresponding to single scattering paths between the central Se atom and a first and second shell of O atoms, and a third and fourth shell of Ca atoms. The local structure around Se in our model consists of two O shells of 3 atoms each, at distances d_1 and d_2 ; and two Ca shells of 3 atoms each, located at d_3 and d_4 , as sketched in Fig. 1. These distances, as well as the coordination numbers and other parameters, are allowed to vary during the fits to minimize the difference between the EXAFS data and the EXAFS equation based on our model.

In Fig. 2 we present the results of the EXAFS fits. The upper panel corresponds to the k^2 -weighted $\chi(k)$ function and the bottom panel represents the Fourier transform magnitude of $\chi(k)$. Sample S2 presents features consistent with more than just one shell of atoms surrounding Se. In this kind of studies, the absence/presence of calcium backscatterers and a well defined structure beyond the first shell provide insight into the degree of disorder associated with disruption of the local calcite structure, and can be taken as indicative of the inability/ability of the contaminant unit to assume a stable structural environment in the host calcite. The Fourier transform magnitude of $\chi(k)$ in Fig. 2 shows a well defined local structure around Se, which is fully compatible with our VASP model, in which Se is effectively incorporated into the calcite structure.

The possibility of fitting three more shells around Se, in good agreement with our structural calculated model, constitutes clear evidence that calcite has effectively incorporated Se as Se(IV). Moreover, we have considered other possible environments for the Se atom in our sample, which could result in a similar EXAFS signal. The precipitation of calcium selenite $\text{CaSeO}_3 \cdot 2\text{H}_2\text{O}$ was discarded for several reasons: the solutions used were under-saturated with respect to this phase, our neutron diffraction data show no evidence of precipitation of a second phase other than calcite, and eventually, the inter-atomic distances in $\text{CaSeO}_3 \cdot 2\text{H}_2\text{O}$ differ from the ones obtained in our fits [5].

References

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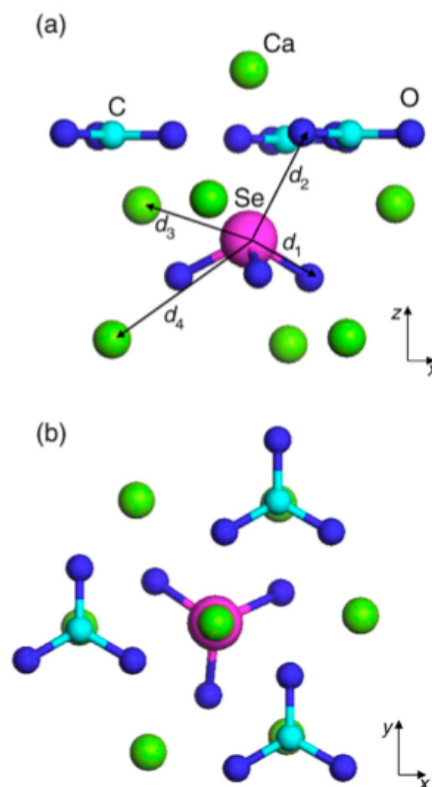


Fig. 1 Local structure around a Se(IV) atom in calcite, resulting from the VASP simulations. (a) Projection along the y direction; (b) projection along the z direction.

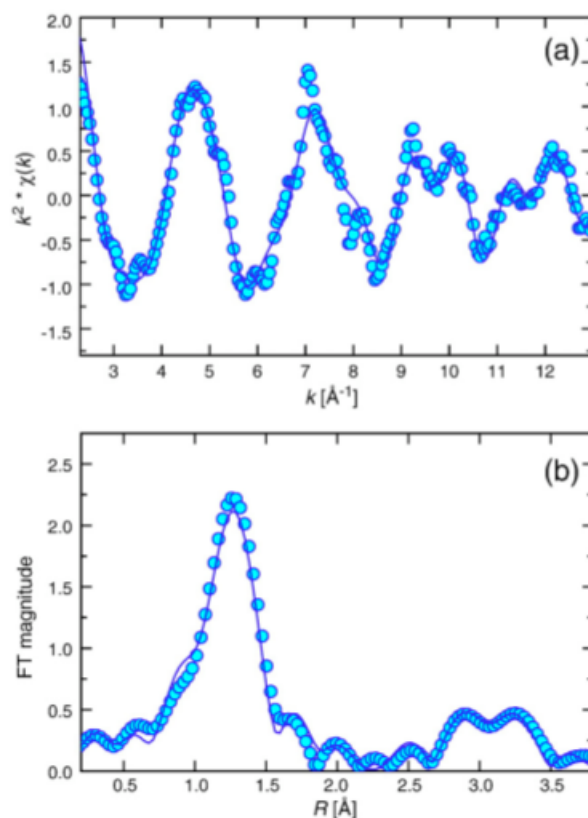


Fig. 2 EXAFS results for selenite incorporated in calcite. Symbols denote raw data and solid lines correspond to the fits to our model based on VASP simulations. (a) k^2 -weighted $\chi(k)$ function; (b) Fourier transform magnitude of $k^2\chi(k)$.