



	Experiment title: X-ray absorption spectroscopy study of the state of Se and Fe in pyrite	Experiment number: A28-1 1350
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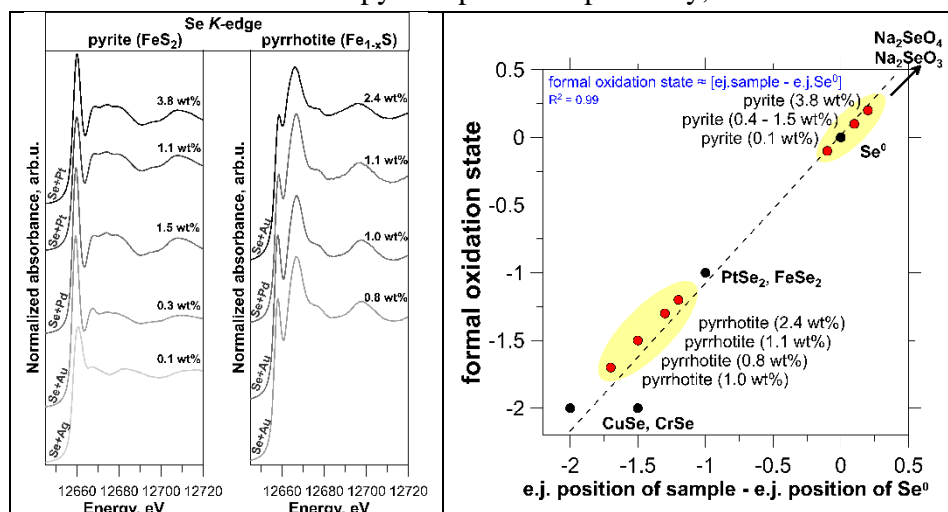
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Introduction and goals: Selenium is a toxic and, in particular, radiotoxic element (^{79}Se) released as a by-product during the refinement of the enriched ore deposits (i.e., phosphatic black shales) and degrading of nuclear waste repositories respectively. In the ores of different origins, Se together with noble and critical elements (Pt, Pd, Au, Ag) often enriches pyrite FeS_2 and pyrrhotite Fe_{1-x}S . The solubility of Se in Fe sulphides can reach 12 wt%. The main goal of this study was to investigate the state of Se (and Fe) in pyrites containing high concentrations of Se which are close to the solubility limit at the given temperature. The results of this study can be used for (1) physical-chemical modelling of Se migration and precipitation in natural systems; (2) compilation with literature data which will allow building a model capable to describe the solubility of Se in pyrite; (3) development of ores refinement technologies; (4) environmental science; (5) investigation of the matrices for radioactive wastes [1,2,3]. **Experiment:** The experimental samples included five Se-bearing pyrites and four Se-bearing pyrrhotites. For this study, only homogeneous samples obtained in the anoxic conditions via the salt flux method of synthesis were selected. Pyrite grains contained 0.1 – 3.8 wt% of Se admixture, pyrrhotite grains contained 0.8 – 2.4 wt% (microprobe detection limit = 0.03 wt%). Se-doped crystals were studied by means of XAS (XANES/EXAFS) at Se *K*-edge in order to reveal the state of Se in iron sulphides.

Se oxidation state: preliminary results of XANES spectroscopy The collected experimental XANES spectra of Se in pyrite and pyrrhotite are shown in Fig. 1. The positions of the edge jump and white line are 12658 and 12659.4 – 12660.5 eV for pyrite spectra respectively, and 12656.3 – 12656.8 and 12657.9 – 12658.4 eV for pyrrhotite spectra respectively.



Spectra of samples of pyrite containing 1.5 – 3.8 wt% of Se are similar independently on the presence of the second admixture (Pt or Pd) indicating the absence of clusterization of Pt/Pd and Se. Spectra of the samples containing 0.1 – 0.3 wt% of Se together with Au and Ag as additional components are different indicating the possible clusterization of Au/Ag and Se. The comparison of experimental spectra with the spectra of the standards recorded in this study (CrSe , PtSe_2 , and K_2SeO_4) and standards from

Fig. 1. Normalized Se *K*-edge XANES spectra of pyrites and pyrrhotites.

Fig. 2. Formal oxidation state of Se in standards, pyrite, and pyrrhotite as a function of e.j. position.

literature [4] shows that the formal oxidation state of Se in pyrite is close to 0 and Se in pyrrhotite is close to –

1 (Fig. 2). The increase of the Se content is directly correlated with the increase of the Se charge in pyrite and pyrrhotite.

Se local atomic environment: preliminary results of EXAFS spectroscopy: The preliminary EXAFS spectra fitting demonstrated that Se mostly substitutes for S in the pyrite and pyrrhotite structures. In general, the first coordination shell of the absorbing atom expands in comparison with the pure structures of pyrite and pyrrhotite. The distances to the rest coordination shells are close to the original distances between S and neighbouring atoms [5,6]. Neither Pt nor Pd was detected in the Se vicinity in the pyrite structure. Two preliminary fittings are shown in Fig. 1.

However, the Se-S interatomic distances in the first coordination shell of Se in pyrite are different for all the measured samples. In general, the increase of Se content from 0.5 to 1.1 wt% leads to the increase of Se-S interatomic distance from 2.24 [3,4] to 2.28 Å (this study, 1.1 wt%).

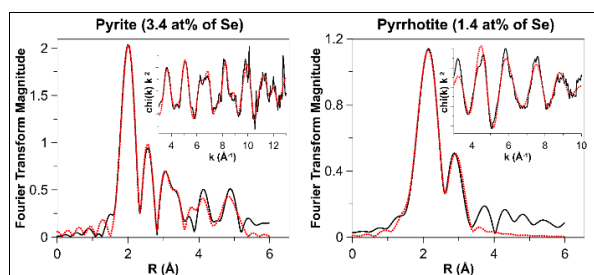


Fig. 2. Results of Se K-edge EXAFS spectra fits performed using ARTEMIS program. The figures show Fourier Transforms (FTs) of the k^2 -weighted background-subtracted EXAFS spectra (not corrected for phase shift), inserts: k^2 -weighted EXAFS spectra. Black lines – experimental spectra, dotted red lines – simulated spectra.

The further increase of Se concentration from 1.1 to 3.8 wt% leads to the substantial decrease of Se-S interatomic distance from 2.28 to 2.2 Å (this study, samples containing from 1.1 to 3.8 wt% respectively). This dependence could be accounted for by the changes in pyrite unit cell parameters. It also can be explained with the formation of Se-Se pairs (Se clustering) at the critical concentration of Se in pyrite of ~ 1 wt%. In that case, the changes in Se-S distances could be artificial and take place because this model does not consider Se-Se clustering. In order to test the clusterization model FDMNES and FEFF simulations were applied, and both methods demonstrated a consistent result. In the most concentrated sample of pyrite, the best simulation of the experimental XANES spectrum was archived when 70% of Se

substituted S in the anionic subshell and 30% of Se formed Se-Se clustering (Se was substituting for 2 atoms of S and one atom of Fe in the vicinity from each other). Fitting of the EXAFS spectrum of this sample has shown that the presence of < 1 atom of Se in the nearest Se vicinity substantially reduces the parameters of the goodness of the fit. The further decrease of the concentration can be accounted for by the presence of 20 and 10% of Se-Se pairs (bonding).

Conclusions and applications

What is the mechanism of Se incorporation in iron sulfides at the concentration close to the solubility limit?

In the anoxic conditions, Se⁰ mostly incorporates in the pyrite structure in the anionic subshell, however at the concentration of Se ≥ 1 wt% the second minor form of Se occurrence appears. According to the preliminary results, the latter was identified as Se-Se clustering within the pyrite structure. This form of Se occurrence in pyrite has not been described yet. Se⁻ incorporates in the pyrrhotite structure substituting S⁻ in the anionic position. Se-Fe interatomic distance increases from 2.44 to 2.53 Å.

Iron sulphides are often present in the radioactive wastes together with Se in the anoxic conditions. The result of this study together with the results published in the literature show that both minerals can contain structurally-bonded selenium that substituted S in the anionic subshell only at low Se content.

Is the state of Se coupled with PGEs?

The presence of Pt-Se and Pd-Se clusterization in the iron sulphides can be ruled out. Apparently, the Pt-Se and Pd-Se enrichment often observed in the natural deposits takes place simultaneously, or in the natural pyrites Se changes the parameters of the unit cell of pyrite which favours Pt and Pd incorporation. The last assumption can be tested via microdiffraction measurements.

The state of Se is coupled with the states of Ag/Au in the synthetic pyrites.

Does the state of Se depend on the state of Fe?

The comparison of the Fe K-edge spectrum of the most Se-concentrated pyrite sample and the spectrum of the pure pyrite demonstrated that the presence of hypothetical 1-2 at% of Fe³⁺ is below the detection limit of the XANES method.

[1] Yakovleva et al., 2003. Mineralogical Magazine, 67(2), 355–361; [2] Franz, 1983. Neues Jahrbuch für Mineralogie, Monatshefte, 3, 130-134 [in German]; [3] Manceau et al., 2020. ACS Earth and Space Chemistry, 4(3), 379-390; [4] Ryser et al., 2005. Geochemical Transactions, 6(1), 1-11; [5] Brostigen, Kjekshus, Acta Chem Scand, 23(6), 2186-2188 (1969); [6] Wyckoff, Interscience Publishers, New York, 1, 85-237 (1963).