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The mode of incorporation of As(-I) and Se(-I) in natural pyrite revisited

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ABSTRACT: Pyrite (FeS₂) from coal, sedimentary rocks, and hydrothermal ore deposits generally contains hazardous selenium (Se) and arsenic (As) that are released in natural waters through oxidative dissolution of the host. Knowing how As and Se are structurally incorporated into pyrite has important implication in controlling or preventing their release because trace metal(loid) substitution accelerates the dissolution of pyrite. Previous extended X-ray absorption fine structure (EXAFS) studies have reported that nominally monovalent arsenic clusters at the sulfur site forming As-As pairs at 3.2 Å, whereas monovalent Se does not form Se-Se pairs at this distance for unknown reason. Here, we revisit this question using As and Se K-edge X-ray absorption near-edge structure (XANES) and EXAFS spectroscopy complemented with atomistic calculations. We find that neither As nor Se atoms can be differentiated from S atom at 3.2-3.3 Å, the cluster and dilute model-fits to As- and Se-EXAFS data yielding equivalent least-squares solutions. Thermodynamic calculations of Fe₄₈As₃S₉₃ (3.8 wt.% As) and Fe₄₈Se₃S₉₃ (4.0 wt.% Se) structures show that the formation of As-As pairs is energetically favorable and the formation of Se-Se pairs unfavorable. Thus, the equilibrium distribution of As and Se predicted by calculation agrees with published EXAFS data. However, this agreement is incidental because EXAFS fits are ambiguous, the same EXAFS spectra being fit indifferently with a cluster and

a dilute model. Regarding Se, the dilute model-fit is probably correct since Se-Se pairs are precluded thermodynamically. The situation is less clear for As. The lowest energy atomic arrangement of As in $\text{Fe}_{48}\text{S}_{93}\text{As}_3$ is similar to the local structure of As in arsenopyrite (FeAsS), thus supporting the cluster model. However, the energy gain to total energy provided by the formation of As clusters decreases with decreasing As concentration, making them thermodynamically less favorable below 1.0 wt.%.

INTRODUCTION

Arsenic and selenium often substitute for sulfur in pyrite (FeS_2). Arsenic commonly amounts to several thousand mg/kg FeS_2 (ppm) in sedimentary pyrite,¹⁻⁷ and can reach up to 10-20 weight-percent (wt.%) in gold deposits.⁸⁻¹⁰ The As-Au association has been described in hydrothermal, epithermal, porphyry Cu and Au, Carlin-type and massive volcanogenic gold deposits.^{9, 11, 12} In contrast, Se rarely exceeds a few hundred mg/kg. Selenious pyrite (Se-pyrite) occurs most frequently in coal¹³⁻¹⁶ and shale^{17, 18} rocks.

The crystal chemistry of As and Se in pyrite has attracted much interest in the last two decades for economic and environmental reasons. Pyrite often contains valuable metals, such as Ni, Cu, Sb, and Ag, in addition to Au, and their concentrations are broadly correlated with As.^{12, 19-21} However, the mining and smelting of sulfide ores and the processing and combustion of coal release hazardous metal(loid)s, including Hg and Tl besides As and Se.²²⁻³³ It is important to know the modes of incorporation of As and Se in pyrite and their association with trace elements at the atomic scale to recover efficiently and safely valuable metals and to develop better methods of sulfide ore roasting, coal cleaning, and mine waste management.

As and Se have a nominal oxidation state of 1- in FeS_2 and substitute for sulfur in the S_2^{2-} dianion units which coordinate Fe in the pyrite crystal structure (Figure 1a).³⁴⁻³⁸ On the basis of their chemical similarity, one would expect As and Se to have similar local structure and atomic distribution. However, As-EXAFS and Se-EXAFS studies on natural pyrite have concluded otherwise.

Savage et al.³⁶ analyzed an arsenian pyrite (As-pyrite) of average composition $\text{FeAs}_{0.02}\text{S}_{1.98}$ (1.2 wt.% As) from gold mineralization using As-EXAFS spectroscopy. EXAFS data were fit with one S atom at 2.25 Å in the first coordination shell ($[\text{AsS}]_1$), and 4 S atoms at 3.10 Å ($[\text{AsS}]_2$) and 3 As atoms at 3.17 Å ($[\text{AsAs}]_2$) in the second anionic shell (Figure 1a). The authors concluded that As occurs in clusters in pyrite and explained the lack of detection of $[\text{AsAs}]_1$ pairs to the close proximity of 3 $[\text{AsFe}]_1$ pairs at 2.32 Å. The lack of $[\text{AsAs}]_1$ pairs is consistent with density functional theory (DFT), which predicts that the AsAs^{2-} unit is energetically less favorable than the AsS^{2-} unit.³⁹ Nano-inclusion

of arsenopyrite (FeAsS), which has [AsS]₁ and [AsAs]₂ pairs in its structure (Figure 1b), was excluded from EXAFS and HRTEM imaging. As clustering in the second S shell around a central As atom was confirmed by Paktunc³⁵ in arsenian pyrite from Carlin-type gold deposit containing 1.5 mol per cent As (FeAs_{0.03}S_{1.97}; 1.6 wt.% As). EXAFS data were fit with 3 [AsAs]₂ pairs at 3.24 Å and 2 [AsS]₂ pairs at 3.34 Å. The two studies agree with ab initio thermodynamic calculations, which show that pyrite can host up to ~6 wt.% of As (FeAs_{0.10}S_{1.90}) in solid solution before unmixing into pyrite-arsenopyrite domains.⁴⁰ A compositional segregation of As atoms at a mean concentration of only 1.0 mol per cent As (FeAs_{0.02}S_{1.98}) was, however, unexpected because no FeAs₂ mineral isostructural to cubic FeS₂ is known.

Ryser et al.¹⁷ analyzed a Se-pyrite grain containing as much as 0.7 wt.% Se (FeSe_{0.01}S_{1.99}) from a mine-waste rock shale using micro XANES and EXAFS spectroscopy. They concluded that Se forms [SeSe]₁ pairs at 2.25 Å from the central Se atom and 12 [SeS]₂ pairs at 3.24 Å. Matamoros-Veloza et al.¹⁸, who also studied a shale pyrite by X-ray microspectroscopy but containing ten times less Se (about 600 ppm), fit the EXAFS spectrum from euhedral grain with a [SeS]₁ pair at 2.34 Å and 6 [SeS]₂ pairs at 3.20 Å. The two model-fits for Se-pyrite agree in next-nearest neighbor identities, but not in nearest. The Se atoms are dispersed locally in the second study and clustered in the nearest S sites in the first study. Se₂²⁻ dianion units in Se-pyrite are structurally possible because cubic FeSe₂, named dzharkenite, occurs naturally in solid solution with pyrite.⁴¹

EXAFS results obtained on As- and Se-pyrite raise several questions. Why would Se form [SeSe]₁ pairs in the nearest S sites and not the next-nearest, and how [SeSe]₁ pairs can form at a Se/S atomic ratio of 0.01/1.99 = 5 × 10⁻³? Does it mean that SeSe²⁻ units are more stable than SeS²⁻ units, in contrast to the AsAs²⁻ and AsS²⁻ units? Why is As locally clustered in the next-nearest S sites at an As/S atomic ratio of 0.02/1.98 = 0.01, but not Se at similar Se/S ratio? Here, we address these questions by combining electron microprobe (EPMA) and synchrotron-based X-ray microfluorescence (SXRF) analysis and As and Se K-edge high energy-resolution XANES (HR-XANES) and EXAFS spectroscopy with quantum-mechanical calculations. Five pyrite specimen were studied, two at the As-edge from hydrothermal veins, two at the As- and Se-edge from epithermal and sedimentary deposits, and one at the Se-edge only from another sedimentary deposit.

MATERIALS AND METHODS

The origin and geological setting of the five pyrite are listed in Table 1. Four specimen (Bol, Ger, Sp, Sw) are massive aggregates of pyrite crystals and one (Ut) is a centimeter-sized single crystal

(Figure S1). Mineralogical purity was verified by X-ray diffraction (Figure S2). The distributions of As and Se were imaged and their point concentrations measured on polished sections by EPMA using a JEOL JXA-8230 microprobe equipped with five wavelength-dispersive spectrometers (WDS) and an energy-dispersive spectrometer (EDS).⁴² As in pyrite Ut and Ger was analyzed also by ICP-AES and Se by ICP-MS to verify the consistency between point and bulk analyses.

Parts of the samples were ground into powder in a glove bag filled with He to prevent oxidation and the powder was pressed into pellets for bulk HR-XANES and EXAFS measurements. HR-XANES data were acquired on beamline ID26 at the European Synchrotron Radiation Facility (ESRF, Grenoble) using a multi-crystal analyzer spectrometer.⁴³ EXAFS data were acquired on beamline BM23 in fluorescence-yield mode using a silicon drift diode detector (SDD). Bulk As-EXAFS was measured on pyrite Bol and Se-EXAFS on pyrite Ut. Growth zones with a wide range of As-Au concentrations were imaged by EPMA in pyrite Bol. A zoned area was relocated by micro SXRF and four As K-edge micro EXAFS spectra were acquired on spots differing in As concentration. The laterally resolved measurements were performed on the microprobe endstation of beamline BM23.⁴⁴ The incident beam was focused to $5 \times 5 \mu\text{m}^2$ with a set of Pt-coated Kirkpatrick-Baez (K-B) mirrors.

The absolute energy of the HR-XANES spectra is referenced at the As and Se K-edges to the first maximum of the derivative (inflection point) taken to 11870.0 eV for As_2O_3 and to 12658.0 eV for elemental Se (Se^0).¹⁷ The precision of the energy is ± 0.1 eV. The reference compounds arsenopyrite (FeAsS) and realgar (As_4S_4) at the As edge, and ferroselite (orthorhombic FeSe_2), achavelite (FeSe), elemental Se, Na_2SeO_3 , and Na_2SeO_4 at the Se edge, were diluted to 500 ppm in boron nitride (BN) to prevent overabsorption.⁴⁵ Additional methodological information (XRD, ICP-ES/MS, EPMA, XANES, EXAFS) is provided in the Supporting Information (SI).

Atomistic models of As and Se incorporation in pyrite were constructed with DFT using the CRYSTAL14⁴⁶ code for periodic systems, and a computational methodology adapted from Smith et al.^{47, 48} The hybrid PWGGA functional PW1PW with 20% HF contribution⁴⁹ was used for all calculations. The PBEsol0 functional, a hybrid version of the PBEsol XC functional comprising 25% Hartree-Fock (HF) exchange,⁵⁰ was used as a check on the reliability of the PW1PW functional. The all-electron split-valence 6-311G Pople's basis set⁵¹ was employed for S. An effective core pseudopotential with s411p411d411 external shell was used for Fe^{52} in pyrite models doped with As. The TZVP basis set of triple-zeta valence quality with polarization functions was employed for Fe^{53} in Se-pyrite models. The As and Se atoms were described with an effective core pseudopotential and the m-pVDZ double-zeta valence with polarization functions basis set.⁵⁴

The PW1PW and PBEsol0 functionals and basis sets were benchmarked by calculating the ionization energies of Fe, S, As and Se (Tables S1-S4), and by assessing the precision of the lattice parameters calculated on single unit cells of known structures (Tables S5-S7). The lattice parameters and interatomic distances derived from our modeling procedure (PW1PW functional) deviate from crystallographic values at most by 1.9% and 2.3% for pyrite,² 1.7% and 2.7% for marcasite (orthorhombic FeS₂),² 0.8% and 1.9% for arsenopyrite (FeAsS),⁵⁵ 1.4% and 2.5% for löllingite (orthorhombic FeAs₂),⁵⁶ 0.16% and 5.03% for dzharkenite (cubic FeSe₂)⁵⁷ (Tables S8-S14). The errors are typical of DFT GGA studies.^{39, 58-60} The distributions of As and Se were modeled in two supercells of dimensions 2 × 2 × 2 and 3 × 2 × 2. The reciprocal space integration was performed by sampling the Brillouin zone with the 6 × 6 × 6 Pack-Monkhorst mesh,⁶¹ resulting in 112 independent *k* points. Parameter space testing and tolerances for Coulomb and exchange sums are reported in Tables S15-17. Additional computational information is provided in SI.

RESULTS AND DISCUSSION

Distribution and concentration of As and Se. Backscattering electron imaging and EPMA mapping show that As and Se are uniformly distributed within the grains of pyrite Ger, Sp, Sw, and Ut (Figure 2). They are free of As- and Se-containing inclusions, such as goldfieldite and colusite sulfide inclusions reported in hydrothermal pyrite.⁶² Pyrite Sp contains minute inclusions of chalcopyrite (CuFeS₂) observed as brighter scattering spots on backscattered electron images. The four pyrite cover a large range of As and Se concentrations (Table 1). As content varies from below the EPMA detection limit of 23 ppm (Sp) to 1590 ppm (Ger), and Se content from below the detection limit of 34 ppm (Sp and Sw) to a maximum of 428 ppm (Ut). Although uniform at the grain scale, As and Se contents vary from grain to grain. As content varies from the detection limit of 23 ppm to 60 ppm in Sw based on the analysis of five grains, and from 50 ppm to 160 ppm in Ut based on the analysis of three grains. Similarly, Se content varies from 318 ppm to 428 ppm in Ut based on three grain analyses.

Growth-zoning compositional variations are observed on the BSE image and EPMA maps of pyrite Bol (Figure S3). On the basis of eight point analyses, As content among the zones varies between 0.15 and 1.14 wt.%, and Se content varies from below the detection limit of 34 ppm to 70 ppm (Table 1). Scatter plots of the fluorescence counts between two elements were derived from each pixel of the EPMA maps, and the co-occurrence between two elements was evaluated from the linear Pearson correlation coefficient ρ . Elemental scatter analysis shows that As and Se are negatively correlated

with S ($\rho(\text{As-S}) = -0.84$, $\rho(\text{Se-S}) = -0.64$), and positively correlated together ($\rho(\text{As-Se}) = 0.67$) (Figure S4). Gold (Au) was detected at a concentration of 60 ppm in one spot out of the eight analyzed (detection limit = 47 ppm). The distribution of Au is heterogeneous within pyrite, being localized in growth bands enriched in As (Figure S3). Scatter analysis shows that Au is, however, weakly correlated to As and Se ($\rho(\text{As-Au}) = 0.29$, $\rho(\text{Se-Au}) = 0.22$) and not to Fe ($\rho = -0.01$). Elemental correlations have limited chemical significance here, because Au is about three orders of magnitude less concentrated than As and more than four orders less than Fe. Analytical precision is not sufficient to calculate ρ confidently. In addition, the Au and Se fluorescence counts on the EPMA maps represent noise when point concentrations are below the detection limit. These points on the As-Au and Fe-Au correlation plots bias the ρ value. We conclude that the strong negative correlation between abundant As (0.15 – 1.14 wt.%) and major S ($\rho(\text{As-S}) = -0.84$) is evidence for As substitution at the S site. Se probably replaces also S, the lower Pearson correlation ($\rho(\text{Se-S}) = -0.64$) being attributed to the lower Se content, and larger ρ uncertainty thereof.

Formal oxidation state and local structure of As and Se from HR-XANES. Pyrite Bol, Sw, Ut, and Sp were measured at the As K-edge and pyrite Ut, Sp, and Ger at the Se K-edge. The As absorption white line is at 11866.2 eV and the Se white line at 12658.4 eV for all pyrites (Figures 3a and 3b). These edge energies are in the range of those for reduced As and Se compounds and several electronvolts lower than the K edges of oxidized As and Se species (Figures 3c and 3d, Tables S18 and S19). Of the reference spectra, those of arsenopyrite (FeAsS) at the As edge and of arsenopyrite (2 ppm Se) and marcasite (orthorhombic FeS₂, 12 ppm Se) at the Se K-edge provided the best match to the pyrite spectra, confirming the nominal -1 oxidation state of both As and Se in pyrite (Figures 4a-c). Comparison of the pyrite and reference spectra identifies three “indicator” features denoted A, B, and C in Figure 4a.

Region A refers to the energy of the white line. The As edge is at 11865.9 eV for arsenopyrite and 11866.2 eV for pyrite, and the Se edge is at 12657.8 eV for arsenopyrite, 12658.2 eV for marcasite, and 12658.4 eV for pyrite. Region B is situated 32-42 eV above the edge. The pyrite spectra show an absorption hump at this place, which is absent in arsenopyrite and marcasite. The edge energy and structure differences make it possible to distinguish a pyrite host with a corner-linked framework and cubic structure, from arsenopyrite and marcasite with a chain framework and a lower symmetry crystallographic structure (Figure 1). This finding was verified by calculating ab initio the arsenopyrite, marcasite, and pyrite spectra with the finite difference method (FDM) as implemented in FDMNES.⁶³

The code calculates the final state potential in real space from a cluster of atoms. The form of the potential is not approximated, in contrast to the alternative muffin-tin approach,^{64, 65} thus providing a better description of scattering phenomena. The As and Se clusters had a radius of 7 Å and were built from crystallographic structures^{2, 55} by replacing S and As with As and Se at the center (As pyrite, Se pyrite, Se marcasite, and Se arsenopyrite). Relaxation of the As and Se sites with CRYSTAL14 did not change the results. Figures 4d-f show that the two XANES fingerprints, edge energy and absorption hump, of As and Se substitution at the S site in pyrite are reproduced theoretically.

Region C is situated 8 eV above the edge energy and corresponds to the first absorption structure after the white line. As-XANES of pyrite has a higher absorption amplitude at 11874.0 eV relative to arsenopyrite. The increase in amplitude is particularly noticeable for Ut (Figure 3a). The energy value of this feature is close to the edge energy of As₂O₅ (11873.6 eV), which suggests that Ut at least, and perhaps all pyrites, contain some As(V). This species is attributed to the oxidation of arsenic exposed on the surface of pyrite grains.³⁵

Local structure of As and Se from EXAFS. Bulk EXAFS spectra measured at the As (pyrite Bol) and Se (pyrite Ut) K-edges are essentially the same, differing only in the amplitude of the oscillations at $k < 4 \text{ \AA}^{-1}$ and $k = 10 \text{ \AA}^{-1}$ (Figure 5a). They have the same frequency and structure, meaning that As and Se have similar short range order in pyrite. Comparison with the EXAFS spectrum of arsenopyrite (FeAsS) shows that the local coordination of As in this mineral does not replicate that of As and Se in pyrite, in agreement with HR-XANES (Figure 5b). Because Bol is zoned, four micro As-EXAFS spectra were measured at points of interests (POI) selected from the micro As-SXRF map (Figure S5a). There is a factor of three in count rate between the richest (spot 6) and the least (spot 8) As-rich point (Figure S5b). The four spectra have the same frequency and structure and they average out to the bulk spectrum (Figure S6). Thus, zoning reflects varying geochemical conditions during crystallization and does not appear to correlate with the chemical form of As.

Careful study of the As-pyrite spectra from Savage et al. (Clio-2 sample)³⁶ and Paktunc et al. (grain 218)³⁵, and the two Se-pyrite spectra from Matamoros-Veloza et al. (POI_{a,b})¹⁸ indicates a considerable degree of similarity with our spectra. Since the EXAFS spectra in the previous studies were fit with S atoms in the first shell (i.e., [AsS]₁ and [SeS]₁ pairs), this infers that As and Se are also bonded to S in our samples. Although this consistency check shows good agreement among different studies in the first anionic shell analysis of As and Se, discrepancies exist in the analysis of the second anionic shell. Savage et al.³⁶ and Paktunc³⁵ concluded that As is clustered forming [AsAs]₂ pairs,

whereas Matamoros-Veloza et al. (POIa,b)¹⁸ observed [SeS]₂ pairs only. How can two EXAFS spectra that look similar (i.e., As-pyrite and Se-pyrite) lead to distinct results? We show below that the As- and Se-EXAFS spectra have two least-squares minima in the parameter space.

To obtain robust structural solutions, care was taken to not overparametrize the model-fits. The limit of the number of free parameters in EXAFS fits can be calculated by the Nyquist formula $N = (2\Delta R\Delta k)/\pi$. Nine parameters were adjusted (Table 2), for a number of degrees of freedom in the refinements of $N = [(2 \times (16.0 - 2.7 \text{ \AA}^{-1}) \times (3.6 - 1.4 \text{ \AA}))]/\pi = 18.6$ for As-pyrite and $N = [(2 \times (13.8 - 3.4 \text{ \AA}^{-1}) \times (3.6 - 1.4 \text{ \AA}))]/\pi = 14.6$ for Se-pyrite. Figures 6 and 7 show that the As- and Se-EXAFS spectra can be fit indifferently with a dilute (model 1) and a cluster (model 2) model. In model 1, As and Se are surrounded by 5.9-6.5 S₂ at 3.08-3.09 Å and 5.5-6.1 S₂ at 3.33 Å, and in model 2 by 6.3-6.6 S₂ at 3.15-3.16 Å and 4.4-5.7 As₂/Se₂ at 3.16 Å. The metric parameters of the S₁, Fe₁, and Fe₂ shells around As and Se are practically identical in the two models (Table 2). Also included in Figures 6 and 7 are the residual of each fit, which indicates the portion of the spectra unfit by the structural model; the lower the residual, the better the fit. The overlay plots of the fit residuals for each model are identical, therefore the two models are equivalent. Consideration of As or Se in the first shell (i.e., As₂²⁻ or Se₂²⁻ dianions) resulted in the fit residual being more than doubled (model 3 in Figures 6 and 7). The As-S₁ distance is 2.27 Å and the Se-S₁ distance is 2.24 Å, compared to the S-S₁ distance of 2.16 Å in pyrite (Table 2). The differences in bond length match the difference of atomic size between S (1.03 Å), As (1.20 Å), and Se (1.16 Å).

In pyrite, the S₂ shell is split into two sub-shells at 3.08 Å and 3.33 Å. In model 1, the two S₂ distances remain unchanged relative to pyrite while the S₁, Fe₁ and Fe₂ distances are relaxed as a result of the As and Se for S substitution. In model 2, the S₁, Fe₁, S₂, and Fe₂ distances are relaxed and an As₂/Se₂ shell at 3.16 Å is detected at the same distance as the S₂ shell. This local structure is not unrealistic because the As distances to smaller S₂ atoms are not shorter on average than the As distances to bigger As₂ atoms in arsenopyrite (FeAsS).⁵⁵ Note that EXAFS does not preclude longer As-As and Se-Se distances at about 3.4 Å from existing, but it does not have the sensitivity to detect them. We conclude that the dilute and cluster models are equiprobable from the standpoint of EXAFS analysis. Since EXAFS cannot answer if As and Se are segregated at the local scale, this possibility is examined next by quantum chemical computations.

Equilibrium segregation of As and Se in pyrite. Twelve unique cases of As incorporation schemes and eight unique cases of Se incorporation schemes were tested in total (Figures 8 and S7).

Their total and relative energies with respect to the least favorable configuration are given in Table 3, with the lattice parameters being reported in Table S20 and Cartesian coordinates in the SI. Formation of As_2^{2-} and Se_2^{2-} dianions (i.e., $[\text{AsAs}]_1$ and $[\text{SeSe}]_1$ pairs) is energetically unfavorable by more than 35 meV/cell (6 kcal/mol, models 2Se-2, 3Se-2, 2As-2, 3As-2). The As-As avoidance in the first S shell had been predicted by Blanchard et al.³⁹ using DFT. Our results show that this theoretical prediction holds for the $[\text{SeSe}]_1$ pair. The equilibrium segregation of As and Se in the second S shell was examined by substituting two As/Se atoms for sulfur in a $2 \times 2 \times 2$ supercell ($\text{Fe}_{32}(\text{As/Se})_2\text{S}_{62}$), and three As/Se atoms for sulfur in a $3 \times 2 \times 2$ supercell ($\text{Fe}_{48}(\text{As/Se})_3\text{S}_{93}$). The two models have an (As/Se)/S atomic ratio of 0.03, an As concentration of 3.8 wt.%, and a Se concentration of 4.0 wt.%. The FeS_6 octahedra have six short S-S edges of 3.08 Å in length and six long S-S edges of 3.32 Å in length (Figure 1a).² Distribution of the As/Se atoms on the long and short edges was varied to examine the energetic preference for clustering on either edge dimension (Figure 8). The main results of this broad evaluation of energy structures are the following:

- As tends to cluster in the second S shell, but not Se, regardless of the number and position of the $[\text{SeSe}]_2$ pairs on octahedral edges.
- A cluster of 3 As atoms is energetically more favorable than a cluster of 2 As atoms (e.g., models 3As-3 and 3As-5).
- A cluster of 3 As atoms grouped on the same octahedral face, forming an $[\text{As}]_3$ triad as in arsenopyrite (Figure 1b), is energetically more favorable than a cluster of 3 As atoms distributed over two octahedral faces (e.g., models 3As-5 and 3As-7).
- Energies of the 3As models show a monotonic trend in function of the dimension of the S-S edge. Larger energy changes (i.e., higher stability) occur for models in which As atoms are distributed on both short and long S-S edges (e.g., models 3As-4, 3As-5, and 3As-6, and models 3As-7 and 3As-8).
- The As-As distances in the second lowest energy structure (model 3As-7) are 3.07 Å, 3.15 Å, and 3.33 Å, close in value to the arsenopyrite $[\text{As}]_3$ triad distances of 3.04 Å, 3.19 Å, and 3.34 Å.⁵⁵ Model 3As-7 differs by 6 meV/cell from the lowest energy model 3As-8.

Generation of the local order of As in arsenopyrite engenders confidence in the calculations. Also, the fact that the $[\text{As}]_3$ arrangement was not found for Se is consistent with the lack of selenious compound structurally analog to arsenopyrite (i.e., FeSeS). Our results also disallow the coexistence of $[\text{SeSe}]_1$ and $[\text{SeSe}]_2$ pairs, and of $[\text{SeSe}]_1$ and $[\text{SeS}]_2$ pairs, in pyrite. $[\text{SeSe}]_1$ and $[\text{SeSe}]_2$ pairs occur in the pyrite isomorph dzharkenite (cubic FeSe_2), and therefore can be expected to be energetically

favorable in selenious pyrite. Our results simply suggest that cubic FeS_2 and FeSe_2 are not miscible at the atomic scale. This finding may explain why the two compounds do not form a complete solid-solution at the macroscopic scale,⁴¹ the two structures being in this case intergrown at the microscopic scale.

The absence of $[\text{SeSe}]_1 + [\text{SeS}]_2$ pairs in our models conflicts with the results of Ryser and co-workers,¹⁷ who observed their co-existence in a pyrite grain using EXAFS (POI g spectrum). On the basis of our results, if Se occurs in the first S shell, then it should also occur in the second S shell to form an FeSe_2 local structure. The FeSe_2 hypothesis can be dismissed because the POI g spectrum differs from that of dzharkenite. Therefore, the alternative consists of hypothesizing that S atoms, not Se, are present in the first shell. This ambivalence was tested by reanalyzing the $\text{Se}_1 + \text{Fe}_1$ contribution to EXAFS for POI g . Results reproduced in Figure S8 show that the model-fit of Ryser and co-workers¹⁷ is overparametrized, thus the mathematical solution non-unique. When physically meaningful structural constraints are enforced to suppress correlations between parameters, S atoms give a better fit to data than Se atoms. This is in line with Matamoros-Veloza et al.,¹⁸ who fit their pyrite data with a $[\text{SeS}]_1$ pair. We conclude that there is a generally good agreement between theoretical predictions and experiments for Se. Se atoms do not cluster in pyrite at the investigated Se/S ratio ≤ 0.03 (4.0 wt.%), and are predicted to demix as cubic FeSe_2 if they do at a higher molar ratio.

In contrast to Se, the lowest energy structures are those in which As occurs in pairs and triads. Formation of an $[\text{As}]_3$ triad in a $3 \times 2 \times 2$ supercell allows an energy gain of 41-47 meV/cell or 5-6 meV per sulfur atom (models 3As-7 and 3As-8). The energy change will be lower, the larger the supercell. Therefore, an $[\text{As}]_3$ triad is energetically less likely to form at $\text{As/S} \leq 0.03$ ($[\text{As}] \leq 3.8$ wt.%), as in the pyrite samples studied by Paktunc³⁵ ($\text{As/S} = 0.015$, $[\text{As}] = 1.6$ wt.%), Savage³⁶ ($\text{As/Fe} = 0.010$; $[\text{As}] = 1.2$ wt.%), and here ($0.001 \leq \text{As/S} \leq 0.01$; 0.15 wt.% $\leq [\text{As}] \leq 1.14$ wt.%). Arsenic clusters may also form a metastable solid-solution at the nanometer scale precipitated far from thermodynamic equilibrium. Compositional growth zones in pyrite crystals are in fact metastable, and arsenic may very well be inhomogeneously distributed from the micrometer down to the nanometer scale.

The tendency of As to form arsenopyrite-type clusters provides general insights into the dissolution of arsenian pyrite in acid mine drainage. Bioleaching of pyrite and arsenopyrite flotation concentrate shows that arsenopyrite is the first mineral phase to be oxidized, pyrite dissolution starting at a later stage.⁶⁶ Further, energetics calculation predicts that As for S substitution promotes the

dissolution of pyrite.³⁹ Therefore, the presence of arsenopyrite-type clusters should enhance pyrite dissolution even further with the environmental implications that ensue.

In conclusion, this study highlights a previously unknown limitation of EXAFS spectroscopy for the study of As and Se in sulfide minerals, which warrants the utmost caution in drawing fine structural distinctions. We showed that SeSe^{2-} dianionic pairs are unlikely to exist unless Se is clustered as FeSe_2 nanoinclusions in the FeS_2 framework. In this case, $[\text{SeSe}]_1$ pairs coexist with $[\text{SeSe}]_2$ pairs and Fe is bonded to six Se atoms. Arsenic clusters are thermodynamically easier to form than Se clusters, because of the existence of the FeAsS phase. In this case, the lowest energy bonding environment resembles the local structure of FeAsS , in which Fe is bonded to three As atoms on one octahedral face and to three S atoms on the other octahedral face.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Materials and methods, supplementary tables and figures, EXAFS spectra (PDF)

Cartesian coordinates of the DFT models (XLS)

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Notes

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FIGURE CAPTIONS

Figure 1. Polyhedral structure and bonding environment of sulfur in pyrite (a) and arsenopyrite (b). Pyrite has a cubic structure consisting of corner-sharing FeS₆ octahedra.² Arsenopyrite has a monoclinic structure consisting of single chains of edge-sharing Fe(As₃S₃) octahedra cross-linked by sharing corners.⁵⁵ In pyrite, sulfur is bonded to one S atom at 2.16 Å (S₂²⁻ dianion) and to three Fe atoms at 2.26 Å ([SFe]₁ pair). The second sulfur shell ([SS]₂ pair) is split in two subshells at 3.08 Å

(short edges in orange) and 3.32 Å (long edges in green). In arsenopyrite, the As atoms form [As]₃ triads on octahedral faces.

Figure 2. Backscattered electron images of pyrite from Bolivia (a), Utah (b), Spain (c), Germany (d), and Switzerland (e), and distributions of As and Se in pyrite Ut, Sp, Ger, and Sw measured by EPMA. The red rectangles indicate the location in the grains of the SXRF maps. Map size: 300 × 80 pixels; pixel size: 2 × 2 μm²; probe diameter: 2 μm; dwell time 500 ms; electron voltage = 20 kV, current = 500 nA. The pyrite from Bolivia is zoned. The brighter zones in pyrite Sp are chalcopyrite (CuFeS₂) inclusions.

Figure 3. As (a) and Se (b) HR-XANES spectra of pyrite. As (c) and Se (d) HR-XANES of reference compounds.

Figure 4. Experimental (a-c) and calculated (d-f) HR-XANES spectra of pyrite measured at the As (a,d) and Se (b,c,e,f) K-edge.

Figure 5. EXAFS spectra of pyrite measured at the As and Se K-edge (a), and pyrite and arsenopyrite measured at the As K-edge (b).

Figure 6. As K-edge EXAFS spectra (a-c) and Fourier transform magnitudes (f-h) of pyrite with model-fits. (d,e) Overlay plots of the fit residuals for models 1 and 2 (d) and models 1 and 3. The peak positions of the Fourier transforms are not corrected for phase shift, and consequently are shifted by $\Delta R \sim -0.3$ to -0.4 Å relative to structural R distances. Res is the fit residual as the goodness-of-fit parameter: $Res = [\sum \{|\chi_{exp} - \chi_{fit}|\} / \sum \{|\chi_{exp}|\}] \times 100$.

Figure 7. Se K-edge EXAFS spectra (a-c) and Fourier transform magnitudes (f-h) of pyrite with model-fits. (d,e) Overlay plots of the fit residuals for models 1 and 2 (d) and models 1 and 3.

Figure 8. Bonding environment of As in the Fe₃₂As₂S₆₂ (a) and Fe₄₈As₃S₉₃ (b) equilibrium structures. The S-S edges in yellow are 3.08 Å long and the S-S edges in green are 3.32 Å long in unsubstituted pyrite (Figure 1a). The red line connects the dianionic pair. Distances are in angstrom.

Table 1. List of samples, and As and Se point and bulk concentrations measured by EPMA and ICP-ES/MS

| Code name | Origin | Geological setting | [As] EPMA | [As] ICP-ES | [Se] EPMA | [Se] ICP-MS |
|-----------|--|--------------------------|---|-----------------|----------------------------|-------------|
| Bol | Bolivia, MNHN ^a collection, Paris | Hydrothermal vein | 0.15-1.14 wt.% | na ^b | b.d.l. – 70 ppm | na |
| Sw | St Gotthard tunnel, Switzerland | Hydrothermal vein | b.d.l. ^c - 60 ppm (<i>n</i> =5) | na | b.d.l. ^d | na |
| Ut | Park City, Utah, USA | Hydrothermal: epithermal | 50-160 ppm (<i>n</i> =3) | 250 ppm | 318-428 ppm (<i>n</i> =3) | 500 ppm |
| Sp | Alzo, Gipuzkoa, Spain | Sedimentary | b.d.l. ^c - 30 ppm (<i>n</i> =2) | na | b.d.l. | na |
| Ger | Neumark, Saxony, Germany | Sedimentary - skarn | na | 1590 ppm | na | 80 ppm |

^aMuseum National d'Histoire Naturelle; ^bNot analyzed; ^cBelow detection limit (23 ppm); ^dBelow detection limit (34 ppm).

Table 2. EXAFS parameters and interatomic distances in pyrite relative to a central S atom

| Pyrite ^a | | | As Pyrite Bol – Model 1 | | | | As Pyrite Bol – Model 2 | | | | Se Pyrite Ut – Model 1 | | | | Se Pyrite Ut – Model 2 | | | |
|---------------------|-----------------|---------------------------|--------------------------------------|------------------|--------------|-----------------------------|----------------------------------|------------------|--------------|---------------------------|----------------------------------|------------------|--------------|---------------------------|----------------------------------|------------------|--------------|---------------------------|
| Atom | CN ^b | <i>R</i> , Å ^c | Atom | CN | <i>R</i> , Å | σ^d , Å ² | Atom | CN | <i>R</i> , Å | σ , Å ² | Atom | CN | <i>R</i> , Å | σ , Å ² | Atom | CN | <i>R</i> , Å | σ , Å ² |
| S | 1 | 2.16 | S | 1 ^e | 2.27 | 0.0031 ^f | S | 1 ^e | 2.27 | 0.0031 ^f | S | 1 ^e | 2.24 | 0.0024 ^f | S | 1 ^e | 2.24 | 0.0024 ^f |
| Fe | 3 | 2.26 | Fe | 3 ^e | 2.33 | 0.0031 ^f | Fe | 3 ^e | 2.33 | 0.0031 ^f | Fe | 3 ^e | 2.32 | 0.0024 ^f | Fe | 3 ^e | 2.32 | 0.0024 ^f |
| S | 6 | 3.08 | S | 5.9 ^g | 3.08 | 0.0056 ^f | S | 6.3 ^g | 3.16 | 0.0058 ^f | S | 6.5 ^g | 3.09 | 0.0040 ^f | S | 6.6 ^g | 3.15 | 0.0038 ^f |
| S | 6 | 3.32 | S | 6.1 ^g | 3.33 | 0.0056 ^f | As | 5.7 ^g | 3.16 | 0.0058 ^f | S | 5.5 ^g | 3.33 | 0.0040 ^f | Se | 4.4 ^g | 3.16 | 0.0038 ^f |
| Fe | 3 | 3.45 | Fe | 3 ^e | 3.52 | 0.0056 ^f | Fe | 3 ^e | 3.52 | 0.0058 ^f | Fe | 3 ^e | 3.52 | 0.0040 ^f | Fe | 3 ^e | 3.52 | 0.0038 ^f |
| | | | $\Delta E^h = 7.0$ eV, $Res^i = 3.1$ | | | | $\Delta E = 7.2$ eV, $Res = 3.4$ | | | | $\Delta E = 5.7$ eV, $Res = 3.8$ | | | | $\Delta E = 5.3$ eV, $Res = 4.4$ | | | |

^aAfter Rieder et al. ²; ^bCoordination number; ^cInteratomic distance; ^dDebye-Waller factor; ^eFixed value; ^fParameters constrained identical; ^gSum fixed to twelve; ^hShift of energy threshold; ⁱFit residual. $Res = [\sum\{|\chi_{exp} - \chi_{fit}|\} / \sum\{|\chi_{exp}|\}] \times 100$.

Table 3. Difference of energy between the dilute and the cluster models for the $\text{FeSe}_x\text{S}_{2-x}$ and $\text{FeAs}_x\text{S}_{2-x}$ supercells^a

| Model | Supercell dimension | Number of Se/As atoms | [Se/As] weight % | Description | kcal/mol | eV/cell |
|-------|---------------------|-----------------------|------------------|--|----------|---------|
| 2Se-1 | 222 | 2 | 4.0 | Two Se atoms at long distance | 0.00 | 0.000 |
| 2Se-2 | 222 | 2 | 4.0 | One [SeSe]1 pair | -6.52 | -0.035 |
| 2Se-3 | 222 | 2 | 4.0 | One [SeSe]2 pair on long edge | 0.01 | 0.000 |
| 2Se-4 | 222 | 2 | 4.0 | One [SeSe]2 pair on short edge | -0.19 | -0.001 |
| 3Se-1 | 322 | 3 | 4.0 | Three Se atoms at long distance | 0.00 | 0.000 |
| 3Se-2 | 322 | 3 | 4.0 | One [SeSe]1 pair + one [SeSe]2 pair on short edge | -6.75 | -0.024 |
| 3Se-3 | 322 | 3 | 4.0 | Three [SeSe]2 pairs on a face with three long edges | -0.04 | 0.000 |
| 3Se-4 | 322 | 3 | 4.0 | Three [SeSe]2 pairs on a face with two short and one long edge | -0.43 | -0.002 |
| 2As-1 | 222 | 2 | 3.8 | Two As atoms at long distance | 0.00 | 0.000 |
| 2As-2 | 222 | 2 | 3.8 | One [AsAs]1 pair | -21.25 | -0.115 |
| 2As-3 | 222 | 2 | 3.8 | One [AsAs]2 pair on long edge | 4.73 | 0.026 |
| 2As-4 | 222 | 2 | 3.8 | One [AsAs]2 pair on short edge | 4.54 | 0.025 |
| 3As-1 | 322 | 3 | 3.8 | Three As atoms at long distance | 0.00 | 0.000 |
| 3As-2 | 322 | 3 | 3.8 | One [AsAs]1 pair + one [AsAs]2 pair on short edge | -8.84 | -0.032 |
| 3As-3 | 322 | 3 | 3.8 | One isolated As + one [AsAs]2 pair on long edge | 5.65 | 0.020 |
| 3As-4 | 322 | 3 | 3.8 | Two [AsAs]2 pairs on short edges | 6.64 | 0.024 |
| 3As-5 | 322 | 3 | 3.8 | Two [AsAs]2 pairs on long edges | 7.90 | 0.029 |
| 3As-6 | 322 | 3 | 3.8 | Two [AsAs]2 pairs, one on short and another on long edge | 8.84 | 0.032 |
| 3As-7 | 322 | 3 | 3.8 | Three [AsAs]2 pairs on a face with three long edges | 11.48 | 0.041 |
| 3As-8 | 322 | 3 | 3.8 | Three [AsAs]2 pairs on a face with two short and one long edge | 12.92 | 0.047 |

^aA negative difference of $E(\text{dilute}) - E(\text{cluster})$ is unfavorable.

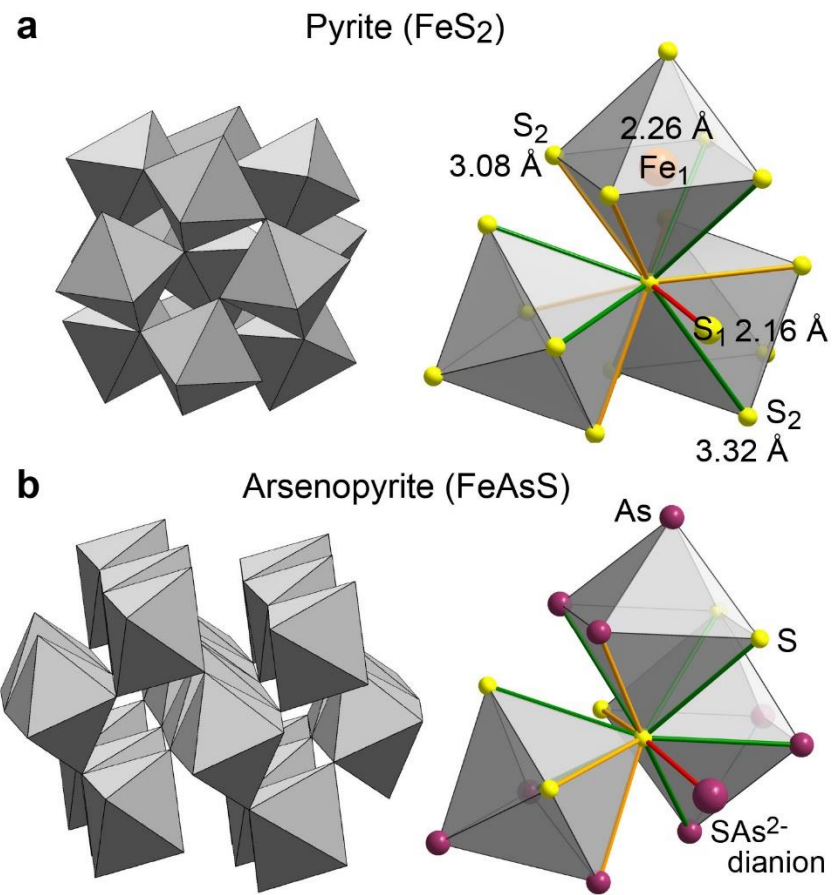


Figure 1

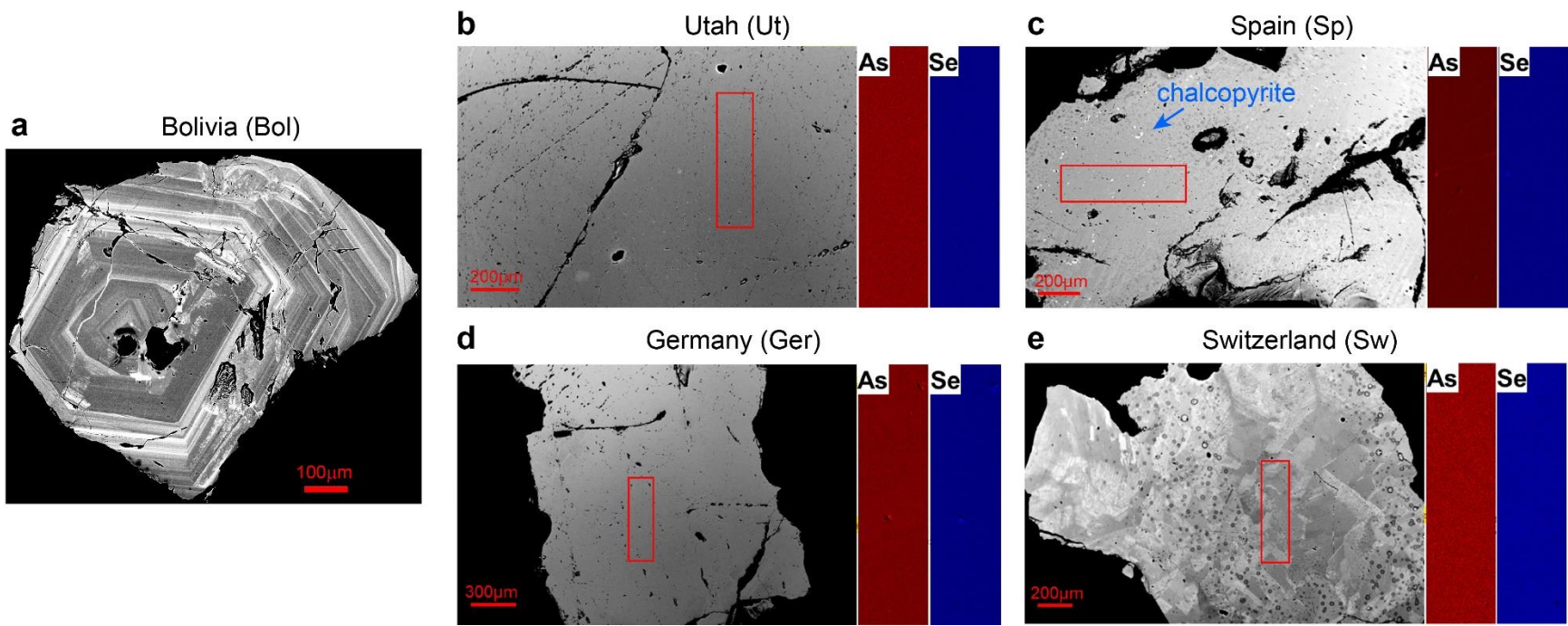


Figure 2

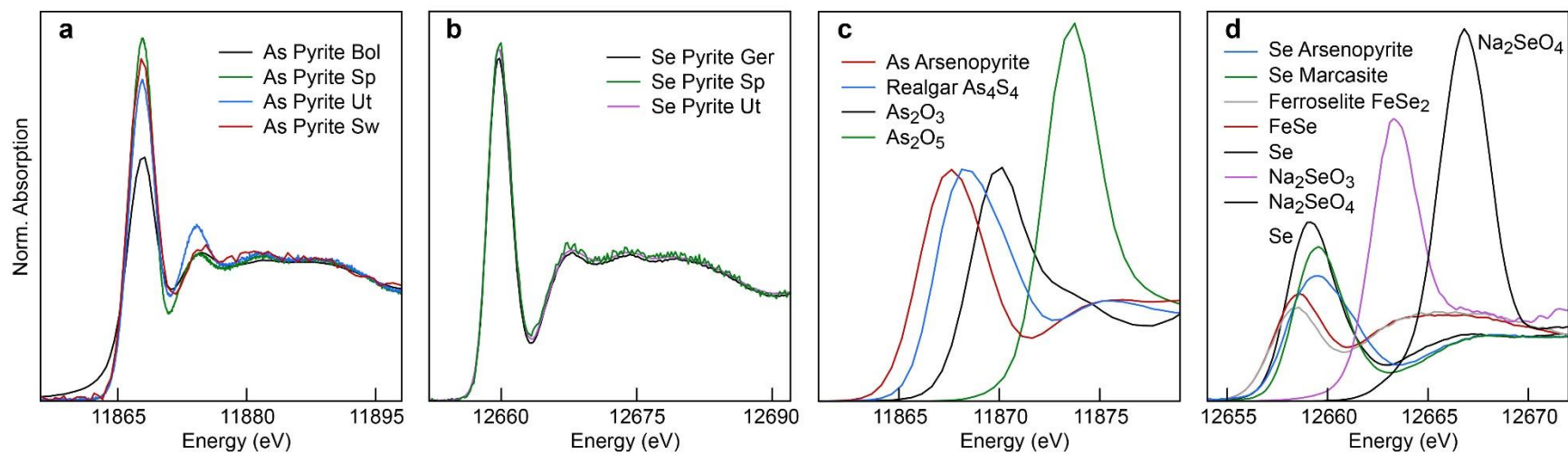


Figure 3

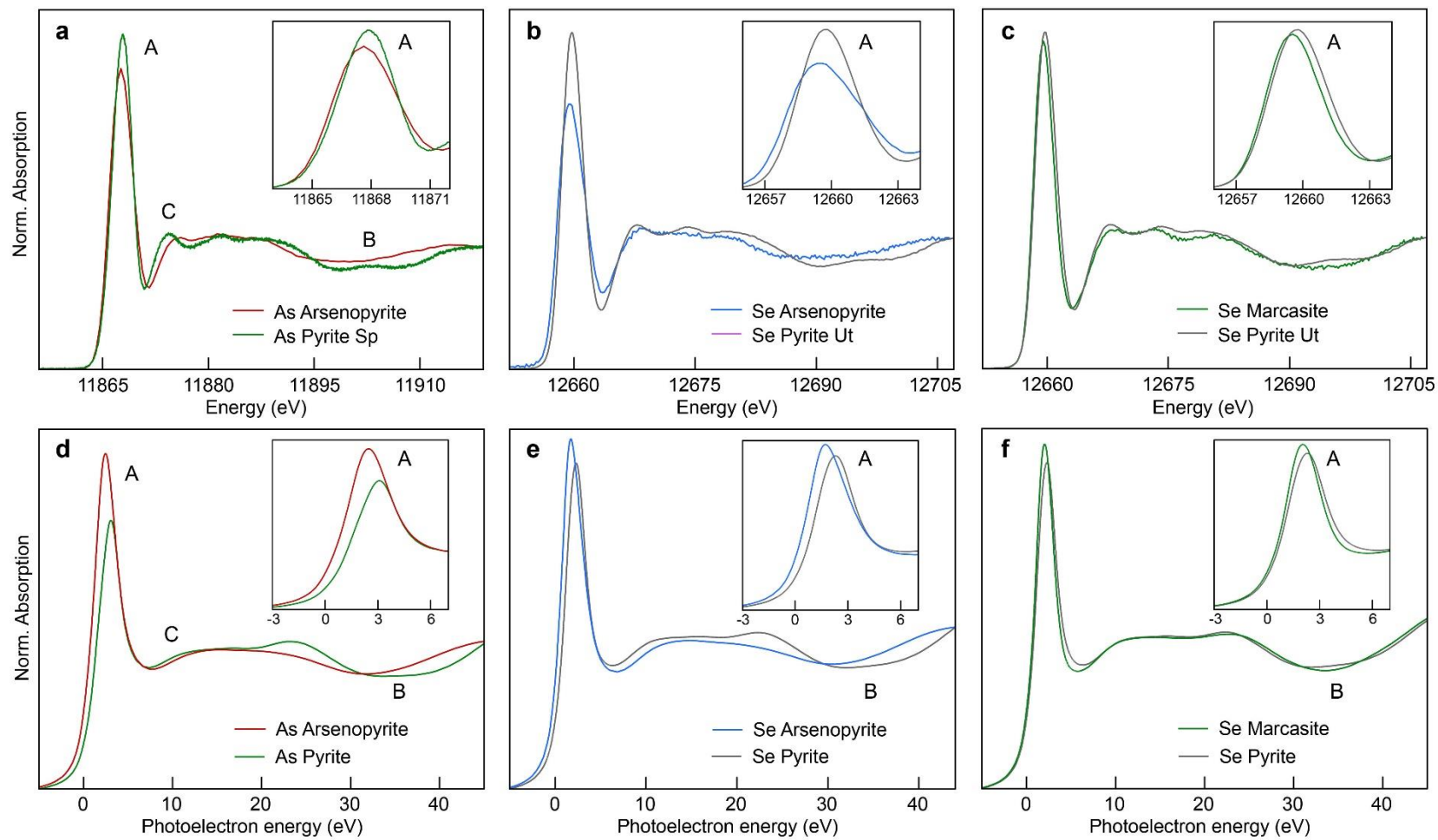


Figure 4

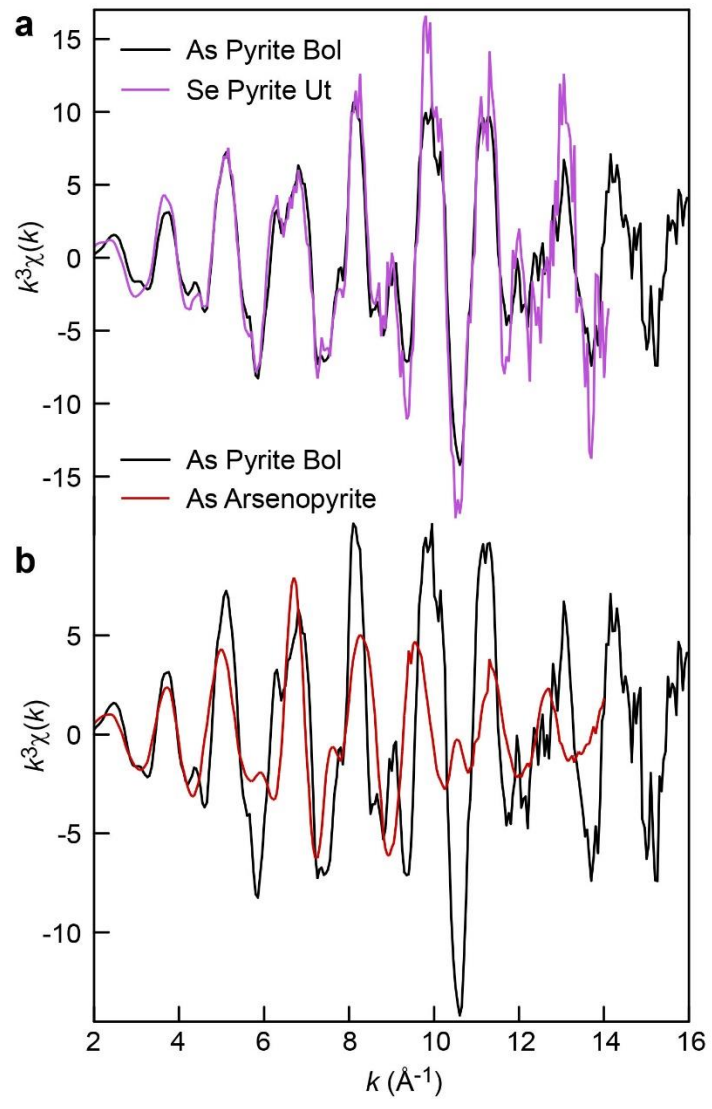


Figure 5

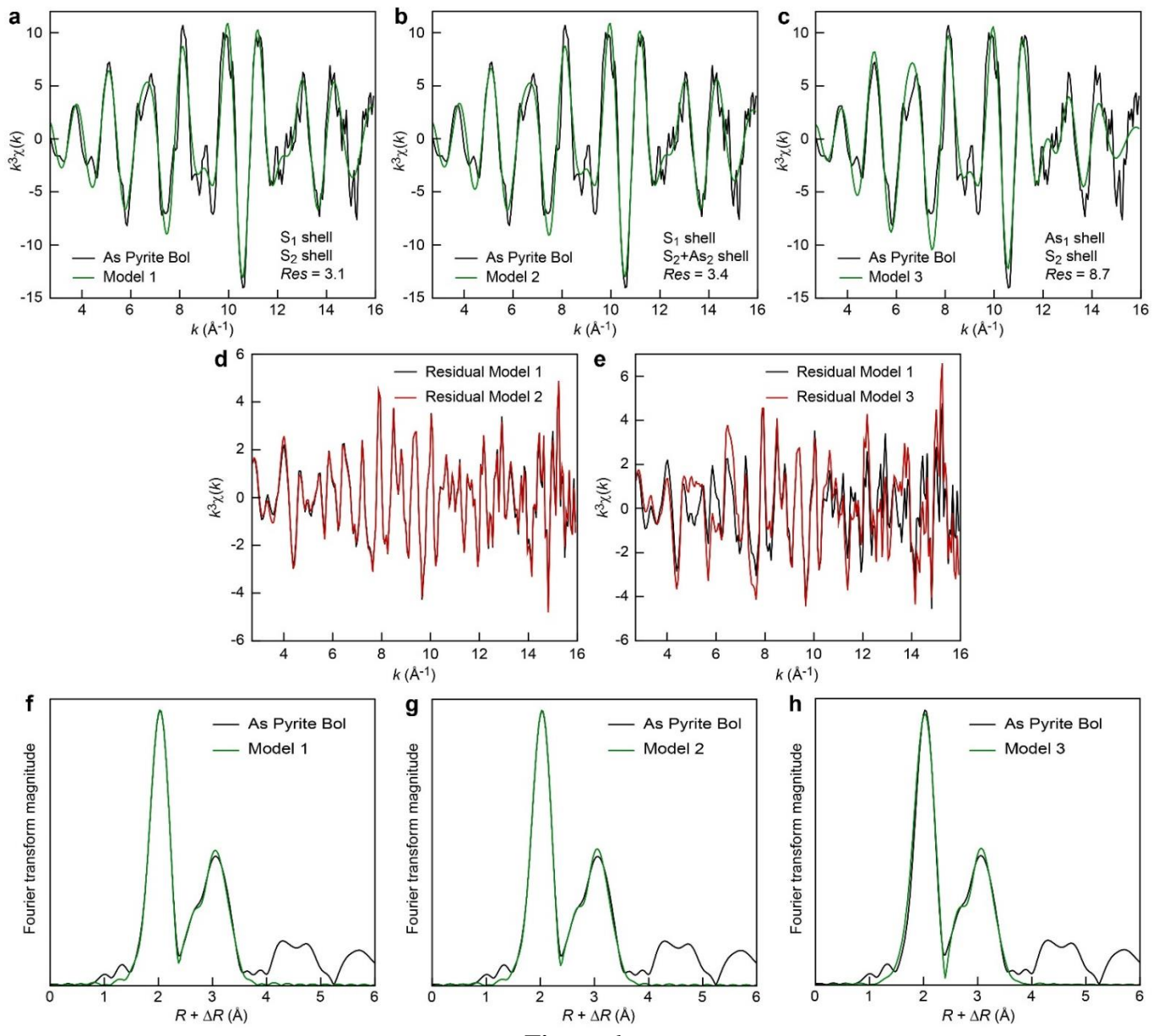


Figure 6

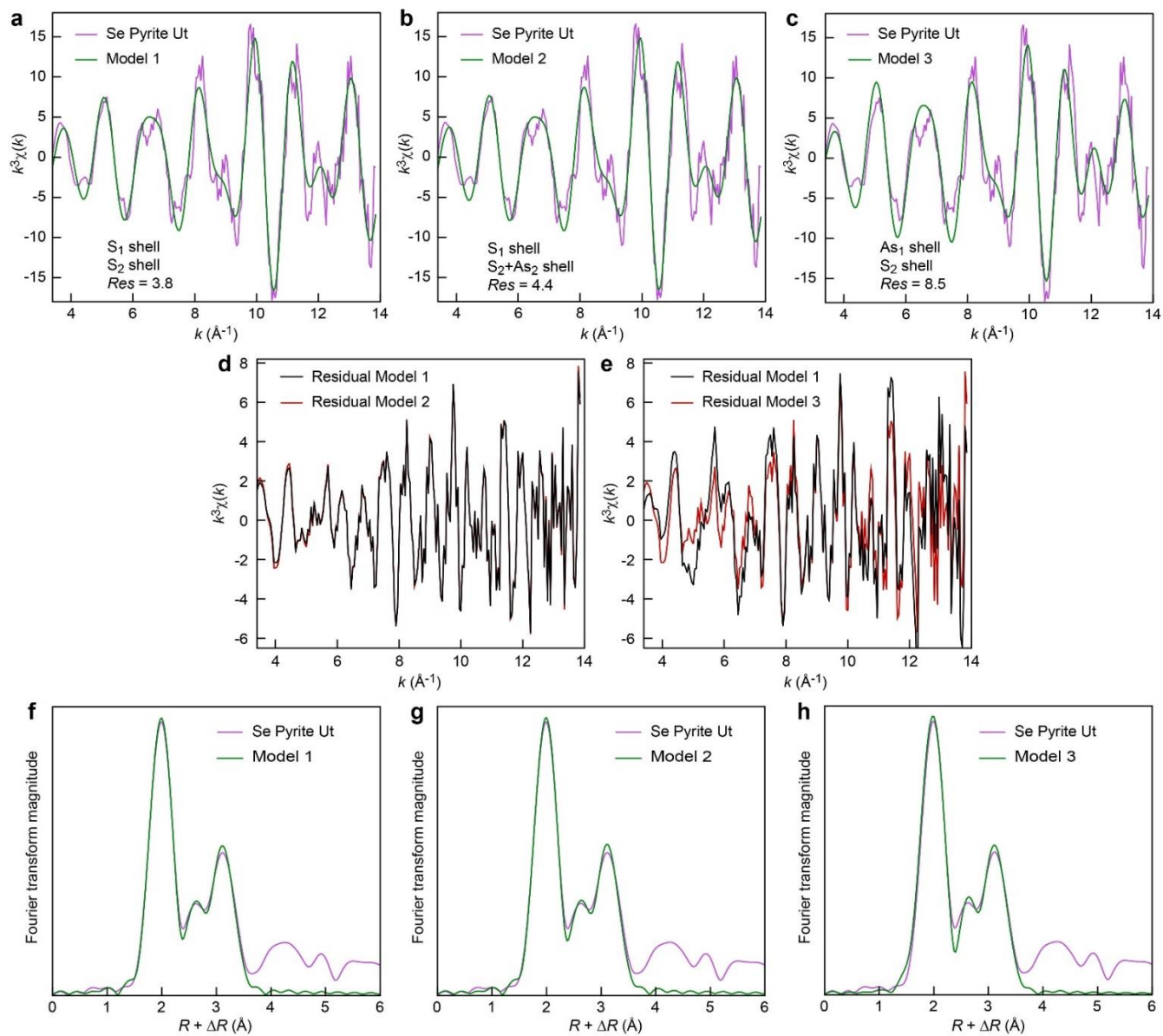


Figure 7

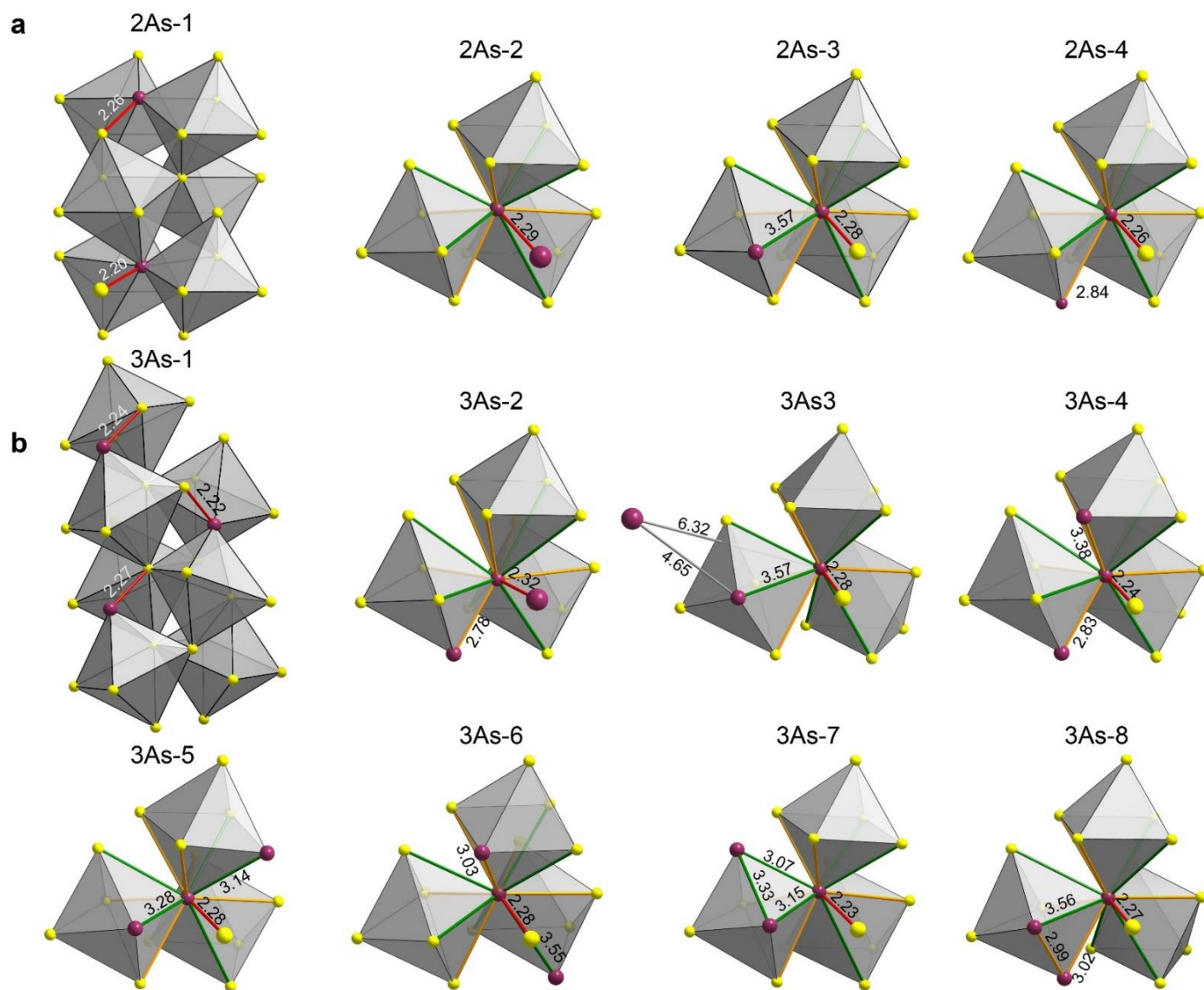


Figure 8

Supplementary information for the article

The mode of incorporation of As(-I) and Se(-I) in natural pyrite revisited

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1. Materials and methods

1.1. Sample preparation

Fragments of pyrite crystals were embedded in epoxy resin and polished for EPMA, SXRF mapping, and micro EXAFS measurement. Other fragments were crushed in an agate mortar inside a glove bag filled with He to prevent oxidation. Powder was stored in a desiccator and pressed into 5-mm diameter pellets for bulk HR-XANES and EXAFS measurements.

1.2. XRD

The X-ray powder diffraction patterns for the five pyrite samples were measured at ISTERre (Grenoble, France) in reflection geometry using a BrukerD8 diffractometer equipped with a selective energy SolXEM (Baltics Instruments) detector. Electron voltage and current were 40 kV and 40 mA. Intensity from the diffracted Cu K α_1 line was measured from 5 to 90° 2 θ with a step size of 0.03° and a dwell time of 6 s per step. The XRD traces are shown in Figure S2a. No mineral impurity was detected.

Arsenic and selenium references were mounted in a glass capillary of 1 mm diameter and characterized in transmission geometry with a Göbel optics. The dwell time was 6 s per step of 0.024°. The XRD traces are shown in Figures S2b and S2c. No mineral impurity was detected.

1.3. ICP-ES/MS

The concentrations of As and Se in bulk pyrite from Utah (Ut) and Germany (Ger) were measured by ICP-ES and ICP-MS, respectively, at Bureau Veritas (Canada). Analytical code AQ270 (ICP-ES/MS with digestion in aqua-regia) was used. Certified standard references and blanks were measured in the same conditions as pyrite. Results are given in Table 1. The percent error is 5% for As and 9% for Se.

1.4. EPMA

Backscattered electron (BSE) images, EPMA and elemental maps of pyrite were recorded with a JEOL JXA-8230 electron microprobe at ISTerre. As, Se, and Au were analyzed with a wavelength-dispersive spectrometer (WDS), and S and Fe with an energy-dispersive spectrometer (EDS). Operating conditions were 20 kV accelerating voltage and 900 nA beam current with a focused beam of 1-3 μm in diameter. The following certified natural and synthetic materials were used for standardization: As: InAs and FeAsS; Se: Se and Bi₂Se₃; Au: Au; Fe: CuFeS₂ and FeS₂; and S: CuFeS₂. The lowest and the highest As and Se contents are reported in Table 1. Elemental maps were acquired for As, Se, Au, Fe, and S (Figures S3 and S4a). Details on analytical precisions and determination of detection limits can be found in Batanova et al.¹

1.5. Bulk HR-XANES

The As and Se K-edge HR-XANES spectra were collected on beamline ID26 of the ESRF. The storage ring was operated in the 7/8 + 1 filling mode, with 200 mA current. Rejection of higher harmonics and reduction of heat load were achieved with a white beam Pd-coated, flat mirror working under total reflection at 2.5 mrad deflecting angle. The energy of the incoming beam was selected with the 111 reflection of a Si double crystal monochromator, and the beam was focused horizontally by a second Pd-coated mirror and vertically by a third Pd-coated mirror. The flux on the sample was approximately 10¹³ photon/s in a beam footprint of ~700 (H) × 80 (V) μm^2 FWHM. The As K α_1 fluorescence line was selected using the 555 reflection of five spherically bent (1 m radius) Si analyzer crystals (diameter = 100 mm) aligned at 69.85° Bragg angle in a vertical Rowland geometry. The Se K α_1 fluorescence line was selected using the Si(844) reflection at a Bragg angle of 85.17°. The diffracted intensity was measured with an avalanche photodiode (APD). The effective energy resolution was 2.3 eV.

Spectra were measured at 10-15 K using a helium flow cryostat. Fifty scans of 20 s were acquired for the As and Se references and from 60 to 90 scans of 30 s for pyrite. The samples were moved horizontally and vertically after every scan to access unexposed material. No changes in spectral features were noted during the course of data collection that would indicate oxidation of pyrite or other radiation damage. Spectra were averaged with the PyMCA software² and reduced with the Labview suite of programs from beamline 10.3.2 at the Advanced Light Source (Berkeley, USA).^{3, 4} They were normalized to a unit step in the absorption coefficient at 11939 eV for As and at 12707 eV for Se.

1.6. Bulk and micro EXAFS

Bulk As and Se K-edge and micro As K-edge EXAFS spectra were collected at room temperature on beamline BM23 of the ESRF. The incoming beam was monochromated with a Si(111) double

crystal monochromator. The footprint on the sample of the unfocused beam was ~ 2.8 (H) \times 0.5 (V) mm^2 FWHM. For micro EXAFS measurements, the monochromatic X-ray beam was focused to $5 \times 5 \mu\text{m}^2$ with a set of Pt-coated Kirkpatrick–Baez (KB) mirrors.⁵ The flux incident on the sample was approximately 5×10^9 photons/sec. Micro EXAFS data were taken on points of interests chosen on a SXRF map measured at 14 keV, 5 μm step size, and 2 s/point measuring time (Figures S5 and S6). No beam damage was observed. EXAFS data were reduced with the Athena software⁶ and fit with WinXAS.⁷ Theoretical amplitude and phase shift functions were generated with FEFF7⁸ using the arsenopyrite structure⁹ for As and Se-substituted arsenopyrite for Se. The amplitude reduction factor (S_0^2) was fixed to 0.9. Fit results are given in Table 2.

1.7. Density Functional Theory (DFT)

Calculations were considered being converged when the total energy obtained in the self-consistent field (SCF) procedure differed by less than 10^{-7} a.u. (E_h) in two successive cycles (0.0027 meV). Default thresholds were used for the geometry optimizations. The two-electron integral tolerance setting 7 7 7 9 30 (TOLINTEG keyword) was preferred because of the recommendation of combined hybrid functionals and pseudopotentials.¹⁰ Other settings were tested to verify that the SCF convergence was well achieved (Table S15, 6 6 6 6 12 is default). The shrinking factor IS also was tested (Tables S16 and S17). A factor of 6 was sufficient to converge the total energy with a precision of 10^{-7} a.u. The ANDERSON's method¹¹ and a FMIXING of 90% were used to accelerate the convergence. No symmetry restriction was applied during geometry optimization.

Basis sets and their abbreviations in Tables are:

Sulfur

Lichanot: all-electron split-valence 6-311G¹²

TZVP: triple-zeta valence with polarization¹³

Durand: effective Durand pseudopotential¹⁴

Iron

Towler: all-electron split-valence 6-411d41G basis set¹⁵

TZVP: Triple-zeta valence with polarization¹³

ECP Heifets: effective core pseudopotential^{16, 17}

Durand: effective Durand pseudopotential¹⁴

Arsenic

pp Heyd: effective core pseudopotential, m-pVDZ double zeta quality with polarization functions¹⁰

TZVP: Triple-zeta valence with polarization¹³

Durand: effective Durand pseudopotential¹⁴

HWLC, val Durand: Hay-Wadt large-core pseudopotential¹⁸ with valence electrons from Durand¹⁴

HWLC, val TZVP: Hay-Wadt large-core pseudopotential¹⁸ with valence electrons from TZVP

HWLC, val Heyd: Hay-Wadt large-core pseudopotential¹⁸ with valence electrons from pp_Heyd¹⁰

Selenium

pp Heyd: effective core pseudopotential, m-pVDZ double zeta quality with polarization functions¹⁰

TZVP: Triple-zeta valence with polarization¹³

2. Supplementary tables

Table S1. Comparison between experimental and calculated ionization energies for S. Energy is in kcal/mol.

| | | S ¹⁺ | | S ²⁺ | | S ¹⁻ | | S ²⁻ | |
|----------------------|---------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|
| | | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % |
| Experiment | | 238.28 | - | 536.82 | - | -4761 | - | 165.37 | - |
| Basis set Functional | | | | | | | | | |
| Lichanot | PBEsol0 | 277.13 | 16.31 | 508.01 | -5.37 | -74.78 | 57.07 | 102.03 | -38.30 |
| | PW1PW | 276.48 | 16.03 | 509.90 | -5.01 | -71.74 | 50.69 | 106.84 | -35.40 |
| TZVP | PBEsol0 | 273.63 | 14.84 | 506.37 | -5.67 | -64.60 | 35.68 | 123.28 | -25.45 |
| | PW1PW | 273.76 | 14.89 | 509.07 | -5.17 | -62.14 | 30.51 | 127.87 | -22.68 |
| Durand | PBEsol0 | 286.43 | 20.21 | 516.36 | -3.81 | -78.51 | 64.90 | 114.44 | -30.80 |
| | PW1PW | 285.57 | 19.85 | 518.62 | -3.39 | -75.24 | 58.04 | 119.40 | -27.80 |

Table S2. Comparison between experimental and calculated ionization energies for Fe. Energy is in kcal/mol.

| | | Fe ¹⁺ | | Fe ²⁺ | | Fe ³⁺ | |
|----------------------|---------|------------------|------------------|------------------|------------------|------------------|------------------|
| | | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % |
| Experiment | | 181.76 | - | 372.58 | - | 704.97 | - |
| Basis set Functional | | | | | | | |
| Towler | PBEsol0 | 98.08 | -46.03 | 425.68 | 14.25 | 796.65 | 13.00 |
| | PW1PW | 92.65 | -49.03 | 422.34 | 13.35 | 796.34 | 12.96 |
| TZVP | PBEsol0 | - | - | 431.68 | 15.86 | 791.09 | 12.22 |
| | PW1PW | - | - | 428.67 | 15.05 | 790.75 | 12.17 |
| ECP_Heifets | PBEsol0 | 124.94 | -31.26 | 435.25 | 16.82 | 798.44 | 13.26 |
| | PW1PW | - | - | 432.36 | 16.05 | 798.60 | 13.28 |
| Durand | PBEsol0 | 59.11 | -67.48 | 424.65 | 13.98 | 830.09 | 17.75 |
| | PW1PW | 56.93 | -68.68 | 425.49 | 14.20 | 835.08 | 18.46 |

Table S3. Comparison between experimental and calculated ionization energies for As. Energy is in kcal/mol.

| | | As ¹⁺ | | As ²⁺ | | As ³⁺ | | As ⁴⁺ | | As ⁵⁺ | | As ¹⁻ | |
|---------------------|------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % |
| Experiment | | 225.14 | - | 427.55 | - | 652.03 | - | 1153.45 | - | 1443.71 | - | -18.58 | - |
| Basis set | Functional | | | | | | | | | | | | |
| pp_Heyd | PBEsol0 | 202.00 | -10.28 | 396.91 | -7.17 | 608.25 | -6.71 | 1164.90 | 0.99 | 1415.94 | -1.92 | -21.34 | 14.86 |
| | PW1PW | 202.20 | -10.19 | 399.56 | -6.55 | 613.82 | -5.86 | 1164.67 | 0.97 | 1426.68 | -1.18 | -19.77 | 6.39 |
| TZVP | PBEsol0 | 206.33 | -8.35 | 396.73 | -7.21 | 606.42 | -6.99 | 1147.54 | -0.51 | 1393.32 | -3.49 | -32.01 | 72.26 |
| | PW1PW | 206.45 | -8.30 | 399.51 | -6.56 | 611.98 | -6.14 | 1147.32 | -0.53 | 1404.77 | -2.70 | -30.51 | 64.16 |
| Durand | PBEsol0 | 222.98 | -0.96 | 426.41 | -0.26 | 643.15 | -1.36 | 1096.45 | -4.94 | - | - | -32.09 | 72.65 |
| | PW1PW | 224.98 | -0.07 | 431.10 | 0.83 | 650.70 | -0.20 | 1096.98 | -4.90 | - | - | -31.81 | 71.19 |
| HWLC, val Heyd | PBEsol0 | 222.05 | -1.37 | 384.76 | -10.01 | 542.72 | -16.76 | 1070.10 | -7.23 | - | - | -57.74 | 210.72 |
| | PW1PW | 223.62 | -0.67 | 387.34 | -9.40 | 546.53 | -16.18 | 1070.81 | -7.16 | - | - | -58.07 | 212.48 |
| HWLC, val TZVP | PBEsol0 | 62.89 | -72.07 | 393.71 | -7.91 | 602.00 | -7.67 | 1119.48 | -2.95 | - | - | -168.58 | 807.18 |
| | PW1PW | 204.90 | -8.99 | 398.43 | -6.81 | 609.28 | -6.56 | 1120.05 | -2.90 | - | - | -27.69 | 48.99 |
| HWLC, val Durand | PBEsol0 | 222.88 | -1.00 | 424.60 | -0.69 | 639.18 | -1.97 | 1092.61 | -5.27 | - | - | -33.09 | 78.04 |
| | PW1PW | 224.85 | -0.13 | 429.19 | 0.38 | 646.61 | -0.83 | 1093.05 | -5.24 | - | - | -32.84 | 64.16 |

Table S4. Comparison between experimental and calculated ionization energies for Se. Energy is in kcal/mol.

| | | Se ¹⁺ | | Se ²⁺ | | Se ³⁺ | | Se ⁴⁺ | | Se ⁵⁺ | | Se ⁶⁺ | | Se ¹⁻ | |
|------------|------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % | Energy | Difference, % |
| Experiment | | 224.25 | - | 487.51 | - | 729.03 | - | 987.78 | - | 1570.90 | - | 1882.09 | - | -46.57 | |
| Basis set | Functional | | | | | | | | | | | | | | |
| pp_Heyd | PBEsol0 | 255.19 | 13.80 | 462.56 | -5.12 | 690.10 | -5.34 | 935.06 | -5.34 | 1575.63 | 0.30 | 1851.21 | -1.64 | -65.50 | 40.64 |
| | PW1PW | 253.65 | 13.11 | 463.47 | -4.93 | 693.75 | -4.84 | 941.59 | -4.68 | 1575.70 | 0.31 | 1863.50 | -0.99 | -61.97 | 33.07 |
| TZVP | PBEsol0 | 265.31 | 18.31 | 468.62 | -3.87 | 697.47 | -4.33 | 947.97 | -4.03 | 1527.69 | -2.75 | 1776.41 | -5.62 | -82.82 | 77.84 |
| | PW1PW | 263.52 | 17.51 | 469.96 | -3.60 | 701.78 | -3.74 | 954.54 | -3.36 | 1527.76 | -2.75 | 1788.87 | -4.95 | -79.34 | 70.37 |

Table S5. Results of basis set and functionals testing for pyrite single cell. First two combinations were chosen for As-pyrite and Se-pyrite calculations, respectively.

| Pyrite FeS ₂ | | | |
|----------------------------------|------------------|---------------------------|----------------|
| Basis sets | Functional | Lattice parameter a , Å | Difference, % |
| Experiment (Rieder et al., 2007) | | 5.416 | - |
| S: Lichanot Fe: ECP_Heifets | PW1PW | 5.518 | 1.89 |
| S: Lichanot Fe: TZVP | PW1PW | 5.471 | 1.01 |
| S: Lichanot Fe: Towler | PBEsol0 PW1PW | 5.418 5.480 | 0.06 1.17 |
| S: TZVP Fe: Towler | PBEsol0 PW1PW | 5.330 5.393 | -1.58 -0.42 |
| S: TZVP Fe: TZVP | PBEsol0 PW1PW | 5.340 5.402 | -1.40 -0.27 |
| S: TZVP Fe: ECP_Heifets | PBEsol0 PW1PW | 5.363 5.437 | -0.97 0.38 |
| S: Durand Fe: Durand | PBEsol0 PW1PW | 5.674 5.767 | 4.76 6.47 |

Table S6. Results of basis set and functionals testing for arsenopyrite single cell.

| Arsenopyrite FeAsS | | | | | | | | | |
|--------------------------|------------|---------|--------------------|---------|------------------|---------|----------------------|------------------|------|
| Basis sets | Functional | a , Å | Lattice parameters | | | | angle β , ° | Difference, % | |
| | | | Difference, % | b , Å | Difference, % | c , Å | | | |
| Experiment (Bindi, 2012) | | 5.761 | - | 5.684 | - | 5.767 | - | 111.721 | - |
| S: lichenot | PBEsol0 | 5.642 | -2.07 | 5.646 | -0.67 | 5.667 | -1.73 | 112.434 | 0.64 |
| As: pp_Heyd | PW1PW | 5.714 | -0.82 | 5.717 | 0.58 | 5.737 | -0.53 | 112.308 | 0.53 |
| Fe: ECP_Heifets | | | | | | | | | |
| S: lichenot | PBEsol0 | 5.637 | -2.15 | 5.637 | -0.84 | 5.660 | -1.86 | 112.590 | 0.78 |
| As: TZVP | PW1PW | 5.706 | -0.96 | 5.703 | 0.34 | 5.726 | -0.72 | 112.421 | 0.63 |
| Fe: ECP_Heifets | | | | | | | | | |
| S: lichenot | PBEsol0 | 5.618 | -2.48 | 5.610 | -1.31 | 5.635 | -2.30 | 112.595 | 0.78 |
| As: TZVP | PW1PW | 5.683 | -1.36 | 5.669 | -0.27 | 5.697 | -1.22 | 112.455 | 0.66 |
| Fe: Towler | | | | | | | | | |
| S: lichenot | PBEsol0 | 5.619 | -2.47 | 5.615 | -1.21 | 5.643 | -2.15 | 112.389 | 0.60 |
| As: pp_Heyd | PW1PW | 5.684 | -1.33 | 5.677 | -0.13 | 5.707 | -1.05 | 112.219 | 0.45 |
| Fe: Towler | | | | | | | | | |
| S: TZVP | PBEsol0 | 5.580 | -3.14 | 5.587 | -1.71 | 5.609 | -2.74 | 112.377 | 0.59 |
| As: TZVP | PW1PW | 5.643 | -2.05 | 5.644 | -0.70 | 5.674 | -1.62 | 112.215 | 0.44 |
| Fe: TZVP | | | | | | | | | |
| S: Durand | PBEsol0 | 5.743 | -0.31 | 5.808 | 2.17 | 5.734 | -0.57 | 114.650 | 2.62 |
| As: Durand | PW1PW | 5.912 | 2.62 | 6.003 | 5.62 | 5.951 | 3.18 | 116.137 | 3.95 |
| Fe: Durand | | | | | | | | | |
| S: Lichenot | PBEsol0 | 5.622 | -2.42 | 5.611 | -1.29 | 5.629 | -2.40 | 112.698 | 0.87 |
| As: HWLC, val Durand | PW1PW | 5.673 | -1.53 | 5.662 | -0.39 | 5.681 | -1.50 | 112.540 | 0.73 |
| Fe: Towler | | | | | | | | | |
| S: Lichenot | PBEsol0 | 5.632 | -2.24 | 5.627 | -1.00 | 5.651 | -2.02 | 112.595 | 0.78 |
| As: HWLC, val TZVP | PW1PW | 5.687 | -1.29 | 5.681 | -0.05 | 5.706 | -1.06 | 112.430 | 0.63 |
| Fe: Towler | | | | | | | | | |

Table S7. Results of basis set and functionals testing for dzharkenite single cell.

| Dzharkenite FeSe ₂ | | | |
|-------------------------------|------------|--------------------------------|---------------|
| Basis sets | Functional | Lattice parameter <i>a</i> , Å | Difference, % |
| Experiment (Mandarino, 1995) | | 5.783 | - |
| Se: pp_Heyd | PW1PW | 5.792 | 0.16 |
| Fe: TZVP | PBEsol0 | 5.721 | 1.12 |
| Se: pp_Heyd | PW1PW | 5.822 | 0.63 |
| Fe: ECP_Heifets | | | |
| Se: pp_Heyd | PBEsol0 | 5.705 | 1.40 |
| Fe: Towler | PW1PW | 5.774 | 0.21 |

Table S8. Optimized versus experimental lattice parameter and interatomic distances of pyrite. PW1PW functional, Lichanot basis set for S and ECP_Heifets basis set for Fe were applied for calculations.

| Parameter | Optimized structure | Rieder et al., 2007 | difference, % |
|--------------|---------------------|---------------------|---------------|
| <i>a</i> , Å | 5.518 | 5.416 | 1.89 |
| S-S, Å | 2.15 | 2.16 | -0.46 |
| Fe-S, Å | 2.31 | 2.26 | 2.21 |
| S-S, Å | 3.15 | 3.08 | 2.27 |
| S-S, Å | 3.38 | 3.32 | 1.81 |

Table S9. Optimized versus experimental lattice parameter and interatomic distances of pyrite. PW1PW functional, Lichanot basis set for S and TZVP basis set for Fe were applied for calculations.

| Parameter | Optimized structure | Rieder et al., 2007 | difference, % |
|--------------|---------------------|---------------------|---------------|
| <i>a</i> , Å | 5.471 | 5.416 | 1.02 |
| S-S, Å | 2.15 | 2.16 | -0.46 |
| Fe-S, Å | 2.29 | 2.26 | 1.33 |
| S-S, Å | 3.12 | 3.08 | 1.30 |
| S-S, Å | 3.35 | 3.32 | 0.90 |

Table S10. Optimized versus experimental lattice parameter and interatomic distances of marcasite. PW1PW functional, Lichanot basis set for S and ECP_Heifets basis set for Fe were applied for calculations.

| Parameter | Optimized structure | Rieder et al., 2007 | difference, % |
|--------------|---------------------|---------------------|---------------|
| <i>a</i> , Å | 4.508 | 4.446 | 1.39 |
| <i>b</i> , Å | 5.516 | 5.425 | 1.68 |
| <i>c</i> , Å | 3.443 | 3.386 | 1.68 |
| S-S, Å | 2.18 | 2.21 | -1.36 |
| S-Fe, Å | 2.28 | 2.24 | 1.79 |
| | 2.30 | 2.25 | 2.22 |
| S-S, Å | 3.05 | 2.97 | 2.69 |
| | 3.19 | 3.12 | 2.24 |

| | | | |
|--|------|------|------|
| | 3.19 | 3.12 | 2.24 |
| | 3.19 | 3.12 | 2.24 |
| | 3.19 | 3.12 | 2.24 |
| | 3.29 | 3.23 | 1.86 |
| | 3.29 | 3.23 | 1.86 |
| | 3.29 | 3.23 | 1.86 |
| | 3.29 | 3.23 | 1.86 |
| | 3.44 | 3.39 | 1.47 |
| | 3.44 | 3.39 | 1.47 |

Table S11. Optimized versus experimental lattice parameter and interatomic distances of marcasite. PW1PW functional, Lichanot basis set for S and TZVP basis set for Fe were applied for calculations.

| Parameter | Optimized structure | Rieder et al., 2007 | difference, % |
|-----------|---------------------|---------------------|---------------|
| a , Å | 4.482 | 4.446 | 0.84 |
| b , Å | 5.484 | 5.425 | 1.09 |
| c , Å | 3.409 | 3.386 | 0.68 |
| S-S, Å | 2.18 | 2.21 | -1.36 |
| S-Fe, Å | 2.26 | 2.24 | 0.89 |
| | 2.28 | 2.25 | 1.33 |
| S-S, Å | 3.03 | 2.97 | 2.02 |
| | 3.16 | 3.12 | 1.28 |
| | 3.16 | 3.12 | 1.28 |
| | 3.16 | 3.12 | 1.28 |
| | 3.16 | 3.12 | 1.28 |
| | 3.26 | 3.23 | 0.93 |
| | 3.26 | 3.23 | 0.93 |
| | 3.26 | 3.23 | 0.93 |
| | 3.26 | 3.23 | 0.93 |
| | 3.41 | 3.39 | 0.59 |
| | 3.41 | 3.39 | 0.59 |

Table S12. Optimized versus experimental lattice parameter and interatomic distances of arsenopyrite. PW1PW functional, all-electron split-valence Lichanot basis set for S, pp_Heyd basis set for As and ECP_Heifets basis set for Fe were applied for calculations.

| Parameter | Optimized structure | Bindi, 2012 | difference, % |
|-------------------|---------------------|-------------|---------------|
| a , Å | 5.714 | 5.761 | -0.82 |
| b , Å | 5.717 | 5.684 | 0.58 |
| c , Å | 5.737 | 5.767 | -0.52 |
| angle β , ° | 112.31 | 111.72 | 0.53 |
| As-S, Å | 2.36 | 2.37 | -0.42 |
| As-Fe, Å | 2.38 | 2.37 | 0.42 |
| | 2.39 | 2.41 | -0.83 |
| | 2.40 | 2.41 | -0.41 |
| As-As, Å | 3.02 | 3.04 | -0.66 |

| | | | |
|---------|------|------|-------|
| | 3.18 | 3.19 | -0.31 |
| | 3.18 | 3.19 | -0.31 |
| | 3.35 | 3.35 | 0.00 |
| | 3.35 | 3.35 | 0.00 |
| As-S, Å | 3.05 | 3.06 | -0.33 |
| | 3.05 | 3.11 | -1.93 |
| | 3.30 | 3.32 | -0.60 |
| | 3.33 | 3.33 | 0.00 |
| | 3.35 | 3.33 | 0.60 |
| | 3.35 | 3.38 | -0.89 |

Table S13. Optimized versus experimental lattice parameter and interatomic distances of löllingite. PW1PW functional, pp_Heyd basis set for As and ECP_Heifets basis set for Fe were applied for calculations.

| Parameter | Optimized structure | Ondrus et al., 2001 | difference, % |
|--------------|---------------------|---------------------|---------------|
| <i>a</i> , Å | 5.224 | 5.268 | -0.84 |
| <i>b</i> , Å | 6.001 | 5.963 | 0.64 |
| <i>c</i> , Å | 2.86 | 2.9 | -1.38 |
| As-As, Å | 2.47 | 2.47 | 0.00 |
| As-Fe, Å | 2.35 | 2.41 | -2.49 |
| | 2.35 | 2.41 | -2.49 |
| | 2.38 | 2.37 | 0.42 |
| As-As, Å | 2.86 | 2.9 | -1.38 |
| | 2.86 | 2.9 | -1.38 |
| | 3.28 | 3.29 | -0.30 |
| | 3.28 | 3.29 | -0.30 |
| | 3.28 | 3.29 | -0.30 |
| | 3.28 | 3.29 | -0.30 |
| | 3.41 | 3.4 | 0.29 |
| | 3.41 | 3.4 | 0.29 |
| | 3.41 | 3.4 | 0.29 |
| | 3.41 | 3.4 | 0.29 |
| | 3.78 | 3.81 | -0.79 |
| | 3.78 | 3.81 | -0.79 |
| | 3.74 | 3.77 | -0.80 |

Table S14. Optimized versus experimental lattice parameter and interatomic distances of dzharkenite. PW1PW functional, pp_Heyd basis set for Se and TZVP basis set for Fe were applied for calculations.

| Parameter | Optimized structure | Mandarino, 1995 | difference, % |
|--------------|---------------------|-----------------|---------------|
| <i>a</i> , Å | 5.792 | 5.783 | 0.16 |
| Se-Se, Å | 2.40 | 2.28 | 5.03 |
| Fe-Se, Å | 2.41 | 2.42 | -0.31 |
| Se-Se, Å | 3.27 | 3.29 | -0.76 |
| Se-Se, Å | 3.55 | 3.55 | 0.0 |

Table S15. TOLINTEG parameter, total energy, cell parameter and volume in single unit cell of pyrite. Basis sets applied for calculations were: Lichanot for S, ECP_Heifets for Fe. PW1PW functional was used for all calculations.

| TOLINTEG | Total energy, Eh | Total energy, kcal/mol | a , Å | volume, cm ³ |
|-------------------------------------|------------------|------------------------|---------|-------------------------|
| Experiment (Rieder et al., 2007) | - | - | 5.416 | 158.87 |
| 6 6 6 6 12 | -3681.8115 | -2310371.6 | 5.5107 | 167.35 |
| 7 7 7 7 14 | -3681.8088 | -2310369.9 | 5.5183 | 168.04 |
| 7 7 7 9 30 | -3681.8114 | -2310371.5 | 5.5179 | 168.00 |
| 8 8 8 8 16 | -3681.8109 | -2310371.2 | 5.5194 | 168.14 |
| 9 9 9 9 18 | -3681.8122 | -2310372.1 | 5.5178 | 168.00 |
| 10 10 10 10 20 | -3681.8155 | -2310374.1 | 5.5174 | 167.95 |
| 11 11 11 11 22 | -3681.8149 | -2310373.7 | 5.5159 | 167.82 |

Table S16. Shrinking factors, k-point density and total energy in supercells 2 x 2 x 2 for pyrite (Fe₃₂S₆₄). Basis sets applied for calculations were: Lichanot for S, ECP_Heifets for Fe. PW1PW functional and TOLINTEG 777930 were applied.

| Shrinking factor | # k-points | Total energy, Eh | Total energy, kcal/mol | Energy difference, kcal/mol |
|------------------|------------|------------------|------------------------|-----------------------------|
| SHRINK 4 4 | 14 | -29454.49091433 | -18482972.10059 | - |
| SHRINK 6 6 | 40 | -29454.49091430 | -18482972.10057 | 0.00002 |
| SHRINK 8 8 | 90 | -29454.49091431 | -18482972.10058 | -0.00001 |
| SHRINK 10 10 | 172 | -29454.49091432 | -18482972.10059 | -0.00001 |
| SHRINK 12 12 | 294 | -29454.49091432 | -18482972.10058 | 0.00000 |
| SHRINK 14 14 | 464 | -29454.49091430 | -18482972.10057 | 0.00001 |
| SHRINK 16 16 | 690 | -29454.49091421 | -18482972.10051 | 0.00006 |
| SHRINK 18 18 | 980 | -29454.49091432 | -18482972.10059 | -0.00007 |

Table S17. Shrinking factors, k-point density and total energy in supercells 3 x 2 x 2 for pyrite (Fe₄₈S₉₆). Basis sets applied for calculations were: Lichanot for S, ECP_Heifets for Fe. PW1PW functional and TOLINTEG 777930 were applied.

| Shrinking factor | # k-points | Total energy, Eh | Total energy, kcal/mol | Energy difference, kcal/mol |
|------------------|------------|------------------|------------------------|-----------------------------|
| SHRINK 4 4 | 36 | -44181.73636383 | -27724458.146073 | - |
| SHRINK 6 6 | 112 | -44181.73636379 | -27724458.146049 | 0.000024 |
| SHRINK 8 8 | 260 | -44181.73636380 | -27724458.146052 | -0.000004 |
| SHRINK 10 10 | 504 | -44181.73636379 | -27724458.146049 | 0.000003 |
| SHRINK 12 12 | 868 | -44181.73636379 | -27724458.146051 | -0.000002 |
| SHRINK 14 14 | 1376 | -44181.73636379 | -27724458.146049 | 0.00000 |
| SHRINK 16 16 | 2052 | -44181.73636380 | -27724458.14605 | 0.00000 |
| SHRINK 18 18 | 2920 | -44181.73636380 | -27724458.14605 | 0.00000 |

Table S18. Se K-edge absorption energies in eV at the inflection point

| Compound | This study ^a | Ryser et al. (2005) | Matamoros-Veloza et al. (2014) ^b |
|----------------------------------|-------------------------|---------------------|---|
| Ferroselite (FeSe ₂) | 12657.2 | 12657.0 | 12656.3 |
| Achavelite (FeSe) | 12657.4 | | |
| Arsenopyrite (FeAsS:Se) | 12657.8 | | |
| Elemental Se (Se ⁰) | 12658.0 | 12658.0 | 12658.0 |
| Marcasite | 12658.2 | | |
| Pyrite | 12658.4 | | |
| Na ₂ SeO ₃ | 12662.2 | 12662.0 | 12662.3 |
| Na ₂ SeO ₄ | 12665.5 | 12664.0 | 12665.4 |

^aUncertainty 0.1 eV; ^bUncertainty 0.4 eV

Table S19. As K-edge absorption energies in eV

| Compound | Inflection point | White line energy |
|---|------------------|-------------------|
| Arsenopyrite (FeAsS) | 11865.9 | 11867.6 |
| Pyrite (FeS ₂) | 11866.2 | 11867.9 |
| Realgar (As ₄ S ₄) | 11866.8 | 11868.4 |
| As ₂ O ₃ | 11868.6 | 11870.0 |
| As ₂ O ₅ | 11872.3 | 11873.6 |

Table S20. Calculated lattice parameters

| Model | Supercell | <i>a</i> , Å | <i>b</i> , Å | <i>c</i> , Å | α , ° | β , ° | γ , ° |
|-------|-----------|--------------|--------------|--------------|--------------|-------------|--------------|
| 2Se-1 | 222 | 10.964 | 10.964 | 10.964 | 90.043 | 90.043 | 90.043 |
| 2Se-2 | 222 | 10.964 | 10.964 | 10.964 | 89.958 | 90.042 | 89.958 |
| 2Se-3 | 222 | 10.964 | 10.964 | 10.964 | 90.000 | 90.000 | 89.957 |
| 2Se-4 | 222 | 10.964 | 10.964 | 10.964 | 90.000 | 89.995 | 89.956 |
| 3Se-1 | 322 | 16.456 | 10.964 | 10.964 | 89.956 | 90.016 | 89.985 |
| 3Se-2 | 322 | 16.456 | 10.964 | 10.964 | 89.958 | 90.014 | 89.983 |
| 3Se-3 | 322 | 16.456 | 10.964 | 10.964 | 89.986 | 89.986 | 89.986 |
| 3Se-4 | 322 | 16.445 | 10.964 | 10.964 | 89.984 | 89.986 | 89.985 |
| 2As-1 | 222 | 11.070 | 11.042 | 11.062 | 89.986 | 89.941 | 90.125 |
| 2As-2 | 222 | 11.075 | 11.080 | 11.023 | 89.705 | 90.157 | 90.013 |
| 2As-3 | 222 | 11.056 | 11.060 | 11.060 | 90.034 | 90.086 | 90.061 |
| 2As-4 | 222 | 11.050 | 11.066 | 11.059 | 90.056 | 90.356 | 89.956 |
| 3As-1 | 322 | 16.589 | 11.052 | 11.064 | 89.962 | 89.989 | 90.017 |
| 3As-2 | 322 | 16.608 | 11.035 | 11.071 | 89.895 | 89.990 | 89.926 |
| 3As-3 | 322 | 16.583 | 11.056 | 11.061 | 90.036 | 90.077 | 89.982 |
| 3As-4 | 322 | 16.586 | 11.057 | 11.059 | 90.016 | 89.984 | 90.225 |
| 3As-5 | 322 | 16.585 | 11.063 | 11.056 | 89.943 | 90.029 | 90.072 |
| 3As-6 | 322 | 16.591 | 11.059 | 11.059 | 89.976 | 89.977 | 89.963 |

| | | | | | | | |
|-------|-----|--------|--------|--------|--------|--------|--------|
| 3As-7 | 322 | 16.580 | 11.065 | 11.055 | 89.899 | 89.847 | 89.931 |
| 3As-8 | 322 | 16.578 | 11.061 | 11.056 | 90.040 | 90.176 | 90.137 |

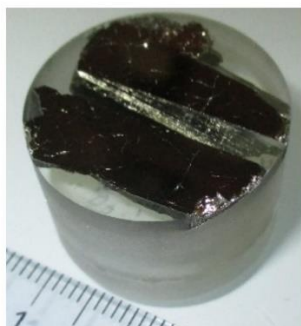
3. Supplementary figures



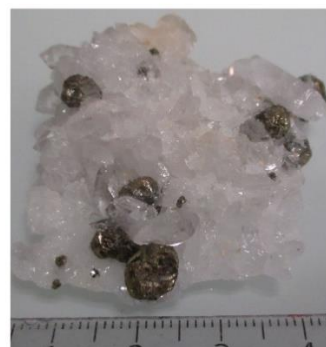
Bolivia (Bol)



Spain (Sp)



Utah (Ut)



Switzerland (Sw)



Germany (Ger)



Arsenopyrite



Ferroselite



Marcasite

Figure S1. Photographs of pyrite and three references: arsenopyrite (FeAsS), ferroselite (orthorhombic FeSe₂), and marcasite (orthorhombic FeS₂).

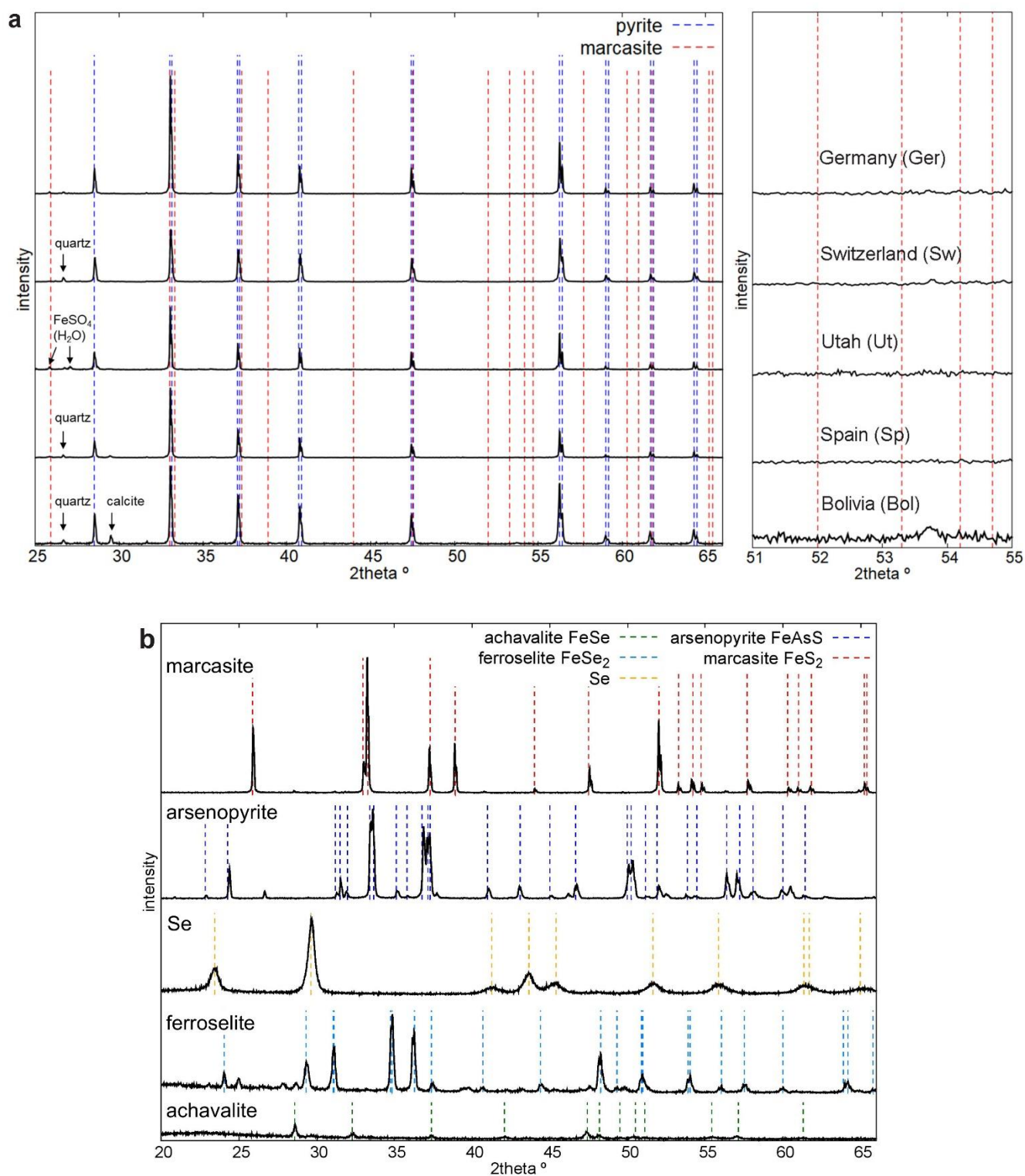
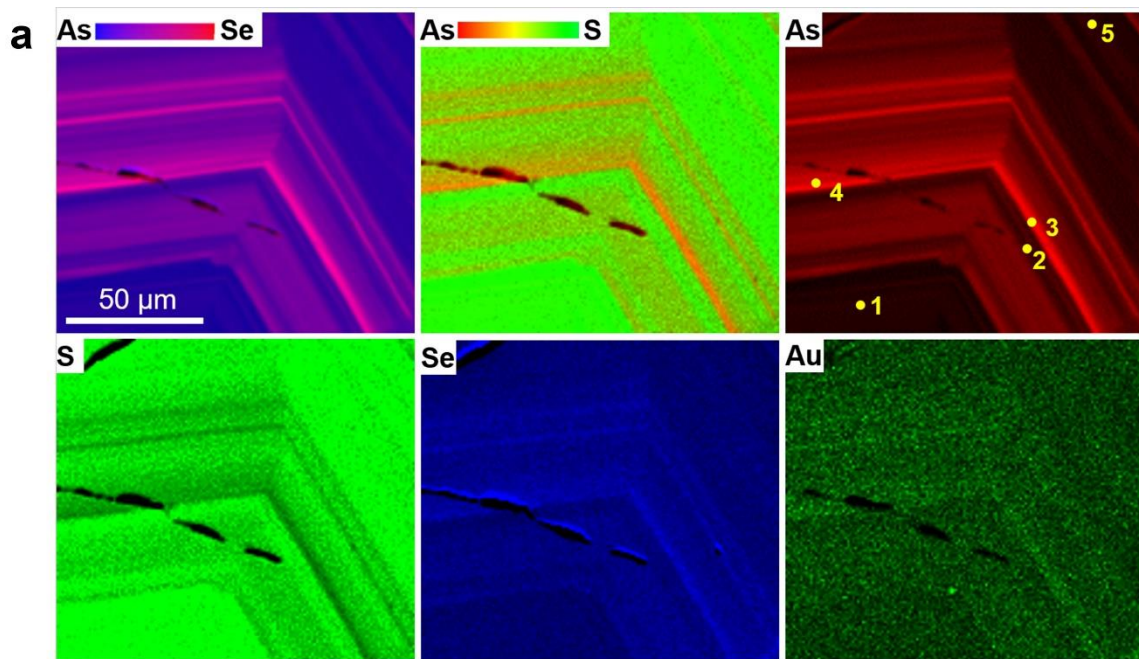


Figure S2. XRD patterns of pyrite (a) and references (b). Blue dashed lines in (a) indicate the reflections of pyrite (cubic FeS₂) and red dashed lines the reflections of marcasite (orthorhombic FeS₂). On the right is an enlargement of the angular region where the second most intense *hkl* reflection of marcasite (211)

occurs (52°) and which does not overlap with any reflection from pyrite. No marcasite impurity is detected in this diagnostic region.



b

| | Fe | S | As | Se | Ni | Cu | Zn | Au | Total |
|-----------------|-------|-------|--------|--------|--------|--------|--------|--------|--------|
| Detection limit | - | - | 0.0019 | 0.0014 | 0.0021 | 0.0021 | 0.0021 | 0.0047 | |
| spot 1 | 46.39 | 52.77 | 0.674 | 0.006 | b.d.l. | 0.073 | b.d.l. | 0.006 | 99.93 |
| spot 2 | 46.63 | 53.32 | 0.276 | 0.002 | b.d.l. | 0.013 | b.d.l. | b.d.l. | 100.24 |
| spot 3 | 46.45 | 52.79 | 1.072 | 0.007 | b.d.l. | 0.011 | b.d.l. | b.d.l. | 100.33 |
| spot 4 | 46.23 | 52.94 | 1.143 | 0.007 | b.d.l. | 0.081 | b.d.l. | b.d.l. | 100.41 |
| spot 5 | 46.60 | 53.32 | 0.404 | 0.004 | 0.001 | 0.031 | b.d.l. | b.d.l. | 100.36 |

Notes: b.d.l. – below detection limit.

Figure S3. (a) Two color and one color EPMA maps of the distribution of As, Se, S and Au in the zoned pyrite from Bolivia (Bol). Spots with numbers indicate the location of the EPMA analyses. Map size: 115 (V) x 135 (H) μm^2 ; pixel size: 1 x 1 μm^2 ; probe diameter: 1 μm ; dwell time 2 sec; electron voltage = 20 kV, current = 500 nA. (b) EPMA analyses (wt.%).

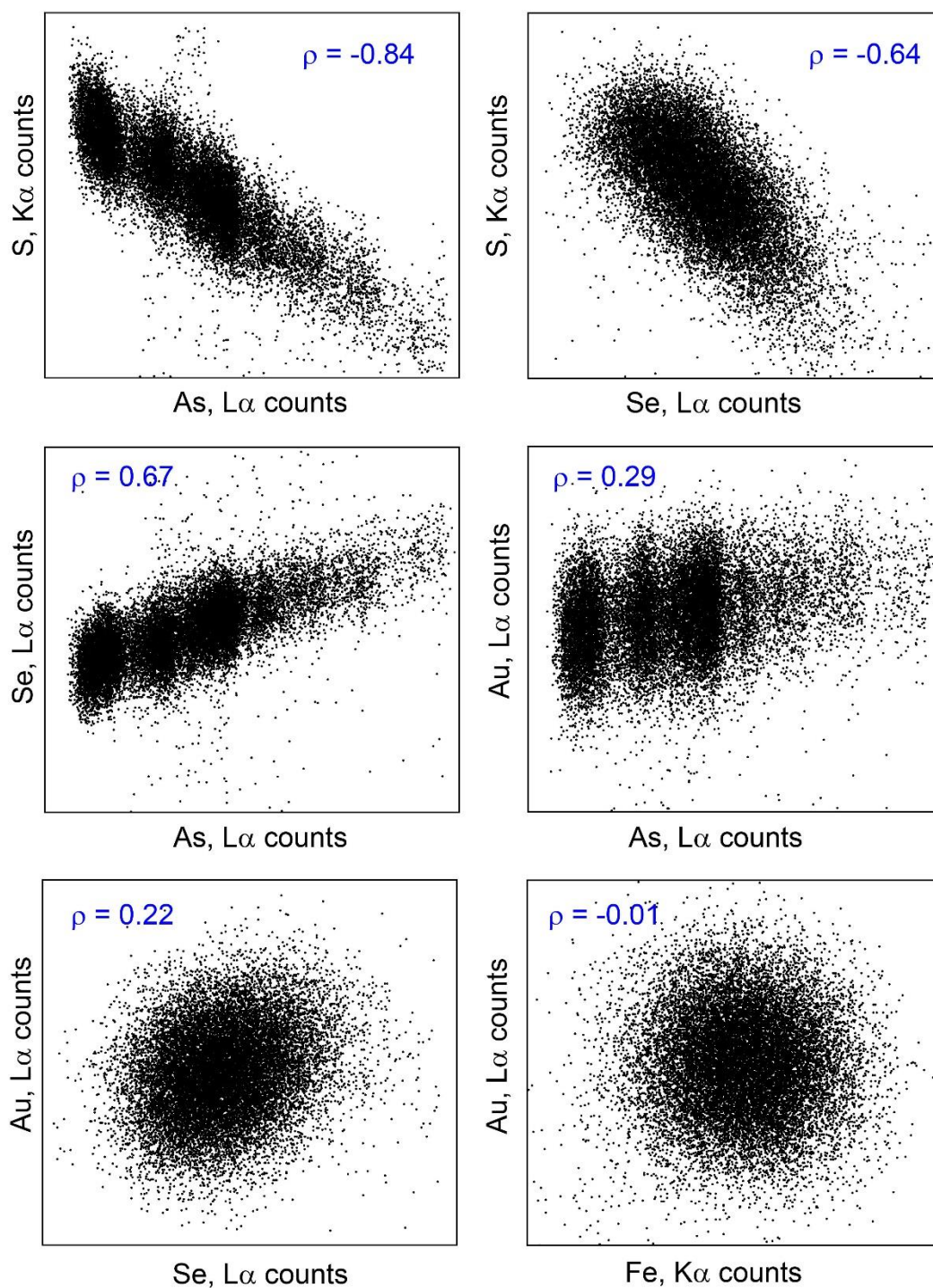


Figure S4. Scatter plots of S, Fe, As, Se, and Au fluorescence counts derived from the EPMA maps of Figure S3 and Pearson correlation coefficients ρ .

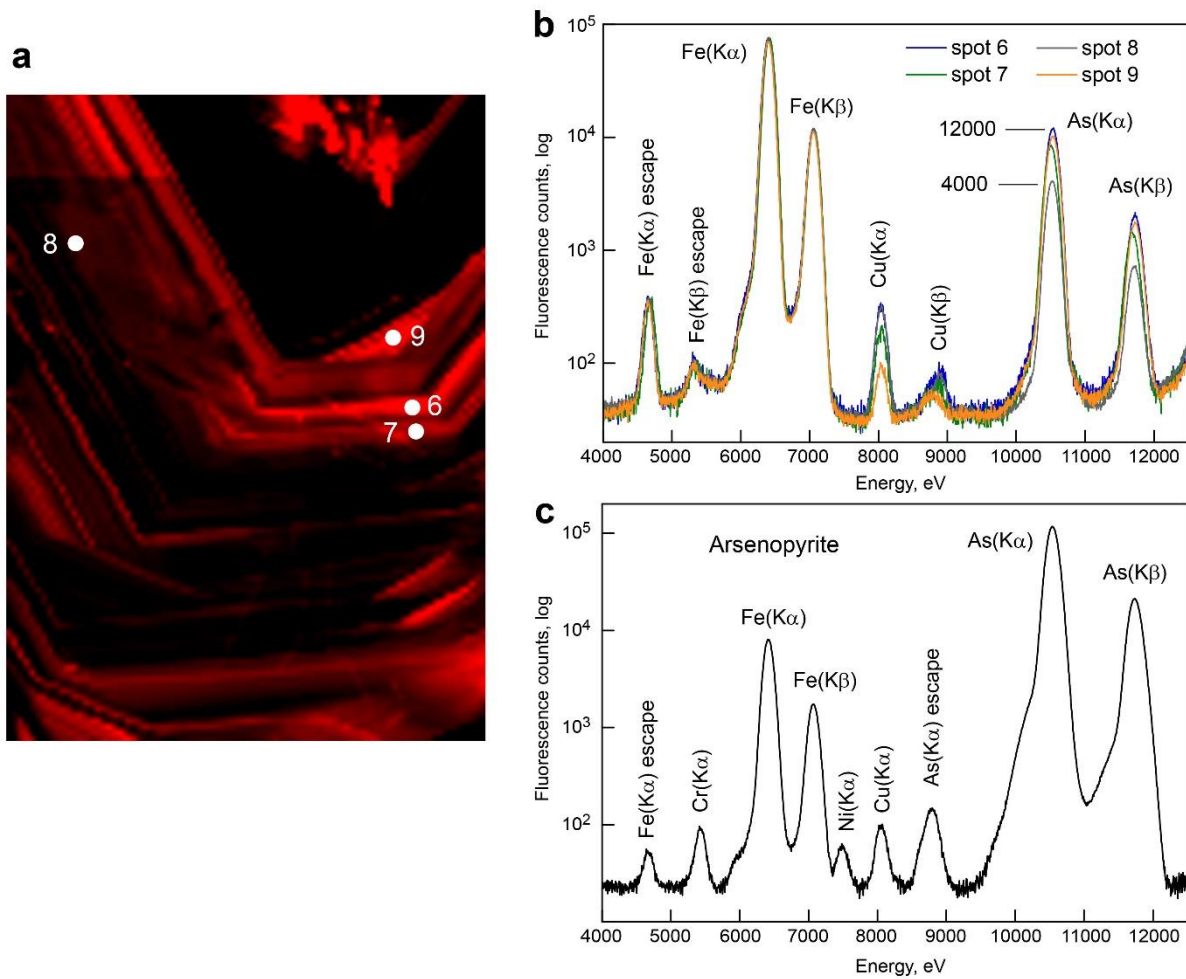


Figure S5. (a) SXRf map of the distribution of As in pyrite from Bolivia (Bol). Map size: 100 (V) x 60 (H) μm^2 . (b) Micro SXRf spectra from spots marked 6-9. (c) Bulk SXRf spectrum from arsenopyrite diluted in boron nitride (BN).

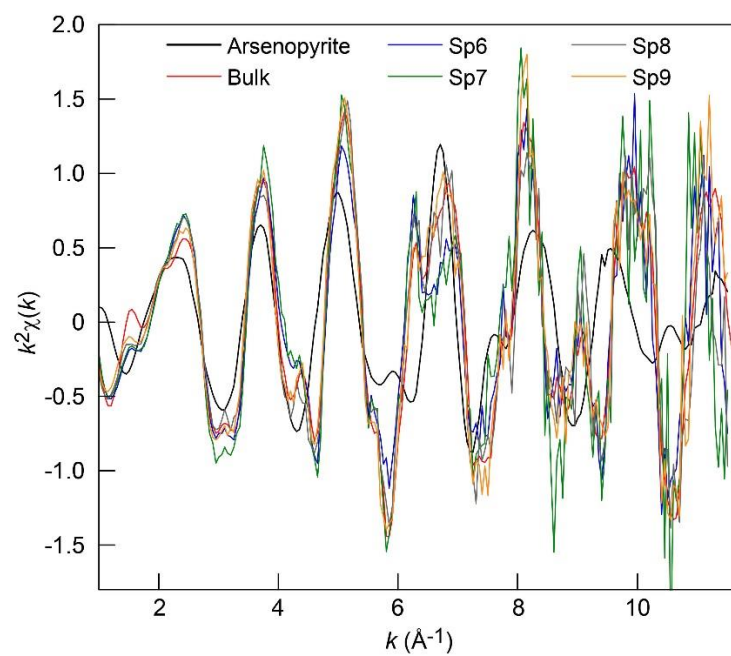


Figure S6. As K-edge micro EXAFS spectra measured on spots 6-9.

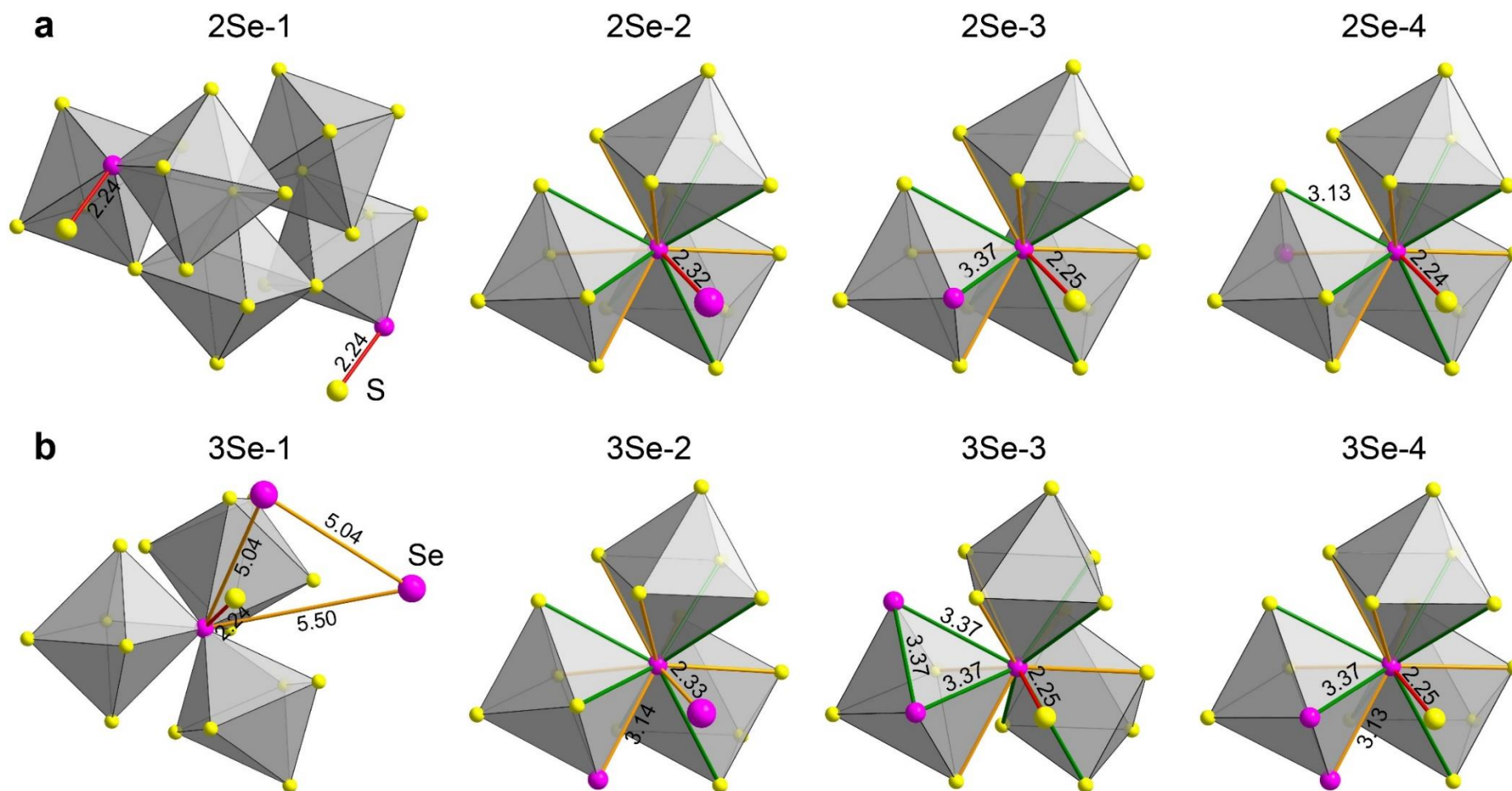


Figure S7. Bonding environment of Se in the $\text{Fe}_{32}\text{Se}_2\text{S}_{62}$ (a) and $\text{Fe}_{48}\text{Se}_3\text{S}_{93}$ (b) equilibrium structures. The S-S edges in yellow are 3.08 Å long and the S-S edges in green are 3.32 Å long in unsubstituted pyrite. The red line connects the dianionic pair. The DFT Se-Se₂ distance of 3.14-3.14 Å on short edges is similar to the EXAFS distance of 3.16 Å for model 2 (Table 2). EXAFS does not have the sensitivity to detect the second Se-Se₂ distance at 3.37 Å on long edges.

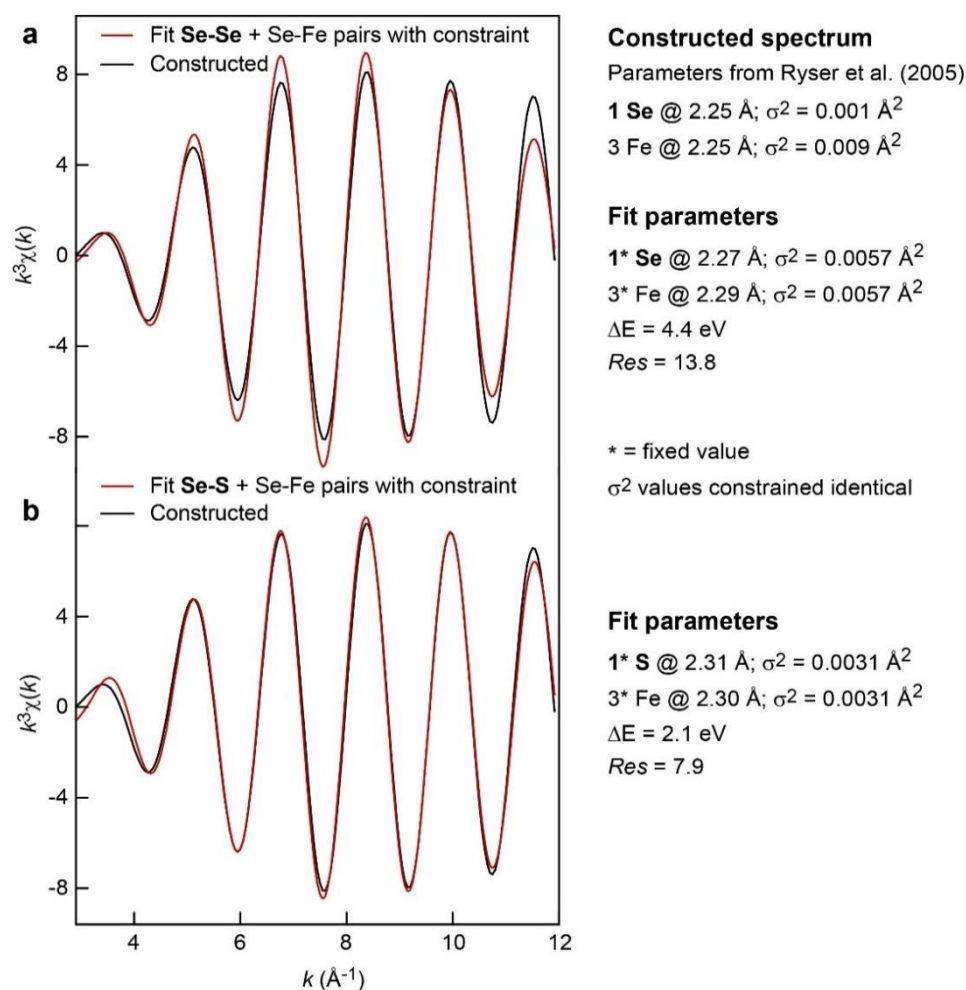


Figure S8. Fit of the first EXAFS shell for sample 2 POI *g* from Ryser et al.¹⁹ The first shell was fit originally with 1 Se at 2.25 Å and 3 Fe at 2.25 Å and the two Debye-Waller factors σ adjusted independently. Data analysis shows that the fit was underconstrained and the coordination number (*CN*) and Debye-Waller (σ) parameters correlated. The EXAFS function was refitted here by covarying the two σ values to suppress correlations. In (a) the first shell contains 1 Se and 3 Fe as in the original fit, and in (b) the Se atom was replaced with S. Results show that the 1S + 3Fe model provides a better fit to data. We conclude from this that [SeSe]₁ pairs are unlikely to exist in sample 2 POI *g* and that Se most likely forms a SeS dianion group.

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6. EXAFS spectra

| k ³ -weighted As-EXAFS | | k ³ -weighted Se-EXAFS | |
|-----------------------------------|----------|-----------------------------------|----------|
| 2.0000 | 0.26616 | 2.0000 | 0.79829 |
| 2.0500 | 0.39624 | 2.0500 | 0.94560 |
| 2.1000 | 0.49244 | 2.1000 | 1.0307 |
| 2.1500 | 0.62861 | 2.1500 | 1.0777 |
| 2.2000 | 0.76271 | 2.2000 | 1.0826 |
| 2.2500 | 0.98235 | 2.2500 | 1.0915 |
| 2.3000 | 1.1905 | 2.3000 | 1.1656 |
| 2.3500 | 1.3954 | 2.3500 | 1.2407 |
| 2.4000 | 1.5132 | 2.4000 | 1.2305 |
| 2.4500 | 1.5907 | 2.4500 | 1.1320 |
| 2.5000 | 1.5609 | 2.5000 | 0.86891 |
| 2.5500 | 1.4164 | 2.5500 | 0.50212 |
| 2.6000 | 1.2083 | 2.6000 | 0.13255 |
| 2.6500 | 0.77657 | 2.6500 | -0.26528 |
| 2.7000 | 0.33466 | 2.7000 | -0.76171 |
| 2.7500 | -0.25579 | 2.7500 | -1.3097 |

| | | | |
|--------|----------|--------|----------|
| 2.8000 | -0.78737 | 2.8000 | -1.8355 |
| 2.8500 | -1.2198 | 2.8500 | -2.2814 |
| 2.9000 | -1.5274 | 2.9000 | -2.5474 |
| 2.9500 | -1.6071 | 2.9500 | -2.6568 |
| 3.0000 | -1.5976 | 3.0000 | -2.6140 |
| 3.0500 | -1.5973 | 3.0500 | -2.4971 |
| 3.1000 | -1.6419 | 3.1000 | -2.3552 |
| 3.1500 | -1.8581 | 3.1500 | -2.1781 |
| 3.2000 | -2.0263 | 3.2000 | -1.9817 |
| 3.2500 | -2.1374 | 3.2500 | -1.7655 |
| 3.3000 | -2.0677 | 3.3000 | -1.3348 |
| 3.3500 | -1.6056 | 3.3500 | -0.61562 |
| 3.4000 | -0.69313 | 3.4000 | 0.37972 |
| 3.4500 | 0.25093 | 3.4500 | 1.5993 |
| 3.5000 | 1.2780 | 3.5000 | 2.7271 |
| 3.5500 | 2.0393 | 3.5500 | 3.6033 |
| 3.6000 | 2.7763 | 3.6000 | 4.2319 |
| 3.6500 | 3.0515 | 3.6500 | 4.3552 |
| 3.7000 | 3.1067 | 3.7000 | 4.0872 |
| 3.7500 | 3.1547 | 3.7500 | 3.8606 |
| 3.8000 | 2.8496 | 3.8000 | 3.5537 |
| 3.8500 | 2.0341 | 3.8500 | 2.9682 |
| 3.9000 | 1.1905 | 3.9000 | 1.7557 |
| 3.9500 | 0.050863 | 3.9500 | -0.21023 |
| 4.0000 | -0.90771 | 4.0000 | -1.1319 |
| 4.0500 | -1.5305 | 4.0500 | -2.1138 |
| 4.1000 | -1.8800 | 4.1000 | -2.9864 |
| 4.1500 | -2.3348 | 4.1500 | -3.4378 |
| 4.2000 | -2.5036 | 4.2000 | -3.4491 |
| 4.2500 | -2.2935 | 4.2500 | -3.5551 |
| 4.3000 | -2.0885 | 4.3000 | -2.9777 |
| 4.3500 | -1.6766 | 4.3500 | -2.7266 |
| 4.4000 | -1.7180 | 4.4000 | -2.6194 |
| 4.4500 | -2.0713 | 4.4500 | -2.4049 |
| 4.5000 | -2.6801 | 4.5000 | -2.6267 |
| 4.5500 | -3.4607 | 4.5500 | -3.3521 |
| 4.6000 | -3.6702 | 4.6000 | -3.2854 |
| 4.6500 | -3.4240 | 4.6500 | -3.3018 |
| 4.7000 | -1.9083 | 4.7000 | -1.4318 |
| 4.7500 | -0.29493 | 4.7500 | 0.17050 |
| 4.8000 | 1.6841 | 4.8000 | 1.6898 |
| 4.8500 | 3.4136 | 4.8500 | 3.7550 |
| 4.9000 | 4.6399 | 4.9000 | 4.6745 |
| 4.9500 | 5.2130 | 4.9500 | 5.3861 |
| 5.0000 | 6.1376 | 5.0000 | 5.9509 |
| 5.0500 | 6.9637 | 5.0500 | 7.0060 |
| 5.1000 | 7.2470 | 5.1000 | 6.8002 |
| 5.1500 | 6.9194 | 5.1500 | 7.5756 |
| 5.2000 | 5.9423 | 5.2000 | 5.8610 |
| 5.2500 | 5.1046 | 5.2500 | 5.6884 |
| 5.3000 | 3.5979 | 5.3000 | 3.6158 |
| 5.3500 | 2.0693 | 5.3500 | 1.2811 |
| 5.4000 | 0.069989 | 5.4000 | 0.040582 |

| | | | |
|--------|-----------|--------|----------|
| 5.4500 | -1.7929 | 5.4500 | -2.3178 |
| 5.5000 | -3.0620 | 5.5000 | -3.8000 |
| 5.5500 | -3.5339 | 5.5500 | -4.8479 |
| 5.6000 | -4.0887 | 5.6000 | -5.0913 |
| 5.6500 | -4.0167 | 5.6500 | -5.4134 |
| 5.7000 | -5.3636 | 5.7000 | -5.0293 |
| 5.7500 | -6.9250 | 5.7500 | -6.5259 |
| 5.8000 | -8.0400 | 5.8000 | -7.8269 |
| 5.8500 | -8.2341 | 5.8500 | -7.5178 |
| 5.9000 | -7.1403 | 5.9000 | -7.0566 |
| 5.9500 | -5.9404 | 5.9500 | -4.7290 |
| 6.0000 | -4.2905 | 6.0000 | -3.5815 |
| 6.0500 | -3.2413 | 6.0500 | -0.90567 |
| 6.1000 | -1.9562 | 6.1000 | 0.84439 |
| 6.1500 | -0.12405 | 6.1500 | 2.5368 |
| 6.2000 | 1.7767 | 6.2000 | 3.3244 |
| 6.2500 | 3.0902 | 6.2500 | 3.6316 |
| 6.3000 | 3.2769 | 6.3000 | 4.3131 |
| 6.3500 | 2.6038 | 6.3500 | 2.6509 |
| 6.4000 | 1.7326 | 6.4000 | 2.7221 |
| 6.4500 | 2.2010 | 6.4500 | 1.4240 |
| 6.5000 | 2.5108 | 6.5000 | 2.6028 |
| 6.5500 | 3.7087 | 6.5500 | 2.6989 |
| 6.6000 | 3.8455 | 6.6000 | 4.1819 |
| 6.6500 | 4.3133 | 6.6500 | 3.3907 |
| 6.7000 | 4.8254 | 6.7000 | 4.9749 |
| 6.7500 | 5.2282 | 6.7500 | 4.4594 |
| 6.8000 | 6.3380 | 6.8000 | 6.0585 |
| 6.8500 | 5.9066 | 6.8500 | 5.1488 |
| 6.9000 | 5.1261 | 6.9000 | 4.5620 |
| 6.9500 | 5.0682 | 6.9500 | 2.6317 |
| 7.0000 | 3.8286 | 7.0000 | 1.0440 |
| 7.0500 | 2.3723 | 7.0500 | 0.74569 |
| 7.1000 | -0.093105 | 7.1000 | -2.0813 |
| 7.1500 | -2.8204 | 7.1500 | -2.7736 |
| 7.2000 | -5.9806 | 7.2000 | -6.8532 |
| 7.2500 | -7.2432 | 7.2500 | -8.2583 |
| 7.3000 | -6.8103 | 7.3000 | -7.2454 |
| 7.3500 | -6.7082 | 7.3500 | -5.4410 |
| 7.4000 | -7.0758 | 7.4000 | -6.3527 |
| 7.4500 | -6.9946 | 7.4500 | -6.2466 |
| 7.5000 | -6.8165 | 7.5000 | -6.1353 |
| 7.5500 | -6.3441 | 7.5500 | -6.7658 |
| 7.6000 | -4.6438 | 7.6000 | -4.3765 |
| 7.6500 | -3.0112 | 7.6500 | -3.7602 |
| 7.7000 | -2.1338 | 7.7000 | -2.4431 |
| 7.7500 | -0.76941 | 7.7500 | -2.1632 |
| 7.8000 | -0.65473 | 7.8000 | -2.1219 |
| 7.8500 | -1.5031 | 7.8500 | -2.7195 |
| 7.9000 | -0.18552 | 7.9000 | -1.6914 |
| 7.9500 | 2.1588 | 7.9500 | 1.0890 |
| 8.0000 | 6.4714 | 8.0000 | 6.1445 |
| 8.0500 | 9.7006 | 8.0500 | 9.9183 |

| | | | |
|--------|----------|--------|----------|
| 8.1000 | 10.657 | 8.1000 | 9.9178 |
| 8.1500 | 10.459 | 8.1500 | 11.498 |
| 8.2000 | 9.6748 | 8.2000 | 9.5717 |
| 8.2500 | 9.3580 | 8.2500 | 12.636 |
| 8.3000 | 6.9566 | 8.3000 | 8.7415 |
| 8.3500 | 4.7569 | 8.3500 | 7.0991 |
| 8.4000 | 1.6793 | 8.4000 | 3.2567 |
| 8.4500 | -1.5539 | 8.4500 | 1.1611 |
| 8.5000 | -3.9910 | 8.5000 | -2.1571 |
| 8.5500 | -3.5303 | 8.5500 | -2.9457 |
| 8.6000 | -3.5021 | 8.6000 | -3.1676 |
| 8.6500 | -3.0120 | 8.6500 | -2.6443 |
| 8.7000 | -3.6894 | 8.7000 | -1.6841 |
| 8.7500 | -4.3190 | 8.7500 | -5.3677 |
| 8.8000 | -5.2845 | 8.8000 | -3.9108 |
| 8.8500 | -4.7537 | 8.8500 | -4.8447 |
| 8.9000 | -3.1674 | 8.9000 | -0.25019 |
| 8.9500 | -1.2276 | 8.9500 | -1.9238 |
| 9.0000 | -1.8260 | 9.0000 | 0.37759 |
| 9.0500 | -0.56155 | 9.0500 | -0.46755 |
| 9.1000 | -0.36057 | 9.1000 | -3.1691 |
| 9.1500 | -2.6416 | 9.1500 | -4.9440 |
| 9.2000 | -3.8554 | 9.2000 | -8.1887 |
| 9.2500 | -5.8516 | 9.2500 | -6.3057 |
| 9.3000 | -6.9440 | 9.3000 | -9.4222 |
| 9.3500 | -7.0953 | 9.3500 | -11.060 |
| 9.4000 | -7.0426 | 9.4000 | -10.729 |
| 9.4500 | -5.6286 | 9.4500 | -6.8438 |
| 9.5000 | -3.0549 | 9.5000 | -6.1101 |
| 9.5500 | 0.36686 | 9.5500 | 0.60362 |
| 9.6000 | 2.8004 | 9.6000 | 1.1010 |
| 9.6500 | 6.5784 | 9.6500 | 3.4045 |
| 9.7000 | 7.7103 | 9.7000 | 9.7957 |
| 9.7500 | 9.4691 | 9.7500 | 15.959 |
| 9.8000 | 9.9380 | 9.8000 | 16.615 |
| 9.8500 | 9.2164 | 9.8500 | 14.028 |
| 9.9000 | 9.5655 | 9.9000 | 16.171 |
| 9.9500 | 10.626 | 9.9500 | 10.314 |
| 10.000 | 6.9965 | 10.000 | 9.6327 |
| 10.050 | 6.6688 | 10.050 | 10.408 |
| 10.100 | 5.7293 | 10.100 | 7.9521 |
| 10.150 | 7.2677 | 10.150 | 9.5880 |
| 10.200 | 5.3881 | 10.200 | 7.2901 |
| 10.250 | 3.4387 | 10.250 | 0.71264 |
| 10.300 | -2.2982 | 10.300 | -4.6975 |
| 10.350 | -5.8703 | 10.350 | -8.5842 |
| 10.400 | -9.2306 | 10.400 | -13.201 |
| 10.450 | -11.322 | 10.450 | -13.734 |
| 10.500 | -12.674 | 10.500 | -17.842 |
| 10.550 | -13.590 | 10.550 | -16.526 |
| 10.600 | -14.174 | 10.600 | -17.544 |
| 10.650 | -13.735 | 10.650 | -16.427 |
| 10.700 | -11.464 | 10.700 | -11.374 |

| | | | |
|--------|-----------|--------|----------|
| 10.750 | -8.2448 | 10.750 | -7.0344 |
| 10.800 | -4.3659 | 10.800 | -4.0859 |
| 10.850 | -3.2943 | 10.850 | -4.4864 |
| 10.900 | -0.13950 | 10.900 | -0.25827 |
| 10.950 | 2.9273 | 10.950 | 0.34795 |
| 11.000 | 6.5308 | 11.000 | 7.5629 |
| 11.050 | 8.1810 | 11.050 | 9.1282 |
| 11.100 | 9.1027 | 11.100 | 11.082 |
| 11.150 | 9.5960 | 11.150 | 8.4138 |
| 11.200 | 8.6832 | 11.200 | 9.3127 |
| 11.250 | 9.6212 | 11.250 | 7.3250 |
| 11.300 | 9.6674 | 11.300 | 14.185 |
| 11.350 | 8.9892 | 11.350 | 11.587 |
| 11.400 | 7.4469 | 11.400 | 10.299 |
| 11.450 | 3.9599 | 11.450 | 7.8726 |
| 11.500 | 0.44762 | 11.500 | 3.5633 |
| 11.550 | -0.95937 | 11.550 | -0.83420 |
| 11.600 | -2.4085 | 11.600 | -7.1820 |
| 11.650 | -3.3124 | 11.650 | -7.9555 |
| 11.700 | -4.5783 | 11.700 | -6.7431 |
| 11.750 | -3.9655 | 11.750 | -7.1201 |
| 11.800 | -4.4998 | 11.800 | -4.4345 |
| 11.850 | -3.0126 | 11.850 | 0.56694 |
| 11.900 | -2.2824 | 11.900 | -0.72288 |
| 11.950 | -0.048844 | 11.950 | 1.1418 |
| 12.000 | -1.0915 | 12.000 | 2.0238 |
| 12.050 | -3.6917 | 12.050 | 0.090986 |
| 12.100 | -3.2344 | 12.100 | -1.1576 |
| 12.150 | -3.1282 | 12.150 | -3.3562 |
| 12.200 | -4.7111 | 12.200 | -5.2304 |
| 12.250 | -2.3019 | 12.250 | -8.4865 |
| 12.300 | -1.0214 | 12.300 | -1.5842 |
| 12.350 | 0.32290 | 12.350 | -2.7759 |
| 12.400 | 0.080365 | 12.400 | -4.6243 |
| 12.450 | -1.5143 | 12.450 | -3.3260 |
| 12.500 | 0.18834 | 12.500 | -5.8521 |
| 12.550 | 1.0020 | 12.550 | -0.85200 |
| 12.600 | -1.0671 | 12.600 | -0.99685 |
| 12.650 | -0.032443 | 12.650 | 0.10999 |
| 12.700 | -1.1906 | 12.700 | -2.7454 |
| 12.750 | 1.0653 | 12.750 | 2.5813 |
| 12.800 | 3.5748 | 12.800 | -0.55342 |
| 12.850 | 2.4904 | 12.850 | 5.3239 |
| 12.900 | 1.2055 | 12.900 | 2.9285 |
| 12.950 | 3.1667 | 12.950 | 11.961 |
| 13.000 | 4.3522 | 13.000 | 9.1107 |
| 13.050 | 6.7235 | 13.050 | 12.655 |
| 13.100 | 5.9964 | 13.100 | 9.2925 |
| 13.150 | 4.8332 | 13.150 | 9.2028 |
| 13.200 | 2.7348 | 13.200 | 8.1624 |
| 13.250 | 1.3229 | 13.250 | 3.8166 |
| 13.300 | -0.71824 | 13.300 | 7.7472 |
| 13.350 | -1.3552 | 13.350 | -3.7454 |

| | | | |
|--------|----------|--------|---------|
| 13.400 | -2.2247 | 13.400 | -2.7199 |
| 13.450 | -3.0564 | 13.450 | -2.7324 |
| 13.500 | -4.0179 | 13.500 | -5.1474 |
| 13.550 | -5.1273 | 13.550 | -8.8529 |
| 13.600 | -4.8137 | 13.600 | -5.8019 |
| 13.650 | -6.1890 | 13.650 | -13.225 |
| 13.700 | -7.3673 | 13.700 | -13.746 |
| 13.750 | -6.2048 | 13.750 | -10.505 |
| 13.800 | -4.6294 | 13.800 | -1.1338 |
| 13.850 | -5.9750 | 13.850 | -1.2276 |
| 13.900 | -3.4949 | 13.900 | -6.8623 |
| 13.950 | 0.70274 | 13.950 | -2.9457 |
| 14.000 | 1.1562 | 14.000 | -8.2199 |
| 14.050 | 4.5725 | 14.050 | -4.8167 |
| 14.100 | 4.5363 | 14.100 | -3.4426 |
| 14.150 | 7.1013 | | |
| 14.200 | 5.2192 | | |
| 14.250 | 5.2430 | | |
| 14.300 | 6.3670 | | |
| 14.350 | 5.4506 | | |
| 14.400 | 2.9672 | | |
| 14.450 | 2.1376 | | |
| 14.500 | 2.9301 | | |
| 14.550 | 2.3790 | | |
| 14.600 | 1.1721 | | |
| 14.650 | -1.3919 | | |
| 14.700 | 2.0720 | | |
| 14.750 | 0.58659 | | |
| 14.800 | 1.8174 | | |
| 14.850 | 2.3578 | | |
| 14.900 | -4.2839 | | |
| 14.950 | -4.6901 | | |
| 15.000 | -6.2599 | | |
| 15.050 | -5.5322 | | |
| 15.100 | -1.9332 | | |
| 15.150 | -5.1721 | | |
| 15.200 | -7.3530 | | |
| 15.250 | -7.3808 | | |
| 15.300 | -2.1165 | | |
| 15.350 | -2.8451 | | |
| 15.400 | -1.2475 | | |
| 15.450 | -0.82886 | | |
| 15.500 | 2.9280 | | |
| 15.550 | 1.9028 | | |
| 15.600 | 2.5773 | | |
| 15.650 | 2.3333 | | |
| 15.700 | 0.98683 | | |
| 15.750 | 4.6828 | | |
| 15.800 | 4.2982 | | |
| 15.850 | 2.2402 | | |
| 15.900 | 3.5881 | | |
| 15.950 | 4.1250 | | |