

Arsenic in iron disulfides in a brown coal from the North Bohemian Basin, Czech Republic

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Abstract

Arsenic in the coal studied is not bound to coal macerals, it is concentrated in the inorganic part of coal, specifically in the iron sulfides. This paper reports the results of five crystal structure refinements that include natural (2) and synthetic (3) sulfides, pyrite (3) and marcasite (2). Powder (3) and single-crystal (2) intensities used in the refinements were obtained by diffraction of X-rays (4) and synchrotron radiation (1). The refined occupancy factors of sulfur and the unit-cell parameters favor the possibility that As substitutes for S in both disulfides.

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1. Introduction

During coal combustion, toxic trace elements escape into the environment, and arsenic is one of them; for a discussion see Finkelman (1982), Spears et al. (1994), or Yudovich and Ketris (2005). A better knowledge of the distribution and speciation of arsenic in coal might aid in regulating the combustion process and minimizing the damage to the environment.

There are reviews dealing with As in coal and coal ashes, both regional (Hokr, 1977; Bouška, 1981) and international (Swaine, 1990; Yudovich and Ketris, 2005). The range reported varies from less than 1 ppm up to the order of 1%, and Czech coals are listed among those enriched in As. A recent summary of trace elements in the Czech coals is due to Pešek et al. (2005). Although it is acknowledged that As may be bound organically or as $(\text{AsO}_4)^{3-}$, it is sulfides that are mentioned most often as carriers of arsenic, specifically pyrite, marcasite, or arsenopyrite. They also are responsible for the content of inorganic sulfur in the coal and, together with associated other sulfides, for contents of trace elements such as Bi, Cd, Cu or Pb.

A closely related question is the solubility of As in pyrite and marcasite as phases. The data available show

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that the content of arsenic in natural iron disulfides varies widely. Vaughan and Craig's (1978) review lists maximum contents of arsenic in natural marcasite and pyrite as 0.78 and 5 wt.%, respectively. Higher contents come from Fleet et al. (1989) who reported up to 8 wt.% As in pyrite from stratabound and stratiform deposits, and from Fleet and Mumin (1997) who found an arsenian gold-bearing pyrite from the Carlin Trend deposit with As contents as high as 16.5 wt.%. An arsenian pyrite from the Carlin-type deposits Twin Creeks, Nevada, with lower As contents (1–2.4 wt.%) was mentioned by Simon et al. (1999). A coarsely zoned arsenian pyrite with As contents ranging between 0 and 5 wt.% was described from the Cretaceous gold mineralization in the Mother Lode Gold district, California (Savage et al., 2000). Ondruš et al. (2003) reported exceptionally high contents of up to 17.35 wt.% As in pyrite and up to 10.63 wt.% in marcasite from the Jáchymov hydrothermal vein deposit, and Zachariáš et al. (2004) found up to 4.5 wt.% As in pyrite from the hydrothermal vein gold deposit at Roudný.

Like their natural counterparts, synthetic disulfides also exhibit a broad range of As contents. Clark (1960) carried out a detailed study of phase relations in the dry Fe–As–S system and estimated the solubility limit of As in pyrite as 0.53 wt.% at 600 °C. Much higher values come from Fleet and Mumin (1997) who conducted hydrothermal experiments in the Fe–As–S–Au system and synthesized marcasite with As contents of 10.5 and 12.6 wt.% and pyrite with As contents ranging from 2.9 to 7.7 wt.%.

2. The problem

The references mentioned suggest that if a coal contains As, it will likely be concentrated in the inorganic part. So, the first question is to ascertain whether As in a coal sample from the North Bohemian Basin behaves as expected or not.

The second question is, if As indeed is associated with the disulfides, what is the nature of incorporation of As in the structure of pyrite or marcasite from this particular coal.

Generally, it is not clear which of the two disulfides can dissolve more As, and in both phases, the substitution mechanism is uncertain. Is the presence of As due to (1) substitution for sulfur, (2) substitution for iron, or (3) heterogeneous microinclusions of arsenopyrite, which has a different crystal structure than pyrite? On the basis of EMP, TEM and EXAFS analyses, Simon et al. (1999) concluded that in natural pyrite As substitutes for S. Ondruš et al. (2003) also noticed a negative correlation

between As and S in pyrite and marcasite from Jáchymov, as did Zachariáš et al. (2004) in pyrite from Roudný. In contrast, Fleet and Mumin (1997) noticed a considerable deficiency of Fe in some gold-bearing arsenian pyrites and hinted at the possibility that As substitutes for Fe. Wolthers et al. (1998) mentioned the redox sensitivity of arsenic that might govern the mode of incorporation of As in the structure of pyrite. Ruppert et al. (2005) examined disulfides from a coal seam — a material closest to the one presently studied. After adjusting the percentages (Ruppert et al., Table 2) to a sum of 100.0%, sulfur and arsenic exhibit a highly significant negative correlation (correlation coefficient -0.82) indicating a replacement relationship.

However, all the substitutions mentioned are based on chemical data rather than on direct evidence. Therefore, we opted for tools of crystal-structure refinement to show whether the presence of As in the presently studied pyrite or marcasite can be confirmed and, if so, to elucidate the nature of its bonding in the crystal structure.

3. Materials and methods

The sample of Miocene coal was collected at the Důl ČSA Mine (North Bohemian Basin). In addition to sulfides dispersed in the coal, the sample contained a concretion with visible crystals of pure marcasite, several mm in size. The concretion was treated separately.

The coal sample, several kg in weight, was finely ground and separated by a centrifugation technique (Density Gradient Centrifugation technique — DGC, Crelling, 1994) into 28 density fractions ranging from 1.0830 g/cm³ to 1.6213 g/cm³, and a residue with a density exceeding 1.6213 g/cm³. The DGC residue was sedimented in heavy liquids to obtain a fraction enriched in iron disulfides — the sulfide concentrate. The total content of As in all samples studied was determined by AAS using hydride generation; the technique was standardized on the South African certified reference material SARM 20.

As reference material, pyrite (As-containing and As-free) and marcasite (As-free) were prepared synthetically. As-free pyrite was synthesized from synthetic pyrrhotite and sulfur by iodine transport in a temperature gradient. A long (120 mm) evacuated silica tube was placed in a horizontal tube furnace with electronically regulated temperature measured with a Ni–NiCr thermocouple. The hot spot was kept at 740 ± 3 °C. As-containing pyrite was grown at 610 °C in a standard collapsible Au tube under hydrostatic pressure of 100 MPa. Starting materials were synthetic pyrrhotite and As_{0.1}S_{0.9} glass. A 1 M NaCl solution served as the

hydrothermal medium. Marcasite was synthesized at 200 °C by a reaction of hydrogen sulfide with ferric sulfate according to the modified method of Allen et al. (1912). The synthesis was performed in a steel pressure vessel with a PTFE (Teflon) insert. Sodium thiosulfate solution was placed directly in the PTFE insert and the ferric sulfate solution was kept separately in a smaller quartz tube (Drábek and Rieder, 2005).

Crystals of iron disulfides were studied under an electron microscope (Philips XL 30 instrument equipped with an EDAX) and analyzed by the EDX technique (conditions: 20 kV, 0.8 μ A beam current, standardless method, ZAF correction).

Powder diffraction data were collected on a standard X-ray diffractometer (Stoe, CoK α radiation); synchrotron data were measured at ESRF in Grenoble. All samples were powdered under acetone and packed in capillaries. Powder data were treated with the Rietveld computer program WYRIET (Schneider, 1994).

Before data collection on the single-crystal diffractometer, precession photographs were taken to avoid twinned or imperfect crystals. Diffraction intensities were collected on a Kuma KM-4 automated four-circle diffractometer with a κ -geometry using graphite-monochromatized MoK α radiation. The intensities were collected over the range $2\theta=0.0$ – 35.0° employing the ω – 2θ scan with an ω –scan speed of $0.15^\circ/\text{s}$ in the step-scan mode. 60 steps were measured for each reflection, 10 steps on each side of the reflection were considered as background. Three standard reflections were monitored after every 100 reflections.

Data treatment, refinement and Fourier synthesis were carried out with the JANA2000 program package (Petříček and Dušek, 2000). As a first step, the data were corrected for Lorentz and polarization effects and for absorption, using the shape of the crystal. From a total of 1023 reflection intensities measured, 728 were classified as observed, that is the intensity had to exceed 3 sigma. The reflections were merged according to the $Pa3$ space group, yielding 77 independent reflections, which were used in the refinement.

4. Distribution of arsenic in the sample of coal from the North Bohemian Basin

The density distribution (density profile) of the micronized coal sample is shown in Fig. 1. It is a typical coal profile with the peak representing the vitrinite macerals; the tail to the left of the peak represents the liptinite macerals, whereas the tail to the right represents the inerinite macerals. It can be seen that the most coal-rich density fractions, that is those around the peak between 1.18 and 1.43 g/cm³, also have the lowest As contents (15 to 111 ppm, respectively). The As content is somewhat higher (184 to 382 ppm) in the density fractions between 1.45 and 1.62 g/cm³. Because the As content is much greater (2350 ppm) in the >1.62 g/cm³ DGC residue, it is clear that very little As is bound to the organic portion of the coal. The fact that the DGC residue with 2350 ppm As is composed dominantly of iron disulfides and that the sulfide concentrate with 4200 ppm As also is composed of iron disulfides

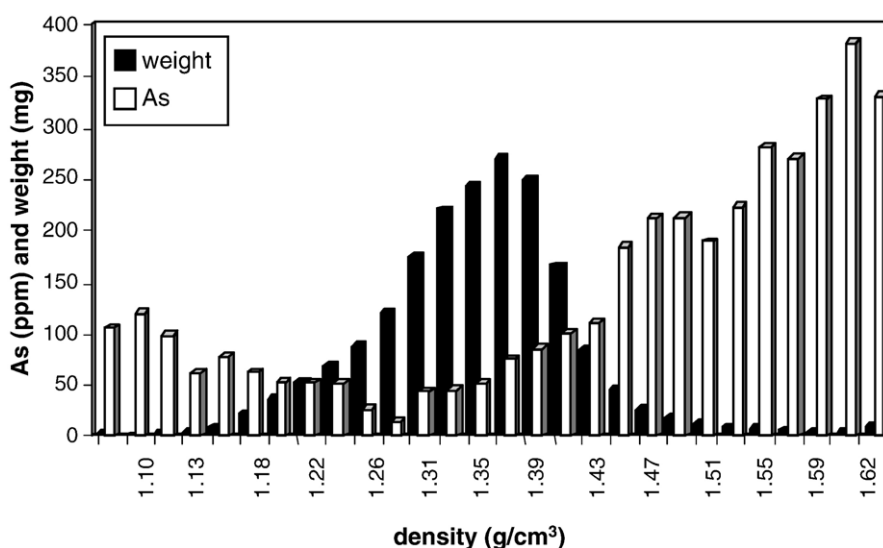


Fig. 1. Weight of individual density fractions and their As content in the brown coal studied. Fractions were prepared by the density gradient centrifugation technique.

makes it almost certain that As is associated with the iron disulfides.

5. Arsenic in iron disulfides from the coal sample

The sulfide concentrate is a mixture of 78 vol.% pyrite and 22 vol.% marcasite (Rietveld refinement). However, due to the similar appearance of both phases in hand specimen and their fine-grained nature, they could not be separated from one another so that their respective contents of As could be determined. Under the microprobe, the two disulfides cannot be distinguished, and individual grains exhibit a considerable inhomogeneity of their As contents. While some grains contain practically no As (below detection limit), other grains have up to 7 at.% As. This is documented in Fig. 2 which shows distribution maps of Fe, S, and As. Likewise, in several grains of natural marcasite from the concretion, contents as high as 1.1 at.% As were observed, even though the overall content of As in the sample is 138 ppm.

For a material like this, X-ray data can only provide information about a mean mineralogical and chemical composition of a powder or a single-crystal. Still, we thought structure refinement might provide some useful information about the role of arsenic in the structure of the disulfides.

6. Crystal structures

It has long been known (Bragg, 1913; Finklea et al., 1976; Bayliss, 1977) that in pyrite, iron atoms are octahedrally coordinated by sulfur, and the immediate neighborhood of each S atom contains three Fe atoms and one S. Two neighboring FeS_6 octahedra share one S atom, and another sulfur atom in each octahedron is bonded to a sulfur atom from a neighboring octahedron by a relatively short covalent bond (2.14 Å). The structure of marcasite (Buerger, 1931; Brostigen et al., 1973) has the same first coordinations as pyrite, but the mutual relationships between the octahedra are different. The

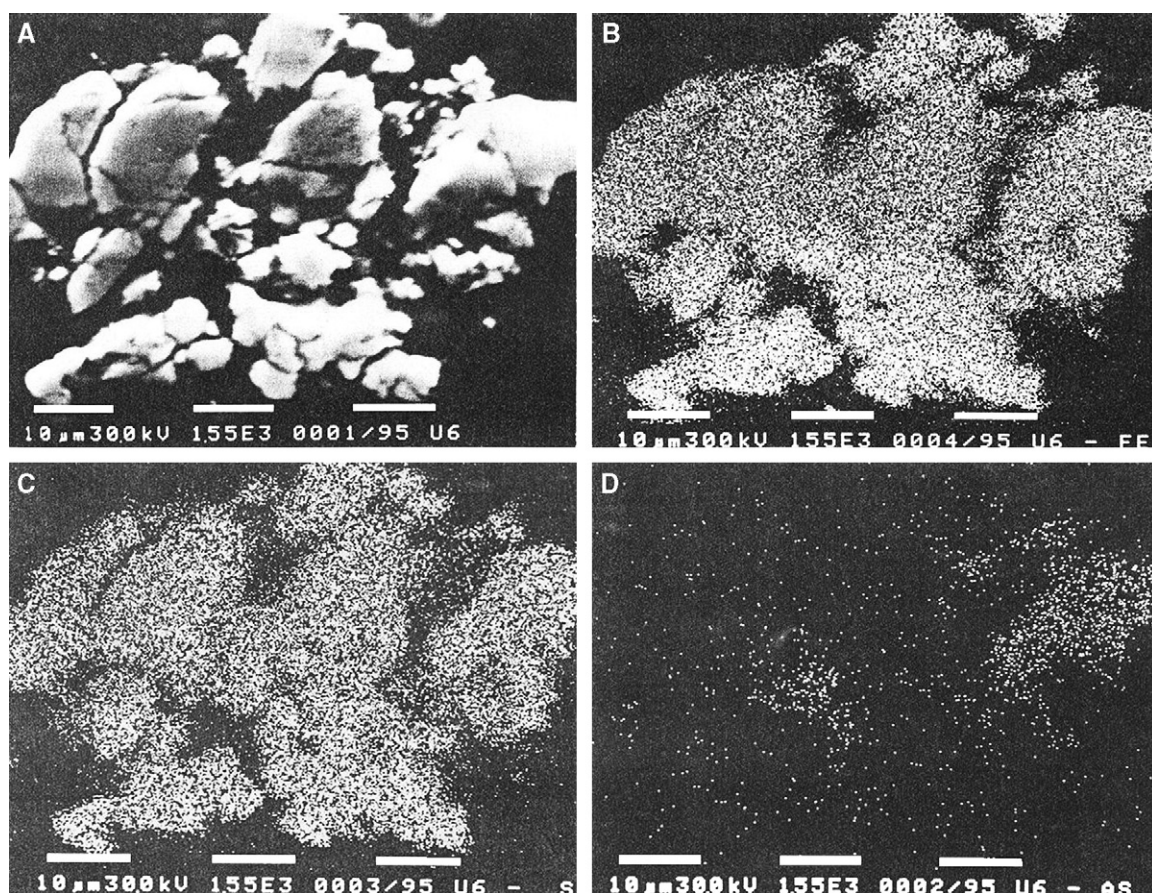


Fig. 2. BSE photograph of the iron sulfide concentrate from the brown coal sample (A) and the corresponding X-ray distribution maps of Fe (B), S (C) and As (D). Each of the horizontal white bars is 10 µm in length.

Table 1

Rietveld structure refinement for two marcasite samples compared to single-crystal data of Brostigen et al. (1973)

	As-marcasite	As-free marcasite	Marcasite
	Natural concretion	Synthetic	Natural
	–	–	Brostigen et al. ^c
	X-rays ^a	Synchrotron ^b	X-rays
Unit-cell parameters			
<i>a</i> (Å)	4.449 (1)	4.4446 (2)	4.4431 (9)
<i>b</i> (Å)	5.432 (1)	5.4246 (2)	5.4245 (9)
<i>c</i> (Å)	3.391 (1)	3.3864 (1)	3.3871 (6)
Atom coordinates ^d			
<i>x</i> (S)	0.202 (1)	0.2004 (2)	0.20008(6)
<i>y</i> (S)	0.380 (1)	0.3787 (2)	0.37820(5)
Occupancy factor ^e			
<i>n</i> (Fe)	0.26 (1)	0.253 (1)	0.25
<i>n</i> (S)	0.60 (1)	0.486 (2)	0.5
Temperature factor			
<i>B</i> ₁₁ (Fe)	2.5 (4)	1.67 (3)	0.306 (4)
<i>B</i> ₂₂ (Fe)	2.2 (6)	1.64 (4)	0.280 (4)
<i>B</i> ₃₃ (Fe)	2.0 (3)	1.68 (3)	0.317 (4)
<i>B</i> ₁₂ (Fe)	0.0 (4)	0.00 (3)	0.007 (6)
<i>B</i> ₁₁ (S)	1.7 (5)	1.43 (4)	0.360 (6)
<i>B</i> ₂₂ (S)	1.9 (6)	1.31 (5)	0.334 (4)
<i>B</i> ₃₃ (S)	1.9 (3)	1.60 (4)	–0.369 (5)
<i>B</i> ₁₂ (S)	0.0 (5)	0.00 (3)	–0.049 (9)
Bond lengths (Å)			
Fe–S ₁	2.248 (2)	2.239 (1)	2.2359 (3)
Fe–S ₂	2.252 (2)	2.252 (1)	2.2540 (2)
S ₂ –S _{3a}	2.223 (2)	2.215 (1)	2.2152 (4)
S ₂ –S ₃	2.953 (2)	2.972 (1)	2.9748 (4)
S ₃ –S ₄	3.134 (2)	3.123 (1)	3.1206 (4)
S ₂ –S ₄	3.230 (2)	3.228 (1)	3.2282 (3)
S ₂ –S ₆	3.391 (1)	3.386 (1)	3.3871 (0)
Agreement factor			
Derived Bragg <i>R</i> (%)	6.9	7.1	2.2
Marcasite (vol.%)	100	95	100
Pyrite (vol.%)	0	5	0
Wavelength (Å)	1.7889	0.62061	0.7107
2θ range (°)	20.0–80.0	9.500–49.995	–

Errors (one e.s.d.), given in units of the last decimal place, appear in parentheses.

^a Diffractometer STOE.

^b ESRF, Grenoble.

^c Based on data of Brostigen and Kjekshus (1970a,b) and Brostigen et al. (1973). Marcasite is reported to contain 10 ppm As (among similar concentrations of other impurities).

^d Iron occupies Wyckoff position *a*, and sulfur occupies position *g*.

^e The occupancy factor follows from the multiplicity of the space group and the multiplicity of the special position. Ideal values for *n* (Fe) and *n*(S) are 1/4 and 1/2, respectively.

structure of marcasite is similar to that of arsenopyrite, and Brostigen and Kjekshus (1970b) and Tossell et al. (1981) anticipated an extensive isomorphous substitution $\text{As} \rightleftharpoons \text{S}$ along the join. The structural relations between pyrite and marcasite have also been examined by Dódy et al. (1996) who used the HRTEM technique. They found shear zones in pyrite and documented fine-scale intergrowths of micro-domains of pyrite and marcasite, on the scale of several planes of atoms. Dódy et al. (1996) also studied a pyrite with up to 2.7 at.% As and showed that the distribution of As in individual domains is homogeneous throughout, whether their structure is ordered or not; thus there appears to be no association of As with the shear zones.

The structures of the presently studied natural marcasite from concretions and of synthetic marcasite were refined by the Rietveld technique, in the space group *Pnnm*. The refinement of natural marcasite was based on X-ray diffraction data; synthetic marcasite was refined from synchrotron data. The results appear in Table 1. A complete description of the structure can be reduced to two different Fe–S bond lengths and four different S–S bonds in one octahedron (specifically, Fe–S₁, Fe–S₂, S₂–S₃, S₃–S₄, S₂–S₄, and S₂–S₆; the “inter-octahedral” bond is designated S₂–S_{3a}). The results are accompanied by the data of Brostigen and Kjekshus (1970a,b) and Brostigen et al. (1973).

An elevated occupancy factor of sulfur is what one would expect if there is a substitution of a “heavier” atom (such as As) for sulfur. Indeed, the factor is 0.60(1) for the As-containing natural sample as opposed to 0.486(2) for synthetic As-free marcasite.

We performed one Rietveld refinement of pyrite (from the sulfide concentrate) and two single-crystal refinements (Table 2). Both single crystals are synthetic; one contains arsenic (0.6 wt.% As), the other is As-free.

The bond lengths do not betray the nature of the substitution of As in pyrite, and neither do the polyhedral volumes, the only parameter that may be an indication is, again, the occupancy factor of sulfur. It refined as 0.43 ± 2 for natural pyrite, higher than the ideal value of 0.33. In the As-containing synthetic single-crystal, the refined occupancy of S is only slightly higher than the ideal value; however, when the occupancy of Fe was open to variation, the calculation yielded an unrealistic lower-than-ideal occupancy of Fe. Like in marcasite, all effects observed are what one would expect if As substitutes for S.

Additional indirect evidence is offered by cell metrics. The unit-cell volume of loellingite (Lutz et al., 1987) is about 10% larger than that of marcasite (Brostigen et al., 1973), and its cause must be As substituting for S, because the rest of both structures remains the same. The unit cell

Table 2
Structure refinements of pyrite from X-ray diffraction data

	As-pyrite	As-pyrite	As-free pyrite
	Natural	Synthetic	Synthetic
	Sulfide concentrate	—	—
	Powder	Single-crystal	Single-crystal
Unit-cell parameters			
<i>a</i> (Å)	5.429 (1)	5.428 (1)	5.416 (1)
Atom coordinates ^a			
<i>x</i> (S)	0.385 (2)	0.3848 (1)	0.38488 (8)
Occupancy factor ^b			
<i>n</i> (Fe)	0.17 (3)	0.166	0.166
<i>n</i> (S)	0.43 (2)	0.338 (2)	0.334 (2)
Temperature factor			
<i>B</i> ₁₁ (Fe)	1.99 (8) ^c	0.77 (2)	0.70 (2)
<i>B</i> ₂₂ (Fe)		0.77 (2)	0.70 (2)
<i>B</i> ₃₃ (Fe)		0.77 (2)	0.70 (2)
<i>B</i> ₁₂ (Fe)		0.01 (1)	0.00 (1)
<i>B</i> ₁₁ (S)	0.97 (9) ^c	0.82 (2)	0.78(2)
<i>B</i> ₂₂ (S)		0.82 (2)	0.78 (2)
<i>B</i> ₃₃ (S)		0.82 (2)	0.78 (2)
<i>B</i> ₁₂ (S)		−0.01 (10)	0.01 (10)
Bond lengths (Å)			
Fe–S	2.274 (4)	2.2683 (5)	1.2632 (4)
S–S	2.143 (5)	2.1665 (6)	2.1597 (6)
Agreement factors			
Derived Bragg <i>R</i> (%)	9		
<i>R</i> _{obs} (%) ^d		1.91	1.73
Marcasite (vol.%)	22	0	0
Pyrite (vol.%)	78	100	100
Wavelength (Å)	1.7889	0.7107	0.7107
2θ range (°)	20.0–80.0	0.0–35.0	0.0–35.0

Errors (one e.s.d.), given in units of the last decimal place, appear in parentheses.

^a Sulfur occupies Wyckoff position *c*.

^b The occupancy factor follows from the multiplicity of the space group and the multiplicity of the special position. Ideal values for *n* (Fe) and *n*(S) for pyrite are 1/6 and 1/3, respectively.

^c Isotropic temperature factor.

^d $R_{\text{obs}} = \sum ||F_o| - |F_c|| / \sum |F_o|$.

of marcasite whose Fe is being substituted by As would likely decrease in size, not increase. (Inasmuch as a pyrite-like FeAs₂ phase is not known, we have no analogous data for the cubic disulfide/diarsenide.) If As substitution for S indeed inflates the unit cells, then the presently obtained unit-cell data fit the pattern: the unit-cell volume of all As-free phases is smaller than the volume of phases that do contain As. In order to put pyrite and marcasite data on a

comparable scale, we calculated *relative unit-cell volumes* (actual unit-cell volume divided by unit-cell volume of the same phase without As) and *relative sulfur occupancies* (actual occupancy of sulfur divided by occupancy of sulfur in the same phase without As). We obtained six data pairs, for three entries from Table 2 and three entries from Table 1. The correlation coefficient is a positive 0.66.

7. Conclusions

- (1) Fractions of brown coal (North Bohemian Basin) were prepared by the DGC technique, and those that contain coal macerals (densities between 1.18 and 1.43 g/cm³) display the lowest As concentrations (between 15 and 111 ppm). Fractions with a higher density (between 1.45 and 1.62 g/cm³) contain 184 to 382 ppm As, respectively. This makes it clear that very little As, if any, is bound in the organic part of coal.
- (2) The average As content in the residue after DGC separation is 2350 ppm, and sulfide concentrate prepared from this residue by sedimentation contains 4200 ppm As. Thus it appears that As in coal is associated dominantly with the sulfides. However, the distribution of As in individual grains of the sulfide concentrate is strongly variable; some grains contain practically no As (below detection limit), others have up to 7 at.% As.
- (3) The sulfide concentrate is a mixture of pyrite (78 vol.%) and marcasite (22 vol.%), whereas the concretion consists of pure marcasite.
- (4) As-free marcasite was prepared synthetically, and its refinement is based on high-quality synchrotron data.
- (5) The nature of substitution of arsenic in iron disulfides could not be unequivocally solved by the tools of structure analysis. Nonetheless, in four refinements of As-containing sulfides (two pyrites, two marcasites) the occupancy factor of sulfur exceeds the ideal value, indicating a substitution by a heavier atom. In two synthetic As-free samples (one pyrite, one marcasite), the occupancy of sulfur does not exceed the ideal values. Likewise, unit-cell volumes of As-containing disulfides are larger than those of their As-free counterparts. Both these lines of evidence favor the substitution of arsenic for sulfur rather than for iron.

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