

Supergene iron sulpho-selenides from the Zapadno-Ozernoe copper-zinc massive sulphide deposit, South Urals, Russia: a new solid-solution series between pyrite FeS₂ and dzharkenite FeSe₂

V. A. YAKOVLEVA^{1,*}, E. V. BELOGUB² AND K. A. NOVOSELOV²

¹ Saint-Petersburg State University, Saint-Petersburg, Universitetskaya nab. 7/9, 199034, Russia

² Institute of Mineralogy of Urals Branch of RAS, Miass, 456301, Russia

ABSTRACT

Supergene Fe sulpho-selenides (pyrite, dzharkenite and their intermediate compositions) were discovered in the oxidation zone of the Zapadno-Ozernoe copper-zinc massive sulphide deposit, South Urals, in association with other rare supergene sulphides, such as galena, tetrahedrite, metacinnabarite, tiemannite, Pb sulpharsenides of the jordanite group, undetermined sulphosalts of Hg and Ag, and native elements, such as S, Au and Se. This is the second known occurrence of dzharkenite. The results of the investigation of Fe sulpho-selenides using electron microprobe analysis, X-ray diffraction (XRD) and reflected light microscopy show the existence of a limited solid-solution series between pyrite and dzharkenite, which has not been described before.

KEYWORDS: pyrite, dzharkenite, oxidation, massive sulphide, selenide, sulphide.

Introduction

THE Zapadno-Ozernoe copper-zinc massive sulphide deposit (discovered in 1980) is situated in the Verkhneural'sk ore district of the South Urals. The formation of the deposit is considered to be the result of hydrothermal activity in the northern part of the East-Magnitogorsk palaeo-ocean volcanic arc. A stratigraphic section of the Zapadno-Ozernoe deposit from bottom to top is as follows: (1) basalt and rhyolite lavas, volcanic breccias and tuffs, effusive rocks and tuffs of rhyolites of the Karamalitash formation D₂ef–gv; (2) andesites of the Ulutau formation D₂gv.

The Zapadno-Ozernoe deposit comprises 15 ore bodies on two stratigraphic levels: on the border between the Karamalitash and Ulutau formations, and within the Ulutau formation.

The ore-bearing structures seem to be related to a central volcano. Ore body No. 5 of the deposit is characterized by a highly developed oxidation

zone, with a high Au content (up to 25 ppm). Gold-bearing gossans formed over ore body No. 5 were exploited during 1998 by the Bashkirian Gold-mining Company. Gold was extracted from the ore using a cyanide leaching method.

The upper part of the massive sulphide ores of ore body No. 5 is located ~30–40 m below the modern erosion level. The mineral composition of the sulphide ores is as follows: pyrite, chalcopyrite, sphalerite and minor quantities of galena, tennantite and arsenopyrite. Pyrrhotite, bornite, covellite, chalcocite, marcasite, native gold and germanite are rare.

The morphology of the supergene zone is cap-like, with walls represented by gossans and sulphate-bearing volcanic rocks, and a stratified lower part composed of quartz, sulphide-quartz, quartz-baryte and pyrite sands. The exploration of the deposit allowed the features of the supergene profile structure and composition to be determined. According to Surin *et al.* (1997) and original data of the present authors (Belogub *et al.*, 2000), the supergene profile includes, from top to base: bleached zone; 'iron cap'; 'red zone' – distant replacement of volcanic rocks by

* E-mail: barbara_mail@yahoo.com
DOI: 10.1180/0026461036720106

jarosite and alunite; 'green zone' – low-sulphate zone of beudantite-baryte-quartz ochres and sands; smectitization and beudantitization of volcanic rocks; 'grey zone' – quartz, quartz-baryte and quartz-baryte-cerussite sands, which are characterized by local disruption of the supergene sequence; 'black zone' – quartz + secondary sulphides sand with native sulphur lenses, up to 2.5 m thick; quartz crust with tetrahedrite impurity, up to 10 cm thick; leaching zone represented by residual pyrite sand, up to 1 m thick and more; and, secondary copper enrichment zone (not seen in the open pit). For further details, see Belogub *et al.* (2003).

Methods of analysis

The reflected light microscopy data were obtained at the Ore Microscopy laboratory of Saint-Petersburg State University using a POLAM R-312 microscope and microspectrophotometer MSF-10, with WTiC as the standard. The microprobe analyses of Fe sulpho-selenides were obtained at the Electron Microscopy and Microanalysis laboratory of St.-Petersburg State University with a Philips SEM 501 B using energy dispersive EDAX 9100 and the standards of C.M. Taylor Corporation, USA. The X-ray analysis of Fe sulpho-selenides was undertaken in the Institute of Mineralogy Laboratory, Miass, Russia. Sulphur isotopes were measured at the Isotope Geosciences Laboratory (NERC, UK), using a VG ISOGAS SIRA 10. Sulphur isotopic compositions are reported in ‰ relative to Canyon Diablo troilite.

Supergene Fe sulpho-selenides

From a mineralogical point of view, the 'black zone' is the most interesting in the supergene profile of the Zapadno-Ozernoe copper-zinc massive sulphide deposit. Its characteristic feature is its unique mineral composition which distinguishes it as a distinct stratigraphic unit of the supergene profile. The quartz-sulphide sand of the 'black zone' is a black sand-like mass composed of quartz, pyrite and dzharkenite of various compositions, with minor amounts of other rare supergene sulphides, such as galena, tetrahedrite, metacinnabarite, tiemannite, sulpharsenides of Pb of the jordanite group, and undetermined sulphosalts of Hg and Ag.

Sulphides and selenides form grains of irregular form, up to 1 mm in size (Fig. 1). In reflected

light, Fe sulpho-selenides are pinkish-yellow, isotropic, with rather high indices of reflection (Table 1). The compositions of the Fe sulpho-selenides vary gradually from core to edge. The probe diameter of the microspectrophotometer used is 0.3 mm, so the reflectance data presented display only approximate values of *R*, and do not

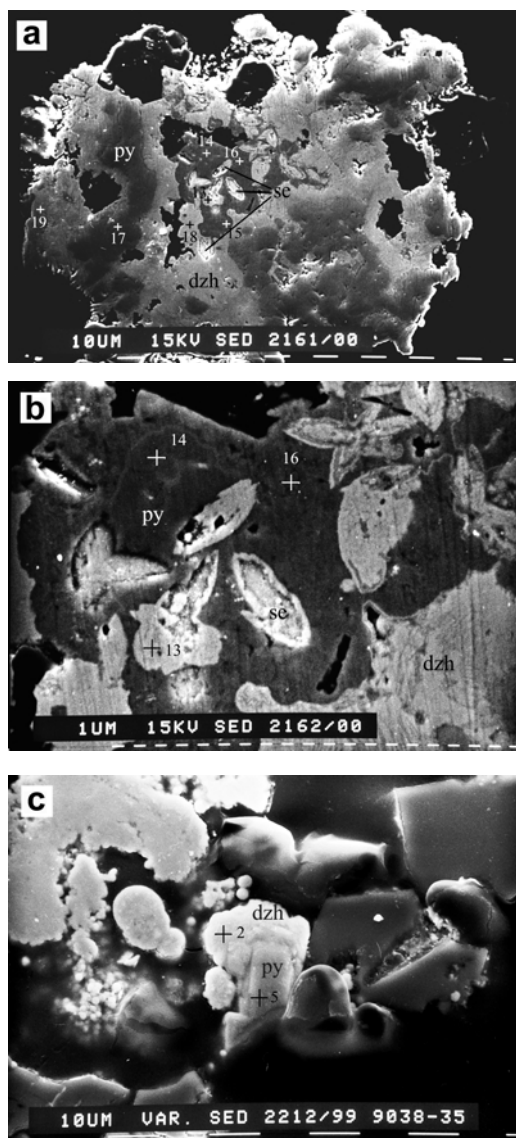


FIG. 1. Sulpho-selenides from the Zapadno-Ozernoe deposit: (a, c) dzharkenite rim around pyrite relic, (b) pyrite and dzharkenite with native Se (py: pyrite, dzh: dzharkenite, se: native selenium).

SOLID-SOLUTION BETWEEN PYRITE AND DZHARKENITE

TABLE 1. Approximate values of R of Fe sulpho-selenides (air, average from 12 measurements).

λ (nm)	R (%)	λ (nm)	R (%)
400	39.0	560	40.3
420	38.1	580	41.1
440	37.1	600	41.6
460	36.4	620	42.1
480	36.4	640	42.9
500	37.7	660	43.3
520	38.5	680	43.5
540	39.2	700	43.7

refer to specific compositions of individual minerals. The reflectance spectrum of the Fe sulpho-selenide deposit is close to that of dzharkenite from the Suluchekinskoe deposit (the type locality of dzharkenite) in form, but the latter is characterized by higher values of the reflectance indices (Fig. 2).

In quartz-sulphide sands of the 'black zone', pyrite and dzharkenite are closely associated with pyrrhotite-like Fe monosulphide with a high isomorphous capacity, containing Ag, Sb, As and Se (up to 15 wt.% in total).

Dzharkenite, the Se analogue of pyrite, was discovered in the ores of the Suluchekinskoe selenium-uranium deposit located in the Dzharkenskaya depression (southeast Kazakhstan) (Yashunsky *et al.*, 1995). At the type locality, dzharkenite occurs as black octahedral crystals up to 100 μm in size in the cement of sand, together with goethite and ferroselite (Yashunsky *et al.*, 1995). Only the ferroselite

was previously known. Ferroselite contains S up to 10 wt.% (Chvileva *et al.*, 1988), dzharkenite from the type locality contains no S (Yashunsky *et al.*, 1995), the Se content of pyrite does not exceed 2–5 wt.% (Burianova, 1956; Chvileva *et al.*, 1988).

In the supergene 'black' zone of the Zapadno-Ozernoe deposit, quartz and pyrite are of at least two generations: residual, hypogene grains and secondary, supergene grains. The former are characterized by porous, cellular structures due to the processes of supergene acid leaching of massive sulphide ore. Supergene quartz forms excellent transparent crystals, up to 0.5 mm in size. Supergene pyrite forms (1) spherical aggregates and (2) flakey accumulations at the margins of hypogene pyrite. Hypogene and supergene pyrite are distinguished from each other by their chemical composition. The former is usually almost chemically pure or contains minor quantities of As and Se (up to 3 wt.% in total); the latter is enriched with Se in a solid-solution series with dzharkenite. Microprobe analyses of secondary pyrite, dzharkenite and their intermediate compositions are listed in Table 2. (It is worth noting the high quality of our analyses. The ED spectra were obtained over a period of 100 live seconds, which is twice as long as necessary for 2% relative precision. Variations in Fe sulpho-selenide compositions exceed this value considerably (2% relative)).

The data show that we must have a solid-solution series between pyrite and dzharkenite. This is confirmed by Fig. 3 which reveals a strict inverse correlation between the S and Se contents in this series. A clear 'gap' in the series is seen which may be connected with the possible limited replacement of S_2^{2-} and Se_2^{2-} groups in Fe sulpho-selenides. So the distinction between pyrite and dzharkenite is made according to the '50%' rule. Analysis 13 in Table 2 corresponds to 'maximum' dzharkenite, with the dzharkenite end-member content equal to 80.5 mol.%. Along with stoichiometric compounds, where the composition can be calculated to the formula $\text{Fe}(\text{S},\text{Se})_2$ (analyses 1, 2 in Table 2), there are non-stoichiometric compounds which when calculated using the formula mentioned above, reveal a significant lack of Fe and a surplus of anion groups. This partially accords with Prokhorov (1970) and Chvileva *et al.* (1988) who revealed the dependence of pyrite stoichiometry on its genesis conditions. In particular, they found the limits of pyrite composition to be from

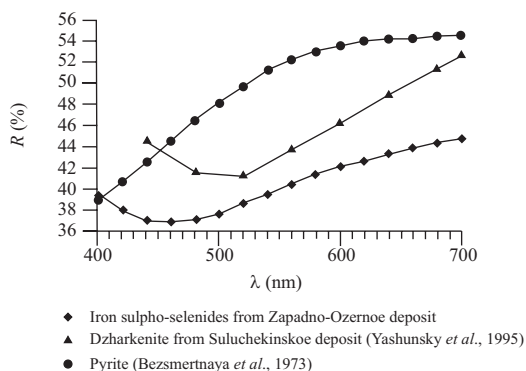


FIG. 2. Reflectance spectra of Fe sulpho-selenides from Zapadno-Ozernoe deposit in comparison with dzharkenite and pyrite.

TABLE 2. Analyses of Fe sulpho-selenides from the supergene zone of Zapadno-Ozernoe copper-zinc massive sulphide deposit (wt.%).

Analyses	Fe	Se	S	As	Sum	Formulae on the basis of $\Sigma(S+Se) = 2$
1	29.02	62.11	8.06		99.19	$Fe_{1.00}^{2+}(Se_{1.52}S_{0.48})_{\Sigma 2.00}$
2	34.97	43.30	22.00		100.27	$Fe_{1.01}^{2+}(S_{1.12}Se_{0.88})_{\Sigma 2.00}$
3	32.26	41.96	25.51		99.73	$(Fe_{0.61}^{2+}Fe_{0.26}^{3+})_{\Sigma 0.87}(S_{1.20}Se_{0.80})_{\Sigma 2.00}$
4	42.15	5.36	52.65		100.16	$(Fe_{0.64}^{2+}Fe_{0.24}^{3+})_{\Sigma 0.88}(S_{1.92}Se_{0.08})_{\Sigma 2.00}$
5	43.83	3.66	53.29		100.78	$(Fe_{0.76}^{2+}Fe_{0.16}^{3+})_{\Sigma 0.92}(S_{1.94}Se_{0.06})_{\Sigma 2.00}$
6	42.75	5.01	52.38		100.14	$(Fe_{0.70}^{2+}Fe_{0.20}^{3+})_{\Sigma 0.90}(S_{1.93}Se_{0.07})_{\Sigma 2.00}$
7	31.01	54.62	14.18		99.81	$(Fe_{0.94}^{2+}Fe_{0.04}^{3+})_{\Sigma 0.98}(S_{1.22}Se_{0.78})_{\Sigma 2.00}$
8	33.83	43.98	22.21		100.02	$(Fe_{0.91}^{2+}Fe_{0.06}^{3+})_{\Sigma 0.97}(S_{1.11}Se_{0.89})_{\Sigma 2.00}$
9	30.64	56.61	12.54		99.79	$(Fe_{0.97}^{2+}Fe_{0.02}^{3+})_{\Sigma 0.99}(Se_{1.30}S_{0.70})_{\Sigma 2.00}$
10	30.78	53.67	14.94		99.39	$(Fe_{0.88}^{2+}Fe_{0.08}^{3+})_{\Sigma 0.96}(Se_{1.19}S_{0.81})_{\Sigma 2.00}$
11	31.63	52.43	15.71		99.77	$(Fe_{0.94}^{2+}Fe_{0.04}^{3+})_{\Sigma 0.98}(Se_{1.15}S_{0.85})_{\Sigma 2.00}$
12	27.33	63.89	7.97		99.19	$(Fe_{0.79}^{2+}Fe_{0.14}^{3+})_{\Sigma 0.93}(Se_{1.53}S_{0.47})_{\Sigma 2.00}$
13	26.71	66.44	6.45		99.60	$(Fe_{0.76}^{2+}Fe_{0.16}^{3+})_{\Sigma 0.92}(Se_{1.61}S_{0.39})_{\Sigma 2.00}$
14	40.75	6.51	50.93	2.53	100.72	$(Fe_{0.58}^{2+}Fe_{0.28}^{3+})_{\Sigma 0.86}(S_{1.87}Se_{0.10}As_{0.03})_{\Sigma 2.00}$
15	40.04	10.87	48.45		99.36	$(Fe_{0.67}^{2+}Fe_{0.22}^{3+})_{\Sigma 0.89}(S_{1.83}Se_{0.17})_{\Sigma 2.00}$
16	42.46	4.91	52.81		100.18	$(Fe_{0.67}^{2+}Fe_{0.22}^{3+})_{\Sigma 0.89}(S_{1.93}Se_{0.07})_{\Sigma 2.00}$
17	41.77	10.68	46.95		99.40	$(Fe_{0.82}^{2+}Fe_{0.12}^{3+})_{\Sigma 0.94}(S_{1.83}Se_{0.17})_{\Sigma 2.00}$
18	29.30	62.69	9.03		101.02	$(Fe_{0.94}^{2+}Fe_{0.04}^{3+})_{\Sigma 0.98}(Se_{1.48}S_{0.52})_{\Sigma 2.00}$
19	34.36	44.22	20.58		99.16	$Fe_{1.02}^{2+}(S_{1.07}Se_{0.93})_{\Sigma 2.00}$
FeS ₂ theor.	46.55		53.45			FeS ₂
FeSe ₂ theor.	26.13	73.87				FeSe ₂

FeS_{1.84}–FeS_{2.10} (or Fe_{1.09}S_{2.00}–Fe_{0.95}S_{2.00} if calculated on the basis $\Sigma(S+Se) = 2.00$) corresponding with the decrease of the formation

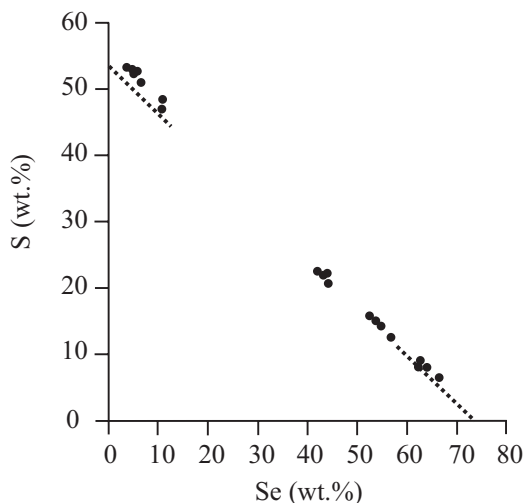


FIG. 3. Correlation between the S and Se contents in Fe sulpho-selenides from the Zapadno-Ozernoe massive sulphide deposit. The dotted line shows the miscibility range of FeS₂ and FeSe₂ in the synthetic system (Franz, 1983).

temperature (in general from high temperature hydrothermal to supergene pyrite). Our results exceed this range. The most non-stoichiometric composition is Fe_{0.86}(S,Se,As)_{2.00} (analysis 14 in Table 2). It is worth noting that the decrease in the Fe/S ratio in Fe sulphides during the supergene process was thermodynamically substantiated by Sato (1992). The lack of Fe in supergene Fe sulpho-selenides seems to be conditioned by the partial replacement of bivalent Fe by trivalent Fe under the scheme: $3Fe^{2+} \rightarrow 2Fe^{3+} + \square$, with the formation of minerals with the general formula $Fe_{1-x}\square_x(S,Se)_2$. From the assumption above, the crystal-chemical formulae of pyrite and dzharckenite were calculated (Table 2). The replacement of bivalent Fe by trivalent Fe is possible, taking into consideration the location of the 'black zone' on the border between stagnant waters without free molecular oxygen and running oxygen-bearing waters. Figures 3 and 4 illustrate the correlation of Se content with relative trivalent Fe and the lack of Fe in sulpho-selenides. In spite of the absence of a strict dependence between the values being considered, two distinct groups of points stand out in these diagrams. The first corresponds to a small amount of Se in minerals and maximum

non-stoichiometry of the mineral composition. The second is characterized by commensurate amounts of S and Se and an insignificant lack of Fe, close to analyses and calculations. Such a distribution of points on diagrams might be evidence of greater isomorphous capacity of dzharkenite with respect to pyrite, rather than *vice versa*. This purpose is confirmed with the displacement of the 'gap' in the isomorphous series towards pyrite (Fig. 3).

The synthetic system $\text{FeS}_2\text{--FeSe}_2$ was studied by Franz (1983). He stated these compounds to be of limited miscibility with a maximum at 530°C (the incongruent melting point of sulpho-selenides). The 'gap' in the solid solution series $\text{FeS}_2\text{--FeSe}_2$ at this temperature is 10–68 mol.% FeSe_2 which corresponds to the absence of compositions between $\text{Fe}(\text{S}_{1.8}\text{Se}_{0.2})$ and $\text{Fe}(\text{Se}_{1.36}\text{S}_{0.64})$. Natural Fe sulpho-selenides discovered in the supergene zone of the Zapadno-Ozernoe deposit reveal a greater range of isomorphous miscibility, i.e. greater possible FeS_2 content in FeSe_2 , so the 'gap' in the series is reduced to 10–40 mol.% FeSe_2 (Fig. 3).

Unfortunately detailed X-ray investigation of Fe sulpho-selenides from Zapadno-Ozernoe massive sulphide deposit seems to be impossible for the present due to a high degree of dispersion of material and mutual intergrowths of minerals and consequent difficulties in picking out mono-

mineral fractions. An attempt was undertaken to estimate the dzharkenite structure on the basis of X-ray analyses of pyrite-dzharkenite aggregates. All the grains analysed were found to be mixtures of pyrite, greigite and dzharkenite. The peaks are broad, and this has an adverse affect on the quality of the measurements. Pyrite is often characterized with increased a parameter, up to 0.01 Å. When being indexed as for pyrite, dzharkenite reveals high values of the a parameter: in different grains it varies from 5.54 up to 5.77 Å. These values are close to PDF data for dzharkenite ($a = 5.7830$ Å, PDF card No. 1246). The XRD data for dzharkenite from the Zapadno-Ozernoe deposit need to be refined.

Our thermodynamic calculations in the system Fe-S-Se- H_2O show that FeSe_2 precipitation is permitted under supergene conditions near the oxidizing/reducing boundary (Fig. 5). This may occur via either of two principal mechanisms: (1) $\text{FeS}_2 + 2\text{Se}^0 \rightarrow \text{FeSe}_2 + 2\text{S}^0$. The condition for this process to occur is a reducing environment with pH 2.2–6.0 (corresponding with redox and Eh-pH characteristics of the environment, the right hand side of the equation may contain not S^0 but SO_4^{2-} or H_2S). In this case the compounds of intermediate composition $\text{Fe}(\text{S},\text{Se})_2$ are likely to occur. In nature this reaction is expressed in the substitution of pyrite and native selenium with dzharkenite (Fig. 1). (2) $\text{Fe}^{2+} + 2\text{Se}^0 + 2\text{e}^- \rightarrow \text{FeSe}_2$. This reaction could have occurred in a strongly reducing environment in the narrow interval of pH 1.1–2.2. This process should result in the formation of pure FeSe_2 (probably with a minor S content) after native Se. It is unlikely to have been realized in the supergene processes of the Zapadno-Ozernoe deposit because of the absence of pure dzharkenite.

The form and the structure of sulphide and selenide grains in quartz-sulphide sands of the 'black zone', their low degree of crystallization, the fact that their compositions are often non-stoichiometric, and their low Fe/(S,Se) ratio in conjunction with lightened isotope composition of S (the extreme value of δS^{34} is -17.20%), are indicative of their genesis under supergene conditions.

In our opinion, there is no reason why the complete solid-solution series between FeS_2 and FeSe_2 should not exist. The ionic radii (1.84 and 1.98 Å, respectively) and electro-negativity values of S^{2-} and Se^{2-} (2.6 and 2.5, respectively) are very close, (Pauling, 1932, taken from Bokiy, 1971). The high degree of miscibility of FeS_2 with

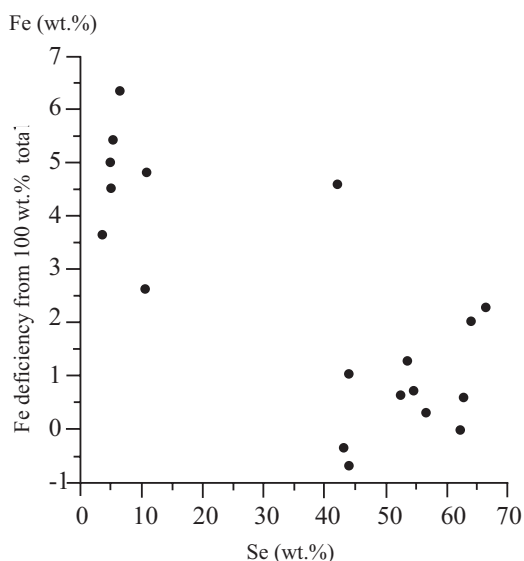


FIG. 4. Correlation of the Fe deficiency from 100 wt.% total with Se content in Fe sulpho-selenides.

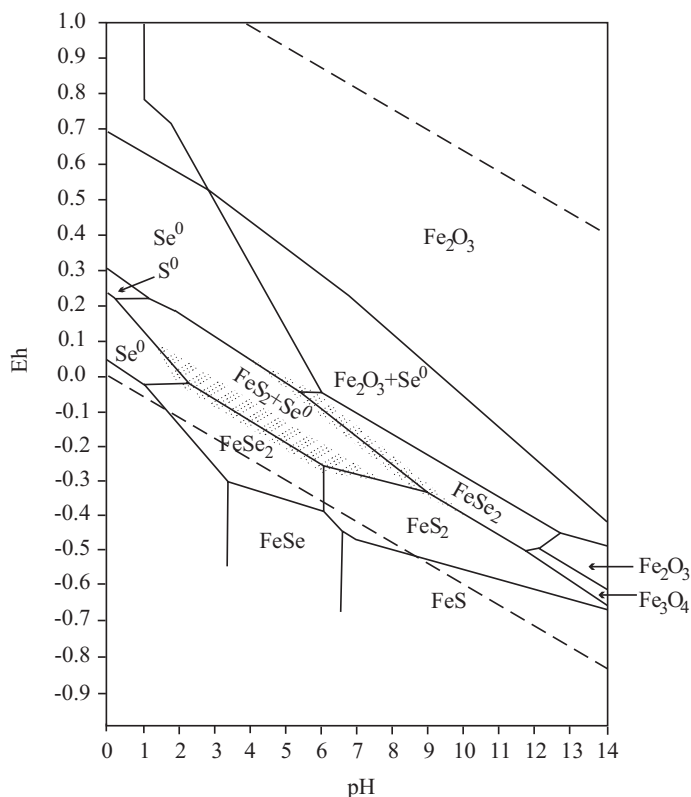


FIG. 5. Persistency field Eh-pH diagram for the system Fe-S-Se-H₂O at 25°C and 1 atm for total dissolved S of 10⁻³ and Se of 10⁻⁵ activities. The dotted lines correspond to the Eh-pH boundary of the stability field of H₂O at 1 atm. The dissolved components are not shown at the diagram. Hatching shows the approximate areas of possible intermediate compositions between FeS₂ and FeSe₂.

FeSe₂ obtained from experiments and varying compositions of pyrite and dzharkenite from the supergene zone of the Zapadno-Ozernoe deposit, as well as thermodynamic calculations, all make it feasible.

Conclusions

The discovery of secondary Fe selenides in the supergene zone of the Zapadno-Ozernoe copper-zinc massive sulphide deposit allows us to reconsider current opinion on the occurrence of Fe selenides as minerals of hydrothermal uranium-bearing deposits. The presence of minerals of intermediate composition between pyrite and dzharkenite are evidence of the existence of limited solid-solution series between the minerals indicated (and probably complete solid-solution series under certain conditions). The data obtained on the composition

of Se-bearing pyrite allow us to correct the limits of pyrite non-stoichiometry. The investigation of the mineralogy of supergene zones of ore deposits and the processes of enhancement, decomposition and precipitation of minerals under supergene conditions, provides a new perspective for such data.

Acknowledgements

We wish to record our thanks to A.R. Nesterov of St.-Petersburg State University, for his invaluable assistance in the investigation of the compositions of supergene minerals and for help with the photomicrographs. We also wish to thank Dr B. Spiro, who helped to obtain the S isotope distribution data, M.M. Boldyreva for her advice on the subject of ore microscopy, and E. Zenovich for XRD analyses of such difficult material. We are grateful to Dr J.F.W. Bowles and Dr C. Rice

for their assistance, comments and critical reviews of this manuscript. Part of this study was supported by the programme 'Universities of Russia'.

References

- Belogub, E.V., Novoselov, K.A., Yakovleva, V.A. and Spiro, B. (2000) Supergene sulphides from Zapadno-Ozernoe massive sulfide deposit. *Transactions of the Institute of Mineralogy, Miass, Russia*, **10**, 27–34 (in Russian).
- Belogub, E.V., Novoselov, C.A., Spiro, B. and Yakovleva, B.A. (2003) Mineralogical and S isotopic features of the supergene profile of the Zapadno-Ozernoe massive sulphide and Au-bearing gossan deposit, South Urals. *Mineralogical Magazine*, **67**, 339–354
- Bezsmertnaya, M.S., Chvileva, T.N., Agroskin *et al.* (1973) *The Identification Guide of Ore Minerals by their reflection Spectra*. Nedra, Moscow, Russia, 504 pp. (in Russian).
- Bokiy, G.B. (1971) *Crystal Chemistry*. Nauka, Moscow, Russia (in Russian)
- Burianova, E.Z. (1956) About ferroselite. *Proceedings of the USSR Mineralogical Society*, **3**, 85–90 (in Russian).
- Chvileva, T.N., Bezsmertnaya, M.S., Spiridonov, E.M. *et al.* (1998) *The Identification Guide of Ore Minerals in Reflected Light*. Nedra, Moscow, Russia, 504 pp. (in Russian).
- Franz, E.-D. (1983) Die chemische Zusammensetzung von Mischkristallen mit begrenzter Mischbarkeit am Beispiel des Fe(Se,S)₂ im System FeS₂-FeSe₂. *Neues Jahrbuch für Mineralogie, Monatshefte*, 130–134.
- Prokhorov, V.G. (1970) *Pyrite*. Krasnoyarsk, Russia, 187 pp. (in Russian).
- Sato, M. (1992) Persistency-field Eh-pH diagrams for sulphides and their application to supergene oxidation and enrichment of sulphide ore bodies. *Geochimica et Cosmochimica Acta*, **56**, 3133–3156.
- Surin, S.V., Krilatov, V.A. and Kuchkildin, K.H. (1997) *Detailed investigation of gossans of Zapadno-Ozernoe copper massive sulphide deposit*. Report on geological exploration work in 1991–1997. Funds. Uchaly, Russia (in Russian).
- Yashunsky, Yu.V., Ryabeva, E.G. Abramov, M.V. and Rasulova, S.D. (1995) Dzharckenite FeSe₂ – the new mineral. *Proceedings of the Russian Mineralogical Society*, **1**, 85–90 (in Russian).

[Manuscript received 11 January 2002:
revised 18 February 2003]

