EASILY OXIDIZABLE CHALCOPYRITE FROM BLACK SMOKERS OF THE RAINBOW HIDROTHERMAL FIELD (MID–ATLANTIC RIDGE, 36°14'N)

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Anomalous chalcopyrite from newly discovered sulphide tubes of deep sea hydrothermal vents known as black smokers in the Rainbow field has been studied by a series of methods (X-ray spectral microprobe analysis, mineragraphy, scanning electron microscopy, and X-ray micro-diffraction method). In contrast to common chalcopyrite, the mineral quickly tarnishes in polished sections (high-copper sulphides of chalcocite-digenite series were detected in the oxidized film). The newly polished surface is isotropic in reflected light; the reflectance spectra belongs to chalcopyrite type, but R coefficients are much lower than standard ones (by 10-15%). The interval of values of micro-indentation VHN significantly exceeds those in common chalcopyrite (114-235 to 181-203 kgs/mm^2). These characteristics indicate that the mineral is similar to two easily oxidizable cubic sulphides of the chalcopyrite group, talnakhite and putoranite. In the chemical composition, more copper than iron was noted in the limits expressed by the empirical formula $Cu_{1-x}(Fe,Co,Ni)_{1+x}S_2$, where x changes from 0 to 0.09 at a constant ratio Me/S = 1. The mineral is identified as standard chalcopyrite by X-ray powder diffraction. There are two different reflection parts. The first ones are sharp and correspond to cubic cell with a = 5.25 Å. The second ones are wide that means disorder in chalcopyrite structure. Thus, X-ray diffraction data also confirms the similarity of easily oxidizable chalcopyrite to talnakhite and putoranite.

3 tables, 4 figures, 24 references.

In recent decades of the last century in high-temperature deposits of the Norilsk type and in dunite pegmatites of Bushveld, four sulphides have been found. They are close to chalcopyrite, but are distinguished from it by a deficiency of sulphur: their ratio Me/S>1, whereas in chalcopyrite it is equal to 1. Two of these minerals, talnakhite and putoranite, belong to the cubic system. They can be oxidized easily in the open air in polished sections. Both minerals were originally described as cubic chalcopyrite (Bud'ko, Kulagov, 1963; Genkin *et al.*, 1966; Filimonova *et al.*, 1974).

In sulphide silts of the Red Sea in the Atlantis II deep, isotropic chalcopyrite was discovered and described; the proposed name was isochalcopyrite (Missack *et al.*, 1989). This name appears in the Mineralogy Database on the Internet as a mineral species that was not registered in the IMA Commission on New Minerals and Mineral Names (CNMMN).

During study of oceanic sulphide ores from black smokers of the Rainbow hydrothermal field (Mid-Atlantic Ridge, 36°14'N), an isotropic chalcopyrite, that oxidized easily in polished sections in the open air, was encountered; similar to the above-mentioned cubic minerals by properties. The results of its detailed study are given below.

General characteristic of studied mineral

The samples of ores were picked up from a depth of nearly 2300 m by deep-water inhabited apparatus (DIA) «Mir-1» during run 47 of the scientific-research ship «Academician Mstislav Keldysh» in 2002. They represent the small tubes, branches of larger tubes. Their age, when studied, was not more than two years, since during the preceding run in 2000, the intense activity of black smokers was not yet fixed in this section of the ore field.

Studied tubes belong to the copper type represented mainly by minerals of the Cu-Fe-S and Cu-S systems in contrast to the zinc type, in which sphalerite and iron sulphides predominate. The tubes were small in sizes: their length

was 5−12 cm, diameter was from 2 up to 8 cm, the thickness of the walls of the largest specimens was 30 mm. In the centre of the tubes there were one or more channels (Fig. 1).

Minerals and their structural-textural correlations in tubes were studied in polished sections made without heating, in reflected light under ore microscope and scanning electron microscope JEM-100C (IGEM). The results have shown that the tube walls had a distinct zoned structure that was described in detail in the special article (Borodaev et al., 2004). All copper tubes have a similar scheme of zoning; only the width of the zones varies. From the channel to the tube surface are the following zones: I — a zone composed of recently discovered Y phase, that is close to isocubanite (Mozgova et al., 2002); II — chalcopyrite zone represented by an easily oxidizable variety of this mineral, which is described in this work; III — bornite zone, and IV — a zone formed by an assemblage of copper sulphides (chalcocite, digenite, etc.).

The chalcopyrite zone that is of interest to us in comparison with other zones has a significantly larger width reaching 5-8 mm in some tubes. The structure of this zone (as well as the first one) is radiate-fibrous with the size of separate elongated grains up to 400 mμ. In newly polished sections in reflected light, a mineral composing this zone has a yellow colour and looks like common chalcopyrite, and is not easily distinguished by reflection and colour from the Y phase in contact with it. Because of quick oxidation in the open air, chalcopyrite looks pinkish-brown, and a border with the Y phase becomes clearly visible (Fig. 2a). At the contact between them, the lattice structure formed by lamellas of tarnished chalcopyrite in the matrix of Y phase is observed (Fig. 2b).

During the study of easily oxidizable chalcopyrite in newly polished sections it was determined that in reflected light the mineral behaves like an isotropic one: anisotropy was not observed even in immersion. Reflection was measured with automatic spectrophotometer MSFU-3121; Si was the standard; objective was 20x0.40. The results have shown (Table 1, Fig. 3a) that the reflectance spectrum of chalcopyrite from the Rainbow is very close to the same spectrum of chalcopyrite and cubic minerals of this group. At the same time, the values of reflection of studied mineral are much lower (on average 10-15%) than the corresponding values of common chalcopyrite and slightly less than the reflection coefficients of talnakhite (on average 2-3%) and putoranite (on average 1-2%). Measurement of reflection values of chalcopyrite covered by an oxidation film has shown the
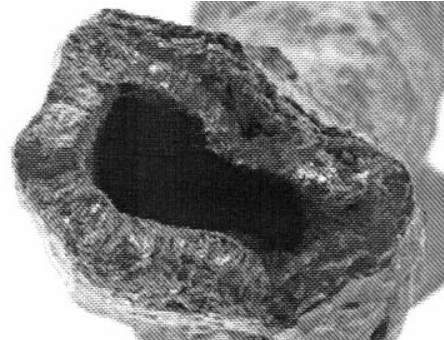

Fig. 1. Cross-section of zoned cooper tube with easily oxidizable chalcopyrite (specimen FMM No. 4412-M1-6). 1.5x
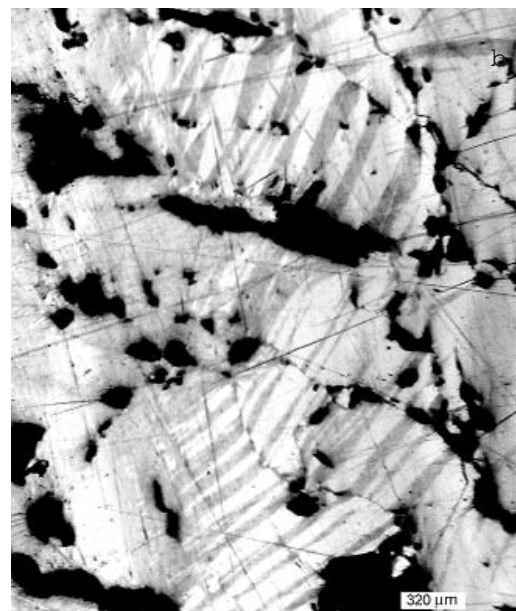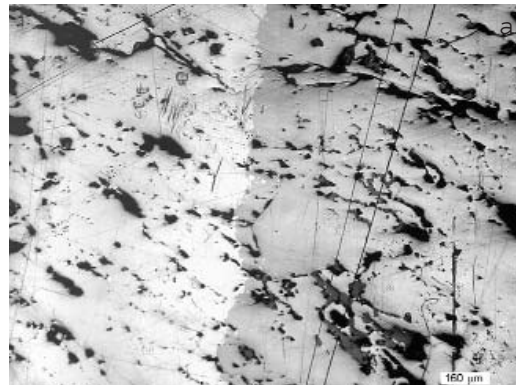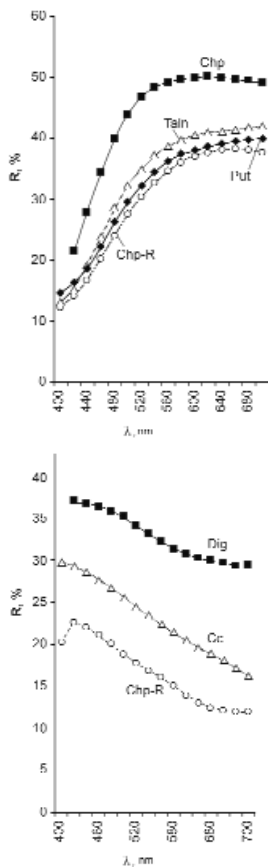

Fig. 2. Contact of a zone of easily oxidizable chalcopyrite with a zone of Y phase. Polished section in reflected light: a — zone of Y phase (white), zone of easily oxidizable chalcopyrite (grey); b — lattice structure of an aggregate directly on the contact of both zones: lamellae are easily oxidizable chalcopyrite (grey), matrix is Y phase (white)

a *Fig. 3. eflectance spectra for easily oxidizable chalcopyrite in comparison with published data (Chvileva et al., 1988): a) newly polished easily oxidizable chalcopyrite from Rainbow (Chp-R), putoranite (Put), talnakhite (Taln), and common chalcopyrite (Chp); b) reflectance spectra for chalcopyrite covered by oxidation film from Rainbow (Chp-R), digenite (Dig), and chalcosine (Cc)*

b

Table 1. **Reflectances of newly polished chalcopyrite from Rainbow (1), putoranite (2)*, talnakhite (3)*, and common chalcopyrite (4)***

λ, nm	1	2	3	4
400	12.3	14.6	13.0	—
420	14.1	16.1	15.2	21.3
440	16.6	18.7	19.2	27.9
460	20.2	22.3	23.9	34.2
480	23.9	26.1	28.6	39.8
500	27.4	29.4	32.1	43.8
520	30.3	32.2	34.9	46.7
540	32.5	34.4	37.1	48.3
560	34.5	36.1	38.7	49.1
580	36.0	37.3	39.7	49.7
600	36.9	38.0	40.4	49.9
620	37.5	38.6	40.8	50.0
640	38.0	39.0	41.2	49.9
660	38.2	39.4	41.4	49.7
680	38.0	39.6	41.8	49.4
700	37.5	39.8	42.0	49.1

***Note:** analysis marked by * done after Chvileva et al., 1988*

strong decrease of R coefficients in comparison with a newly polished surface (on an average of 20-25% in the long-wave part of the spectrum) and opposite inclination of reflectance spectrum, which is similar to spectra of digenite and chalcocite by configuration (Table 1, Fig. 3b).

Micro-indentation VHN of the studied chalcopyrite, which was obtained with PMT-3 instrument at load 30 g, is was within the limits 114-235 kgs/mm^2; according to reference data (Anthony *et al.*, 1990), it is lower than corresponding values of talnakhite (261-277 kgs/mm^2) and putoranite (263 kgs/mm^2) and significantly exceeds the fluctuation of values of chalcopyrite (181-203 kgs/mm^2).

Thus, easy oxidizability in the open air as well as optical characteristics indicate a considerable distinction of described chalcopyrite from Rainbow from common chalcopyrite and its similarity to cubic minerals of the chalcopyrite group.

Chemical composition

Chemical analyses were performed with X-ray spectral microprobe instrument CAME-BAX-SX-50 and energy-dispersive spectrometer Link ISIS on electron microscope JEM-100C. Conditions of mesurements on CAME-BAX-SX-50 were: 20 kV, 30 nA; standards (element, line) were: CuS (CuKα), FeS (FeKα, SKα).

Results obtained in comparison with data on isochalcopyrite and theoretical chemical compositions of the chalcopyrite group minerals are given in Table 2. Chemical composition of the studied mineral varied within small limits (wt %): Cu 31.23-34.75; Fe 27.87-32.26; S 34.98-36.03. Admixtures of Co (to 0.34, in one analysis up to 3.56 wt %) and Ni (0.25-1.49 wt %) were noted in insignificant amounts. In single instances Au (to 0.4 wt %) and Ag (0.1 wt %) were detected. Analyses were calculated on the formula of chalcopyrite, CuFeS$_2$. Intervals of fluctuation of formula coefficients are as follows: Cu from 0.90 to 1.01, (Fe + Co + Ni) from 0.99 to 1.08, which allows the presenting of the general empirical formula as Cu$_{1-x}$(Fe,Co,Ni)$_{1+x}$S$_2$, where x changes approximately within the limits of 0 to 0.09. At the maximum value of x = (0.09) the composition of the end-member in atomic percents is as follows: Cu — 22.75, Fe — 27.25, S — 50; which deviates from the ideal one (Cu — 25, Fe — 25, S — 50 at %) by 2.25 at % in metal contents. The ratio Me/S remains close to 1 in contrast to isochalcopyrite and the chalcopyrite group minerals, where it is always more than 1. On the triangle diagram Cu-Fe-S (Fig. 4), chem-

Table 2. **Chemical composition (wt %) of easily oxidizable chalcopyrite from Rainbow (data of electron micro-probe analysis in comparison with reference data)**

№ of sample.	№ an	Cu	Au	Ag	Fe	Co	Ni	Zn	S	Total
					Homogeneous chalcopyrite					
4-10	8	31.23	0.37	–	27.87	3.56	1.49	–	35.06	99.58
4-10	6	32.39	0.24	0.10	32.36	0.34	0.20	0.02	35.53	101.18
4412-9	6	33.35	–	0.03	31.45	n.d.	n.d.	–	35.77	100.60
4412-9	5	33.56	–	–	32.16	n.d.	n.d.	–	35.68	101.40
4412-9	32*	34.09	–	–	31.22	n.d.	n.d..	–	36.03	101.34
4-10	9	34.17	0.09	–	30.07	0.11	0.25	0.12	35.38	100.19
4412-6	15*	34.75	–	–	30.25	n.d.	n.d.	–	34.56	99.56
Average		33.36	0.10	0.02	30.77	0.57	0.28	0.02	35.43	100.55
				Lamellae from disintegration structures						
4412-9	3L	32.63	0.40	–	31.85	n.d.	n.d.	0.02	35.55	100.45
4412-6	7L	33.01	–	0.03	31.75	n.d.	n.d.	0.15	35.64	100.58
4412-6	10L	33.21	–	–	31.42	n.d.	n.d.	0.02	34.98	99.63
Average		32.63	0.13	0.01	31.42	0.06			35.39	100.22
			Isochalcopyrite (Atlantis II, the Red Sea) (Missack et al., 1989)							
Homogeneous		34.04	–	–	32.20	–	–	0.15	33.87	100.26
Lamellae (grain centre)**(L-1)		31.69	–	–	34.51	–	–	0.20	33.85	100.25
Lamellae (grain edge)***(L-2)		33.08	–	–	32.81	–	–	0.26	33.88	100.03
		Theoretical chemical composition of the chalcopyrite group minerals (Anthony et al., 1990)								
Chalcopyrite $CuFeS_2$		34.56			30.52				34.92	100.00
Putoranite 4* $Cu_{18}(Fe,Ni)_{18}S_{32}$		35.68			31.22		0.51		32.49	99.9
Putoranite 5* $Cu_{16}(Fe,Ni)_{19}S_{32}$		32.99			32.11		1.63		33.14	99.87
Talnakhite $Cu_9(Fe,Ni)_8S_{16}$		37.15			29.10		0.75		33.31	100.31
Mooihoekite $Cu_9Fe_9S_{16}$		36.02			31.66				32.32	100.00
Haycockite $Cu_4Fe_9S_8$		32.18			35.35				32.47	100.00

N	Cu	Fe	Co	Ni	Zn	Σ Fe, Co,Ni	S	ΣMe	Me/S	Cu/Fe
					Formula coefficients (calculation on 4 atoms in formula).					
					Homogeneous chalcopyrite					
8	0.90	0.92	0.11	0.05		1.08	2.01	1.99	0.99	0.83
6	0.92	1.05	0.01	0.01		1.07	2.01	1.99	0.99	0.86
6a	0.95	1.02				0.95	2.02	1.98	0.98	0.93
5	0.95	1.04				1.04	2.01	1.99	0.99	0.91
32*	0.97	1.01				1.01	2.03	1.97	0.97	0.96
9	0.98	0.98		0.01		0.99	2.02	1.98	0.98	0.99
15*	1.01	1.00				1.00	1.99	2.01	1.01	1.01
Average	0.96	1.00	0.02	0.01		1.03	2.01	1.99	0.98	0.93
				Lamellae from disintegration structures						
3L	0.94	1.04				1.04	2.02	1.98	0.98	0.90
7L	0.94	1.03				1.03	2.02	1.98	0.98	0.91
10L	0.96	1.03				1.03	2.00	1.99	1.00	0.93
Average	0.95	1.04				1.04	2.02	1.99	0.99	0.91
			Isochalcopyrite (Atlantis II, the Red Sea) (Missack et al., 1989)							
Homogeneous	0.99	1.06					1.95	2.05	1.05	0.93
L-1	0.92	1.14			0.01		1.94	2.07	1.07	0.80
L-2	0.96	1.08			0.01		1.95	2.05	1.05	0.88

	Cu	Fe	Ni	S	ΣMe	Me/S	Cu/Fe
		Chemical composition of the chalcopyrite group minerals					
Chalcopyrite	1	1		2	2	1	1
Putoranite 4*	18		18	32	36	1.12	1
Putoranite 5*	16		19	32	35	1.09	0.84
Talnakhite	9		8	16	17	1.06	1.12
Mooihoekite		9	9	16	18	1.12	1
Haycockite	4	5		8	9	1.12	0.8

Note. *Analysts: I.A. Bryzgalov (CAMEBAX, MSU); *N.V. Trubkin (Link, IGEM RAS); ** − average from 5 analyses; *** − average from 3 analyses; 4* − average from 7 analyses; 5* − average from 12 analyses; n.d. -not detected; dash − not determined*
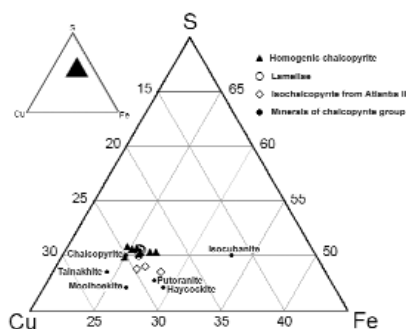
Fig. 4. Distribution of chemical compositions of easily oxidiz-able chalcopyrite (homogenous and lamellae in structures of decomposition of solid solution) from Rainbow, isochalcopy-rite from Atlantis II (Missack et al., 1989), and the chalcopyrite group minerals (Anthony et al., 1990) on the triangle Cu-Fe-S-diagram (at %)

ical compositions of analysed chalcopyrite from Rainbow lies on intersection answering to a ratio of Me/S = 1. From the theoretical composition of chalcopyrite they moved slightly towards an increase of Fe content, towards isocubanite. Points of theoretical compositions of all other minerals of the group are below this intersection on the diagram.

X–ray data

Material extracted from the part of the chal-copyrite zone of a tube analysed with an elec-tron microprobe instrument was used for X-ray study. Registration of the spectrum was carried out by an automatic diffractometer Rigaku D/Max-2000/PC, Cu-K$_\alpha$ radiation, at continu-ous scanning with a rate of 0.1° (2θ)/s. Correction by means of the Si standard was used in the calculation.

The results of the X-ray study in compari-son with standard data for tetrahedral chal-copyrite and cubic chalcopyrite are given in Table 3. Comparison with the chalcopyrite standard gives satisfactory coincidence of X-ray powder patterns and calculated sizes of unit cells.

At the same time, the X-ray diffraction pattern of the studied sample had a number of peculiarities (Table. 3). Some of its reflexes are visibly widened. It is obvious from the third column, where the full width at the half of maximum (FWHM) is given for each reflection; FWHM grows with increase of reflection angle. There are the mainly weak ones that belongs to chalcopyrite tetragonal system (reflections No. 4, 6, 10). As it is evident from the table, sharp and strong reflections correspond to reflections of cubic chalcopyrite.

In addition, X-ray powder patterns were made by Debye-Scherrer method (diameter of camera is 114) with Si standard. The results obtained on material extracted from previously analysed samples on a newly polished section correspond to tetragonal chalcopyrite. On the X-ray powder pattern obtained from microamounts of oxidized chalcopyrite covered by a grey film there are several additional weak lines (intensity of 1-2) in small angle region. Among them the lines with interplanar distances 2.558 and 2.193 are similar to reflexes (2.54, 2.59, and 2.16) of standard X-ray powder pattern of anilite, Cu_7S_4, which belongs to high-copper sul-phides of the chalcocite-digenite series: chal-cocite, djurleite, anilite, digenite, with Cu/S from 2 to 1.125 (Gablina et al., 2000).

Discussion

As was mentioned above, in studied chal-copyrite the maximum deviation from the stoi-chiometric ideal formula is 2.25 at % for metals. This is within the limits (2.4 at %) of the chemical composition of chalcopyrite from continental deposits, obtained by processing of the publil-shed reference data (Lafitte, Maury, 1982). As is known from experimental data, the close limits (from $CuFeS_2$ to $Cu_{0.9}Fe_{1.1}S_2$) were detected in hydrothermal conditions for a very narrow range of chalcopyrite solid solution at 350 °C and 300 °C in the Cu-Fe-S (Sugaki et al., 1975) and Cu-Fe-Zn-S (Ueno et al., 1980) systems. Consequently, chalcopyrite from Rainbow does not differ by chemical composition from common natural and synthetic chalcopyrites in spite of isotropy, easy oxidizability, low values of reflectance and micro-indentation hardness.

In putoranite and talnakhite the same change of properties was presumably connect-ed with the filling of vacancies in chalcopyrite crystal structure by additional metal atoms (Filimonova et al., 1974; 1980), since these min-erals are distinguished from chalcopyrite by a surplus of metals (Me/S>1). The explanation of the unusual characteristics of chalcopyrite from Rainbow are evidently also explained by peculiarities of crystal structure. It is most probably the widening of some reflexes on X-ray diffraction patterns is caused by the defects in crystal structure. Judging by the above-mentioned similarity of strong and sharp peaks of obtained X-ray powder pattern to reflections of cubic chalcopyrite, the distribu-tion of cations by sulphur tetrahedra differs slightly from the cubic one. It means a tenden-cy for statistic distribution of different cations

Table 3. X-ray diffraction data for easily oxidizable chalcopyrite in comparison with standards

Studied sample № 4412-6				Standard of chalcopyrite (83-0983 JCPDS)			Standard of cubic chalcopyrite (75-0253 JCPDS)		
№	I	d	FWHM*	I	d	hkl	I	d	hkl
1	100	3.04	0.169	100	3.036	112	999	3.0183	111
2	4	2.65	0.474	4.3	2.643	200	66	2.614	200
3	20	1.871	0.258	16.8	1.869	220	487	1.8483	220
4	32	1.857	0.275	32.5	1.854	204			
5	17	1.593	0.301	18.2	1.5916	312	269	1.5763	311
6	9	1.576	0.339	4.8	1.5712	116			
7	1.5	1.520	0.726	1	1.5181	224	11	1.5091	222
8	2.5	1.3578	0.502	1	1.3506	323			
9	4	1.3225	0.438	3.5	1.3216	400	52	1.3070	400
10	1.8	1.3033	0.567	1.8	1.3013	008			
11	3.2	1.2132	0.488	2.6	1.2118	332	76	1.1993	331
12	5	1.2052	0.423	5.1	1.2038	316			
13	1.4	1.1601	0.715	0.2	1.1687	208	7	1.1687	420
	$I\overline{4}2d$			$I\overline{4}2d$			$F\overline{4}3m$		
	$a = 5.289(2)$			$a = 5.2864(1)$			$a = 5.228$		
	$c = 10.422(6)$			$c = 10.4102(1)$			$V = 142.89$		
	$V = 291.56$			$V = 290.9$					

*Note: *FWHM — full width at half maximum*

in tetrahedra. In common tetragonal chalcopyrite, copper and iron atoms have strictly ordered distribution, but in cubic chalcopyrite they are completely disordered. The indistinct character of peaks on X-ray diffraction pattern determines with a high degree of probability is determined by the incomplete order of different cations between different positions.

A question about details of this phenomenon demands an additional study with use of microdiffraction methods and high-precision electron microscopy. Since chalcopyrite belongs to semi-conductors and has antiferromagnetic properties (Vaugan, Kreig, 1978), the study of magnetic and electromagnetic characteristics is also perspective.

Obtained data allow the consideration of some peculiarities of the oxidation process of described chalcopyrite. It is known, that a question about the valency of copper and iron in chalcopyrite was disputed for a long time, and results from the Messbauer spectra of this mineral are discrepant. Nevertheless, recently the formula of chalcopyrite was presented in the form of $Cu^+Fe^{3+}S_2$, where iron is in higher oxidation degree and copper is univalent (Vaugan, Kreig, 1978). If this formula is used as the basis, then in chalcopyrite from Rainbow only copper atoms can be exposed to oxidation: $Cu^+ \rightleftarrows Cu^{2+}$. Possibly, the process is not complete. A surplus of Cu^+ atoms formed during this process diffuses on the surface of a polished section for maintenance of charge balance; where it forms a film of high-copper sulphides of the chalcocite-digenite series, in which univalent copper dominates.

Thus, the process of copper oxidation is accompanied by copper diffusion. In this connection, it is essential to emphasize that copper in the crystal structures of Cu-bearing minerals often has high mobility. So, in high-copper fahlores, according to X-ray data (Makovicky, Skinner, 1976), part of the copper ions is in motion, without fixing on definite sites; this in many respects determines the nonstoichiometry of these minerals (Mozgova, Tsepin, 1983). It is also known that on the surface of polished sections of Cu-bearing minerals during their exposure to the open atmosphere, new formations of copper sulphides in the form of bushy aggregates and films appear (Mozgova *et al.*, 1994).

Previously published studies show that the Cu-Fe-S system, which was intensively studied during the last century (Merwin, Lombard, 1937; Schlegel, Schuller, 1952; Hiller, Probsthain, 1956; Yund, Kullerud, 1966; Cabri, 1973; Likhachev, 1973, *etc.*), still holds many riddles demanding further study with a variety of methods.

Acknowledgements

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