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## TETRAGONAL $\text{Cu}_2\text{S}$ IN RECENT HYDROTHERMAL ORES OF RAINBOW (MID ATLANTIC RIDGE, 36° 14'N)

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The ores samples were investigated taken from active chimneys of the Rainbow hydrothermal field (MAR, 36° 14' N) at a depth of 2,276 m in Cruise R/V 47 of research vessel «Academician Mstislav Keldysh» (2002). Optical, microprobe and X-ray analytical methods were used. The basic method of mineral identification was X-ray analysis (Debye powder photomethod). Samples were fragments of small hydrothermal chimneys having a zonal structure: in direction from the channel to the external wall, isocubanite zone («phase Y») is replaced by chalcopyrite zone, then follows bornite zone, which to the periphery gradually passes into a copper sulfide zone. For the first time the tetragonal form of  $\text{Cu}_2\text{S}$  — metastable isomorph of chalcocite, which stability is limited by the field of high pressure (above 0.8 kilobar) and temperature (above 102°C) — was discovered in modern ocean ore. Tetragonal  $\text{Cu}_2\text{S}$  was identified in one sample in a mixture with chalcocite and djurleite, in the other — in a mixture with bornite. The parameters of its lattice cell designed from an X-ray powder pattern are:  $a = 4.0042\text{Å}$ ,  $c = 11.3475\text{Å}$ ,  $V = 181.938\text{Å}^3$ , average composition of 4 measurements is  $\text{Cu}_{2.02}\text{S}$ . The find of high-temperature tetragonal isomorph of chalcocite in modern deep-water active smokers seems natural. Formation of Rainbow sulfide ore occurs under the pressure of water column more than 2000 m and at temperature of 250–362°C. Tetragonal chalcocite is not met in earlier investigated by us inactive (relict) constructions of more ancient Logachev field. After the extinction of hydrothermal activity  $\text{Cu}_2\text{S}$  soon passes into non-stoichiometric sulfide minerals more stable in sea-water ambient.

Until recently, only three minerals were known in the system Cu-S: chalcocite, digenite and covellite. The studies of fiftieth-eightieth years of the last century (Djurle, 1958; Roseboom, 1962, 1966; Morimoto *et al.*, 1969; Skinner, 1970; Goble, 1980; Goble, Robinson, 1980; Mumme *et al.*, 1988, etc.) have shown that quite often under these names other minerals are interpreted, close to them by composition, structure and ranges of stability. Now, ten natural compounds of the system Cu-S and two synthetic phases, unstable at usual temperature (hexagonal chalcocite and cubic digenite) are known. Non-stoichiometric minerals — ratio Cu/S in them varies from 1 to 2 — predominate among copper sulfides (Table 1). The big variety of non-stoichiometric minerals in the system Cu-S is conditioned by the fact that even insignificant deviation of copper sulfide structure from stoichiometry is accompanied by structural reorganization of their crystal lattice, i.e. formation of a new mineral individual. The deviation from stoichiometry is conditioned by partial entry of bivalent (oxidized) copper into the crystal lattice of minerals (Belov, 1953; Eliseev *et al.*, 1964; Goble, 1985), which is usually

related to oxygen presence in the mineral-forming system. N.V. Belov considered the digenite formula as  $\text{Cu}^{+}_{1.6}\text{Cu}^{2+}_{0.2}\text{S}$ . By analogy to this, E.N. Eliseev *et al.* (1964) have proposed for non-stoichiometric copper sulfide the general formula:  $\text{Cu}^{+}_{2-y}\text{Cu}^{2+}_{0.5y}\text{S}$ , in which the content of bivalent copper grows proportionally to the number of defects in the sulfide structure. As a result, in the presence of oxygen, Cu/S ratio changes, though the sum of valencies of cations and anions is preserved in the structure. Later this assumption has been confirmed by studies of lattice cell sizes and character of electron bonds by the method of monocrystal survey (Goble, 1985). R.Goble in quoted work has shown that the content of bivalent copper in sulfide increases with decrease of Cu/S ratio. Stability of the majority of non-stoichiometric sulfides is rather limited and phase transformations are frequently irreversible. These features, as well as ability of non-stoichiometric copper sulfides to fast phase transformations at insignificant oscillations of physical or chemical parameters of environment, allow to use them as indicators of mineralogenesis conditions and subsequent transformations under the

Table 1. Structure, composition, limits of stability temperature of minerals of the system Cu-S (Djurle, 1958; Roseboom, 1966; Morimoto, Koto, 1969; Skinner, 1970; Potter, Evans, 1976; Potter, 1977; Grace, Cohen, 1979; Goble, 1980; Goble, Robinson, 1980; Mumme *et al.*, 1988, *etc.*)

Mineral	Composition	System	Symmetry of sulfur sublattice	Stability limits °C	Phase transformation product
Chalcocite (high)	Cu <sub>2.00</sub> S	Hexagonal	HSCP	102±2 — 452±3	Digenite (high)
Chalcocite (low)	Cu <sub>1.993-2.001</sub> S	Monoclinic	HSCP	< 0 — 102±2	Chalcocite (high)
Tetragonal Cu <sub>2-x</sub> S (x = 0-0.04)	Cu <sub>1.96-2.00</sub> S	Tetragonal	CFC	102 — 340* 340 — 500(?)**	Chalcocite (high) Digenite (high)
Djurleite	Cu <sub>1.93-1.96</sub> S	Monoclinic	HSCP	< 0 — 93±2	Chalcocite + Digenite
Roxsbyite	Cu <sub>1.72-1.82</sub> S	Monoclinic	HSCP	< 0 — 65-70	Digenite (low)
Digenite (high)	Cu <sub>2</sub> S	Cubic	CFC	> 1000	Melt
Digenite (low)	Cu <sub>1.75-1.78</sub> S	Rhombic	CFC	18 — 76-83	Digenite (high)
Anilite	Cu <sub>1.75</sub> S	Rhombic	CFC	< 0 — 30	Digenite (low)
Geerite	Cu <sub>1.5-1.6</sub> S	Rhombic (pseudocubic)	CVC	n.d.	n.d.
Spionkopite	Cu <sub>1.4</sub> S	Hexagonal	HSCP	< 0 — 157	Covellite
Yarrowite	Cu <sub>1.1</sub> S	Hexagonal	HSCP	< 0 — 157	Covellite
Covellite	CuS	Hexagonal	HSCP	< 0 — 507	Digenite (high)

Notes:

CFC — cubic face-centered, CVC — cubic volume-centered, HSCP — hexagonal supercompact packing.

\* — at pressure > 1 kilobar, \*\* — at pressure > 9 kilobar. (Grace, Cohen, 1979), the rest — at 1 bar, n.d. — not determined.

impact of endogenous and exogenous factors (Gablina, 1993, 1997). The nanoscale particles, frequently characteristic of copper sulfide segregations, similarity of structure and optical characteristics, low stability (possibility of phase transformations at storage and preparation of samples) hardly hinder the study of these minerals, require the specific approach and application of a complex of methods. The most informative among them is X-ray analysis.

Tetragonal form of Cu<sub>2</sub>S-Cu<sub>2-x</sub>S — a metastable compound met in natural ores, but not having the status of a mineral — occupies a special place among copper sulfides. In literature it is referred to as «tetragonal phase», «tetragonal form of Cu<sub>2</sub>S» or «tetragonal chalcocite». For the first time this compound was received in experiments on a high-temperature synthesis of copper sulfide (Djurle, 1958; Roseboom, 1962; Janosi, 1964). As these studies have shown, the synthetic tetragonal form of chalcocite is a metastable phase originating at polymorphic transition of high-temperature hexagonal chalcocite into cubic modification (at 430–450° C after different authors) or into monoclinic (at 102° C). It was established (Roseboom, 1966) that the tetragonal phase forms a solid solution from Cu<sub>2</sub>S to Cu<sub>1.96</sub>S. Synthesized at increased temperatures (above ~100° C), it can be tempered at room temperature, but with time it passes into low-temperature polymorphs — monoclinic chalcocite or djurleite — depending on initial structure. As the experiments have shown, the samples synthesized at most high temperatures (above 350° C) are the most stable at usual conditions. Tetragonal form Cu<sub>1.96</sub>S in experiments (Roseboom, 1966) was safe even after four years of stay at room tempera-

ture. E. Roseboom in the quoted work states the assumption that tetragonal form of Cu<sub>1.96</sub>S is more stable at usual conditions than tetragonal Cu<sub>2</sub>S, which stability is limited to the field of high pressures (more than 0.8 kilobar). In an experimental work (Grace, Cohen, 1979), the field of stability of tetragonal Cu<sub>2</sub>S is determined in limits 102–500° C and 1–13.5 kilobar. Researchers consider the limit of the field to a certain measure conditional because of lack of data (Grace, Cohen, 1979). The restriction of tetragonal Cu<sub>2</sub>S stability by the field of high pressure is reflected in its density: specific weight of tetragonal Cu<sub>2</sub>S, determined by B. Skinner (1970), is 5.932, that is much higher than specific weight of usual (monoclinic) chalcocite (5.783) and djurleite (5.747±0.005). Under optical characteristics, the tetragonal form does not differ from usual chalcocite and is only diagnosed on the basis of X-raying. The roentgenogram of the tetragonal form essentially differs from roentgenograms of monoclinic chalcocite and djurleite (Table 2). The most typical for it are reflections 2.740 and 2.302.

Studies of features of natural distribution of Cu-S system sulfides have shown that non-stoichiometric copper sulfides are typomorphic minerals of exogenous ore — copper sandstones and shales, zones of secondary sulfide enriching and oxidation. The stoichiometric chalcocite is more typical for ores of endogenous origin (Gablina, 1997). Metastable tetragonal form of Cu<sub>2</sub>S-Cu<sub>2-x</sub>S in the nature is registered extremely rarely and usually in high-temperature formations: in sulfide crusts, which have precipitated on well casings from thermal salt brines of Solton Sea (Skinner *et al.*, 1967) and in the exocontact of the magmatogenic deposit of Talnakh (Gablina, 1992).

Table 2. Interplanar distances in tetragonal Cu<sub>2</sub>S in polymineral mixtures: with monoclinic chalcocite and djurleite (Test 2); with bornite and admixture of djurleite (Test 5)

Sample 4393-2 (Test 2)		Djurleite (Roseboom, 1962)		Monocline chalcocite (Potter, Evans, 1976) <sup>2)</sup>		Tetragonal Cu <sub>2</sub> S (Janosi, 1964)			Sample 4412-6 (Test 5)		Bornite (Berry, Thom- pson, 1962)	
I	d, Å	I <sup>1)</sup>	d, Å	I	d, Å	I	d, Å	hkl	I	d, Å	I	d, Å
		1	4.28						15	4.18*		
10	3.81*	1	3.89	25	3.735							
		2	3.752									
		2	3.586	13	3.599							
20	3.41*	5	3.386									
		1	3.35	6	3.336							
				18	3.315							
20	3.29	3	3.282	35	3.276	16	3.27	1 0 2	30	3.27	40	3.31
		3	3.192	18	3.188				40	3.17	60	3.18
		2	3.100	25	3.158							
30	3.03*	3	3.04	13	3.057				30	3.02*	5	3.01
		3	3.01	18	2.952							
				13	2.933							
		2	2.89	6	2.886							
30	2.816*	1	2.82			20	2.827	1 1 0	30	2.819	20	2.80
100	2.751	6	2.785	13	2.765	100	2.740	1 0 3	90	2.753	50	2.74
				9	2.732							
		1/2	2.73	35	2.726							
		1	2.69	18	2.668							
		1	2.654	18	2.620							
		1/2	2.595									
50	2.540*	1	2.557	6	2.562							
				13	2.533							
		1/2	2.514	18	2.527				40	2.510	40	2.50
		1	2.477	18	2.477							
40	2.408**	1/2	2.41	50	2.407							
				70	2.403							
		9	2.387	35	2.399							
90	2.317			25	2.330	80	2.302	1 0 4	70	2.309		
30	2.273	1/2	2.289	13	2.242	30	2.259	1 1 3				
				35	2.210							
		1/2	2.142	6	2.182				20	2.134	20	2.13
		1/2	2.107	9	2.120							
		1	2.069									
		1/2	2.047	6	2.028							
80	2.003**			9	2.012	30	1.998	2 0 0	50	2.004		
				9	1.981							
80	1.972**	9	1.964	70	1.975	30	1.967	2 0 1				
		9	1.957	13	1.952							
				6	1.911				100	1.937	100	1.937
				70	1.881	35	1.883	2 0 2	30	1.886		
				100	1.880							
				9	1.877							
70	1.874*	10	1.871	9	1.875							
				6	1.799							
20	1.773			6	1.788	12	1.764	1 1 5	20	1.764		
60	1.714**	1	1.693	9	1.709	30	1.704	2 1 2	40	1.706		
				13	1.704							
				13	1.687				10	1.664	30	1.652
50	1.616					12	1.614	2 1 3	20	1.613		
50	1.488*	1	1.514			6	1.495	1 0 7	30	1.488*		
40	1.407					30	1.401	2 1 5	20	1.405		
									10	1.368	20	1.370
40	1.331					8	1.330	1 0 8	10	1.327	5b	1.335
10	1.283*	12	1.283									
20	1.264	6	1.26			18	1.260	1 1 8	20	1.262	50b	1.258
20	1.239					12	1.234	3 1 2	20	1.238		
30	1.200					16	1.196	1 0 9	10	1.197	10b	1.198
									20	1.116	50	1.119
30	1.093					18	1.087	3 0 6				

\* — djurleite lines or strengthened by it; \*\* — the same for chalcocite

<sup>1)</sup> — in 10-score scale

<sup>2)</sup> — the strongest lines (above 5) are shown out of 93 in the quoted work

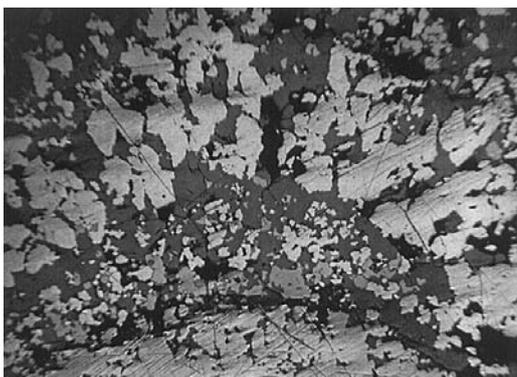


FIG. 1. Copper sulfide (light) in the peripheral zone of active channel wall. Gray — bornite, dark gray — sulfates. Polished section.  $\times 90$

In a single case, the find of tetragonal  $\text{Cu}_{1.96}\text{S}$  was mentioned in hypogene formations on a wall of adit of the Mina Maria in Chile (Clark, Sillitoe, 1971). Authors of this work do not exclude that their find can appear to be an artifact. However, in experiments on leaching of synthetic chalcocite at usual temperature and pressure, a tetragonal form occurred as a transition to digenite, and then to anilite (Whiteside, Goble, 1986).

### Materials and methods of studies

Samples from active chimneys of the Rainbow hydrothermal field (MAR,  $36^{\circ} 14' \text{N}$ ) discovered in 1997, were investigated. Samples were collected in the zone of «smokes» at a depth of 2,276 m with the help of deep-water device «Mir-1» in Cruise VR/V 47 of research vessel «Academician Mstislav Keldysh» in the summer of 2002. The authors have investigated two samples: # 4393-2 and # 4412-6. Samples were small tubes in diameter to 7 cm, broken off from larger active chimneys or their aggregates. The dimensions of the last change at length from several tens of centimeters to one and a half meters at diameter to 25 cm. Chimneys are covered with a red crust of iron hydroxides and have hollow channels with smooth surfaces.

Optical, microprobe and X-ray methods of analyses were used. Optical studies were conducted on an ore microscope in polished sections, which were produced from cross cuts of chimneys without heating. Chemical compositions of minerals were investigated on the microanalyser «Camebax SX-50» in the Moscow State University (analysis conditions: accelerating potential 20 kV, sound current 10 milliamperes, standards for Fe and S — natural pyrite, for Zn — synthetic ZnSe, for other elements — pure metals), and also in the Moscow State Building University on the microanalyser «Camebax microbeam». Quantitative analysis was conducted with the help of

program ZAF-4. Conditions of the analysis: accelerating potential 20 kV, analyzed field 1.5–2 microns, standards for Fe and S — natural pyrite, for other elements — pure metals. Ti, Ni, Ag, Au, Zn, Pb, Sb, As, Bi, Mg, Co, Se, Ce, La were determined in addition to basic elements (Cu, Fe, S). Errors of the analysis (mass %): Cu  $\pm$  0.2-0.6, Fe  $\pm$  0.1-0.2, S  $\pm$  0.15-0.26. Contents of other elements are within the limits of error ( $< 2\sigma$ ) and are not cited in the work.

The basic method of mineral identification was X-ray analysis (Debye powder photomethod) for which microsamples were selected under the microscope mainly from the sites investigated by the microprobe. Conditions of the analysis: chamber RKD-57.3 in the unfiltered Fe-radiation, time of exposition — 6 h. Intensity was determined visually by a 100-score scale. Analyses were made in X-ray laboratory of IGEM of the Russian Academy of Sciences.

### Received Results

Two samples were investigated. One of them — a fragment of a tube, elliptic in cross-section, 65 x 35 mm with wall thickness of 10 mm; another one — a part of a three-channel tube with the cross-section of 35 x 35 mm and height of 80 mm, diameter of channels from 0.5 mm to 18 mm. Tubes have a zonal structure: in the direction from the channel to the external wall isocubanite zone («phase Y») is replaced by chalcopyrite, followed by bornite zone, which to the periphery gradually passes into the zone of copper sulfides (Borodaev *et al.*, in print). In the reflected light, the zone of copper sulfides includes two non-continuous subzones of irregular width (in bulges to 1.5-2 mm): bluish-gray, adjoining to the bornite zone, and more light, gray peripheral subzone.

The first subzone is composed of mixtures of copper sulfides with bornite, which probably represents the chilled high-temperature solid solutions of chalcocite — bornite series and/or products of their disintegration. In the direction to the bornite zone, blue color of mixture very gradually passes in pink. Sometimes fine sliced structures of solid solution disintegration appear in the transition area to the bornite zone, visible in reflected light at magnification  $\times 210$ . However, in the direction from periphery to the centre, the blue matrix with pink lamellae is very gradually replaced with pink matrix with blue lamellae.

In the second subzone, sulfides of chalcocite — digenite series predominate, on periphery usually submerged in anhydrite «cement» (Fig. 1). They are mainly presented by monoclinic chalcocite or its fine mixture with tetragonal phase of  $\text{Cu}_2\text{S}$ . Sometimes non-stoichiometric minerals — djurleite and digenite (diagnosed conditionally) — occur on the periphery of chalcocite zone, forming polymineral mixtures with monoclinic

Table 3. Composition of minerals in the mixture of tetragonal phase, monoclinic chalcocite and djurleite from Rainbow active chimneys

Sample (X-ray analysis test)	Analysis	Cu	Fe	S	Total	Formula	Minerals (according to X-ray analysis, data, see Table 2)
4393-2(Test 2)	15	79.642	0.158	19.393	99.193	Cu <sub>2.07</sub> S	Monoclinic chalcocite and tetragonal phase
4393-2(Test 2)	17	79.464	0.437	19.739	99.640	Cu <sub>2.03</sub> S	Monoclinic chalcocite and tetragonal phase
4393-2(Test 2)	18	79.556	0.083	20.018	99.657	Cu <sub>2</sub> S	Monoclinic chalcocite and tetragonal phase
4393-2(Test 2)	19	78.411	0.201	19.818	98.430	Cu <sub>2</sub> S	Monoclinic chalcocite and tetragonal phase
	Average of 4	79.268	0.220	19.742	99.230	Cu <sub>2.02</sub> S	Monoclinic chalcocite and tetragonal phase
4393-2	33*	77.749	0.054	21.114	98.917	Cu <sub>1.86</sub> S	Digenite (?)
44393-2(Test 2)	20	78.154	0.413	20.101	98.668	Cu <sub>1.96</sub> S	Djurleite
4393-2(Test 2)	34*	79.547	0.083	20.621	100.251	Cu <sub>1.96</sub> S	Djurleite
4393-2(Test 2)	35*	78.599	0.106	20.552	99.257	Cu <sub>1.93</sub> S	Djurleite
	Average of 3	78.512	0.164	20.597	99.273	Cu <sub>1.95</sub> S	Djurleite
Theoretical composition of chalcocite			79.86	-	20.14		Cu <sub>2</sub> S
Composition of djurleite (Roseboom 1966)			79.53	-	20.47		Cu <sub>1.96</sub> S

\* — analyses made by the Moscow State University, the others — by the Moscow State Building University

chalcocite and/or tetragonal Cu<sub>2</sub>S. In rare cases, spionkopite and yarrowite replacing listed above copper sulfides are registered.

Tetragonal Cu<sub>2</sub>S is interpreted in roentgenograms in both investigated samples: in one of them (sample 4393-2, test 2) — in a mixture with chalcocite and djurleite, in the other (sample 4412-6, test 5) — in a mixture with bornite (Table 2).

Test 2 for X-raying was selected from the most homogeneous massive part of the copper sulfide zone. Optical characteristics of the analyzed copper sulfide in reflected light (gray color, weak anisotropy) are identical to usual chalcocite, it has xenomorphic-granular structure with the size of separate grains 0.01 to 0.2 mm, rarely larger. Its average composition (from 4 measurements) is Cu<sub>2.02</sub>S (Table 3). In some sites, in the light microscope at magnification x210, the irregular sliced structure is observed (bluish-gray lamellae in gray matrix). In the electronic microscope, the difference between these phases is not fixed because of structural similarity. The data of X-raying of test 2 indicated in Table 2 allow to interpret them as a mixture of three minerals: usual (monoclinic) chalcocite, its tetragonal form and djurleite. Judging by maximum intensity of the basic peaks of tetragonal form of Cu<sub>2</sub>S in the roentgenogram, it predominates in the mixture. Parameters of lattice cell of this phase, designed from the X-ray powder pattern of test 2 are: a = 4.0042 Å, c = 11.3475 Å, V = 181.938 Å<sup>3</sup>, they are close to those published for tetragonal Cu<sub>1.96</sub>S: a = 4.008 Å, c = 11.268 Å (Djurle, 1958). Bluish-gray plates in inhomogenous sites are probably represented by djurleite, which presence is confirmed by the data of X-ray and microprobe studies. The average composition of djurleite (3 measure-

ments) corresponds to formula Cu<sub>1.95</sub>S (Table 3).

Test 5 was taken from the peripheral zone of sample 4412-6, being a thin mixture of copper sulfides and bornite. At usual magnifications in reflected light it has grayish-blue color and looks homogeneous, only local indistinct plots of more intensive bluish-gray color can be noted. In the immersion at magnification x950, a very fine structure of breakup of the mixture is observed: brownish laths to 20 microns thick (bornite) are submerged in a bluish matrix (copper sulfide). The matrix has emulsion-sliced structure of the second order disintegration: it consist of very thin emulsion and bluish-gray laths with higher reflection. Laths are basically thin and short, but separate laths are to 40 microns long. To the periphery, the number and size of bornite laths gradually decreases to complete disappearance. The brownish phase is present at separate sites as thin emulsion.

Under the electronic microscope, the disintegration structure is not fixed. Etching with HNO<sub>3</sub> reveals xenomorphic-granular structure of the mixture with grains 0.05 to 0.25 mm. Grains increase and acquire subradial orientation in the direction from periphery, rich in copper sulfides, to the contact with the chalcopyrite zone. Each grain is usually characterized by fine mosaic fissuring and consists of allotriomorphic aggregate of more fine (0.01-0.03 mm) polygonal isometric grains. Grain borders cross plates of disintegration. The described structures can result from crystallization of solid solution originally segregated as a colloid. The breakup of solid solution probably preceded the crystallization of colloid.

The X-raying identified bornite and tetragonal form of chalcocite approximately in equal ratio in the mixture by intensity of the basic lines (Table 2).

Table 4. Chemical compositions of mixture of copper sulfides and bornite from active chimneys of the Rainbow (sample #4412-6, test #5)

No analysis	Cu	Fe	S	Sum	Formula	Minerals	Chalcocite/ bornite (n,S)
1	72.682	4.346	21.491	98.519	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.10}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	0.867
2	73.242	3.882	20.617	97.741	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.21}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	0.768
4	72.012	4.564	21.254	97.830	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.20}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	0.973
5	73.012	3.430	21.232	97.674	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.02}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	0.592
6	70.032	6.275	22.078	98.385	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.26}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	1.879
7	68.811	7.737	22.998	99.546	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.39}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	3.397
11	71.025	5.440	21.776	98.242	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.18}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	1.345
12	70.346	5.455	22.413	98.214	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.01}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	1.267
13	69.168	6.722	22.853	98.743	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{2.10}\text{S}$	Mixture bornite with tetragonal phase of $\text{Cu}_2\text{S}$	2.080
14	69.333	6.309	23.218	98.860	$\text{Cu}_3\text{FeS}_4 + \text{Cu}_{1.92}\text{S}$	Mixture bornite with djurleite (?)	1.659

Analyses made by the Moscow State Building University

Several additional reflections allow to assume the presence of djurleite admixture. The composition of two major phases of the mixture (9 measurements) was designed on the basis of stoichiometric formula of bornite, though usually the composition of bornite in association with chalcocite differs from the stoichiometry towards enrichment in copper and impoverishment in sulfur. This probably explains the overestimation in some cases of the copper content in the structure of tetragonal chalcocite (Table 4).

Quantitative relations of copper sulfides and bornite in the mixtures, designed by sulfur, oscillate in a wide range: from 0.592 to 3.397 (Table 4). It is known that copper sulfides of chalcocite – digenite series easily form solid solutions with bornite. Already at temperature above 65° C, synthetic bornite and digenite form limited solid solutions and above 330° C — unlimited solid solutions, which at fast cooling can be chilled and exist in a metastable state (Kullerud, 1959). No doubt that the investigated mixtures represent the initial products of breakup of chalcocite – bornite solid solutions and wide oscillations of quantitative ratios of coexisting phases can indicate high temperatures of their formation.

## Discussion

Thus, the metastable tetragonal form of chalcocite, which is stable in a limited field of high pressure (above 0.8 kilobar) and temperature (above ~100° C) was detected for the first time in modern hydrothermal ocean ores. At low temperature and atmospheric pressure, this unstable compound with time passes into low-temperature polymorphs of the corresponding composition. As follows from generalization of published experimental data (Gablina, 1993), stability of tetragonal modification of  $\text{Cu}_2\text{S}$  directly depends on synthesis temperature and the most stable are tetragonal structures of composition  $\text{Cu}_{1.96}\text{S}-\text{Cu}_2\text{S}$  synthesized at temperature above 350-400° C. The find of high-temperature dense polymorph of chalcocite in modern deep-water active smoker is natural, as well as its association with solid solutions of chalcocite – bornite series. Formation of

Rainbow sulfide ore occurs under pressure of water column more than 2000 m and at increased temperatures: the measured temperatures of fluids in the Rainbow hydrothermal field are 250–362° C (Bogdanov et al., 2002). In similar conditions, the tetragonal form has been earlier established in sulfide crusts of thermal salt brines of Solton Sea, where it was present as lamellae of solid solution breakup in bornite. The temperature of salt brines is 300–350° C. In 30 months at room temperature, the tetragonal phase in samples of sulfide crusts has completely passed into chalcocite (Skinner et al., 1967).

In experiments on leaching and dissolution of chalcocite by iron sulfate at usual temperature and pressure, the tetragonal phase formed as a short-time transition product (Whiteside, Goble, 1986). It was observed at low concentration of iron sulfate ( $10^{-2}$ – $5 \cdot 10^{-2}$  M) in the solution. The further leaching resulted in transformation of tetragonal phase into digenite, then anilite and other non-stoichiometric sulfides with increasing shortage in copper. At higher concentration of iron sulfate in the solution ( $> 10^{-1}$ ), the initial product of chalcocite leaching was djurleite. The fact that tetragonal  $\text{Cu}_2\text{S}$  was met in Rainbow sulfide constructions not only in mixtures with monoclinic chalcocite and djurleite, but also in products of breakup of the high-temperature chalcocite – bornite solid solutions, indicates that in this case it is not a result of oxidation and leaching of chalcocite, but an initial hydrothermal mineral preserved in specific thermodynamic conditions of functioning of deep-water thermal sources. This conclusion is also confirmed by the fact that the tetragonal chalcocite is not met in investigated in detail inactive (relict) constructions of more ancient Logachev field. There, products of chalcocite oxidation — djurleite, anilite, geerite, spionkopite, yarrowite and covellite — develop together with rare relics of chalcocite (Gablina et al., 2000). Currently, roxsbyite as a product of djurleite oxidation is established by the X-ray analysis. Apparently, tetragonal polymorph of chalcocite could be considered a typomorphic mineral of active «smokers», but nevertheless it remains an exotic find, since after the extinction of hydrothermal

activity it is soon converted in non-stoichiometric sulfide minerals more stable against the impact of sea-water ambient. Already now admixture of djurleite and presumably digenite — initial products of chalcocite oxidation — are present in the mixture of monoclinic chalcocite and its tetragonal form in the investigated samples; on the external wall of chimneys these minerals are substituted by low-copper sulfides — spionkopite and yarrowite.

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