# ORICKITE FROM THE KHIBINY
# ALKALINE COMPLEX (KOLA PENINSULA)
# AND ITS STRUCTURE FEATURES

Igor V. Pekov
*Lomonosov Moscow State University, Geological faculty; GEOKHI RAS, Moscow; igorpekov@mail.ru*

Vasiliy O. Yapaskurt, Igor A. Bryzgalov, Natalia V. Zubkova
*Lomonosov Moscow State University, Geological faculty, Moscow*

The hydrous sulfide of Fe and Cu, orickite, was found for the second time in the world at the Khibiny alkaline massif (Kola Peninsula, Russia). It was discovered at the Koashva mountain, in cavities of hydrothermally altered peralkaline pegmatite with natrolite, aegirine, astrophyllite, lorenzenite, fluorapatite, fluorite, burbankite, sphalerite, chlorbartonite, amicite, vishnevite, elpasolite and other minerals. Orickite forms hexagonal laminar crystals (up to 1.5 mm) of bronze-yellow color with metallic luster. Chemical composition of the mineral (wt.%, electron microprobe data) is: Na $0.0-0.2$, K $0.1-0.2$, Ca $0.05-0.2$, Tl $0.0-0.3$, Fe $27.7-31.7$, Cu $29.9-33.8$, Zn $0.2-0.9$, S $28.8-34.0$, O $5.2-8.6$. The average empirical formula of the best studied sample is: $Ca_{0.01}Cu_{1.01}Fe_{1.03}Zn_{0.01}S_{1.95} \cdot 0.83H_2O$. The simplified formula of orickite is: $CuFeS_2(H_2O)_{1-x}$, where $0 \leq x \leq 0.8$. According to X-ray powder diffraction patterns, for orickite is suggested, as the most probable, hexagonal symmetry, space group $P6_3mc$ and structure model corresponding to wurtzite with disordered distribution of $H_2O$ molecules that form layers (or their "fragments"), statistically substituting pairs of layers [(Fe,Cu)-S]. The Khibiny orickite represents intergrowth of two polytypic modifications, one of which (predominant) corresponds to wurtzite-2H ($a = 3.71(4)$, $c = 6.16(3)$ Å — according to single-crystal data; $a = 3.700(2)$, $c = 6.137(6)$ Å — according to X-ray powder data), and the second one — to wurtzite-4H (according to X-ray powder data: $a = 3.700(2)$, $c = 12.267(12)$ Å).
3 tables, 2 figures, 17 references.
Keywords: orickite, hydrous sulfides, wurtzite structure type, alkaline pegmatites, Khibiny massif, Kola Peninsula.

Orickite, a hudrous sulfide of iron and copper, discovered by R. Erd and J. Czamanske (Erd, Czamanske, 1983), was known up till now only in high-alkaline pegmatoids of small diatreme of Coyote Peak (California, USA), composed mainly of phlogopite, schorlomite, aegirine, sodalite, pectolite and natrolite. Interesting feature of these rocks is unique variety of sulfides containing as species-forming components alkaline metals and/or $H_2O$ molecules: these are djerfisherite, bartonite, chlorbartonite, rasvumite, erdite, coyoteite and orickite. The latter was studied very insufficiently: absence of individuals suitable for single-crystal X-ray investigation allowed us to judge about structural features only by X-ray powder-diffraction pattern. Even, inspite of its bad quality (diffused lines), it was revealed undoubted relationship of orickite with wurtzite-2H that made it possible to characterize a new mineral as hexagonal one with parameters of unit cell $a = 3.695(10)$, $c = 6.16(1)$ Å, V $= 72.8$ Å$^3$. However, the authors did not exclude for it also ortho rhombic pseudohexagonal symmetry. On the basis of electron microprobe data (Table 1, an. 1) for orickite it was established

the formula $Na_xK_yCu_{0.95}Fe_{1.06}S_2 \cdot zH_2O$ ($x$, $y <$ 0.03, $z < 0.5$) (Erd, Czamanske, 1983), which is often written in simplified form: $CuFeS_2 \cdot 0.5H_2O$.

We made the second find of orickite — on the Koashva mountain in the Khibiny alkaline massive (Kola Peninsula, Russia). The mineral was found in 2007 by I.V. Pekov and A.S. Podlesnyi in peralkaline pegmatite uncovered in a quarry operating for the apatite deposit Koashva. By the present time this pegmatite, located at the level $+100$ m at south-western part of the quarry, is destructed by mining workings.

The pegmatite body was represented by a lens with about 3 m in length, situated in urtite near the contact with nepheline-apatite rock. Its marginal zone was composed mainly of microcline and aegirine with minor amounts of nepheline, sodalite, alkali amphibole, eudialyte, titanite, lamprophyllite, lorenzenite, and fluorapatite. The major part of pegmatite volume is its cavernous core, formed by hydrothermal minerals, among which substantially predominated natrolite and green thin needle-shaped, aegirine, and subordinate components were represented by astro-
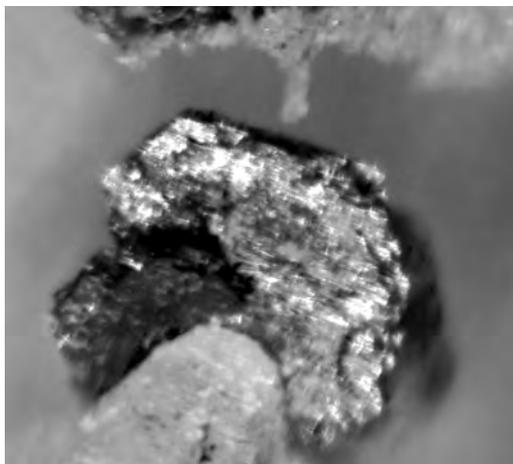
*Fig. 1. Orickite crystal (0.4 mm across) on natrolite. Koashva Mountain, Khibiny massif, Kola Peninsula, Russia. Photo: I.V. Pekov and A.V. Kasatkin.*

phyllite, fluorapatite, intermediate members of ilmenite-pyrophanite series, titanite, lorenzenite, fluorite, burbankite, and sphalerite, as well as solid bitumen in the form of spherical aggregations. In small amounts were present pectolite, chlorbartonite, tainiolite, lamprophyllite, barytolamprophyllite, vinogradovite, leucophanite, amicite, vishnevite, elpasolite, labuntsovite-Mn, catapleiite, zircon, pyrochlore, galena, orickite, and Na-bearing Fe-rich chlorite-like mineral.

Orickite occurs in caverns of aegirine-natrolite aggregates. It forms lamellar hexagonal crystals (Fig. 1) typically, not perfect, bended and split in different degree with uneven surface, and their intergrowths, including fan-like or similar to open book. Size of its crystals is typically up to 0.5 mm, and intergrowths — up to 2 mm. Well-shaped crystals of orickite are found for the first time. Their main habit form is pinacoid {001}, we did not manage to determine indexes of side faces. Mineral individuals are soft, flexible, easily split along plane of perfect, mica-like cleavage {001}, giving thin flakes. The orickite color is bronze-yellow, luster is metallic. Under the influence of air the mineral gradually darkens and becomes dull.

Chemical composition of the Khibiny orickite was determined by means of electron microprobe method for several crystals in two laboratories.

At the chair of petrology of Moscow State University (analyst V.O. Yapaskurt) the mineral was studied using scanning electron microscope Jeol JSM-6480LV with combined system microanalysis (Table 1, an. 2). Analysis was carried out in conjugated regime: contents of metals and sulfur were measured using energy-dispersive spectrometer INCA-Energy 350 (window ATW-2), oxygen — by wave dispersive four-crystal spectrometer INCA-Wave 500. Conditions of analysis: accelerating voltage 15 kV, beam current 45.8 nA, beam area from 12 to 100 $\mu m^2$, duration of accumulation of energy-dispersive spectrum — 100 sec. (dead time 32%), duration of accumulation of signal at measurement of oxygen concentration at peak — 20 sec., at background — 10 sec. Standards: Cu, Fe, S — CuFeS2; Zn — ZnS; Ca, O — $CaWO_4$.

At the chair of mineralogy of Moscow State University (analyst I.A. Bryzgalov) the mineral was studied by wos method using a Camebax SX 50 microanalyzer (Table 1, an. 3). Accelerating voltage 15 kV, beam current 30 nA, duration of accumulation of signal at peak is 10 sec, at background — 5 sec at each side. Analyses were carried out by defocused beam at the area of 10 × 10 $\mu$m. Standards: Cu — covellite; Fe, S — FeS; Na — albite; K — $KTiPO_5$; Tl — lorandite.

Contents of the main components — Cu, Fe and S, obtained for the Khibiny orickite in two laboratories, are very close to each other and differ slightly from corresponding data for the specimen from Coyote Peak (Table 1). Concentrations of Na and K vary, but are low, in the Khibiny mineral are discovered also small admixtures of Ca and Tl. Content of oxygen in orickite from Khibiny is considerably higher, than in Californian one: calculated on its content average amount of $H_2O$ in our specimen is $0.83H_2O$ per formula (unit $Cu + Fe + Zn + S = 4$), while in the mineral from Coyote Peak it varies in the limits of $(0.18 - 0.61)H_2O$. Thus, the simplified orickite formula can be modified as follows: $CuFeS_2(H_2O)_{1-x}$, where the value $x$ ranges, according to empiric data, from 0.0 to 0.8.

We tried to study single-crystal of Khibiny orickite using a Xcalibur S CCD diffractometer, MoKα-radiation. Unfortunately, all tested crystals proved to be useless for structural analysis due to curring and/or splitting. However, for the first time we determine parameters of orickite unit cell by the single-crystal method: the mineral is hexagonal, $a = 3.71(4)$, $c = 6.16(3)$ Å.

Powder X-ray diffraction study of the Khibiny orickite was carried out by Gandolfi

*Table 1.* **Chemical composition of orickite from Coyote Peak, California, USA (1), and Khibiny, Kola Peninsula, Russia (2−3)**

| Component | 1 | 2 | 3 |
|---|---|---|---|
| | | wt.% | |
| Na | 0.4 (0.2−0.5) | bdl | 0.08 (0.00−0.2) |
| K | 0.2 (0.05−0.25) | bdl | 0.14 (0.1−0.2) |
| Ca | | 0.15 (0.05−0.2) | non determ. |
| Fe | 31.0 (30.0−32.2) | 28.90 (27.7−31.7) | 29.45 (28.1−29.9) |
| Cu | 31.7 (30.8−32.7) | 32.01 (29.9−33.8) | 30.91 (30.3−31.7) |
| Zn | 0.49 (0.2−0.9) | non determ. | |
| S | 33.6 (33.1−34.4) | 31.30 (28.8−34.0) | 31.41 (30.2−32.4) |
| O | 1.5−5.1 | 6.60 (5.2−8.6) | non determ. |
| [$H_2O$ calc] | [1.7−5.7] | [7.43] | |
| Total | 96.9 *(without oxygen)* | 99.45 [100.28][*] | 92.10[**] |
| | number of atoms per formula, calculation for $(Cu + Fe + Zn + S) = 4$ | | |
| Na | 0.03 | — | 0.01 |
| K | 0.01 | — | 0.01 |
| Ca | | 0.01 | |
| Fe | 1.06 | 1.03 | 1.06 |
| Cu | 0.95 | 1.01 | 0.98 |
| Zn | | 0.01 | |
| S | 1.99 | 1.95 | 1.96 |
| $H_2O$ | 0.18−0.61 | 0.83 | |

*Note: 1 − Erd, Czamanske, 1983, 2, 3 − our data for two different crystals (average for 6 analyses in each case).*
*[*] − value of analytical total in square brackets includes not O but $H_2O$; [**] − total includes also 0.11 % Tl (average for 6 analysis with range: 0.0−0.3 % ); bdl − below detection limit by electron microprobe method; non determ. − component was not determined.*

metod using single-crystal diffractometer STOE IPDS II (the chair of crystallography St. Petersburg State University), equipped by IP detector. MoKα-radiation was used. Our powder diffraction pattern in its strongest reflections is very close to the X-ray powder pattern of the Californian orickite, but additionally includes 7 more reflections (Table 2). All its reflections, excluding one with $d = 1.938$ Å, are well indexed in the hexagonal cell suggested in (Erd, Czamanske, 1983) and based upon the cell of wurtzite-2*H*. Refined by 17 lines from 18 ones (excluding the above mentioned with $d = 1.938$ Å) parameters of unit cell of orickite from Khibiny are: $a = 3.700(2)$, $c = 6.137(6)$ Å, $V = 72.8(2)$ Å$^3$. Lines of X-ray powder pattern of our specimen, as well as Californian one, are brooden and diffuse.

With support on new X-ray data, we tried to analyze in more details, than authors of the first description, the specific features of orickite structure.

In 1988 was described a new mineral chvilevaite, $Na(Cu,Fe,Zn)_2S_2$, trigonal, $a = 3.873$, $c = 6.848$ Å (Kachalovskaya *et al.*, 1988), and then it was characterized its crystal structure,

which proved to be derivative from wurtzite structure, but with another law of alternating of layers of three types: S, transition metals (Cu, Fe, Zn) and Na; this induced lowering of symmetry from $P6_3mc$ for wurtzite to $P3m1$ for chvilevaite (Kaplunnik *et al.*, 1990; Fig. 2). Very close structure, although other space groups, has the whole family of chvilevaite-like synthetic sulfides and selenides: $Na(CuFe)S_2$, $Li(CuFe)S_2$, $Li(CuFe)Se_2$ — $P$-$3m1$ (Ramirez *et al.*, 2001), $Na(Cu_{1.54}V_{0.46})S_2$ — $P$-$3$ (Mujica *et al.*, 1996). It is interesting that change of layers of Na or Li atoms for the layers of more large K, Cs or Tl results in transition from the structural type of trigonal chvilevaite to the structural type of tetragonal bukovite (Ramirez *et al.*, 2001), to which is related murunskite $K(CuFe)S_2$, also occurring at the Koashva mountain (Pekov *et al.*, 2009) in pegmatites of the same type that orickite does, but only less altered by late hydrothermal processes.

Based on chemical composition, stoichiometry, dimensions of unit cells, and structural similarity to wurtzite, one of the authors of the present article in 2006 suggested that orickite could be an analogue of chvilevaite with layers of molecules $H_2O$ instead of

*Table 2.* **X-ray powder data for orickite, wurtzite-2*H* and wurtzite-4*H***

| hkl(2H) | Orickite | | | | | Wurtzite-2H | | | | Wurtzite-4H | | hkl (4H) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Koashva Mount, Khibiny massif (our data) | | | Coyote Peak (Erd, Czamanske, 1983) | | synthetic (Swanson, Fuyat, 1953) | | calculated accord. to (Kisi, Elcombe, 1989) | | calculated accord. to(Chao, Gault, 1989) | | |
| | $I_{meas.}$ | $d_{meas.}$, Å | $d_{calc.}$, Å | $I_{meas.}$ | $d_{meas.}$, Å | $I_{meas.}$ | $d_{meas.}$, Å | $I_{calc.}$ | $d_{calc.}$, Å | $I_{calc.}$ | $d_{calc.}$, Å | |
| 100 | 100 | 3.199 | 3.204 | 90 | 3.20 | 100 | 3.309 | 100 | 3.311 | 25 | 3.311 | 100 |
| — | | | 3.100* | | | | | — | — | 100 | 3.200 | 101 |
| 002 | 85 | 3.078 | 3.069 | 100 | 3.08 | 86 | 3.128 | 62 | 3.130 | 64 | 3.130 | 004 |
| 101 | 41 | 2.853 | 2.840 | 60 | 2.84 | 84 | 2.925 | 98 | 2.927 | 75 | 2.927 | 102 |
| — | | | 2.522* | | | | | — | — | 11 | 2.594 | 103 |
| 102 | 15 | 2.224 | 2.216 | 15 | 2.20 | 29 | 2.273 | 36 | 2.275 | 9 | 2.274 | 104 |
| — | 27 | 1.938* | 1.948* | | | | | — | — | 33 | 1.997 | 105 |
| 110 | 40 | 1.854 | 1.850 | 70 | 1.85 | 74 | 1.911 | 71 | 1.911 | 78 | 1.911 | 110 |
| 103 | 19 | 1.736 | 1.724 | 55 | 1.73 | 52 | 1.764 | 69 | 1.765 | 58 | 1.765 | 106 |
| 200 | | | 1.602 | | | 10 | 1.654 | 10 | 1.655 | 3 | 1.655 | 200 |
| — | | | 1.589* | | | | | — | — | 13 | 1.641 | 201 |
| 112 | 13 | 1.593 | 1.584 | 30 | 1.583 | 45 | 1.630 | 44 | 1.631 | 50 | 1.631 | 114 |
| 201 | 8 | 1.550 | 1.550 | 3 | 1.543** | 12 | 1.599 | 13 | 1.600 | 12 | 1.600 | 202 |
| 004 | | | 1.534 | | | 2 | 1.564 | 1 | 1.565 | 2 | 1.565 | 008 |
| 202 | 4 | 1.417 | 1.420 | | | 5 | 1.462 | 7 | 1.463 | 2 | 1.463 | 204 |
| 104 | 5 | 1.370 | 1.384 | | | 1 | 1.414 | 1 | 1.415 | 0.4 | 1.415 | 108 |
| 203 | 7 | 1.265 | 1.261 | 10 | 1.261 | 14 | 1.296 | 21 | 1.297 | 19 | 1.297 | 206 |
| 210 | 3 | 1.213 | 1.211 | | | 6 | 1.251 | 7 | 1.251 | 2 | 1.251 | 210 |
| 211 | 4 | 1.187 | 1.188 | | | 3 | 1.226 | 9 | 1.227 | 8 | 1.227 | 212 |
| 105 | 4 | 1.149 | 1.146 | 5 | 1.146 | 4 | 1.170 | 14 | 1.171 | 14 | 1.171 | 1.0.10 |
| 212 | 4 | 1.119 | 1.127 | | | 8 | 1.161 | 6 | 1.162 | 2 | 1.162 | 214 |
| 204 | | | 1.108 | | | <1 | 1.136 | 0.4 | 1.137 | 0.2 | 1.137 | 208 |
| 300 | 5 | 1.070 | 1.068 | | | 13 | 1.103 | 9 | 1.104 | 12 | 1.104 | 300 |
| 213 | 12 | 1.042 | 1.042 | 5 | 1.043 | 6 | 1.072 | 20 | 1.073 | 21 | 1.073 | 216 |
| symmetry and parameters of unit cell, Å | | | | | | | | | | | | |
| | hex., $P6_3mc$ (?) | | | hex., $P6_3mc$ (?) | | hex., $P6_3mc$ | | hex., $P6_3mc$ | | hex., $P6_3mc$ | | |
| | $a$ 3.700 | | | $a$ 3.695 | | $a$ 3.820 | | $a$ 3.8227 | | $a$ 3.8227 | | |
| | $c$ 6.137 | | | $c$ 6.16 | | $c$ 6.254 | | $c$ 6.2607 | | $c$ 12.52 | | |

*Note. The Table does not include reflexes of theoretical X-ray powder patterns of wurtzite with intensites <10, which are not observed upon experimental X-ray powder patterns. For wurtzite-2H they are (hkl−d, Å) 114−1.211 and 301−1.087, and for wurtzite-4H: 002−6.260, 006−2.087, 112−1.828, 107−1.574, 203−1.539, 116−1.409, 205−1.381, 109−1.282, 0.0.10−1.251, 211−1.245, 207−1.215, 118−1.211, 213−1.199, 215−1.119, 301−1.094, 302−1.087 ana 1.0.11−1.076. Strike line means that reflex is impossible by symmetry (P6_3mc) for wurtzite-2H.*
*\* − reflexes possible for modification of orickite corresponding in unit cell dimensions to wurtzite-4H, but not to wurtzite-2H;*
*\*\* − reflex with d = 1.543 Å is considered in original work as 004 (Erd, Czamanske, 1983) but, basing upon relationships of intensities in calculated X-ray powder patterns of wurtzite, this is most probably 201.*

Na atoms, which could arise as a result of leaching from the latter of Na and hydration: $Na(Cu,Fe)_2S_2 \rightarrow (Cu,Fe)_2S_2 \cdot 0.nH_2O$ (Pekov, 2006).

However, investigation of orickite, found in 2007 at the Khibiny massif, shows, that this mineral and chvilevaite most probably are not direct structural analogues. Thus, at X-ray powder pattern of chvilevaite are present strong reflexes 001 and 111, as well as weaker lines 003 and 113 (Kachalovskaya *et al.*, 1988), impossible according to symmetry for wurtzite ($P6_3mc$, $a$ = 3.823, $c$ = 6.261 Å; Kisi, Elcombe, 1989). These reflections are absent for orickite (Table 2), if we ignore weak reflex with $d$ = 1.370 Å at the X-ray powder pattern of the Khibiny specimen, which one could interpret as 113. However, it could be considered most probably as 104: appearance of the weak line 113 with simultaneous absence of
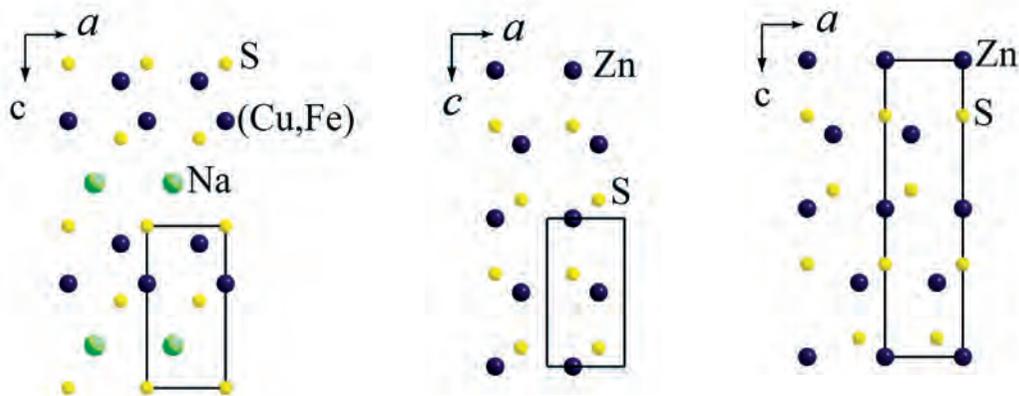
*Fig. 2. Crystal structures of chvilevaite (a), wurtzite-2H (b) and wurtzite-4H (c) in the ac projection. Parameters of the unit cell are shown. Drawn using data from: a — Kaplunnik et al., 1990; b — Kisi, Elcombe, 1989; c — Chao, Gault, 1989.*

strong reflex 111 seems to be hardly probable. We simulated with the help of program LAZY PULVERIX (Yvon *et al*., 1977) X-ray powder patern of $CuFeS_2(H_2O)_{0.83}$ — hypothetical analogue of chvilevaite, at which Na is replaced for $H_2O$ with preserving symmetry *P3m*1, and parameters of unit cell (as well as occupancy of $H_2O$ position) correspond to the Khibiny orickite. Comparison of this theoretical X-ray powder pattern with experimental one of the Khibiny orickite (Table 3) shows essential differences which have systematic character. At the first place they are represented by absence at orickite a reflex 001 ($d$ = 6.14 Å) and very high intensity of reflex 002 ($d$ = 3.078 Å), whereas at hypothetical chvilevaite-like $CuFeS_2(H_2O)_{0.83}$ reflection 001 should be very strong, and reflection 002 — weak. We should also note an absence at the experimental X-ray powder pattern of orickite reflexes 003 and 111, impossible according to symmetry of wurtzite ($P6_3mc$), but rather intensive for its derivatives, crystallized in space groups *P-3m*1, *P3m*1 and *P-3* (X-ray powder patterns of the mentioned above synthetic chvilevaite-like phases were also simulated by us).

Set of reflexes and their intensities for orickite are the most similar with ones for wurtzite-2*H*. It was noted by R. Erd and J. Czamanske (Erd, Czamanske, 1983), and now it is confirmed by us at the X-ray powder pattern of higher quality (Table 2).

In contrast to the Californian orickite, the Khibiny one has rather strong reflex with $d$ = 1.938 Å, which violates the pattern corresponding to unit cells of both wurtzite-2*H* type and chvilevaite (Table 2 and 3). However it is well indexed as 105 while doubling the parameter *c* (Table 2). Appearance of this reflex might serve as indication for the fact, that the Khibiny orickite according to unit cell dimensions is an analogue of wutzite-4*H*, but the latter has relative intensities of reflexes 100 and 101 substantially another than for wurtzite-2*H* (Table 2). If an absence of reflex 111 ($d_{calc.}$ = 3.100 Å) yet could be explained in the frame of the model "4*H*" by its merge with the reflex 004 ($d_{calc.}$ = 3.069 Å) into single broad line with d ≈ 3.08 Å, the high intensity of the reflex 100 (the strongest reflection at all X-ray powder patterns of orickite) clearly indicate to better correspondence to the model of wurtzite-2*H*. Thus, it is possible to assume with considerable probability, that orickite as well as wurtzite are characterized by polytypism, and the Californian specimen by dimensions of its unit cell corresponds to wurtzite-2*H*, and the Khibiny one is represented by intergrowths of the same polytype, having the minimum possible by volume unit cell, with another one, with the doubled *c* parameter is in correspondence with the model of wurtzite-4*H* (Fig. 2). Calculation of parameters of its unit cell by 18 lines, including reflex with $d$ = 1.938 Å, results in: $a$ = 3.700(2), $c$ = 12.267(12) Å, V = 145.5(3) Å$^3$. Judging from relations of reflex intensities at the X-ray powder pattern of the Khibiny specimen, the polytype with small unit cell predominates.

Due to absence at the orickute X-ray powder pattern of other reflexes, first at the low-angle area ($d$ > 3.25 Å), it is possible to con-

**Table 3.** Comparison of experimental X-ray powder data of orickite from Khibiny and calculated data of hypothetical analogue of chvilevaite with composition $CuFeS_2(H_2O)_{0.83}$, space group $P3m1$ and parameters of unit cell $a = 3.700$, $c = 6.137$ Å

| Orickite | | CuFeS₂(H₂O)₀.₈₃ | | hkl |
|---|---|---|---|---|
| $I_{meas.}$ | $d_{meas.}$, Å | $I_{calc.}$ | $d_{calc.}$, Å | |
| | | 80 | 6.137** | 001** |
| 100 | 3.199 | 100 | 3.204 | 100 |
| 85 | 3.078 | 9 | 3.069 | 002 |
| 41 | 2.853 | 56, 27 | 2.840 | 011, 101 |
| 15 | 2.224 | 57, 14 | 2.216 | 102, 012 |
| | | 18 | 2.046** | 003** |
| 27 | 1.938* | | | |
| 40 | 1.854 | 69 | 1.850 | 110 |
| | | 9, 9 | 1.771** | 111**, 11-1** |
| 19 | 1.736 | 16, 35 | 1.724 | 013, 103 |
| | | 11 | 1.602 | 200 |
| 13 | 1.593 | 4, 4 | 1.584 | 112, 11-2 |
| 8 | 1.550 | 3, 8 | 1.550 | 021, 201 |
| | | 1 | 1.534 | 004 |
| 4 | 1.417 | 3, 12 | 1.420 | 202, 022 |
| 5 | 1.370 | 4, 1 | 1.384 | 104, 014 |
| | | 13, 13 | 1.372** | 113**, 11-3** |
| 7 | 1.265 | 5, 11 | 1.261 | 203, 023 |
| | | 1 | 1.227** | 005** |
| 3 | 1.213 | 4, 4 | 1.211 | 210, 120 |
| 4 | 1.187 | 2, 1, 2, 1 | 1.188 | 21-1, 12-1, 121, 211 |
| | | 1, 1 | 1.181 | 114, 11-4 |
| 4 | 1.149 | 4, 4 | 1.146 | 105, 015 |
| 4 | 1.119 | 1, 4, 1, 4 | 1.127 | 21-2, 12-2, 122, 212 |
| | | 0.5, 1 | 1.108 | 204, 024 |
| 5 | 1.070 | 8 | 1.068 | 300 |
| | | 1, 1 | 1.052 | 301, 031 |
| 12 | 1.042 | 2, 2, 5, 5 | 1.042 | 123, 21-3, 12-3, 213 |

*Note.* * — *reflex impossible for crystals corresponding unit cell dimensions to wurtzite-2H;*
** — *reflexes impossible by symmetry in space group P6₃mc.*

clude, that there are no or slightingly little polytypes with greater value of the parameter $c$ (correspoanding to wurtzite-6*H*, -8*H*, etc.) in studied specimens. By analogy with all above mentioned natural and synthetic compounds with studied structures, as well as in terms of parameters of orickite unit cell, it is possible with great possibility to assume, that Cu and Fe in it are disordered.

From systematic extinction of reflexes of X-ray powder pattern (even values of l in the series 00*l* and *hhl*) and in terms of structural archetype of orickite is most probably represented by the wurtzite-2*H* type, one might assume, that the most possible space group for orickite is the same: $P6_3mc$. Corresponding to the same rule of special extinction the space groups $P6_3/mmc$, $P-62c$, $P-31c$ and $P31c$ are not confirmed in structural models based upon wurtzite-2*H*. Transition to other lower-symmetry variants (first attention was attracted by space groups $P-3m1$, $P3m1$ and $P-3$, corresponding to chvilevaite and related synthetic phases — see above) invariably leads to appearance at the theoretical X-ray powder patterns of additional strong reflexes that are absent for orickite.

In nature are known also other hexagonal and trigonal sulfides of copper and iron with stoichiometry of (Cu,Fe):S = 1:1 — they are nukundamite, $(Cu,Fe)_4S_4$ ($P-3m1$, $a = 3.783$, $c = 11.195$ Å; Rice *et al.*, 1979; Sugaki *et al.*, 1981), and idaite, $Cu_3FeS_4$ (?) (hexagonal, $a = 3.90$, $c = 16.95$ Å; Frenzel, 1959; Rice *et al.*, 1979). However the first one is close by its structure not to wurtzite but to covellite (Sugaki *et al.*, 1981), and the second one is studied insufficiently and its structural features are not known. According to X-ray powder patterns nukundamite and idaite differ strongly from orickite.

Where is $H_2O$ in orickite? We tried to simulate crystal structures of the compound $CuFeS_2(H_2O)_{1-x}$ (with $x < 0.5$) with ordered distribution of $H_2O$ molecules, which would have metrics of wurtzite-2*H* unit cell. It proved to be, that this is possible only at lowering of symmetry with disappearance of the $c$ plane. This inevitably results in disappearance of systematic extinctions and, correspondingly, in appearance at theoretical X-ray powder patterns of strong reflexes that are absent for orickite (the examples are represented by structures of chvilevaite and related synthetic compounds; see Table 3, Fig. 2). Another way — multiple increase of one or of both parameters of the unit cell — also leads to appearance of additional reflections, which are absent at the X-ray powder patterns of orickite. Thus, experimental X-ray powder patterns of this mineral are satisfied only by structure of wurtzite itself. From this, as well as from diffusivity of reflexes, observed by the authors of first description of orickite (Erd, Czamanske, 1983) and by us, follows the conclusion, that distribution of $H_2O$ molecules in its structure, which in the whole analogous to

wurtzite structure (in the first place to poly-type 2*H*), is most probably disordered. Presumably, they form layers (or their "fragments"), statistically replacing pairs of layers [(Fe,Cu)-S]. Exactly such disorde can be a cause of wide variations of oxygen content, revealed as a result of electron microprobe investigation.

It is not excluded, that just presence of $H_2O$ molecules makes more stable wurtzite structure of sulfide of iron and copper: no data found in literature on compounds with wurtzite structure and compositions close to $(CuFe)S_2$.

We should note that we have no reasons to assume presence of oxygen in orickite not in the form of neutral $H_2O$ molecules, but in some other form ($O^{2-}$, $OH^-$). Stoichiometry of $(Cu,Fe):S = 1:1$ is distinctly preserved and is in accordance with wurtzite type of X-ray powder pattern, that implies charge-balanced sulfide part of the structure. Appearance in this layered mineral of the charged O-bearing component (anion) would require existence of compensator in the form of additional cation, as, for example, in mixed-layered hydroxide-sulfides of the valleriite family (Organova, 1989), which in orickite, judging from electron-microprobe data, is absent.

The hudrous sulfides are generally typical for late stages of mineral formation just in high-alkaline systems (Pekov, 2006). At the Khibiny massif they are represented by two layered sulfides of Cu and Fe found in hydrothermally altered hyperagpaitic pegmatites at the Koashva mountain — these are wilhelmramsayite, $Cu_3FeS_3 \cdot 2H_2O$ (Pekov *et al.*, 2006), and orickite. Presumably, such minerals could form in nature by two ways: as products of alteration of an hydrous sulfides with alkaline metals — as result of leachihg of the latters accompanied by hydration, or as a result of direct crystallization from aqueous solution (fluid). The first mechanism is well illustrated at the example of the evolution series of layered sulfides caswellsilvertite $NaCrS_2 \rightarrow$ schöllhornite $Na_{0.3}CrS_2 \cdot H_2O \rightarrow$ cronosite $Ca_{0.2}CrS_2 \cdot 2H_2O$, in which the first stage is represented by the process of leaching of 70% Na with replacing it by $H_2O$ molecule, and the second one — by exchange of the remaining Na for Ca and introduction between Cr,S-layers (with their moving apart) one more $H_2O$ molecule (Britvin *et al.*, 2001). For orickite both direct crystallization from hydrothermal solution and transformation

(leaching of Na with hydration) under the influence of this solution upon the hypothetical phase $Na_{1-x}(CuFe)S_2$ seem possible. In the last case small amount of Na found in orickite from Coyote Peak and Khibiny could be relict, and K, Ca, Tl — products of natural ion exchange.

## References

*Britvin S.N., Guo Iy.S., Kolomenskiy V.D., Boldyreva M.M., Kretser Yu.L., Yagovkina M.A.* Cronosite, $Ca_{0.2}(H_2O)_2CrS_2$ — a new mineral from the enstatite achondrite Norton County // Zap. VMO. **2001**. № 3. P. 29—36. (in Russian).

*Chao G.Y., Gault R.A.* The occurrence of two rare polytypes of wurtzite, 4*H* and 8*H*, at Mont Saint-Hilaire, Quebec // Can. Miner. **1998**. V. 36. P. 775—778.

*Erd R.C., Czamanske G.K.* Orickite and coyoteite, two new sulfide minerals from Coyote Peak, Humboldt County, California // Amer. Miner. **1983**. V. 68. P. 245—254.

*Frenzel G.* Ein neues Mineral: Idait, natuerliches $Cu_5FeS_6$ // N. Jb. Miner. Abh. **1959**. Bd. 93. S. 87—114. (in German).

*Kachalovskaya V.M., Osipov B.S., Nazarenko N.G., Kukoev V.A., Mazmanyan A.O., Egorov I.N., Kaplunnik L.N.* Chvilevaite — new alkaline sulfide of the composition $Na(Cu,Fe,Zn)_2S_2$ // Zap. VMO. **1988**. Is. 2. P. 204—207. (in Russian).

*Kaplunnik L.N., Petrova I.V., Pobedimskaya E.A., Kachalovskaya VM., Osipov B.S.* Crystal structure of natural alkaline sulfide chvilevaite $Na(Cu,Fe,Zn)_2S_2$ // Doklady AN SSSR. **1990**. V. 310. P. 90—93. (in Russian).

*Kisi E.H., Elcombe M.M.* U parameters for the the wurtzite structure of ZnS and ZnO using powder neutron diffraction // Acta Crystallogr. C. **1989**. V. 45. P. 1867—1870.

*Mujica C., Llanos J., Carvajal G., Wittke O.* Synthesis and crystal structure of $Na_2Cu_3VS_4$ // Eur. J. Solid State Inorg. Chem. **1996**. V. 33. P. 987—992.

*Opranova N.I.* Crystal Chemistry of Disproportionate and Modulated Mixed-Lay-

ered Minerals. M.: Nauka. **1989**. 144 p. (in Russian).

*Pekov I.V.*, *Chukanov N.V.*, *Boldyreva M.M.*, *Dubinchuk V.T.* Wilhelmramsayite, $Cu_3FeS_3$ $\cdot 2H_2O$ — a new mineral from the Khibiny massif, Kola Peninsula // Zap. VMO. **2006**. № 1. P. 38−48. (in Russian).

*Pekov I.V.*, *Zubkova N.V.*, *Lisitsin D.V.*, *Pushcharovsky D.Yu.* Crystal chemistry of murunskite // Doklady RAS. **2009**. V. 424. P. 385−387. (in Russian).

*Pekov I.V.* Alkali and hydrous sulfide minerals: classification and genetic aspect of crystal chemistry // 19th General Meeting of IMA. Kobe, **2006**. P. 298.

*Ramirez R.*, *Mujica C.*, *Buljan A.*, *Llanos J.* A family of new compounds derived from chalcopyrite. Common patterns in their electronic and crystal structures //

Boletin de la Sociedad Chilena de Quimica. **2001**. V. 46. P. 235−245.

*Rice C.M.*, *Atkin D.*, *Bowles J.F.W.*, *Criddle A.J.* Nukundamite, a new mineral, and idaite // Miner. Mag. **1979**. V. 43. P. 194−200.

*Sugaki A.*, *Shima H.*, *Kitakaze A.*, *Mizota T.* Hydrothermal synthesis of nukundamite and its crystal structure // Amer. Miner. **1981**. V. 66. P. 398−402.

*Swanson H.E.*, *Fuyat R.K.* Standard X-ray diffraction powder patterns // National Bureau of Standards Circular. **1953**. V. 539. P. 14−15.

*Yvon K.*, *Jeitschko W.*, *Parthe E.* LAZY PULVERIX — a computer program, for calculating X-ray and neutron diffraction powder patterns // J. Appl. Cryst. **1977**. V. 10. P. 73−74.