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Orickite and coyoteite, two new sulfide minerals from Coyote Peak, Humboldt County, California

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Abstract

Orickite and coyoteite occur with rare alkali iron sulfides in a mafic alkalic diatreme near Orick, Humboldt County, California. Both minerals are very rare, and only a few milligrams of each have been found.

Orickite, $Na_xK_yCu_{0.95}Fe_{1.06}S_2 \cdot zH_2O$ ($x,y < 0.03$, $z < 0.5$), is hexagonal; $a = 3.695$, $c = 6.16$Å (both ±0.01Å); D = 4.212 g cm^{-3} for Z = 4. The six strongest lines in the X-ray diffraction powder pattern are [*d* in Å, *I*, (*khl*): 3.08, *100*, (002); 3.20 *90*, (100); 2.84, *60*, (101); 1.73, *55*, (103); 1.583, *30*, (112); 2.20, *15*, (102). The mineral is brass yellow and opaque, weakly pleochroic, but strongly anisotropic (from grayish brown to grayish blue) in reflected light. Orickite is compositionally near iron-rich chalcopyrite, but the mineral may be related to synthetic chalcogenides having a distorted wurtzite–(2*H*) structure.

Coyoteite, $NaFe_3S_5 \cdot 2H_2O$, is triclinic, $P1$ or $P\bar{1}$; $a = 7.409(8)$, $b = 9.881(6)$, $c = 6.441(3)$Å, $\alpha = 100°25(3)'$, $\beta = 104°37(5)'$, $\gamma = 81°29(5)'$; D = 2.879 g cm^{-3} for Z = 2. The six strongest lines in the powder pattern are: 5.12,*100*,($\bar{1}11$); 7.13,*90*,(100); 3.028,*80*,(220); 3.080,*70*,(002); 9.6,*60*,(010); 5.60,*60*,($0\bar{1}1$). Coyoteite is black and opaque; in reflected light it is pale brownish gray, faintly pleochroic, and strongly anisotropic (from gray to dull golden orange). The mineral is unstable under normal atmospheric conditions.

Introduction

Several unusual minerals have been found in a mafic alkalic diatreme at Coyote Peak near Orick, Humboldt County, California. Previous papers have introduced the minerals erdite, $NaFeS_2 \cdot 2H_2O$ (Czamanske *et al.*, 1980; Konnert and Evans, 1980), bartonite, $K_6Fe_{21}S_{26}(S,Cl)$ (Czamanske *et al.*, 1981; Evans and Clark, 1981), djerfisherite, $K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$, and rasvumite, FKe_2S_3 (Czamanske *et al.*, 1979), also found at this locality. Here we introduce two new minerals: orickite, $Na_xK_yCuFeS_2 \cdot zH_2O$ [$x,y < 0.03$, $z < 0.5$], and coyoteite, $NaFe_3S_5 \cdot 2H_2O$. In addition to these, several as yet undescribed, hydrated, Na–Fe and Na–Cu–Fe sulfides are present at Coyote Peak. These alkali-bearing sulfides are geologically ephemeral and are extremely rare in their occurrence. The only other locality where some of these same alkali sulfides have been found is the Khibina massif on the Kola Peninsula, USSR (Chukhrov, 1978; Czamanske *et al.*, 1979).

Orickite (or′ik-īt) is named for the small coastal lumbering town nearest the locality. Coyoteite (kī-ō′ti-īt) is named for the local prominence, Coyote Peak, which also gives its name to the U. S. Geological Survey 15-minute quadrangle map of the area. Both names and minerals have been approved by the IMA Commission on New Minerals and Mineral Names. We emphasize the rarity of these two new minerals; our study is based on only a few grains of each found in several specimens. Our studied holotype material will be deposited at the Smithsonian Institution (National Museum of Natural History), Washington, D. C., and, barring new discoveries, we have no other material to distribute for scientific studies. This is particularly regrettable in the case of orickite as it has interesting relations with chalcopyrite, wurtzite, and some synthetic chalcogenides having a distorted wurtzite structure (Schäfer and Nitsche, 1974).

Occurrence and paragenesis

Both minerals occur in small (1–4 cm diameter) "pegmatitic" clots, thought to have crystallized late in the consolidation of the Coyote Peak magma. These clots are enriched in Na, K, and H^2O relative to their host rocks and characteristically contain phlogopite, schorlomite, aegirine, sodalite, cancrin-

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ite (vishnevite), pectolite, natrolite, magnetite, and, very rarely, calcite. Associated sulfides are pyrrhotite (61.2 wt.% Fe, 39.1 wt.% S) and one or more of the alkali–iron sulfides djerfisherite, rasvumite, bartonite, and erdite.

Coyoteite and orickite are rarer and finer grained than these associated sulfides; coyoteite was found only in specimen 77-CYP-134, and orickite only in specimens 77-CYP-134 and 78-CYP-250. The maximum observed dimension for either mineral is 0.4 mm; many grains of orickite are small laths of only approximately 15 × 150 μm. Although grains of orickite have been found within clear sodalite (Fig. 1) and one calcite crystal, the two minerals typically occur as isolated individuals within a nondescript dark-gray matrix of complex mineralogy and cellular to lamellar texture. This matrix has the aspect of leaching and depletion. Attempts to define better the mineralogy of the matrix through microprobe and X-ray studies suggest that very fine-grained pyrite, hematite, native sulfur, and a complex ferric sulfate(?) phase may all be present, presumably as alteration products.

No relations have been observed that place coyoteite and orickite within the paragenetic sequence of the other sulfide phases. On the basis of the composition of coyoteite and its occurrence (solely within what appears to be a late-formed unstable matrix), coyoteite was probably among the last sulfide phases to form.

Orickite

Chemistry

Both orickite and coyoteite were analyzed with the ARL EMX-SM electron microprobe in Menlo Park, California, using the theoretical data-reduction program FRAME (Yakowitz *et al.*, 1973); standards and operating conditions are noted in Tables 1 and 6. All the orickite analyzed was from specimen 77-CYP-134 from which several polished-section mounts were prepared. Orickite in one of these mounts was analyzed both in Menlo Park and in Ottawa, Canada (by J. H. G. Laflamme of the Canada Centre for Mineral and Energy Technology). Table 1 incorporates both sets of data, for which mean values differ by less than one weight percent. From the averaged analysis, the formula of orickite is $Na_xK_yCu_{0.95}Fe_{1.06}S_2{\cdot}zH_2O$, where x and y are both less than 0.03 and z is less than 0.5. This composition, neglecting the alkalis and water, is identical with that of an iron-rich chalcopyrite (Table 2). Hall (1975) showed that the minerals of the chalcopyrite series are metal-rich rather than sulfur poor. Until the crystal structure of orickite is known, we shall follow Hall in basing the atomic ratios on two atoms of sulfur. Before further discussion of the chemical composition and relations of orickite, however, we first consider the presence of oxygen and alkalis in the mineral.

Table 1. Electron-microprobe analysis of orickite

	Wt %*	Range	Recalc. to 100%	Atomic ratio (S=2)
Na	0.4	(0.17– 0.53)	0.4	0.03
K	0.2	(0.05– 0.25)	0.2	0.01
Cu	31.7	(30.8 –32.7)	32.7	0.95
Fe	31.0	(30.0 –32.2)	32.0	1.06
S	33.6	(33.1 –34.4)	34.7	2.00
Total	96.9**		100.0	

* Average of six grains analyzed in two laboratories at 15 and 20 kV using $CuFeS_2$ as the standard. Six to ten spots per grain were occupied.

** Does not include 1.5–5.1 weight percent oxygen (detected qualitatively by analysis with a TAP crystal). Sought for, but not detected: Al, Ca, Cl, Co, Mg, and Ni.

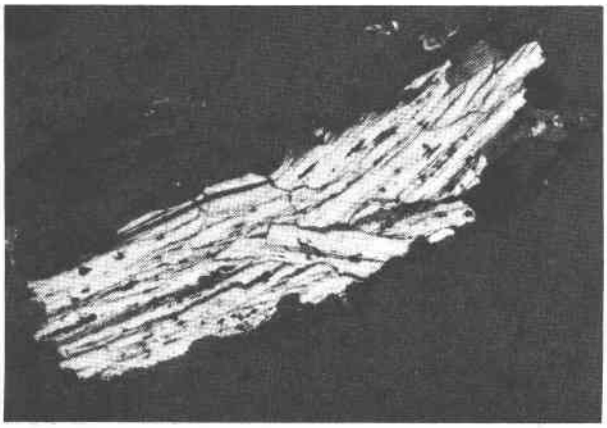

Fig. 1. Intergrown crystals of orickite in sodalite (dark gray). The long dimension of the photograph is 0.44 mm.

Oxygen. Using routine analytical procedures, summations notably below 100 wt.% were obtained for both orickite and coyoteite. Because of our earlier experience with erdite, $NaFeS_2{\cdot}2H_2O$ (Czamanske *et al.*, 1980), we suspected the presence of water or hydroxyl ion. Subsequent analysis with a TAP crystal, using Fe_2O_3 for comparison (360 counts/sec) and FeS for background (3 counts/sec), showed that orickite contains up to 5 wt.% oxygen. Due to the extremely limited amounts of sample available for both minerals, we were unable to conduct other tests for the presence of water or

Table 2. Chemical compositions of orickite and chalcopyrite

	Weight %			Atom %					Mol % FeS ($CuFeS_2$–FeS)
	Cu	Fe	S	Cu	Fe	S	Cu/Fe	Me/S	
$CuFeS_2$	34.63	30.43	34.94	25.0	25.0	50.0	1.00	1.00	0.0
Orickite*	32.9	32.2	34.9	23.7	26.4	49.9	0.90	1.01	10.2
Fe-rich cp**	32.9	32.3	34.8	23.7	26.5	49.8	0.90	1.01	10.6
Fe-rich cp†	31.1	33.2	35.7	22.3	27.0	50.7	0.83	0.97	17.4
Fe-rich cp††	31.0	34.3	34.6	23.3	28.2	49.5	0.79	1.02	17.4

* Analysis from Table 1, omitting alkalis and oxygen, and recalculated to 100 wt%.

** Synthetic. Data of Sugaki et al. (1975): Run No. 074 (at 300°C). (See also Hutchinson and Scott (1981).

† Natural. Data of Picot and Fevrier (1980) for chalcopyrite from the East Pacific Rise (Gulf of California).

†† Natural. Data of Karpenkov et al.(1974) for chalcopyrite from the Talnakh and Oktyabrsk Cu-Ni sulfide deposits, USSR. Average of twenty analyses (modified here to exclude Ni, 0.27 wt%, and Co, 0.02).

hydroxyl ion. The amount of oxygen in orickite appears to vary from grain to grain because summations of analyzed elements range from 94.9 to 98.5 wt.%. This range in summations was obtained from freshly polished surfaces, and because these surfaces show only slight tarnish after more than two years exposure, significant oxidation or hydration of orickite during the course of our study seems unlikely. Skinner and Barton (1960) showed that small amounts of oxygen (up to 0.2 wt.% oxygen) can substitute for sulfur in wurtzite formed at low temperatures. No report of oxygen in either natural or synthetic chalcopyrite is known to us. The maximum amount of oxygen measured in orickite is less than half that needed to form a single mole of water or hydroxyl ion. The role and limits of oxygen (and probably hydrogen) in orickite must await discovery of more material or synthesis of the mineral. Here we consider orickite on an oxygen-free basis.

Alkalis. Na and K also were found to vary in amount from grain to grain, independent of the variation in summation (apparent oxygen content). If Na and K were combined as alkaline hydroxides or oxides, their maximum concentration determined requires less than one-third of the minimum apparent oxygen content. Although alkaline solutions containing Na^+ and K^+ ions have been employed in many syntheses of chalcopyrite (*e.g.*, Barnard and Christopher, 1966; Lee *et al.*, 1975; Moh, 1975; Sugaki *et al.*, 1975), no Na or K has been reported in the resulting products. On the other hand, on the basis of luminescence and reflectance spectra, Shalimova *et al.* (1974a,b) found that K^+ ions were incorporated into sphalerite grown from hydrothermal solutions of KOH. The K^+ ions introduced into the ZnS produced stacking faults and point defects. Colaitis *et al.* (1976) have proposed that a defect structure of wurtzite might be produced by the incorporation of Ce^{3+} ions into that structure. While Na and K may play a role in the wurtzite-like structure of orickite, they are of little compositional importance, and we ignore them in discussing the relation of orickite to the other chalcopyrite-like minerals.

Although various Na–Cu and K–Cu sulfides are known (Burschka, 1979a,b; Brown *et al.*, 1980), none have any apparent relations with orickite. More closely related chemically to orickite, and discussed later in this paper, are some Na- and K-bearing copper–iron sulfides from the Khibina massif, described by Dobrovol'skaya *et al.* (1977, 1979).

Chemical properties. Orickite is insoluble or slightly soluble in cold 1:1 HNO_3 or HCl but is readily soluble in hot acids of the same concentration. Lack of material precluded thermal studies of orickite.

Synthesis. Orickite has not been found as a synthetic phase so far, despite extensive studies of the Cu–Fe–S and related systems (Barton, 1973; Cabri, 1973; Lee *et al.*, 1975; Moh, 1975; Sugaki *et al.*, 1975; Dutrizac, 1976; Vorob'ev and Borisovskii, 1980). Its absence probably arises from causes similar to the difficulty in synthesizing either cubanite or haycockite: according to Cabri (1973), slow cooling over geologic time may be required to form these orthorhombic structures from a high-temperature *fcc* phase. The difficulties of both synthesis and recognition of the phases formed, and the importance of the cooling rate in the formation of the various polymorphs of metal-enriched chalcopyrite, were demonstrated by McConnell (1978) and Putnis (1978). We have not attempted to synthesize orickite.

Physical properties

Orickite is brass yellow with a black streak and metallic luster. There is a good cleavage on {001} and the mineral has conchoidal fracture. The hardness could not be measured, although the mineral is easily scratched with a steel needle. The specific gravity could not be measured, due to contamination by epoxy resin, but the calculated density is 4.212 g cm^{-3} with Z = 4. Orickite is weakly magnetic.

Optical properties

In polished section orickite is bright, pale yellow, similar in color to, or slightly lighter than, chalcopyrite. The lamellar cleavage of orickite is distinctive (Fig. 1). Reflection pleochroism is weak, from pale to slightly deeper yellow, with maximum absorption with the cleavage trace parallel to the plane of the polarizer (NS for our microscope). Anisotropism is strong (in contrast to chalcopyrite); colors change from grayish brown to grayish blue. There are no internal reflections, and no external form is observed in polished sections. Good polished surfaces are obtained on orickite; this fact and other observations suggest that its hardness is more like that of chalcopyrite (4) than of erdite (1½). Polished surfaces or orickite remained bright for at least a year in Menlo Park, California.

Reflectivity values in air (measured by John Jambor, Canada Centre for Mineral and Energy Technology), were obtained by comparison with N.P.L. silicon standard N2538.42. Because only small grains were available for measurement, a 60× objective had to be used and the areas measured were rectangular. Each grain was aligned parallel to a crosshair, and a total of 14 or 15 wavelength readings were taken throughout the spectrum (450–662 nm). The sample was then replaced immediately by the Si standard, and the same wavelength readings were taken without changing the settings of the light source. From graphical plots, maximum reflectance values for orickite are 34.7, 39.9, 42.8, and 46.9 (at 470, 546, 589, and 650 nm, respectively, with elongation EW). On the best plots, reflectance shows a straight-line variation that contrasts with the reflectance curves of chalcopyrite (Araya *et al.*, 1977). The quality of the grains and the high magnifications needed are such that minimum-reflectance values are not given. With grains in the NS position, reflectance values are so similar to those for EW that a meaningful difference could not be established.

X-ray crystallography

The poor quality of the orickite crystals limited the information that we have been able to gather. The X-ray powder diffraction patterns show diffuse and relatively broad lines, and the reflections in the single-crystal X-ray precession photographs are streaked and appear as short arcs except in the *hk*0 net. Only Laue arcs and no zero-order ring appear in cone-axis [*c*] photographs. Nevertheless, preliminary data were sufficient to characterize orickite as having a wurtzite–(2*H*) unit cell with a = 3.695, c = 6.16Å (both ±0.01Å), and V = 72.8$Å^3$. The largest coherent crystal analyzed (0.05 × 0.38 mm) was extracted from specimen 77-CYP-134 and was used to obtain *hk*0, *h*0*l*, 0*kl*, and cone-axis [*c*] photographs with Zr-filtered Mo radiation. This crystal detached from the goniometer head during preparation of the 0*kl* net and was lost; it became necessary to duplicate and continue data collection with a single crystal of poorer quality from another specimen (78-CYP-250). A fragment from the second crystal was used for the X-ray powder photograph.

Table 3 lists the X-ray powder diffraction data; the pattern is simple and may be indexed completely by using the wurtzite–(2*H*) cell. The data are compared with those of the synthetic compound Cu^2FeSiS^4, described by Schäfer and Nitsche (1974) as being an orthorhombic superstructure of wurtzite. The reflections indicating orthorhombic symmetry in Cu^2FeSiS^4 are all very weak (intensities less than 3). Although these reflections could not be found in the orickite pattern (with exposures as long as 65 hours), such weak lines in our pattern would be sufficiently diffuse to go undetected.

The I(100):I(002) ratio is reversed from that found for wurtzite by Short and Steward (1955), who demonstrated that grinding affects the relative intensities of these peaks. The orickite used for the

Table 3. X-ray powder diffraction data for orickite and related compounds

Calculated* (WTZ 2H)		Observed						Calculated†† (WTZ-ST)	
		Wurtzite (2H)**		Orickite***		Cu_2FeSiS_4 †			
hkℓ	$d_{hk\ell}$(Å)	$d_{hk\ell}$(Å)	I	I	$d_{hk\ell}$(Å)	$d_{hk\ell}$(Å)	I	$d_{hk\ell}$(Å)	hkℓ
---	---	---	---	---	---	4.708	1	4.732	011
---	---	---	---	---	---	4.428	3	4.438	101
100	3.200	3.309	100	90	3.20	3.207	100	3.200	200,120
002	3.080	3.128	86	100	3.08	3.074	28	3.080	002
101	2.840	2.925	84	60	2.84	2.844	85	2.840	201,121
---	---	---	---	---	---	2.598	1	2.598	112
---	---	---	---	---	---	2.363	1	2.366	022
102	2.219	2.273	29	15	2.20	2.219	13	2.219	202,122
110	1.848	1.911	74	70	1.85	1.852	48	1.848	040,320
103	1.728	1.764	52	55	1.73	1.725	26	1.728	203,123
200	1.600	1.654	10	---	---	1.603	6	1.600	400,240
112	1.584	1.630	45	30	1.583	1.585	16	1.584	042,322
201	1.549	1.599	12	3	1.543	1.551	3	1.549	401,241
004	1.540	1.564	2					1.540	004
202	1.420	1.462	5	---	---				
104	1.388	1.414	1	---	---				
203	1.262	1.296	14	10	1.261				
210	1.209	1.251	6	---	---				
211	1.187	1.226	3	---	---				
114	1.183	1.210	10						
105	1.149	1.1703	4	5	1.146				
212	1.126	1.1611	8	---	---				
204	1.110	1.1364	<1	---	---				
300	1.067	1.1029	13	---	---				
213	1.042	1.0724	6	5	1.043				
006	1.027	---	---	---	---				
302	1.008	1.0401	5						
205	0.9761	0.9979	6	---	---				

* Indexing based on the wurtzite-(2H) structure. The $d_{hk\ell}$ values (≥0.975) are calculated for orickite with a=3.695Å, c=6.16.

** Synthetic α-ZnS; data from Swanson and Fuyat (1953). Diffractometer; CuKα radiation.

*** Specimen 78-CYP-250. Film 947: Debye-Scherrer camera (114.6 mm dia.); FeKα radiation; Si used as internal standard; 65 hours exposure. Intensities estimated visually.

† Synthetic Cu_2FeSiS_4; data from Schäfer and Nitsche (1974). Guinier camera; CuKα radiation; a=6.411Å, b=7.404, c=6.140 (a and b interchanged from Schafer and Nitsche).

†† Indexing based on the wurtz-stannite structure (Schäfer and Nitsche, 1974). The $d_{hk\ell}$ values (≥1.540Å) are calculated for orickite with a=6.40Å, b=7.39, c=6.16.

powder photograph was not ground but was crushed between two glass slides and further crushed during mixing with the mounting medium, using a steel needle. A spherical mount reduced the effects of preferred orientation.

Discussion

Relation to chalcopyrite-like minerals. Disregarding the minor alkalis and oxygen, orickite lies near chalcopyrite on the chalcopyrite–cubanite join in the central part of the Cu–Fe–S system, just outside the field of the intermediate solid solution shown by Cabri (1973, p. 447, Fig. 5). In their study of the structure of haycockite, Rowland and Hall (1975) pointed out that all minerals with compositions in the central part of the Cu–Fe–S system have, at some temperature, a sphalerite-like arrangement of close-packed layers of sulfur atoms tetrahedrally coordinated to the copper and iron atoms. Hall (1975) stated further that the metal-rich minerals in this part of the Cu–Fe–S system are related to chalcopyrite by the presence of additional metal atoms at interstitial sites of the cubic close-packed sulfur lattice. He noted that relative unit-cell volumes (V/Z) increase with increasing metal/sulfur ratio and that the formulas for these minerals are all stoichiometric. The close relation of orickite to these chalcopyrite-like minerals may be seen in Table 4, in which all formulas are based on 16 sulfur atoms for comparison. The composition of orickite (with Na, K, and O neglected) lies about halfway between $CuFeS^2$ and iron-rich chalcopyrite, (Dutrizac (1976) suggested that about 18 mole percent FeS (in the pseudobinary system $CuFeS^2$-FeS) is the limiting composition for iron-rich chalcopyrite. The compositional limits of chalcopyrite were also discussed by Barton and Skinner (1979)).

A further similarity between orickite and the chalcopyrite-like minerals is that the strongest line in all their X-ray diffraction patterns, at 3.04–3.08Å, corresponds to the {111} plane of hexagonal close-packed sulfur in sphalerite. In chalcopyrite this is the {112} plane which is the most important polysynthetic twinning plane in its deformational twinning (Kelly and Clark, 1975) and corresponds to the {001} plane of wurtzite and orickite. All the chalcopyrite-like minerals have been placed (Table 5) in a wurtzite–(2*H*) pseudocell, using the vectors corresponding to $[111]^{sph}$ and $[01\bar{1}]^{sph}$ as $[001]^{wtz}$ and $[100]^{wtz}$, respectively. When the chalcopyrite-like minerals, together with sphalerite and wurtzite, are arranged in order of increasing C/A (Table 5), it may be seen that orickite and the synthetic compound Cu^2FeSiS^4 are set apart by their high C/A ratios. Even allowing for the uncertainty of the axial parameters of orickite, the lowest possible C/A (1.66) suggests that the true structure of orickite may not be identical to that of wurtzite.

Table 5. Comparison of axial ratios of chalcopyrite-like and ZnS minerals in wurtzite–2*H* setting

	a(Å)	c(Å)	A(Å)	C(Å)	C∧A	C/A
Mooihoekite	10.585*	5.383	3.774	6.146	90.80°	1.628
Sphalerite	5.409**	—	3.824	6.246	90.00°	1.633
Putoranite	5.30***	—	3.748	6.120	90.00°	1.633
Talnakhite	10.593*	—	3.745	6.116	90.00°	1.633
Haycockite	10.705*	31.630	3.761	6.155	89.16°	1.637
Chalcopyrite	5.292†	10.407	3.711	6.077	89.21°	1.638
Fe-rich cp	5.30††	10.42	3.716	6.085	89.20°	1.639
Wurtzite	3.820†††	6.260	3.820	6.260	90.00°	1.639
Cu_2FeSiS_4	6.411ψ	6.140	3.702	6.140	90.00°	1.658
Orickite	6.40ψψ	6.16	3.695	6.16	90.00°	1.667

* Natural mineral (Hall, 1975). $A=a_{wtz}$, $C=c_{wtz}$ in wurtzite-2H setting.

** Synthetic φ-ZnS (Skinner and Barton, 1960).

*** Natural mineral (Filiminova et al., 1980).

† Synthetic stoichiometric chalcopyrite (cp) (Adams, 1974).

†† Iron-rich chalcopyrite from the Talnakh and Oktyabrsk Cu-Ni sulfide deposits, USSR (Karpenkov et al., 1974).

††† Synthetic α-Zns (Swanson and Fuyat, 1953).

ψ Synthetic (Schäfer and Nitsche, 1974).

ψψ This study.

Relation to wurtz–stannite compounds. This high axial ratio is our best present evidence that orickite may be related to a large group of ternary and quaternary chalcogenides which possess a distorted wurtzite structure. This structure is an orthorhombic supercell of wurtzite that arises from an ordered arrangement of cations on former Zn sites and has $a^{orth} \simeq 2a^{wtz}$, $b^{orth} \simeq 3a^{wtz}$, and $c^{orth} \simeq c^{wtz}$. Compounds with this structure are strongly pseudohexagonal and have axial ratios in the wurtzite

Table 4. Comparison of orickite with other chalcopyrite-like minerals

Mineral	Formula (S=16)	Me/S	V/Z(Å^3)	D	Reference
Chalcopyrite	$Cu_8Fe_8S_{16}$	1.000	72.9	4.18	Adams (1974
Synthetic	$Cu_8Fe_4Si_4S_{16}$	1.000	72.9	3.14	Schafer and Nitsche (1974)
Orickite*	$Cu_{7.6}Fe_{8.5}S_{16}$	1.005	72.8	4.19	This study
Fe-rich cp	$Cu_{7.2}Fe_{9.1}S_{16}$	1.020	73.2	4.20	Karpenkov et al. (1974)
Talnakhite	$Cu_9Fe_8S_{16}$	1.063	74.3	4.28	Hall (1975)
Putoranite	$Cu_9Fe_9S\ _{16}$	1.125	74.4	4.43	Filimonova et al. (1980)
Mooihoekite	$Cu_9Fe_9S_{16}$	1.125	75.4	4.37	Hall (1975)
Haycockite	$Cu_8Fe_{10}S_{16}$	1.125	75.7	4.33	Hall (1975)

* Na, K, and O omitted.

subcell that are all close to or exceed 1.65. The name "wurtz–stannite" was applied to the distorted wurtzite structure by Schäfer and Nitsche (1974). Orickite may be the first mineral representative of the wurtz–stannite structure type.

A wurtzite analog to chalcopyrite was first found in β-$NaFeO^2$ by Bertaut and Blum (1954) and Bertaut, Delapalme, and Bassi (1964). Because of the presence of sodium and oxygen in orickite, we considered the possibility of an interlayered structure consisting of slabs of β-$NaFeO^2$ and $CuFeS^2$, analogous to the slabs found in valleriite (Evans, 1968). However, the contents of Na, K, and O in orickite are far too low to permit such a possibility.

Na–K–Cu–Fe sulfides from the Khibina massif. Rasvumite grains from the Khibina massif (Czamanske *et al.,* 1979) contain small amounts of a phase similar in appearance to orickite. The grains are too small to obtain an X-ray diffraction pattern, but electron-microprobe analyses of two grains show (weight percent): Cu 23.2, 21.6; Fe 37.4, 38.8; S 28.4, 30.2; O 11.8, 9.4 (by difference). The average composition of these grains is quite distinct from that of orickite but is close to that of a hypothetical hydroxycubanite, $CuFeS^3(OH)^2$ (ideally Cu 20.80, Fe 36.57, S 31.49, and O 11.14). This phase was found independently by Dobrovol'skaya *et al.* (1979) in the Khibina massif, where it occurs with both rasvumite and djerfisherite. Dobrovol' skaya *et al.* (1977, 1979) also found and partially described several other Na- and K-bearing lamellar copper-iron sulfides in complexly intergrown material in the Khibina massif. One of these sulfides has a chalcopyrite-like structure and a composition near Cu^2FeS^3, but neither this phase nor any of the others has a composition or X-ray data near to that of orickite.

Coyoteite

Chemistry

The electron–microprobe data in Table 6 were obtained on five discrete grains from specimen number 77-CYP-134 for which was found a nearly constant high sodium content. The largest of these grains was only 0.2 × 0.4 mm in size. Many other grains, similar to appearance to coyoteite, were found to contain lesser amounts of sodium, presumably as a result of alteration and leaching. One relatively large analyzed grain was removed from the polished section for X-ray diffraction and other studies.

Table 6. Electron-microprobe analyses of coyoteite

	Wt %*	Range	Calc. compn. $NaFe_3S_5 \cdot 2H_2O$
Na	5.99	(5.94 - 6.01)	5.94
Fe	44.0	(43.7 - 44.3)	43.31
S	41.3	(40.9 - 41.7)	41.44
H_2O	8.71**		9.31
Total	100.00		100.00

* Average of five grains analyzed at 10kV, using synthetic FeS and a natural crocidolite (4.63 wt % Na) as standards. Six to ten spots per grain were occupied.

** By difference. K<0.2 wt%; sought for by wavelength dispersive spectrometry, but not detected: Cl, Cu, Mg, and Ni.

As in the case of orickite, all analyses sum to about nine weight percent too low. Qualitative analyses with a TAP crystal confirmed that oxygen is present in coyoteite. No other element with an atomic number greater than 11 was detected in the energy-dispersive spectra, and so we assume that oxygen and hydrogen account entirely for the nine-percent deficiency in the analyses. There must, therefore, be two atoms of oxygen per formula, although the further question of whether these exist as water or hydroxyl ion remains unresolved. By analogy with erdite, we offer the provisional formula $NaFe_3S_5 \cdot 2H_2O$ for coyoteite. We could find no published record of a hydrous or anhydrous sodium–iron sulfide near this composition.

Coyoteite is insoluble, or very slowly soluble, in cold 1:1 HCl or HNO_3, but it dissolves readily in hot acids of these concentrations. It alters to undetermined decomposition products in a matter of months. Neither thermal studies nor a qualitative determination of water could be made with the limited material at hand.

Physical properties

Coyoteite is black in incident light and has a black streak; its luster is metallic, and the mineral is opaque in the smallest fragments. No crystal forms were observed in the polished sections. Coyoteite has perfect $\{\bar{1}11\}$ cleavage, which most grains display conspicuously in polished sections. An unusual chevron pattern is commonly developed by opposing sets of cleavage lamellae (Fig. 2). The measured specific gravity ranges from 2.5–2.6 but

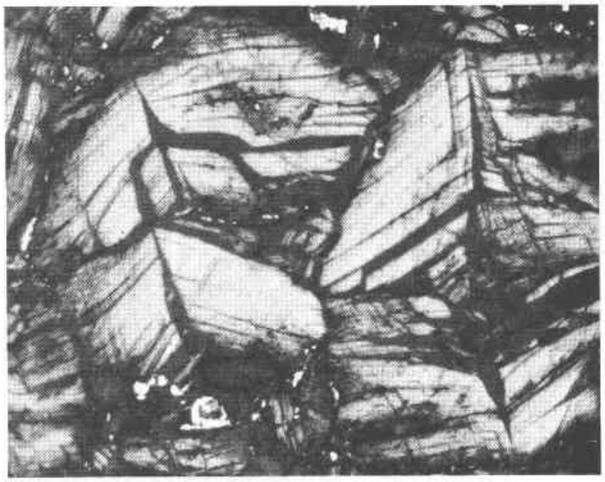

Fig. 2. Coyoteite crystals showing chevron pattern developed by opposing cleavage sets. Continuous parallel lines are polishing scratches. The long dimension of the photograph is 0.26 mm.

these values are low because of minor contamination by epoxy resin along the cleavage lamellae. The calculated density is 2.879 gcm^{-3} for Z = 2. Coyoteite is moderately magnetic.

Optical properties

Under the ore microscope, coyoteite is pale brownish gray with a pink tint. Reflection pleochroism is faint, from grayer to pinker. Anisotropism is strong; colors between crossed polars change from gray to dull golden orange. Internal reflection is absent. Although reflectance and hardness have not been measured, the hardness is estimated to be near that of erdite (approximately 1½ (Mohs)). Coyoteite is so soft that the most carefully polished surfaces of the mineral show scratches (Fig. 2).

X-ray crystallography

X-ray precession photographs (Mo radiation, Zr filter) of an analyzed single crystal show coyoteite to be triclinic, space group $P1$ or $P\bar{1}$. The crystal, however, proved to be of poor quality, and reflections are streaked and diffuse. A small piece of the crystal was detached, crushed (but not ground), and used to obtain the powder diffraction data (Table 7). The unit-cell dimensions refined by least-squares analysis of the X-ray powder diffraction data are (estimated standard deviations in parentheses): a = 7.409(8), b = 9.881(6), c = 6.441(3)Å, α = 101°25(3)′, β = 104°37(5)′, γ = 81°29(5)′, and V = 446.2(5)Å^3.

Discussion

The data that we could obtain from coyoteite were limited both by the scarcity and ephemeral nature of the mineral; it alters to undetermined decomposition products. Until more and better crystallized material is either found or synthesized, it is impossible to know whether the mineral con-

Table 7. X-ray powder diffraction data for coyoteite

Calculated*		Observed**	
hkℓ	d (Å) hkℓ	d (Å) hkℓ	I
010	9.662	9.6	60
100	7.127	7.13	90
001	6.163	6.15	20
110	6.055	----	----
$0\bar{1}1$	5.590	5.60	60
$\bar{1}10$	5.461	----	----
$\bar{1}01$	5.311	5.31	40
$\bar{1}\bar{1}1$	5.129	5.12	100
011	4.875	----	----
020	4.831	4.827	15
$\bar{1}11$	4.290	----	----
120	4.215	4.199	20
101	4.204		
$0\bar{2}1$	4.113	----	----
$\bar{1}\bar{2}1$	4.016	----	----
$1\bar{1}1$	3.911	3.910	50
$\bar{1}20$	3.813	----	----
111	3.801	----	----
200	3.564	----	----
021	3.552	3.552	50
$\bar{2}\bar{1}1$	3.463	3.456	20
$\bar{2}01$	3.451		
030	3.221	3.222	15
003	3.081	3.080	70b
220	3.028	3.029	80b
$\bar{1}\bar{2}2$	2.882	2.884	10
012	2.816	2.808	20
201	2.815		
$\bar{2}\bar{1}2$	2.709	2.707	20b
$\bar{1}31$	2.529	2.528	10
230	2.528		
		2.404	30
		2.365	30
		2.104	10
		1.901	80
		1.877	20
		1.862	20

* All calculated hkℓ's listed for $d_{hk\ell} \geq$ 3.500Å. All $d_{hk\ell} \geq$ 2.500Å are indexed. Indices from least-squares analysis of X-ray powder data using the digital computer program of Appleman and Evans (1973).

** Specimen No. 77-CYP-134. Film No. 904: Fe/Mn radiation; λFeKα = 1.93728Å. Debye-Scherrer camera diameter 114.6 mm; film corrected for shrinkage.

tains hydroxyl and (or) hydrate water. From the properties that we have been able to determine, we can find no other mineral or synthetic compound that is closely related to coyoteite. Its perfect cleavage, however, suggests that coyoteite has a layered structure that together with the chemical composition, would place coyoteite near to (but distinct from) the valleriite series of minerals.

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