Isocubanite, a new definition of the cubic polymorph of cubanite $CuFe_2S_3$

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Abstract

Isocubanite is a cubic polymorph of cubanite $CuFe_2S_3$, discovered in the submarine sulphide deposits of the East Pacific Rise (EPR) and the Red Sea, in association with chalcopyrite, pyrrhotine, pyrite, sphalerite or wurtzite and anhydrite. It was previously obtained artificially and mentioned as *iss*, 'intermediate solid solution of $CuFe_2S_3$ composition'. Crystals are cubic with $a = 5.303(3)$ Å and strongest lines in the X-ray powder pattern are 3.059 (10) 111, 1.876 (7) 220, 1.602 (5) 311. Euhedral grains range from a few microns up to 400 μm, with a Vickers microhardness of 175(25) kg/mm^2 for $P = 100$ g. Isocubanite is usually intimately intergrown with iron- and zinc-rich chalcopyrite and is opaque with a metallic lustre and a bronze colour. Pinkish brown and isotropic in polished sections; reflectance values (SiC standard) are: 420 nm 22.73%, 460 nm 26.87, 500 nm 31.34, 540 nm 34.79, 580 nm 37.35, 620 nm 39.11, 660 nm 40.32, 700 nm 41.33, 740 nm 41.91, 780 nm 42.50. Electron microprobe analyses gave (wt. %): Fe 41.64–42.49, Cu 20.79–21.52, Zn 0.77–1.09, S 35.49–35.82, corresponding to the formula $(Cu,Zn)Fe_2S_3$.

Isocubanite is characteristic of high-temperature (> 200 °C) present-day submarine sulphide deposits where hot hydrothermal fluids are quenched by seawater as in EPR deposits or by cooler brines as in Atlantis II Deep, in the Red Sea; it is unstable and therefore unusual in fossil ores. This cubic phase was previously observed and described more or less accurately as *cubic cubanite*, *cubanite II*, *chalcopyrrhotite* and *iss*; the name isocubanite, proposed in order to clarify the nomenclature, and this new description, were approved by the IMA Commission on New Minerals and Mineral Names.

KEYWORDS: isocubanite, cubanite, new mineral, East Pacific Rise, Red Sea.

Introduction

DURING a study of present-day submarine sulphide deposits, discovered in the East Pacific Rise (EPR 21 °N) and the Red Sea (Atlantis II Deep), a cubic polymorph of cubanite $CuFe_2S_3$ has been observed in association with chalcopyrite, pyrrhotine, pyrite, sphalerite or wurtzite and anhydrite (Noltner, 1979; Picot *et al.*, 1980; Haymon and Kastner, 1981; Styrt *et al.*, 1981; Oudin, 1981, 1983*a*; Pottorf and Barnes, 1983; Lafitte and Maury, 1983; Koski *et al.*, 1984; Zierenberg *et al.*, 1984; Oudin *et al.*, 1984; Lafitte *et al.*, 1984).

This polymorph can be obtained artificially by heating orthorhombic cubanite between 200 and 270 °C (Cabri *et al.*, 1973; Fleet, 1970; Sawada *et al.*, 1962; Yund and Kullerud, 1961). It is frequently mentioned in the literature as *iss*, 'intermediate solid solution of $CuFe_2S_3$ composition' (Amcoff, 1981; Barton, 1973; Cabri, 1973; Kojima and Sugaki, 1984; Sugaki *et al.*, 1975).

It was apparently first reported by Ramdohr (1928) and then by Odman (1933) under the name of *cubanite II*. Later, Genkin *et al.* (1965) almost certainly recorded this phase in the ores of the Noril'sk and Talnakh deposits, as fine rims on the periphery of orthorhombic cubanite. The minerals were not analysed, but X-ray data and reflectivities show they are identical with the East Pacific Rise and the Red Sea cubic polymorph of cubanite.

The name *chalcopyrrhotit* was first used by Blomstrand (1870) for a material proved later to be

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TABLE 1. *X-ray powder data and parameters for natural and artificial isocubanites*

	1			2		3		4	
hkl	I/I_o	d_{obs}	d_{calc}	I/I_o	d_{obs}	I/I_o	d_{obs}	I/I_o	d_{obs}
111	10	3.059	3.062	10	3.061	10	3.052	10	3.049
200	2	2.647	2.652	3	2.655	4	2.643	3	2.640
220	7	1.876	1.875	8	1.881	8	1.867	8	1.867
311	5	1.602	1.599	7	1.602	7	1.594	7	1.594
222				1	1.536	1b	1.526	1	1.524
400	2	1.327	1.326	3	1.328	4	1.321	1	1.321
a (Å)		5.303(3)			5.31		5.286(1)		5.283(1)

1 - Isocubanite from EPR(21°N); present study.
2 - Isocubanite from Norilsk (Genkin *et al.*, 1965).
3 - Artificial isocubanite (Cabri *et al.*, 1973).
4 - Artificial isocubanite (MacLean *et al.*, 1972).

FIG. 1. Isocubanite (medium grey) with lamellae and rim of Fe–Zn-rich chalcopyrite, associated with wurtzite in EPR 21 °N sample. Polished section photograph (× 120).

cubanite by Geijer (1924) and then discredited; a study of the topotype material by the Department of Mineralogy of the British Museum (Natural History) also proved that it was a mixture without isotropic material (M. H. Hey, pers. comm.). Unfortunately, Borchert (1934), observing that *cubanite II* was a mixture of thin lamellae of chalcopyrite in an isotropic phase close to cubanite, named this material *chalcopyrrhotite*. This name was later used by Ramdohr (1960) for several occurrences of this phase, although he thought that the choice of the name was unfortunate. In submarine sulphide samples, this mineral has variously been called chalcopyrrhotite, *iss*, cubic cubanite or even (incorrectly) cubanite.

In order to clarify the nomenclature, it is therefore proposed that this cubic polymorph of cubanite be named isocubanite as it is not a constituent of Blomstrand's *chalcopyrrhotit* but identical to Genkin's cubic cubanite. This name was approved before publication by the Commission on New Names and Mineral Names of the International Mineralogical Association.

Crystallographic properties

A homogeneous fragment, free of chalcopyrite lamellae or rims, from an East Pacific Rise 21° N 'black smoker' chimney, was selected under the microscope and oriented with a precession camera using Mo-$K\alpha$ radiation. Isocubanite is cubic *Fm3m* with $a = 5.303(3)$ Å. No reflections from chalcopyrite were observed (Cabri *et al.*, 1973).

An X-ray powder diagram was obtained using a 114.6 mm diameter Gandolfi camera and Fe-$K\alpha$ radiation; data are presented in Table 1, along with those from Noril'sk isocubanite and from cubic cubanites obtained by heating and quenching orthorhombic cubanites.

It can be seen from this table that the d_{hkl} and a parameters of artificial isocubanites are systematically smaller than for natural isocubanites. As for East Pacific Rise isocubanite, this could be related to small amounts of zinc (ionic radius: 0.60 Å) replacing copper (ionic radius: 0.57 Å) (Oudin, 1981). The X-ray pattern is also very close to that of cubic chalcopyrite (Genkin *et al.*, 1965).

Physical properties

Pure isocubanite (i.e. devoid of chalcopyrite inclusions) is very rarely observed; it is usually intimately intergrown with iron- and zinc-rich chalcopyrite which appears as lamellae and/or rims (Fig. 1); both textures can be interpreted as due to

TABLE 2. *Reflectivities (%) of isocubanite in air and oil*

λ_{nm}	air	oil	λ_{nm}	air	oil
420	22.73	12.94	620	39.11	25.83
440	24.65	14.58	640	39.70	26.37
460	26.87	16.40	660	40.32	26.80
480	29.23	18.30	680	40.91	27.72
500	31.34	20.08	700	41.33	27.48
520	33.16	21.56	720	41.58	27.66
540	34.79	22.73	740	41.91	27.87
560	36.19	23.75	760	42.46	28.08
580	37.35	24.58	780	42.50	27.42
600	38.25	25.32	800	41.66	25.54

TABLE 3. *Electron microprobe analyses (wt.%) of isocubanite, in one sample from EPR(21°N), associated with pyrrhotine and wurtzite.*

S	35.62	35.49	35.57	35.71	35.82
Fe	42.49	41.99	41.64	42.21	41.93
Zn	1.09	1.02	0.96	0.85	0.77
Cu	21.52	20.79	21.23	21.27	21.27
total	100.72	99.29	99.40	100.04	99.78

exsolution of chalcopyrite from isocubanite (see Brett, 1964). It is opaque with a metallic lustre and a bronze colour, usually as euhedral grains; cubo-octahedra are frequently observed (Fig. 2); grain size varies from a few microns up to approximately 400 μm. The Vickers microhardness is 175(25) kg/mm^2 for P = 100 g.

In polished section, the mineral is pinkish-brown and, in direct contact with pyrrhotine, appears slightly browner and softer. It is isotropic and the reflectance values, measured in air and oil (n = 1.5155 for λ = 589 nm) using a prism monochromator and a SiC standard, are given in Table 2. The reflectivities are very different from those of chalcopyrite and pyrrhotine; they are close to $R_{\min}$ of cubanite, but this mineral is clearly anisotropic. Iron- and zinc-rich chalcopyrite associated with isocubanite has a lower reflectivity than normal chalcopyrite (Fig. 3).

Chemical properties

Isocubanite was analysed using a CAMEBAX electron microprobe, with Cu, ZnS and FeS as standards; the results are presented in Table 3. All the analyses show zinc contents ranging from 1.09 to 0.77 wt. % within the same sample and the corresponding formulae, on the basis of three atoms of sulphur, are from $Cu_{0.91}Fe_{2.05}Zn_{0.05}S_3$ to $Cu_{0.90}Fe_{2.02}Zn_{0.03}S_3$. In East Pacific Rise samples, the isocubanite Zn-content varies from nil up to approximately 1 wt. %. However, Red Sea isocubanite may contain up to 2 wt. % Zn; moreover it has been proved experimentally that a significant amount of zinc can be accommodated in isocubanite (Wiggins and Craig, 1980; Kojima and Sugaki, 1985).

It has been suggested by Oudin (1981) that the ZnS content of isocubanite is temperature dependent in East Pacific Rise samples, as shown by the experimental work of Hutchison and Scott (1981) who studied the solubility of ZnS in *iss* coexisting with pyrite and pyrrhotine, in the Cu-Fe-Zn-S system at high temperature.

Temperature estimates using the ZnS content of EPR 21° N isocubanite (associated with wurtzite and pyrrhotine), extrapolated to lower temperatures, are close to the measured exit temperature of the hydrothermal fluids (Scott, 1983). Isocubanite forming the inner conduit of a chimney shows a decrease in Zn content towards the chimney centre (from 0.8 to 0.5 wt. %). However, isocubanite is not buffered by zinc- and iron sulphides and temperature cannot be estimated (S. Scott, pers. comm.).

Iron-rich chalcopyrite associated with isocubanite also contains zinc (up to 2 wt. %) which may explain the variations from stoichiometric composition observed when plotted on the Cu-Fe-S diagram of Lafitte and Maury (1983). Up to 0.04 wt. % selenium has been analysed in some Red

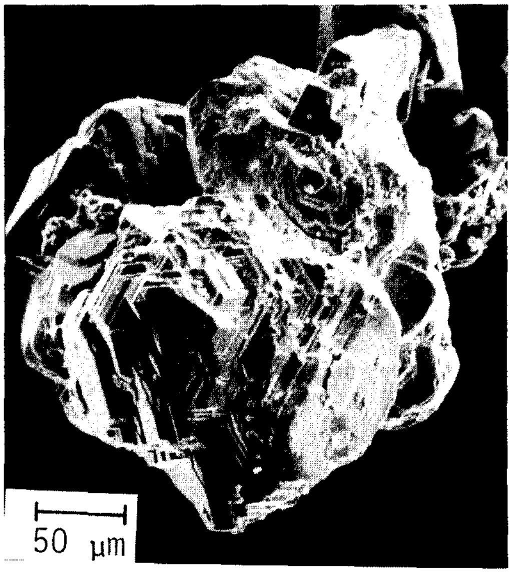

FIG. 2. Aggregate of idiomorphic grains of isocubanite associated with minor pyrite (P). SEM photograph.

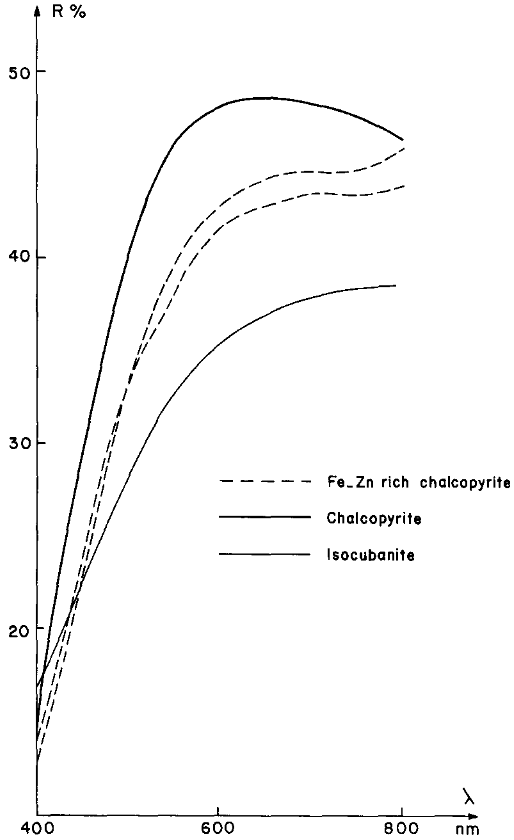

FIG. 3. Reflectivity of isocubanite and associated Fe-Zn-rich chalcopyrite, as compared with chalcopyrite.

Sea isocubanites (Oudin, 1987). Nickel was also sought but not detected.

Occurrence and stability in ore deposits

Isocubanite is an unstable phase and therefore unusual in fossil ores. It was described by Ramdohr (1960) in numerous contact metasomatic deposits, sometimes in deposits metamorphosed by lava flows, or in stony meteorites.

Isocubanite is characteristic of high-temperature (> 200 °C) present-day submarine sulphide deposits (Oudin, 1983*b*). Quenching by seawater (East Pacific Rise) or cooler brines and sediments in the Atlantis II Deep (Red Sea) and the presence of minor amounts of zinc probably prevents an early breakdown of the mineral. However, in fossil analogues of East Pacific Rise deposits, such as massive sulphides from Cyprus or Oman, isocubanite has not been identified; but lattice textures in chalcopyrite, outlined by dissolution or by a network of microcrystalline pyrite in Oman samples, have been interpreted as ghost textures of isocubanite-chalcopyrite intergrowths (Lescuyer *et al.*, in press). This interpretation is supported by observations in Red Sea samples from the presently accumulating hydrothermal sediments of Atlantis II Deep, of partly destabilized isocubanite-chalcopyrite grains displaying a lattice texture outlined by minute pyrite inclusions associated with other destabilization products (Oudin, in prep.). A similar interpretation has been given by Ixer *et al.* (1984) for minute inclusions of associated chalcopyrite-pyrrhotine or chalcopyrite-cubanite in pyrite from Oman, which have also been observed in modern samples from the Galapagos Ridge (Oudin, 1982).

Zn-bearing isocubanite is most probably replaced by chalcopyrite containing minute star-shaped exsolutions of sphalerite (Oudin and Constantinou, 1984; Sugaki *et al.*, 1987) in fossil ores.

Conclusions

The cubic polymorph of cubanite $CuFe_2S_3$ has rarely been identified in fossil ores; it is referred in the literature under several names including *cubanite II*, *cubic cubanite*, *chalcopyrrhotite* and *iss* (intermediate solid solution). Its occurrence in modern submarine mineralizations made a new definition and description of its crystallographic and chemical properties desirable. The name isocubanite is given in order to avoid the confusion arising from the use of several different names, sometimes covering mixtures or badly defined products. Type material will be deposited in the Mineralogical Collection of the Ecole Nationale Supérieure des Mines, Paris.

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