COOKEITE FROM THE MUIANE PEGMATITE, ZAMBEZIA, MOZAMBIQUE

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This paper describes a cookeite occurring as large rosettes crystallized in an open vug in the Muiane granite pegmatite in Zambezia, Mozambique. Optical properties, chemical composition, X-ray powder pattern, single crystal data and infra-red absorption are given. The mineral represents a pseudo-hexagonal one-layer semi-random cookeite with noticeable contents of beryllium and boron.

Introduction

The mineral cookeite is known to occur in the granite pegmatites of the Alto Ligonha region in Zambezia, Mozambique. In describing the mineral collection of the Geological Survey of Mozambique in Lourenço Marques, Behier (1957) mentions the ocurrence of small hexagonal-looking flakes on the surfaces and in the cavities of some altered tourmaline crystals from the Muiane pegmatite. According to him, these mica-like crystals evidently represent either cookeite or manandonite. Because a qualitative spectroscopic test showed absence of boron, he concludes that the mineral must be cookeite. Similar cookeite incrustations were found also on the surfaces of some quartz crystals from the same pegmatite. The observation by Behier was verified by Cotelo Neiva & Correia Neves (1960) in the Muiane pegmatite. According to Correia Neves (personal communication), the occurrence of cookeite is not restricted to the Muiane pegmatite alone but the mineral is found also in other pegmatite localities of the region, for instance in Naipa. As described by v. Knorring (1963), cookeite occurs in several pegmatites of the region also in pseudomorphs after spodumene. Chemical and X-ray powder data for such pseudomorphs from the Muiane, Maridge and Namivo localities reported by him show that these pseudomorphs consist mainly of cookeite, in addition to minerals of the montmorillonite and kaolinite series.

In the Zambezia pegmatites cookeite was found merely as an alteration product belonging to the latest stages of crystallization. To the knowledge of the authors, the material of the mineral available from the region was not well suited for single crystal X-ray work. In Muiane, however, the manager of the mine, Mr. Eurico Lopes da Silva, now of the Geological Survey of Mozambique in Lourenço Marques, found a specimen of coarse grained mica-like mineral grown in an open vug. Evidently, the mineral represents no secondary alteration product of any pre-existing minerals but belongs to the primary low temperature crystallization of the pegmatite mass. On a visit to the Muiane mine in 1963, Mr. Lopes da Silva handed over the specimen to one of us (Th. G. S.). Preliminary X-ray tests showed the mineral to belong to the 14 Å layer silicates and a qualitative spectroscopic test made by Mr. A. Löfgrén, of the Geological Survey of Finland, showed it to be a LiAl-silicate with some boron and beryllium. It was suspected that the mineral might represent the rare species manandonite which would deserve a closer inspection. Therefore, the specimen was subjected to a more detailed chemical, optical and X-ray study. The X-ray study was based mainly on the general survey of the chlorite polytypism published by Brown & Bailey (1962). The results obtained for presentation in this paper proved the mineral to be cookeite with a minor content of boron and beryllium.

MORPHOLOGY AND OPTICAL PROPERTIES

In the specimen studied, cookeite occurs as rosettes of six-sided flakes, ca. 1 cm in diameter, projecting out of a coarse flaky matrix of the same mineral. Fig. 1 illustrates the shape of such a rosette. The crystals are soft like talc with a perfect basal cleavage. The flakes are flexible, not elastic. Single flakes in a rosette are entirely clear, transparent, very slightly yellowish in color and too thin to show any other crystal faces except the basal plane and the hexagonal-looking prism faces. Under the microscope the crystals prove to represent twins in the way illustrated in Fig. 2. The margins of the complex twin appear slightly 'zoned' just reflecting oscillating strain conditions in the last stages of crystallization. The position of the optic axial plane is indicated in the figure. The twinning and the position of the optic axial plane found in the Muiane cookeite is similar to that described by Landes (1925) for cookeite from Buckfield, Maine, and by Lacroix (1922) for manandonite from Antandrokomby, Madagascar. The same kind of twinning was observed by the authors in a specimen of cookeite from Hebron, Maine, and of manandonite from Sahatany Valley, Madagascar. These two specimens were kindly made available for comparison by Professor Hugo Strunz, of the Technical University of Berlin.

Fig. 1. Cookeite rosette from the Muiane pegmatite. Half natural size. Drawn by Toini Mikkola.

The following optical properties were obtained for the Muiane mineral:

$\alpha=1.584$, $\beta=1.588$, $\gamma=1.598$, all with ± 0.001 (immersion method in sodium light). These values correspond to $\gamma-\alpha=0.014$ and $2V=65°$. Optical γ is virtually perpendicular to the cleavage flake. Optically positive. A measurement with the U-stage conoscope yielded $2V\gamma=60°\pm 2°$. Optical α parallel to the crystallographic b-axis. The trace of the optic axial plane on 001 is parallel to the trace of the prism face.

Optical data for cookeite have been published by Landes (1925), Quensel (1937, 1956), Brammall et al. (1937), Ginzburg (1953), Zwyagin & Nefedov (1954) and Herman et al. (1961). Leaving aside the exceptional cookeite from Varuträsk (Quensel, op. cit.) which occurs as a pseudomorph after spodumene, the range of variation of the refractive indices is found as follows: $\alpha=1.565-1.576$, $\beta=1.579-1.584$, $\gamma=1.590-1.600$. The variation of $\gamma-\alpha$ ranges from 0.014 to 0.030. Accordingly, the refractive indices of the Muiane mineral are among the highest and the birefringence among the lowest recorded for cookeite. All statements to be found in literature indicate the mineral to be optically positive. Values given for 2V are but few varying from moderate to large. The data available so far are too scanty to allow correlation of optical properties with chemical composition.

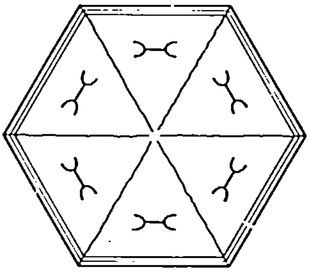

Fig. 2. Basal section of the Muiane cookeite showing twinning and optic axial plane.

CHEMICAL COMPOSITION

The cookeite from Muiane was chemically analyzed by one of us (O.v.K.) with the result summarized in Table 1. Because the mineral represents no alteration product of rubellite or other Li-minerals, the specimen studied did not contain such minerals. Traces of quartz present in the specimen were carefully avoided. Therefore, it is felt justified to consider the result of the analysis to reflect the true composition of the uncontaminated cookeite. The Table indicates also the unit cell content based on O+OH+F=18. Neglecting the minor amount of iron, the formula of the mineral will be

$$Al_{2.00}[(OH)_{1.91}F_{0.09}\,|\,Al_{0.76}Be_{0.22}B_{0.06}Si_{2.96}\,O_{9.79}(OH)_{0.21}].$$
$$Ca_{0.01}Na_{0.01}Li_{1.11}Al_{1.97}(OH)_{6.00}.$$

This formula, written in the way proposed by Strunz (1966), may be simplified to the theoretical formula

$Al_2[(OH)_2\,|\,AlSi_3O_{10}].LiAl_2(OH)_6$ with Z=2.

The chemical formula found for the Muiane cookeite and the unit cell data to be given below yield a specific gravity of 2.65. The value measured for the mineral with Berman balance is slightly lower, viz. 2.61.

Compared with the theoretical formula of cookeite, the actual composition of the Muiane mineral is characterized by noticeable contents of boron and beryllium. Remarkably enough, cookeite seems to be generally devoid of these two elements despite the fact that it is a typical constituent of granite pegmatites where it often represents a secondary alteration product of elbaite (rubellite). In most cookeite descriptions published in literature the presence or absence of boron and beryllium has not been mentioned. The only previous case in which a boron content was given in cookeite is that reported by Herman et al. (1961). For the mineral from Manono in Katanga these authors have found spectroscopically 0.08% B_2O_3. On the other hand, the only previous statement of the occurrence of beryllium in cookeite was found in the paper by Zwyagin & Nefedov (1954). In a cookeite from northwestern U.S.S.R. (locality not specified) these authors mention that a spectroscopic test showed the mineral to contain a small amount of beryllium the content of which was not quantitatively determined. Small amounts of boron and beryllium will, of course, easily escape detection if spectroscopic tests are not made. In analyzing cookeite we recommend testing spectroscopically the presence of boron and beryllium and, if necessary, carrying out a quantitative determination. A possible contamination of the analyzed material by tourmaline, beryl, etc. must be taken into consideration. In the case of the Muiane mineral such a contamination is excluded. The mineral is the most boron- and beryllium-rich cookeite found so far. According to the most reliable analysis of manandonite, the boron analogue to cookeite, published by Lacroix (1922), boron substitutes for silicon in the structure of that mineral. Intermediate members of a hypothetical cookeite-manandonite series are not known.

X-RAY CRYSTALLOGRAPHY

The X-ray powder pattern of the Muiane cookeite was recorded with the Philips Norelco diffractometer using filtered copper radiation and internal silicon standard. The finely powdered material was placed in the usual way on a glass plate and the powder pattern recorded. The result is summarized in Table 2. For a platy material like cookeite the preferred orientation effect could be expected to exaggerate the intensities of the 001 type reflections. Therefore, the intensities of the 001 reflections are given in the Table separately from those of the other types of reflections. For the 001 type reflections the intensities were based on that of 003 which was taken as one hundred and for the other types of reflections on that of $20\bar{2}$ which was taken as ten. The ratio $I_{003}:I_{20\bar{2}}$ as it appears on the chart is approximately 10:1. To measure more accurately the intensities of the weakest 001 reflections, a cleavage flake of the mineral was placed in a rotating specimen holder and the intensities recorded. In that way also the intensities of the reflections 009 and 00,10 could be measured.

Data for the powder pattern of cookeite have been given by Ginzburg (1953), Zwyagin & Nefedov (1954), Herman et al. (1961) and, most recently, by Brown & Bailey (1962). The d-values of the powder pattern of the Muiane mineral are virtually identical with those listed by the last named authors. For that reason the indexing of the reflections given by Brown and Bailey was adopted in Table 2. The data of this table for the Muiane mineral correspond to the following unit cell dimensions: $a_0 = 5.16 \pm 0.02$ Å, $b_0 = 8.92 \pm 0.02$ Å, $c_0 = 14.21 \pm 0.06$ Å, $\beta = 97°15' \pm 10'$. These values agree well with the cell parameters obtained from a series of rotation, Weissenberg and precession photographs. The β-angle was measured on b-axis precession photographs using the sharp reflections with $k = 3n$. The systematic extinctions found for these reflections agree with the space group C2/m (Cm, C2). As has been pointed out by Brown & Bailey (op. cit.), the result indicates only the symmetry of one chlorite layer, not of the entire structure. No doubling of the c-axis was traced in any of the single crystal photographs nor in the powder pattern of the 001 reflections recorded of single cleavage flakes. The reflections with $k \neq 3n$ are not sharp but appear as streaks parallel to c^* indicating a semi-random stacking sequence. According to the nomenclature adopted by Brown and Bailey, the Muiane mineral represents a pseudo-hexagonal one-layer semi-random cookeite. The data published by Brammall et al. (1937) and by Brown & Bailey (1962) indicate that, so far, no regular stacking sequences have been found for cookeite.

INFRA-RED ABSORPTION

The infra-red absorption spectrum of the Muiane mineral was recorded using apparatus and technique described by Sahama & Lehtinen (1967). The spectrophotometer tracing obtained which illustrates the absorption spectrum in the wavelength range 7–24 μ is reproduced in Fig. 3. A comparison of this spectrum with the infra-red absorption data for layer silicates compiled, e. g., by Moenke (1962, 1966) reveals the fact that, by means of its infra-red absorption, cookeite is easily distinguished from the other layer silicates studied. As has been demonstrated by Stubičan and Roy (1961), the infra-red absorption spectrum of layer silicates is affected by isomorphous substitutions in the structure. Thus, assignments can be made of the ions involved in a vibration which give rise to a particular absorption band. The infra-red absorption spectrum of manandonite recorded of the Sahatany Valley mineral shows, however, no noticeable difference from that of the Muiane cookeite. A qualitative spectroscopic test made by Mr. A. Löfgrén showed the Sahatany Valley mineral to be rich in boron and, consequently, to represent manandonite. It seems that, in the wavelength range studied, the substitution of boron for silicon does not produce any shifting of bands in the absorption spectrum. Cookeite and manandonite cannot be distinguished from each other by infra-red absorption.

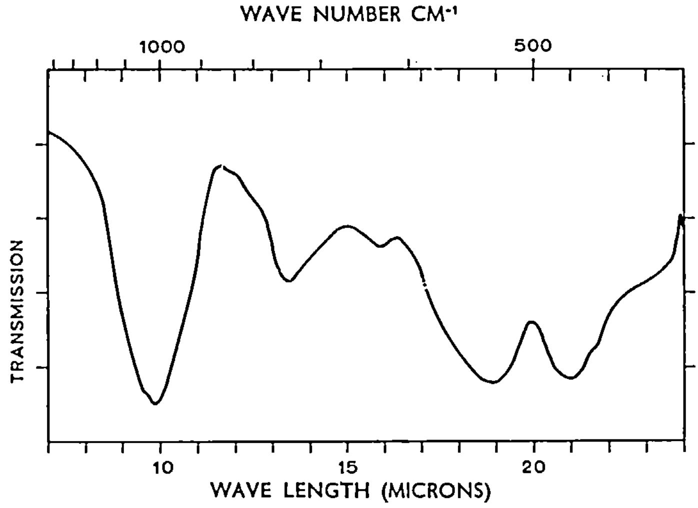

Fig. 3. Infra-red absorption spectrum of the Muiane cookeite.

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Table. 1. Chemical composition of cookeite from Muiane, Zambezia, Mozambique Analysis by Oleg v. Knorring

Original analysis		Based on O+OH+F=18	
SiO_2	34.15 %	Si	2.96
BeO	1.06	Be	0.22
B_2O_3	0.38	B	0.06
Al_2O_3	46.35	Al	4.73
Fe_2O_3	0.09	Fe	–
TiO_2	none	Ca	0.01
MgO	trace	Na	0.01
CaO	0.16	Li	1.11
Na_2O	0.10	F	0.09
K_2O	trace		
Li_2O	3.18	OH	8.12
F	0.35	O	9.79
H_2O+	14.06		
H_2O-	0.42		
Sum	100.30		
—O	0.15		
Total	100.15		

Table 2. Powder pattern of cookeite from Muiane, Zambezia, Mozambique

hkl	d	I based on $I_{003}=100$	I based on $I_{20\bar{2}}=10$
001	14.03	17	–
002	7.03	29	–
003	4.70	100	–
020,110	4.44	–	6
004	3.52	87	–
005	2.816	47	–
200	2.555	–	7
$20\bar{2}$	2.503	–	10
006	2.347	11	–
202	2.315	–	9
007	2.013	18	–
$20\bar{5}$	1.990	–	<2
204	1.959	–	4
008	1.761	7	–
206	1.634	–	3
009	1.566	2	–
060	1.486	–	3
00,10	1.410	6	–

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