

## Kassite from the Diamond Jo quarry, Magnet Cove, Hot Spring County, Arkansas: The problem of cafetite and kassite

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### ABSTRACT

Small (<0.5 mm), brownish-pink platy rosettes and yellow spherules, in cavities in nepheline syenite at the Diamond Jo quarry, Magnet Cove, Hot Spring County, Arkansas, have been identified as kassite,  $\text{CaTi}_2\text{O}_4(\text{OH})_2$ , a mineral previously known only from the Kola Peninsula, USSR. The Magnet Cove kassite is orthorhombic, in space group *Ammm*, *A2mm*, *A222*, or *A2122*, with unit-cell parameters  $a = 12.10$ ,  $b = 31.65$ ,  $c = 4.95$  Å, and  $Z = 16$ ;  $d_{\text{calc}} = 3.28$  g/cm<sup>3</sup>. Principal X-ray powder lines [ $d$  in Å, ( $I$ )] are 7.85(10), 3.26(7), 2.565(7), 1.910(8), 1.898(6). The X-ray powder and single-crystal data and density correspond to those reported by earlier workers for cafetite,  $(\text{Ca},\text{Mg})(\text{Fe},\text{Al})_2\text{Ti}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ , from Kola, but the chemical and physical properties correspond to those given in their description of kassite. These earlier workers may have intermixed samples during their X-ray study of kassite and cafetite.

### INTRODUCTION

The Magnet Cove complex, an alkalic intrusion in Cretaceous sedimentary rocks in Hot Spring County, Arkansas, forms a roughly circular body about 3 mi (about 5 km) wide. The inherent chemistry of the igneous rocks, their reaction with surrounding country rocks, and protracted weathering during Tertiary time have produced an extensive variety of unusual minerals, including concentrations of less common elements such as Ti, Zr, Sc, U, Nb, V, and REEs. The geochemistry and petrology of these rocks have been studied and described in detail by Williams (1891) and by Erickson and Blade (1963).

The Magnet Cove alkalic rocks are similar to those alkalic rocks found in the Afrikanda massif in the Kola Peninsula in the USSR, near the Finnish border. Here Kukharensko et al. (1959) discovered the new mineral cafetite,  $(\text{Ca},\text{Mg})(\text{Fe},\text{Al})_2\text{Ti}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ , and a second "undetermined mineral," then briefly described as a calcium titanate that occurred as pale-yellow, platy rosettes. Later, in an intensive study of the geochemistry and mineralogy of the Afrikanda massif, Kukharensko et al. (1965) described this latter mineral as a second new species, kassite,  $\text{CaTi}_2\text{O}_4(\text{OH})_2$ .

We found kassite at the Diamond Jo quarry in Magnet Cove, Hot Spring County, Arkansas. The identification of our mineral with that described by Kukharensko is unequivocal, but some confusion exists in the original description of the properties of the two species cafetite and kassite. In this paper we describe the Magnet Cove kassite and try to resolve the confusion in the Russian description.

### OCCURRENCE AND PROPERTIES OF KASSITE FROM MAGNET COVE

The Diamond Jo quarry is cut into a nepheline syenite pegmatite that is in contact with the surrounding sedimentary rock at the southern edge of the Magnet Cove complex. Malcolm Ross and M.J.K. Flohr of the U.S. Geological Survey made a modal analysis of the gray, fine-grained nepheline syenite in which the kassite was found, which showed that the syenite contains mainly light-colored minerals such as microcline, clinopyroxene, nepheline, and garnet. Titanian garnet, aegirine pyroxene, sodalite, pyrite, calcite, magnetite, and sphene occur as accessory constituents. The rock contains many small vugs or miaroles in which well-formed crystals of these and other minerals are found. Two types of kassite have been found—(1) brownish-pink, platy rosettes, 0.5 mm in diameter or less, implanted on white feldspar surfaces (Fig. 1A), and (2) yellow spherules, 0.1 mm or less in diameter, scattered on pectolite or other late-formed crystals (Fig. 1B). In other cavities, many previously unrecognized crystallized minerals have been found; these include kupletskite, fluorophlogopite-3T, catapleite, labuntsovite, lorenzenite, and several undescribed species containing Ti, Nb, Zr, and REEs. The kassite is rare and known only in minute quantities from this locality (we have not seen more than a dozen groups such as shown in Fig. 1). Thus, microscopic techniques have been used to characterize this mineral, because bulk chemical analysis is precluded.

In a scanning-electron microscope (SEM), a kassite rosette gave an energy-dispersive X-ray spectrum (EDX) that

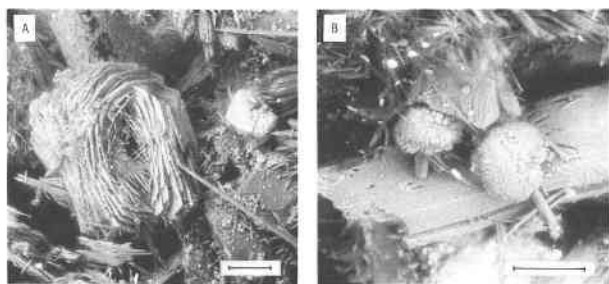


Fig. 1. Scanning-electron microscope images of kassite from Diamond Jo quarry, Magnet Cove region, Arkansas: (A) brownish-pink rosette on feldspar surface; (B) yellow spherules on pectolite crystals. Scale bars represent 0.1 mm.

showed as principal constituents Ca and Ti cations in about a 1:2 ratio. In addition, only trace amounts of Na, Nb, and Fe were registered. A preliminary Gandolfi X-ray pattern of a rosette was found to conform fairly closely with the JCPDS (1980) file card 13-551 for cafetite (see Table 1), one of the two new calcium titanate minerals from Kola described by Kukhareno et al. (1959, 1965).

The X-ray powder data were measured from a Gandolfi pattern (camera diameter, 114.7 mm;  $\text{CuK}\alpha$  radiation), by using a Nonius Guinier Viewer for  $2\theta$  angles and a Nonius Model II Microdensitometer for intensities. These data are listed in Table 1 and are compared there with data published by Kukhareno et al. (1965) for cafetite and kassite (JCPDS, 1980, cards 13-551 and 20-243, re-

Table 1. X-ray powder data for kassite and cafetite

Magnet Cove <sup>1</sup> kassite		Kola Peninsula <sup>2</sup>			
d(obs)	I(rel)	"cafetite"		"kassite"	
d(obs)	I(rel)	d(obs)	I(rel)	d(obs)	I(rel)
7.85 Å	10	7.86 Å	10	7.7 Å	2
4.49	1			7.2	3
4.22	.5			5.2	3
3.94	1			4.99	1
3.70	2	3.75	2	4.78	5
3.59	3			4.54	1
3.26	7	3.27	8	4.18	1
3.18	1			3.85	1
3.10	1	3.09	1	3.64	4
2.99	4	3.00	1	3.31	10
2.91	2			2.90	1
2.79	3	2.79	3	2.63	2
		2.63	4	2.52	1
2.565	7	2.562	8	2.41	1
2.510	.5			2.31	2
2.410	1	2.408	3	2.29	4
2.385	2	2.388	1	2.05	3
2.332	3			1.975	1
2.291	2			1.949	3
2.234	1			1.789	1
2.109	3	2.108	4	1.765	10
2.038	.5			1.682	1
1.910	8	1.914	7	1.655	1
1.898	6			1.634	1
1.849	3			1.610	2
1.804	2	1.801	2	1.519	3
1.772	.5			1.504	4
1.718	1			1.445	1
1.697	1	1.696	1	1.307	1
1.599	.5			1.223	2
1.577	1	1.573	4	1.198	2
1.555	2			1.164	2
1.532	3	1.535	2	1.151	1
1.473	1			1.141	1
1.416	1	1.420	3	1.094	1
		1.389	1	1.087	2

<sup>1</sup>Gandolfi method;  $\text{CuK}\alpha$  radiation.

<sup>2</sup>Kukhareno et al. (1965); converted to Å from kX units.

See also JCPDS (1980) (cards 13-551 and 20-243).

Table 2. Properties of kassite and cafetite

Property	Magnet Cove	Kola Peninsula (Kukhareno, et al., 1965)	
		"cafetite"	"kassite"
Name	kassite	"cafetite"	"kassite"
Formula	$\text{CaTi}_2\text{O}_4(\text{OH})_2$	$(\text{Ca},\text{Mg})(\text{Fe},\text{Al})_2\text{-Ti}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$	$\text{CaTi}_2\text{O}_4(\text{OH})_2$
Habit	platy rosettes; spherules	acicular laths; fibrous	platy rosettes
Color	brownish pink to yellow; adamantine luster	yellowish to colorless; adamantine luster	yellowish; adamantine luster
Crystal system	orthorhombic, A-centered	orthorhombic	orthorhombic
Unit cell, Å*			
a	12.10(2)	(b) 12.12(3)	8.99(3)
b	31.65(3)	(a) 31.34(5)	9.55(3)
c	4.95(1)	4.96(1)	5.26(1)
V (Å <sup>3</sup> )	1899.	1884.01	451.59
Density, g/cm <sup>3</sup>	3.28 (calc.) (Z=16)	3.28 (meas.)	3.42 (meas.)
Optics	Biax. neg. X ⊥ plate	Biax. neg. Y ⊥ lath	Biax. neg. Z ⊥ plate (?)
α		1.95	1.95
β		2.08	2.13
γ		2.11	2.21
	2V ~ -30°	2V -30°	2V -58°

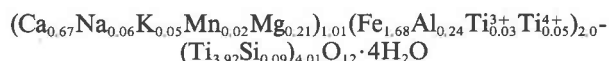
\*Estimated standard deviations indicated in parentheses for last significant digits; those for Magnet Cove estimated from quality of precession photographs.

spectively). A close correspondence can be seen between our data for kassite and the data reported for cafetite.

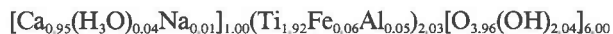
We have obtained poor but clearly resolved precession single-crystal patterns for our mineral, from which an orthorhombic unit cell can be measured. Table 2 presents these data and unit-cell constants and other data reported by Kukhareno et al. (1965). Our unit-cell constants for the Magnet Cove kassite crystals correspond closely to those published for cafetite. We found the kassite lattice to be A centered, which allows the possible space groups  $Ammm$ ,  $A2mm$ ,  $A222$ , or  $A2_122$ . These patterns permit some low-angle lines of the powder pattern to be indexed, but not enough to make possible the refinement of unit-cell parameters.

#### THE PROBLEM OF KASSITE AND CAFETITE

Tables 1 and 2 seem to indicate a correspondence between the Magnet Cove mineral and either cafetite or kassite, but initially it is not clear which. A major inconsistency exists between the chemistry and crystallography of the two species. Kukhareno et al. (1965) presented a quantitative chemical analysis of "cafetite" that led to the following formula:



or approximately  $(\text{Ca},\text{Mg})(\text{Fe},\text{Al})_2\text{Ti}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ . Although Kukhareno et al. reported the presence of major Fe (with Ca and Ti, hence the name cafetite), we found barely a trace of Fe in our mineral. On the other hand, Kukhareno et al. (1965) gave for "kassite" the following formula:



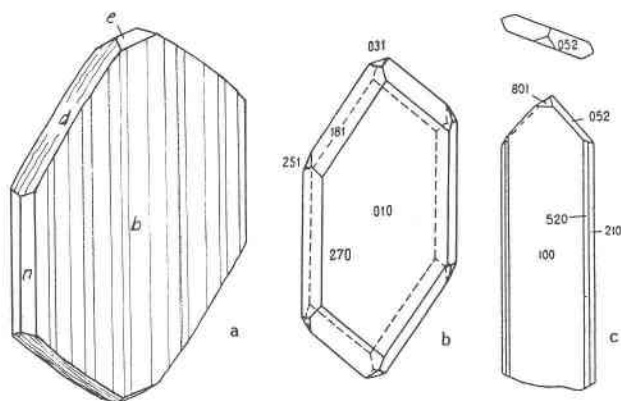


Fig. 2. Crystal habit of (a) kassite from the Diamond Jo quarry, (b) "kassite," and (c) "cafetite," reproduced from Kukharenko et al. (1965). The probable forms shown in (a) are  $b\{010\}$ ,  $n\{120\}$ ,  $d\{101\}$ , and  $e\{051\}$ .

or approximately  $\text{CaTi}_2\text{O}_4(\text{OH})_2$ . This formula agrees with our EDX analysis.

The implication is strong that these earlier workers, who studied the two minerals together, somehow mixed up their data. The crystal habit, chemistry, and physical properties of the Magnet Cove mineral conform with those of the Russian "kassite," but the single-crystal and X-ray powder data correspond with those given for "cafetite." The Russian study was attributed by Kukharenko (who presumably wrote the reports) to four investigators: A. A. Kukharenko, who made the field and laboratory mineralogical studies; V. V. Kondratyeva, who did the X-ray studies; and V. M. Kovyatsina and E. H. Baranovoi, who made the chemical analyses. If we postulate that someone accidentally interchanged the two samples, the confusion is largely eliminated. We have kept the name cafetite for the Fe-bearing mineral, and we conclude that our mineral is kassite (named for N. G. Kassin, who discovered the Afrikanda massif).

The questions of density, crystal habit, and optical properties also are confusing. Because of the microscopic amount of the Magnet Cove sample at hand, the density of kassite could not be measured directly, but, by using the kassite formula, the calculated density was found to be  $3.28 \text{ g/cm}^3$ . Kukharenko et al. reported this density for "cafetite," whereas for "kassite" they reported a higher density (Table 2). The Magnet Cove kassite is predominantly flattened on (010) and forms six-sided plates (Fig. 2a). Four of the plate edges are blunt, curved, and rough and show no reliable signals in the optical goniometer. The plate angles conform best to the form  $d\{101\}$ . The two lateral edges give poor but recognizable signals for a prism  $n\{120\}$ . Similarly, a small dome  $e\{051\}$  also could be measured. This habit is on the whole similar to that illustrated by Kukharenko et al. (1965) for "kassite" (Fig. 2b). We have been unable to reconcile his measured goniometer angles for six different forms with our unit cell. The major forms that he shows (aside from the plate) have

a small angle to the pinacoid form {010} and may represent vicinal or growth surfaces. Some SEM images seem to show a prism is lying closer to  $b$  than  $n$ , which may represent a form such as {150} or {160}, although optical signals for such faces could not be detected. The figure of "cafetite" from Kukharenko et al. is also shown in Figure 2c for comparison.

We have not attempted to measure the refractive indices of Magnet Cove kassite, but the biaxial acute figure centered on the plate normal is clearly negative, as would be expected for a crystal that most probably has a layer structure. Kukharenko et al. (1965) reported  $\gamma$  normal to the plate ( $\parallel[010]$ ), which appears anomalous. The optic angle may vary somewhat if any interlayer hydration occurs.

## CONCLUSION

In the nepheline syenite at the Diamond Jo quarry, Hot Spring County, Arkansas, we have found crystals of a calcium titanate hydroxide mineral. From its morphology, chemistry, and physical properties, the mineral can be identified with kassite from the Kola Peninsula, USSR. The X-ray unit cell and powder-diffraction data correspond with the data reported for cafetite from Kola. We conclude that the crystallographic data published for cafetite and kassite were inadvertently interchanged in the original description (Kukharenko et al., 1965) and that this confusion has been repeated in the subsequent literature and mineral compilations. Thus, in *Mineralogy* (1967), in Strunz (1977), in Rudashevskii et al. (1977), in the JCPDS (1980) file, in Semenov (1981), and in reports by Fleischer (1960, 1965), the X-ray powder and single-crystal data for cafetite are given for kassite and vice versa.

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