ATHABASCAITE: A NEW COPPER SELENIDE MINERAL FROM MARTIN LAKE, SASKATCHEWAN*

D. C. HARRIS, L. J. CABRI AND S. KAIMAN
Mines Branch, Department of Energy, Mines and Resources,
Ottawa, Canada

ABSTRACT

Athabascaite is a new copper selenide from the Lake Athabasca area, northern Saskatchewan. Electron probe microanalyses gave $Cu_{5.11}Se_{4.0}$ and $Cu_{5.10}Se_{3.48}S_{0.52}$.

The x-ray powder data can be indexed on an orthorhombic cell with $a = 8.227$, $b = 11.982$, $c = 6.441$ Å. The strongest lines are 3.235(10), 3.015(6), 1.997(8), 1.893(5), 1.817(3), 1.664(4). With $Z = 4$, G. (calc.) is 6.59.

The mineral occurs as lath-shaped inclusions in umangite and as stringers and veinlets in hematite-stained carbonate vein material in basalt. In reflected light it is strongly bireflecting with colours in air ranging from light grey to bluish grey, like klockmannite. Anisotropism very distinct with polarization colours white to dark blue. Reflectivity and microhardness values are given. Attempts to synthesize the mineral above 100°C were unsuccessful.

INTRODUCTION

A possibly new copper selenide from the Lake Athabasca area was first recognized in 1949 by Mr. S. Kaiman, Extraction Metallurgy Division, Mines Branch, Ottawa, while studying the radioactive minerals of the Athabasca area of northern Saskatchewan. At this time, Dr. J. W. Earley was investigating the selenide minerals for a Ph.D. thesis, at the University of Toronto, and samples containing the unknown copper selenide were sent to him for identification. Unfortunately, the material was insufficient for anything but qualitative chemical tests, polished section observations, and x-ray powder diffraction. The powder diffraction data are recorded in the Peacock Atlas (Berry & Thompson 1962) under No. 154, as an unknown copper selenide. Due to the small grain size and scarcity of the material, further studies were discontinued.

The recent installation of an electron-probe microanalyzer in the Mineral Sciences Division has provided an opportunity to re-examine the mineral and to obtain sufficient data to establish the unknown copper selenide as a new species.

LOCALITY

Samples containing the new copper selenide were initially sent to S. Kaiman by Eldorado Mining and Refining Limited. The samples originated from the Martin Lake Mine located at the northeast corner of

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Martin Lake, Saskatchewan, in the neck of land between Beaverlodge Lake and Martin Lake, which is south of the road from Beaverlodge to Uranium City. The selenides occur in pitchblende ore and in hematite-stained carbonate vein material in the basalt of the Martin formation. Further information on the geology and mineralogy can be obtained from Robinson (1955) and Smith (1952).

PHYSICAL PROPERTIES

Athabascaite occurs sparsely as inclusions in, and replacements of, umangite, and as stringers and veinlets in the carbonate vein material. Where associated with the umangite, the mineral forms elongated lath-shaped grains (Fig. 1) which range up to 100 microns in length and 40 microns in width. Several of the lath-shaped crystals, at first glance, appear as remnants containing cores of umangite that is finer grained than the surrounding material. This feature suggests that the umangite may have recrystallized during the formation of the new mineral.

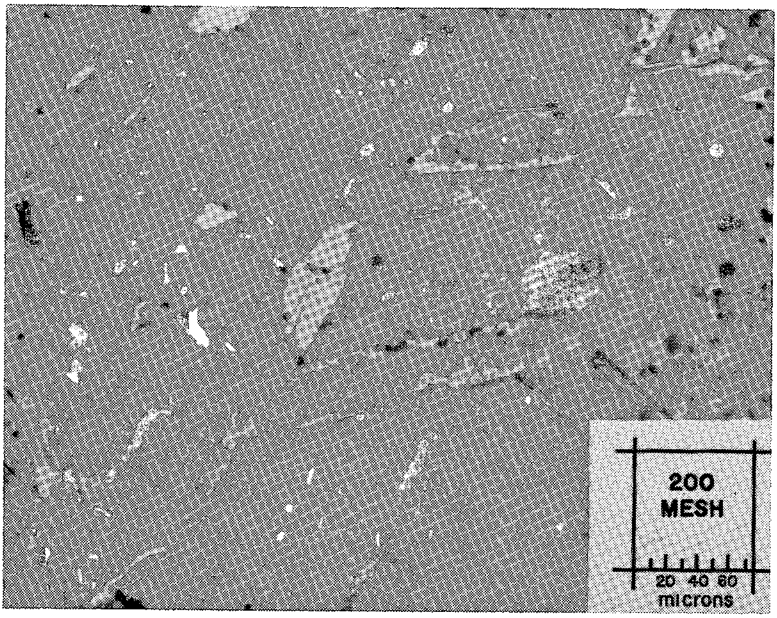

FIG. 1. Photomicrograph showing lath-shaped grains of athabascaite (light grey to white) in umangite (grey). Note the strong bireflectance exhibited by the grains in different orientations.

The veinlets or stringers in the carbonate veins contain massive areas up to 300 microns in diameter. The veinlets consist of an aggregate of randomly oriented crystals which seldom exceed a few microns. In this environment, the mineral is essentially pure, with only the odd trace of umangite.

The optical properties of the mineral are striking, and are characterized by distinct bireflectance, as seen in Fig. 1, and strong anisotropism. The bireflectance somewhat resembles that of klockmannite, varying from a light grey to bluish grey. The polarization colours (nicols crossed) vary from a creamy white to a distinct dark blue. This property enables one to recognize and distinguish the mineral from klockmannite, which, like graphite, varies from a light blue to bright yellow between crossed nicols.

A comparison of the reflectivity properties of the athabascaite and other known copper selenides is given in Table 1. The apparatus used for measuring the reflectivities was a Leitz MPE microscope photometer equipped with type FS-9-A photomultiplier tube, two six-volt storage batteries connected in parallel, and a Veril B200 continuous-band interference filter. Silicon was used as a reference standard. Ten measurements were made to obtain the range and average values given in Table 1. These included grains of athabascaite which occur both as inclusions in umangite and as stringers in the carbonate veins, which, as will be shown later, represent both sulphur- and non-sulphur-bearing varieties. No difference in reflectivity were noted for the two types of athabascaite. The reflectivity of athabascaite is distinct enough to distinguish the mineral from the other known copper selenides.

A comparison of the microhardness with other known copper selenides is likewise listed in Table 1. The microhardness for athabascaite was determined with a Leitz Durimet hardness tester equipped with polarizing filters and rotating stage. Ten indentations were made using a 15-gram weight. Microhardness values for the other copper selenides were extracted from the literature (Cameron 1961; Sindeeva 1964). This property does not appear to be distinct enough to characterize the mineral.

As mentioned above, athabascaite is closely associated with umangite. Other metallic minerals identified in the sections are clausthalite, eucairite, berzelianite, sulphur-bearing berzelianite, klockmannite, eskebornite, tyrrellite, native copper and silver, pitchblende, hematite and pyrite. The gangue minerals are calcite, barite, quartz and feldspar. A manuscript with new data on several of the above rare selenides is in preparation.

ELECTRON PROBE ANALYSIS

The composition of athabascaite was determined with a Materials Analysis Company (MAC) electron-probe microanalyzer operated at a voltage of 25 kV and a specimen current of approximately 0.04 micro-

TABLE 1. MICROHARDNESS AND REFLECTIVITY OF ATHABASCAITE AND KNOWN COPPER SELENIDES

Mineral	Microhardness VHN (in kg/mm²)	Reflectivity			
		470 nm	546 nm	589 nm	650 nm
Athabascaite	Av. 78.1†	Max. 24.7–26.1 (25.5)	23.9–26.9 (25.8)	22.8–26.2 (25.0)	21.6–25.6 (24.0)
	Range 68.8–93.5	Min. 18.9–19.5 (19.2)	17.6–18.3 (17.9)	16.4–17.1 (16.7)	14.3–15.2 (14.6)
Klockmannite Argentina M 17025 (ROM)	60–82*	Max. 19.3–28.9 (23.0)	18.6–28.6 (22.8)	17.0–27.1 (21.2)	15.0–24.3 (18.9)
		Min. 15.2–16.1 (15.8)	13.8–15.5 (14.8)	12.4–14.0 (13.2)	10.0–12.1 (11.2)
Umangite N.W.T.	77–128*	Max. 18.3–18.8 (18.5)	14.3–15.8 (15.3)	13.3–14.7 (14.2)	14.5–14.7 (14.5)
		Min. 16.9–17.9 (17.5)	11.9–12.2 (12.1)	10.4–11.1 (10.8)	14.3–15.5 (14.9)
Berzelianite C.S.S.R.	85*	28.1–28.7 (28.4)	27.4–28.1 (27.7)	25.1–25.6 (25.4)	21.8–22.3 (22.0)

†15 g weight, 10 grains measured.
*not determined in this study.

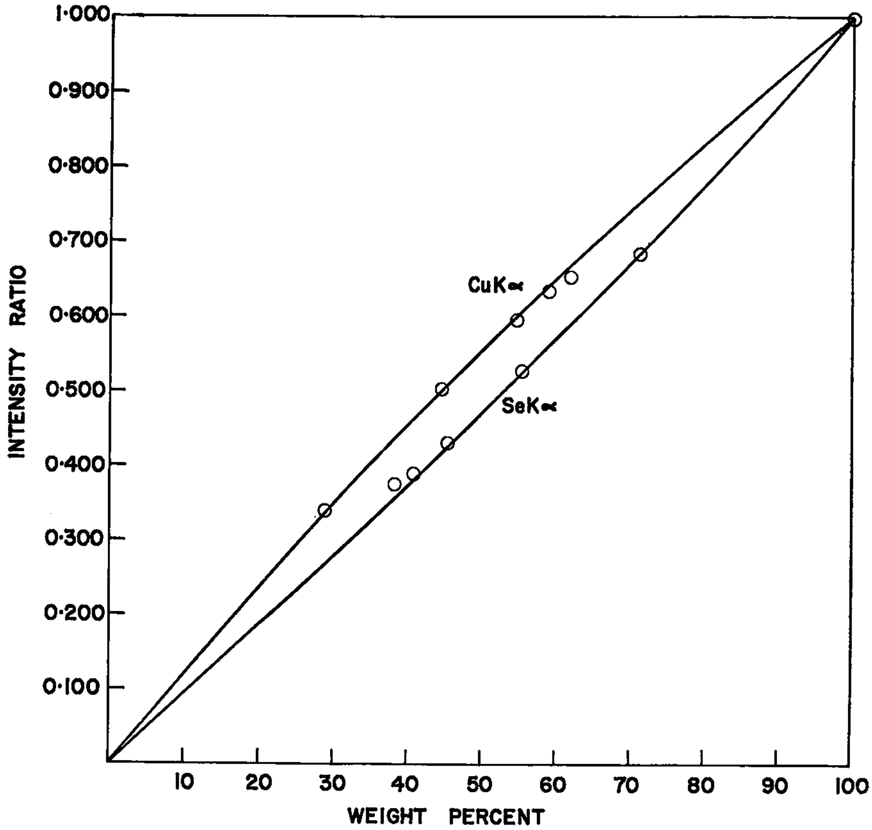

FIG. 2. Electron probe calibration curve for synthetic copper selendides.

amperes. Synthetic copper selenides of compositions Cu_2Se, $Cu_{1.801}Se$, Cu_3Se_2, CuSe and $CuSe_2$ were used as standards. The synthetic samples were found to be homogeneous and calibration curves of the standards are shown in Fig. 2.

The composition of the mineral was determined by analyzing several grains in five polished sections; the average values are given in Table 2.

TABLE 2. ELECTRON PROBE ANALYSIS OF ATHABASCAITE AND RELATED COPPER SELENIDES

Mineral	Cu	Se	S	Total
Athabascaite in umangite	51.1 ± 0.5	49.7 ± 1.0	—	100.8
In wall rock	52.0 ± 0.5	44.0 ± 1.0	2.7 ± 0.5	99.7
Theoretical Cu_5Se_4	50.15	49.85	—	100.0
Theoretical umangite Cu_3Se_2	54.70	45.30	—	100.0
Theoretical klockmannite CuSe	43.58	56.42	—	100.0

Sulphur was detected only where athabascaite occurs as stringers or veinlets in the carbonate veins in the wallrock. The sulphur content varies slightly from grain to grain, with an average value of approximately 2.7 per cent. Synthetic copper selenides of compositions $Cu_{1.8}Se$, with variable amounts of sulphur replacing the selenium, were used as standards for the sulphur analysis.

The empirical composition of athabascaite may be written as $Cu_{1.278}Se$, but re-calculation to whole numbers yields two possible formulae: $Cu_{5.112}Se_4$ and $Cu_{8.946}Se_7$, which are close to Cu_5Se_4 and Cu_9Se_7, respectively.

X-RAY DIFFRACTION DATA

Attempts to obtain sufficient fragments for single-crystal studies were unsuccessful. The *x*-ray powder pattern (Fig. 3), which distinguishes the mineral from all other copper selenides, can be indexed satisfactorily on an orthorhombic cell yielding dimensions $a = 8.227 \pm 0.01$, $b = 11.982 \pm 0.02$, $c = 6.441 \pm 0.01$. The unit cell parameters were refined by a least-squares computer program.

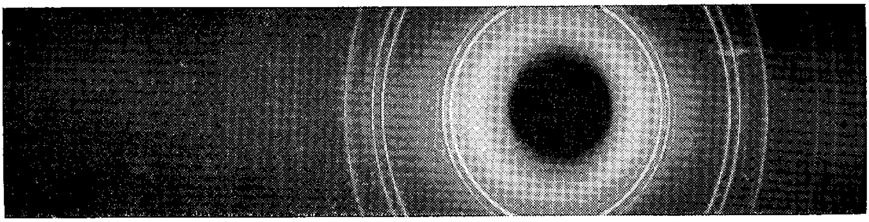

FIG. 3. *X*-ray powder diffraction pattern of athabascaite. Ni-filtered Cu radiation.

It is to be noted that the cell dimensions originally proposed for umangite, $a = 4.28$, $b = 6.40$, $c = 12.46$ Å, are nearly $a/2$, c, b of athabascaite. However, Morimoto (1966) recently determined the crystal structure of umangite and confirmed a tetragonal cell with dimensions $a = 6.406 \pm 0.002$ Å and $c = 4.279 \pm 0.002$ Å. Since suitable material was not available for single-crystal work in this study, the cell dimensions of athabascaite can only be proposed from attempts to index the powder pattern.

Table 3 compares the *x*-ray powder data obtained in this study using a 114.6-mm diameter Debye-Scherrer camera and Ni-filtered Cu radiation with the data given in the Peacock Atlas. The main differences in the data are the apparent doubling of certain lines which were not observed in 1949 nor in the present study. Whether the extra lines obtained by Earley are due to impurities or sample preparation, is difficult to say.

TABLE 3. X-RAY DIFFRACTION DATA FOR ATHABASCAITE

Orthorhombic $a = 8.227$ $b = 11.982$ $c = 6.441$		Ni-filtered Cu radiation			
		Martin Lake (This Study)		J. W. Earley (Peacock Atlas)	
hkl	*d*(calc.)	*I*(est)	*d*(meas.)	*I*(est)	*d*(meas.)
010	11.982	½	12.10		
020	5.991	½	6.00		
200	4.113	½	4.11		
201	3.467	3	3.44		
211	3.330	½	3.34		
002	3.220	10	3.235	8	3.25
				8	3.20
012	3.110	1	3.112		
040	2.996	6	3.015	4	3.04
				4	2.99
230	2.866	2	2.870	½	2.85
300	2.742	2	2.744		
231 141	2.618 2.579	½	2.606		
320	2.493	2	2.490	½	2.49
050	2.396	½	2.391		
042	2.193	½	2.200		
013	2.113	2	2.105		
060	1.997	8	1.997	10	2.00
033	1.891	5	1.893	½	1.899
				2	1.884
223	1.814	3	1.817	½	1.811
233	1.718	½	1.720		
440	1.696	2	1.694	½	1.710
422	1.665	4	1.664	3	1.658
				½	1.419
600	1.371	3	1.374	1	1.368
630	1.297	3	1.294	1	1.295
225	1.204	2	1.205	1	1.208
613	1.150	2	1.149	½	1.153
2.10.1 093 660	1.132 1.131 1.130	2	1.132	1	1.133
006	1.073	½	1.074	1	1.077
				½	1.037
				½	0.999
				½	0.963
				½	0.950
				½	0.919
				½	0.884
				½	0.857

The x-ray data obtained in this study are more complete, since a 114.6-mm diameter camera was used in place of the smaller camera and, apart from the four extra lines observed by Earley, the patterns are in excellent agreement.

Based on the unit-cell dimensions given above and a theoretical formula of Cu_5Se_4, the cell contains four formula units and gives a calculated density of 6.59 g/cc; with a theoretical formula of Cu_9Se_7, the cell contains two formula units and gives a calculated density of 5 85 g/cc. Both of these densities are in the same general range as densities for the known copper selenides—umangite Cu_3Se_2(6.59), klockmannite CuSe(6.12) and berzelianite $Cu_{1.85}Se$(6.96), all g/cc. Unfortunately, it was not possible to concentrate sufficient pure athabascaite for a density determination. Since single crystal work could not be done, the formula Cu_5Se_4 has been tentatively selected for athabascaite, based on closer calculated density value.

THE Cu-Se BINARY SYSTEM

The compilations of early work on the Cu-Se system by Hansen & Anderko (1958) and Elliott (1965) are now superseded by the more definitive work of Heyding (1966). Bernadini & Catani (1968) generally confirmed Heyding's work, although most of their reported temperatures of transition, melting, etc. were higher.

None of the phase diagrams report the existence of a phase corresponding to Cu_5Se_4. Several attempts at synthesizing this phase in the "dry" system proved unsuccessful. The lowest temperature tried was 100°C for 55 days, after previous heating at about 350°C, followed by grinding and pelletizing. The phases present in all cases were klockmannite and umangite. Attempts to speed reaction rates by shaking the sample in a "wiggle-bug" for an hour and then annealing at 100°C were also unsuccessful. Attempts to synthesize Cu_5Se_4 at 100°C with 3% S also failed.

It is difficult, at present, to decide whether these experiments in the "dry" system suggest a low-temperature stability field for athabascaite or whether this is just due to the wrong experimental conditions or insufficient annealing times. Umangite has a low breakdown temperature (135°C) and its successful synthesis at 120°C took 120 days with two grinding and pelletizing operations after initial heating at 500°C and 350°C. The minimum time required to produce homogeneous umangite at that temperature is not known. Other related minerals, however, such as empressite (AgTe) which has been shown to decompose at 210°C (Honea 1964), has not been successfully synthesized when heated for three months at 194°C and 170°C in the "dry" system (Cabri 1965).

In connection with umangite, mentioned above, an attempt was made to see if it departed much from stoichiometry by "appearance-of-phase runs." The experiments, although not conclusive, indicate that, at 120°C, umangite can take up a slight excess of Cu but not excess of Se. The boundaries determined were: 59.840 ± 0.166 at.% Cu on the Se-rich side, and 60.891 ± 0.166% at.% Cu on the Cu-rich side.

The name athabascaite (Ă. THE BĂSKĂ-ĂIT) is for Lake Athabasca in northern Saskatchewan and Alberta, a famous Canadian mineral locality. The name has been approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material is preserved at the National Mineral Collection, Ottawa and the Royal Ontario Museum, Toronto.

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