

# ESKEBORNITE, TWO CANADIAN OCCURRENCES

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## ABSTRACT

The first Canadian occurrence of eskebornite from Martin Lake and the Eagle Group, Lake Athabaska area, Northern Saskatchewan is reported. Electron microprobe analyses show that the formula is  $\text{CuFeSe}_2$ . The x-ray powder diffraction patterns are identical to that of eskebornite from Tilkerode, Germany, the type locality.

Eskebornite occurs as island remnants in, and replaced by, umangite which occurs in pitchblende ores in the basalt of the Martin formation and in granitized mafic rocks of the Eagle group. The mineral can be readily synthesized at  $500^\circ\text{C}$  from pure elements in evacuated silica glass tubes. Reflectance and micro-indentation hardness measurements are given.

## INTRODUCTION

Eskebornite, a copper iron selenide, was first discovered and named by P. Ramdohr in 1949 while studying the selenide minerals from the Tilkerode area, Harz Mountain, Germany. The mineral has also been reported from Sierra de Cacheuta and Sierra de Umango, Argentina (Tischendorf 1960). More recently, other occurrences of eskebornite have been described: by Kvačėk *et al.* (1965) in the selenide paragenesis at the Slavkovice locality in the Bohemian and Moravian Highlands, Czechoslovakia; and by Agrinier *et al.* (1967) in veins of pitchblende at Chaméane, Puy-de-Dôme, France.

Earley (1950) and Tischendorf (1959, 1960) made observations on eskebornite from the Tilkerode locality, but, even today, certain data are still lacking in the characterization of eskebornite, in particular its crystallographic symmetry. The purpose of this paper is to record the first occurrence of eskebornite in Canada and to present electron microprobe analyses, reflectance and micro-indentation hardness measurements.

## GENERAL DESCRIPTION

Eskebornite was identified by the first author in polished sections during the investigation of other selenide minerals from the Martin Lake mine, Lake Athabasca area, northern Saskatchewan, from which a new

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copper selenide mineral, athabascaite, has been described (Harris *et al.* 1970). The Martin Lake mine is located at the northeast corner of Martin Lake, on the neck of land between Beaverlodge Lake and Martin Lake, south of the road from Beaverlodge to Uranium City. The second author identified eskebornite during the investigation of some rare ore minerals in a polished section containing selenide minerals from the Eagle group of claims, an area north of Hal Lake, which is about 1500 feet west of the Eagle shaft, Lake Athabasca area. The sample (part of the tyrrellite type locality material) was presented by Dr. S. C. Robinson to Prof. W. Uytendogaardt. The description of the locality is from Robinson (1955).

Eskebornite occurs as island remnants in, and replaced by, umangite (Fig. 1). The remnants range up to 200 microns in diameter and frequently contain small inclusions of eucairite (Fig. 1, 2 and 3). Other minerals identified in the sections, although not in contact with the eskebornite, are hematite, klockmannite, clausenthalite and tyrrellite. A minority of eskebornite grains in the Eagle specimen contain numerous tiny (less than 1 micron diameter) inclusions of a white mineral which could not be identified.

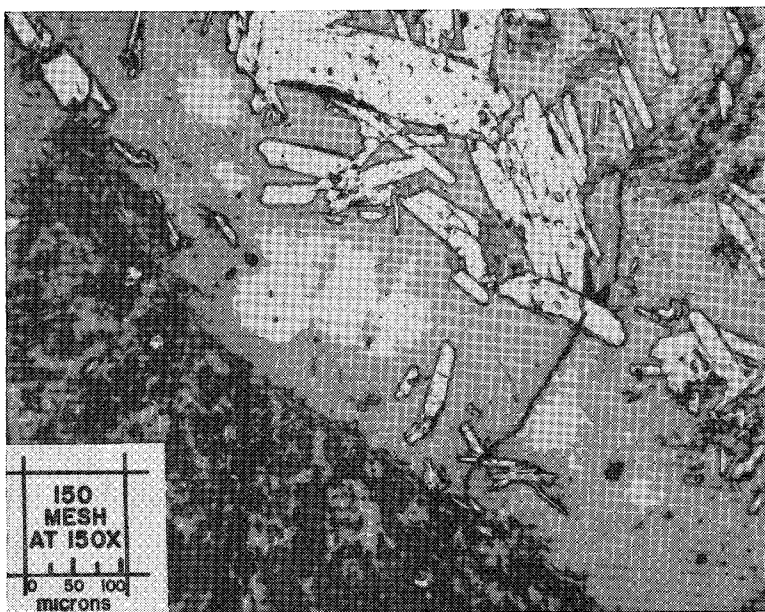


FIG. 1. Photomicrograph showing island remnants of eskebornite from Martin Lake (light grey) and hematite laths (white) in umangite (dark grey). Note the small white inclusions of eucairite in eskebornite.

The minerals occur in pitchblende ore and in hematite-stained carbonate vein material in the basalt of the Martin formation and in granitized mafic rocks of the chlorite-epidote type of the Eagle group. Further information on the geology and mineralogy can be obtained from Robinson (1955) and Smith (1952).

In reflected light, the bireflectance of the Martin Lake eskebornite is weak and varies from creamy yellow to yellowish brown. Anisotropism is moderate and varies from yellowish to tan. The colours are slightly enhanced under oil, with bireflectance varying from yellowish cream to brownish cream, somewhat similar to that of pyrrhotite. Anisotropism varies from greyish white to dark brown. The bireflectance and the anisotropism of the Eagle eskebornite are distinctly stronger than for the Martin Lake eskebornite, but show the same colours. Tischendorf (1960) observed two optically distinguishable varieties of eskebornite from the Tilkerode locality which he called eskebornite I and II, although the two varieties are not distinguishable in x-ray powder patterns. Eskebornite I was reported to have a creamy brown colour which contrasts with the dirtier brown of eskebornite II. Eskebornite II had a more creamy yellow-

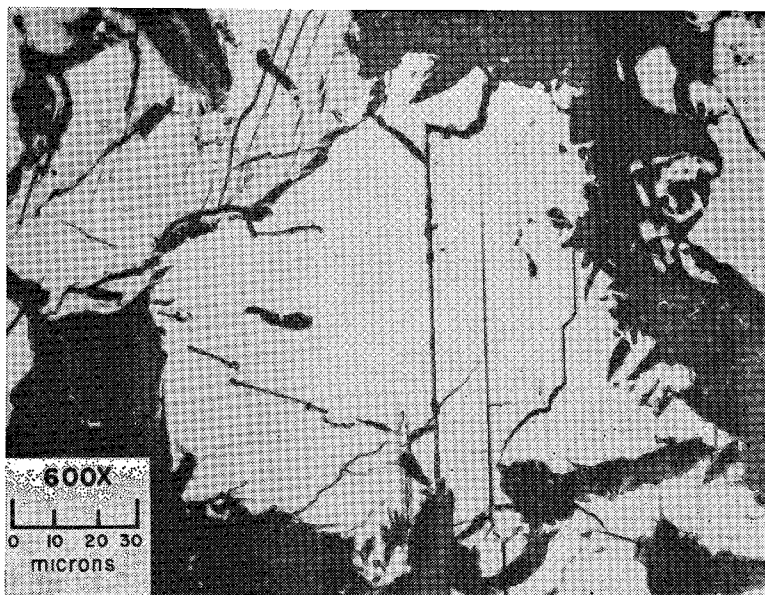


FIG. 2. Photomicrograph of eskebornite from Martin Lake (grey) in umangite (black). The small white inclusions in eskebornite are eucairite. Note the cleavage or fracturing in eskebornite.

brown reflectance and is reported as being definitely brighter. As also noted by Tischendorf, eskebornite I showed a well-developed hexagonal cleavage not observed in the other variety. It is possible, however, that the two optically distinguishable varieties are the same mineral, but in different optical orientations, particularly since Tischendorf mentioned that intermediate members frequently occur which cannot always be successfully identified. Synthetic eskebornite prepared in this study showed what appeared to be two varieties, but with the same composition and x-ray powder pattern.

As noted by Ramdohr, the Tilkerode material shows a strong hexagonal cleavage from which he assumed hexagonal or pseudohexagonal properties for the mineral. The Martin Lake material (Fig. 2) and the Eagle group material (Fig. 3) show a development of a cleavage, but whether it is correct to classify it as hexagonal cleavage or octahedral parting is difficult to say.

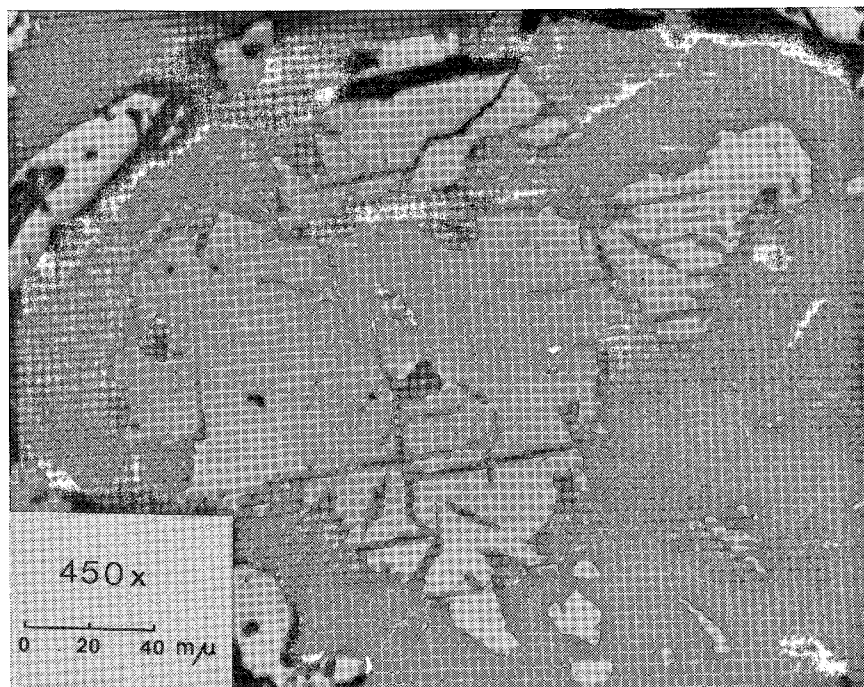


FIG. 3. Photomicrograph of eskebornite from the Eagle Group (grey) and hematite (white) in umangite (very dark grey). The small white inclusions in eskebornite are eucairite. Note the cleavage or fracturing in eskebornite.

Earley (1950) observed that small particles of eskebornite from the Tilkerode locality scraped from a polished section are magnetic and cling to a magnetized needle. Kvaček made no mention of the magnetism of the Czechoslovakian material, but Agrinier noted that the Chaméane mineral is non-magnetic. Eskebornite from the Lake Athabasca area is not attracted to a magnet.

#### REFLECTANCE AND MICRO-INDENTATION HARDNESS

The apparatus used for measuring the reflectance of the Martin Lake eskebornite was a Leitz Ortholux-Pol microscope, a Leitz MPE microscope photometer equipped with a Dumont, type-6467 photomultiplier tube, two six-volt storage batteries connected in parallel, and a Veril B200 continuous-band interference filter. A 16.5:1 objective with a numerical aperture of 0.40 was used. The reflectance values of the three largest grains for the four standard wavelengths, using silicon as a standard, are given in Table 1. The reflectance of the Eagle group eskebornite was measured with a Leitz MPV microscope photometer, mounted on a Leitz Ortholux-Pol microscope and equipped with Knott type-9592A photomultiplier tube and a Veril B200 continuous-band interference filter. A 16:1 objective with a numerical aperture of 0.40 was used. The method described by Cameron (1963) was applied to determine the optical symmetry of the Eagle eskebornite. On the basis of the reflectance

TABLE 1. ESKEBORNITE: REFLECTANCE AND MICRO-INDENTATION HARDNESS

Wavelength (nm)	470	546	589	650	Micro-indentation
					Hardness
Martin Lake					VHN (kg/mm <sup>2</sup> )
max.	26.2-30.7	30.4-33.3	31.8-34.2	33.4-36.8	155-252
	27.9	31.7	32.7	34.5	Av. = 204
min.	24.4-27.2	28.2-29.1	29.5-30.1	31.2-32.8	
	25.6	28.7	29.8	31.8	
Eagle group					
max. ( $R_o$ )	30.6	34.6	36.2	37.9	144-202
min. ( $R'_e$ )	20.4	24.4	26.7	29.0	

values in air the mineral is uniaxially positive. The reflectance values for the four standard wavelengths as measured on the grain showing maximum bireflectance, using carborundum as a standard, are given in Table 1. The silicon and carborundum standards were supplied by the Commission on Ore Microscopy of the International Mineralogical Association and had been calibrated by the National Physical Laboratory in Great Britain. The reflectance values for silicon and carborundum were taken from the NPL report, references N2528 and N2538 respectively, dated August 22, 1966.

The micro-indentation hardness of eskebornite was determined with the aid of Leitz Durimet hardness testers equipped with polarizing filters and rotating stage. A load of 15 grams with an indentation time of 20 seconds was used. A total of seven indentations in the Martin Lake eskebornite and of 10 indentations in the Eagle eskebornite were made, for which the range of values are given in Table 1.

#### CHEMISTRY OF ESKEBORNNITE

Ramdohr originally assumed that the composition of eskebornite was FeSe from its optical similarity to pyrrhotite and well-developed hexagonal cleavage. The fact that eskebornite also contained copper was established accidentally by Earley (1950), who noted the similarity of the x-ray powder pattern to that of certain Fe-Cu-Se fusions which had been made for another purpose. A polished section of eskebornite and two small chips from the Tilkerode locality were sent to Prof. M. A. Peacock, University of Toronto by Ramdohr in 1948, from which Earley made his observations. Since none of this material was in sufficient amounts for quantitative analysis, Earley prepared sixteen fusions by heating Fe, Cu and Se in various proportions in evacuated glass tubes. This study indicated that the composition of eskebornite approached  $\text{CuFeSe}_2$ . In spite of Earley's work, Ramdohr (1955) later suggested a composition of  $\text{Fe}_3\text{CuSe}_4$  for eskebornite.

Tischendorf (1960) reviewed the previous work on eskebornite, but made no mention of the synthetic work of Earley. In an attempt to determine the composition of eskebornite, he made a preliminary spectrographic analysis on milligram amounts of natural material and made several synthetic fusions. Results of this work led Tischendorf to the conclusion that there must be a certain range of composition for eskebornite with the general formula  $(\text{Cu,Fe})_{1.1n}\text{Se}_n$ , whereby the mole ratio Cu:Fe is approximately 1:1, or slightly copper deficient.

Since eskebornite occurs in very small amounts and is generally intergrown with other selenides, the only reliable method of analysis is with the microprobe. In this study, the analysis of the Martin Lake eskebornite was performed on a Materials Analysis Company (MAC) electron microprobe, and the data processed by a computer program which applied corrections for absorption, fluorescence and atomic number. Synthetic  $\text{CuSe}$  and  $\text{CuFeSe}_2$  were used as standards. Several analyses were made on each grain and no fewer than six grains were examined in the polished section. The results are given in Table 2. The analysis of the Eagle eskebornite was carried out on a Cambridge Instrument Company electron microprobe (type Geoscan), and the data processed by a slightly modified computer program as published by Springer (1967) which applied correction for absorption, continuous and characteristic fluorescence, and atomic number. Copper and iron metal, and synthetic  $\text{Ag}_2\text{Se}$  were used as standards. Several analyses were made on two grains. The results are given in Table 2.

The electron microprobe analyses show that the ideal formula of eskebornite is close to  $\text{CuFeSe}_2$ , as originally suggested by Earley from his synthetic studies. Using the composition obtained from the microprobe analysis, synthetic fusions were prepared, both for the purpose of establishing the phase relationships, and with the aim of obtaining suitable fragments for single-crystal studies. One such charge of composition  $\text{CuFeSe}_2$  was prepared from high-purity elements and fused in the following manner. The material was heated at  $400^\circ\text{C}$  for  $1\frac{1}{2}$  hours, then to  $800^\circ\text{C}$  for another  $\frac{1}{2}$  hr and finally to  $500^\circ\text{C}$  for 1 day. The sample was then ground, pelletized, and reheated to  $500^\circ\text{C}$  for 25 days,  $417^\circ\text{C}$  for 7 days and finally to  $474^\circ\text{C}$  for 20 days. Polished section examination revealed a trace of  $\text{FeSe}_2$ , and showed that the eskebornite consisted of multiple randomly oriented single-crystal fragments. The synthetic work suggests that eskebornite is probably non-stoichiometric at  $500^\circ\text{C}$ , with a slight deficiency of Fe and Se.

TABLE 2. ESKEBORNITE: ELECTRON MICROPROBE ANALYSES

	<i>Martin Lake</i>		<i>Eagle Group</i>	
	Wt. %	At Prop.	Wt. %	At Prop.
Cu	$23.62 \pm 0.2$	1.06	$23.0 \pm 0.5$	0.993
Fe	$19.75 \pm 0.2$	1.01	$19.7 \pm 0.4$	0.969
Se	$55.96 \pm 0.3$	2.00	$57.5 \pm 0.4$	2.000
	99.32		100.2	

## CRYSTALLOGRAPHY

The x-ray powder diffraction patterns of eskebornite from Martin Lake and the Eagle group agree very well with the data obtained by Earley and published by Berry & Thompson (1962), and that of Tischendorf (1960) for eskebornite from Tilkerode locality. Agrinier *et al.* (1967) and Kvaček *et al.* (1965) also noted that their x-ray powder agreed with those of Tischendorf. The Lake Athabasca area material is closely intergrown with umangite and it is thus difficult to obtain a clear pattern. In Table 3, the x-ray data for synthetic  $\text{CuFeSe}_2$  are compared with those published by Tischendorf. The measurements were obtained by the first author from a 114.6 mm-diameter Debye-Scherrer camera with Fe-filtered Co radiation.

In spite of the distinct anisotropism and hexagonal or pseudo-hexagonal properties of eskebornite, the mineral gives a cubic-like x-ray powder

TABLE 3. ESKEBORNITE: X-RAY POWDER DATA

Synth. $\text{CuFeSe}_2$ Co Radiation, 114.6 mm dia. Camera.		Eskebornite (Tischendorf) CoK Radiation, 60 mm dia. Camera.	
<i>I</i> (est.)	<i>d</i> (meas.)	<i>I</i>	<i>d</i> (meas.)
8	5.53	st	5.55
1	3.90	ss	3.86
10	3.17	sst	3.18
1	3.04		
5	2.746	ss	2.76
8	2.459	m	2.47
9	1.945	sst	1.947
6	1.836	s-m	1.838
8	1.662	st	1.662
3	1.590	ss	1.592
4	1.529	ss	1.530
1/2	1.475		
7	1.380	m	1.380
5	1.337	ss	1.337
1/2	1.300		
7	1.266	m	1.263
5	1.233	ss	1.231
4	1.204		
1	1.167		
7	1.126	m-st	1.127
3	1.103	sss	1.105
7	1.063	m	1.062
4	1.025	ss	1.025
6	.976	m	.976
		m-st	.934
		ss	.922



pattern which can be indexed successfully on a cubic lattice with a cell parameter of  $5.52\text{\AA}$ . Tischendorf noted that both eskebornite I and II gave the same powder pattern, and had a primitive cubic lattice with  $a = 5.53 \pm 0.01\text{\AA}$ . In spite of the anisotropism, all previous workers have accepted cubic symmetry.

In an effort to determine the structure of eskebornite by single-crystal methods, several fragments were examined from the synthetic fusions, but they all proved to be unsuitable.

However, since the composition of eskebornite, as determined by the electron microprobe, is close to  $\text{CuFeSe}_2$ , it could be that the structure of eskebornite is related to that of the chalcopyrite-type. Since the x-ray powder data of eskebornite can be indexed on a cubic lattice, it is possible that its symmetry is tetragonal with the  $c$  dimension being twice that of the  $a$  dimension, giving  $a$   $5.52$ ,  $c$   $11.04\text{\AA}$ .

Final confirmation will have to await single-crystal studies.

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