AN OCCURRENCE OF A SULPHUR-BEARING BERZELIANITE

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Berzelianite is a selenide of copper with the formula $Cu_{2-x}Se$. The binary Cu–Se system has been investigated by a number of workers, the most recent of which are Earley (1950), Borchert & Patzak (1955), Heyding (1966) and Bernardini & Catani (1968). From the phase diagram, the cubic $Cu_{2-x}Se$ phase has a very narrow homogeneity range at room temperature, centered at approximately $Cu_{1.8}Se$, within the limits $0.15 \leq x \leq 0.25$. To date, no one has reported on the stability relations in the ternary system Cu–S–Se.

During an investigation of the selenide minerals from Martin Lake, Lake Athabasca area, northern Saskatchewan, in which a new copper selenide mineral, athabascaite was found (Harris *et al.* 1969), electron microprobe analysis showed that some of the berzelianite contained sulphur. The purpose of this paper is to report this first occurrence of a naturally-occurring sulphur-bearing berzelianite.

GENERAL DESCRIPTION

The most common selenides from the Martin Lake locality are umangite, berzelianite and clausthalite. Other minor selenides are klockmannite, eucairite, tyrrellite, eskebornite and athabascaite. The selenides occur in pitchblende ore and in hematite-stained carbonate vein material in the basalt of the Martin formation. The berzelianite that occurs in the pitchblende ore is sulphur-free and it occurs as inclusions in, and replacements of, umangite. The sulphur-bearing berzelianite occurs as stringers and veinlets in the vein material. The mineral is associated with athabascaite, which in this environment is also sulphur-bearing, and with minor umangite. Sulphur was not detected in the umangite.

ELECTRON MICROPROBE ANALYSIS

The analyses were performed on a Materials Analysis Company (MAC) electron microprobe operated at 25 kilovolts. The $K\alpha$ characteristic radiation was used for each element. Synthetic copper selenides of compositions $Cu_{1.801}Se$, $Cu_{1.806}Se_{.826}S_{.173}$ and $Cu_{1.799}Se_{.699}S_{.300}$ were used to construct calibration curves. Several grains were analyzed, and the average

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TABLE 1. ELECTRON MICROPROBE ANALYSIS OF BERZELIANITE

	Elements Wt. %			
	Cu	Se	S	Total
Martin Lake, Vein material	64.2	30.3	5.7	100.2
Martin Lake, Pitchblende ore	57.9	41.1	—	99.0
West Moravia CSSR	59.4	39.8	—	99.2

analysis is given in Table 1. For comparison, analysis of a berzelianite from the well-known locality in West Moravia, Czechoslovakia is given.

The synthetic standards were prepared from high purity Cu, Se, S, all initially heated at 300° C for about 1 hr., then at 600° C for 1 day. The samples were then ground and pelletized, reheated at 600° C for 18 days and then followed by 1 day at 500° C. This procedure produced single phases which, from electron microprobe examinations, were found to be homogeneous.

OTHER PROPERTIES

Although the reflectivity of the sulphur-bearing berzelianite was not measured, no differences in optical properties could be observed between it and normal berzelianite under a comparison microscope.

To determine the influence that sulphur may have on other properties, the microhardness and unit-cell dimensions were measured; the results are given in Table 2.

TABLE 2. MICROHARDNESS AND CELL EDGE FOR BERZELIANITE

Sample	Formula	VHN(Kg/mm²)	Cell edge (Å)
129 Synthetic	$Cu_{1.801}Se$	27.2–35.2 31.1	5.746 ± .001
155 Synthetic	$Cu_{1.806}Se_{.826}S_{.173}$	27.1–34.7 30.8	5.724 ± .002
159 Synthetic	$Cu_{1.799}Se_{.699}S_{.300}$	26.2–34.2 30.1	5.702 ± .001
157 Synthetic	$Cu_{1.680}Se_{.499}S_{.501}$	—	5.653 ± .002
Martin Lake, Vein material	$Cu_{1.797}Se_{.683}S_{.317}$	36.6–47.3 41.8	5.696 ± .003
Martin Lake, Pitchblende ore	$Cu_{1.751}Se$	44.5–47.1 45.8	5.740 ± .001
W. Moravia CSSR	$Cu_{1.854}Se$	28.9–36.0 31.6	5.748 ± .002

The microhardness values were determined with a Leitz Durimet hardness tester using a 15-gram weight and an indentation time of 20 seconds. For comparison, the microhardness values of the synthetic samples were measured. As can be seen in Table 2, this property is not sufficiently sensitive to sulphur content.

For the unit-cell dimensions, a 114.6-mm.-diameter Debye-Scherrer diffraction camera was used with Ni-filtered Cu radiation. The patterns were indexed on a cubic lattice and the parameters were refined by a least-squares computer program.

According to Borchert & Patzak (1955), the unit-cell parameter of $Cu_{2-x}Se$ varies linearly from 5.745 Å for $Cu_{1.85}Se$ to 5.730 Å for $Cu_{1.80}Se$. This amount of variation was not observed in this study for the non-sulphur berzelianites. However, a nearly linear relationship was observed between the unit-cell parameters and the atomic percent sulphur in the (Se,S) position. This variation is shown in Fig. 1.

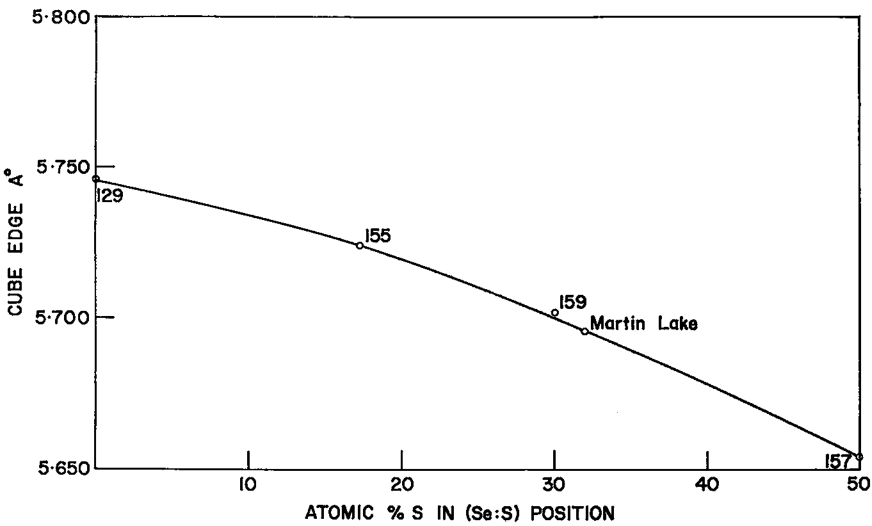

FIG. 1. Relationship between unit-cell parameters and atomic percent sulphur in the (Se,S) position.

DISCUSSION

This is the first reported occurrence of a sulphur-bearing berzelianite. The substitution of sulphur for selenium and *vice versa* is certainly not uncommon. Experiments in the synthetic system show that at least 50 atomic percent sulphur can substitute for selenium in berzelianite, with retention of the cubic structure, but with decreasing unit-cell parameter.

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WERNERITE AND FELDSPAR FROM MADAGASCAR

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Six samples of wernerite and six of feldspar were separated from the werneritic and feldspathic pyroxenites of S. E. Madagascar. These pyroxenites (Precambrian) occur in association with charnockites and have been considered to be metamorphosed sediments (Lacroix 1941; de La Roche 1956 & 1958). Wernerite and feldspar were studied optically and chemically and the *x*-ray powder diffraction patterns of the selected samples were also determined.

These wernerites are whitish grey, granular and majority of them show two sets of perfect cleavages and also show more or less greasy luster. In thin sections, they are colourless but some of them are slightly stained by impurities. Some of the crystals show twin-lamellae, which represent the clear passage of feldspar to wernerite. They are uniaxial negative showing moderately high relief with ϵ, varying from 1.551 to 1.568 and ω, varying from 1.580 to 1.607. They show strong birefringence which varies from 0.029 to 0.039. The specific gravity varies from 2.65 to 2.77 (Table 1).

The feldspars are greyish white in colour with vitreous luster. In thin sections, they are colourless, some partially altered. They have one distinct cleavage parallel to (001). They show low relief with the refractive indices varying, α, from 1.555 to 1.559 and γ, from 1.562 to 1.566. Birefringence varies from 0.005 to 0.009. They show albite twinning and the anorthite content varies between 52% and 62%. Their optic axial