

EPHESITE,  $\text{Na}(\text{LiAl}_2)(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$ , A TRIOCTAHEDRAL  
MEMBER OF THE MARGARITE GROUP, AND  
RELATED BRITTLE MICAS<sup>1</sup>

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ABSTRACT

A new analysis of ephesite from the Postmasburg district, South Africa, shows that the lithium content is much higher than previously determined. Ephesite is a trioctahedral member of the margarite group with formula  $\text{Na}(\text{LiAl}_2)(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$ ; lithium fills the vacant octahedral position as calcium is replaced by sodium. X-ray study shows it to be of the  $2M_1$  type with  $a$  5.12<sub>0</sub>,  $b$  8.85<sub>3</sub>,  $c$  19.30<sub>3</sub> Å.,  $\beta$  95°5'. Replacements involved in bityite, the lithium-beryllium member of the group, are discussed.

INTRODUCTION

The accepted formula of margarite, the best known of the brittle micas, is  $\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$ , which requires CaO 14.09 percent, yet of the 72 published analyses we have found of members of the group, only 7 show more than 13.0 percent CaO, whereas 41 show contents in the range 10–12 percent. It was recognized long ago that many margarites contained a little sodium, but the mechanism of substitution was not understood.

J. Lawrence Smith (1851, 1869) described a sodium-rich brittle mica from the emery deposits of Gumuch-Dagh near Ephesus, Asia Minor, for which he proposed the name ephesite (Table 1, nos. 1–3). Little attention was paid to this material, which was considered to be a mixture (Dana's System, 6th Ed., p. 707) until Phillips (1931) described ephesite ("soda-margarite") from the Postmasburg district, South Africa. The analyses he published (Table 1, nos. 4 and 5) showed high  $\text{Na}_2\text{O}$  and also 0.9 and 1.5 percent  $\text{Li}_2\text{O}$ . Consideration of these analyses, plus the six old analyses of margarite in which  $\text{Li}_2\text{O}$  contents of 0.23 to 0.45 percent  $\text{Li}_2\text{O}$  had been reported, caused one of us (WTS) to speculate that the charge unbalance caused by the replacement of Ca by Na in margarite might be compensated by the introduction of Li into the vacant octahedral position in margarite. If this were correct, the reported analyses for lithium were much too low; it had been known for a long time that it was difficult to extract all the lithium from silicates, that margarite is an unusually difficult mineral to decompose (Smith, 1851), and that lithium had often been missed and reported as sodium in old analyses. Accordingly, a redetermination was undertaken by R. E. Stevens of the alkalis in ephesite from the Postmasburg district. Professor C. E. Tilley kindly

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. ANALYSES OF EPHESITE

	1	2	3	4	5	6
SiO <sub>2</sub>	31.54	30.04	30.70	29.4	28.9	—
TiO <sub>2</sub>	—	—	—	0.1	} 51.6	—
Al <sub>2</sub> O <sub>3</sub>	57.89	56.45	55.67	50.6		—
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	.55		—
FeO	1.34	1.00	—	.35		—
MgO	—	—	—	.4	—	—
MnO	—	—	—	.1	—	—
Li <sub>2</sub> O	—	—	—	1.5	0.9	2.76
CaO	1.89	2.11	2.55	1.4	—	—
Na <sub>2</sub> O	4.41 <sup>1</sup>	4.41 <sup>1</sup>	5.52	8.65	9.2	7.56
K <sub>2</sub> O	—	—	1.10	tr	0.3	0.06
H <sub>2</sub> O <sup>+</sup>	3.12	3.09	4.91	5.3	—	—
H <sub>2</sub> O <sup>-</sup>	—	—	—	1.25	—	—
F	—	—	—	0.2	—	—
	100.19	97.10	100.45	99.80		
Less O=F <sub>2</sub>				0.08		
				99.72		

<sup>1</sup> Including a little K<sub>2</sub>O.

1-2. Smith (1851), from Gumuch-Dagh near Ephesus, Asia Minor

3. Smith (1869), from Gumuch-Dagh

4-5. Phillips (1931), from Postmasburg, South Africa

4. H. G. Weall, analyst

5. Phillips, analyst

6. R. E. Stevens, new analysis from Postmasburg, sample furnished by C. E. Tilley

furnished a small amount of this ephesite, with the statement that none of Phillips' analyzed material remained, but that the material sent was similar. Determination by R. E. Stevens of the alkalis on this material (Table 1, no. 6) showed, as expected, a much higher content of lithium.

A new analysis of ephesite was evidently needed, but no further work could then be done because of lack of material. Fortunately, during examination of a large stockpile of manganese ore at Baltimore, Maryland, during World War II, Fleischer found ephesite in Postmasburg ore, and he, E. P. Henderson, and Schaller collected a large supply, which made possible the re-examination of this material.

#### CHEMISTRY OF POSTMASBURG EPHESITE

The ephesite in the Postmasburg samples from the stockpile occurs as disseminated pinkish flakes, greatly resembling the pink muscovite from the Harding mine, New Mexico. It is associated with brown mangan-

diaspore as a minor constituent of the black ore, which consists mainly of massive braunite with occasional well-developed cubes of bixbyite. In our material the flakes of ephesite have a maximum size of 5 mm across, although Phillips (1931) reported crystals up to 13 mm in diameter and 10 mm in length, a size reached by the material sent to us by Tilley.

Optical study by Schaller gave indices of refraction:  $\alpha$  1.592,  $\beta$  1.624,  $\gamma$  1.625, close to the values reported by Phillips. The specific gravity was determined pycnometrically by Mrs. A. C. Vlisidis to be 2.984.

Single crystal studies of the Postmasburg ephesite samples by Malcolm Ross (U. S. Geological Survey) using Buerger precession techniques showed that all five crystals examined are the  $2M_1$  polytype. The unit-cell data are as follows: space group  $C2/c$  or  $Cc$ ,  $a=5.12_0$ ,  $b=8.85_3$ ,  $c=19.30_3$  Å,  $\beta=95^\circ 5'$ , and  $V=871.5\text{Å}^3$ , the calculated specific gravity is 2.965. Most crystals are twinned by a  $180^\circ$  rotation about  $[310]$  or  $[3\bar{1}0]$ .

In preparing a sample for analysis, it was crushed to a size of about 0.5 cm, then, as suggested to us by C. S. Ross, it was rolled on a steel plate with a steel roller, thus crushing the more brittle manganese oxides to a finer powder. After sieving, final purification by standard procedures yielded 20 grams of pure mineral.

A complete analysis by M. K. Carron, along with determinations by R. E. Stevens and determinations of the alkalis by W. W. Brannock by flame photometry, is given in Table 2. The analysis was made by conventional procedures, except that it was found necessary to repeat the extraction of alkalis. A 0.5-g portion of the sample was ground to an impalpable powder, mixed with 4 g  $\text{CaCO}_3$  and 1 g  $\text{BaCl}_2$ , and sintered in the usual way. After leaching, filtering, and washing with 1,000 ml of hot water in small portions, the insoluble residue was ignited, ground with an additional 4 g  $\text{CaCO}_3+1$  g  $\text{BaCl}_2$ , and resintered. The sinter was leached, filtered, and washed with 500 ml of hot water in small portions. The results obtained by this modified J. Lawrence Smith method were as follows:

	<i>One sintering</i>	<i>Two sinterings</i>
$\text{Li}_2\text{O}$	3.10, 3.06	3.52
$\text{Na}_2\text{O}$	7.33, 7.38	7.44
$\text{K}_2\text{O}$	0.13, 0.16	0.15

It will be noted that only a little additional  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , but much  $\text{Li}_2\text{O}$  were obtained by the retreatment; very likely still more would have been obtained by further treatment, as also indicated by the higher figures found by flame photometry.

Calculation of the formula from the average analysis of Table 2 is shown in Table 3. It is apparent that the formula of ephesite is  $\text{NaLiAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$ , *i.e.*, ephesite is a trioctahedral sodium-lithium member of the margarite group, in which valence compensation for the substitution of Ca by Na is by introduction of Li into octahedral coordination.

#### THE POSSIBLE ISOMORPHOUS SERIES MARGARITE-EPHESITE

The lack of analyses of margarite with near-theoretical contents of CaO and the many analyses that show less CaO, especially in the range

TABLE 2. ANALYSES OF EPHESITE FROM THE POSTMASBURG DISTRICT, SOUTH AFRICA

Analyst	Carron (modified J. L. Smith method)	Stevens	Brannock flame photometry	Average	Calculated for ideal formula
$\text{SiO}_2$	30.86	30.88	—	30.87	30.96
$\text{Al}_2\text{O}_3$	51.68	52.40	—	51.68	52.55
$\text{Fe}_2\text{O}_3$	.47		—	.47	—
FeO	.04		—	.04	—
$\text{TiO}_2$	.03		—	.03	—
MnO	.12	—	—	.12	—
MgO	.09	—	—	.09	—
$\text{Li}_2\text{O}$	3.52	—	3.80	3.66	3.85
CaO	.02	.02	—	.02	—
BaO	.17	—	—	.17	—
$\text{Na}_2\text{O}$	7.44	—	7.94	7.69	7.99
$\text{K}_2\text{O}$	.15	—	.17	.16	—
$\text{H}_2\text{O}^+$	4.92	—	—	4.92	4.65
$\text{H}_2\text{O}^-$	.06	—	—	.06	—
	99.57			99.98	100.00

10–12 percent, tempt one to speculate that these are actually intermediate members of a series margarite-ephesite, in which lithium was missed or was present in larger amounts than reported. Only five of the older analyses report  $\text{Li}_2\text{O}$  in more than traces and these show 0.23 to 0.45 percent.

Spectrographic analyses made in 1950 of five margarites by K. J. Murata showed that lithium was present in all.<sup>1</sup> The alkalis in these samples were determined by flame photometer by W. W. Brannock, with

<sup>1</sup> A sample from Gumuch Dagh, Asia Minor (U. S. Nat. Mus. R4924) (the type locality of ephesite) was found to contain approximately  $\text{K}_2\text{O}$  8,  $\text{Na}_2\text{O}$  1,  $\text{Li}_2\text{O}$  <0.1 percent; it is presumably muscovite.

results given in Table 4. These analyses show that the proposed mechanism of substitution is in fact operative and emphasize the necessity of determining  $\text{Li}_2\text{O}$  in all margarite analyses. They show, however, that other mechanisms of valence compensation are also operating, the contents of  $\text{Li}_2\text{O}$  found in analyses 2-5 being only roughly half that required by the mechanism  $\text{NaLi}=\text{Ca}$ ., where the dot denotes a vacant position.

The analyses therefore indicate that in the possible series  $\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH}_2\text{-Na}(\text{LiAl}_2)(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2)$  only a small portion is now known to exist.

#### COMPLEX SUBSTITUTIONS INVOLVING LI AND BE

The unexpectedly high values for  $\text{BeO}$  in analyses 4 and 5, Table 4, suggested a complex substitution involving Be; this was confirmed by an analysis published by Beus (1956) ( $\text{BeO}$  1.18,  $\text{Li}_2\text{O}$  0.47%), three analyses published by Kutukova (1959) ( $\text{BeO}$  3.26, 1.88, 2.67;  $\text{Li}_2\text{O}$  0.78, 0.72, 0.31%) and an analysis of "bowleyite" by Rowledge and Hayton (1948) ( $\text{BeO}$  7.30,  $\text{Li}_2\text{O}$  2.39%). The last was promptly recognized by two abstractors as being identical with the micaceous mineral bityite. The substitutions involved have been discussed by Strunz (1956)

TABLE 3. ATOMIC RATIOS OF AVERAGE ANALYSIS OF EPHESITE

	Weight percent		Atomic ratios
$\text{SiO}_2$	30.87	Si	2.011
		Al	1.989
		$\Sigma$	4.000
$\text{Al}_2\text{O}_3$	51.68	Al	1.975
$\text{Fe}_2\text{O}_3$	.47	Fe	.023
$\text{FeO}$	.04	Fe	.002
$\text{TiO}_2$	.03	Ti	.002
$\text{MgO}$	.09	Mg	.010
$\text{MnO}$	.12	Mn	.006
$\text{Li}_2\text{O}$	3.66	Li	.958
		$\Sigma$	2.976
$\text{CaO}$	.02	Ca	.002
$\text{Na}_2\text{O}$	7.69	Na	.970
$\text{K}_2\text{O}$	.16	K	.012
$\text{BaO}$	.17	Ba	.004
		$\Sigma$	0.988
		O	10.00
$\text{H}_2\text{O}^+$	4.92		
$\text{H}_2\text{O}^-$	.06	OH	2.135
	99.98		

TABLE 4. NEW PARTIAL ANALYSES OF MARGARITES (WEIGHT PERCENT)

No	Li <sub>2</sub> O <sup>1</sup>	Na <sub>2</sub> O <sup>1</sup>	K <sub>2</sub> O <sup>1</sup>	BeO <sup>2</sup>	Published analyses <sup>3</sup>			
					Li <sub>2</sub> O	Na <sub>2</sub> O	K <sub>2</sub> O	CaO
A	—	—	—	—	0.00	0.00	0.00	14.09
1	0.12	1.19	0.49	0.00x	—	—	—	—
2	.19	.71	.17	0.00x	—	0-1.25	—	10.80-11.92
3	.29	3.62	.79	0.00x	0-0.32	1.91-2.46	—	10.02-10.38 <sup>4</sup>
4	.36	1.72	1.25	.3	0.0.36	0.96-2.66	0.25-0.58	10.70-12.13
5	.44	2.44	.89	.2	—	—	—	—
B	—	—	—	—	.77	1.60	—	11.28

<sup>1</sup> Flame photometer analysis by W. W. Brannock.

<sup>2</sup> Semiquantitative spectrographic analysis by K. J. Murata.

<sup>3</sup> From Dana's *System of Mineralogy*, 6th Ed., p. 637.

Doelter, *Handb. Mineralchem.*, 2, part 2, p. 1044-1048 (1917).

Hintze, *Handb. Mineralchem.*, 2, p. 643, 654-655 (1897).

<sup>4</sup> A recent analysis by Aoki and Shimada (1965) of margarite from Chester gives Li<sub>2</sub>O 0.39, Na<sub>2</sub>O 0.92, CaO 10.89.

A. Theoretical composition of margarite, CaAl<sub>2</sub>(Al<sub>2</sub>Si<sub>2</sub>)O<sub>10</sub>(OH)<sub>2</sub>

1. Margarite, Laurel Creek, Rabun County, Georgia (USNM 48633).
2. Margarite, Naxos, Greece (USNM R 4483).
3. Margarite, Chester, Mass.
4. Margarite, var. emerylite, Unionville, Penn. (USNM R 4485).
5. Margarite (USNM 79936).

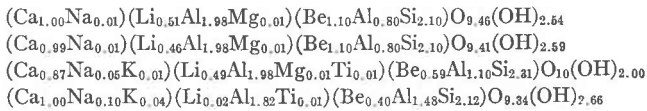
B. Theoretical composition of margarite end-member 80, ephesite end-member 20, if K<sub>2</sub>O is absent.

and Ginzburg (1957); we therefore give only the structural formulas (as given by the authors) of these five beryllium-lithium-bearing members of the group for comparison.

Beus	$\left\{ \begin{array}{l} (\text{Ca}_{0.80}\text{Na}_{0.24}\text{K}_{0.04})(\text{Li}_{0.12}\text{Al}_{1.64}\text{Fe}_{0.04}\text{Mg}_{0.12})(\text{Be}_{0.18}\text{Al}_{1.92}\text{Si}_{1.90}) \\ (\text{O}_{10.0}(\text{OH})_{2.22}\text{F}_{0.14}) \\ (\text{Ca}_{0.94}\text{Na}_{0.14}\text{K}_{0.04})(\text{Li}_{0.19}\text{Al}_{1.89}\text{Mg}_{0.10}\text{Cr}_{0.03})(\text{Be}_{0.30}\text{Al}_{1.69}\text{Si}_{2.01}) \\ (\text{O}_{10}(\text{OH})_{1.63}\text{F}_{0.37}) \\ (\text{Ca}_{0.93}\text{Na}_{0.03}\text{K}_{0.01})(\text{Li}_{0.09}\text{Al}_{2.06}\text{Fe}_{0.01}\text{Mg}_{0.03})(\text{Be}_{0.42}\text{Al}_{1.54}\text{Si}_{2.04}) \\ (\text{O}_{10.13}(\text{OH})_{1.69}\text{F}_{0.28}) \\ (\text{Ca}_{0.95}\text{Na}_{0.07}\text{K}_{0.02})(\text{Li}_{0.20}\text{Al}_{2.06}\text{Fe}_{0.02}\text{Mg}_{0.06})(\text{Be}_{0.52}\text{Al}_{1.48}\text{Si}_{2.00}) \\ (\text{O}_{10.03}(\text{OH})_{1.77}\text{F}_{0.20}) \end{array} \right.$	
Kutukova		
Rowledge and Hayton (calc. by Strunz and Ginzburg)		
		$\left\{ \begin{array}{l} (\text{Ca}_{0.98}\text{Na}_{0.04})(\text{Li}_{0.61}\text{Al}_{1.97}\text{Fe}_{0.01})(\text{Be}_{1.12}\text{Al}_{0.75}\text{Si}_{2.13})(\text{O}_{10}(\text{OH})_{2.43}) \end{array} \right.$

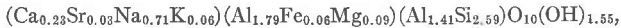
Four new analyses have been published by Gallagher and Hawkes (1966) from pegmatites in Rhodesia and Uganda; these contained BeO 7.2, 7.2, 3.8, 2.5; Li<sub>2</sub>O 2.0, 1.8, 1.9, and 0.05 percent), the first two being close in composition to that analyzed by Rowledge and Hayton. The

calculated formulas are:



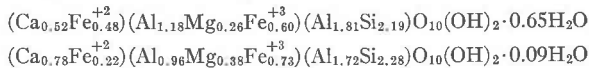
Strunz generalizes the formula derived from the analysis by Rowledge and Hayton to the form  $\text{CaLiAl}_2(\text{AlBeSi}_2)\text{O}_{10}(\text{OH})_2$ , the mechanism being  $\text{LiBe}=\text{Al}$ . It will be noted, however, that whereas the ephesite analysis is very close to the trioctahedral end-member, the bityite analysis is that of an intermediate member.

Two other members of the margarite group should be mentioned, the status of which is not yet clear. One is a "soda-margarite" described by Afanas'ev and Aidinyan (1952), ( $\text{Na}_2\text{O}$  5.64,  $\text{K}_2\text{O}$  0.68,  $\text{CaO}$  3.28,  $\text{SrO}$  0.62,  $\text{BaO}$  0.19 percent). The analysis has been calculated to the formula:



which has a very different Si/Al ratio than the other members of the group, the substitution being  $\text{NaSi}=\text{CaAl}$ . The indices of refraction,  $\alpha=1.586$ ,  $\beta=1.612$ ,  $\gamma=1.613$ ,  $2V=50^\circ$ , are closer to those of ephesite than to those of margarite. The DTA curve shows a single endothermic break at  $810^\circ\text{--}840^\circ\text{C}$ , whereas ephesite from Postmasburg has one at  $930^\circ\text{C}$  (Heystek and Schmidt, 1954) and margarite one at  $960^\circ\text{C}$  (Ginzburg, 1955). Further work is needed; particularly the material should be checked for the possible presence of lithium and beryllium. This is the only margarite analysis that shows Si appreciably deviating from 2.00.

The second is "ferroferrimargarite," described by Ginzburg (1955) as a high-iron margarite. Two analyses are recalculated to give formulas:



The DTA curve showed a single endothermal break at  $990^\circ\text{C}$ . The formulas are somewhat doubtful because  $\text{FeO}$  was not determined, and it is uncertain whether the mineral belongs to the margarite group.

#### ACKNOWLEDGMENTS

We thank Professor C. E. Tilley of Cambridge University for the gift of material and Dr. George Switzer of the U. S. National Museum for making available specimens of margarite. We are deeply indebted to our colleagues W. W. Brannock, R. E. Stevens, and Angelina C. Vlisidis for their analyses, and to Malcolm Ross for the X-ray work.

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