EPHESITE, $Na(LiAl_2)(Al_2Si_2)O_{10}(OH)_2$, A TRIOCTAHEDRAL MEMBER OF THE MARGARITE GROUP, AND RELATED BRITTLE MICAS[1]

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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 $Na(LiAl_2)(Al_2Si_2)O_{10}(OH)_2$; 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_0, b 8.85_3, c 19.30_3 A., β 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 $CaAl_2(Al_2Si_2)O_{10}(OH)_2$, 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 Na_2O and also 0.9 and 1.5 percent Li_2O. Consideration of these analyses, plus the six old analyses of margarite in which Li_2O contents of 0.23 to 0.45 percent Li_2O 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 alkalies in ephesite from the Postmasburg district. Professor C. E. Tilley kindly

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[1] Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. ANALYSES OF EPHESITE

	1	2	3	4	5	6
SiO_2	31.54	30.04	30.70	29.4	28.9	—
TiO_2	—	—	—	0.1		—
Al_2O_3	57.89	56.45	55.67	50.6	51.6	—
Fe_2O_3	—	—	—	.55		—
FeO	1.34	1.00	—	.35		—
MgO	—	—	—	.4	—	—
MnO	—	—	—	.1	—	—
Li_2O	—	—	—	1.5	0.9	2.76
CaO	1.89	2.11	2.55	1.4	—	—
Na_2O	4.41[1]	4.41[1]	5.52	8.65	9.2	7.56
K_2O	—	—	1.10	tr	0.3	0.06
H_2O^+	3.12	3.09	4.91	5.3	—	—
H_2O^-	—	—	—	1.25	—	—
F	—	—	—	0.2	—	—
	100.19	97.10	100.45	99.80		
Less $O = F_2$				0.08		
				99.72		

[1] Including a little K_2O.

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 alkalies 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: α 1.592, β 1.624, γ 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 crustal 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, $\beta = 95°5^1$, and $V = 871.5$Å^3, the calculated specific gravity is 2.965. Most crystals are twinned by a 180° rotation about [310] or [3̄10].

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 alkalies 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 alkalies. A 0.5-g portion of the sample was ground to an impalpable powder, mixed with 4 g $CaCO_3$ and 1 g $BaCl_2$, 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 $CaCO_3 + 1$ g $BaCl_2$, 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:

	One sintering	Two sinterings
Li_2O	3.10, 3.06	3.52
Na_2O	7.33, 7.38	7.44
K_2O	0.13, 0.16	0.15

It will be noted that only a little additional Na_2O and K_2O, but much Li_2O 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 $NaLiAl_2(Al_2Si_2)O_{10}(OH)_2$, *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 co-ordination.

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	Stevens	Brannock flame photometry	Average	Calculated for ideal formula
	(modified J. L. Smith method)				
SiO_2	30.86	30.88	—	30.87	30.96
Al_2O_3	51.68		—	51.68	52.55
Fe_2O_3	.47	52.40	—	.47	—
FeO	.04		—	.04	—
TiO_2	.03		—	.03	—
MnO	.12	—	—	.12	—
MgO	.09	—	—	.09	—
Li_2O	3.52	—	3.80	3.66	3.85
CaO	.02	.02	—	.02	—
BaO	.17	—	—	.17	—
Na_2O	7.44	—	7.94	7.69	7.99
K_2O	.15	—	.17	.16	—
H_2O^+	4.92	—	—	4.92	4.65
H_2O^-	.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 Li_2O 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.[1] The alkalies in these samples were determined by flame photometer by W. W. Brannock, with

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[1] A sample from Gumuch Dagh, Asia Minor (U. S. Nat. Mus. R4924) (the type locality of ephesite) was found to contain approximately K_2O 8, Na_2O 1, $Li_2O < 0.1$ 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 Li_2O in all margarite analyses. They show, however, that other mechanisms of valence compensation are also operating, the contents of Li_2O found in analyses 2–5 being only roughly half that required by the mechanism $NaLi = Ca.$, where the dot denotes a vacant position.

The analyses therefore indicate that in the possible series $CaAl_2(Al_2Si_2)O_{10}(OH_2-Na(LiAl_2)(Al_2Si_2)O_{10}(OH)_2$ only a small portion is now known to exist.

COMPLEX SUBSTITUTIONS INVOLVING LI AND BE

The unexpectedly high values for BeO in analyses 4 and 5, Table 4, suggested a complex substitution involving Be; this was confirmed by an analysis published by Beus (1956) (BeO 1.18, Li_2O 0.47%), three analyses published by Kutukova (1959) (BeO 3.26, 1.88, 2.67; Li_2O 0.78, 0.72, 0.31%) and an analysis of "bowleyite" by Rowledge and Hayton (1948) (BeO 7.30, Li_2O 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
SiO_2	30.87		Si	2.011
			Al	1.989
			Σ	4.000
Al_2O_3	51.68		Al	1.975
Fe_2O_3	.47		Fe	.023
FeO	.04		Fe	.002
TiO_2	.03		Ti	.002
MgO	.09		Mg	.010
MnO	.12		Mn	.006
Li_2O	3.66		Li	.958
			Σ	2.976
CaO	.02		Ca	.002
Na_2O	7.69		Na	.970
K_2O	.16		K	.012
BaO	.17		Ba	.004
			Σ	0.988
			O	10.00
H_2O^+	4.92			
H_2O^-	.06		OH	2.135
	99.98			

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

No	Li_2O[1]	Na_2O[1]	K_2O[1]	BeO[2]	Published analyses[3]			
					Li_2O	Na_2O	K_2O	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[4]
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

[1] Flame photometer analysis by W. W. Brannock.

[2] Semiquantitative spectrographic analysis by K. J. Murata.

[3] 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).

[4] A recent analysis by Aoki and Shimada (1965) of margarite from Chester gives Li_2O 0.39, Na_2O 0.92, CaO 10.89.

A. Theoretical composition of margarite, $CaAl_2(Al_2Si_2)O_{10}(OH)_2$

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).
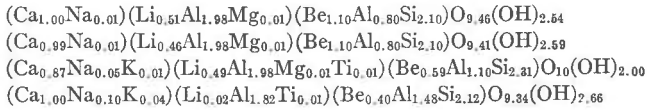5. Margarite (USNM 79936).

B. Theoretical composition of margarite end-member 80, ephesite end-member 20, if K_2O 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 $\Big\{$ $(Ca_{0.80}Na_{0.24}K_{0.04})(Li_{0.12}Al_{1.64}Fe_{0.04}Mg_{0.12})(Be_{0.18}Al_{1.92}Si_{1.90})\cdot$
$(O_{10.0}(OH)_{2.22}F_{0.14})$

Kutukova $\Big\{$ $(Ca_{0.94}Na_{0.14}K_{0.04})(Li_{0.19}Al_{1.89}Mg_{0.10}Cr_{0.03})(Be_{0.30}Al_{1.69}Si_{2.01})$
$(O_{10}(OH)_{1.63}F_{0.37})$

$(Ca_{0.98}Na_{0.08}K_{0.01})(Li_{0.09}Al_{2.06}Fe_{0.01}Mg_{0.08})(Be_{0.42}Al_{1.54}Si_{2.04})$
$(O_{10.13}(OH)_{1.59}F_{0.28})$

$(Ca_{0.95}Na_{0.07}K_{0.02})(Li_{0.20}Al_{2.06}Fe_{0.02}Mg_{0.06})(Be_{0.52}Al_{1.48}Si_{2.00})$
$(O_{10.03}(OH)_{1.77}F_{0.20})$

Rowledge and Hayton
(calc. by $\Big\{$ $(Ca_{0.98}Na_{0.04})(Li_{0.61}Al_{1.97}Fe_{0.01})(Be_{1.12}Al_{0.75}Si_{2.13})(O_{10}(OH)_{2.43})$
Strunz and Ginzburg)

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_2O 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
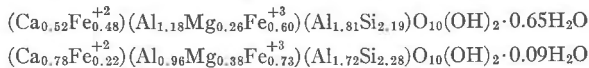
calculated formulas are:

$$(Ca_{1.00}Na_{0.01})(Li_{0.51}Al_{1.98}Mg_{0.01})(Be_{1.10}Al_{0.80}Si_{2.10})O_{9.46}(OH)_{2.54}$$
$$(Ca_{0.99}Na_{0.01})(Li_{0.46}Al_{1.98}Mg_{0.01})(Be_{1.10}Al_{0.80}Si_{2.10})O_{9.41}(OH)_{2.59}$$
$$(Ca_{0.87}Na_{0.05}K_{0.01})(Li_{0.49}Al_{1.98}Mg_{0.01}Ti_{0.01})(Be_{0.59}Al_{1.10}Si_{2.31})O_{10}(OH)_{2.00}$$
$$(Ca_{1.00}Na_{0.10}K_{0.04})(Li_{0.02}Al_{1.82}Ti_{0.01})(Be_{0.40}Al_{1.48}Si_{2.12})O_{9.34}(OH)_{2.66}$$

Strunz generalizes the formula derived from the analysis by Rowledge and Hayton to the form $CaLiAl_2(AlBeSi_2)O_{10}(OH)_2$, the mechanism being $LiBe = Al$. 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), (Na_2O 5.64, K_2O 0.68, CaO 3.28, SrO 0.62, BaO 0.19 percent). The analysis has been calculated to the formula:

$$(Ca_{0.23}Sr_{0.03}Na_{0.71}K_{0.06})(Al_{1.79}Fe_{0.06}Mg_{0.09})(Al_{1.41}Si_{2.59})O_{10}(OH)_{1.55},$$
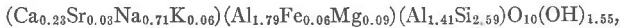
which has a very different Si/Al ratio than the other members of the group, the substitution being $NaSi = CaAl$. The indices of refraction, $\alpha = 1.586$, $\beta = 1.612$, $\gamma = 1.613$, $2V = 50°$, are closer to those of ephesite than to those of maragrite. The DTA curve shows a single endothermic break at 810°–840°C, whereas ephesite from Postmasburg has one at 930°C (Heystek and Schmidt, 1954) and margarite one at 960°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:

$$(Ca_{0.52}Fe_{0.48}^{+2})(Al_{1.18}Mg_{0.26}Fe_{0.60}^{+3})(Al_{1.81}Si_{2.19})O_{10}(OH)_2 \cdot 0.65H_2O$$
$$(Ca_{0.78}Fe_{0.22}^{+2})(Al_{0.96}Mg_{0.38}Fe_{0.73}^{+3})(Al_{1.72}Si_{2.28})O_{10}(OH)_2 \cdot 0.09H_2O$$

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

REFERENCES

AFANAS'EV, G. D. AND N. KH. AIDINYAN (1952) Sodium margarite from the Northern Caucasus. *Akad. Nauk SSSR, Izv., Ser. Geol.*, **1952, No.2,** 138–140 [in Russian].
AOKI, YOSHIKAZU AND NOBUTAKA SHIMADA (1965) Margarite from the Shin-Kiura mine,

Oita Prefecture. *Kobutsugaki Zasshi*, **7**, 87–93 [in Japanese] [Chem. Abs., **64**, 10935 (1966)].

BEUS, A. A. (1956) Characteristics of the isomorphous entry of beryllium into the crystal structure of minerals. *Geokhimiya* **1956**, 67–80 [Transl. *Geochemistry* **1956**, 62–77].

GALLAGHER, M. J. AND J. R. HAWKES (1966) Beryllium minerals from Rhodesia and Uganda. *Bull. Geol. Surv. G. Brit.* **25**, 59–75.

GINZBURG, A. I. (1955) A new mineral of the brittle mica group1 *Trudy Mineral. Muz. Akad. Nauk SSSR*, **7**, 70–75 (in Russian); [Abs. *Amer. Mineral.* **42**, 582 (1957)].

——— (1957) Bityite, a lithium-beryllium margarite. *Trudy Mineral. Muz. Akad. Nauk SSSR*, **8**, 128–131 [in Russian].

HEYSTEK, H. AND E. R. SCHMIDT (1954) The technique of differential thermal analysis and its application to some South African minerals. *Trans. Geol. Soc. S. Afr.* **56**, 149–176.

KUTUKOVA, E. I. (1959) Beryllium-containing margarite from the Middle Urals. *Trudy Inst. Mineral., Geokhim., Kristallokhim. Redkikh Elem.* **3**, 79–84 [in Russian].

PHILLIPS, F. C. (1931) Ephesite (soda-margarite) from the Postmasburg district, South Africa. *Mineral. Mag.* **32**, 482–485.

ROWLEDGE, H. P. AND J. D. HAYTON (1948) Two new beryllium minerals from Londonderry. *J. Roy. Soc. W. Aust.* **33**, 45–52 [Abs. *Zentralbl. Mineral.* **1949**; *Amer. Mineral.* **35**, 1091 (1950)].

SMITH, J. L. (1851) Emery. *Amer. J. Sci.*, **11**, 53–66.

——— (1869) The lesleyite of Chester County, Penna., and its relation to the ephesite of the emery formation near Ephesus, Asia Minor. *Amer. J. Sci.* **48**, 254–255.

STRUNZ, HUGO (1956) Bityit, ein Berylliumglimmer. *Z. Kristallogr.* **107**, 325–330.