METASTABLE OSUMILITE- AND PETALITE-TYPE PHASES IN THE SYSTEM MgO-Al$_2$O$_3$-SiO$_2$

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Abstract

Two new compounds have been synthesized metastably in the system MgO-Al$_2$O$_3$-SiO$_2$. One has a structure similar to that of osumilite and other related phases such as the synthetic compound Na$_2$O·5MgO·12SiO$_2$. It has a composition along the line SiO$_2$-MgAl$_2$O$_4$, probably close or equal to MgO·Al$_2$O$_3$·4SiO$_2$ as deduced from the phase assemblages. On the other hand, the measured mean index of refraction (1.535), according to the Gladstone-Dale relationship, suggests a composition containing less SiO$_2$ such as 4MgO·4Al$_2$O$_3$·7SiO$_2$. The other compound, whose composition is unknown, yields a powder x-ray diffraction pattern similar to those of petalite, Li$_2$O·Al$_2$O$_3$·8SiO$_2$, and lithium disilicate, Li$_2$O·2SiO$_2$. The two metastable phases form during devitrification of glass of certain bulk compositions at relatively low subsolidus temperatures. Upon further heating they are gradually replaced by assemblages which are more stable for these bulk compositions and include cordierite and a silica modification with or without protoenstatite.

Introduction

There are eleven known principal compounds in the system MgO-Al$_2$O$_3$-SiO$_2$, neglecting their polymorphs of identical composition stable under different conditions. These compounds are shown as open circles in Fig. 1 and may be classified as follows:

1. Oxides:
   MgO periclase
   Al$_2$O$_3$ corundum and other modifications
   SiO$_2$ cristobalite and other modifications
2. Binary compounds:
   MgO·Al$_2$O$_3$ spinel
   2MgO·SiO$_2$ forsterite
   MgO·SiO$_2$ enstatite and other modifications
   Al$_2$O$_3$·SiO$_2$ sillimanite and other modifications
   3Al$_2$O$_3$·2SiO$_2$ mullite
3. Ternary compounds:
   2MgO·2Al$_2$O$_3$·5SiO$_2$ cordierite
   4MgO·5Al$_2$O$_3$·2SiO$_2$ sapphirine
   3MgO·Al$_2$O$_3$·3SiO$_2$ pyrope

Many of these compounds may, under appropriate conditions, exhibit extensive ranges of solid solution. Some of them, such as pyrope and sillimanite, are stable only at elevated pressures, but all are stable phases within a certain *PT* range. The phases which were found to be stable in the laboratory at atmospheric pressure between 800° C. and 1300° C. are connected by the tie lines shown in Fig. 1.

In addition to these stable phases there are metastable ones, i.e. phases which form and disappear again at constant pressure and temperature.

As early as 1918 Rankin and Merwin described an "unstable or μ-form of the ternary compound $Mg_2Al_4Si_5O_{18}$," which was later called "μ-cordierite" by Karkhanavala and Hummel (1953), who attributed a β-spodumene structure to this phase. Recent studies by Schreyer and Schairer (1961A) indicate that this phase actually has a quartz-type structure, and that it belongs to a series of metastable solid solutions covering at least 60% of the range of the join SiO_2-$MgAl_2O_4$ (spinel). On the basis of these results the term metastable quartz solid solutions or quartz$_{ss}$ was used in describing this series of compounds. The term "metastable" seems to be preferable to "unstable," because there is no evidence that these phases have no range of stability at any temperature and pressure. It is conceivable, for instance, that quartz solid solutions are stable at some very high
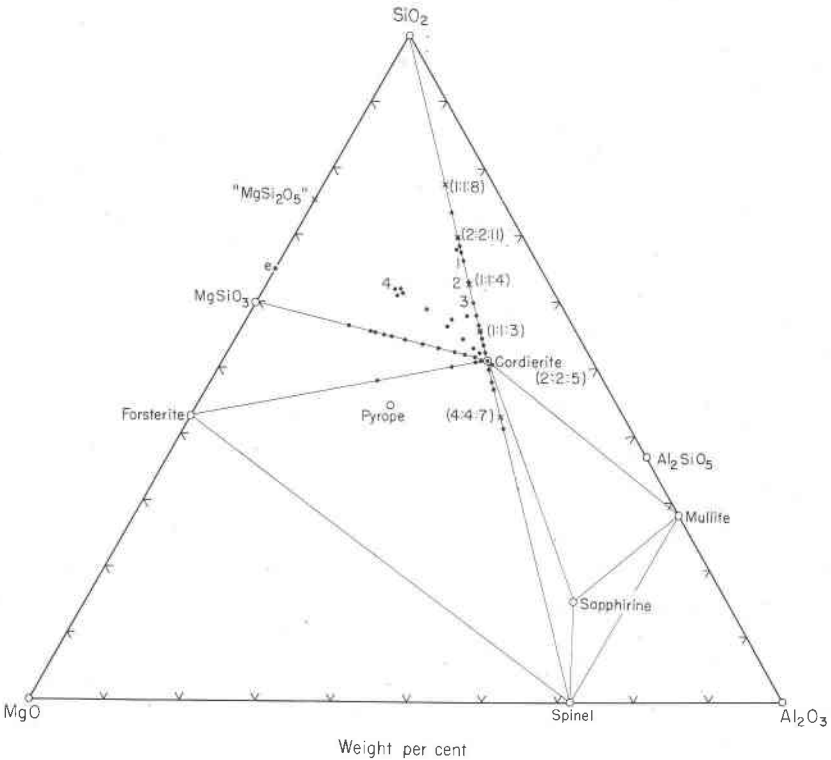

FIG. 1. Crystalline compounds in the ternary system MgO-Al_2O_3-SiO_2. The tie lines connect phases which were found to be stable in the laboratory at subsolidus temperatures between 800° and 1300° C. at 1 atmosphere. Solid dots indicate compositions studied; those accompanied by Nos. 1–4 have yielded the new metastable compounds. Crosses indicate compositions of theoretical compounds. "e" is the composition of the binary eutectic $MgSiO_3$-SiO_2 as reported by Bowen and Andersen (1914) .

pressure and temperature outside the stability range of coesite. Metastable quartz solid solutions are obtained by devitrifying glasses of compositions within the system $MgO-Al_2O_3-SiO_2$ at relatively low subsolidus temperatures between 800° and 1250°. Depending on the composition of these glasses, as many as three other crystalline phases may coexist metastably with the quartz solid solution. Among these early products of crystallization two crystalline phases were found which had not been known previously in the system $MgO-Al_2O_3-SiO_2$. The first phase is structurally akin to the recently discovered natural mineral osumilite (Miyashiro, 1956); the second phase shows similarities in the x-ray pattern to the mineral petalite, $LiAlSi_4O_{10}$.

It is the purpose of this paper to describe the mode of formation and some of the physical properties of these two new compounds. However, it must be emphasized that the data to be reported can represent only a preliminary characterization, the main difficulty being that none of the phases could be synthesized entirely alone but they were found only in intimate intergrowth with other crystalline products with or without residual glass. They were not found in coexistence with stable liquid.

The 46 compositions studied in the course of an experimental investigation of the ternary compound cordierite (Schreyer and Schairer, 1961B) are shown as solid dots in Fig. 1. Numbers 1–4 refer to those compositions that yielded the new metastable compounds to be described. The percentages of oxides for these four compositions are given in Table 1.

The Osumilite-type Phase

A phase with an osumilite-type structure was obtained by crystallizing glass of composition No. 1 at 1000° for 10 days and then at 1250° for 4 days. It was also obtained from glass of composition No. 2 after crystallization at 1050° for 6 days, and in traces from glass of composition No. 3 after only 20 hours at 1000°. It may be of significance that adjacent compositions along the line SiO_2-spinel containing more or less SiO_2 than compositions Nos. 1–3 did not yield the osumilite-type phase although crystallized under identical conditions. The phase was always associated with a metastable quartz$_{ss}$ (usually a very siliceous member), cordierite, and small amounts of high-cristobalite. The assemblages obtained after different periods of crystallization are summarized in Table 1. It can be seen from this compilation that the best conditions for the formation of the osumilite-type phase from this rather narrow range of compositions lies between 1050° and 1250°. At lower temperatures, with the exception of composition No. 3, the phase did not form; at higher temperatures it broke down to yield the more stable phases for these bulk compositions, i.e., cordierite and cristobalite. It is believed that the phase would also

TABLE 1. SUBSOLIDUS CRYSTALLIZATION PRODUCTS OF VARIOUS GLASSES
IN THE SYSTEM MgO-Al_2O_3-SiO_2

No.	Composition of glass in weight per cent			Heat treatment of glass		Phases as determined optically and by x-ray
	MgO	Al_2O_4	SiO_2			
1	9.65	24.40	65.95	1000°	3 days	Much quartz$_{ss}$, residual glass.
				1000° 1250°	10 days+ 4 days	Much osumilite-type phase, much cordierite, moderate amount quartz$_{ss}$, little cristobalite.
				1000° 1250° 1300°	10 days+ 4 days+ 3 days	Much cordierite, much cristobalite, moderate amount quartz$_{ss}$.
2	10.49	26.51	63.00	1050°	6 days	Much osumilite-type phase, much cordierite, moderate amount quartz$_{ss}$, trace cristobalite.
				1050° 1330°	6 days+ 15 days	Much cordierite, much cristobalite.
3	11.34	28.66	60.00	1000°	20 hours	Much quartz$_{ss}$, trace osumilite-type phase, trace cordierite, much residual glass.
				1000°	38 hours	Much quartz$_{ss}$, moderate amount cordierite, trace osumilite-type phase, little residual glass.
				1000° 1250°	13 days+ 1 day	Much cordierite, trace osumilite-type phase, trace cristobalite.
				1000° 1250° 1400°	13 days+ 1 day + 4 days	Much cordierite, moderate amount cristobalite.
4	20.50	17.50	62.00	850°	1 day	All glass.
				900°	140 min.	Moderate amount petalite-type phase, moderate amount quartz$_{ss}$, little pyroxene, residual glass.
				900°	1–5 days	Much petalite-type phase, much cordierite, moderate amounts quartz$_{ss}$ and pyroxene.
				900° 1000°	5 days+ 1 day	Much petalite-type phase, much cordierite, moderate amounts quartz$_{ss}$ and pyroxene.
				900° 1000° 1250°	5 days+ 1 day + 1 day	Much cordierite, much pyroxene, much cristobalite.

break down after longer heat treatment at the temperature of its forma-
tion, although this has not been demonstrated. The fact that all three co-
existing phases (Schreyer and Schairer 1961A, B) as well as the glass used
as starting material lie on the join SiO_2-$MgAl_2O_4$ indicates that the new
phase must also have a composition along this line. It appears from the
crystalline assemblages obtained from composition No. 1 after different

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TABLE 2. X-RAY DATA OF THE NEW METASTABLE COMPOUNDS IN THE
SYSTEM MgO-Al₂O₃-SiO₂ (COPPER Kα RADIATION)

$$\text{TABLE 2. X-Ray Data of the New Metastable Compounds in the System MgO-Al}_2\text{O}_3\text{-SiO}_2\text{ (Copper K}\alpha\text{ Radiation)}$$

Note: The data are incomplete because some of the reflections are hidden by
stronger lines of other coexisting crystalline phases.

Osumilite-type phase obtained by crystallizing glass of composition No. 1 at 1000° for 10 days and then at 1250° for 4 days			Petalite-type phase. Data compiled from several crystalline materials of composition No. 4		
d	2θ	I (estim.)	d	2θ	I (estim.)
7.11	12.45	15	7.20	12.30	8
5.54	16.00	25	4.65	19.10	<1
5.01	17.70	55	4.08	21.80	8
3.72	23.91	30	3.79	23.50±	20
3.59	24.81	30	3.69	24.10	100
3.20	27.87	100	3.58	24.85	25
2.92	30.62	40	2.99	29.90	8
2.765	32.38	40	2.78	32.20	6
2.71	33.10	15	2.55	35.20	11
			2.47	36.40±	8
			2.39	37.70	8
			2.06	44.00±	5±
			1.95	46.50	6
			1.93	47.00	8
			1.90	47.75	5

heat treatments (Table 1) that the breakdown of the osumilite-type phase
at higher temperatures leads to the formation of more cordierite and
cristobalite, whereas the amount of quartz$_{ss}$ remains constant. The con-
clusion seems justified, therefore, that the unknown phase has a composi-
tion between that of cordierite and cristobalite.

Despite the presence of three other crystalline phases the new com-
pound is characterized by at least nine distinct peaks in the powder x-ray
diffraction pattern. These peaks are compiled in Table 2 and are also
marked "O" in Fig. 2B. No differences in the x-ray properties were ob-
served among the osumilite-type phases crystallized from the three
compositions (Nos. 1–3) at different temperatures. All the unmarked
peaks shown in pattern B can be accounted for as being due to cordierite,
quartz$_{ss}$, and high-cristobalite. It is apparent from Fig. 2, A and B, that
all of the "O" peaks can be matched with corresponding peaks in the
osumilite pattern. In a number of cases, however, the osumilite lines in
pattern B are covered by stronger lines of the other coexisting phases.
Furthermore there are minor differences in positions as well as intensities
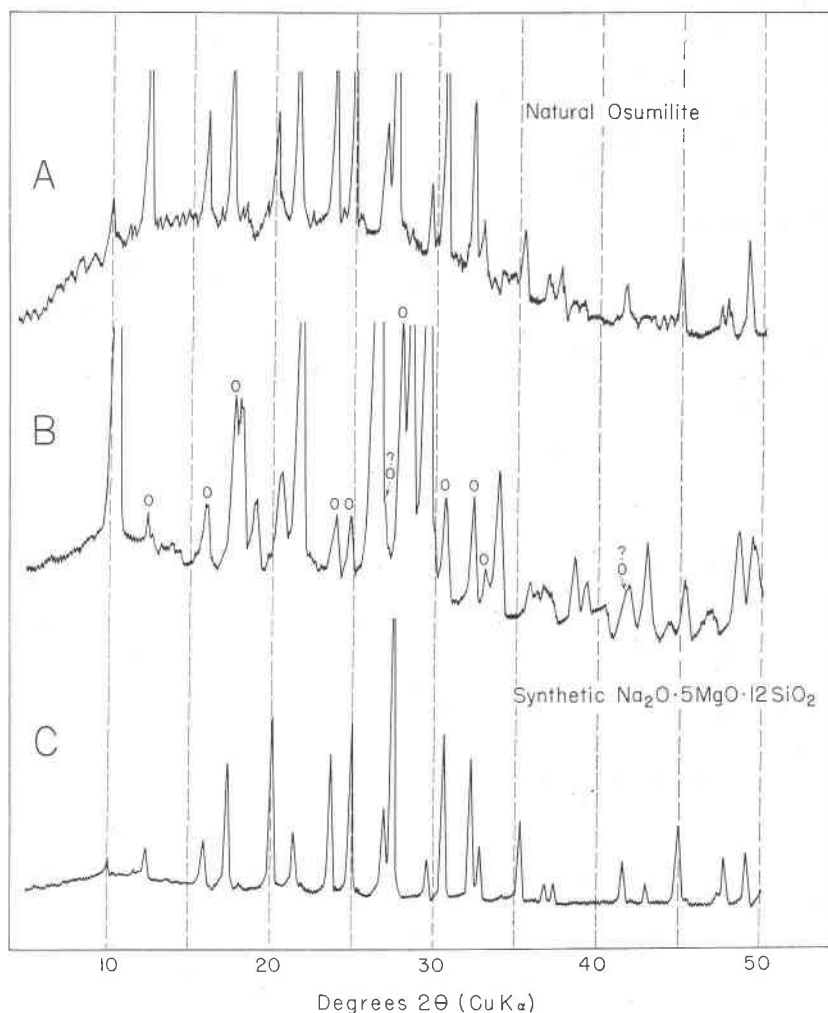of lines. The pattern of osumilite is in turn very similar to that of a com-

FIG. 2. Powder x-ray diffraction patterns between 5° and 50° 2θ for copper Kα radiation of:

A. Natural osumilite, Japan. The sample available at the Geophysical Laboratory was a gift from Dr. Kenzo Yagi, and is presumably from Sakkabira, from where the mineral was first identified by Miyashiro (1956).

B. Devitrification product of composition No. 1 after heating at 1000° for 10 days and 1250° for 4 days. Peaks marked "0" cannot be attributed to the phases cordierite, quartz$_{ss}$ and cristobalite present in the crystalline aggregate, but are caused by the unknown osumilite-type compound.

C. Synthetic $Na_2O \cdot 5MgO \cdot 12SiO_2$ (Schairer, Yoder, and Keene, unpublished data); the pattern was provided by Dr. H. S. Yoder, Jr., of the Geophysical Laboratory.

pound $K_2O \cdot 5MgO \cdot 12SiO_2$ (Roedder, 1951), and even more so to that of the sodium analogue $Na_2O \cdot 5MgO \cdot 12SiO_2$ (Schairer, Yoder and Keene, unpublished data). By permission of the latter authors the latter pattern is given as Fig. 2C. Except for differences of the relative intensities, especially at low angles 2θ, patterns A and C are identical, and the peaks "O" of pattern B show unmistakable similarities to both of them. On the basis of Miyashiro's (1956) indexing of natural osumilite the cell edges of the new metastable osumilite-type compound were calculated from the x-ray data given in Table 2 as $a = 10.12$ Å, $c = 14.36$ Å.

According to Miyashiro (1956) osumilite is isostructural with milarite $KCa_2(Be,Al,Si)_3 \cdot (Si,Be)_{12}O_{30} \cdot \frac{1}{2} H_2O$, and most recently Tennyson (1960) has pointed out that the mineral armenite $BaCa_2Al_3(Al_3Si_9O_{30}) \cdot 2H_2O$, found in the Armen Mine at Königsberg, Norway (Neumann, 1941), probably also belongs to this structural type.

There are thus at least five crystalline compounds of drastically different bulk compositions which nevertheless are presumably isostructural. The problem of relating these bulk compositions to each other by conceivable lattice substitutions is treated schematically in Table 3. On the basis of the milarite-osumilite relations and the structural data given by Miyashiro (1956) a basic formula for osumilite-type phases is suggested. The mineral armenite can easily be fitted into this scheme as already shown by Neumann (1941) in his comparison with milarite; however, there seems to be more H_2O^+ than available structural sites.

Starting from the basic formula (Table 3) the alkali-magnesium-silicates (1:5:12) are arrived at by filling both the 12-coordinated positions and the water positions within the double rings, i.e. all the available positions inside the ring channels, with alkalies and all the 4- and 6-coordinated positions with Mg.

The main difficulty in relating the new compound synthesized in the system $MgO-Al_2O_3-SiO_2$ to the basic formula is the complete lack of alkalies or other large ions like Ca^{2+} of Ba^{2+}. Let us assume then that all the possible alkali positions are vacant. Thus, by substituting 4Al for $2Na+3Mg+Si$ in 1:5:12, a composition $2MgO \cdot 2Al_2O_3 \cdot 11SiO_2$ (2:2:11) is obtained, which is practically identical to one of the 46 compositions investigated (Fig. 1). This composition, however, had not yielded the osumilite-type phase at any temperature. It is assumed next, therefore, that some of the Mg may occupy positions inside the channel as Ca does in osumilite. By this operation, which corresponds to a substitution $Mg+2Al$ for 2Si in 2:2:11, the formulas 1:1:3, 4:4:7, and 1:1:4 (Fig. 1) are obtained, thus filling respectively one-half, all, or one-quarter of the available sites. Only the last of these formulas falls within the compositional range, from which the new phase was crystallized; in fact, this

TABLE 3, LATTICE SUBSTITUTIONS IN OSUMILITE-TYPE COMPOUNDS

Basic formula	Structural Formula						Oxide Formula
	$(Alk\ or\ Me^{2+})^{XII}$	Me_2^{VI}	Me_3^{IV}	$(Be, Al, Si)_{12}^{IV}$	O_{30}	$(H_2O\ or\ Alk)$	
Milarite (Miyashiro, 1956)	K	Ca_2	$(Be, Al, Si)_3$	$(Si, Be)_{12}$	O_{30}	$\frac{1}{2}H_2O$	—
Osumilite (Miyashiro, 1956)	(K, Na, Ca)	$(Mg, Fe^{2+})_2$	$(Al, Fe^{3+}, Fe^{2+})_2$	$(Si, Al)_{12}$	O_{30}	H_2O	—
Armenite (Neumann, 1941)	Ba	Ca_2	Al_3	Al_3Si_9	O_{30}	$2H_2O$	$BaO \cdot 2CaO \cdot 3Al_2O_3 \cdot 9SiO_2 \cdot 2H_2O$
1:5:12	Na	Mg_3	Mg_3	Si_{12}	O_{30}	Na	$Na_2O \cdot 5MgO \cdot 12SiO_2$
Conceivable osumilite-type phases in $MgO \cdot Al_2O_3 \cdot SiO_2$	—	Mg_2	Al_3	$AlSi_{11}$	O_{30}	—	$2MgO \cdot 2Al_2O_3 \cdot 11SiO_2$
	Mg	Mg_2	Al_3	Al_3Si_9	O_{30}	—	$MgO \cdot Al_2O_3 \cdot 3SiO_2$
	Mg	Mg_2	Al_3	Al_5Si_7	O_{30}	Mg	$4MgO \cdot 4Al_2O_3 \cdot 7SiO_2$
	$\frac{1}{2}Mg$	Mg_2	Al_3	Al_2Si_{10}	O_{30}	—	$MgO \cdot Al_2O_3 \cdot 4SiO_2$

formula almost coincides with composition No. 2, which had yielded the highest amount of the new compound at the lowest temperature. It might thus be concluded from this line of evidence that the new metastable osumilite-type compound of the system MgO-Al_2O_3-SiO_2 has a composition approaching the formula $MgAl_2Si_4O_{12}$ or $MgO \cdot Al_2O_3 \cdot 4SiO_2$. This would also be in agreement with the previous statement that the unknown composition is likely to lie between cordierite and cristobalite. The assumption that some of the positions within the channels of the osumilite-type phase are vacant or only partly occupied is in agreement with Miyashiro's (1956) predictions that in osumilite the water content may not be essential and the quantity of (K,Na,Ca) may vary to some extent.

Optically the new osumilite-type compound is characterized in the synthetic products by a feathery arrangement of very thin needles and prisms of straight extinction and negative elongation. Their intergrowth with other phases as well as their thinness made exact optical determinations impossible. However, it can be stated with confidence that the phase has a mean refractive index of about 1.535 and a birefringence similar to or lower than that of quartz. Osumilite according to Miyashiro (1956) is uniaxial positive with $\epsilon = 1.549$–1.551, $\omega = 1.545$–1.547, $\epsilon - \omega = 0.004$. Milarite (Larsen and Berman, 1934) is uniaxial negative only at high temperatures ($\epsilon = 1.529$, $\omega = 1.532$, $\epsilon - \omega = 0.003$), whereas at ordinary temperature it is biaxial negative with small 2V. Armenite (Neumann, 1941) is also biaxial negative with refractive indices slightly higher than those of osumilite. Single crystals of osumilite are usually elongated parallel to the c-axis, but may also be tabular on {0001} (Miyashiro, 1956). If the elongation of the needles of the new osumilite-type compound follows the one or the other of these two directions, the optical character would respectively be either negative or positive. Although no clear decision between these alternatives can be offered, it seems more likely that the elongation parallels c and the crystals are optically negative like milarite and armenite. The fact that osumilite and also $K_2O \cdot 5MgO \cdot 12SiO_2$ (Roedder, 1951) are positive indicates optical relations among osumilite-type solid solutions similar to those of the gehlenite-akermanite series or of the metastable quartz solid solutions (Schreyer and Schairer, 1961A). Sensibly isotropic phases or others with very low birefringence like certain milarites (Koenigsberger and Müller, 1921) may be expected. The fact that biaxial crystals appear in this group of supposedly isostructural hexagonal minerals points to the possibility that for certain compositions under appropriate conditions ordering of the lattice with concomitant lowering of the symmetry may occur. An order-disorder relationship of this kind is now well known for the cordierite lattice, to which the osumilite lattice is related (six-fold single rings in cor-

TABLE 4. FICTIVE DENSITIES, REFRACTIVE INDICES, AND K VALUES OF CONCEIVABLE OSUMILITE-TYPE PHASES IN THE SYSTEM MgO-Al$_2$O$_3$-SiO$_2$
(An application of the law of Gladstone and Dale)

Theoretical formula*	Molecular weight on the basis of 30 oxygens	Computed density d	K†	Computed mean refractive index $n = d \cdot K + 1$
2MgO·2Al$_2$O$_3$·11SiO$_2$	945.28	2.468	0.20791	1.513
MgO·Al$_2$O$_3$·4SiO$_2$	955.25	2.494	0.20813	1.519
MgO·Al$_2$O$_3$·3SiO$_2$	967.32	2.525	0.20837	1.526
4MgO·4Al$_2$O$_3$·7SiO$_2$	989.46	2.583	0.20875	1.539

* For derivation see Table 3.
† Computed from

$$K = k_1 \frac{p_1}{100} + k_2 \frac{p_2}{100} + \text{etc.};$$

for $K_{Al_2O_3}$ the value 0.214 as given by Larsen and Berman (1934) for feldspars, feldspathoids, etc. was used.

dierite versus six-fold double-rings in osumilite, Miyashiro, 1956).

The knowledge of the approximate mean refractive index of the new osumilite-type compound enables us to check its proposed composition by means of the Gladstone-Dale relation between index of refraction, density, and chemical composition of a crystalline compound as described by Larsen and Berman (1934). The results of these calculations are compiled in Table 4. First the molar volume of the unknown phase was calculated from the cell edges a and c as 383.06 cm^3. Division of the molecular weights of the four theoretical osumilite formulas by this molar volume leads directly to the fictive densities d, which through a simple relationship with the specific refractive energies K yield the fictive refractive indices n of the four conceivable osumilite-type phases. It can be seen that the closest agreement between fictive and measured (1.535) refractive indices exists for the formula 4MgO·4Al$_2$O$_3$·7SiO$_2$ (4:4:7), which is based on the assumption that all structural vacancies are occupied by Mg^{2+}. This formula, however, is in contrast to the probable 1:1:4 composition of the unknown compound as deduced from the phase assemblages (see before). No explanation for this discrepancy can be offered at present. The deviation of the computed refractive index for the 1:1:4 formula (1.519) from the measured value seems too large for a compound consisting only of three oxides. It should also be noted that for the ternary compound cordierite (2MgO·2Al$_2$O$_3$·5SiO$_2$) computed and measured refractive indices agree within ±0.002. The exact composition of the new metastable osumilite-type phase, therefore, is yet unknown. According to

the phase assemblages in the bulk compositions from which it crystal-lized it has to lie along the line SiO_2-$MgAl_2O_4$.

The finding of a ternary compound with an osumilite-type structure in the system MgO-Al_2O_3-SiO_2, although metastable, enhances the possibil-ity of encountering osumilite-like compounds in the systems K_2O-MgO-Al_2O_3-SiO_2 and Na_2O-MgO-Al_2O_3-SiO_2. Lattice substitutions such as the ones proposed in Table 3 may lead to rather extensive binary or even ternary ranges of solid solutions in these systems, some of which may well have a true range of stability.

The Petalite-type Phase

A metastable phase with distinctly different physical properties was ob-tained from glass of composition No. 4 (Fig. 1) at relatively low devitrifi-cation temperatures. The other compositions immediately adjacent to No. 4 have not been crystallized at similar temperatures, but it is likely that they would also yield this phase. The conditions under which the un-known phase formed, persisted, and finally disappeared in composition No. 4 are summarized in Table 1. This indicates an optimum temperature of formation of about 900°–1000° C. Like the osumilite-type phase this compound could not be obtained entirely alone, but was found only in association with other products (Table 1). On account of the location of composition No. 4 within the phase triangle cordierite-$MgSiO_3$-SiO_2 no definite conclusions concerning the chemical composition of the unknown phase can be drawn from these assemblages.

In x-ray pattern the phase is characterized by a rather strong peak triplet around 24° 2θ for copper Kα radiation and a number of weaker lines, which are all listed in Table 2. It is likely, however, that some of the weaker lines of the unknown compound are covered by lines of the three possible coexisting phases and thus cannot be recognized. All the peaks which could not be attributed to any of the two coexisting phases in the material crystallized at 900° for 140 minutes are marked "P" in Fig. 3B. The weaker lines are very diffuse and may actually consist of more than one reflection, so that only approximate values for d and 2θ could be de-termined.

Known compounds yielding x-ray patterns similar to that of the un-known phase were found to be the natural mineral petalite, $LiAlSi_4O_{10}$, and synthetic Li-disilicate, $Li_2Si_2O_5$. The patterns of these two compounds are shown as Fig. 3, A and C. The unknown peaks labelled "P" in Fig. 3B show certain resemblances to both of these patterns; however, it can-not be decided which might be the closer relationship.

The main similarity between the two patterns A and C in Fig. 3 is also the peak triplet around 24° 2θ. However, there are dissimilarities regard-
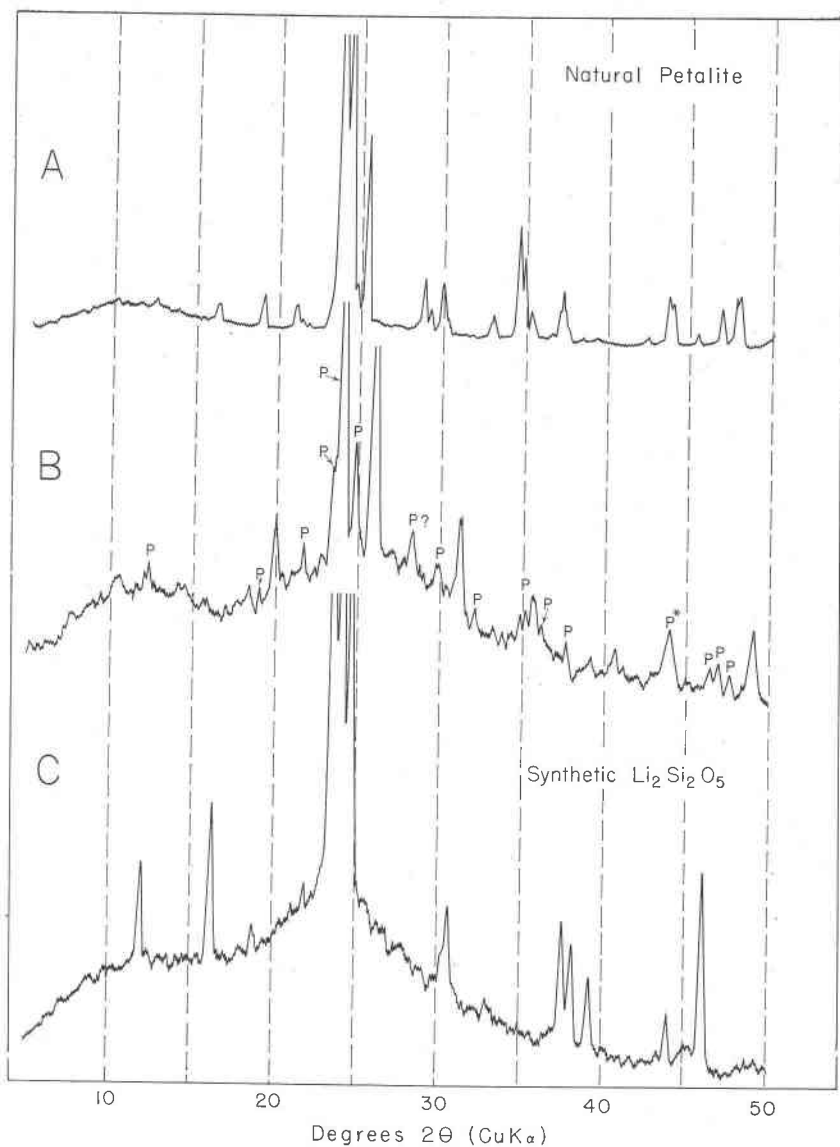
FIG. 3. Powder x-ray diffraction patterns between 5° and 50° 2θ for copper Kα radiation of:

A. Natural petalite, Londonderry, Western Australia. Sample provided by Dr. B. J. Skinner of the U. S. Geological Survey.

B. Devitrification product of composition No. 4 after heating at 900° C. for 140 minutes. Peaks marked "P" cannot be attributed to the phases quartz$_{ss}$ and enstatite, which are present in the crystalline aggregate, but belong to the unknown petalite-type compound. The asterisk marks a peak whose intensity is only in part due to the unknown phase P.

C. Synthetic Li$_2$O·2SiO$_2$. Sample provided by Drs. B. J. Skinner and D. B. Stewart of the U. S. Geological Survey.

ing the weaker reflections. Petalite is monoclinic pseudo-orthorhombic, space group $P2/a$ (Zemann-Hedlik and Zemann, 1955), and Li-disilicate is orthorhombic, space group $Ccc2$ or $Cccm$ (Donnay and Donnay, 1953); yet there are certain similarities in the lengths of the unit cell edges of petalite and Li-disilicate, especially if one uses the pseudo-orthorhombic orientation for the petalite cell as originally indicated by Gossner and Mussgnug (1930). Furthermore the form of Li-disilicate presented here may not be the only polymorph. A structural transition in Li-disilicate was mentioned by Kracek (1939); however, no x-ray data were given. There might thus be a polymorphic form of Li-disilicate which is structurally still more akin to petalite. A close structural relationship between these two compounds would not be so surprising, since simple substitution of three more Li for Al in petalite leads directly to the disilicate.* This might indicate the possibility of a solid solution between these two compounds in the system $Li_2O-Al_2O_3-SiO_2$ at some low temperature. Petalite was synthesized hydrothermally by Roy, *et al.* (1950) between 300° and 650° C at pressures between 1000 and 35,000 p.s.i. According to these authors petalite becomes unstable above 680° C. at about 10,000 p.s.i. and gives rise to a β-spodumene solid solution. Li-disilicate melts incongruently to Li-metasilicate Li_2SiO_3 and liquid at 1033° (Kracek, 1939).

The Mg^{2+} ion is known to have a similar size as Li^+ and, therefore, can replace the latter ion in certain compounds, at least metastably (Schreyer and Schairer, 1961A). This seems to be the case here also.

The Mg-analogue of petalite, $LiAlSi_4O_{10}$, would be $MgAl_2Si_8O_{20}$ or $MgO \cdot Al_2O_3 \cdot 8SiO_2$ (1:1:8, Fig. 1). This composition lies not very far beyond the most siliceous melt we have investigated along the line SiO_2-$MgAl_2O_4$. There is, however, no indication in the latter composition of any low temperature formation of the unknown petalite-type phase synthesized from composition No. 4. A substitution of Mg+Al for Li+Si in petalite leads to a theoretical formula $MgAl_2Si_3O_{10}$ or $MgO \cdot Al_2 \cdot 3SiO_2$ (1:1:3). This composition (Fig. 1) has been studied in the course of our work on cordierite. It has not yielded the unknown petalite-type phase, but crystallized completely to a metastable quartz solid solution at the lowest possible devitrification temperature. The phase assemblage of composition No. 4 after crystallization at 900° for 5 days and at 1000° for 1 day in the absence of residual glass seems to indicate that the unknown composition of the petalite-type compound does not lie along the line

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* After completion of the manuscript a paper by Friedrich Liebau (Untersuchungen an Schichtsilikaten des Formeltyps $A_m(Si_2O_5)_n$. I. Die Kristallstruktur der Zimmertemperaturform des $Li_2Si_2O_5$: *Acta Cryst.*, **14**, 389–395, 1961) appeared in which a very close structural relationship between $Li_2Si_2O_5$ and $LiAlSi_4O_{10}$ is demonstrated on the basis of single-crystal x-ray studies.

SiO_2-spinel but more towards the MgO-SiO_2 side of the ternary diagram.

The simplest compound on the join $MgSiO_3$-SiO_2 has a theoretical formula $MgSi_2O_5$ or $MgO \cdot 2SiO_2$ (Fig. 1). This compound "Mg-disilicate" is simply the Mg-analogue of Li-disilicate or may also be arrived at by a substitution of $2Mg$ for $Li + Al$ in petalite. A phase "Mg-disilicate," however, has not been reported in the literature. Its composition would melt to cristobalite and liquid at the temperature of the binary eutectic $MgSiO_3$-SiO_2, $1543° \pm 2°$ C. (Bowen and Andersen, 1914),* and only two immiscible liquids would coexist between 1695° and some very high temperature (Greig, 1927). It is not impossible that the unknown metastable phase has this composition. The fact, however, that glass of the composition "e" (Fig. 1) upon crystallization at 800° C. did not yield the unknown phase but only a pyroxene structurally close to clinoenstatite, makes it rather unlikely that the unknown petalite-type phase is a binary compound along the join $MgSiO_3$-SiO_2. It is more likely that its true composition lies somewhere in the ternary compositional range between the theoretical formulas $MgSi_2O_5$, 1:1:8 and 1:1:3. It can be said with certainty that the formation of the petalite-type phase requires bulk compositions with excess normative SiO_2 in addition to $MgSiO_3$. The phase has never been obtained from any of the compositions along the lines $MgSiO_3$-cordierite or cordierite-SiO_2 (Fig. 1).

Under the microscope the new compound seems to form round lumps most intimately intergrown with the other devitrification products as well as residual glass. For this reason it was impossible to determine its optical properties. It appears that the phase has a mean refractive index in the vicinity of 1.580 and rather low birefringence. In comparison the optical properties of the Li phases are as follows:

Petalite: Biaxial positive; $\alpha = 1.504$, $\beta = 1.510$, $\gamma = 1.516$;
birefringence $\gamma - \alpha = 0.012$ (Winchell, 1951).
Li-disilicate: Biaxial positive; $\alpha = 1.547$, $\beta = 1.550$, $\gamma = 1.558$ (Kracek, 1930)

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* This temperature was checked by means of a mixture of the eutectic composition as given by Bowen and Andersen (1914): 87.5% $MgSiO_3$, 12.5% SiO_2 or 35.15% MgO, 64.85% SiO_2 in weight per cent (composition "e" in Fig. 1). It was found that this composition remained fully crystalline below $1553° \pm 5°$ C. Above this temperature only small amounts of cristobalite coexisted with liquid up to $1563° \pm 5°$ C. It is concluded from this behavior that the temperature of the binary eutectic $MgSiO_3$-SiO_2 is slightly higher than reported by Bowen and Andersen (1914) and may be given as $1553° \pm 5°$ C. This value was obtained with a Pt-Pt90Rh10 thermocouple calibrated with pure Pd with the melting point 1549.5° C. It should be noted that a melt of the composition "e" can be quenched as a glass only if small charges are dropped instantaneously into mercury. If larger amounts of liquid contained in a Pt crucible are cooled more slowly in a water bath, crystallization to protoenstatite takes place, whereas the normative SiO_2 remains in a state which is amorphous to x-rays but can be detected readily under the microscope as round globules of a very low refractive index (SiO_2 glass?).

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