

ON SUB SOLIDUS RELATIONS OF SILICATES

III. A contribution to the chemistry of melilites.

By

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Abstract. Based upon the structure determination of melilite and upon substitution experiments, the general melilite formula $A_2M'_2(BC_2M_3)$ or $A_2(BC_2M_6)M'$ is proposed. The substitution possibilities in the different sites are shown by experiments.

Introduction

In this paper, being a part of the study on the mineral physics and chemistry of the melilite group, a series of melilite syntheses are presented. The syntheses were made to shed light on the details of the melilite structure, they form a supplement to the structure determinations by RAAZ (1930), by WARREN (1930) and by SMITH (1953) as shown by high accuracy X-ray powder analysis.

Experimental technique

Most of the melilites used in this work were made by sintering. The ionic migration along surfaces of a sintering batch is relatively rapid. Metastable phases may form, but due to the rapid ionic migration they are decomposed more rapidly than in a melt.

The alkali-free melilites were produced at 1200° C and 1300° C. With two intermediate grindings the products appeared to be homogeneous when examined optically and by X-ray powder analysis. The NaF-melilites were produced by reaction between an alkali-free melilite and a considerable excess of NaF. The decomposition temperature of NaF melilites is so low that attempts to produce them by melting and crystallization from the melt were largely unsuccessful;

the melts contained undissolved Al_2O_3 or MgO . It is possible that syntheses under hydrothermal conditions would yield more successful results. The only melilite produced by melting and crystallization from the melt is CaNaOFSiBeSiO_5 . The preparation data for the melilites of this work are shown in table 1.

X-ray analysis technique

The artificial melilites were examined with the microscope and by X-ray powder analysis. Cameras of 9 cm. diameter of the self-centering type described by NEUMANN and BARSTAD (1953) were used for identification purposes, and a 22,92 cm. quadruple Nonius camera was used for high accuracy determination of the unit cell sizes.

Much care was taken to obtain the best possible results from the high accuracy determinations. For this type of camera the accuracy of the geometrical conditions of the reflection of the X-ray beam is essential, and the adjustment of the setup is relatively time consuming. When correctly adjusted, however, high accuracy is readily obtained throughout almost the whole range of reflections. The $K\alpha_1$ and $K\alpha_2$ lines are well separated at the zero point of the film. By screening the beam just in front of the specimen holder an almost pure $K\alpha_1$ beam can be obtained. The combined $K\alpha_1$ and $K\alpha_2$ beam was used for all the exposure for the present work and the resolving power was better than a θ value of $0,025^\circ$ at convenient intensity conditions. The accuracy of the reading of the lines is better than $0,015^\circ$ of θ .

A refined technique was developed for making powder specimens

Table 1. Preparation data for melilites.

Name	Formula	Temp.	Time	Batch
Åkermanite	$\text{Ca}_2\text{O}_2\text{MgSi}_2\text{O}_5$	1300°	8 days	oxides-carbonates
Gehlenite	$\text{Ca}_2\text{O}_2\text{AlSiAlO}_5$	1300°	8 days	oxides-carbonates
Be-gehlenite	$\text{Ca}_2\text{O}_2\text{SiBeSiO}_5$	1200°	8 days	oxides-carbonates
NaF Be-gehlenite	CaNaOFSiBeSiO_5	800°	1 day	oxides-carbonates
NaF åkermanite	$\text{CaNaOFMgSi}_2\text{O}_5$	520°	14 days	åkermanite + NaF
NaF gehlenite	CaNaOFSiAlO_5	520°	14 days	gehlenite + NaF
Na-oxy-gehlenite	$(\text{Ca}, \text{Na})_2\text{O}_2\text{AlSiAlO}_5$	1120°	8 days	oxides-carbonates
K-oxy-gehlenite	$(\text{Ca}, \text{K})_2\text{O}_2\text{AlSiAlO}_5$	1100°	1 day	oxides-carbonates

of uniform thickness and free from grains: The powder to be examined was ground in an agate mortar until a very fine product was obtained using acetone as a grinding liquid. The specimen holder was placed upon a thin plastic foil and a special glue was applied to the four windows of the specimen holder. The glue was made from a commercial multipurpose cellulose acetate glue mixed with acetone in the ratio one part glue to four parts acetone. After a few minutes the powder was attached to the window by means of a few extra drops of the special glue. The necessary amount of powder to produce a satisfactory X-ray record is 15–20 milligrams. The plastic foil on the back of the specimen holder gives a reflection band that normally does not disturb the X-ray pattern. If this reflection band is unwanted the specimen holder may be dried at 100° C for a few hours. After the drying the plastic foil may be torn off, when a little carefully made, the powder window remains well preserved because the glue does not stick to the plastic foil when dried.

An especially made double scale with 1/10 mm divisions was exposed to the films just before the exposure by X-rays. All the exposures were made with $\text{Pb}(\text{NO}_3)_2$ as an internal standard. Analytical $\text{Pb}(\text{NO}_3)_2$ from British Drug House with $a_0 = 7,8560 \text{ \AA}$ was used. The advantages of using an exposed scale and an internal standard are obvious: either corrections for small changes in the distance from the specimen holder to the zero point (actual camera diameter), nor corrections for the variation of the window thickness, nor for the film shrinkage are necessary.

To check the method used here, a correlation has been made between gehlenite, åkermanite and the 60 åkermanite 40 gehlenite mixed crystal of this work and the determinations made by ANDREWS (1948), by ERVIN and OSBORN (1949) and by NEUVONEN (1952). (Figure 1 and table 2). The values obtained by NEUVONEN (1952) on synthetic åkermanite—gehlenite mixed crystals agree well with the data of ERVIN and OSBORN (1949), indicating perfect accordance to Vegard's law. The data of the present work show better agreement with those obtained by ANDREWS (1948). Neuvonen has shown by calculation that the non-ideal mixing in the åkermanite—gehlenite series actually found by him cannot be recorded by normal X-ray powder analysis because the effect upon the unit-cell size is lower than the accuracy of the present X-ray measurements. Therefore an appa-

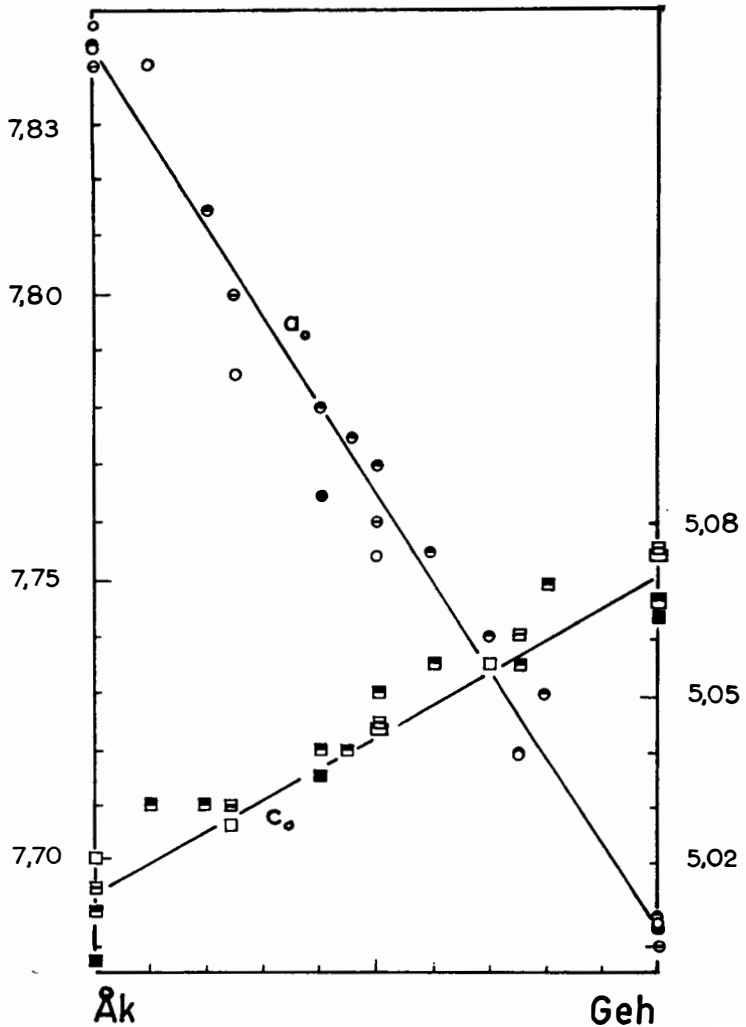


Fig. 1. Values of a_0 and c_0 in the series åkermanite-gehlenite. a_0 values: ○ Andrews (1948), ● Ervin and Osborn (1949), ⊖ Neuvonen (1952), ● present work. c_0 values: □ Andrews, ■ Ervin and Osborn, ⊖ Neuvonen, ■ present work.

rent linearity exists in the relationships of the unit-cell constants of the åkermanite-gehlenite series.

The developed films were projected by an air cooled modified Liesegang slide projector and the readings were made at a magnifi-

Table 2. Values of a_0 and c_0 of the mixed-crystal series åkermanite-gehlenite.

	0	20	25	30	40	50	55	60	75	80	90	100	
Åkermanite	100	80	75	70	60	50	45	40	25	20	10	0	
a_0	{ 7,690		7,719	7,74	7,755	7,754	7,775	7,78	7,787	7,815	7,84	7,844	Andrews (1948)
	{ 7,694	7,73				7,77	7,775	7,78	7,800			7,846	Ervin and Osborn (1949)
	{ 7,685		7,720			7,760		7,765				7,840	Neuvonen (1952)
	{ 7,689											7,844	Present work
c_0	{ 5,067		5,055	5,055	5,055	5,045	5,04	5,04	5,027	5,03	5,03	5,010	Andrews (1948)
	{ 5,077	5,07				5,05	5,04	5,04	5,030			5,020	Ervin and Osborn (1949)
	{ 5,076		5,060			5,045		5,035				5,015	Neuvonen (1952)
	{ 5,063											5,000	Present work

cation of roughly ten times. This method yields a spread of less than 0,05% of the values of the calculated unit-cell edge length for all the reflections used for the calculations.

Observations on earlier work on the chemistry and structure of melilites

SHEPHARD and RANKIN (1911) and FERGUSON and MERWIN (1919) first determined the correct proportional formula of gehlenite and åkermanite respectively. The earlier formulas by Bourgeois, Vogt, Zambonini, Doelter and others have only historical interest. A compilation of the different melilite formulas introduced before 1911 is presented in C. Doelter: *Handbuch der Mineralchemie*, Dresden and Leipzig 1917.

WINCHELL (1924) introduced the general formula R_5O_7 for melilites. BERMAN (1929) wrote it $X_2Y_3O_7$, and later MACHATSCHKI (1930) suggested the general melilite formula $X_2YZ_2(O, OH)_7$. This formula has been generally accepted later.

However this formula may lead to misinterpretations of the substitution mechanisms of melilites if the reader is not conversant with the details of the melilite structure. This has been done several times in the literature and therefore there is justification for a revision of the general formula of melilites introduced by Machatschki.

Before doing this, the atomic structure of melilite should be briefly surveyed:

RAAZ (1930) and WARREN (1930) independently determined the atomic structure of melilite on synthetic gehlenite and on natural melilite material respectively. BARTH and POSNJAK (1931) explained the relation between gehlenite and åkermanite on the theory of variate atom equipoints. WARREN and TRAUTZ (1930) showed that hardystonite, $Ca_2O_2ZnSiSiO_5$, is a melilite also. ZACHARIASEN (1930 and 1931) pointed out that the minerals leukophane and melinophane are melilite-like compounds and O'DANIEL and TSCHWEISCHWILI (1945—48) showed that $Na_2F_2LiBeBeF_5$ is isotype with melilite. Recently the present author (1960) pointed out that the minerals leukophane and melinophane are mixed crystals between the $Ca_2O_2SiBeSiO_5$ melilite and åkermanite and gehlenite respectively and with a partial substitution of Ca_2O_2 groups by Na_2F_2 groups.

The unit-cell constants of the åkermanite—gehlenite mixed crystals were determined by ANDREWS (1948) and ERVIN and OSBORN (1949). SMITH (1953) reexamined the melilite structure using a crystal from the same locality as that of Warren's material and supplied accurate data for the interatomic distances.

According to Smith the melilite structure consists of sheets of MgO_4 , AlO_4 , and SiO_4 tetrahedra oriented parallel to the 001 plane. The sheets are held together by weaker Ca—O bonds and, therefore, the only cleavage plane of the melilites is the 001 plane.

In accordance with the ideas of MACHATSCHKI (1930) the åkermanite formula has been written $\text{Ca}_2\text{MgSi}_2\text{O}_7$, and the formulas for iron-åkermanite and hardystonite $\text{Ca}_2\text{FeSi}_2\text{O}_7$ and $\text{Ca}_2\text{ZnSi}_2\text{O}_7$. This is one of the reasons why melilites have been classified with the sorosilicates. The minerals of the soro-silicate group, with few exceptions, have isolate Si_2O_7 double tetrahedra, but in melilites isolated Si_2O_7 groups do not exist. The melilite structure is a sheet structure and melilites should be classified as phyllosilicates as pointed out e.g. by STRUNZ (1957).

The sheet is made up of oxygen tetrahedra of different sizes. In the unit-cell three different tetrahedra may be distinguished, and according to SMITH (1953) they are called tetrahedron I, tetrahedron II and tetrahedron III. In this paper the site inside tetrahedron I will be called the B site and the site inside the tetrahedra II and III the C site.

Tetrahedron I is the largest one having a metal-to-oxygen distance of 1,88 Å in the melilite studied by Smith. The tetrahedra II and III are almost identical in size with a mean metal-to-oxygen distance of 1,63 Å.

Both Warren and Smith pointed out that it is very improbable that Si occupies the B site (inside tetrahedron I). Tetrahedron I is larger than are II and III and it is in all probability occupied by the larger ions Mg, Fe and Zn. (This is unique and to the present author's knowledge magnesium is not found in four-fold coordination in any other mineral group. The ionic radius of magnesium in this coordination is not known but 0,64—0,65 Å seems to be about right). It is possible that this statement actually should be restricted to the mineral specimens studied by Warren and by Smith. The melilite $\text{Ca}_2\text{O}_2\text{SiBeSiO}_5$ (CHRISTIE (1961)) seems to have a structure identical

to that of gehlenite, $\text{Ca}_2\text{O}_2\text{AlSiAlO}_5$, as will be discussed later in this paper. If only Si and Be occupy the center of the sheet tetrahedra, the larger tetrahedron I in all probability will be occupied by the larger Si ion whereas the smaller Be ion takes place inside the smaller tetrahedra II and III.

In the melilites, the oxygen polyhedron around the Ca ion is strongly distorted, and there are two sets of Ca-O distances, 2,44 Å and 2,70 Å. The extreme length of the one set of Ca-O distances indicates a homopolar character of this very bond.

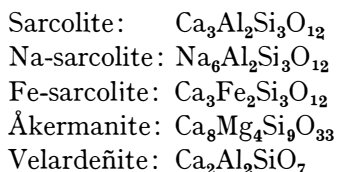
There may be an analogy between some details in the structure of the mineral afwillite (MEGAW (1952)) and that of melilite. In afwillite Si occurs in isolated tetrahedra connected by Ca-O bonds. Ca is situated inside a distorted polyhedron, and three different polyhedra may be distinguished in the afwillite structure. One set of the Si-O distances are longer than the other ones and hydrogen ions are situated around the oxygen of the long Si-O bond. The bond between the OH group and the nearest Ca ion of afwillite is also longer than the Ca-O bonds.

Smith reported that the corner of the SiO_4 tetrahedron not shared with other SiO_4 tetrahedra of the sheets have insufficient Pauling valence bonds to justify the location of an ionically bound oxygen ion. It is, therefore, probably that the F ions of the NaF melilites and the OH ions of the NaOH melilites occupy the 'free' apexes of the sheet tetrahedra rather than other sites of the structure.

Chemically the formation of NaF melilites from CaO melilites may be expressed as a substitution of Na_2F_2 for Ca_2O_2 . It will be shown later in this paper that strict rules may be laid down for the formation of melilites if the bonds between the sheets are written $\text{A}_2\text{M}'_2$ and the constituents forming the sheets are written BC_2M_5 . (This formulation is not quite correct because the M' ions also take part in the formation of the sheets as apexes of the tetrahedra. From structure point of view the general formula $\text{A}_2(\text{BC}_2\text{M}_6)\text{M}'$ should be preferred, the A-M' bonds representing the longer Ca-O bonds of the melilite studied by SMITH (1956). In this paper, dealing with the chemical conditions for the formation of melilites, the formula $\text{A}_2\text{M}'_2(\text{BC}_2\text{M}_5)$ is used for the sake of convenience. Consequently the complete general formula of melilites should be written $\text{A}_2\text{M}_2(\text{BC}_2\text{M}_5)$. Åkermanite, in this notation, is written $\text{Ca}_2\text{O}_2(\text{MgSi}_2\text{O}_5)$ and gehlenite is written $\text{Ca}_2\text{O}_2(\text{AlSiAlO}_5)$.

It will presently be shown by the experimental evidence of this paper that the $A_2M'_2$ part of the formula and the BC_2M_5 part must be uncharged or almost uncharged. A charge of the BC_2M_5 part of the formula of more than + 0,3 per mole is not accepted in the molecule of melilites known so far, and leads to breakdown of the melilite structure.

Natural melilites normally contain some alkali metals and, therefore, the mechanism of the substitution of Na for Ca has been subject to considerable interest. SCHALLER (1915) considered natural melilites to be mixed crystals of the following end members:



The name velarde\~{n}ite was proposed by Schaller for pure $Ca_2Al_2SiO_7$. However, SHEPHERD and RANKIN (1911) who were the first ones to produce this mineral, called it gehlenite. The name velarde\~{n}ite is not used in the literature any longer.

BUDDINGTON (1922) showed that there is full solid solution between \AA kermanite and gehlenite and the mixture nine parts sarcolite one part Na-sarcolite in the temperature range $1000^\circ-1500^\circ$ C.

WINCHELL (1924) pointed out that there could be no mixed crystal formation between the melilites and the sarcolites because of the great difference in chemical composition, and he proposed the existence of a $Na_2Si_3O_7$ melilite end member. GOLDSMITH (1948), following this idea, tried to make mixed crystals between $Na_2Si_3O_7$ and \AA kermanite and gehlenite respectively. He found that there is no $Na_2Si_3O_7$ melilite and that \AA kermanite takes nothing of this molecule in solid solution. Gehlenite takes only 15 % by weight of $Na_2Si_3O_7$ in solid solution at the solidus temperature.

The substitution of Na for Ca in natural melilites cannot be explained by the abovementioned mechanism alone. Goldsmith, therefore, suggested that the substitution of Na for Ca must be followed by a substitution of OH for O.

SMITH (1953) pointed out that this explanation was not satisfactory and showed that there is no direct connection between the alkali content and the water content of natural melilites.

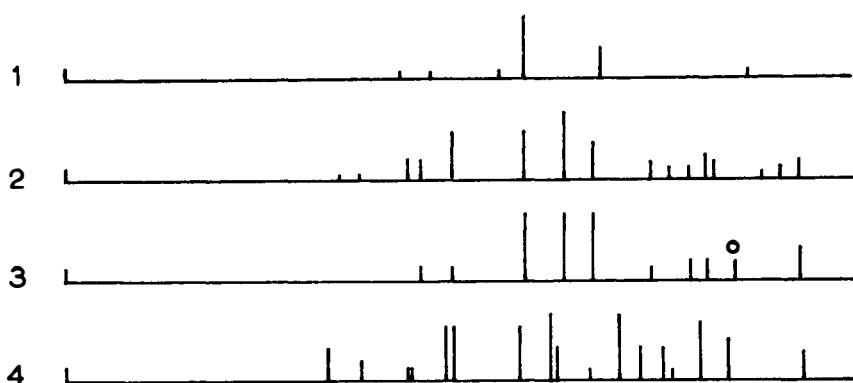


Fig. 2. X ray powder patterns of 1) high wollastonite, 2) nepheline, 3) "sodium melilite" of Nurse and Midgley (1953), pattern constructed from d values. Line marked o cannot be ascribed to the high wollastonite or the nepheline pattern, 4) pattern of a melilite with $a_0 = 8,511 \text{ \AA}$ and $c_0 = 4,809 \text{ \AA}$ given by Nurse and Midgley for "sodium melilite". Intensities of lines taken to be the same as for gehlenite.

NURSE and MIDGLEY (1953) claimed to have produced CaNaAlSiO_7 and $\text{CaKAlSi}_2\text{O}_7$ melilites, this is in conflict with the results of GOLDSMITH (1948). The existence of such melilites is questionable in the opinion of the present author. Nurse and Midgley reported the best temperature of formation for $\text{CaNaAlSi}_2\text{O}_7$ melilite to be around 1000°C . The present author has repeated this experiment using very long time for the heat treatment and no other phases than nepheline and high wollastonite could be detected in the product. The X-ray powder pattern of the sodium melilite of Nurse and Midgley cannot be indexed on the basis of the unit-cell values given by them and the pattern is quite different from that of a melilite. Moreover, all the lines in the sodium melilite pattern reported by Nurse and Midgley can be ascribed to lines in either the nepheline or the high-wollastonite pattern as shown by figure 2 and table 3.

There is a slight discrepancy between the higher d -values of the presented nepheline pattern and the corresponding values of the sodium melilite pattern of Nurse and Midgley. This may be due to slight differences in the unit-cell of the nephelines (caused by differences in chemistry and temperature of formation) or to pure technical reasons.

Table 3. Interplanar spacings in Å units of "Sodium melilite" by Nurse and Midgley (1953), of nepheline and of high wollastonite.

"Sodium melilite"	Nepheline	High wollastonite
—	—	vvw 5,7
—	10 5,55	—
—	10 5,02	—
—	—	vvw 4,37
—	30 4,31	—
vvw 4,17	50 4,17	—
—	—	vw 4,04
vvw 3,80	80 3,81	—
—	10 3,74	vw 3,42
s 3,21	60 3,25	s 3,23
s 2,98	100 2,99	—
s 2,81	60 2,84	m 2,80
vw 2,548	30 2,56	—
—	20 2,49	—
—	—	vw 2,44
w 2,392	20 2,39	—
w 2,319	40 2,33	—
—	30 2,30	—
w 2,267	—	—
—	10 2,145	—
—	20 2,110	—
m 2,069	30 2,080	—
vw 2,014	—	vw 1,989
s 1,965	—	vs 1,970
vw 1,908	20 1,920	—
vw 1,862	10 1,875	—
vw 1,831	10 1,834	vvw 1,828
vw 1,788	20 1,790	—
—	—	vvw 1,748
s 1,736	—	—
wm 1,700	—	vvw 1,703
wm 1,677	20 1,688	vvw 1,680
—	10 1,630	—
ms 1,603	20 1,612	vvw 1,609
m 1,584	10 1,595	—
—	—	vvw 1,539

Table 4. Failed melilite syntheses. All four molecules should yield melilites according to the earlier $A_2BC_2O_7$ melilite formula. They do not fulfill the conditions for formation of melilites forwarded in this paper.

Formula	Charge per mole of BC_2M_5	Reference
$Gd_2O_2MgBeSiO_5$	- 2	This work
$Na_2O_2SiSi_2O_5$	+ 2	{ Winchell (1924) Goldsmith (1948)
$AlO_2AlAl_2O_5$	- 1	Goldsmith (1948)
$NaO_2AlSi_2O_5$	+ 1	Nurse and Midgley (1953)

Thus, when the present writer took up the study of melilites, many conflicting ideas had been published. BUDDINGTON's experiments on alkali melilites (1922) had been rather ignored by later authors, although his conclusions never had been proved to be incorrect. The $Na_2Si_3O_7$ melilite end member introduced by WINCHELL (1924) was shown by GOLDSMITH (1948) to be non-existent and finally the existence of the $CaNaAlSi_2O_7$ melilite seems questionable so far.

According to the general formula of melilites introduced in this paper, the sodium melilite of Nurse and Midgley should be written $CaNaO_2AlSi_2O_5$. Here the BC_2M_5 part of the formula is electrically charged and this is against the condition for the formation of melilite. Therefore, this compound is included in table 4 displaying failed syntheses of melilites.

Results of the syntheses and discussion

The present syntheses have been based upon the formula $A_2M'_2BC_2M_5$. The substitution experiments have been made to find the maximum charge per mole of the BC_2M_5 part of the formula of melilite and to explore the accepted variation of the atomic radii in the different sites of the structure.

a) Substitutions in the $A_2M'_2$ part of the general formula of melilites.

GOLDSMITH (1948) showed that 15% by weight of the $Na_2Si_3O_7$ molecule is taken in solid solution in gehlenite. The substitution mechanism may be explained in two ways:

General formula	1)		2)	
	$\text{Na}_2\text{Si}_3\text{O}_7$	gehlenite	$\text{Na}_2\text{Si}_3\text{O}_7$	gehlenite
A_2	$\text{Na}_2 \longrightarrow$	Ca_2	$\text{Na}_2 \longrightarrow$	Ca_2
M'_2	$\text{O}_2 \longrightarrow$	O_2	$\text{O}_2 \longrightarrow$	O_2
B	$\text{Si} \longrightarrow$	Al	$\text{Si} \searrow$	Al
C_2	$\text{Si} \longrightarrow$	Si	$\text{Si} \longrightarrow$	Si
	$\text{Si} \longrightarrow$	Al	$\text{Si} \longrightarrow$	Al
M_5	$\text{O}_5 \longrightarrow$	O_5	$\text{O}_5 \longrightarrow$	O_5

In case 1) one Si ion from $\text{Na}_2\text{Si}_3\text{O}_7$ enters the B site of gehlenite. This is not very probable because the small Si ion would preferably be situated in the smaller C site, leaving the B site for the larger Al ion. Therefore, case 2) gives a more satisfactory explanation implying that all Si of the $\text{Na}_2\text{Si}_3\text{O}_7$ molecule enters the C sites and that the Al situated in this position at the same time migrates from the C site to the B site.

The failure of åkermanite to take any $\text{Na}_2\text{Si}_3\text{O}_7$ in solid solution is readily understood from the substitution mechanism of 2).

General formula	$\text{Na}_2\text{Si}_3\text{O}_7$	åkermanite
A_2	$\text{Na}_2 \longrightarrow$	Ca_2
M'_2	$\text{O}_2 \longrightarrow$	O_2
B	$\text{Si} \searrow$	Mg
C_2	$\text{Si} \longrightarrow$	Si
	$\text{Si} \longrightarrow$	Si
M_5	$\text{O}_5 \longrightarrow$	O_5

No Al is present in the C sites of åkermanite. Thus no C sites in åkermanite will be available for the B site ions of the fictitious $\text{Na}_2\text{Si}_3\text{O}_7$ melilite, contrary to what is found in gehlenite.

When $\text{Na}_2\text{Si}_3\text{O}_7$ is taken in solid solution in gehlenite the BC_2M_5 part of the general formula is not electrically neutral any longer. Experiments by the present author clearly indicate that the maximum charge of the BC_2M_5 is temperature dependent and, therefore, that the amount of $\text{Na}_2\text{Si}_3\text{O}_7$ taken into solid solution in gehlenite also

Table 5. Solubility of the $\text{Na}_2\text{Si}_3\text{O}_7$ molecule in gehlenite. The run at 600°C was made under hydrothermal conditions, and therefore the percentage of $\text{Na}_2\text{Si}_3\text{O}_7$ dissolved in gehlenite may be too low if some $\text{Na}_2\text{Si}_3\text{O}_7$ has been leached out by the water vapor. The initial material for this 14 days/ 6 kbar water pressure run was gehlenite with 15% $\text{Na}_2\text{Si}_3\text{O}_7$ in solid solution. The material for the 1000°C run was gehlenite mixed with 30% of an oxide/carbonate mixture of $\text{Na}_2\text{Si}_3\text{O}_7$ proportions. The material was heated for 2 weeks. Determination of the amount of dissolved $\text{Na}_2\text{Si}_3\text{O}_7$ was made by X-ray analysis and by measurement of the index of refraction and is accurate within $\pm 1\%$ of $\text{Na}_2\text{Si}_3\text{O}_7$ dissolved.

Temperature $^\circ\text{C}$	% dissolved $\text{Na}_2\text{Si}_3\text{O}_7$	Charge of BC_2M_5	Reference
1154	15	+ 0.30	Goldsmith (1948)
1000	10	+ 0.20	Present work
600	7.5	+ 0.15	Present work

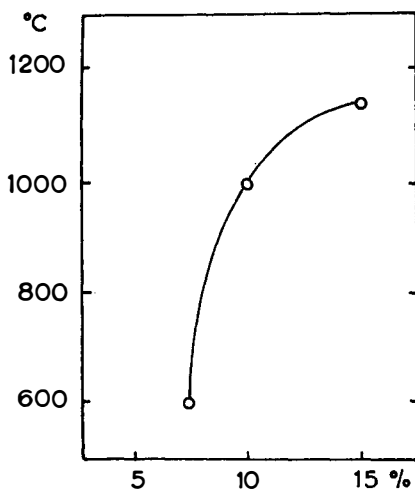


Fig. 3. Solubility of the $\text{Na}_2\text{Si}_3\text{O}_7$ molecule in gehlenite at different temperatures, data from table 5.

depends upon the temperature. Table 5 and figure 3 displays the percentage of $\text{Na}_2\text{Si}_3\text{O}_7$ dissolved in gehlenite.

The mixed crystal series at $1060^\circ - 1500^\circ\text{C}$ between melilite and the sarcolite and Na-sarcolite molecule of BUDDINGTON (1922) is explained by the small charge of the BC_2M_5 part of the general formula. The mixture 9 parts sarcolite 1 part Na-sarcolite may be transformed into the melilite formula yielding a charge of + 0,25 per mole of the BC_2M_5 part of the formula, which is within the accepted range at this temperature. Buddington also showed

that up to 60% of the pure sarcolite molecule is taken in solid solution in gehlenite. The temperature of formation of homogeneous crystals was about 1100°C in Buddington's experiments and the charge of the BC_2M_5 part of the general formula is + 0,29 for this

Table 6. Interplanar spacings in Å units of the mixed crystal gehlenite — $15 \text{ Na}_2\text{Si}_3\text{O}_7$

$a_0 = 7,667 \pm 0,004 \text{ Å}$ (7,689) $c_0 = 5,075 \pm 0,033 \text{ Å}$ (5,063)		Numbers in brackets are corresponding values for pure gehlenite	
hkl	$d_{calc.}$	$d_{obs.}$	Int.
110	5,422	5,423	w
001	5,075	5,076	s
011	4,232	4,230	vw
020	3,835	3,832	vw
111	3,706	3,706	s
120	3,430	3,430	m
021	3,059	3,057	s
121	2,841	2,839	vs
220	2,711	2,712	m
030	2,556	2,556	vw
002	2,538	2,537	m
130	2,425	2,425	s
012	2,409	2,409	w
221	2,391	2,391	m
112	2,299	{ 2,298	vw
122	2,298		vw
031	2,283	2,284	m
040	1,917	1,917	m

mixed crystal, again being in very good agreement with the data from table 5.

NEUVONEN (1955) has pointed out that there is a connection between the Al content of melilites and their alkali content. His conclusions are based upon the assumption that there exists a $\text{CaNaO}_2\text{AlSi}_2\text{O}_5$ melilite, in fact being nothing but a 50/50 mixture of gehlenite and $\text{Na}_2\text{Si}_3\text{O}_7$. Within the limits of solubility found by Goldsmith and by the present author, the results presented by Neuvonen are in good agreement with the earlier published data.

The substitutions in the $\text{A}_2\text{M}'_2$ part of the general formula can be followed by changes in index of refraction, density, unit-cell dimensions, and other physical properties. The changes in the unit-cell

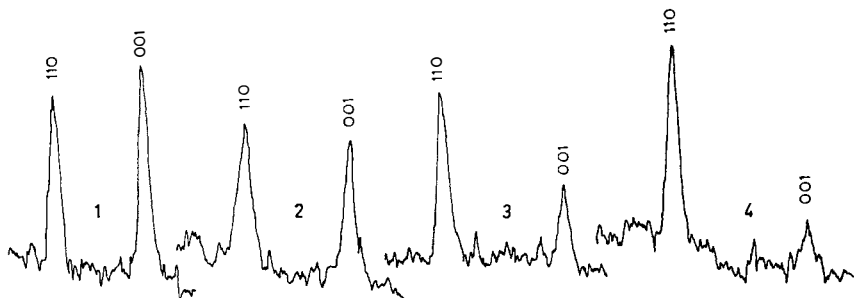


Fig. 4. Intensity of the lines 110 and 001 of the x-ray powder pattern of gehlenite with various amounts of $\text{Na}_2\text{Si}_3\text{O}_7$; 1) 15%, 2) 10%, 3) 5%, 4) 0%.

dimensions are particularly interesting because they confirm the structure determination, and the substitution mechanism can be followed very accurately.

The A ions are situated between the sheets of the melilite structure and therefore substitutions in the A site affect the c_0 value relatively much more than the a_0 value. It is possible that substitutions of the ions in the apexes of the tetrahedra in the sheets likewise would cause the same effect.

If $\text{Na}_2\text{Si}_3\text{O}_7$ is dissolved in gehlenite there is a substitution of Si for Al in the C site of the formula, but this substitution is not likely to affect the a_0 value but little. Ca is replaced by Na, and because the ionic radii of Ca and Na are almost identical, the c_0 value should also be unaffected by this substitution. The sheet becomes charged, however, and will therefore cause a contraction of the sheet in the direction of a_0 . This can be shown by the changes induced when $\text{Na}_2\text{Si}_3\text{O}_7$ is taken in solid solution to 15% by weight: the c_0 value increases roughly 0,2% in agreement with the ionic radii relations of Ca and Na, the a_0 value decreases around 0,3% reflecting a slight contraction of the sheets. The unit-cell dimensions and the d-values of the X-ray pattern of the mixed crystal 85 gehlenite — 15 $\text{Na}_2\text{Si}_3\text{O}_7$ are displayed in table 6.

When Na substitutes for Ca in melilites there is a slight change in the intensity relations of the lines of the powder pattern, this is particularly marked in the two nearby lines 110 and 001: the intensity of 110 decreases and the intensity of 001 increases (figure 4). Results of intensity calculations for these lines confirm the differences actually found.

The solubility relations of $K_2Si_3O_7$ in gehlenite are different from those of $Na_2Si_3O_7$. Na has roughly the same radius as Ca; from ionic radius standpoint there is no limit, therefore, to the general substitution of Na for Ca. The limit is actually set by the reluctance of the structure to accept a charge of more than + 0,3 per mole of the BC_2M_5 part of the general formula.

K, however, is larger than Ca, and the solubility of the $K_2Si_3O_7$ molecule in gehlenite is governed by the available space in the A site of the melilite structure. The highest amount of the $K_2Si_3O_7$ molecule taken in solid solution in gehlenite at 1200° C is 6 mole per cent as shown by figure 5. The index of refraction of the melilite in the different runs were:

Composition of batch	% gehlenite	100	96	92	88
	% $K_2Si_3O_7$	0	4	8	12
	ω	1.667	1.635	1.660	1.660
	ϵ	1.657	1.635	1.653	1.653
X-ray powder pattern		melilite	melilite	melilite + extra lines	melilite + extra lines

Several attempts were made to synthesize the pure NaF-åkermanite and the corresponding gehlenite. All the trials were unsuccessful, probably because the crystallization of the NaF melilites is extremely slow at temperatures below the melting point, which seems to be around 550° C. No complete reaction in the sub-solidus region was observed within the time involved in the heatings, mostly two weeks, and unreacted Al_2O_3 or MgO were almost always observed in these runs.

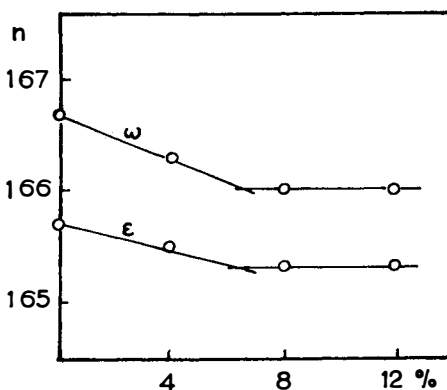


Fig. 5. Index of refraction of gehlenite with various amounts of $K_2Si_3O_7$ in the batch.

The reaction between åkermanite or gehlenite and NaF melilite batch yielded mixed crystals which at 520° C contained equal amounts

Table 7. Interplanar spacings in Å units of the mixed crystal 94 gehlenite — 6 K₂Si₃O₇

			Numbers in brackets are corresponding values for pure gehlenite
a ₀ = 7,703 ± 0,004 Å		(7,689)	
c ₀ = 5,072 ± 0,003 Å		(5,063)	
hkl	d _{calc.}	d _{obs.}	Int.
110	5,448	5,446	m
001	5,072	5,069	w
011	4,236	4,236	vw
020	3,852	3,854	vw
111	3,713	3,714	s
120	3,446	3,444	s
021	3,067	3,066	s
121	2,850	2,852	vs
220	2,724	2,724	m
030	2,567	2,568	vw
002	2,536	2,536	m
130	2,436	2,436	s
012	2,409	2,409	w
221	2,399	2,398	m
112	2,369	2,369	vw
031	2,291	2,290	w
040	1,926	1,926	m

of Ca₂O₂ and Na₂F₂. Batches with more than 50% NaF melilite yielded mixed crystals whose index of refraction did not differ from that of the mixed crystals formed from the 50/50 batch. Reaction between åkermanite or gehlenite and a large excess of NaF yielded identical results, and there seems therefore to be a limited substitution possibility of Na₂F₂ for Ca₂O₂ in melilites. The substitution is probably temperature dependent and seems to be 50% at 520° C.

The substitution of Na₂F₂ for Ca₂O₂ cannot be followed by X-ray analysis because of the similarity of the ionic radii of Ca and Na and of O and F. However the indices of refraction change with Na₂F₂ substituting for Ca₂O₂

There seems to be a 50/50 substitution limit for Na₂F₂ in Be-gehlenite as well. (As for Be-gehlenite, see following chapter).

Table 8. Interplanar spacings in Å units of strontiogehlenite, data from Brisi and Abbatista (1960).

$a_0 = 7,82 \text{ \AA}$ $c_0 = 5,27 \text{ \AA}$		
hkl	d	Int.
110	5,52	10
001	5,26	14
200	3,91	8
111	3,82	18
210	3,49	8
201	3,14	28
211	2,91	100
220	2,76	7
002	2,63	20
310	2,47	25
211	2,45	7
112	2,38	6
301	2,33	5
311	2,24	6
202	2,18	5
212	2,10	26
400	1,952	8

BRISI and ABBATISTA (1960) have reported the existence of strontiogehlenite. The unit-cell dimensions are: $a_0 = 7.82 \text{ \AA}$ and $c_0 = 5.27 \text{ \AA}$. This again shows the relation between the unit-cell dimensions and the chemistry of the melilites. In the A site Ca is replaced by the larger Sr, the a_0 value is changed relatively less than is the c_0 value.

Formula	Ionic radius of A	a_0	c_0
$\text{Ca}_2\text{O}_2\text{AlSiAlO}_5$	1,01 Å	7.69	5,07
$\text{Sr}_2\text{O}_2\text{AlSiAlO}_5$	1,16 Å	7.82	5.27

DEAR (1960) reported the existence of strontio-åkermanite in his study on the system SrO-MgO-SiO. The unit-cell dimensions of this melilite is according to Dear $a_0 = 8.025$ and $c_0 = 5.181$. These results are in good agreement with what should be expected from the data given by Brisi and Abbatista for strontiogehlenite. The calculated d-values by Dear (table 10) are inaccurate when based upon the unit-

Table 9. Interplanar spacings in Å units of strontio-åkermanite, data from Dear (1960).

$a_0 = 8,025 \text{ \AA}$ $c_0 = 5,181 \text{ \AA}$			
hkl	$d_{calc.}$	$d_{obs.}$	Int.
110	5,68	5,70	32
001	5,18	5,19	5
011	4,35	4,35	5
020	4,02	4,02	9
111	3,825	3,825	23
120	3,589	3,585	9
021	3,172	3,175	45
121	2,950	2,950	100
220	2,838	2,840	7
002	2,590	2,585	24
130	2,539	2,539	36
221	2,462	2,462	12
012			
031			
112	2,366	2,366	10
131			
230	2,225	2,238	5
022	2,175	2,170	7
122	2,100	2,095	43
231	2,050	2,060	7
040	2,000	2,007	10

cell dimensions given by him. The intensity relations and the good agreement with the indexing makes it evident, however, that Dear really has produced a melilite. In his studies Dear found no Sr-analog to diopside and he concluded that no such minerals exists. The present author, however, in an unsuccessful attempt to make Sr-åkermanite at 1300° C, 8 days, produced a compound that in all probability is a strontio-pyroxene. Its powder pattern is almost identical to that of a diopsidic pyroxene and the unit-cell constants are: $a_0 = 9.8 \text{ \AA}$, $b_0 = 9.0 \text{ \AA}$, $c_0 = 5.3 \text{ \AA}$ and $\beta \sim 73^\circ$. The corresponding values for diopside are: $a_0 = 9.750 \text{ \AA}$, $b_1 = 8.930 \text{ \AA}$, $c = 5.249 \text{ \AA}$ and $\beta = 74^\circ 10'$ given by KUNO and HESS (1953). There is probably a temperature-dependent relationship between strontio-diopside and strontio-åker-

manite similar to that of diopside and åkermanite treated in a later paper of this series.

The substitution possibilities in the $A_2M'_2$ group of melilites thus seem to be:

1) Ca in the A site may be completely replaced by Sr as has been shown by BRISI and ABBATISTA (1960) and by DEAR (1960). It is not clear if Ca may be replaced by Cd. From structure point of view this is probable but the few attempts made by the present author to produce a cadmium melilite failed.

An oxide/chloride batch to yield the composition $Cd_2O_2MgSi_2O_5$ heated at $1300^\circ C$ for 8 days yielded two phases, one which may possibly be $CdSiO_3$ and one which is probably a cadmium pyroxene giving an X-ray pattern very similar to that of a monoclinic pyroxene with the unit-cell constants $a_0 = 9.7 \text{ \AA}$, $b_0 = 9.0 \text{ \AA}$, $c_0 = 5.4 \text{ \AA}$ and $\beta \sim 73.50$. There is probably a similar relationship between the stability range of Cd-diopside and Cd-åkermanite as it is between diopside and åkermanite.

2) Ca may be replaced by Na, to a certain extent also by K. This substitution is very limited if Na and K are supplied from the $Na_2Si_3O_7$ and $K_2Si_3O_7$ molecules and depends on both the gehlenite content of the melilite and on the temperature.

If the substitution of Ca by Na or K is accompanied by a substitution of F, probably also OH, for O in equimolecular proportions, Ca seems to be substituted in amounts up to 50% by Na and up to 6% by K.

The A site is chiefly occupied by Ca in natural melilites (ionic radius 1.01 \AA). Na may also occupy this site (ionic radius 1.01 \AA) and Sr is fully accepted (ionic radius 1.16 \AA), but the substitution of K (ionic radius 1.40 \AA) is very limited. It is probable, but yet not proved, that Cd (ionic radius 1.01 \AA) may occupy the A sites, Ba (ionic radius 1.40 \AA) is expected to do so in limited amounts, probably not higher than does K. Three-valent Gd, being of the same size as Ca, is not accepted in the A site (table 4).

b) Substitutions in the BC_2M_5 part of the general formula of melilites.

The B site of the melilite structure (tetrahedron I in the notation of SMITH (1953)) is of particular interest. In åkermanite it is occupied by Mg, in iron-åkermanite by Fe^{2+} and in hardystonite by Zn. It is

possible that a $\text{Cd}_2\text{O}_2\text{ZnSi}_2\text{O}_5$ melilite may exist, affording an example of a mineral in which Cd enters one position in the structure and Zn another, and where Cd and Zn do not substitute for each other.

It was pointed out that the smallest metal ions of the melilite sheets occupy the C sites (tetrahedra II and III) and the larger metal ions occupy the B sites (tetrahedron I). Therefore the atomic arrangement of åkermanite corresponds to the formula $\text{Ca}_2\text{O}_2\text{MgSiSiO}_5$ rather than to $\text{Ca}_2\text{O}_2\text{SiMgSiO}_5$, and accordingly gehlenite should be written $\text{Ca}_2\text{O}_2\text{AlSiAlO}_5$ rather than $\text{Ca}_2\text{O}_2\text{SiAlAlO}_5$.

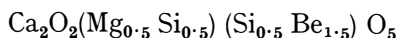
New experiments show that Mg may be completely replaced by Be. When Be partially substitutes for Mg in åkermanite, there are three elements to occupy the B and the C sites: Be, Mg and Si. The larger ones occupy the B and the smaller ones the C sites. Mg is the largest ion (radius 0.64 Å), Be the smallest one (radius 0.33 Å) and Si is intermediate (radius 0.4 Å). As a consequence the Be ions preferably occupy the B site, and the substitution of Be for Mg is accompanied by the following replacements in the structure:

- 1) Si in the C sites are replaced by Be.
- 2) The Si ions leaving the C site enter those of the B sites being vacant because of the Be — Mg substitution.

Thus the complete substitution of Be for Mg leads to a phase that chemically, and written in the old general melilite formula, is analog to åkermanite, but which in reality is similar to gehlenite:

	Old notation	Notation of this paper
Åkermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$	$\text{Ca}_2\text{O}_2\text{MgSi}_2\text{O}_5$
Be-melilite	$\text{Ca}_2\text{BeSi}_2\text{O}_7$	$\text{Ca}_2\text{O}_2\text{SiBeSiO}_5$
Gehlenite	$\text{Ca}_2\text{AlSiAlO}_7$	$\text{Ca}_2\text{O}_2\text{AlSiAlO}_5$

From a structure point of view the åkermanite—Be-melilite mixed crystal series is interesting. Here the B sites are occupied partly by the bi-valent Mg (radius 0.64 Å), partly by the tetra-valent Si (radius 0.4 Å) whereas the C sites are occupied partly by the tetra-valent Si and the bi-valent Be (radius 0.33 Å). Thus the formula of the 50/50 mixed crystal is



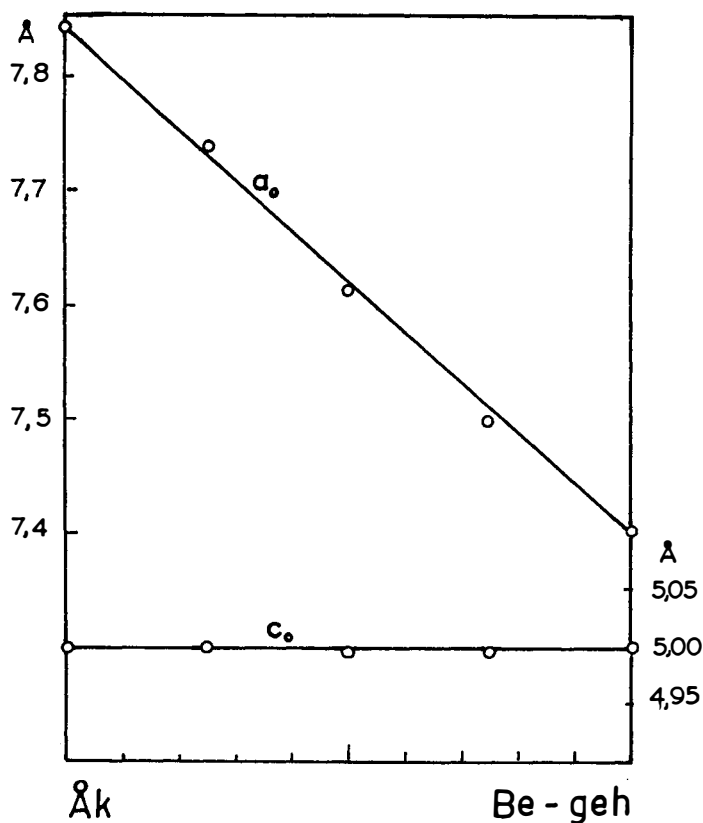


Fig. 6. Values of a_0 and c_0 in the mixed crystal series åkermanite–Be-gehlenite. Data from table 14.

These extraordinary conditions do not affect the change of the unit-cell dimensions to an extent that can be traced by X-ray high precision powder analysis. From figure 6 it is seen that the value of a_0 decreases upon increasing Be content indicating a contraction of the sheet. The A site is occupied by Ca in all mixed crystals of this series and consequently the c_0 values is less affected.

Be-gehlenite, $\text{Ca}_2\text{O}_2\text{SiBeSiO}_5$, is an end member of natural melilites. ZACHARIASEN (1930 and 1931) showed that leucophane and melinophane are melilites. Both melinophane and leucophane contain sodium and fluorine as a result of the substitution of NaF for CaO. Be is found as a result of a mixed crystal formation with Be-gehlenite.

Table 10. Interplanar spacings in Å units of the mixed crystal 75 åkermanite — 25 Be-gehlenite.

$a_0 = 7,738 \pm 0,004 \text{ \AA}$ $c_0 = 5,001 \pm 0,003 \text{ \AA}$			
hkl	$d_{calc.}$	$d_{obs.}$	Int.
110	5,472	5,469	m
001	5,001	4,998	w
011	4,200	4,200	vw
020	3,869	3,872	w
111	3,693	3,692	m
120	3,461	3,459	s
021	3,060	3,058	s
121	2,846	2,845	vs
220	2,736	2,735	w
030	2,579	2,581	m
002	2,501	2,501	w
130	2,447	2,448	vw
221	2,400	2,401	vw
012	2,380	2,379	m
031	2,293	2,293	m
112	2,274	2,274	w
131	2,198	2,198	w
122	2,027	2,027	s
040	1,935	1,934	s
231	1,911	1,911	vw

Table 11. Interplanar spacings in Å units of the mixed crystal 50 åkermanite — 50 Be-gehlenite.

$a_0 = 7,613 \pm 0,004 \text{ \AA}$ $c_0 = 4,995 \pm 0,003 \text{ \AA}$			
hkl	$d_{calc.}$	$d_{obs.}$	Int.
110	5,383	5,385	m
001	4,995	4,995	w
011	4,167	4,164	vw
020	3,807	3,809	w
111	3,662	3,661	m
120	3,405	3,406	s
021	3,021	3,022	s
121	2,813	2,815	vs
220	2,692	2,692	vw
030	2,537	2,538	m
002	2,498	2,499	vw
130	2,408	2,408	vw
012	2,373	2,373	m
221	2,370	2,371	vw
112	2,266	2,266	w
031	2,262	2,262	m
131	2,169	2,169	w
122	2,014	2,014	s
231	1,884	1,884	vw
040	1,870	1,870	s

In the leucophane studied by Zachariasen a negligible amount of Mg is present (0.27% MgO in the chemical analysis) and the C site is occupied by Be almost quantitatively (10.03% BeO in the analysis) Hence this leucophane is a Be-gehlenite. There are roughly equal amounts of Ca and Na indicating a near to 50/50 substitution, and 16% of the tetrahedra corners are occupied by F and OH. This value seems to be somewhat low to account fully for the CaO — NaF/NaOH substitution type, but minor errors in the chemical analysis may be the reason for this. It should be mentioned that the refractive indices of leucophane are different from those of Be-gehlenite, this again indicating that they are not structurally identical.

According to Zachariasen some Al is present in melinophane,

Table 12. Interplanar spacings in Å units of the mixed crystal 25 åkermanite — 75 Be-gehlenite.

$a_0 = 7,497 \pm 0,004 \text{ \AA}$ $c_0 = 4,995 \pm 0,003 \text{ \AA}$			
hkl	$d_{calc.}$	$d_{obs.}$	Int.
110	5,272	5,272	m
001	4,995	4,997	vw
011	4,150	4,148	vw
020	3,728	3,731	w
111	3,627	3,626	m
120	3,334	3,335	s
021	2,998	2,997	s
121	2,774	2,776	vs
220	2,636	2,636	vw
002	2,498	2,498	vvw
030	2,485	2,486	m
012	2,368	2,367	w
130	2,358	2,358	vw
221	2,331	2,332	vw
112	2,257	2,257	vw
031	2,225	2,225	w
131	2,132	2,133	vw
122	2,001	2,001	s
040	1,864	1,864	m
231	1,851	1,851	vw

Table 13. Interplanar spacings in Å units of Begehlenite, $Ca_2O_2SiBeSiO_5$.

$a_0 = 7,402 \pm 0,004 \text{ \AA}$ $c_0 = 4,998 \pm 0,003 \text{ \AA}$			
hkl	$d_{calc.}$	$d_{obs.}$	Int.
110	5,234	5,232	m
001	4,993	4,991	vw
011	4,139	4,142	vw
020	3,701	3,701	w
111	3,613	3,615	m
120	3,310	3,310	s
021	2,973	2,974	s
121	2,759	2,757	vs
220	2,617	2,616	vw
002	2,497	2,498	vvw
030	2,468	2,468	m
012	2,365	2,365	w
130	2,341	2,340	vw
221	2,318	2,319	vw
112	2,253	2,253	vw
031	2,212	2,212	w
131	2,120	2,120	vw
122	1,994	1,994	s
231	1,631	1,631	vw
040	1,851	1,851	m

indicating that this mineral is a member of the mixed crystal series gehlenite — Be-gehlenite. Here the Na/Ca ratio is roughly 40/60 and the F content is correspondingly lower.

More accurate analyses are necessary to permit a closer treatment of the crystal chemistry of natural Be-containing melilites. It seems, however, that Zachariassen's leucophane is very similar to pure Be-gehlenite. Thus, the unit-cell dimensions of that leucophane are: $a_0 = 7.38 \text{ \AA}$ and $c_0 = 4.98 \text{ \AA}$, and those of Be-gehlenite are $a_0 = 7.402 \text{ \AA}$ and $c_0 = 4.998 \text{ \AA}$.

Figure 7 shows the composition of melinophane and leucophane in their relation to the end-members gehlenite, åkermanite and Be-gehlenite.

Table 14. Variation of the unit cell dimensions in Å units of the series åkermanite — Be-gehlenite.

% Åk	100	75	50	25	0
% Be-geh.	0	25	50	75	100
a_0	7,844	7,738	7,613	7,497	7,402
c_0	5,000	5,001	4,995	4,995	4,998

The valency of the ions in the B sites and in the C sites may vary from + 1 to + 4 in the melilite structure. If the BC_2M_5 part of the formula is to be kept uncharged, the valency of the ion in the B site determines the valency of the ions of the C sites. If the valency of the ion in the B site is changed in one direction, the valency of the ions in the C sites must change in the opposite direction. The following list of artificial melilites may elucidate this.

Name	$A_2M'_2B C_2 M_5$	valency of B site ion	valency of C site ions
No name	$Na_2F_2LiBeBeF_5$	+ 1	+ 4
Åkermanite	$Ca_2O_2MgSiSiO_5$	+ 2	+ 8
Gehlenite	$Ca_2O_2AlSiAlO_5$	+ 3	+ 7
Be-gehlenite	$Ca_2O_2SiBeSiO_5$	+ 4	+ 6

The C sites may be occupied:

- by ions of the same valency, $Na_2F_2LiBe_2F_5$, and åkermanite, $Ca_2O_2MgSi_2O_5$.
- by bi- and tetra-valent ions, Be-gehlenite, $Ca_2O_2SiBeSiO_5$.
- by tri- and tetra-valent ions, gehlenite, $Ca_2O_2AlSiAlO_5$.

The present author has not been able to make melilites where all the C sites are filled by Al, but such melilites might be produced artificially. They are not known to occur in nature.

The smallest ion to occupy the B sites seems to be Si (radius 0.4 Å) in Be-gehlenite. Mg (radius 0.64 Å) and Li (radius 0.66 Å) form intermediate values and Fe^{2+} (radius 0.72 Å) and Zn (radius 0.71 Å) are apparently the largest ions accepted in the B site. The present author tried to make the $Ca_2O_2TiAlAlO_5$ melilite, but no other phases than perovskite, $CaTiO_3$, and corundum, Al_2O_3 , could be detected in the

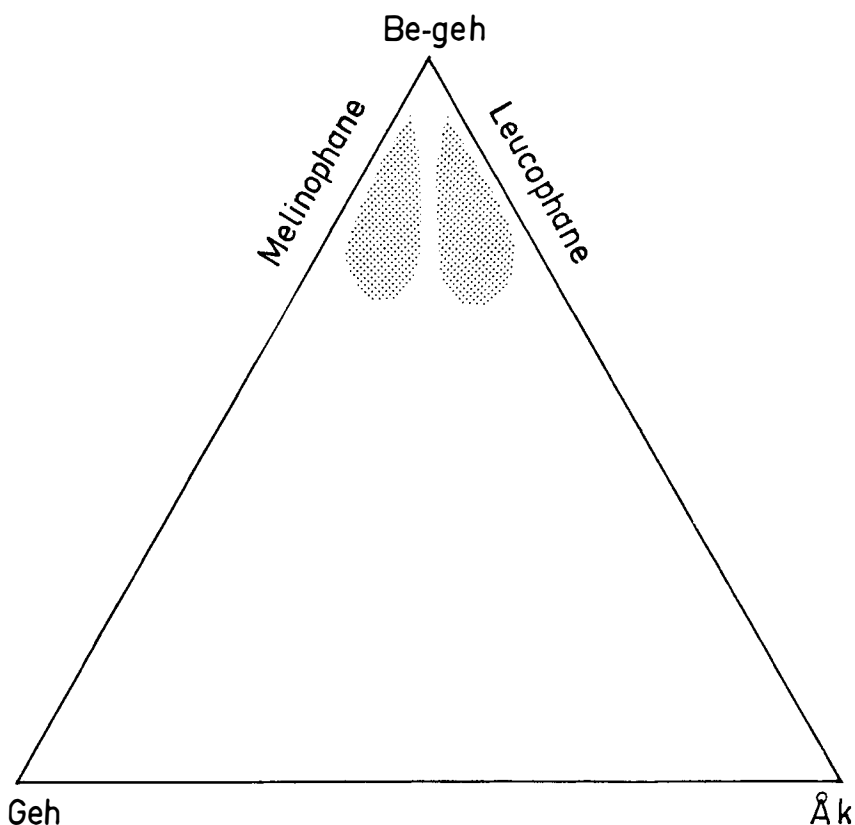


Fig. 7. Location of the minerals melinophane and leucophane in the system gehlenite—åkermanite—Be-gehlenite with substitution of Na_2F_2 for Ca_2O_2 .

heated product. The reasons for this may be the reluctance of the structure to accept Al to occupy all the C sites, or simply that the temperature conditions for the formation of such a melilite was not fulfilled. Nevertheless, some Ti may be found in melilites.

The smallest ion recorded in the C site of melilites is Be (radius 0.33 Å). Si forms an intermediate size (radius 0.4 Å) and Al (radius 0.49 Å) seems to be the largest ion accepted in the C site. Attempts to produce a Ga—Ge gehlenite, $\text{Ca}_2\text{O}_2\text{GaGeGaO}_5$, were unsuccessful and the heated products contained mainly a body-centered cubic phase with $a_0 = 12.254 \pm 0.009$ Å. This phase is probably a Ga—Ge garnet, $\text{Ca}_3\text{Ga}_2(\text{GeO}_4)_3$.

The M and M' sites may be occupied by O and F, probably also OH, although this has not been proved by experiments. The F and OH groups are probably situated at the corner of the tetrahedra that are not shared with other tetrahedra.

LITERATURE

- ANDREWS, K. W., (1948): The lattice parameters and interplanar spacings of some artificially prepared melilites. *Min. Mag.* 28, pp. 374–379.
- BARTH, T. F. W. and POSNJAK, E. (1931): The spinel structure: An example of variate atom equipoints. *Jour. Washington Acad. Sci.* vol. 21, pp. 225–258.
- BERMAN, H., (1929): Composition of the melilite group. *Am. Mineralogist.* 14, pp. 389–407.
- BOWEN, N. L., SCHAIRER, J. F., and POSNJAK, E., (1933): The system CaO-FeO-SiO₂. *Am. Jour. Sci.* 26, pp. 193–284.
- BRISI, C., and ABBATISTA, F., (1960): Ricerche sulle melilite. — Nota I. Struttura e proprietà della stroncio-gehlenite. *Ann. Chim.* 50, pp. 1061–1065. (Roma).
- BUDDINGTON, A. F., (1922): On some natural and synthetic melilites. *Am. Jour. Sci.* 3, pp. 35–87.
- CHRISTIE, O. H. J., (1961): On sub solidus relations of silicates II: Preliminary note on the chemistry of melilites. *Norsk Geol. Tidsskr.* 41, pp. 322–324.
- DEAR, P. S., (1960): Solid state equilibria for the ternary system strontia-magnesia-silica. *Bull. Virginia Polytechn. Inst.* 54 no. 1, 1960.
- ERVIN, G., and OSBORN, E. F., (1949): X-ray data on synthetic melilites. *Am. Mineral.* 34, pp. 717–722.
- FERGUSON, J. B., and BUDDINGTON, A. F., (1920): The binary system åkermanite-gehlenite. *Am. Jour. Sci.* 4th. Ser. 50, pp. 131–140.
- GOLDSMITH, J. R., (1948): Some melilite solid solutions. *Jour. Geol.* 56, pp. 437–477.
- KUNO, H. and HESS, H. H. (1953): Unit cell dimensions of clinoenstatite and pigeonite in relation to other common clinopyroxenes. *Am. Jour. Sci.* 251, pp. 741–752.
- MACHATSCHKI, F. (1930): Die Summenformel der Melilithe. *Centr. bl. f. Min. Geol. u. Pal. Abt. A.* (1930), pp. 284–292.
- MEGAW, HELEN D. (1952): The structure of Afwillite, Ca₃(SiO₃OH)₂ · 2H₂O. *Acta Cryst.* 5, pp. 477–491.
- NEUMANN, H. and BARSTAD, J. (1953): A selfcentering x-ray camera for powder diagrams. *Norsk Geol. Tidsskr.* 32, pp. 57–59.
- NEUVONEN, K. J. (1952): Thermochemical investigation of the åkermanite-gehlenite series. *Bull. Comm. Geol. Finlande.* 158.
- (1955): On the composition of natural melilites, *Compt. Rend. Soc. geol. Finlande*, 28.

- NURSE, R. W. and MIDGLEY, H. G., (1953): Studies on the melilite solid solutions. *Jour. Iron and Steel Inst.* 174, pp. 121—131.
- O'DANIEL, H. and TSCHESCHWILI, L. (1945—1948): Zur Struktur von Gehlenit $\text{Ca}_2(\text{AlSiAlO}_7)$ — Åkermanit $\text{Ca}_2(\text{MgSi}_2\text{O}_7)$ und ihrer Modellsubstanz $\text{Na}_2(\text{LiBe}_2\text{F}_7)$. *N. Jahrb. Min. Geol. und Pal. Abt. A.* (1945—1948), pp. 65—70.
- RAAZ, F., (1930): Über den Feinbau des Gehlenit. Ein Beitrag zur Kenntnis der Melilithe. *Sitzungsber. Akad. d. Wissenschaften Wien. Abt. I* 139, pp. 645—671.
- SCHALLER, W. T. (1916): Mineralogic Notes. *Nova Scotia Geol. Survey Bull.* 670, 3d Ser. pp. 109—128.
- SHEPHERD, E. S. and RANKIN, G. A. (1911): Preliminary report on the ternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$; a study of the constitution of portland cement clinker, with optical study by E. F. Wright. *Jour. Ind. Engn. Chem.* 3, p. 224.
- SMITH, J. V. (1953): Reexamination of the crystal structure of melilite. *Am. Mineral.* 38, pp. 643—661.
- STRUNZ, H. (1957): *Mineralogische Tabellen*. Ed. Akad. Verlagsges. Geest & Portig K.-G. Leipzig. 1957.
- WARREN, B. E. (1930): The structure of melilite, $(\text{Ca}, \text{Na})_2(\text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_7$. *Zeitschr. Krist.* 74, pp. 131—138.
- WARREN, B. E. and TRAUTZ, O. R. (1930): The structure of Hardystonite $\text{Ca}_2\text{ZnSi}_2\text{O}_7$. *Zeitschr. Krist.* 75, pp. 525—528.
- WINCHELL, A. N. (1924): The composition of Melilite. *Am. Jour. Sci.* 5th Ser. 8, pp. 375—384.
- ZACHARIASEN, W. H. (1930): On meliphanite and leucophanite. *Zeitschr. Krist.* 74, pp. 226—229.
- (1932): Meliphanite, Leucophanite and their relation to Melilite. *Norsk Geol. Tidsskr.* 12, pp. 577—581.
- Geochemical Tables of the Elements for 1958. *Bull. Geol. Soc.* vol. 69.

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