

## ON SUB-SOLIDUS RELATIONS OF SILICATES

### I. The Lower Breakdown Temperature of the Åkermanite Gehlenite Mixed Crystal Series at Moderate Water Pressure

By

OLAV H. J. CHRISTIE

(Mineralogisk-Geologisk Museum, Oslo NÖ)

**A b s t r a c t.** Some sub solidus relations in systems of åkermanite gehlenite compositions in the range 200° C — 700° C have been studied. Åkermanite was reported to decompose to wollastonite and monticellite at approximately 700° C (HARKER and TUTTLE, 1956). At 6 kbar water pressure and 500° C, wollastonite and clinopyroxene form from åkermanite. At the same pressure and ca. 450° C. clinopyroxene and xonotlite seem to be the stable mineral association. The decomposition temperature of the åkermanite-gehlenite mixed crystal series at 4.8 bar to 6.7 kbar depends upon the composition of the mixed crystal and is situated between 500° C and 650° C. The decomposition products are vesuvianite and hydrogarnet, hydrogarnet, or hydrogarnet and xonotlite in addition to clinopyroxene and wollastonite formed from the åkermanite-rich batches. The hydrogarnets formed during the experiments are mixed crystals in the series hydrogrossular - hydropyrope.

#### Previous work

Åkermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) and gehlenite ( $\text{Ca}_2\text{AlSiAlO}_7$ ) are the two most important end members of the melilite group.

*Åkermanite* was described by J. H. L. VOGT (1884), who found it as an artificial mineral in slags. ZAMBONINI (1910) described natural åkermanite from Vesuvius, and FERGUSON and BUDDINGTON (1919) determined the chemical composition of it.

*Gehlenite* was described by FUCHS (1815). It was subject to closer study by RANKIN and WRIGHT (1915). The composition of natural melilites was studied by WINCHELL (1924), by BERMAN (1929), and by GOLDSMITH (1947 and 1948).

The minerals of the system åkermanite-gehlenite, in this paper referred to as melilite, form a series of mixed crystals with a minimum melting point at 74 per cent åkermanite (FERGUSON and BUDDINGTON, 1919; OSBORN and SCHAIRER, 1941). This explains the frequent occurrence of zoning in both natural and synthetic melilites.<sup>1</sup>

The breakdown of åkermanite at atmospheric pressure in certain temperature ranges has been reported by several authors. CARSTENS and KRISTOFFERSEN (1931) obtained a mixture of åkermanite, diopside, and glass, from åkermanite glass. Similar results are mentioned by BOWEN, SCHAIRER and POSNJAK (1933) and by OSBORN and SCHAIRER (1941). Osborn and Schairer found the lower stability of åkermanite to be 1325° C at atmospheric pressure. Below this temperature diopside formed as a decomposition product.

HARKER and TUTTLE (1956) investigated the lower limit of stability of åkermanite at high pressure. They found the breakdown products to be wollastonite ( $\text{CaSiO}_3$ ) and monticellite ( $\text{CaMgSiO}_4$ ) in the range 30–60 kpsi water pressure. These results were extrapolated to zero pressure under the assumption that no other products than wollastonite and monticellite formed from åkermanite.

The lower stability limit of gehlenite under atmospheric pressure was studied by TAVASCI (1939) and by MALQUORI and CIRILLI (1943) with special application to reactions in hydraulic cements. No attempt was made to transfer the results to geological conditions.

### **Technique and results of the present experiments**

The present study is an investigation of the lower stability temperatures of melilite at moderate water pressure. The starting materials for the experiments were prepared by heating the oxides at 1300° C with repeated intermediate grindings until a homogeneous material was obtained. Cold seal bombs, or Morey bombs, were used for the heating experiments. The water pressure was supplied by a manual high pressure pump of conventional design. The pressure readings

<sup>1</sup> See following note on the chemistry of melilites.

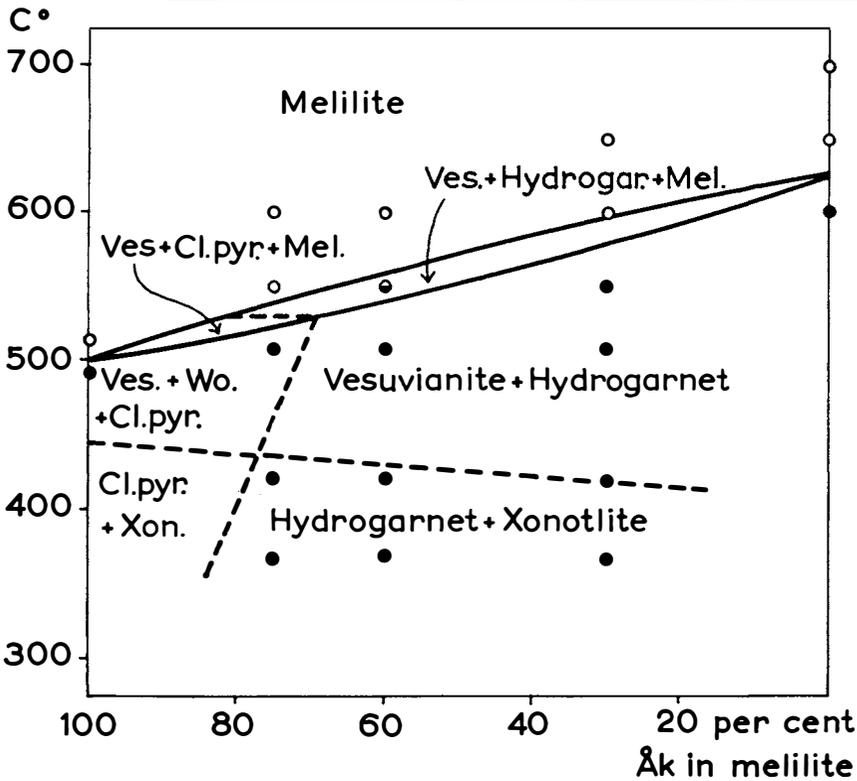


Fig. 1. The low temperature breakdown relations of sodium free åkermanite-gehlenite mixed crystals at 4.8 kbar to 6.7 kbar water pressure. Data from Table 1.

have an accuracy of plus minus ten per cent. The temperature of the furnaces was controlled within plus minus five degrees centigrade by controllers of the falling bridge type. The products were examined by microscope and by nine-centimeter X-ray powder cameras.

There is always a possibility that metastable phases may develop in mineral synthetic experiments. To determine a stability limit both decomposed products and undecomposed ones are heated at identical conditions and if they yield the same end products, this is taken as a proof that true equilibrium is obtained. In the present writer's opinion, however, true equilibrium cannot be stated by thermal experiments, true equilibrium can only be determined by energy calculations.

Table 1.

Products formed by decomposition from åkermanite gehlenite mixed crystals during heating experiments.

Per cent åkermanite in melilite	Water pressure kbars.	Temperature °C	Time	Products
100	4.5	500	9 days	Mel + cl.pyr + wo
100	4.8	550	9 days	Mel
75	6.0	650	11 days	Mel
75	5.5	600	8 days	Mel
75	5.1	550	12 days	Mel
75	6.7	509	10 weeks	Ves + cl.pyr
75	6.5	447	8 weeks	Gar + xon
75	6.5	369	14 weeks	Gar + xon
60	5.5	600	8 days	Mel
60	5.1	550	9 days	Mel + ves + tr. gar
60	6.7	509	10 weeks	Ves + gar
60	6.5	447	8 weeks	Gar + xon
60	6.5	369	14 weeks	Gar + xon
30	6.0	650	10 days	Mel
30	5.5	600	8 days	Mel
30	5.1	550	10 weeks	Mel
30	6.7	509	10 weeks	Gar + ves
30	6.5	447	8 weeks	Gar + xon
30	6.5	369	14 weeks	Gar + xon + tr. bruc
0	6.3	700	6 days	Mel
0	6.0	650	9 days	Mel
0	5.5	600	9 days	Mel + tr. unident. prod.

Thermal experiments can under favourable conditions give us an idea of which phase is the stable one at given conditions. Nevertheless metastable assemblages exist for geological time, they exist in nature more as a rule than as an exception.

In this study all the runs between 600° C and 500° C were made with synthetic melilites as well as with unreacted batches. They yielded identical end products.

The chief decomposition products formed from melilite during the experiments were hydrogarnet, vesuvianite, and xonotlite.

*Hydrogarnet*  $(Ca_3Al_2(SiO_4)_3(OH)_3)$  was first described by PABST

(1937), later by BELYANKIN and PETROV (1941) and by HUTTON (1943). YODER (1950) studied the formation of synthetic hydrogrossular in his work on the system grossularite — calcium aluminium hexahydrate and found that there is experimental evidence for a complete replacement of  $\text{SiO}_4$  groups by  $(\text{OH})_4$  groups in grossularite. However, not more than a third of the  $\text{SiO}_4$  groups has been replaced by  $(\text{OH})_4$  groups in the natural hydrogarnets described by Pabst, by Belyankin and Petrov, and by Hutton.

The natural hydrogarnets described are all hydrogrossular; no hydropyrope has been reported either from natural occurrences or from synthetic products. The present experiments show the existence of a solid solution series in the system hydrogrossular — hydropyrope.

The variation of the unit cell in the hypothetical hydrogrossular — hydropyrope series is presented in the tentative diagram of Fig. 2. Provided the plane of unit cell dimensions of Fig. 2 is not curved the length of the unit cell edge of magnesium aluminium hexahydrate (hydropyrope with complete  $(\text{OH})_4$  substitution) is 12.1 Å.

PISTORIUS and KENNEDY (1960) showed that if sufficient water is present to form hydrogarnet an additional increase of the water pressure will not increase the  $(\text{OH})_4$  substitution to any appreciable amount; a variation of the temperature, however, will give rise to a distinct change in the  $(\text{OH})_4$  substitution.

If pyrope behaves like grossularite any mixed crystal in the hydrogrossular — hydropyrope series will have the same  $(\text{OH})_4$  substitution provided the temperature of formation is constant. In that case the  $a_0$  of the unit cell for mixed crystals in the series hydrogrossular — hydropyrope formed at constant temperature will be situated along a line parallel to the constant  $(\text{OH})_4$  lines of the plane of Fig. 2.

Fig. 3 displays the variation in the edge of the unit cell,  $a_0$ , of hydrogarnets formed by decomposition of melilite. The unit cell edge of pure hydrogrossular is derived from the data of PISTORIUS and KENNEDY (1960).

The lines connecting unit cell edges of hydrogarnets formed at constant temperature have the same slope as the lines of constant  $(\text{OH})_4$  substitution of Fig. 2. The slope is derived directly from Fig. 2 and the lines are not drawn to make the best possible conformity with the observed values. It is evident from Fig. 3 that there is a good

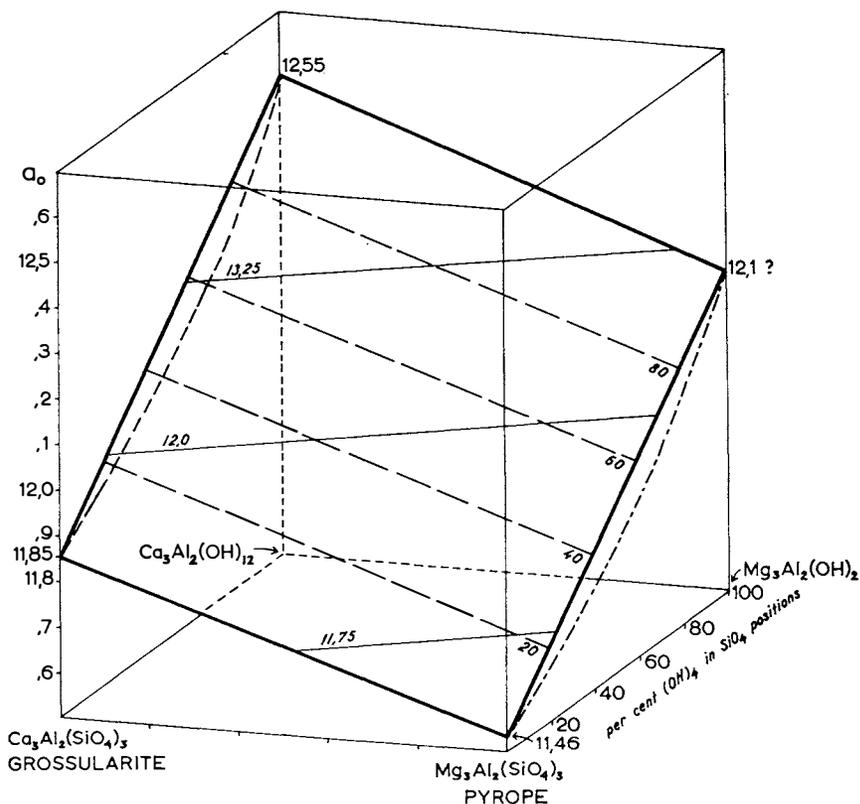


Fig. 2. Length of unit cell edge,  $a_0$ , of grossularite-pyrope hydrogarnets. The uncurved plane corresponds to Vegard's law. Dashed line in the grossularite-hydrogrossular plane is taken from Yoder (1950). Dash-and-dot line in the pyrope-hydropyrope plane are estimated values for the hypothetical hydro-pyrope series. At 10 kbars water pressure hydrogrossular takes no more than 6 per cent hydropyrope in solid solution (Yoder, personal communication 1960). At lower pressure, however, the mutual solubility of the hydrogarnets increases but no quantitative data are available at present. This diagram indicates only the  $a_0$  of possible hydrogrossular-hydropyrope mixed crystals and should not be taken as a suggestion that complete solid solution exists in this system.

agreement between the values predicted from Fig. 2 and the observed values presented in Fig. 3.

The hydrogarnets formed at 369° C have a smaller unit cell than those formed at 447° C. This is probably due to a smaller content of calcium and may be explained by the formation of xonotlite in the low

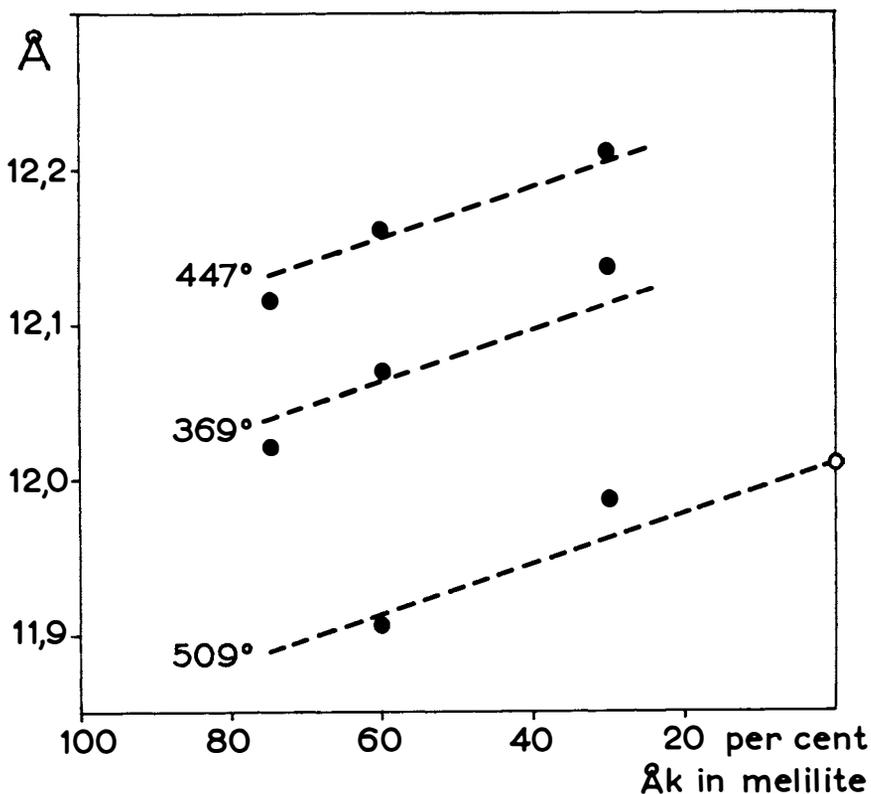


Fig. 3. Unit cell edge,  $a_0$ , for hydrogarnets formed by decomposition of melilite. Dashed lines indicate slope of lines of constant  $(OH)_4$  substitution of fig. 2. O is taken from Pistorius and Kennedy (1960).

Table 2.  
Unit cell size of hydrogarnets formed by decomposition of melilite.

Per cent Åk in melilite	Temperature °C	Unit cell size
75	369	12.02
75	447	12.12
60	369	12.07
60	447	12.16
60	509	11.91
30	369	12.14
30	447	12.21
30	509	11.98

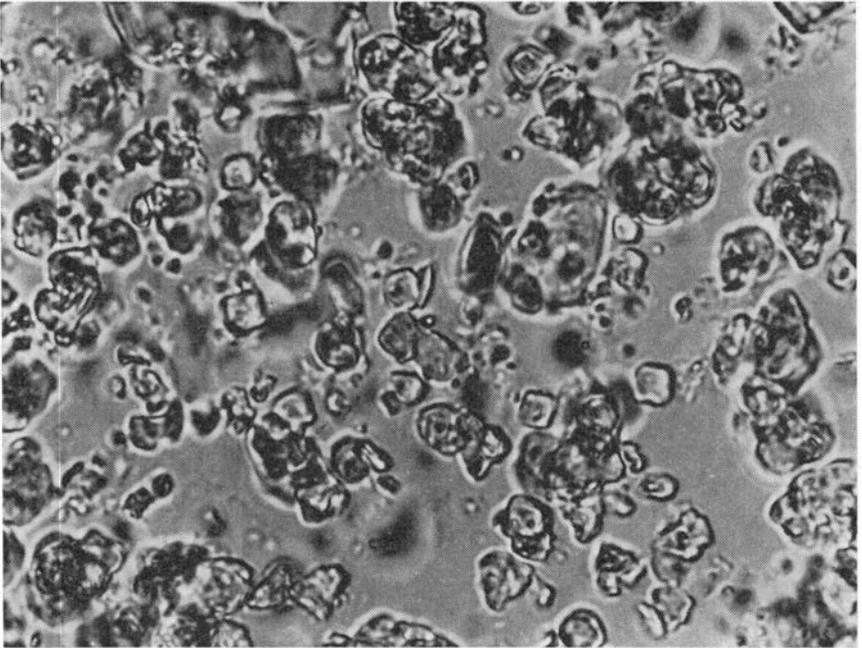


Fig. 4. Hydrogarnets from the system grossularite-pyrope-water formed by decomposition of 30 Åk 60 Geh melilite at 447° C and 6.5 kbar water pressure for 8 weeks. The photo displays 0.1 mm across.

temperature range. The xonotlite requires much calcium, thus making less calcium available for the hydrogarnets.

In one of the runs of 30Åk70Geh at 369° C small amounts of brucite were formed. This might indicate that the hydrogarnet formed at a higher temperature from the same melilite composition is not stable at 369° C.

*Vesuvianite* ( $\text{Ca}_{10}\text{Al}_4\text{Mg}_2\text{Si}_9\text{O}_{34}(\text{OH})_2$ ) is well known from contact metamorphic and regional-metamorphic rocks. It has also been found in volcanic ejectamenta.

MACHATSCHKI (1930) investigated the chemical composition of vesuvianites and WARREN and MODELL (1931) determined the structure of it. Both Machatschki and Warren and Modell emphasize the structural, chemical, and physical similarity between garnet and vesuvianite.

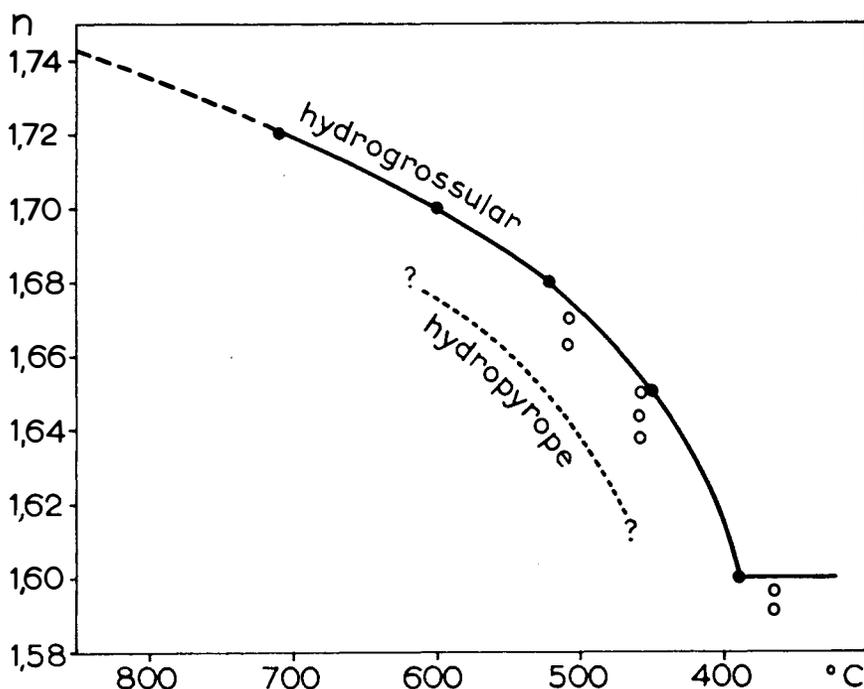


Fig. 5. Refractive index of hydrogarnets formed by decomposition of melilite. Data from table 2 and Yoder (1950).

Vesuvianite is a decomposition product of melilite at 509° C and 550° C. At 447° C and 369° C hydrogarnet and xonotlite, or hydrogarnet alone, formed instead of vesuvianite. The lower critical temperature for the formation of vesuvianite is situated somewhere between 447° C and 509° C. This is confirmed by field experience: vesuvianite occurs mainly in the high temperature contact zones of contact metamorphic rocks.

The refractive index of vesuvianite formed in the present experiments (1.645 — 1.650) is lower than of most natural vesuvianites (1.70 — 1.71). There is also a marked difference in the intensity relation between the line 440, 432, 204, and the line 224, 600, 522 of the X-ray powder pattern of natural and of synthetic vesuvianite. With the present material it has not been possible, however, to show whether or not this phenomenon could be explained from the assumption that vesuvianite, like garnet, is able to form hydro-varieties in which certain  $\text{SiO}_4$  groups are replaced by  $(\text{OH})_4$  groups.

Table 3.  
Refractive index of hydrogarnets formed by decomposition of melilites

Temperature °C	75Åk25Geh	60Åk40Geh	30Åk70Geh
509	—	1.663	1.671
447	1,638	1.642	1.650
369	—	1.595	1.601

*Xonotlite* ( $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ ) never occurred together with vesuvianite during the experiments. Runs at 447° C contained xonotlite, this is above the upper limit of crystallization (390° C) given by FLINT, MCMURDIE and WELLS (1938), but is in good agreement with data recently published by BRUCKNER, ROY and ROY (1960).

The upper stability temperature limit of xonotlite formed in the present experiments decreases with increasing aluminium content of the starting material. This was not expected as the calcium content in mole per cent is constant in all mixtures between åkermanite and gehlenite. However, with increasing aluminium content an increased amount of garnet is formed. Therefore more and more calcium is taken by garnet, and less calcium is left for the residual mixture.

*Clinopyroxene* ( $(\text{Ca}, \text{Mg})_2\text{Si}_2\text{O}_6$ ) was formed from pure åkermanite at 509° C. HARKER and TUTTLE (1956) reported that åkermanite decomposes at 700° C — 750° C and 2—4 kbar water pressure to wollastonite and monticellite. HARKER and TUTTLE (1956) used heating times up to ten days, whereas the present experiments have been extended several weeks at a higher pressure than those of Harker and Tuttle. This point will be discussed in one of the following papers. The åkermanite-rich batch, 75Åk25Geh, yielded clinopyroxene and wollastonite after ten weeks at 500° C and 6.7 kbar water pressure. This clinopyroxene had the composition 70Di30En (determined by extinction angles). Evidently monticellite (density 3.2) forms at lower pressure than does clinopyroxene (density 3.3). The transition pressure seems to be in the range 4.5 kbar to 5 kbar water pressure.

*Wollastonite* ( $\text{CaSiO}_3$ ) formed from åkermanite together with clinopyroxene. Below ca. 450° C wollastonite is not stable but converts into xonotlite (FLINT, MCMURDIE and WELLS, 1938). Below 450° C the stable association formed from åkermanite is xonotlite and clino-

pyroxene. If small amounts of gehlenite are present the clinopyroxenes will take aluminium into solid solution. When the clinopyroxene is saturated with aluminium, hydrogarnet will form.

### Melilites heated in glycerine

Organic material is supposed to be one of the sources for graphite occurring in schists. Organic material may in many cases accelerate mineral reactions, but it is not known if different compounds have specific catalytic effects upon special mineral reactions.

In the present study some runs were made with synthetic melilites heated in Morey bombs in a glycerine atmosphere. The breakdown products have been identified by X-ray analysis. Examination with the microscope was not successful because of amorphous carbon adhering to the mineral grains.

HARKER and TUTTLE (1956) reported breakdown of åkermanite to calcite and diopside in excess of  $\text{CO}_2$  in the range  $800^\circ\text{C} - 1000^\circ\text{C}$ , and 1.5 — 8 kbar  $\text{CO}_2$  pressure. (Estimated values from the diagram of figure 2 in HARKER and TUTTLE (1956)).

There is a breakdown of melilite heated in glycerine in closed Morey bombs at  $485^\circ\text{C} \pm 15^\circ\text{C}$ . The chief decomposition product of these runs was calcite. In one of the runs ( $300^\circ\text{C}$ ) garnet with lattice spacing of pyrope was formed, and in two of the runs boehmite was noticed. Clinopyroxene was not observed in any runs. However, the determination of the decomposition products is not complete, as only X-ray analysis was used for identification.

The decomposition temperature seems to be independent of the Mg-Al ratio of the melilites. As calcite is the only calcium-containing phase detected, except for pyrope, that may have some calcium in solid solution, it is apparently the activity relations of calcium in calcite and in melilite under the given conditions that determine the breakdown temperature of melilite.

Because of the complexity of the interpretation of the physico-chemical conditions of these runs, the experiments have not been carried further. However, they lend support to the idea that organic compounds may accelerate mineral reactions; they may, indeed, act as catalysts by the formation of some minerals typical of the early stages of regional metamorphism. The catalytic effect may be consider-

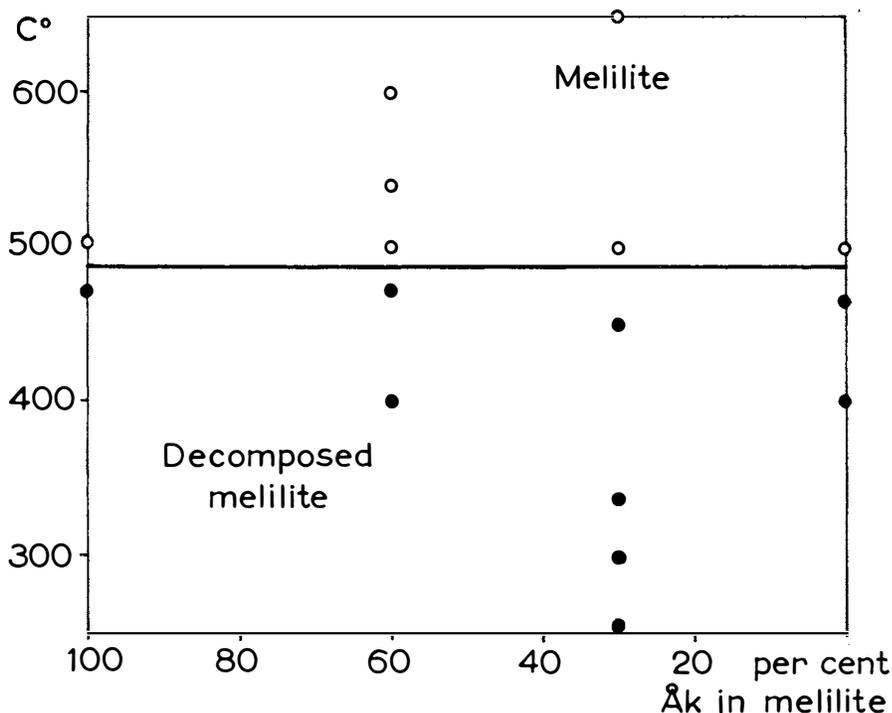


Fig. 6. Decomposition of melilite heated in glycerine in closed Morey bombs.

able, even at low temperatures. Over a period of four days calcite formed from melilite under glycerine pressure at 260° C. Pure gehlenite heated at 200° C for one week showed no presence of calcite, but even at this temperature calcite might form from gehlenite in geological times.

### Melilite rocks

BELYANKIN and PETROV (1941) mention several localities carrying melilite or the minerals formed by the decomposition of melilite: hydrogarnet, and vesuvianite or xonotlite. MASON (1957) described an occurrence of hydrogarnet and melilite in a contact metamorphic limestone. Apart from these descriptions very little is published on natural hydrogarnets formed from melilite-bearing contact rocks.

The melilite dike rocks are better studied. They may be divided into three groups:

Table 4.

Products formed by decomposition from åkermanite gehlenite mixed crystals heated at various temperatures in glycerine atmosphere.

Per cent åkermanite in melite	Temperature °C	Time	Products
100	500	4 days	Mel
100	470	12 days	Cal
60	700	1 day	Mel
60	600	1 day	Mel
60	540	12 days	Mel
60	500	1 day	Mel
60	470	12 days	Cal + Mel
60	400	1 day	Cal + Mal
60	400	12 days	Cal
30	500	4 days	Mel
30	470	12 days	Cal + tr. boehmite
30	400	4 days	Cal
30	340	4 days	Cal + Mel (non equil.)
30	300	4 days	Cal + Garnet
30	260	4 days	Mel + tr. Cal. (non equil.)
30	200	8 days	Mel (non equil.?)
0	500	1 day	Mel
0	370	12 days	Cal
0	400	4 days	Boehmite + tr. Cal.

1) *Modlibovites* and *Farrisites*, containing melilite, but no monticellite, no garnet and no calcite.

2) *Vesecites*, *monticellite-Alnöites* and *biotite-Alnöites*, all of them containing melilite and monticellite, but no garnet and no calcite.

3) *Alnöites*, containing melilite, garnet, and calcite among other minerals.

The *Modlibovites* and *Farrisites* are probably formed at a higher temperature than than are the other dike rocks mentioned, because none of the melilite decomposition products are present.

*Alnöites* represent probably low-temperature high-pressure conditions. In the original alnöite (TÖRNEBOHM, 1882) the CO<sub>2</sub> pressure was so high that calcite formed during the crystallization of the melt, as can be seen from thin sections. Here melilite is sometimes intergrown with calcite lamellae in a very fresh rock. The garnets of the

alnöites have not been closely studied, and it is not known if they are hydrogarnets.

Vesecites, monticellite-Alnöites and biotite-Alnöites probably represent low-pressure conditions. They contain the low-pressure breakdown product of melilite: monticellite.

None of the melilite dike rocks have been studied with respect to the breakdown products of the melilites. Therefore the physical conditions under which the different melilite rocks formed may only be vaguely suggested. Observations on natural melilite rocks may be explained by help of the results obtained by experiments, and a closer study in light of the present data would be of great interest to petrology.

### Acknowledgements

I wish to express my thanks to Norges Teknisk-Naturvitenskapelige Forskningsråd for sponsoring this study and to my father-in-law Mr. Kaare Berntsen, for financial aid during the studies.

### LITERATURE

- D. S. BELYANKIN and V. P. PETROV, (1941): The grossularoid group (hibschite and plazolite). *Am. Mineralogist* 26 (1941) 450.
- H. BERMAN (1929): Composition of the melilite group. *Am. Mineralogist* 14 (1929) 389.
- N. L. BOWEN, J. F. SCHAIRER and E. POSNJAK (1933): The system CaO-FeO-SiO<sub>2</sub>. *Am. Jour. Sci.* 5th ser. 26 (1933) 193.
- D. A. BRUCKNER, D. M. ROY and R. ROY (1960): Studies in the system CaSiO<sub>3</sub>-H<sub>2</sub>O. *Am. Jour. Sci.* 258 (1960) 132.
- C. W. CARSTENS and KR. KRISTOFFERSEN (1931): Schlackenstudien mit besonderer Berücksichtigung der Manganhaltigen Schlacken. *N. Jahrb. Min. Beilageband.* 62A (1931) 163.
- J. B. FERGUSON and A. F. BUDDINGTON (1919): The binary system åkermanite-gehlenite. *Am. Jour. Sci.* 50 (1919) 131.
- E. P. FLINT, H. F. MCMURDIE and L. S. WELLS (1938): Formation of hydrated calcium silicates of elevated temperatures and pressures. — *Jour. Res. Nat. Bur. Std.* 21 (1938) 617.
- J. N. FUCHS (1815): Ueber den Gehlenit, ein neues Mineral aus Tirol. *Journal für Chemie und Physik.* 15 (1815) 377.
- J. R. GOLDSMITH (1947): The system GaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>-NaAlSiO<sub>4</sub>. *Jour. Geol.* 55 (1947) 386.
- (1948) cited in A. N. Winchell: *Elements of optical mineralogy* II, 4th Ed. J. Wiley & Sons. p. 473.

- R. I. HARKER and O. F. TUTTLE; (1956): The lower limit of stability of åkermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ). *Am. Jour. Sci.* 254 (1956) 468.
- C. O. HUTTON (1943): Hydrogrossular, a new mineral of the garnet-hydrogarnet series. *Roy. Soc. New Zealand. Trans. Proc.* 73 (1943) 174.
- F. MACHATSCHKI (1930): Die Summenformel des Vesuvians und seine Beziehungen zum Granat. *Centr. bl. Min. A* (1930) 284.
- G. MALQUORI and V. CIRILLI; (1943): *Ric. Sci. Prog. Tecn. Ec. Nac.* 74 (1943) 85.
- E. F. OSBORN and J. F. SCHAIRER, (1941): The ternary system pseudowollastonite åkermanite gehlenite. *Am. Jour. Sci.* 239 (1941) 715.
- A. PABST (1937): The crystal structure of plazolite. *Am. Mineralogist* 22 (1937) 861.
- C. W. F. T. PISTORIUS and G. C. KENNEDY (1960): Stability relations of grossularite and hydrogrossularite at high temperature and pressure. *Am. Jour. Sci.* 258 (1960) 247.
- F. RAAZ (1930): Über den Feinbau des Gehlenit; ein Beitrag zur Kenntnis der Melilite. *Akad. Wiss. Wien. Math. nat.w. Kl. Sitzungsber. Abt. 1*, 739 (1930) 645.
- G. A. RANKIN and F. E. WRIGHT; (1915): The ternary system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ . *Am. Jour. Sci.* 4th ser. 39 (1915) 1.
- J. V. SMITH (1953): Reexamination of the structure of melilite. *Am. Mineralogist* 38 (1953) 643.
- H. STRUNZ: *Mineralogische Tabellen*, Ed. Verl. ges. Geest und Portig K. G. Leipzig 1957.
- B. TAVASCI; (1939): *Struttura del cemento portland idratato*. *La Chim. et l'Ind.* (Milano) 27 (1939) 660.
- A. E. TÖRNEBOHM (1882): *Mikroskopiska bergartsstudier XVII. Melilitbasalt från Alnö*. *Geol. För. Sthlm. Förh.* VI (1882) 241.
- J. H. L. VOGT (1884): *Studier over slagger I*. *Bih. K. Sv. Vet. Akad.* 9 (1) (1884).
- B. E. WARREN (1930): The structure of melilite  $(\text{Ca, Na})_2(\text{Mg, Al})(\text{Si, Al})_2\text{O}_7$ . *Zeitschr. Krist.* 74 (1930) 131.
- B. E. WARREN and D. I. MODELL (1931): The structure of vesuvianite  $\text{Ca}_{10}\text{Al}_4(\text{Mg, Fe})_2\text{Si}_9\text{O}_{34}(\text{OH})_4$ . *Zeitschr. Krist.* 78 (1931) 422.
- A. N. WINCHELL, (1924): The composition of melilite. *Am. Jour. Sci.* 5th Ser. 8 (1924) 375.
- H. S. YODER (1950): Stability relations of grossularite. *Jour. Geol.* 58 (1950) 221.
- F. ZAMBONINI (1910): *Mineralogia Vesuviana*, *Mem. R. Accad. d. Sc. fis. e. mat. Napoli* (2) 74 no 7, 1909.

Manuscript received June 22, 1960.

Printed December 1961.