

ON SUB SOLIDUS RELATIONS OF SILICATES

IV. The systems åkermanite — sodium-gehlenite and gehlenite — sodium-gehlenite.

By

OLAV H. J. CHRISTIE

(Mineralogisk-Geologisk Museum, Oslo)

A b s t r a c t. The melting phenomena of the mixed crystal series åkermanite — sodium-gehlenite and gehlenite — sodium-gehlenite are given. The lower breakdown relations of this system are principally the same as those of the system åkermanite—gehlenite but the presence of an exsolution area modify the picture somewhat. The åkermanite breakdown relations of Harker and Tuttle (1956) are revised. The decomposition products of åkermanite at 6 kbar water pressure are hydrovesuvianite and clinopyroxene.

Introduction.

The literature on melilites has recently been reviewed by the present author (1961) and shall not be repeated here. In this paper Na-gehlenite denotes the mixed crystal 85 gehlenite 15 $\text{Na}_2\text{Si}_2\text{O}_7$.

Melting phenomena.

The liquidus temperatures of the mixed crystal series åkermanite — Na-gehlenite was studied with a heating stage microscope. The heating stage consisted of a platinum heating spiral mounted in a brass box with windows in it. The brass box was placed upon the microscope stage and the product in the platinum spiral was observed through universal stage objectives to permit a long working distance, thus avoiding damage to the lense due to heat radiation from the heating stage. The temperature was controlled by a set of two variable

transformers and the temperature readings were made with a Leeds and Northrup optical pyrometer calibrated with a National Bureau of Standards platinum thermocouple. The accuracy of the readings is $\pm 5^\circ$ C. The advantages of this technique are mentioned elsewhere and will not be repeated here (see. e. g. J. H. Welch, Build. Res. Stn. Note no. E 657).

The solidus temperatures were determined by heating in conventional tube furnaces supplied with temperature controllers of the falling bridge type. The accuracy of these temperatures is $\pm 3^\circ$ C.

The lower breakdown temperatures and products.

The experimental technique used in this work has been described earlier by the present author (1961) who showed that the products formed at 6 kbar water pressure and 400° C— 600° C by decomposition of mixed crystals in the series åkermanite - gehlenite are vesuvianite, hydrogarnet, diopsidic pyroxene and xonotlite. During the experiments of that work it was found that monticellite was absent in the decomposition mixture formed from åkermanite rich mixed crystals. This was unexpected because HARKER and TUTTLE (1956) have suggested that the only breakdown products formed from åkermanite at low temperature are monticellite and wollastonite. Therefore a more detailed study of the breakdown of åkermanite was included in the planned study of the lower breakdown relations of sodium-oxy-melilites.

It has been known for a long time that melilites seem to be unstable at lower temperatures. CARSTENS and KRISTOFFERSEN (1931) reported that åkermanite glass devitrified to form åkermanite and diopside. Similar results are mentioned by OSBORN and SCHAIRER (1941) who determined the lower stability temperature of åkermanite at atmospheric pressure to be 1325° C. Below this temperature diopside formed as one decomposition product.

Somewhat different results were obtained by BOWEN, SCHAIRER and POSNJAK (1933) who reported that monticellite formed in a glass of åkermanite composition at 1050° C and atmospheric pressure.

NEUVONEN (1952) discussed the breakdown of åkermanite from thermochemical standpoint and arrived at the conclusion that with decreasing temperature the following equilibria should be stable:

- 1) Åkermanite = Diopside + Merwinite
- 2) Diopside + Merwinite = Diopside + Monticellite + Ca_2SiO_4
- 3) Diopside + Monticellite + Ca_2SiO_4 = Monticellite + Wollastonite

This seems to be in good agreement with the results obtained by Bowen, Schairer and Posnjak and by Osborn and Schairer.

Table 1. Melting relations of mixed crystals in the series gehlenite — Na-gehlenite and åkermanite — Na-gehlenite.

% Geh	% Na-geh	Liquidus	Solidus	Reference
100	0	1590°	1590°	Osborn and Schairer (1941)
33	67	1541°	1220°	Goldsmith (1948)
0	100	1462°	1160°	Goldsmith (1948)
% Åk	% Na-geh			
100	0	1454°	1454°	Osborn and Schairer (1941)
67	33	1458°	1280°	This work
33	67	1460°	1205°	This work
0	100	1462°	1160°	Goldsmith (1948)

The heating experiments carried out by Neuvonen have later been completed by HARKER and TUTTLE (1956). They found the åkermanite breakdown products to be wollastonite and monticellite (CaSiO_3 and CaMgSiO_4) in the 2—4 kbar (30.000—60.000 psi) water pressure range. They extrapolated the experimental results to atmospheric pressure and arrived at a decomposition temperature of 720°—750° C. This is not in accordance with the results of Bowen, Schairer and Posnjak and of Osborn and Schairer.

Harker and Tuttle state: 'In the breakdown to wollastonite and monticellite, åkermanite becomes unstable by virtue of its own internal structure and not through any tendency to react with other phases which may be present (as for example, H_2O or CO_2)'. This statement, however, is not tenable outside the pressure range studied by Harker and Tuttle, and it is not tenable when glycerine, probably also other organic compounds, are present, as shown by the present author (1961).

Some runs carried out at 5 kbar water pressure with åkermanite yielded decomposition products identical to those found by Harker and Tuttle — wollastonite and monticellite. At 6 kbar water pressure

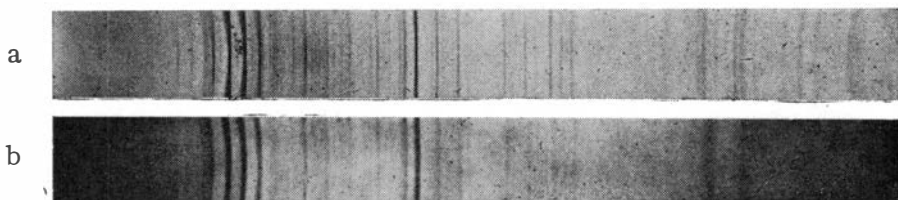


Fig. 1. X-ray identification films of vesuvianite. a) Natural vesuvianite from Vesuvius. b) Vesuvianite formed from åkermanite at 447° C, 6 kbar water pressure, 8 weeks.

other products were found. One of them is clinopyroxene, the other one is a phase having an atomic structure similar to that of vesuvianite.

Vesuvianite has been reported by the present author (1961) as a decomposition product of mixed crystals of the series åkermanite — gehlenite, all of them containing at least some Al being necessary to satisfy the chemical formula of vesuvianite, $\text{Ca}_{10}(\text{Mg, Fe})_2\text{Al}_4(\text{OH}/(\text{SiO}_4)_2 \cdot (\text{Si}_2\text{O}_7)_2$. The observation of vesuvianite as a decomposition product of åkermanite ($\text{Ca}_2\text{O}_2\text{MgSi}_2\text{O}_5$) was indeed so unexpected that the thermal experiments were repeated. The repeated runs confirmed that a mineral with vesuvianite-like structure forms as one decomposition product by the breakdown of åkermanite. The X-ray identification films of vesuvianite thus formed and of natural vesuvianite are shown in figure 1.

The structure of vesuvianite was determined by WARREN and MODELL (1931). They found that vesuvianite consists of columns of garnet structure with intermediate Si_2O_7 groups. The Mg, Fe and Al of vesuvianite are situated in six-fold coordinated sites. According to Warren and Modell there are also sites of four-fold coordination that may be occupied by metal ions. Some vesuvianites contain Be, and from chemical viewpoint Be substitutes for Mg. However, Be does not occupy the general six-fold coordination sites of Mg in vesuvianite but are found in the four-fold coordination sites normally empty in the Be free vesuvianites. Thus, when small ions replace the Mg, Fe or Al ions in vesuvianite, they may enter into the four-fold coordinated sites outside the garnet columns and the Si_2O_7 groups.

No Al is present in åkermanite, and if vesuvianite forms by breakdown of it, the six-fold coordinated sites normally occupied by Al in

Table 2. Interplanar spacings in Å units of vesuvianites. Intensity relations of the vesuvianite formed from åkermanite derived from a photometer curve of the film.

Vesuvianite ASTM 2694 d 2-0874		Vesuvianite formed from åkermanite our film no. 11617	
d values	Int	d values	Int
		5,88	10
		4,79	10
		4,29	10
4,07	20	4,07	10
3,90	20		
3,47	20	3,49	10
3,22	20D		
3,04	60	3,08	20
2,93	60	2,94	40
2,74	100	2,75	80
2,59	80	2,60	100
2,45	70	2,46	60
2,34	40	2,35	20
2,20	20	2,20	10
2,12	60	2,13	20
		2,01	10
		1,940	10
1,88	40	1,890	20
1,81	50		
1,76	50	1,774	20
1,66	70D	1,668	30
1,63	80	1,628	80

vesuvianite must be empty. To preserve electroneutrality other ions must go into the structure.

An obvious suggestion is that the $(\text{OH})_4 - \text{SiO}_4$ substitution mechanism found in hydrogarnets may work in the garnet-like columns in the vesuvianite structure as well. This would affect the physical properties of vesuvianite and reduce the index of refraction considerably. This has actually been found in the vesuvianites formed by breakdown of melilites (CHRISTIE (1961)). The introduction of additional OH groups in the garnet columns of vesuvianite may be followed by a filling up of the empty four-fold sites (occupied by Be in Be-vesuvianites) by Si, thus compensating for the non present Al. This

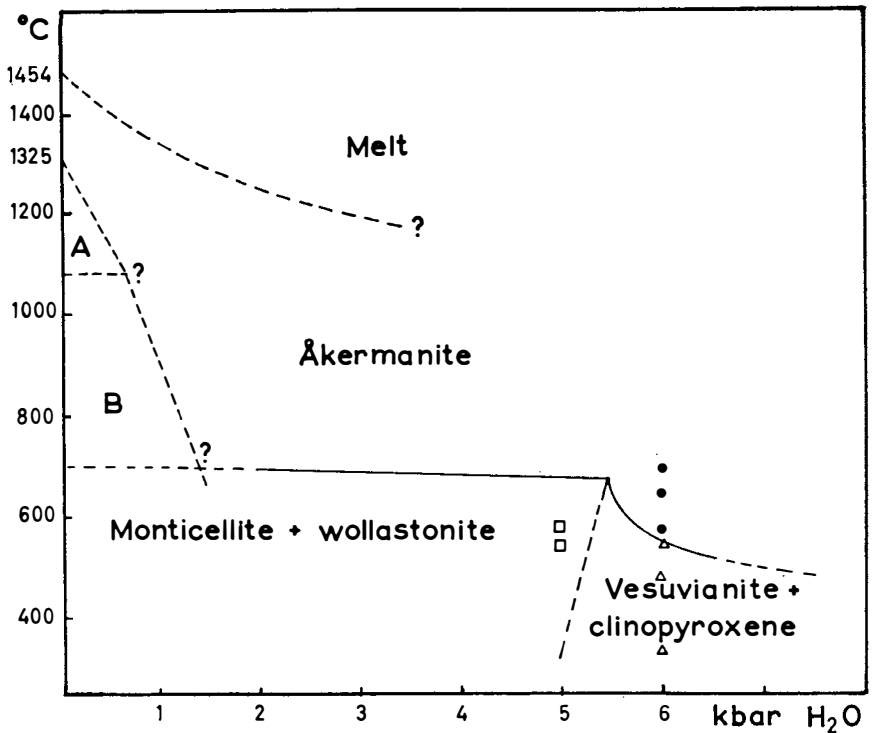


Figure 2. The breakdown relations of åkermanite. Data from Bowen, Schairer and Posnjak (1933), Osborn and Schairer (1941), Neuvonen (1952), Harker and Tuttle (1956) and present work. Δ Vesuvianite + clinopyroxene, \square Monticellite + wollastonite, \bullet undecomposed åkermanite.

explanation is possibly more tenable than the assumption that the mentioned four-fold sites are occupied by hydrogen ions.

There are some differences in the X-ray diffraction line intensities of natural vesuvianite and of vesuvianite formed from åkermanite. Unfortunately the atomic coordinates of the empty four-fold coordination sites of the structure of vesuvianite are not given in the literature, and the experimental material available to the present author is too small to permit a more detailed treatment of this problem. Intensity calculations suggest that the mere replacement of $(\text{OH})_4$ groups for SiO_4 groups in the garnet columns does not explain the actual intensity differences, therefore other ions must be present in the structure that

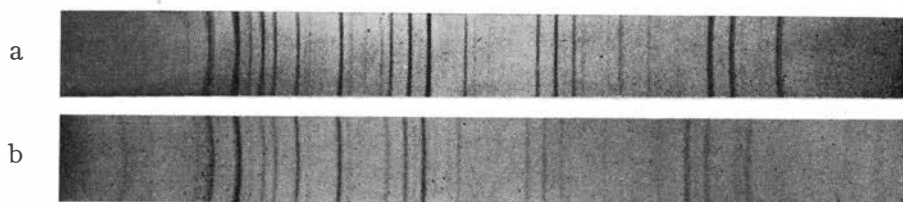


Fig. 3. X-ray identification films of garnets, a) Grossularite, Seiland, Norway, b) hydrogrossularite formed from gehlenite at 447° C, 6 kbar water pressure, 8 weeks.

account for the differences of the X-ray diffraction patterns of the vesuvianites.

Because of the reduced index of refraction (1.645—1.650 to 1.70—1.71 of natural vesuvianite) the present author is inclined to suggest that the vesuvianite-like phase formed by the breakdown of åkermanite is a hydro-vesuvianite where the non-existence of Al in the structure is compensated for by the presence of OH groups, thus exhibiting an analog to hydrogarnet.

The relative amounts of clinopyroxene and vesuvianite formed from åkermanite seem to depend upon the temperature. This is found by the breakdown of åkermanite rich melilites also. Thus, in the runs at 525° C roughly equal amounts of clinopyroxene and vesuvianite form, at 447° C vesuvianite dominates, and at 350° C the only detectable phase is clinopyroxene. The relative amount of pyroxene and vesuvianite has been estimated from the X-ray powder films, and several factors — like disorder phenomena — may effect the quantity estimation. Nevertheless, the general trend seems to be that there is a definite temperature range of optimal formation of vesuvianite at 6 kbar water pressure, — this indicating that both the temperature and the water 'activity' are of importance.

Figure 2 presents the low-temperature breakdown products of åkermanite at various water pressures. The breakdown phenomena below 2 kbar are taken from NEUVONEN (1952) and they are derived from thermochemical aspects. Within the area marked A, OSBORN and SCHAIRER (1941) have found diopside as a decomposition product, and within the area marked B, BOWEN, SCHAIRER and POSNJAK (1933) found monticellite in a devitrified åkermanite glass, confirming the conclusions by Neuvonen. The pressure range 2—4 kbar was

Table 3. Experimental runs. Temperatures marked B: starting material is unreacted batch.

Gehlenite 6 kbar water pressure

Temp °C	Time	Products
700	6 days	Melilite
650	9 days	Melilite
600	9 days	Melilite
568	12 days	Melilite
525	6 weeks	Hydrogarnet
447	8 weeks	Hydrogarnet, (xonotlite)

67 geh 33 Nageh 6 kbar water pressure

680	1 day	Melilite
640	14 days	Melilite
600	14 days	Melilite
568	12 days	Melilite
525	6 weeks	Not identified
525B	6 weeks	Hydrogarnet
447	8 weeks	Hydrogarnet
447B	8 weeks	Reaction not completed, CaCO ₃ present
350	8 weeks	Hydrogarnet
350B	8 weeks	Hydrogarnet + unreacted batch, CaCO ₃

33 geh 67 Nageh 6 kbar water pressure

680	1 day	Melilite
640	14 days	Melilite
600	14 days	Melilite
525	6 weeks	Hydrogarnet
525B	6 weeks	Hydrogarnet
447	8 weeks	Hydrogarnet
447B	8 weeks	Incomplete reaction
350	8 weeks	Hydrogarnet
350B	8 weeks	Hydrogarnet + unreacted batch, CaCO ₃

5 kbar water pressure

568	10 days	Melilite, monticellite, wollastonite (?)
-----	---------	--

Nageh 6 kbar water pressure

680	1 day	Melilite
600	14 days	Melilite
568	12 days	Melilite
525	6 weeks	Hydrogarnet
525B	6 weeks	Hydrogarnet
447	8 weeks	Hydrogarnet
447B	8 weeks	Hydrogarnet
350	8 weeks	Hydrogarnet
350B	8 weeks	Hydrogarnet

5 kbar water pressure

568	10 days	Melilite, monticellite, wollastonite (?)
-----	---------	--

Cont. table 3.

33 Åk 67 Nageh 6 kbar water pressure

680	1 day	Melilite
600	14 days	Melilite
568	14 days	Melilite
525	6 weeks	Vesuvianite
525B	6 weeks	Vesuvianite
447	8 weeks	Hydrogarnet
447B	8 weeks	Vesuvianite, (clinopyroxene)
350	8 weeks	Hydrogarnet
350B	8 weeks	Vesuvianite, (clinopyroxene)
<i>5 kbar water pressure</i>		
568	14 days	Monticellite, melilite, wollastonite

67 Åk 33 Nageh 6 kbar pressure

680	1 day	Melilite
640	14 days	Melilite
600	14 days	Melilite
525	6 weeks	Vesuvianite, clinopyroxene
525B	6 weeks	Vesuvianite, clinopyroxene
447	8 weeks	Vesuvianite
447B	8 weeks	Unreacted batch
350	8 weeks	Vesuvianite
350B	8 weeks	Unreacted batch
<i>5 kbar water pressure</i>		
568	14 days	Melilite, monticellite, wollastonite

Åkermanite 6 kbar water pressure

568	12 days	Melilite
550	9 days	Melilite
525	6 weeks	Vesuvianite, clinopyroxene
500	9 days	Melilite, clinopyroxene, unidentified
447	8 weeks	Vesuvianite, (clinopyroxene)
400	3 weeks	Melilite, clinopyroxene, unidentified
350	8 weeks	Clinopyroxene
<i>5 kbar water pressure</i>		
640	14 days	Monticellite, wollastonite
568	14 days	Monticellite, wollastonite

covered by HARKER and TUTTLE (1956) and the present work brings the results from the range 5–6 kbar.

Neuvonen did not consider the possibility of the formation of hydrous phases from åkermanite, neither did Harker and Tuttle, and the experiments of this work form a supplement to the earlier published data on the breakdown of åkermanite.

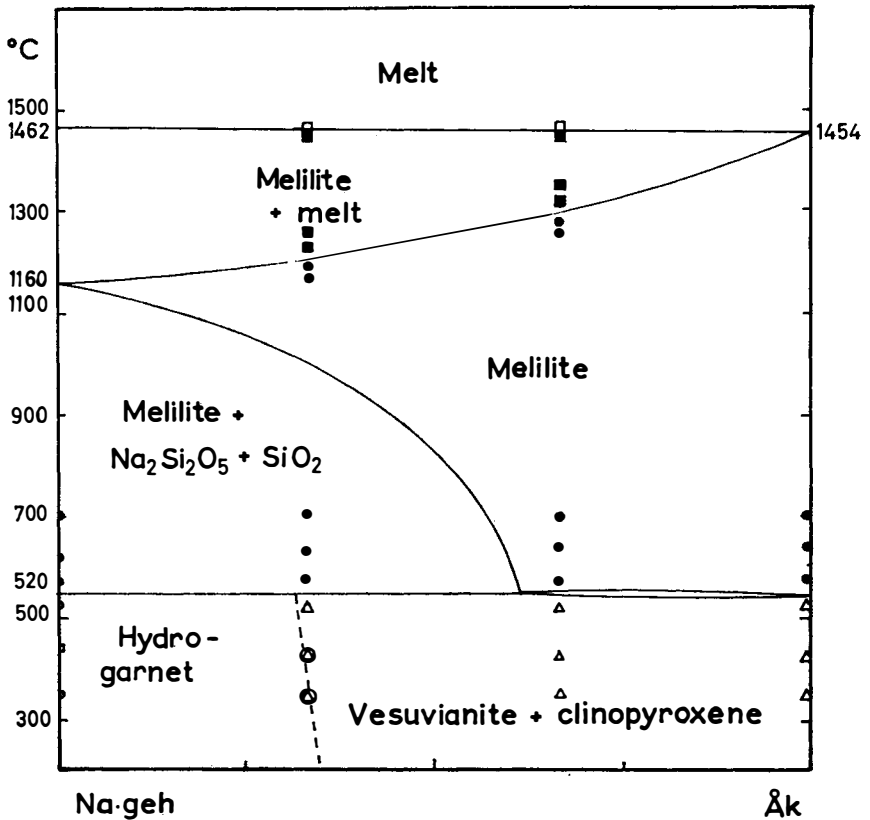


Fig. 4. Breakdown relations of the system åkermanite - Na-gehlenite. Data from table 3. ● undecomposed melilite, ■ melilite + melt, □ melt, ○ hydro-garnet, △ vesuvianite + clinopyroxene. Melting relations at atmospheric pressure.

Gehlenite breaks down to form hydrogrossular in the studied pressure range 5–6 kbar (figure 3.). This indicates that there must be a certain flexibility of the rules of site occupation in the garnet structure. Gehlenite contains too much Al and far too little Si to satisfy the 'dry' grossularite formula, and the presence of water in the system seems to facilitate the formation of hydrogrossular even in chemical environments where the formation of garnets is unexpected.

The presence of water-containing minerals as decomposition products of åkermanite and gehlenite changes the general viewpoint

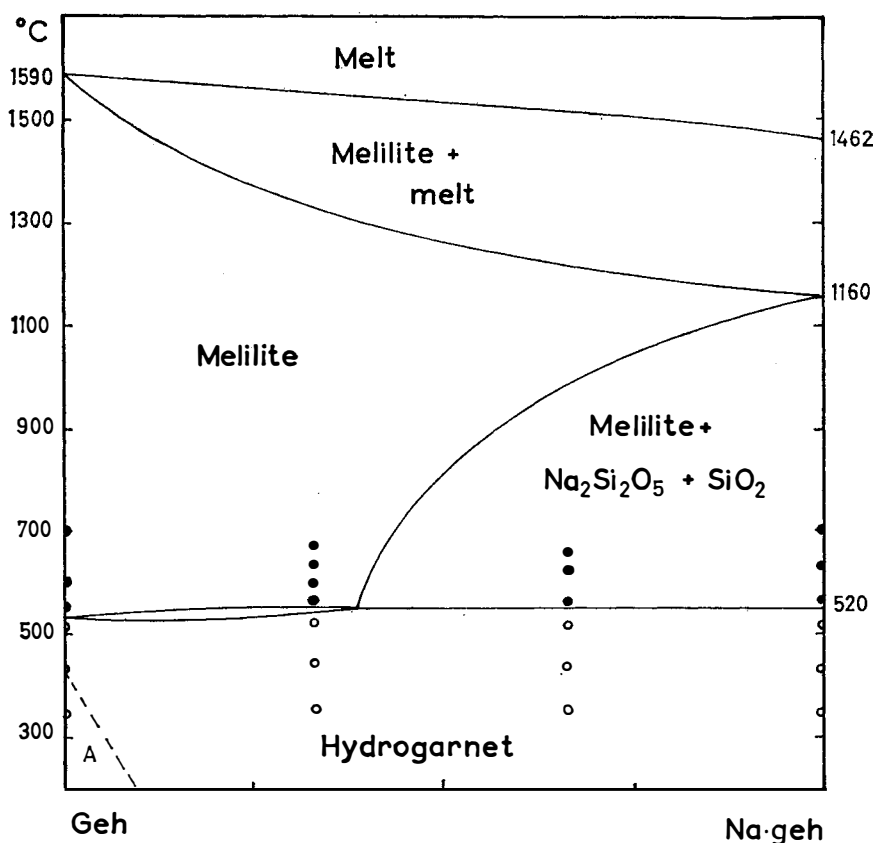


Fig. 5. Breakdown relations of the system gehlenite — Na-gehlenite. Data from table 3. ● undecomposed melilite, ○ hydrogarnet, Solidus and liquidus curve from Goldsmith (1948), solvus curve from Christie (1962). Inside area A xonotlite is formed. Melting relations at atmospheric pressure.

concerning the breakdown of melilites. Whereas the breakdown relations were supposed to be of the same type as that of the plagioclase-epidote stability curve introduced by RAMBERG (1943) (see e. g. HARKER and TUTTLE (1956)) the experimental studies of the present author (1961) have shown that the breakdown of the åkermanite-gehlenite mixed crystal series takes place within a narrow temperature range. The results presented in this work show that the Na-content of the melilite is of no practical importance to the breakdown temperature.

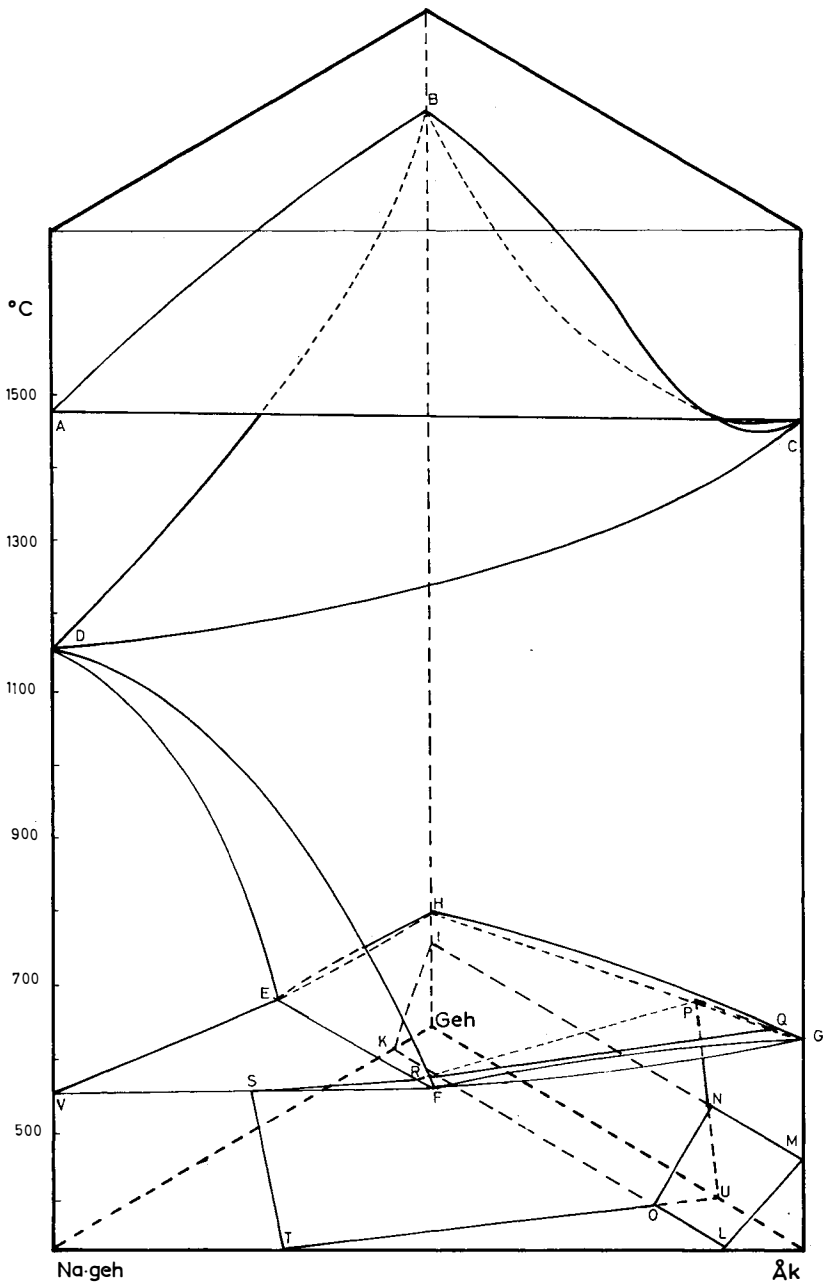


Fig. 6. Tentative diagram for the system gehlenite - åkermanite - Na-gehlenite. ABC: liquidus plane, BCD: solidus plane, DEFGHBCD: space of melilite mixed crystal, DEFV: space of melilite mixed crystals + $\text{Na}_2\text{Si}_3\text{O}_7$ + SiO_2 , SPU · Åk · TS: space of vesuvianite + clinopyroxene, UONIK · Geh: space of xonotlite, Nageh · TUPQRSVEH · Geh: space of hydrogarnets.

During the studies on melilites by the present author it became evident that the amount of the $\text{Na}_2\text{Si}_3\text{O}_7$ molecule taken in solid solution in gehlenite is temperature dependent (1962), and whereas 15 % of the $\text{Na}_2\text{Si}_3\text{O}_7$ molecule is taken in solid solution in gehlenite at 1145°C , only 6–7 per cent is dissolved at the breakdown temperature gehlenite. If the melilite contains some of the åkermanite molecule the amount of the $\text{Na}_2\text{Si}_3\text{O}_7$ taken in solid solution is even less. Therefore, the presence of Na affects the breakdown of the gehlenite – åkermanite mixed crystals very little. In fact, even for the Na-richest gehlenite a depression or raising of the breakdown temperature is not stated with certainty.

The stability field of vesuvianite formed by the breakdown of melilites is considerably extended when Na is present. Thus the border between the hydrogarnet and the vesuvianite + clinopyroxene field is situated at around 66 % Åk in the åkermanite – gehlenite system (CHRISTIE (1961)) and around 33% Åk in the åkermanite – Na-gehlenite system (this work).

Xonotlite present in low-temperature runs of the åkermanite – gehlenite studies (1961) were absent in all present runs but one: gehlenite 350°C and 6 kbar water pressure. This indicates that even small amounts of Na seems to disfavour the formation of xonotlite from melilite at lower temperature.

LITERATURE

- BOWEN, N. L., SCHAIRER, J. F. and POSNJAK, E. (1933): The system $\text{CaO} - \text{FeO} - \text{SiO}_2$. Amer. Jour. Sci. vol. 26, pp. 193–284.
- CARSTENS, C. W. and KRISTOFFERSEN, K., (1931): Schlackenstudien mit besonderer Berücksichtigung der Mangan-haltigen Schlacken. Neues Jahrb. d. Mineral. Beilageband 62A (1933) pp. 163–192.
- CHRISTIE, O. H. J., (1961): On sub solidus relations of silicates. I. The lower breakdown temperature of the åkermanite-gehlenite mixed crystal series at moderate water pressure. Norsk Geol. Tidsskr. vol 41, pp. 225–269.
- (1962): On sub solidus relations of silicates. III. A contribution to the chemistry of melilites. Norsk Geol. Tidsskr. vol. 42, pp. 1–28.
- GOLDSMITH, J. R., (1948): Some melilite solid solutions. Jour. Geol. vol. 56, pp. 437–477.
- HARKER, R. I. and TUTTLE, O. F., (1956): The lower limit of stability of åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$). Amer. Jour. Sci. vol. 254, pp. 468–478.

-
- NEUVONEN, K. J. (1952): Thermochemical investigation of the åkermanite—gehlenite series. Bull. Comm. Géol. Finlande. no. 158.
- OSBORN, E. F. and SCHAIRER, J. F. (1941): The ternary system pseudowollastonite—åkermanite—gehlenite. Amer. Jour. Sci. vol. 239, pp. 715—763.
- RAMBERG, H. (1943): En undersøkelse av Veststrandens regionalmetamorf bergarter. Norsk Geol. Tidsskr. vol. 23, pp. 1—174.
- WARREN, B. E. and MODELL, D. I. (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. vol. 78, pp. 422—432.

Manuscript received June 22, 1961.

Printed May 1962.