PHASE EQUILIBRIUM DATA FOR THE SYSTEM
MgO-MgF$_2$-SiO$_2$

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ABSTRACT

In completely anhydrous melts of the binary system MgO-MgF$_2$ a simple eutectic reaction at 1214° C. was established.

The binary system Mg$_2$SiO$_4$-MgF$_2$ is characterized by the formation of minerals of the humite-clinohumite group. All of them show incongruent high-temperature reactions, norbergite melting with a primary crystallization of chondrodite (stable) or forsterite (metastable) at 1345° C., chondrodite melting with primary crystallization of forsterite at 1450° C. On heating, clinohumite breaks down at 1380° C. to a mixture of forsterite and chondrodite. Humite is only sporadically observed in subsolidus reactions; the equilibrium temperature for the reaction clinohumite+chondrodite⇌humite could not be determined. Metastable crystallization of forsterite (in the place of chondrodite) occurs mostly on heating and fusion of norbergite.

In the ternary system MgO-MgF$_2$-SiO$_2$ some of the minerals of the humite-clinohumite series (on the join Mg$_2$SiO$_4$-MgF$_2$) could be outlined in their crystallization fields, with boundary curves to the fields of primary periclase, sellaite, cristobalite and/or tridymite, forsterite, and clinoenstatite. No magnesium amphibole of the formula Mg$_7$(Si$_8$O$_{22}$)F$_2$ was observed in the melt products.

INTRODUCTION

Phase equilibrium studies in ternary systems of the type oxide-fluoride-SiO$_2$ (oxide and fluoride with the same cation) have been investigated in only a few cases. In the main these investigations have been restricted to the system CaO-CaF$_2$-SiO$_2$. Special attention has been given to the influence of CaF$_2$ on the formation of tricalcium silicate, because of the special importance this substance plays in the hardening process of cements (Eitel (1), Bååk and Ölander (2)).

IMPORTANCE OF THE SYSTEM MgO-MgF$_2$-SiO$_2$

In the last two decades there have been many attempts to synthesize mica and amphibole asbestos. These took into account the necessity of substituting F for the OH-groups, if the process was to be undertaken from the melt at atmospheric pressure. While this method proved successful for mica synthesis, it is questionable whether the synthesis of asbestos is possible in the same manner. In any case, it seemed useful to go into more detail regarding the melting equilibria of this system.

REVIEW OF LITERATURE

The system MgO-SiO$_2$ was studied in 1914 by Bowen and Anderson (3) and supplemented by Greig (4) in 1927. According to these authors a

eutectic exists between periclase and forsterite at 1850° C. and a second between clinoenstatite and cristobalite at 1543° C. Forsterite melts congruently at 1890° C; clinoenstatite melts incongruently at 1557° C. with forsterite as solid phase. Melts rich in SiO_2 beyond the eutectic clinoenstatite-cristobalite unmix at 1695° C. and form two liquid phases.

The system $MgO-MgF_2$ was studied in 1953 by Eitel, Hatch and Denny (5), and x-ray investigation revealed no new compounds. The system MgF_2-SiO_2 could not be studied, because the samples partly showed strong hydrolysis and evaporation. For example, in a melt $MgF_2:SiO_2 = 2:1$, norbergite $Mg_2SiO_4 \cdot MgF_2$ and even forsterite Mg_2SiO_4 were found as reaction products.

Various partly successful attempts have been made to synthesize the minerals of the humite group: norbergite, chondrodite ($2Mg_2SiO_4 \cdot MgF_2$), humite ($3Mg_2SiO_4 \cdot MgF_2$) and clinohumite ($4Mg_2SiO_4 \cdot MgF_2$).*

In 1947 Rankama (6) succeeded in getting norbergite and chondrodite. On the other hand an attempt to synthesize clinohumite failed. (This paper includes a survey of literature since 1851).

In 1954 Karyakin and Gul'ko (7) succeeded in obtaining norbergite, chondrodite and humite, when they melted calcium fluoride and quartz in magnesite crucibles.

Finally, in 1955 van Valkenburg (8) succeeded in synthesizing all of the humite-minerals by using melting reactions or reactions in the solid state.

The system $MgO-MgF_2-SiO_2$ was studied by Fujii and Eitel (9) in 1957 by means of reactions in the solid state. A large number of mixtures was heated at 1200° C. and the reaction products were investigated for the most part by x-ray diffraction. The approximate limits of the individual compounds were represented in a triangular composition diagram. As such are mentioned: periclase, sellaite, norbergite, chondrodite, forsterite, clinoenstatite, and cristobalite. While humite and clinohumite could not be established with certainty in the mixtures heated for three hours, after 42 hours of heating at the same temperature they did appear. Clinohumite was more easily formed than humite.

Preparation of Samples

One of the main difficulties of these investigations was the extraordinarily high sensitivity of magnesium fluoride to moisture. Magnesium fluoride retains surface-adsorbed water up to high temperatures, and H_2F_2 is split off by hydrolysis. For this reason by "open" conditions it is impossible to melt MgF_2 once it has been exposed to the free air without the forming of MgO. The vapor pressure of MgF_2, even at 1400 to

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* In the natural minerals F⁻ is substituted in part by OH⁻.

1500° C., has very little disturbing effect (5). According to new investigations carried out by Günther (10), the vapor pressure is 0.1068 Torr at a temperature of 1282°C. and certainly does not have to be taken into account (at least, when the duration of the experiment is short).

The possibility of forming SiF_4 exists when the mixtures contain both MgF_2 and SiO_2 as shown in various references in literature, and clearly confirmed by our own experiments.

The escaping SiF_4 is hydrolysed instantaneously when moisture is present, and clouds of smoke escape. Therefore it was necessary to control the loss in weight, or better to determine the change in composition by analytical methods.

The greater part of the mixtures were prepared with purest MgO from the Schering Works. For some attempts "magnesium carbonate, p.a. Merck, Darmstadt" was used. Both substances were heated for about half an hour at 1150° C., and as is the case with the other raw materials, preserved above P_2O_5 until their application.

SiO_2 was obtained by hydrolysis of silicon tetrachloride (Institute of Silicon and Fluorcarbon Chemistry, Radebeul) in an ammoniac-water solution. The product was filtered off, slightly washed, dried, and heated at 1150° C. for one hour.

For the first orienting experiments "magnesium fluoride, precipitated, pure" produced by Riedel de Haën, Seelze near Hannover, was used. It is a fluffy white powder. Before its application it was melted as quickly as possible, poured from the crucible, and crushed. During the melting and pouring out, a distinct odor of hydrofluoric acid was noticeable (hydrolysis by adsorbed water and moisture of the air). A great number of experiments were made with a shortly fused "magnesium fluoride, pure, for optical use" of unknown origin. This substance was heavier than the first and it seems likely that it was produced at a higher temperature.

For the last experiments we had at our disposal a "magnesium fluoride, precipitated" (Werkstätten für Photochemie, Berlin-Charlottenburg). It had a slight resemblance to the first mentioned MgF_2; it was likewise quickly fused.

Concerning the degree of purity of the ingredients used, it should be said that MgO and SiO_2 were checked by spectral analysis. As contaminations, MgO contained only about 0.1% CaO; SiO_2 contained about 0.3% Al_2O_3 and below 0.05% of other oxides. MgF_2 was determined by chemical analysis.

The compositions of the samples after one melting are shown in Table 1. The three samples of MgF_2 contained only a small or very small quantity of MgO. The contaminations of the "magnesium fluoride, for optical use" may be far below the limit of analytical determination.

TABLE 1. COMPOSITION OF DIFFERENT SAMPLES OF COMMERCIAL
MAGNESIUM FLUORIDE

A—from Riedel-de Haën;
B—pure, for optical use;
C—from Werkstätten für Photochemie

Weight %	A	B	C	Weight %	A	B	C
MgO	63,79	64,24	64,31	MgF_2†	96,97	99,20	97,02
CaO	1,25	0,12	0,40	MgO†	1,05	0,06	1,54
BaO	0,41	0*	0*	SiO_2	0,17	0,10	0,34
Fe_2O_3	0,15	0,20	0,26	CaO	1,25	0,12	0,40
Al_2O_3				BaO	0,41	—	—
SiO_2	0,17	0,10	0,34	Fe_2O_3	0,15	0,20	0,26
F_2	n.d.	60,49	59,16	Al_2O_3			
Sum	—	125,15	124,47	Sum	100,00	99,68	99,56
$O = F_2$		25,47	24,91				
	—	99,68	99,56				

† Indirectly calculated.
* Not identified by spectral analysis.

Normally, before adding the weighed quantity of MgF_2, the corresponding mixture of MgO and SiO_2 was pulverized and heated for some time at 1350° C.–1400° C. to make the mixtures less voluminous. Likewise by sintering the MgO-SiO_2 mixtures the troublesome development of electrostatic charges in the MgO powder was avoided.

EXPERIMENTAL PROCEDURE

For most of the experiments a SiC resistor furnace with four vertically arranged heating elements was used. With this furnace, work was carried out at temperatures of up to 1450° C. For higher temperatures a molybdenum furnace, which consisted of a molybdenum resistor in sintered Al_2O_3, was at our disposal. The gas-tight construction of this furnace made it possible to work with unprotected platinum.

For the measurement of the temperature a Pt-Pt, 10 Rh thermocouple was used, the hot junction of which was dipped directly into the melt. The cold junction was kept at 20° C. in a Dewar vessel. The thermocouple was compared with a calibrated standard element of the German "Amt für Maasse und Gewichte."

THERMOANALYSIS

The first runs were carried out using the dynamic method. The mixtures of 12 gm. were placed in a platinum crucible with a volume of 20 ml.

As soon as the sample was fused, the melt was stirred with a platinum sheet. At temperatures above 1350° C., however, the stirring had to be abandoned, because the crucible was often welded with the platinum stirrer.

After fusing and stirring, the thermocouple was introduced into the melt, avoiding a contact of the thermocouple with the crucible. Then the power of the furnace was diminished and the cooling curve taken.

This method was applied for the investigation of mixtures rich in MgF_2, which are inclined to a disturbing undercooling in the field of the primary crystallization of MgF_2; an undercooling effect of about 10° could be rather regularly observed. In order to grow single primary crystals, the dynamic method was partly modified. Shortly after the beginning of the primary crystallization the cooling curve was interrupted by removing the thermocouple with the adhering crystals. Relatively large, clear crystal needles of this rapid growth were very suitable for microscopic examination and for x-ray diffraction.

Quenching Method

In mixtures in the neighborhood of the binary system $MgO-SiO_2$, equilibrium is mostly not arrived at with sufficient speed in spite of the presence of magnesium fluoride which is known to be a strong mineralizer. Mixtures with as much as 15 mol% MgF_2 can be kept as clear glasses, if they are quenched with sufficient speed.

It also seemed undesirable in many experiments to work in certain regions of the system with open crucibles. Small tubes of platinum foil (of 0.06 mm. thickness) with a diameter of about 3 mm., and a length of 10 to 15 mm., were welded together and filled with about 100 mg. of substance. The opening was folded together, the platinum tube connected with a ceramic tube by a platinum wire and the whole put into the furnace, which was already at the required temperature.

Then the temperature of the furnace was slowly reduced to the equilibrium temperature in question and held there for some time. After the heat treatment, the samples were removed from the furnace and air-quenched from the fusion temperature.

This method allowed a clear differentiation between larger primary crystals and crystals formed by reaction in the solid state, or crystals simply formed by quenching.

The furnace temperature was controlled by hand by means of a transformer and kept constant to about ±2 to 3° C.

Microscopic Investigation

To identify the different crystalline compounds, the petrographic thin section method has been of great service. Thus periclase (MgO) could be
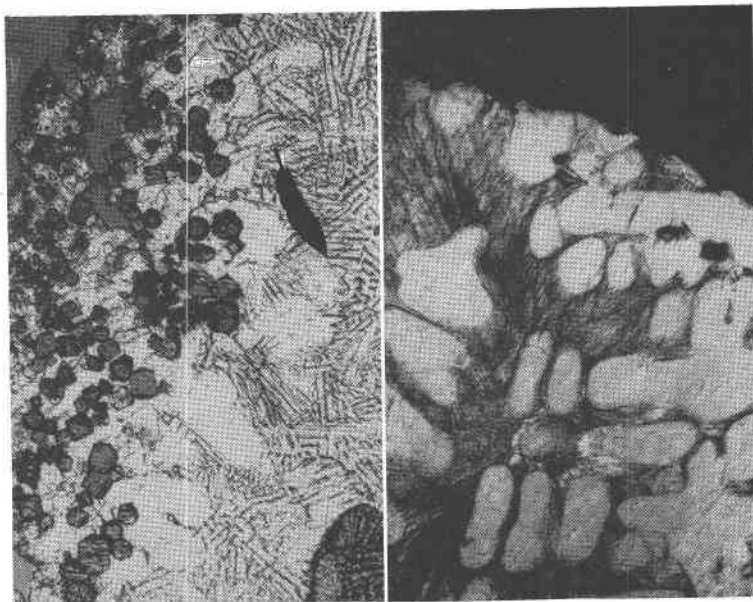
FIG. 1. (left) Periclase grains in periclase-sellaite-eutectic-Analyser 60° (Composition 10 mol. % MgO; 90% MgF₂). ×85

FIG. 2. (right) Sellaite skeletons, between them periclase-sellaite eutectic-Analyser 90°. ×85

clearly distinguished from the other minerals. It showed crystals with well-developed faces, mostly combinations of cubes and octahedra (Fig. 1). Sellaite (MgF₂) also often showed characteristic skeleton forms (Fig. 2) and peculiar cracks, by which, with suitable light incidence, it could nearly always be distinguished from the other minerals. These cracks may be caused by the polymorphic change of MgF₂, observed by Counts, Roy and Osborn (11) by high-temperature x-ray investigation at about 800° C.

SiO₂ could be identified just as easily. It showed irregular grains marked by a very slight birefringence. (Regarding the differentiation between cristobalite and tridymite, see later.)

In some cases it was possible to determine the angle of the optical axes; for norbergite it is 2V = 45° 15'.

X-RAY INVESTIGATION AND CHEMICAL ANALYSIS

X-ray patterns were taken from samples of the fused products as well as from single crystals, after having determined for clearly identified specimens which crystal interferences lie on the equatorial line.

Sometimes only one needle or a few very small, thin needles which could not be investigated by the powder method were at our disposal.

Rotation patterns were made with a camera 57.3 mm. in diameter, the powder patterns in a Debye-Scherrer camera, 114.6 mm. in diameter, and a Guinier camera, 57.3 mm. in diameter. Both Cu Kα, and Co Kα radiation were used. For comparison, the x-ray data of the humite-minerals, as determined by Sahama (12) were used.

The Shell and Craig methods (13) were used for bulk analysis, but fluorine was precipitated as calcium fluoride. From a special sodium carbonate melt all the other ingredients were determined (cf. Thomas (14)).

DISCUSSION OF THE RESULTS

The system MgO-MgF_2

The experiments of this binary system were carried out using the dynamic method. The system proves to be simply eutectic, as shown in Fig. 3.
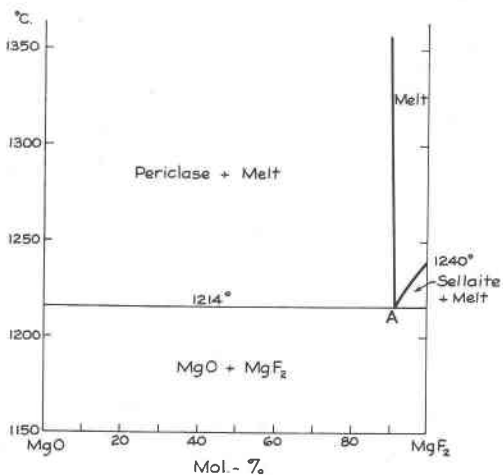

FIG. 3. Phase equilibrium diagram of the binary system MgO-MgF₂.

The fusion point of an especially pure substance "magnesium fluoride, for optical use" was found to be at 1238° C. In consequence of the slight contamination, by extrapolation a value of 1240° C. was obtained, in exact agreement with the value found by Venturello (15). In the literature the values vary between 1221° and 1270° C. To identify the substances, microscopic investigation was sufficient.

Refractive indices and x-ray pattern showed no indication of solid solution.

Under the microscope the eutectic showed sellaite crystals which were interspersed with straight parallel veins (Fig. 1). An addition of as little

as 10 mol% of MgO to MgF_2 brings about periclase as the primary crystallization.

The system MgF_2-SiO_2

The border system MgF_2-SiO_2 is not binary under normal experimental conditions as Eitel, Hatch and Denny (5) had previously observed. Mixtures of MgF_2 and SiO_2 showed, on heating, an intense smoke evolution; the solid reaction products belong to the ternary system $MgO-MgF_2-SiO_2$ (see below).

The white smoke evolved from a mixture of the composition $MgF_2:SiO_2 = 2:1$ on heating to 1300° C. in a platinum crucible was condensed in a water-cooled tube of copper fixed above the crucible. A voluminous white mass was deposited. The result of the analysis was 85.6% SiO_2 and 1.05% MgO. No determination was made for fluorine. The remainder may have consisted of adsorbed water. It is to be supposed that according to the equation

$$2\ MgF_2 + SiO_2 \rightarrow 2\ MgO + SiF_4,$$
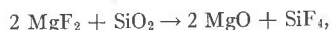
SiF_4 forms first of all, which under the influence of air is hydrolysed to SiO_2 and H_2F_2.

The system $Mg_2SiO_4-MgF_2$

The join $Mg_2SiO_4-MgF_2$ of the ternary system can be considered as a binary system, and minerals of the humite group appear as pseudo-binary compounds. Of the humites, only norbergite and chondrodite could be found as primary crystallization products from melts which bears out the observations of previous authors (6, 9), while clinohumite and humite are only obtained by reaction in the solid state.

According to Fig. 4, there is an eutectic between norbergite and sellaite. Norbergite melts incongruently at 1345° C. with primary crystallization of chondrodite. Forsterite, however, is often formed as a metastable primary crystallization of a melt of norbergite, so norbergite shows a double incongruent melting type. The stable incongruent melting point of chondrodite may be about 1450° C.

Clinohumite appears only below about 1380° C. as shown by x-ray diffraction patterns; at higher temperatures forsterite and chondrodite are formed.

Starting materials with the composition of humite, after heating at 1252° for 8½ hours, showed forsterite, clinohumite and chondrodite. The boundaries of the crystallization range of humite could not be established. The thermoanalysis showed, beside the arrest point at 1215° C., a second one at about 1192° C. The cause of this may be seen from the following:

According to chemical analysis all of the samples contain a little more MgO than corresponds to the proportion 2 MgO:SiO₂ for forsterite. Therefore the observed thermal data are not fully valid for the binary system Mg_2SiO_4-MgF_2 but rather for points lying in the ternary system on the MgO-side of the join Mg_2SiO_4-MgF_2. Thus it may be assumed that the mentioned second thermal effect has to be coordinated to the arrest point of the ternary eutectic periclase-norbergite-sellaite.

The system MgO-MgF_2-Mg_2SiO_4

Beside the eutectic periclase-norbergite-sellaite, E, two reaction points, F and G, exist. The corresponding compositions and temperatures are contained in Table 2. The position and temperature of the ternary eutectic and the reaction point F for periclase, chondrodite, norbergite and melt were relatively accurately determined, while the data for the reaction point G for periclase, chondrodite, forsterite, and melt are to be considered as approximate (see Fig. 5). As is to be expected, the fusion temperatures in the periclase field rise very sharply, so their determination was seldom possible.
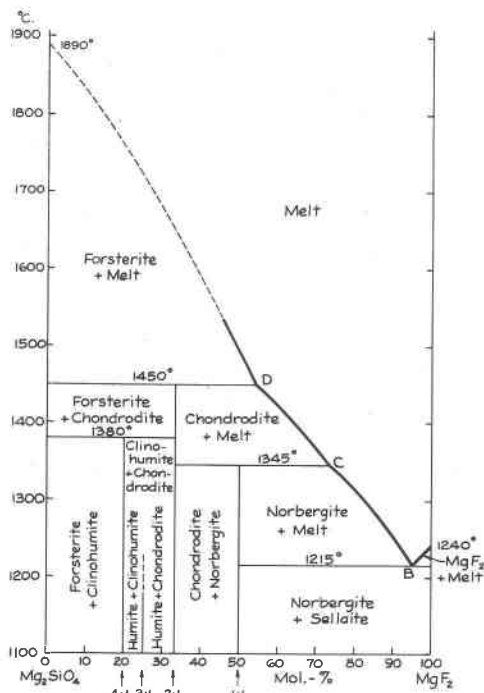

FIG. 4. Phase equilibrium diagram of the binary system Mg_2SiO_4-MgF_2.

TABLE 2. INVARIANT POINTS

Points in Figs. 3, 4, 5	Crystal Phases	Equilibrium	Temp. °C.	Composition		
				MgO	MgF₂	SiO₂
Binary Equilibria						
A	Periclase, Sellaite	Eutectic	1214	9	91	—
B	Norbergite, Sellaite	Eutectic	1215	10	85	5
C	Chondrodite, Norbergite	Reaction Point	1345	33	51	16
D	Forsterite, Chondrodite	Reaction Point	1450	48	28	24
Ternary Equilibria						
E	Periclase, Sellaite, Norbergite	Eutectic	1192	14	82	4
F	Periclase, Chondrodite, Norbergite	Reaction Point	1330	34	53	13
G	Periclase, Forsterite, Chondrodite	Reaction Point	1440	49	29	22
H	Chondrodite, Norbergite, Tridymite	Reaction Point	1250	37	28	35
J	Forsterite, Clinoenstatite, Chondrodite	Reaction Point	1340	44	16	40
K	Clinoenstatite, Chondrodite, Tridymite	Reaction Point	1300	43	16	41
L	Clinoenstatite, Cristobalite, Tridymite	Inversion Point	1470	46	5	49

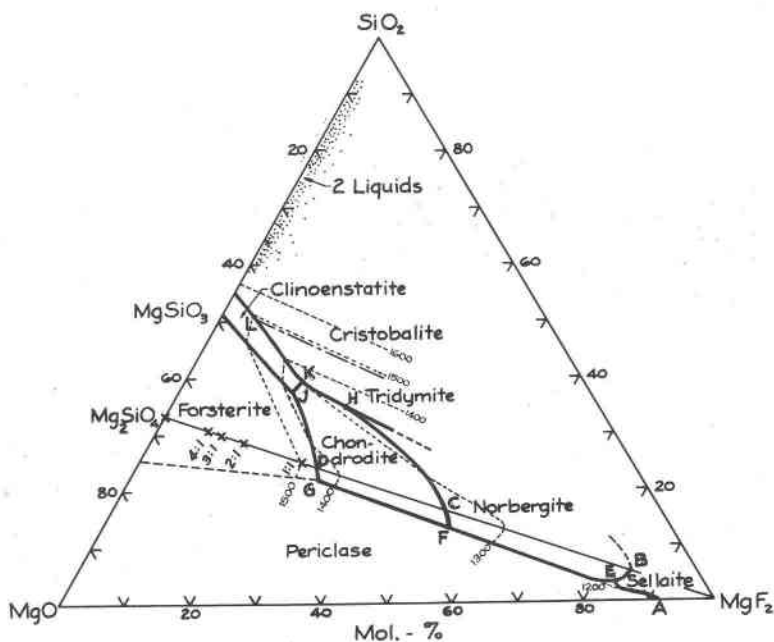Note: The data of Bowen and Anderson (3) and Greig (4) are omitted.

FIG. 5. Phase equilibrium diagram of the ternary system MgO-MgF₂-SiO₂.

The system Mg_2SiO_4-MgF_2-SiO_2

On the side beyond the join Mg_2SiO_4-MgF_2 (Fig. 5) the position of the ternary eutectic could not be determined. In this region such strong reactions take place, at the required temperatures, that methods applied here could not be used. A further difficulty must be noted here, obviously caused by the very great fluidity and low surface tension of the melts. Quite frequently, they crept over the margins of the platinum capsule. In the open atmosphere, the melt was hydrolysed, and MgO formed. This often happened also on nearly imperceptible pores and scratches formed in welding the platinum capsules. Nothing can be said on the entire extension of the sellaite field, but some statements can be made for the fields of chondrodite and norbergite extending toward the MgF_2 apex. The boundary against the SiO_2 field (see Table 2) could be established only approximately. The fields of crystallization of chondrodite and clinoenstatite with their boundaries against forsterite and SiO_2 could be established more precisely.

The question of a clear differentiation between cristobalite and tridymite in the products was rather difficult, especially in milky glasses
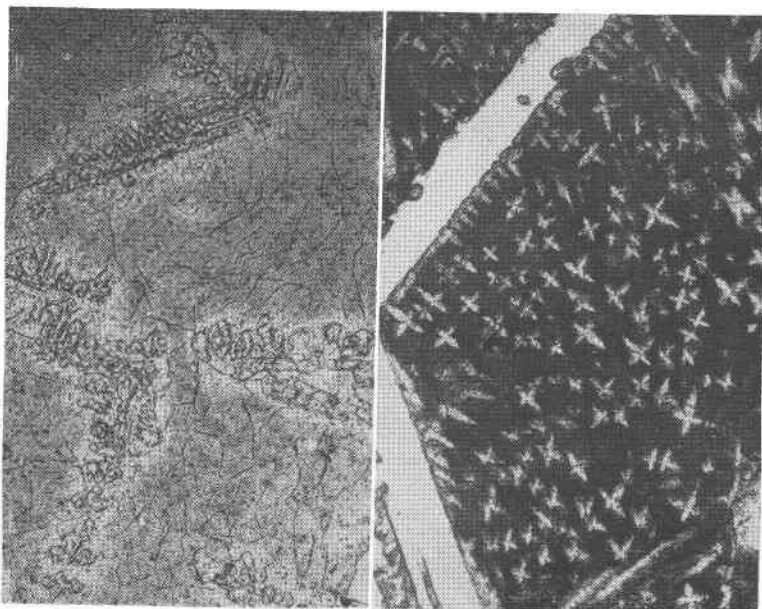

Fig. 6. (left) Cristobalite skeletons embedded in milky glass—Analyser 60° (Composition 35 mol. % MgO; 25% MgF_2; 40% SiO_2). ×85

Fig. 7. (right) Two large norbergite needles, between them quenched substance (sellaite in characteristic dendrites)—Analyser 60° (Composition 15 mol. % MgO; 75% MgF_2; 10% SiO_2). ×85

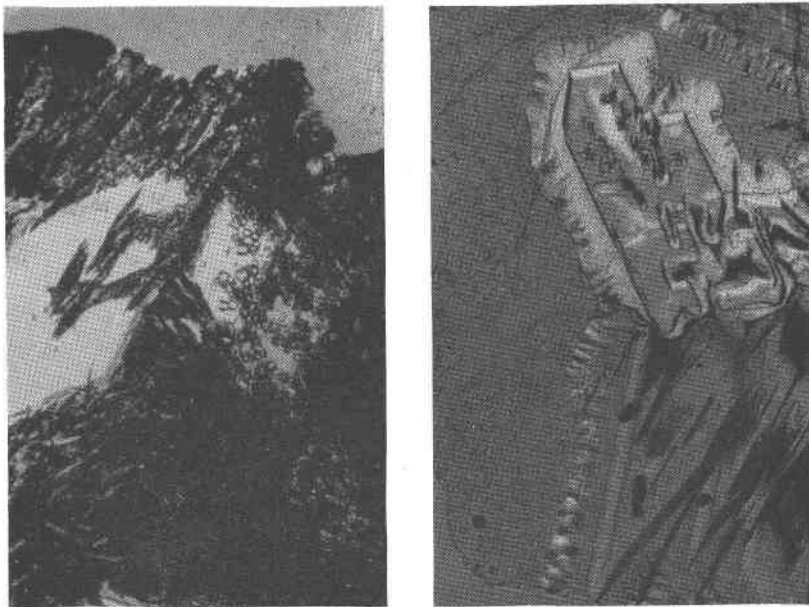Fig. 8. (left) The chondrodite crystal in the middle shows many little periclase grains. Analyser 70° (Composition 40 mol. % MgO; 45% MgF₂; 15% SiO₂). ×85

Fig. 9. (right) Chondrodite crystals surrounded by a fringe of quenched substance embedded in glass.—Analyser 60° (Composition 40 mol. % MgO; 25% MgF₂; 35% SiO₂). ×85

quenched from the melts. Usually the silica is observed in granular aggregates, but sometimes in dendrites (Fig. 6) or octahedral shapes. The x-ray patterns of these crystallizations show the lines of cristobalite, which was also identified by its refractive index. Because of the smallness of the cristobalite crystals in the milky glasses, the index of refraction could not be determined, and the x-ray photographs showed no lines; evidently too little crystalline material was present. In Fig. 5 and Table 2 the inversion tridymite⇌cristobalite is considered to be 1470° C.

Particularly well developed lath-shaped primary crystals of norbergite (together with characteristic sellaite dendrites in the matrix) are seen in Fig. 7.

Chondrodite crystals with many inclusions of periclase grains are observed in Fig. 8, and euhedral chondrodites surrounded by a fringe of quenched material in a glass in Figure 9.

A mixture of the composition of a hypothetical magnesium-amphibole ($6MgO \cdot MgF_2 \cdot 8SiO_2$) was heated to 1315° and 1614° C., but no new phases could be found.

No compositions near, or in, the field of liquid immiscibility on the side $MgO-SiO_2$ was investigated.

Summary

In a part of the system MgO-MgF$_2$-SiO$_2$ the liquidus points were determined. For this purpose dynamic and static methods were applied. The identification of the crystalline phases was undertaken by the microscopic investigation of thin sections, by determination of the refractive indices, and by the x-ray diffraction method.

The position and temperature of the eutectics, incongruent melting points and reaction points were as far as possible determined.

The join Mg$_2$SiO$_4$-MgF$_2$ proved to be a binary system, where the humite-minerals norbergite and chondrodite appear as incongruently melting compounds. Neither here nor in the three-component system could humite and clinohumite be obtained as products of crystallization. No further compounds could be found.

References

1. Eitel, W., (1937), Das System CaO-CaF$_2$-Ca$_2$SiO$_4$: *Z. angew. Mineral.* **1**, 269–284.
2. Bååk, T. and Ölander, A., (1955), The system CaSiO$_3$-CaF$_2$: *Acta Chem. Scand.* **9**, 1350–1354.
3. Bowen, N. L. and Andersen, O., (1914), The binary system MgO-SiO$_2$: *Amer. J. Sci.*, 4 Ser., **37**, 487–500.
4. Greig, J. W., (1927), Immiscibility in silicate melts: *Amer. J. Sci.* 5 Ser., **13**, 1–44.
5. Eitel, W., Hatch, R. A. and Denny, M. V., (1953), Synthetic mica investigations II. Role of fluorides in mica batch reactions: *J. Amer. Cer. Soc.* **36**, 341–348.
6. Rankama, K., (1947), Synthesis of norbergite and chondrodite by direct dry fusion: *Am. Mineral.* **32**, 146–157.
7. Karyakin, L. I. and Gul'ko, N. V., (1954), Formation of Cuspidine and of the Minerals of the Humite Group: *Dokl. Akad. Nauk SSSR*, **96**, 581–584.
8. Valkenburg, A. van, (1955), Synthesis of the humites: *Amer. Miner.* **40**, 339.
9. Fujii, T. und Eitel, W., (1957), Reaktionen im festen Zustand im System MgO-MgF$_2$-SiO$_2$: *Radex-Rdsch.* 1957, 445–469.
10. Günther, K.-G., (1958), Zur Messung von Dampfdrucken und Verdampfungsgeschwindigkeiten an glasbildenden Substanzen: *Glastechn. Ber.* **31**, 9–15.
11. Counts, W. E., Roy, R. and Osborn, E. F., (1953), *Fluoride model systems. II.* The binary systems CaF$_2$-BeF$_2$, MgF$_2$-BeF$_2$ and LiF-MgF$_2$: *J. Amer. Ceram. Soc.* **36**, 12–17.
12. Sahama, T. G., (1953), Mineralogy of the humite group: *Ann. Acad. Sci. Fenn.*, Ser. A, III, Nr. 31.
13. Shell, H. R. and Craig, R. L., (1954), Determination of silica and fluorides in fluorsilicates: *Anal. Chem.* **26**, 996–1001.
14. Thomas, F., (1959), Beiträge zur Bestimmung der Kieselsäure in Fluorsilikaten: *Silikattechnik* **10**, 129–130.
15. Venturello, G., (1940/41), Studio termico-roentgenografico del systema BeF$_2$-MgF$_2$: *Atti reale Accad. Sci.*, Torino, **76** I, 556–565.