THE SYSTEM CaF_2-$CaMgSi_2O_6$

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By

SZU-BIN LIN, B.Sc.

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AUTHOR: Szu-Bin Lin, B.Sc. (National Taiwan University)

SUPERVISOR: Professor B. J. Burley

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SCOPE AND CONTENTS: The equilibrium diagram of the system CaF_2-$CaMgSi_2O_6$ at atmospheric pressure has been constructed by the quenching method. Some special features have been discussed, and the significance to geology and Portland cement manufacturing have been considered.

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ABSTRACT

The melt equilibria of the system CaF_2-$CaMgSi_2O_6$ has been studied at atmospheric pressure by using a modified quenching method. This system is characterized by a simple binary eutectic at CaF_2 43.4, $CaMgSi_2O_6$ 56.5 weight percent at 1082± 2°C; neither solid solution nor intermediate compound was found. Some special features have been discussed in detail.

The results of the study of the system CaF_2-$CaMgSi_2O_6$, together with suppositions regarding the system CaF_2-$CaMgSi_2O_6$-$CaCO_3$, have tentatively been applied to a hypothesis regarding the origin of certain skarns which are considered to be formed by differential melting of impure limestone in regional metamorphic terrains. The applications of this binary system to the theoretical chemistry of Portland cement burning is also incidentally considered.

I. INTRODUCTION

Salt-containing systems have been receiving increasing attention by geologists concerned with models of igneous and metamorphic rocks at temperatures at or near the liquidus, and also by industry, because many minerals can be recrystallized in salt melts. Thus, it is a matter of interest to ascertain the melting equilibria of the binary system CaF_2-$CaMgSi_2O_6$, not only from a purely scientific point of view, but also from its bearing on certain geological features, and incidentally on problems of Portland cement burning.

The basic objective of the study presented here was to construct a precise phase diagram of melt equilibria of the system CaF_2-$CaMgSi_2O_6$. Further, it was tentatively intended to try to evaluate the condition of formation of natural mineral assemblages occurring in certain categories of so-called Skarn rocks. Recently, there is an increasing tendency to propose, both from field evidence and from experimental study, that many pegmatites, especially those present in strongly metamorphosed terrains, and also limestone-contact skarns, may be formed by partial melting or anatexis. An attempt has been made in the present thesis to determine whether certain categories of the so-called skarns in the Grenville province might be formed by partial melting of impure limestone as a result of crustal depression.

The present system can be thought of as a binary join within the quaternary system CaO-MgO-SiO_2-CaF_2, which is important to the theoretical chemistry of the Portland cement industry. The bearing of this system on this problem is also incidentally and briefly considered.

II. PREVIOUS RELATED STUDIES

Little has been done on the phase equilibria of the fluoride-silicate systems. So far, most of the investigations of fluoride-containing systems were conducted for industrial interests, and limited to within systems of the type oxide-fluoride-SiO_2, and the type fluoride-fluoride. Only a few systems of geological significance have been studied.

The ternary system CaO-CaF_2-SiO_2 has been studies in detail because of its importance to the Portland cement industry (Brisi, 1957; Eitel, 1938). The binary system CaO-CaF_2 has been investigated by Eitel (1938) and found to be a simple eutectic, and later revised by Bååk (1954) to show the existence of liquid immiscibility on the CaF_2-rich side of the phase diagram. The system CaO-Ca_2SiO_4-CaF_2 was also investigated by Eitel (1938), and only the initial components and tricalcium silicate (Ca_3SiO_5) were present as primary phases, and no ternary compound was observed. The binary system $CaSiO_3$-CaF_2 within the ternary system CaO-CaF_2-SiO_2 is the analogous system to the binary system $CaMgSi_2O_6$-CaF_2. It was studied in 1910 by Krandeeff and in 1955 by Bååk and Ölander. The former used the method of thermal analysis and found the system to be a simple binary with an eutectic at 48 mole per cent CaF_2 and 1130°C, while the latter used the method of electric conductivity and generally confirmed the result of the former, but the eutectic was given at 59 mole per cent CaF_2 at 1127°C.

However, Bergman and Bychkova (1955) claimed to have identified a ternary compound of the presumed composition $2CaSiO_3 \cdot CaF_2$. on the join CaF_2-$CaSiO_3$ of the system CaO-CaF_2-SiO_2. Brisi (1957) studied the role of cuspidine ($3CaO \cdot 2SiO_2 \cdot CaF_2$) in the system CaO-SiO_2-CaF_2 and definitely denied the existence of fluorosilicates in the partial system $CaSiO_3$-CaF_2, but found that cuspidine was also easily formed by secondary reactions in solid mixtures of the subsystem $CaSiO_3$-CaF_2 and in ternary mixtures of these with free SiO_2 if heated in open crucibles.

Another chemically analogous system is the section $MgSiO_3$-CaF_2 in the ternary system MgO-CaF_2-SiO_2, which was studied by A. S. Berezhnoi (1951) for its significance in manufacturing forsterite refractories. It is a pseudobinary eutectic system with incongruently melting $MgSiO_3$. The partial systems MgO-CaF_2 and Mg_2SiO_4-CaF_2 do not chemically interact.

The liquidus relations of the system CaF_2-$Ca(OH)_2$-$CaCO_3$ at 1000 bars total pressure was studied by Gittins and Tuttle (1964) in order to evaluate the influence of fluorine on the intrusion temperature of carbonatites. The three bounding two-component systems are, or are very close to simple binary eutetics. The CaF_2-$Ca(OH)_2$-$CaCO_3$ system is ternary except for compositions near $CaCO_3$ at high temperatures. No other compound was observed and the system has an isobaric ternary eutectic at $CaF_2$19, $Ca(OH)_2$45, $CaCO_3$36 in weight per cent at a temperature of 575°C.

The system CaF_2-BeF_2 was investigated by W. E. Counts, R. Roy, and E. F. Osborn (1953) as a model of the system ZrO_2-SiO_2 on the basis of the "model" principle of Goldschmidt.

III. EXPERIMENTAL METHODS

A modified quenching method was used for this study. Various mixtures of synthetic crystalline diopside and calcium fluoride were heated in sealed platinum tubes, at temperatures of 1000°C to 1270°C and then quenched with water or air. The resulting products were examined by optical methods and X-ray diffraction.

A) Synthesis of Diopside:

The mixture for the synthesis of diopside was prepared from analytical-grade reagents. The ingredients of this mixture were:

SiO_2: Precipitated silicic acid, H_2SiO_3-nH_2O, was dehydrated at 2500°F (1370°C) for three hours in a graphite crucible. The resulting SiO_2 was ground to pass a 200-mesh screen. The water content was determined by chemical analysis to be below the limit of detecting, and the absence of long-range structural order was determined by X-ray diffraction. The total impurities of the Fisher Certified Reagent silicic acid was stated to be less than 0.07%.

$CaCO_3$: Calcium carbonate ("Analar" from British Drug House L.T.D.) was used as a source of CaO, and was stated to contain $CaCO_3$ not less than 99%. It was supplied as a very fine powder which passed the 200-mesh screen.

MgO: Magnesium oxide (Fisher Certified Reagent; impurities stated as less than 0.6%) was used. It was an exceedingly fine powder, quite easily passing through the 200-mesh screen.

All of the above three reagents were dried in the oven, ground together in the correct stoichiometric proportions, and mixed thoroughly by means of manual and mechanical methods. The resulting mixture was placed in a platinum crucible, which was in turn placed in a larger graphite crucible and segregated from the latter by a layer MgO. The crucible was directly heated to 1500°C in half an hour, and kept for one hour in an induction furnace. The mixture fused and then was held at about 1300°C for one hour; it was subsequently cooled slowly to room temperature over a period of one hour, in order to allow sufficient time for crystallization. The loss of weight after firing was found to be in agreement with the expected weight loss of CO_2 from breakdown of $CaCO_3$. After cooling, the oxides in the Pt crucible became a compact, milky white, crystalline mass. When broken, complete cleavage fragments bounded by (110)($1\bar{1}0$) was often formed.

The synthetic diopside thus formed was investigated by optical methods and the X-ray diffraction powder method. The properties of this synthetic diopside will be described in the next chapter.

B) <u>Preparation of Charges</u>:

The starting materials used in this study consisted of synthetic crystalline diopside and A. R. grade calcium fluoride, the end members of this binary system. Calcium fluoride from Fisher Scientific Company was a white, exceedingly fine powder, easily passing a 250-mesh screen. The diopside was pulverized to pass a 200-mesh screen. Both were dried at 110°C over several days before mixing to prepare the starting mixtures of each composition, ranging from $D_{10}F_{90}$ to $D_{85}F_{15}$.

Batches of each composition were prepared by weighing out different proportions of CaF_2 and $CaMgSi_2O_6$ on a four-place analytical balance. The weighed materials were ground under acetone in an agate mortar. After evaporation of the acetone, each mixture was transferred to a small glass bottle, which was then kept in an oven at 110°C for use.

The platinum cylinders of 0.30 and 0.15mm thickness, with I. D. of 2.5mm and a length of 25mm, were crimped at one end and sealed by arc-welding. After being filled with starting mixtures weighing about 0.04gm, the capsules were flattened to displace excess air, and the open end crimped and welded in order to suppress the tendency of volatilization of calcium fluoride.

It should be noticed that care was taken not to flatten the capsules excessively; too much distortion of platinum capsules resulted in open cracks, or in lines of weakness which opened at the temperatures of reaction, with subsequent leakage of the contents.

In order to ascertain whether or not equilibrium was being obtained, some fused glasses of the starting mixtures were used as starting materials.

C) Quenching Method:

The quenching method was employed throughout this study. By this method the charge is instantly chilled from the temperature of the furnace to approximately that of the room. Any liquid present at the temperature of the run is normally quenched into a glass, and the crystals in equilibrium with liquid become crystals embedded in glass.

All the experiments were performed in a furnace ("Sentry Electric Furnace", Model V) with two horizontally arranged silicon-carbide heating elements, and one horizontally arranged mullite tube having a tapered end. This furnace had a working temperature limit of about 1300°C. Therefore, experimental work was limited to temperatures up to 1270°C. The temperature of the furnace was manually controlled with the aid of a time-proportioning controller (Automatic Timing and Controls Inc.). The temperature was kept constant at about ±2 to 3°C, and was measured with a platinum-platinum, 13% rhodium thermocouple, using both a thermocouple potentiometer ("CROPICO" Type P. 4), and an X-Y recorder (Hewlett-Packard Company, Model 2D-2). The thermocouple was calibrated periodically with the melting point of gold (1063°C). Temperatures reported for individual runs are believed to be accurate to ±2 or 3°C.

The charges were placed in a suitable container, which was connected with the insulating tube of the thermocouple, and the hot junction placed as near as possible to the charges. The container was put into the furnace, which was usually pre-heated to the required temperature and held at constant temperature generally for a period of two to four hours before quenching. All charges were heated and quenched in air at atmospheric pressure.

After the heat treatment, the samples were removed as quickly as possible from the furnace and quenched immediately. Some of the charges were quenched with air, but most were quenched with water, with more satisfactory results.

It should be mentioned that the total time required for removing a charge from the furnace and quenching it to room temperature should be less than three seconds, especially for charges of fluorite-rich compositions. Otherwise, the fluorite will very rapidly crystallize from the melt, since calcium fluoride is well-known to crystallize very rapidly. The results of different quenching rates will be contrasted later.

In general, two to four hours of reaction were found to be enough to obtain equilibrium. For charges near the phase boundaries, longer running times were required to obtain equilibrium. The duration of the run was varied in some cases as a test for attaining equilibrium (as a check on the liquidus temperature). Reaction was also effected in both directions. Glasses were produced, in charges heated slightly above the liquidus, which were subsequently examined by petrographic microscope and X-ray diffraction. These glasses were again sealed into capsules, and heated to temperatures slightly below the liquidus.

The charge was weighed on the same analytical balance, both before placing in the furnace and after quenching, to detect any discrepancy of weight. A nearly constant, but insignificant loss of weight occurred most of the time, of the order of less than one per cent.

Runs with greater weight loss than 1%, or which failed to be quenched within three seconds, were normally not used for constructing the phase diagram.

D) Identification of Products:

The resulting products of quenched charges were examined under a binocular microscope, then crushed under acetone in an agate mortar, and studied in immersion oils with the petrographic microscope. When necessary, the X-ray powder method using a Norelco High Angle Diffractometer with filtered Cu Kα radiation was used for identification purpose. Standard X-ray powder diffraction patterns of the pure end members were first prepared, using α-quartz as internal standard, for comparison with the patterns of the products. An electron probe was also employed in some cases to differentiate between fluorite and glass, and to detect the possibility of solid solution of fluorite.

The equilibrium products of each experiment were composed of one of the following assemblages: diopside and fluorite, diopside and glass, fluorite and glass, or glass alone. The diopside was fairly readily distinguished from fluorite and glass by means of a petrographic microscope, because diopside exhibits strong birefringence, and the distinction was confirmed by X-ray powder diffraction patterns.

However, at the initial stage of identification, isotropism and lack of color made the distinction between fluorites and glasses somewhat difficult. Moreover, their grain size was too fine to permit them to be separated from each other for individual analysis. Therefore, an electron probe was used to determine the local composition of the products, to supplement the examination by optical methods and

X-ray diffraction.

Fluorite has occurred in several habits in the quenched products. Liquids of the CaF_2-rich side can not be completely quenched into glass; secondary fluorite crystallized from liquids during the quenching. In fast quenching, fluorite occurred as submicroscopic, brown nuclei unevenly dispersed in glass (Plate 7), while in slow quenching, it occurred as dirty, minute aggregates dispersed in glassy matrix (Plate 8); both kinds of fluorite were readily identified by X-ray diffraction.

In all the CaF_2-rich runs that were heated at temperatures above the solidus and just below the liquidus, there was seen under the petrographic microscope, many clear, colorless, isotropic globules embedded in a relatively cloudy, isotropic matrix in which the brown, secondary fluorite nuclei described above were unevenly dispersed. At first sight, these globules were thought to be glass representing the result of liquid immiscibility, but actually, the X-ray diffraction patterns of these runs are exactly the same patterns as the pure calcium fluoride, and the refractive index of these globules were also determined to be that of calcium fluoride (1.434). To further clarify this point, electron probe analyses were taken. The result is that all the globules contain Ca, but not Si and Mg, while the matrix contains Ca, Si, and Mg, (Plates 15 to 18). Summarizing these observed facts, it can be concluded that those globules are pure fluorite, while the matrix is glass.

Primary fluorite and diopside, in runs heated below the temperature of the solidus, i.e., the temperature of the eutectic in this system, maintain their original shape during the quench, and all silicate-rich liquids quenched to clear glass. These products were readily identified with petrographic microscope and X-ray diffraction (Plates 11 & 12).

IV. EXPERIMENTAL RESULTS

A) Properties of Synthetic Diopside:

i) Optical properties--Megascopically, the diopside cleavage fragments were dense, homogeneous, translucent, milky-white in color, and with sub-vitreous luster. Petrographic study of then sections showed that the synthetic product was composed of well-crystallized aggregates, with an individual average size of several millimeters. The individual crystals commonly, with four-or eight-sides cross sections, developed a good cleavage parallel to (110) and (1$\bar{1}$0). There were therefore two directions at angles of 87° and 93°; a parting parallel of (010) or (100) was also developed (Plates 1 & 2). The mineral was colorless and non-pleochroic. The refractive indices were determined to be $\alpha=1.664$, $\beta=1.672$ and $\gamma=1.694$, by use of immersion methods with sodium light. Its birefringence was rather strong, and the maximum interference color was about upper second order. The optical sign was positive and the optical angle (2V) was 60°, determined on a universal stage. The maximum extinction angle, $C \wedge Z$, was found to be 40°.

ii) X-ray properties--The powder diffraction patterns match very closely those of other synthetic and natural diopsides reported and filed in the A.S.T.M. Card Index*, and were satisfactorily indexed through comparison with them.

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*American Society for Testing Materials, Card Index File of X-ray Diffraction Data.

Table 1 shows their interplanar spacings and relative intensities estimated from peak height. An X-ray diffraction tracing of the synthetic diopside is shown in Fig. 1.

iii) Chemical composition--A chemical analysis was carried out by J. Muysson in the Rock Analysis Lab., McMaster University. The results are: SiO_2=54.19, MgO=18.88, CaO=25.88, others=1.05 in weight percent.

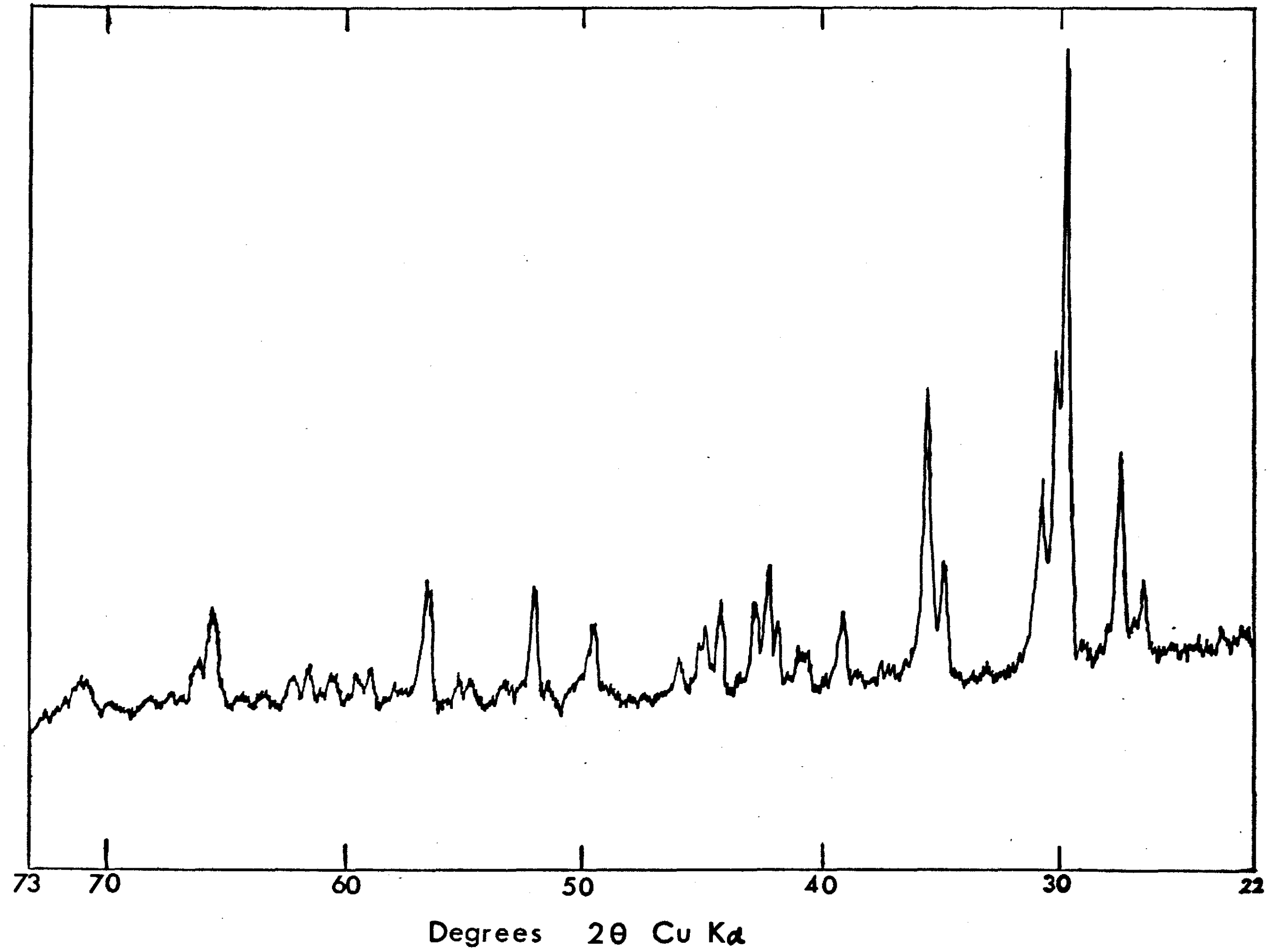

Fig. 1. X-ray diffraction tracing of synthetic diopside. Instrument settings: CuKα radiation at 30Kv, 15ma; 1° divergence slit, 0.003" receiving slit; scale factor 4, multiplier 1.0, time constant 8 sec.; scan speed 1°/min; chart speed 1/8"/min.

TABLE 1

X-ray powder data for synthetic diopside

(hkl)	A.S.T.M. Natural	11-654* diopside	A.S.T.M. Synthetic	3-0860** diopside	Diopside of Present work	
	dA	I/I	dA	I/I	dA	I/I
200	4.69	1				
020	4.47	3				
$11\bar{1}$	4.41	3				
111	3.66	3				
021	3.35	11	3.35	10	3.34	12
220	3.23	25	3.23	20	3.23	45
$22\bar{1}$	2.991	100	3.00	80	2.99	100
310	2.952	25	2.96	10	2.95	50
$31\bar{1}$	2.893	30	2.90	40	2.89	43
130	2.837	1				
$13\bar{1}$	2.566	20	2.57	10	2.564	20
002,$20\bar{2}$	2.528	40	2.53	100	2.515	53
112,221	2.518	30			2.508	55
131	2.392	3			2.385	8
311	2.304	15	2.30	10	2.295	12
112	2.218	13	2.21	10	2.210	8
022,$22\bar{2}$	2.200	11	2.20	10	2.194	9
330	2.157	9	2.15	10	2.149	12
$33\bar{1}$	2.134	15	2.13	20	2.130	20
$42\bar{1}$	2.109	7	2.10	10	2.103	8
420	2.077	1				
041	2.043	13	2.04	20	2.038	20
$40\bar{2}$	2.016	9			2.012	11
202	2.009	9	2.01	10	2.008	17
$13\bar{2}$	1.970	7	1.97	10	1.964	9
331	1.862	3				
510,$42\bar{2}$	1.838	5			1.833	10
222	1.832	3	1.83	10	1.829	14
132	1.815	3				
421	1.777	1				
150	1.755	11	1.75	20	1.751	18
$51\bar{2}$	1.720	1				
$11\bar{3}$,312	1.713	1				
$15\bar{1}$	1.685	1				

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* Mineral from Schwarzenstein, Zillerthal, Tyrol.

** Ref. Clark, C.B., J. Am. Ceram. Soc., 29, 25 (1946).
First and second firing; heated 3 hrs to 1300°C, and held 5 hrs.

TABLE 1 (continued)

(hkl)	A.S.T.M. Natural 11-654* diopside		A.S.T.M. Synthetic 3-0860** diopside		Diopside of Present work	
	dA	I/I	dA	I/I	dA	I/I
042,24$\bar{2}$	1.674	5	1.67	10	1.67	5
31$\bar{3}$	1.659	5	1.66	10	1.651	5
22$\bar{3}$,53$\bar{1}$	1.625	25	1.62	60	1.622	25
440	1.618	5	1.61	10		
530	1.588	3				
600	1.564	3	1.56	10	1.560	8
550	1.551	3	1.55	10	1.550	9
60$\bar{2}$	1.529	1				
402,62$\bar{1}$	1.526	9	1.53	10	1.524	10
13$\bar{3}$	1.504	11	1.50	10	1.499	9
242	1.494	1				
060	1.488	3	1.49	10	1.485	8
33$\bar{3}$	1.468	1				
441	1.463	1				
513	1.447	3				
531	1.424	13	1.42	40	1.420	22
35$\bar{2}$	1.410	7	1.41	20	1.407	9
223	1.391	3				
243	1.374	1				
043	1.345	1				
712	1.330	7	1.33	10	1.328	9
512,710	1.327	3				
53$\bar{2}$	1.317	3			1.317	5
11$\bar{4}$,62$\bar{3}$	1.288	7	1.29	10		
26$\bar{2}$,062	1.282	7				
461,004	1.265	5	1.26	10		
352,153	1.249	3	1.24	10		

B) The System CaF_2-$CaMgSi_2O_6$:

i) General statement--The system CaF_2-$CaMgSi_2O_6$ was binary, simple eutectic, as shown in Fig. 2, drawn from data of quenching experiments, listed in Table 2. The eutectic has the composition CaF_2 43.5, $CaMgSi_2O_6$ 56.5 weight per cent at 1082±2°C. Neither appreciable evidence of solid solution nor any indication of a new compound was observed.

ii) Liquidus--Quenching experiments were made with compositions ranging from $F_{15}D_{85}$ to $F_{90}D_{10}$. For compositions richer in CaF_2 than $F_{70}D_{30}$ and less than $F_{15}D_{85}$, liquidus temperatures cannot be attained with the present apparatus. The liquidus curve was extended by extrapolation to the expected melting points of the end members of this binary system. Petrographic study, X-ray diffraction study and electron probe analysis showed no indication of solid solutions or new compounds.

All the liquids of the diopside-rich side were quenched into clear glass (Plate 3). With addition of CaF_2, the liquid became more difficult to quench into clear glass, and once the liquid was richer in CaF_2 than that of the eutectic composition, crystallization of fluorite from the liquid began during quenching within three seconds. Therefore, when the composition of the fluorite-rich liquid became richer in CaF_2, the sub-microscopic brown nuclei of fluorite which were a product of non-quenchable crystallization, became increasingly visible in the quenched glass, which, in turn, became browner in appearance under the microscope, and megascopically more white and less transparent (Plates 4 & 7). The same phenomenon occurs on a line of constant composition when the temperature of the run is reduced. This is only true, of course, for runs above the liquidus. Glass with a composition richer in CaF_2 than 55%, exhibits spherulitic structure (Plates 5 & 6, 19-22).

As mentioned before, if the length of quenching time is more than three seconds, the brown nuclei of fluorite increase in size quickly into minute, colorless particles dispersed in aggregates in glass; and the whole product, under the microscope, becomes grayish and dirty, due to the difference of the refractive indices of glass and fluorite (Plate 8).

Under the microscope, the fluorite of primary crystallization is characterized by the formation of clear, large, globular grains which were embedded in glass during quenching (Plates 9 & 10), while primary diopside preserved within the clear glass, mostly showed prismatic habit, but some maintained their angular shape (Plates 11 & 12).

When fused glasses were used as starting materials for checking the liquidus temperatures, diopside recrystallized as clusters of prismatic crystals within glass (Plates 13 & 14), and spherical fluorite also formed within glass, as a primary crystallization.

iii) Subsolidus: No glass phase was detected in this system at termperatures lower than 1082±2°C. Below this temperature fluorite and diopside maintained their original shape, if the solidus was approached from a lower temperature, or conversely, they crystallized together from glass, when the solidus was approached from a higher temperature. New compounds such as cuspidine-like phases, was not encountered in this current investigation. However, the systematic study of solid state reactions in this system in open air has not been done.

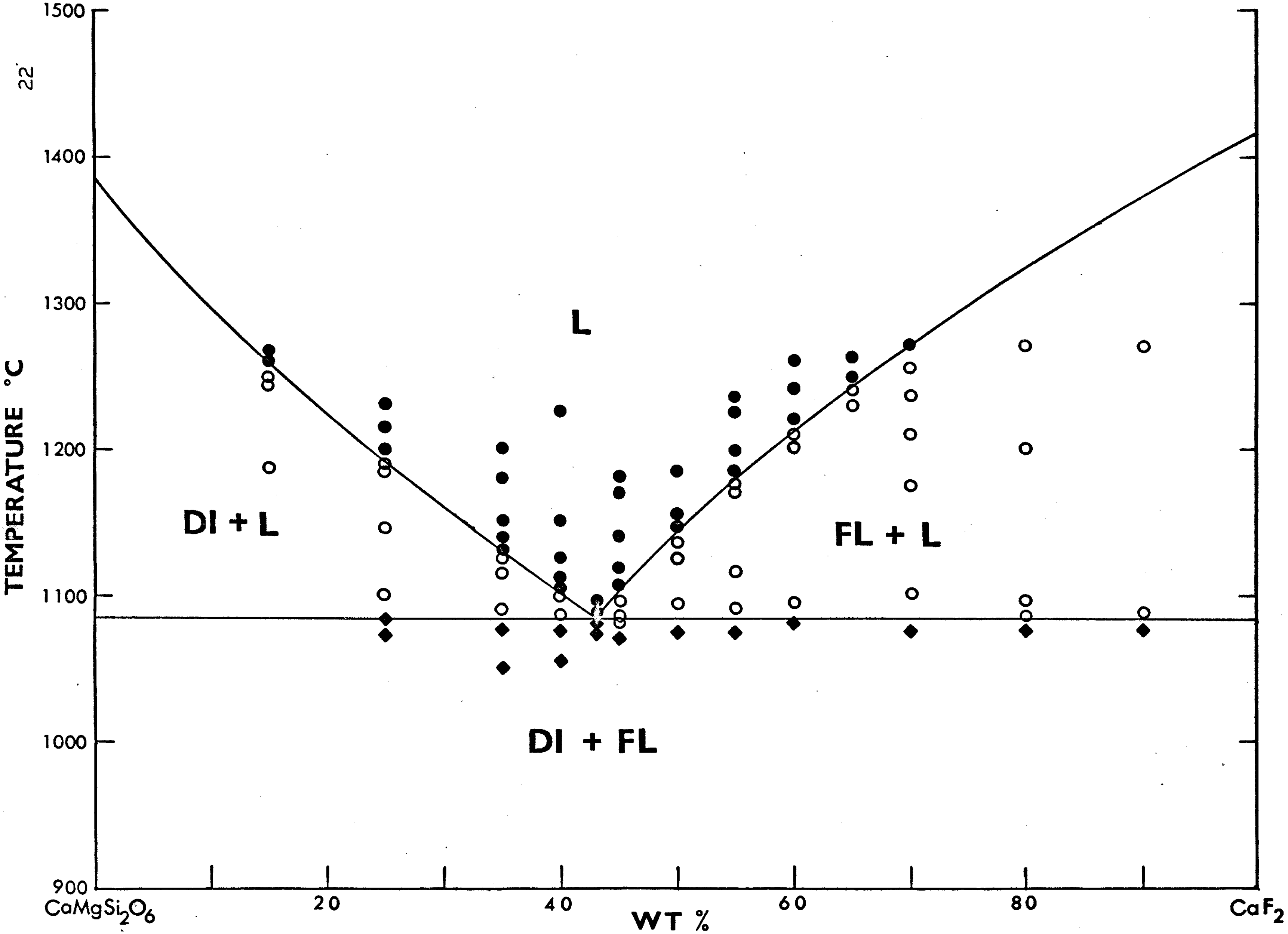

Fig. 2. Equilibrium diagram of the binary system CaMgSi$_2$O$_6$ — CaF$_2$. DI = Diopside, FL = Fluorite, L = Liquid.

TABLE 2

CaF_2-$CaMgSi_2O_6$

EXPERIMENTAL RESULTS

(L=Liquid, F=CaF_2, D=$CaMgSi_2O_6$, vm=very minor, m=minor)

	Composition					
No.	CaF_2 (weight percent)	$CaMgSi_2O_6$	Temperature (°C)	Time (Hr.)	Phase	Remark
1	90	10	1270±2	1	L+F	
2	90	10	1085±2	2	L+F+D	
3	90	10	1075±2	4	F+D	
4	80	20	1270±2	2	L+F	
5	80	20	1200±2	2	L+F	
6	80	20	1095±3	3	L+F	
7	80	20	1085±2	2	L+F+D	
8	80	20	1075±2	4	F+D	
9	70	30	1070±2	2	L	
10	70	30	1255±2	2	L+F	
11	70	30	1235±2	2	L+F	
12	70	30	1210±2	4	L+F	
13	70	30	1175±2	4	L+F	
14	70	30	1100±2	4	L+F+D(vm)	
15	70	30	1075±2	8	F+D	
16	65	35	1262±3	2	L	(Palladium added)
17	65	35	1250±3	2	L	
18	65	35	1240±3	2	L+F(vm)	
19	65	35	1230±3	2	L+F	
20	60	40	1260±3	5	L	
21	60	40	1240±3	2	L	
22	60	40	1220±2	4	L	
23	60	40	1210±2	2	L+F	
24	60	40	1200±2	2	L+F	(Fused glass of No. 22 as starting material)
25	60	40	1095±2	3	L+F	
26	60	40	1080±3	4	F+D+L	
27	55	45	1235±2	2	L	
28	55	45	1225±2	2	L	
29	55	45	1200±2	2	L	
30	55	45	1185±2	2	L	

TABLE 2 (continued)

No.	Composition CaF_2 (weight percent)	 $CaMgSi_2O_6$ 	Temperature (°C)	Time (Hr.)	Phase	Remark
31	55	45	1182±2	2	L(vm)	
32	55	45	1175±2	2	L+F	
33	55	45	1170±2	2	L+F	
34	55	45	1115±2	2	L+F	
35	55	45	1090±2	2	L+F	
36	55	45	1073±2	5	F+D	
37	50	50	1185±2	4	L	
38	50	50	1155±2	2	L	
39	50	50	1145±2	2	L	
40	50	50	1135±2	2	L+F	
41	50	50	1125±2	2	L+F	
42	50	50	1095±2	2	L+F	
43	50	50	1095±3	2	L+F	(Palladium added)
44	50	50	1075±3	4	F+D	
45	45	55	1182±2	4	L	
46	45	55	1170±2	4	L	
47	45	55	1140±2	2	L	
48	45	55	1118±2	4	L	
49	45	55	1105±2	2	L	
50	45	55	1102±2	2	L+F(vm)	
51	45	55	1095±2	2	L+F	
52	45	55	1085±2	2	L+F+D(vm)	
53	45	55	1080±2	4	F+D+L(vm)	
54	45	55	1070±2	4	F+D	
55	43.5	56.5	1095±2	2	L	
56	43.5	56.5	1085±2	4	L+D(trace)	
57	43.5	56.5	1080±2	4	L+F+D	
58	43.5	56.5	1075±2	4	F+D	
59	40	60	1225±2	4.5	L	
60	40	60	1150±2	2	L	
61	40	60	1125±2	2	L	
62	40	60	1110±2	8	L+D(trace)	
63	40	60	1105±2	2	L+D(vm)	
64	40	60	1100±2	2	L+D	
65	40	60	1085±2	2	L+D+F	

TABLE 2 (continued)

No.	Composition (weight percent)		Temperature (°C)	Time (Hr.)	Phase	Remark
	CaF$_2$	CaMgSi$_2$O$_6$				
66	40	60	1075±2	4	F+D	
67	40	60	1055±2	2	F+D	
68	35	65	1200±2	10	L	
69	35	65	1180±2	5	L	
70	35	65	1150±2	2	L	
71	35	65	1137±2	4	L	
72	35	65	1130±2	4	L+D(vm)	
73	35	65	1125±3	4	L+D	
74	35	65	1115±2	4	L+D	
75	35	65	1090±2	2	L+D	
76	35	65	1075±3	4	F+D	
77	35	65	1050±10	8	F+D	
78	25	75	1230±2	2	L	
79	25	75	1215±2	2	L	
80	25	75	1200±3	4	L	
81	25	75	1190±2	4	L+D	
82	25	75	1184±3	4	L+D	(Fused galss of No. 79 as starting material)
83	25	75	1184±3	2	L+D	(Reheated the products of No. 84)
84	25	75	1148±2	4	L+D	
85	25	75	1100±3	4	L+D	
86	25	75	1085±2	4	F+D+L(m)	
87	25	75	1075±3	4	F+D	
88	15	85	1265±2	4	L	
89	15	85	1260±3	5	L	
90	15	85	1250±2	4	L+D	
91	15	85	1245±5	5	L+D	
92	15	85	1187±5	16	L+D	

V. DISCUSSION

A) Efficiency of the Experimental Method:

It is well known that normal quenching methods (Rankin & Wright, 1915) and hydrothermal quenching methods are not suitable for determinations of quenching temperature in rapidly crystallizing systems, such as the CaF_2-rich mixtures, but are suitable for temperature determinations in slowly crystallizing systems, such as the viscous silicate-rich mixtures. By contrast, the method of thermal analysis (County, Roy and Osborn, 1953) and the method of electric conductivity are not accurate for temperature determinations in silicate-rich mixtures, but are accurate for that in CaF_2-rich mixtures (Bääk and Ölander, 1955). Therefore, normal quenching methods and hydrothermal quenching methods are not satisfactory in the present system $CaMgSi_2O_6$-CaF_2, especially on the CaF_2-rich side, because CaF_2 glass is non-quenchable, and the products of CaF_2-rich mixtures become blurred and confused (Plate 8). If the quenching method is modified, however, and improved as mentioned before, so that a sample is quenched from running temperature to room temperature within three seconds, then the mixture of the same composition can be quenched into a glass containing brown nuclei of CaF_2 (Plates 7 & 8). Moreover, the methods of thermal analysis and electric conductivity are inaccurate not only for the silicate-rich side of this system, due to the undercooling of the silicate-rich liquids, but also for the

CaF_2-rich side of this system, due to the volatilization of CaF_2 in open air (Count, Roy and Osborn, 1953). Therefore, a modified quenching method combined with suitable technique of identification is still ideal for studying the phase relation of the system $CaMgSi_2O_6$-CaF_2.

B) Volatilization of Calcium Fluoride:

The weight loss due to volatilization of CaF_2 when crystalline mixtures of CaF_2-containing systems are heated at high temperatures in the open air, has been reported widely in the literature (Brisi, 1957, Count, Roy and Osborn, 1953); hence, experiments often have to be carried out in closed platinum containers. The nature and mechanism of the volatilization of CaF_2 in these mixtures is still not understood well, and it seems to be not simple volatilization. The formation of SiF_4 and/or reactions with the oxygen from air and/or moisture are reportedly involved (Brisi, 1957; Hinz & Kunth, 1960). For example, Brisi (1957) claimed that fluorine was volatilized and replaced by oxygen from air, in addition to the subordinate formation of SiF_4, when crystalline mixtures of the system $CaSiO_3$-CaF_2 were exposed to high temperatures in the open air. As mentioned before, volatilization of CaF_2 also occurred in this study. If the mixture was heated in an open platinum capsule, the mixture partly creeping outside and diopside being left after vaporization of calcium fluoride.

However, the volatilization of CaF_2 is quite easily suppressed by heating the mixture in closed, welded platinum tubing instead of in an open capsule; in this case, only an insignificant weight loss was observed. Even when water poured into the charges during quenching in water through invisible cracks in the platinum tubing, still no significant loss of weight was observed after driving off the water by reheating the charge in an oven at 110°C to a constant weight.

The cause of this nearly constant, insignificant loss of weight was not obvious. It seems to have no apparent relation to original weight, composition of the charge, duration of running, or to quenching, whether with water or air blast. Moreover after the quenched charge was weighed and then put back into the furnace and run again at the original temperature, there was often no further loss of weight. Perhaps like the case of MgF_2, the weight loss may be partly due to the high sensitivity of the fine-grained chemical CaF_2, or even $CaMgSi_2O_6$, to absorb moisture; the mixture may keep surface-absorbed water up to rather high temperatures and release water at higher hemperature (Hinz and Kunth, 1960).

In a study of the system $CaSiO_3$-CaF_2, Bääk and Ölander (1955) also mentioned that no significant loss of fluoride occurred if the components of the mixtures are ignited and cooled before mixing, whereas 3-7% will be lost when melting is performed without first driving off moisture.

As a matter of fact the volatilization of CaF_2 is easily suppressed and the weight loss is not significant. The vapor pressure of CaF_2 at high temperatures should not be high, because CaF_2 is chemically analogous to MgF_2, but with a higher melting point than MgF_2. The vapor pressure of MgF_2 at a temperature of 1282°C is 0.1068 torr

(1torr=1mmHg=0.0013332 bar) which certainly does not have to be taken into account (Hinz and Kunth, 1960). Likewise, the vapor pressure of CaF_2 at high temperature is believed to be so small that it can be neglected in comparison with atmospheric pressure. Therefore, the system $CaMgSi_2O_6$-CaF_2 can be considered to be a condensed system, i.e., a true binary system with no vapor phase to make compositions off the binary join or to shift the original composition of the charge on the binary join. It is not like the (Gittins and Tuttle, 1960) mixtures of $CaCO_3$ and $CaMgSi_2O_6$ which were heated in closed capsules at about 1000°C to 1050°C in a hydrothermal bomb at 1000 Bars. Gas rushed out when these quenched charges were opened. So far, fluoride-containing systems have been widely considered to be condensed system in the literature.

C) Theoretical Calculations

The liquidus curves of the system $CaMgSi_2O_6$-CaF_2 can be calculated on the assumption that only the heat of fusion (ΔH_{fus}, enthalpy of fusion at the melting point) is involved in the change from solid to liquid, because the thermochemical data for $CaMgSi_2O_6$ and CaF_2 are available. The theoretically calculated curves not only can be used as a tentative guide for the experimental determination of the liquidus but also can be used to compare with the experimentally determined curves.

There are several different values of the thermochemical data derived from various sources. The melting point (M.P.) of diopside has been recognized to be 1391°C as a fixed point. Using the method of lowering of freezing point, the heat of fusion (ΔH_{fus}) of diopside has been computed from the system diopside-anorthite and from the system diopside-leucite, and found to be 450 joules per gram and 407 joules per gram respectively; the mean value was taken as 430 joules per gram (Birch et al., 1942). Using this value, a curve of freezing-point depression for diopside, namely the curve (A) in figure 3, was calculated. A direct determination of $^{\circ}H_{fus}$ of diopside by White (1909) gave 106± 15 cal. per gram, i.e., 443±63 joules per gram.

The M.P. and ΔH_{fus} of fluorite were respectively given in the literature to be 1392°C and 220 joules per gram, as a result of computing from the system CaF_2-AlF_3 and CaF_2-$Ca_3(PO_4)_2$ (Birch, et al, 1942). Using these values, we can calculate the curve of freezing point lowering (B) of fluorite in figure 3. However, the true M.P. and ΔH_{fus} of a pure natural fluorite were determined by Naylor (1945), using calorimetry, and found to be 1418°C and 7100 cal. mole. (380.5 joules/gm). Later Bååk (1954) also found the melting point of A. R. chemical CaF_2 to be 1418°C, using the method of electrical conductivity. With these more accurate thermochemical data, curve (C) was calculated and plotted in figure 3. Then the graphic intersections of the pair of lines (A) & (B), and the pair of lines (A) & (C), gave respectively the eutectic points of Eab and Eac.

By comparing with the experimentally determined liquidus, we see that the calculated curves of both (A) & (C) all lie above the determined liquidus curves, but are generally in agreement in tendency

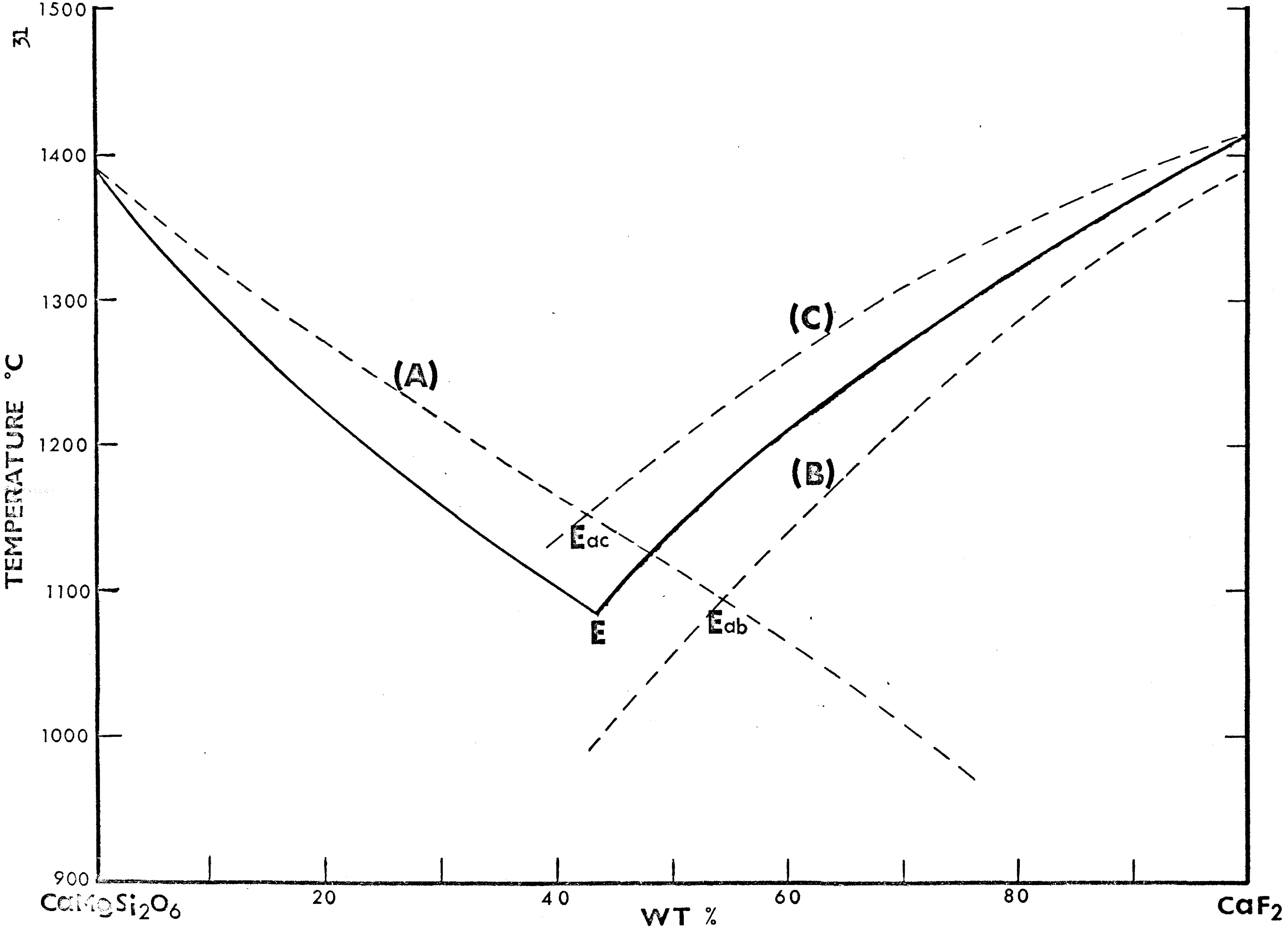

Fig. 3. Comparison of experimentally determined liquidus (solid curve) with theoretically calculated liquidus (dash curve).

of slope. The calculated eutectic Eac ($F_{43}D_{57}$; 1150°C) deviates from the determined eutectic E ($F_{43.5}D_{56.5}$; 1082°C) in temperature, but coincides remarkably in composition. Of course, the deviation of the temperature of the calculated liquidus from that of the determined liquidus is attributable to the heat of mixing of the liquids; and in this case, the molecules of diopside and fluorite mix in the liquid state with evolution of heat. Here, the difference of temperature between Eac and E is about the same order as in the case of the system diopside-anorthite (Bowen, 1915). Therefore, the experimental result can be said to be consistent with the theoretical calculation using Naylor's data.

In contrast to (A) and (C), the calculated liquidus curve (B) lies below the determined liquidus of CaF_2. Consequently, this is inconsistent with the fact that the heat of mixing of diopside and fluorite is exothermic, which requires the experimentally determined liquidus to lie below the theoretically determined liquidus by use of the well-established thermochemical data of diopside. Moreoever, this also gives a eutectic point Eab ($F_{54}D_{46}$; 1095°C) whose composition deviates considerably from the experimentally determined eutectic E. Therefore, these inconsistencies show that the CaF_2 thermochemical data given in the "Handbook of Physical Constants" (G.S.A. Special papers No. 36), i.e., the data used for calculating the curve (B), are not accurate enough, while the accuracy of Naylor's thermochemical data of CaF_2 is indirectly confirmed by the results of this study.

D) Formation of Globules of Calcium Fluoride:

As noted previously, whether the starting materials were a crystalline mixture or glass, the CaF_2 of primary crystallization was characterized by the peculiar formation of clear, round grains which were preserved within the glass after quenching. The physical appearance of two liquids that are immiscible has been discussed in detail by Greig (1927); and the appearance of the isotropic globules enclosed within glass has been recognized as a typical phenomenon exhibited by liquid immiscibility. Nevertheless, all these clear, isotropic globules encountered in this study have been identified to be pure CaF_2 by combined use of the petrographic microscope, the X-ray diffractometer and electron probe; therefore, it should be a solid phase in equilibrium with the coexisting liquid, because the running temperatures were below the melting point of pure CaF_2. This observed fact strongly excludes not only the possibility of the existence of two liquids, but also that of solid solution. In addition, the presence of only one kind of globule (i.e., the absence of another corresponding kind of globule) and the increase in numbers of the same kind of globule when the composition of the charge goes toward the CaF_2 end, were also indications denying the possibility of two liquids. Therefore, the formation of spherical grains of the CaF_2 phase enclosed within the quenched glass is not necessarily a criterion indicating liquid immiscibility.

It is interesting to discuss the nature of the process of the formation of these crystalline globules of CaF_2. Of course, these CaF_2 globules have to grow by concentrating the originally, homogeneously distributed grains of CaF_2 in the starting mixture, or molecular units of CaF_2 in the starting glass. There may be two possible ways to transfer CaF_2 in this system.

If the starting material is the fine-grained, crystalline mixture, the first possible way is that, after the partial melting permitted at that running temperature is completed, the residual grains of CaF_2 migrate themselves perhaps due to a certain kind of attraction, through the melt and toward each common centre, and finally unify together as an enlarged globular cystal; the second possible way is that, after the partial melting is finished, the residual CaF_2 can still be transiently both dissolved in the melt and crystallized out of the melt, and finally crystallized as enlarged globular crystals. In this second way, the residual CaF_2 is transferred by means of molecular or ionic diffusion through the melt medium at the transient interval between being melted into liquid and crystallization from liquid. If the starting material is the fused glass, obviously, the second way described above is the better way; perhaps molecular or ionic diffusion is in effect before the melting of the charge starts. The basic differences between these two ways are: that the residual CaF_2 has been remelted and recrystallized in the second way but not in the first way, and the residual CaF_2 is transferred by means of molecular or ionic diffusion in the second way but not in the first way. The second way is strongly supported by the following observed facts. Under the microscope with the highest magnification, the enlarged globules of CaF_2 were often found to be surrounded by a group of minute, oval granules of CaF_2, looking in appearance like many strings of pearls, converging on it. These minute granules of CaF_2 were much smaller than the original grains of CaF_2 in the starting mixtures, and had no cubic crystal form as did the original CaF_2. Moreover, when these minute granules of CaF_2 were nearer to the enlarged globule of CaF_2, their size became larger and larger. Therefore, although it seems that a residual solid phase should not be melted during running of the starting crystalline mixtures, in fact, the residual CaF_2 in this study has been remelted, transferred by molecular or ionic diffusion and then recrystallized together into an enlarged globular crystal in order to be in equilibrium with the coexisting liquid. Furthermore, in order to confirm this point, palladium was also added to the starting mixtures, and the products showed that palladium was excluded outside the globular crystal of CaF_2.

E) <u>Comparison with Other Analogous Systems</u>:

Comparison among systems of the same type and with chemically analogous substances is also interesting and meaningful. Of special interest here are comparisons with the alkaline earth metasilicate-alkaline earth fluoride joins in the systems: CaO-CaF_2-SiO_2, MgO-CaF_2-SiO_2, MgO-MgF_2-SiO_2, and CaO-MgF_2-SiO_2.

It is interesting to see how the presence of magnesium affects the phase relations in these systems. The system $CaSiO_3$-CaF_2 is a binary, simple eutectic type. The system $CaMgSi_2O_6$-CaF_2 can be thought of as an intermediate system between the system $CaSiO_3$-CaF_2

and the system $MgSiO_3$-CaF_2. The presence of Mg in the system $CaMgSi_2O_6$-CaF_2 still does not change the type of phase diagram of the system $CaSiO_3$-CaF_2, i.e., the types of these two systems still are simple binary eutectics. Likewise, the presence of Mg in the system $MgSiO_3$-CaF_2 still does not change its phase diagram from the simple eutectic type, although it becomes a pseudobinary system (Levin et al., 1964). However, with the total absence of calcium, the pseudobinary system $MgSiO_3$-MgF_2 suddenly becomes quite different with the formation of the intermediate compounds of the humite family. The phase diagram of the system $CaSiO_3$-MgF_2, is not available now, but it might be expected to be a binary, simple eutectic without formation of any new compound or solid solution, according to the results of comparisons of the systems described above. Probably, the most important factor that creates the difference in the phase diagram of these systems, is the great difference between the ionic radii of magnesium (0.66Å) and calcium (0.99Å), although both elements are alkaline earth metals.

F) Effect of Water Pressure:

Before the beginning of the experiments on this dry system, a study of the wet system was first tried, by using hydrothermal bombs. Some tentative runs with the addition of water to the charges have been performed over a composition range near the eutectic, under 1000 bars of P_{H_2O} and at temperatures near 1050°C. All the products were only the initial components, i.e., no fusion occurred at all. Originally, it was hoped to lower the temperature of the solidus down below 1000°C, under 1000 bars water vapor pressure, but this did not occur. Therefore, it can be concluded that the effect of water vapor pressure on the temperature of the eutectic is very slight.

VI. APPLICATIONS

A) Application to the Petrogenesis of Certain Kinds of Skarns:

Diopside is a typical mineral in thermally metamorphosed siliceous limestones and dolomites, and also in some skarns, while fluorite commonly occurs as a vein mineral and also in certain pegmatites, such as granitic pegmatite and pegmatite associated with alkaline rocks. It also occurs in some skarns. However, these two minerals, together with calcite, are the principal minerals present in certain coars-grained skarns which are wide-spread throughout the Grenville province.

Shaw et al. (1963) have made a study of the petrology and geochemistry of the Grenville skarns and have given an interpretation of the origin of the skarns. These skarns are usually found in association with marble, and in regions which have been subjected to high-grade metamorphism. This is indicated by abundant migmatites, pegmatites and granites, and the obliteration of sedimentary features together with the tectonic complexity of the rocks. This indicates that the lower part of the rocks of the Grenville province have been depressed and suffered the highest-grade dynamo-thermal metamorphism and been brought into the zone of anatexis. Meanwhile, the mode of occurrence of the skarns also shows that they are in part metasomatic and in part vein and cavity fillings, often transecting the structures of adjacent rocks. In addition to the processes of in situ metasomatism, metamorphic differentiation and diffusion, it is likely that partial melting, flowage and injection also have to be taken into account in the formation of these skarns.

The skarns concerned, consist mainly of calcium-bearing silicates and calcite with fluorite. From the characteristics of the mineral assemblages of these skarns and their close relationship with marble, it is likely that an impure siliceous dolomitic limestone is the source rock of these skarns, or at least, contribute most of the source materials. Shaw et al. suggested that the skarn-forming fluids were produced by partial remelting of the country rocks by crustal depression of the metamorphic complex into hotter regions. Then the skarn-forming fluids moved upward through fractures and reacted with the cooler country rocks to form skarns.

On the other hand, from experimental investigation of the system $CaO-CO_2-H_2O$, Wyllie and Tuttle (1960) have suggested that partial melting of limestone is likely at igneous contacts, and that impure limestones may be partially melted during high-grade metamorphism. The lowest melting temperature with coexisting calcite-portlandite-liquid-vapor is at 675°C at 1000 bars. The ternary liquid exists in the pressure range 27 to 4000 bars with a minimum temperature from 685°C to 640°C. These values are easily obtainable in the crust of the earth and in the high-grade metamorphic terrain. Fyfe, Turner and Verhoogen (1958) have proposed an upper limit of the granulite facies above 700°C, perhaps of the order of 700° to 800°C, and the range of almandine-amphibolite facies to be from about 500° to near 700° or 750°C. The pelitic assemblages intercalated with the Skarn Series and associated rocks of Grenville province indicate that the metamorphic grade has reached the almandine-amphibolite facies. Therefore, it leaves little reason to doubt that partial melting within the deep region of Grenville province was a highly prevalent process during the high-grade dynamo-thermal metamorphism, but also suggests that, in some cases, skarn may be formed by in situ partial melting perhaps combined with short migration and then by recrystallization, just as the "magmatic" portion of migmatite can arise in place, i.e., the so-called venite.

Furthermore, in addition to those skarns formed as a result of the metasomatic reactions of skarn-forming solutions with country rocks, it would be also probable that, in some cases, the skarn may be just the product of the crystallization of the molten "magma-like" liquids, with very little or no chemical reaction with the country rocks. Here the so-called molten "magma-like" fluid can be thought of as a kind of melt in chemical composition which was simply rich in carbonates with a few subordinate silicates, and approached the normal concept of magma; it also contained abundant volatiles, such as CO_2, Cl_2, F_2, (especially CO_2, in order to keep calcite stable at high temperature), and H_2O, but p-H_2O may not be so predominant as in normal magma. Such skarn-forming fluids migrated and accumulated in low-pressure pods, lenses and veins, and then recrystallized into the coarse grained skarns.

If some skarns belong to the case described as above, then the melting relations in compositions approaching those of skarns will yield information applicable to the problem of genesis of these skarns, just as the phase relations of the system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O which approaches the composition of granites, can be applied to the granite problem. Thus, the minimum melting point of the system whose components are the major mineral phases of the Skarn Series, can approximately represent the minimum temperature of that particular skarn-forming solution, and meanwhile will approximately be equal to temperature of crystallization of the skarn.

The system diopside-fluorite of the present experimental study is one of the bounding binary systems of the ternary system calcite-diopside-fluorite. Calcite, diopside and fluorite together with scapolite are the principal mineral phases present in some categories of the Grenville skarns, i.e., the fluorite skarn, pyroxenite, and pink calcite skarn of Shaw (1963), which are always confined to regions of intense tectonic and migmatitic activity.

As discussed previously, the eutectic temperature of the system fluorite-diopside is 1082±2°C at 1 atmosphere and is very little affected by the presence of a vapor pressure of H_2O, while the eutectic temperature of the system fluorite-calcite is 880±10°C at 1000 bars total pressure (Gittins & Tuttle, 1960). The phase relations of the other bounding binary system calcite-diopside has not been experimentally investigated, but its nature can be inferred from the other related systems and its phase diagram can approximately be constructed by calculation with available thermochemical data, so this system is likely to be of simple binary type (except at the region near calcite at high temperature) with a eutectic at about 1065°C. Likewise, judging from the properties of the components and the nature of the bounding systems, the ternary system fluorite-diopside-calcite is also likely to be of simple ternary eutectic type (except in the region near calcite), and the temperature of the eutectic point can be reasonably estimated to be of the order of 750°C-800°C. Thus, it is probable that the temperature of beginning of melting of this dry system containing only three mineral phases, already lies within the temperature range of the highest grade of metamorphism. However, the important point is that the skarn-forming fluids in fact contained abundant various volatiles which certainly will lower the melting points of the solids; especially, as mentioned before, the melting temperature of calcite is greatly dropped with the presence of coexisting H_2O (but not much affected by total pressure) (Wyllie & Tuttle, 1959, 1960). According to Wyllie et al's phase diagram of the system $CaCO_3$-H_2O, at 1000 bars pressure, the presence of 10 weight percent H_2O drops the melting point of calcite from 1310°C to about 1060°C, while 20 weight percent of H_2O, drops the M.P. to about 1010°C, and 50 weight percent of H_2O, down to about 970°C.

The abundance of water in magma has been estimated to vary from about 0.5 to 8 weight percent. Goranson has also shown that a liquid of typical granitic composition, at elevated temperatures and pressures, can contain about 10 percent of water. It is likely that a pegmatitic fluid could have somewhat more than this amount (Jahn, 1955), as it is enriched in volatile constituents. The skarn-forming fluid also has the same "pegmatitic" characteristics. Therefore, the skarn-forming fluids are also likely to contain more than 10 weight percent water. This amount of water will probably lower the eutectic temperature of the system CaF_2-$CaMgSi_2O_6$-$CaCO_3$ about 200°C, down to about 550° to 600°C. Of course, the other non-volatile and volatile components present in the skarn forming fluids will still lower the temperature an unknown amount. Consequently, the temperature of formation of the Grenville skarns could be around 550°C, which seems to be consistent with the grade of the associated metamorphic rocks, and the temperature of formation of the pegmatites (probably 500-700°C). In brief, the formation of skarns by differential fusion seems to be quite possible.

B) Application to the Portland Cement Industry:

When dealing with the theoretical chemistry of Portland cement preparation, the present system CaF_2-$CaMgSi_2O_6$ can be thought of as a binary join within the quaternary system CaO-MgO-SiO_2-CaF_2, which encompasses most of the phases in Portland cement excepting 3 $CaO \cdot Al_2O_3$. The relationship of these two systems is shown in Fig. 4.

Because CaF_2 plays an important role as a mineralizing agent in the clinkerization process, the presence of CaF_2 as a slight addition to the raw mixes of Portland cement is a powerful measure to improve reactivity. The system CaO-CaF_2-SiO_2 has been investigated

A : Akermanite, $2CaO\cdot MgO\cdot 2SiO_2$
C : Cuspidine, $3CaO\cdot 2SiO_2\cdot CaF_2$
D : Diopside, $CaO\cdot MgO\cdot 2SiO_2$
E : Enstatite, $MgO\cdot SiO_2$
F : Forsterite, $2MgO\cdot SiO_2$
L : Larnite, $2CaO\cdot SiO_2$
Me : Merwinite, $3CaO\cdot MgO\cdot 2SiO_2$
Mo : Monticellite, $CaO\cdot MgO\cdot SiO_2$
R : Rankinite, $3CaO\cdot 2SiO_2$
T : Tricalcium silicate, $3CaO\cdot SiO_2$
W : Wollastonite, $CaO\cdot SiO_2$

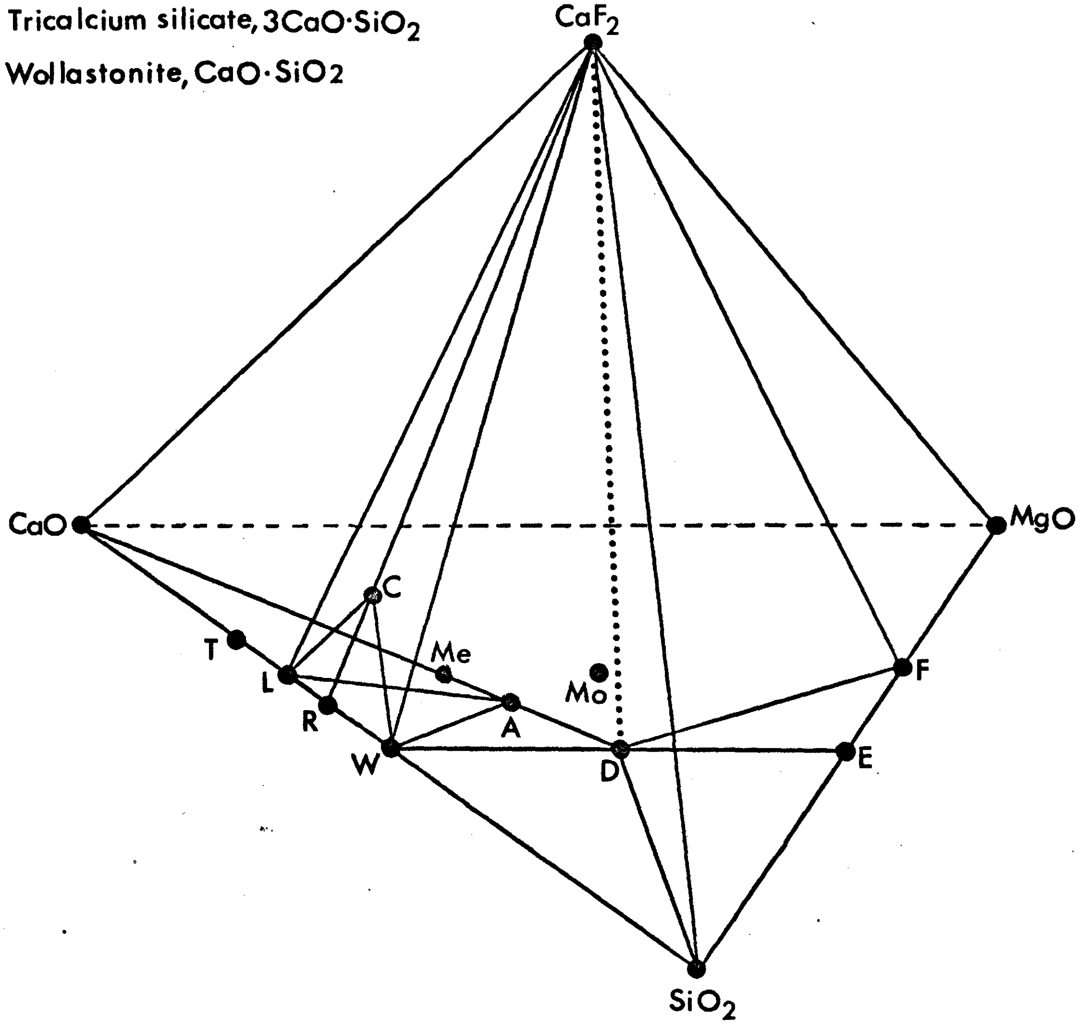

Fig. 4 . The position of the join $CaMgSi_2O_6 - CaF_2$ in the quaternary system $MgO - CaO - SiO_2 - CaF_2$.

in relative detail by other workers; special attention has been paid to the influence of CaF_2 on the formation of tricalcium silicate ($3CaO \cdot SiO_2$) which is the most important constituent of Portland cement clinker, and has an important effect on the hardening process of cements (Eitel, 1937; 1966, Rankin and Wright, 1915).

In addition to CaO, Al_2O_3 and SiO_2, other components, such as MgO, Fe_2O_3 etc. are present in small quantities in the raw cement materials. Therefore, it is an interesting problem to study how the presence of more or less MgO in such raw mixes will affect the results of the reactions. It is apparent that some magnesia-bearing lime silicates, such as diopside, akermanite etc. will be produced, if the amount of MgO in raw mixes of cement increases. This study shows that the type of phase equilibria of the system CaF_2-$CaMgSi_2O_6$ is still the same as that of the system CaF_2-$CaSiO_3$ (Bääk and Ölander, 1955), and therefore small amounts of MgO do not affect the phase relations greatly.

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APPENDIX

Petrographic Microscopic Pictures and Electron-probe Pictures

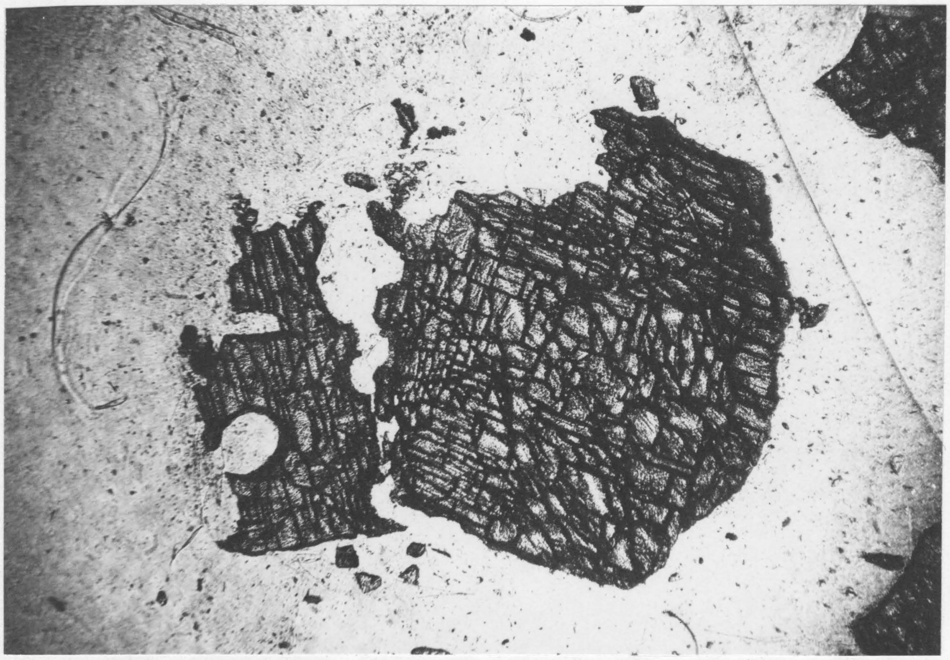

Plate 1. Cleavage fragments of synthetic diopside, using plane polarized light, x 30.

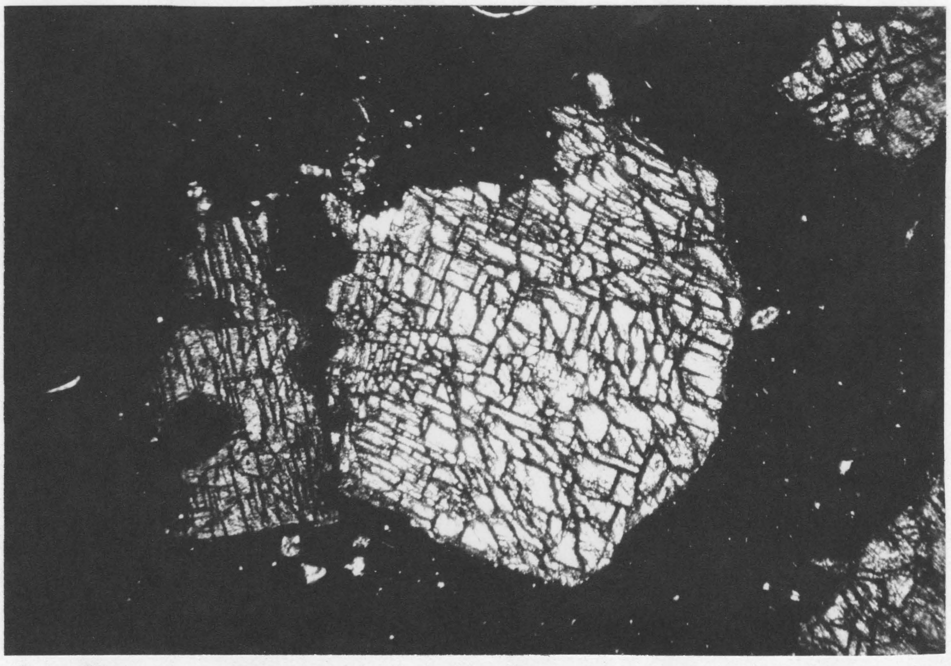

Plate 2. Cleavage fragment of synthetic diopside, using crossed polarized light, x 30.

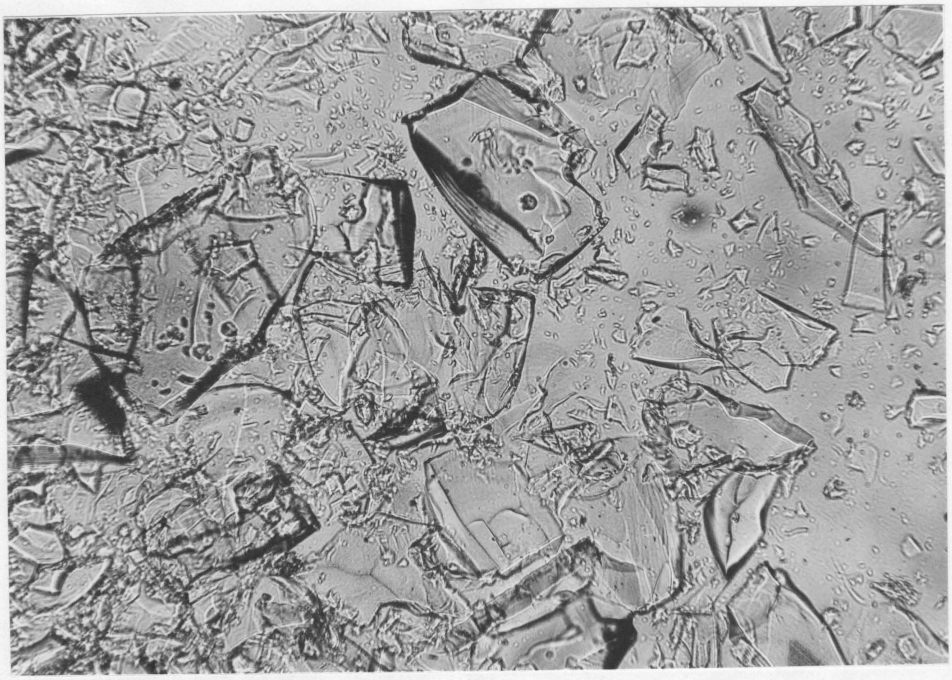

Plate 3. Transparent, clear glass (quenched liquid) of composition $F_{40}D_{60}$, x 80.

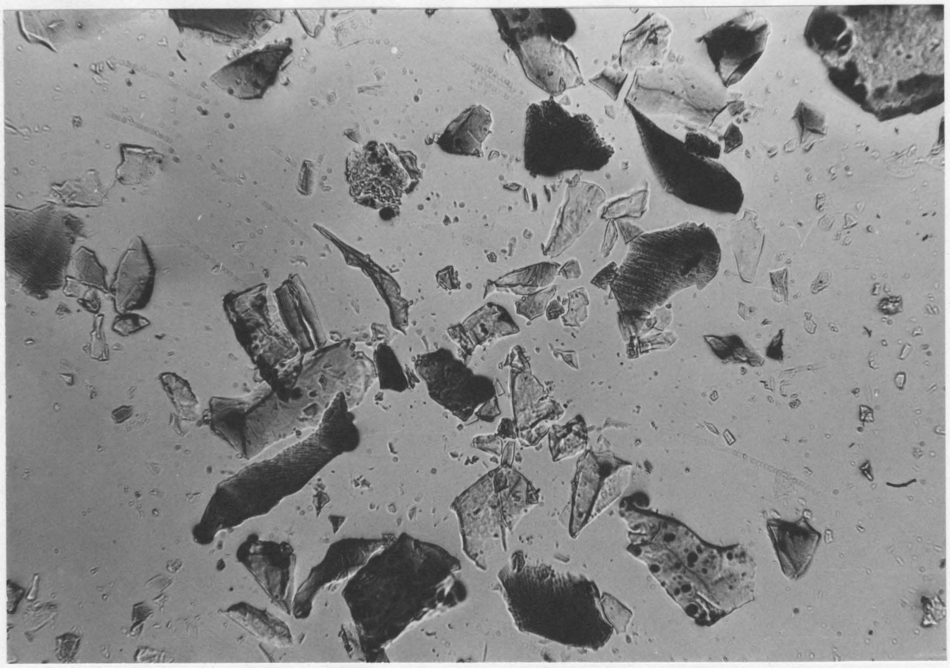

Plate 4. Brownish quenched glass of the CaF_2-rich composition ($F_{55}D_{45}$). Note the presence of sub-microscopic brown nuclei of CaF_2, which crystallize from liquid during quenching, x 125.

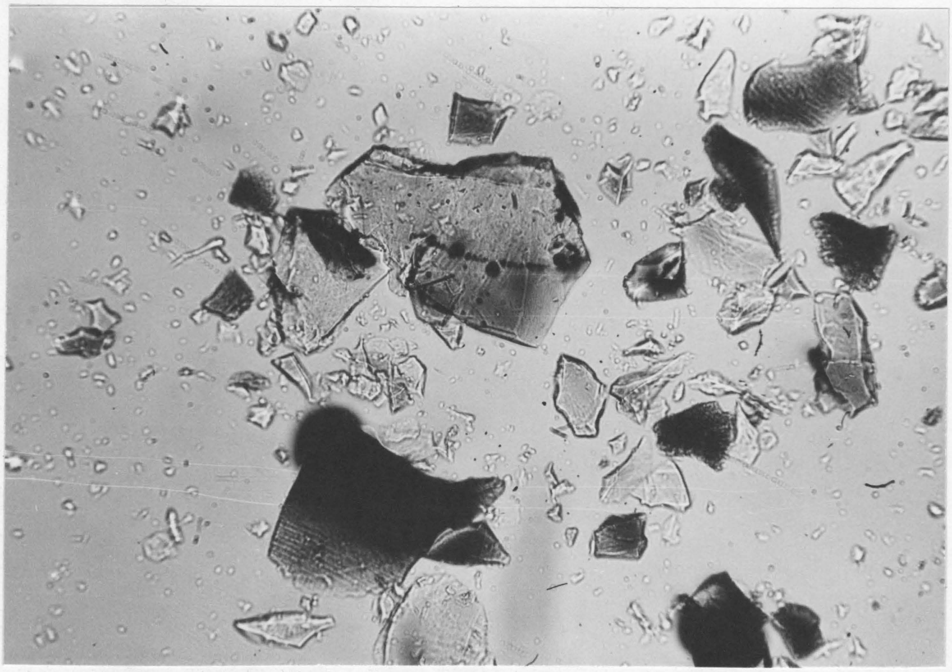

Plate 5. CaF_2-rich glass with spherulitic structure, plane polarized light, x 125.

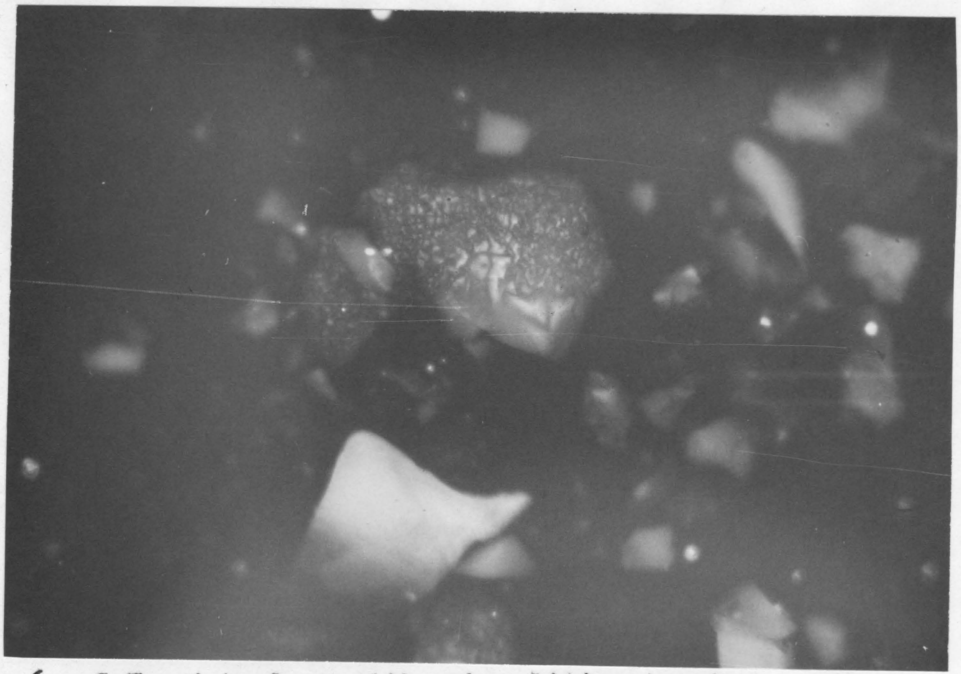

Plate 6. CaF_2-rich glass with spherulitic structure, cross polarized light, x 125.

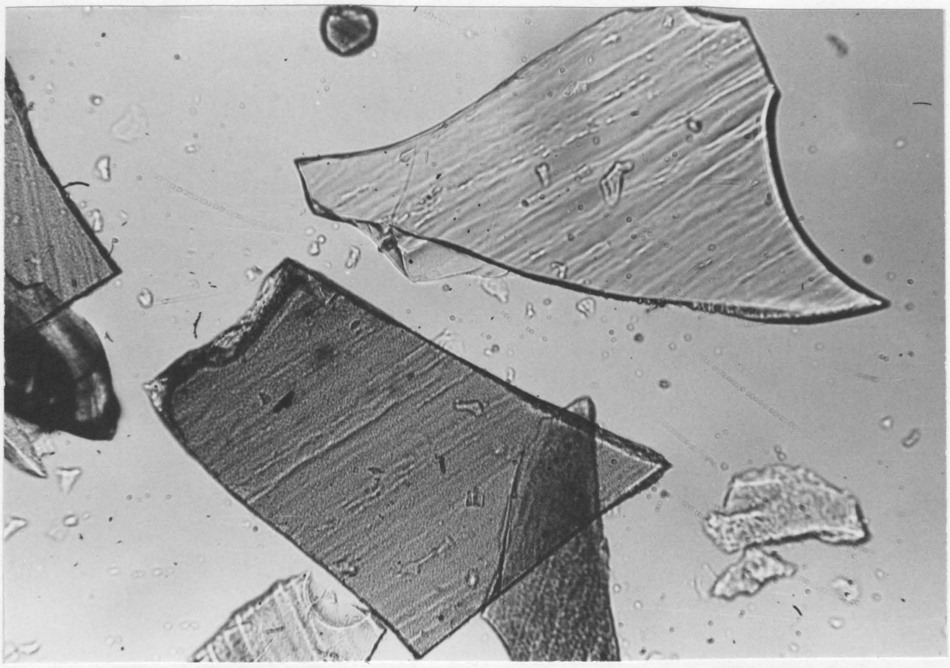

Plate 7. Same as plate 4, but this quenched glass contains less CaF_2 nuclei (i.e. $F_{50}D_{50}$), so it is clearer, x 125.

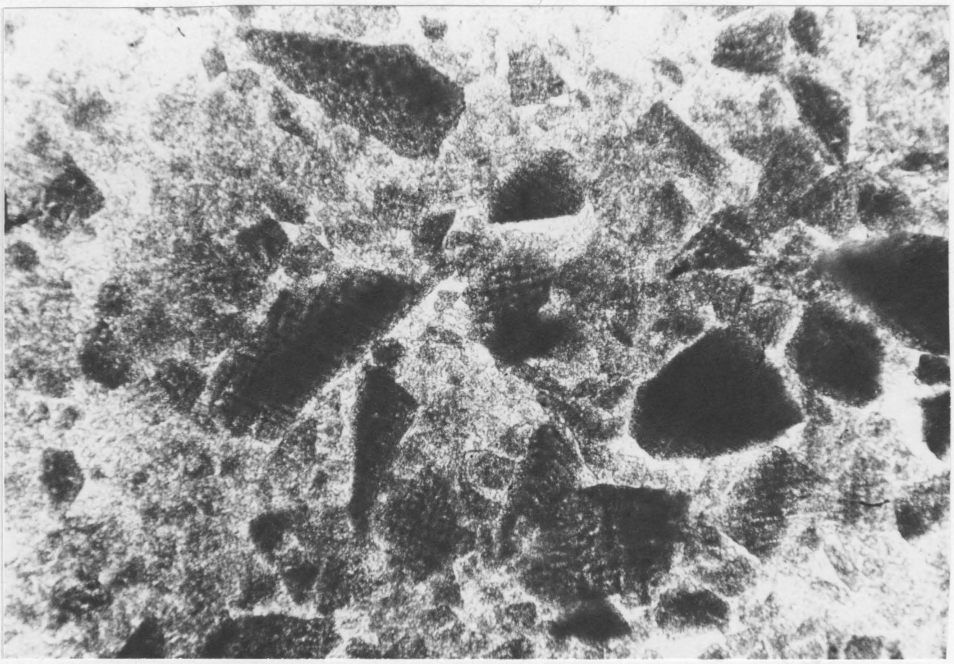

Plate 8. Showing remarkable contrast to plate 7. This quenched product has the same composition as that of plate 7, but failed to quench within 3 seconds; it becomes blurred and dirty in appearance, x 125.

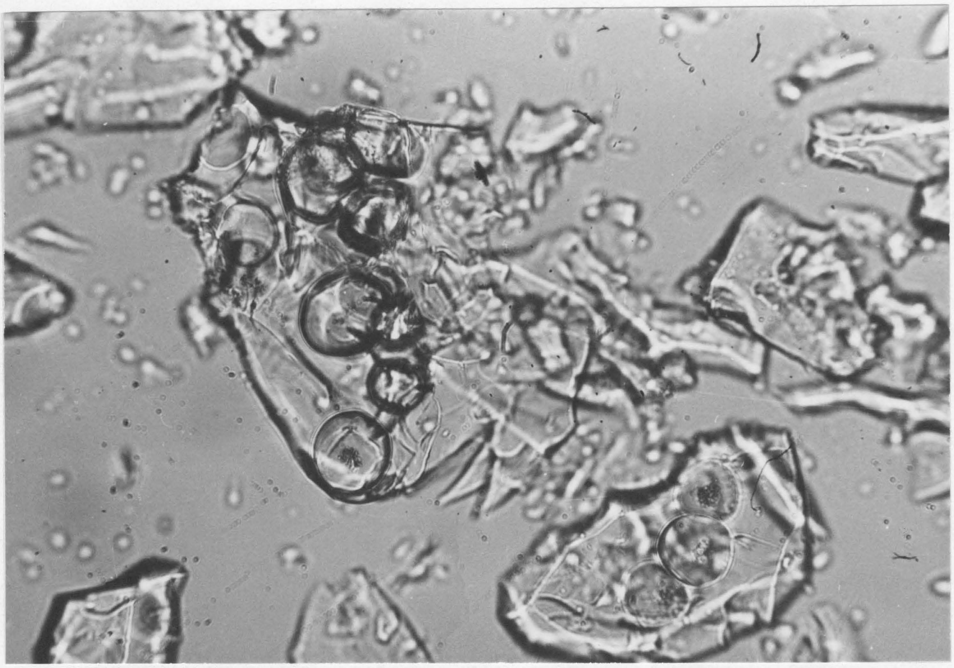

Plate 9. The clear globules of CaF_2 of primary crystallization embedded in transparent glass, the composition of charge is $F_{50}D_{50}$, x 260.

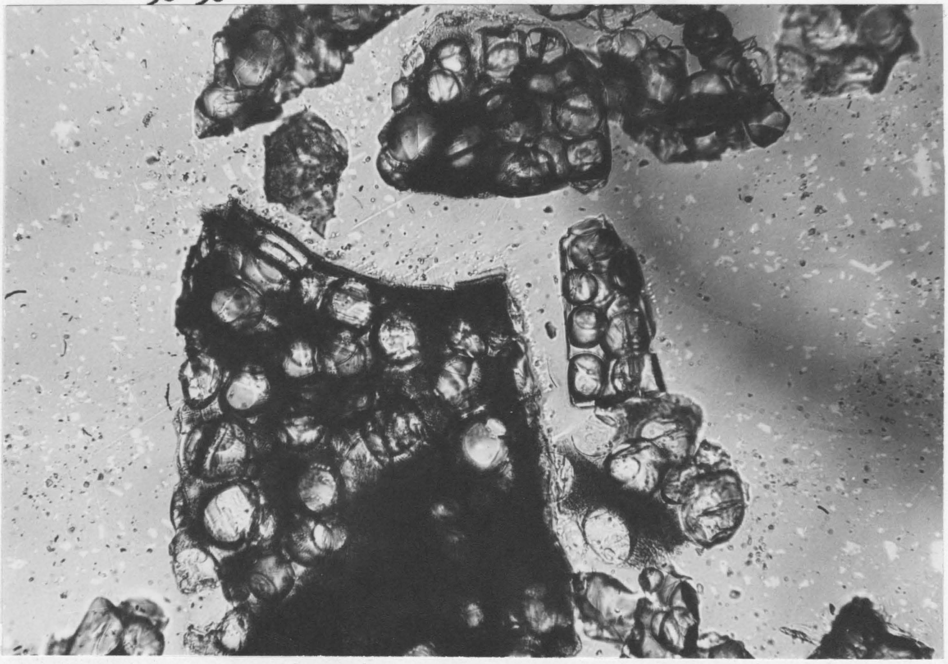

Plate 10. The clear globules of CaF_2 of primary crystallization embedded in brown glass which contains the CaF_2 nuclei of secondary crystallization, the composition of charge is $F_{80}D_{20}$, x 125.

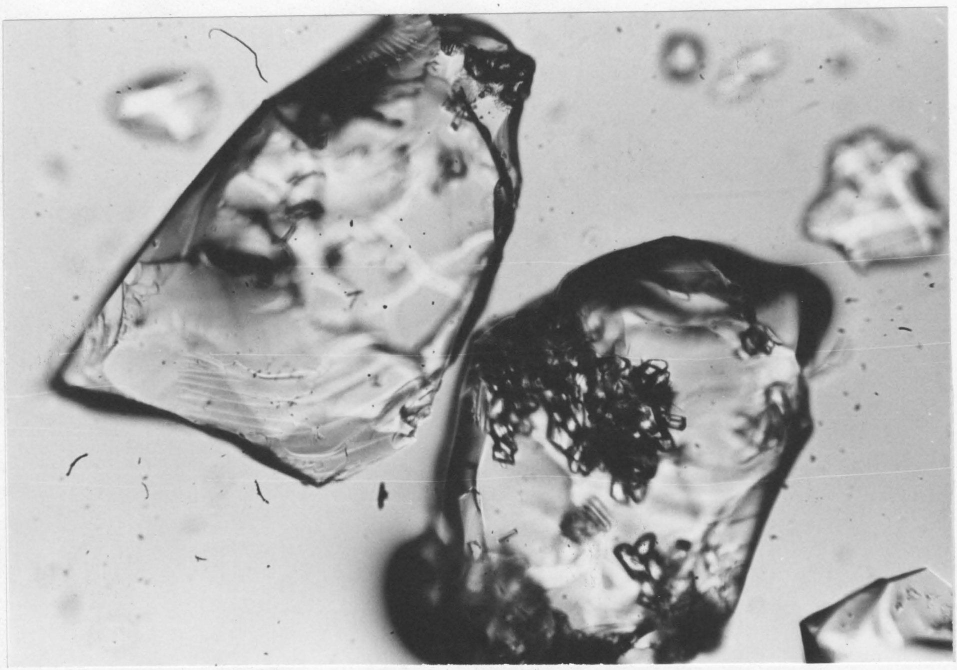

Plate 11. The primary diopside embedded in clear, transparent glass, the composition of this charge is $F_{40}D_{60}$, plane polarized light, x 125.

Plate 12. The same as above, but using cross polarized light, x 125.

Plate 13. Primary diopside recrystallized as clusters of prismatic crystals within glass; using plane polarized light, x 125.

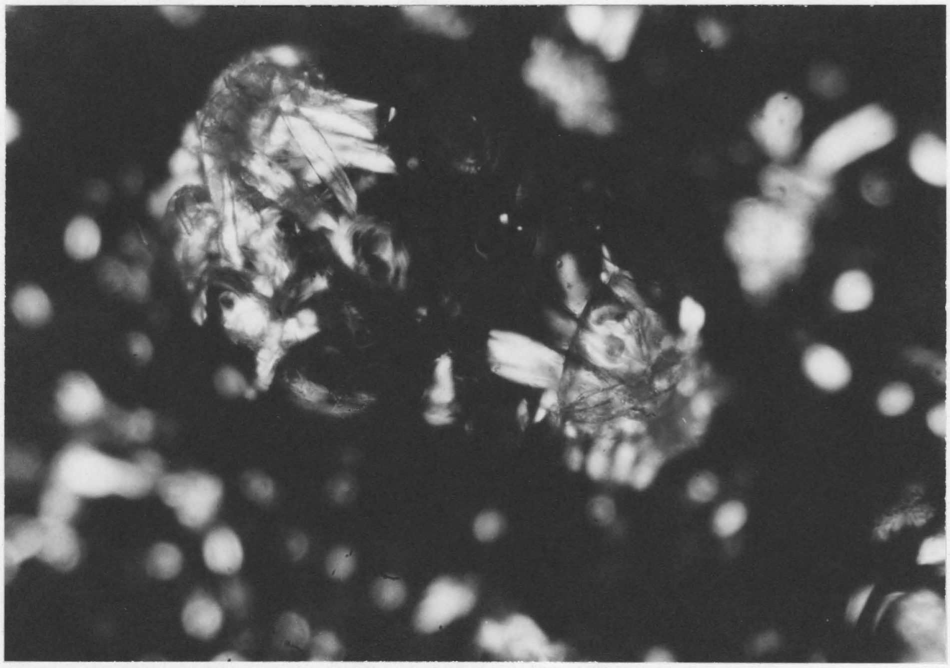

Plate 14. The same as above, but using cross polarized light, x 125.

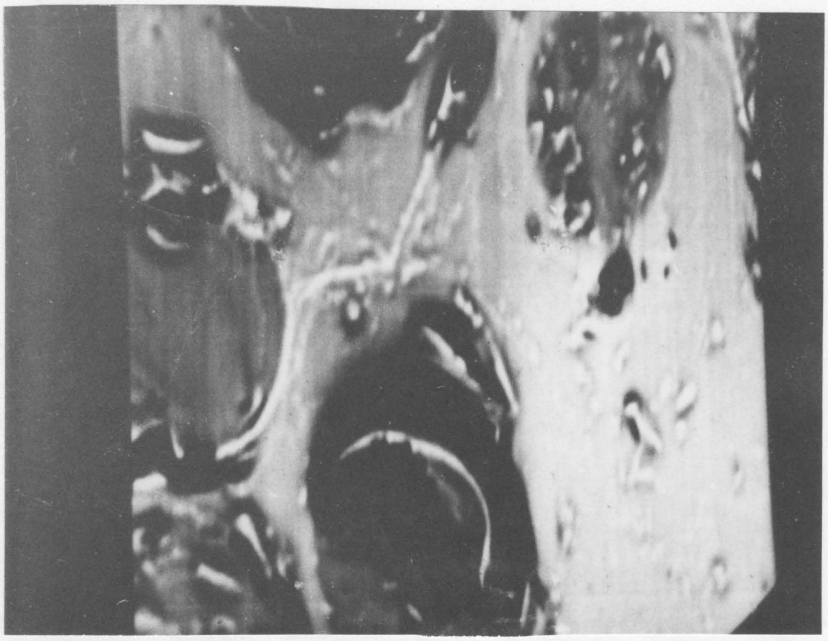

Plate 15. Electron-probe image showing globular CaF_2 crystal (dark area) embedded in glass (white area), by using electron back-scattering, x 2500.

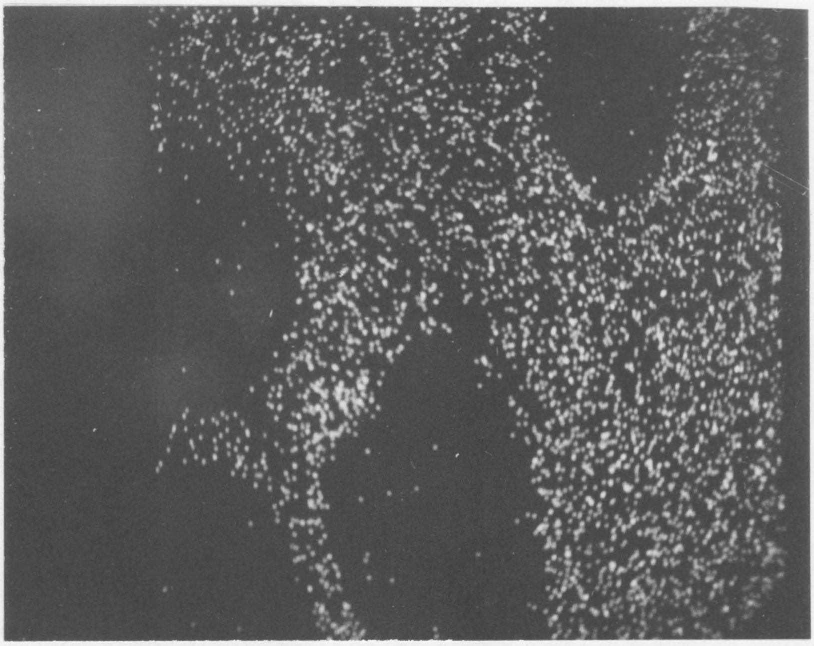

Plate 16. Electron-probe image of the same object as above, but by using SiKα radiation, globular CaF_2 shown by dark area, every white spot indicates an atom of Si, x 2500.

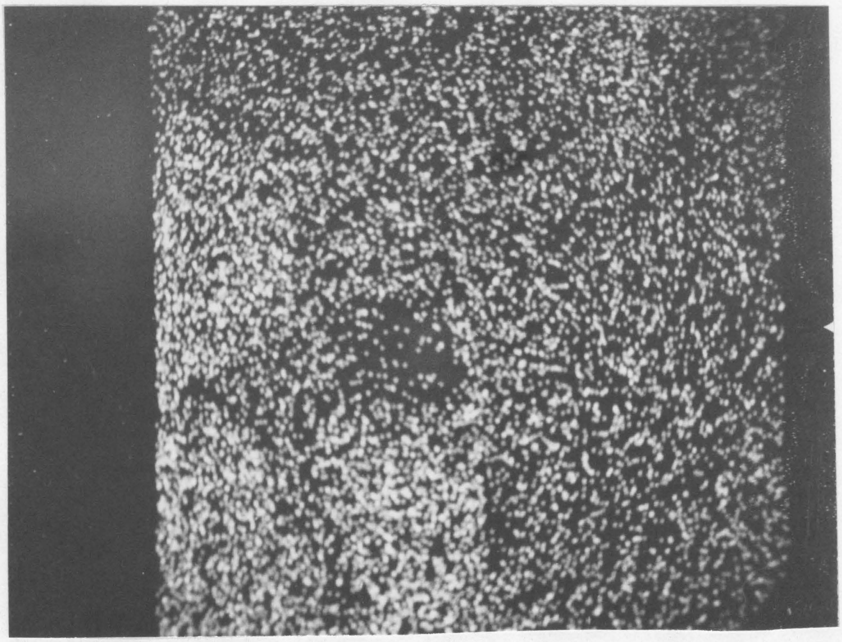

Plate 17. Showing the distribution of Ca atom in the same object as the plate 16 CaKα radiation, x 2500.

Plate 18. Showing the distribution of Mg atom in the same object as the plate 16 MgKα radiation, x 2500.

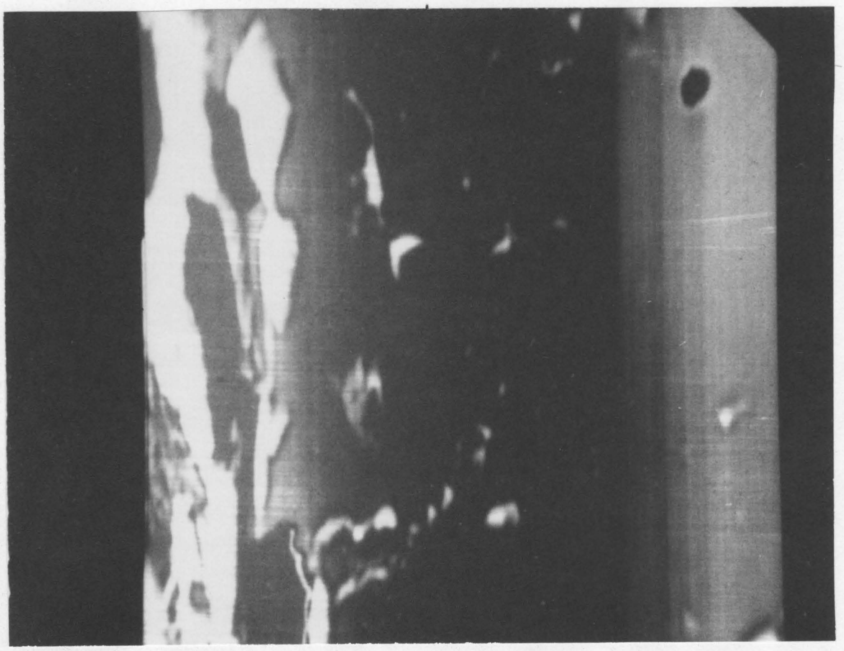

Plate 19. An image of the spherulitic glass, by using electron back-scattering, x 2500.

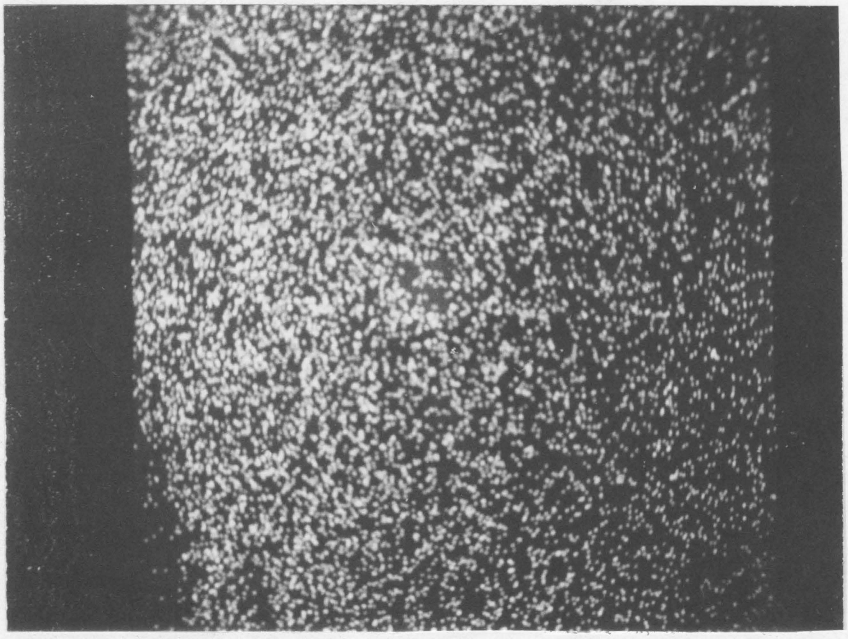

Plate 20. Showing the distribution of Si atom in plate 19, SiKα radiation, x 2500.

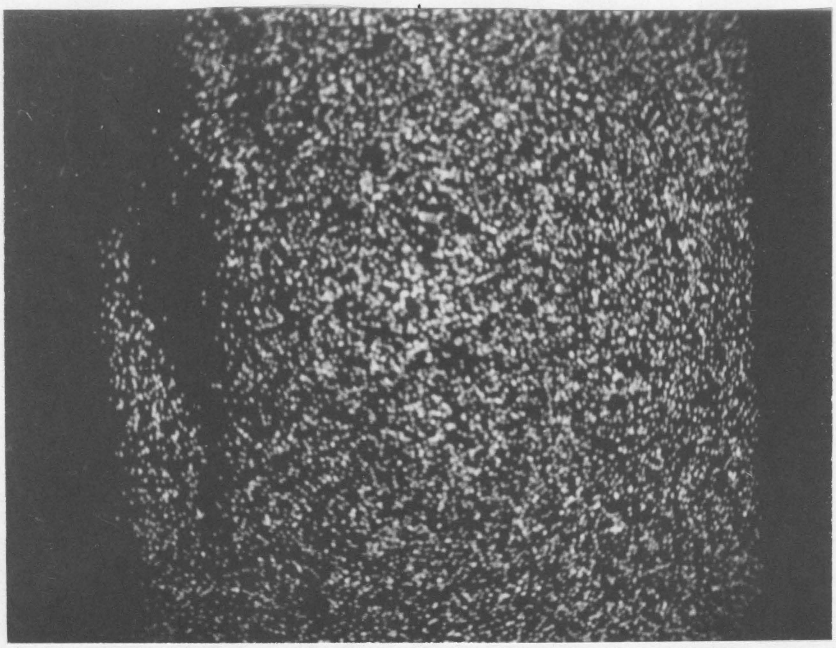

Plate 21. Showing the distribution of Ca atom in plate 19, CaKα radiation, x 2500.

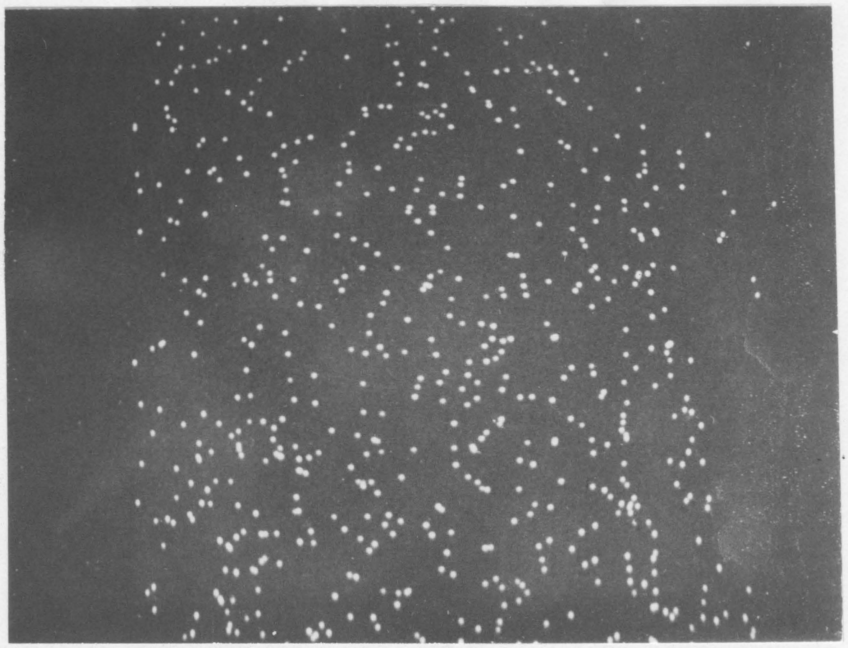

Plate 22. Showing the distribution of Mg atom in the plate 19, MgKα radiation, x 2500.