MINERALOGICAL JOURNAL, VOL. 17, NO. 6, PP. 257–281, APRIL 1995

Hexagonal $CaAl_2Si_2O_8$ in a high temperature solution; metastable crystallization and transformation to anorthite

Toshiya ABE* and Ichiro SUNAGAWA**

**Department of Mineralogical Sciences and Geology, Faculty of Science, Yamaguchi University, Yoshida, Yamaguchi 753, Japan*
***Yamanashi Institute of Gemmology and Jewelry Arts, Tokoji-machi, Kofu 400, Japan*

Abstract

Nucleation, stability and change of hexagonal $CaAl_2Si_2O_8$ crystals in the solution of $anorthite_{70}forsterite_{10}silica_{20}$ wt% were investigated by high temperature in-situ observations, ex-situ runs in a furnace, and examinations of the quenched products.

Hexagonal $CaAl_2Si_2O_8$ was observed to crystallize dominantly in the supercooled liquid at temperatures from 1100 to 1000°C. The incubation time becomes shorter as the temperature decreases. At 1000°C, it nucleates within a few hours. At these temperatures anorthite rarely nucleates in spite of large ΔT (300–400°C), but does at 1250–1150°C (ΔT=150–250°C). Its nucleation, however, needs time more than several hours. The nucleation sequence is explainable with supercooling degree and interfacial free energy difference for each polymorph. It was also demonstrated that the hexagonal polymorph has a metastable liquidus at 1240°C, 160°C lower than that of anorthite. This difference is consistent with that in the An_{100} composition. The crystals of hexagonal $CaAl_2Si_2O_8$ grow steadily below this metastable liquidus. This can exist permanently if anorthite is not present in the system. However, hexagonal $CaAl_2Si_2O_8$ changes easily to anorthite without dissolution once the latter starts crystallization and gets in contact with the former. The contact of the two phases triggers the change from hexagonal to triclinic $CaAl_2Si_2O_8$.

Introduction

Preferential nucleation of a metastable phase has been reported in some silicates; e.g., hexagonal $CaAl_2SiO_6$ (Yoshioka, 1970; Kirkpatrick and Steele, 1973), hexagonal $BaAl_2Si_2O_8$ (Müller, 1977), Mg_2SiO_4 in metastable regions (Kirkpatrick *et al.*, 1981 and 1983), hexagonal $Mg_2Al_4Si_5O_{18}$ (Putnis and Bish, 1983), and Mg_2SiO_4 and $CaTiO_3$ in metastable regions (Nakamura *et al.*, 1990). These were observed when a melt was cooled instantaneously or a glass was heated rapidly. A similar nucleation at $CaAl_2Si_2O_8$ composition was first reported by Davis and Tuttle (1952). As reviewed by Smith and Brown (1988), anorthite is a triclinic $CaAl_2Si_2O_8$ and, under atmospheric pressure, takes a symmetry of $P\bar{1}$ space group at room temperature and $I\bar{1}$ above 240°C. Whereas, polymorphic phases take different structures from that of anorthite; orthorhombic $CaAl_2Si_2O_8$ with space group $P2_12_12$, pseudo-orthorhombic one with $P2_1$, and hexagonal one with $P6/mmm$ or $P6_3/mcm$, and pseudo-hexagonal one with $C2$ (Davis and Tuttle, 1952; Takéuchi and Donnay, 1959, Takéuchi et al 1973; Ito, 1976).

Among them, the hexagonal and the pseudo-hexagonal phases are considered to be essentially the same one but taking slightly modified structures, and the orthorhombic and the pseudo-orthorhombic phases are also the same one. Therefore, only three polymorphs, "triclinic", "hexagonal", and "orthorhombic", should be distinct phases. The triclinic phase, "anorthite", is the stable phase occurring commonly in nature. The hexagonal phase is encountered only in synthetic products, but a similar hexagonal form named as "hexacelsian" is observable in other compositions, $BaAl_2Si_2O_8$, $SrAl_2Si_2O_8$ and so on (Takéuchi, 1958; Pentinghaus, 1975). The orthorhombic phase has been found in nature, at burning dumps at Kopeysk, Chelyabinsk coal basin, southern Urals, Russia, and the name "svyatoslavite" was given by Chesnokov *et al.* (Jamber and Grew, 1991).

Recently, we have investigated the stability and the crystallization of "hexagonal" and "orthorhombic" polymorphs in the $CaAl_2Si_2O_8$ melt by the in-situ observation method (Abe *et al.*, 1991). The followings were clarified. (1) Both pseudo-hexagonal and pseudo-orthorhombic $CaAl_2Si_2O_8$ were identified. (2) Both polymorphs exclusively nucleated and grew prior to the appearance of stable anorthite when the melt was supercooled below 1200°C. (3) Their metastable melting points were measured, which were much lower than that of anorthite. Below the metastable melting points crystals of these metastable phases grew steadily, and above these points they dissolved. (4) In the presence of anorthite, they quickly disappeared. However, it was not conclusive as to whether the metastable phases disappeared through melting process or they directly transformed to the stable anorthite phase.

In our previous work (Abe *et al.* 1991), the system investigated was a pure anorthite melt, in which the growth of anorthite is too rapid to properly observe the change of metastable polymorphs. In a solution system(*1), much slower growth is expected, so that the changes can be traced deliberately even in the presence of anorthite. In addition, there is no report that hexagonal or orthorhombic $CaAl_2Si_2O_8$ appears in other silicate systems except the melt and the flux. This may reflect the nucleation nature of $CaAl_2Si_2O_8$ polymorphs, or may arise from experimentation. These should be examined by the in-situ observation. Our interest is also in the metastable liquidus in a solution system; how it varies depending on a liquid composition. A solution system also has the advantage of liquidus measurement; the in-situ measurement by the morphological changes can be ensured by the ex-situ chemical analysis of glass composition.

Therefore, we planned another experiment on the $CaAl_2Si_2O_8$ polymorphs. This was made at the solution composition of 70% anorthite, 10% forsterite and 20% silica ($An_{70}Fo_{10}Silica_{20}$) in weight, which was chosen because of its wider temperature range of anorthite liquidus. In this study, we focused on which polymorphs appear in the supercooled

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[*1] The term "melt" was sometimes given equivocally to molten silicates, ignoring their composition. In this paper, "melt" was given to the liquid in single component, including a pure liquid of a mineral, and "solution" to the others, such as the liquid in a binary or ternary system.

liquid and how the metastably nucleated $CaAl_2Si_2O_8$ crystals behave in the silicate solution in the absence and presence of anorthite. Particularly, we examined in detail the last one, the change caused by anorthite. These were examined by in-situ observations and X-ray diffractometry on the quenched samples. To carry out a number of long time runs, we also adopted an ex-situ method, syntheses using a furnace and analyses of the quenched products. This method was also used to prepare a series of the quenched products and to trance the change.

Experimental

A starting material was prepared from reagent grade MgO, $CaCO_3$, Al_2O_3 and SiO_2 (Kanto Chemical). The mixture in a composition of $An_{70}Fo_{10}Silica_{20}$ (wt%) was sintered at 1220±30°C to degas. The sintered material, in which anorthite was already present, was pulverized again. The powder was hydrostatically pressed into the shape of a cylindrical rod, of which a slice was used as an experimental charge. Three slices from different places were made into glass individually, and their chemical compositions were checked by EPMA. Table 1 shows the averaged composition of the glasses. As seen from a larger deviation for the glass than for the crystals, the charges might be slightly heterogeneous.

The in-situ observations were made by a similar set-up and procedures with those reported in our previous papers (Abe *et al.* 1987 and 1991), although a video system was not used in the present study. We used a holder made of $Pt_{87}Rh_{13}$ wires (0.6mmø) and heated in Ar atmosphere. The observations were made at the central portion of the holder, $0.5\times0.5mm^2$. The temperature was measured within ±10°C by a Pt-$Pt_{87}Rh_{13}$ thermocouple which was calibrated against the anorthite liquidus in the experimental composition. Quenching was made by stopping the power supply. It led the temperature drop below 800°C within a second. Overgrowth of a metastable phase was not observed.

To prepare products routinely, we also adopted ex-situ runs. They were made in the air condition and with a programmable PID controller (Chino, KP) and vertical SiC furnace. The sample was held in a $Pt_{87}Rh_{13}$ ring (Fig. 1). The ring (with a hole of 3–5mm wide) was made by welding ends of a wire (0.6mmø). The outside of the ring was put in at a set of $Pt_{87}Rh_{13}$ pins, with which the ring was suspended horizontally in the furnace. The sample was charged in the hole of the ring. For this charge, the sample was placed on the ring and inserted into the furnace. Then the temperature was raised slowly, and the sample was molten and held in a form of disc (thick film) inside the ring. The sample was once taken out from the furnace and the holding was checked. If the sample was in contact with the pins, it was abandoned. Thus checked sample was used for the ex-situ run. The temperature was measured within ±5° by a Pt-$Pt_{87}Rh_{13}$ thermocouple calibrated only against the melting point of $CaMgSi_2O_6$. The run product was quenched in the air in most of the experiments to avoid cracks. Neither overgrowth nor nucleation of a metastable phase on quench was detectable. As a precaution, however, quench

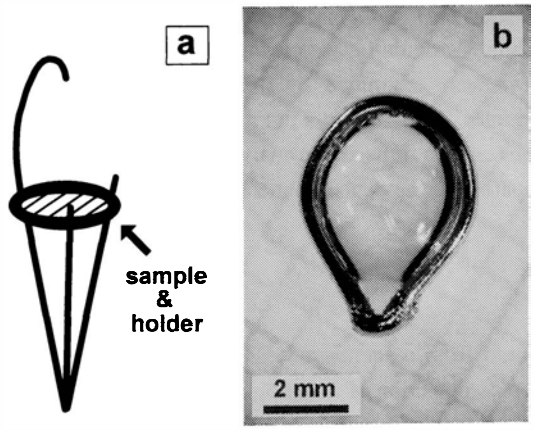


FIG. 1. Ring holder used in the ex-situ runs. The holder is suspended in a furnace horizontally with the help of pins (a). The sample is charged in the hole of the ring (b).

by dropping into oil was adopted in the experiments involved with anorthite seeding.

In this study, phase identification was focused on $CaAl_2Si_2O_8$. Discrimination of $CaAl_2Si_2O_8$ polymorphs was firstly made by their characteristic morphologies in all the experiments. In the in-situ ones, the growth rate difference was also observable and useful for the phase discrimination. The ex-situ run products were immersed in benzene and observed at first with a microscope. Some of them were examined in thin sections, which were sliced vertically to the ring holder. Representative samples of both in-situ and ex-situ runs were examined by X-ray diffractometer (XRD, Rigaku RAD-II VC). XRD measurements were made on the powdered sample spread on a glass plate with Cu target and Ni filter and under conditions of 40kV, 20mA and 1°(2θ)/minute. Diffraction intensity was collected at a step of 0.02°, and a XRD pattern was drawn with a 11-point smoothing. 2θ was calibrated with an external standard, α-SiO_2. A glass plate was used instead of a normal XRD holder in all the measurements. This method was weak against preferred orientation but enabled to measure in a half volume of the run product. We also used an electron probe microanalyser (EPMA, Shimazu V6). In quantitative analyses, EPMA was operated at 15kV acceleration and 15nA specimen current, and characteristic X-rays were measured with wavelength-dispersive detectors. The correction was made by ZAF method.

At first, we searched which $CaAl_2Si_2O_8$ polymorphs nucleate and grow under isothermally supercooled conditions. This needed a long time run, so we used mainly the ex-situ method. The experimental charge was molten completely at 1480°C, 80°C above the liquidus, then cooled in 15 minutes to an isothermal temperature ranging from 1250 to 1000°C. Nucleation only at 1000°C was ensured by the in-situ method, where the cooling to an isothermal condition was reached in a few minutes.

Secondly, we examined a metastable liquidus of hexagonal phase and the change of hexagonal phase in the presence of anorthite. For these purposes, we had to grow a desired polymorph. A hexagonal phase ≤1100°C was prepared by nucleation and growth under an isothermal condition. This preparation was designated as "isothermal". Whereas a hexagonal phase >1100°C was prepared by a kind of seeding, designated simply as "program". Seed crystals were nucleated at 1000°C then the temperature was changed to the desired one, as illustrated in Fig. 2. In the in-situ experiments, two types of program preparation were used. (I) The temperature was changed directly to the growth condition after the nucleation. (II) Crystals were grown and dissolved repeatedly until the small crystal proper as a seed was struck on a thin Pt wire (<0.1mmø) in the liquid and across the in-situ holder. By this procedure, the crystal can be observed steadily without being moved by convection. The growth and dissolution times were changed properly on the observations. In the ex-situ runs, we used only the seeding corresponding to (I); the sample was kept for 2 hours at 1000°C and heated up to the desired temperature in 1 hour. Anorthite in the ex-situ runs was crystallized by "devitrification", i.e., heating a quenched glass directly at an experimental temperature. The glass sample was inserted quickly into the furnace of which electric supply was fixed after 2 hours' preheating at the experimental temperature. In 5 minutes the thermocouple adjacent to the sample indicated the deviation of about –10°C from the nominal temperature. In 10 minutes the temperature was reached nearly isothermal within ±2°C and we began to re-control the

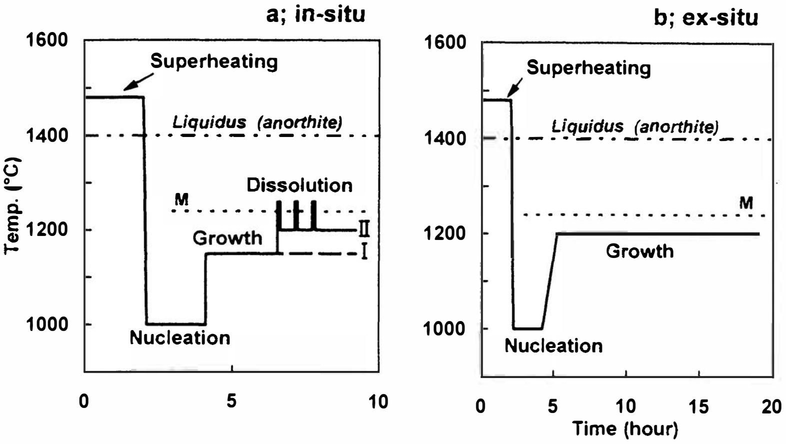


FIG. 2. Temperature-time profile used to grow the metastable phase for the in-situ runs (a) and for the ex-situ (b). These procedures were designated as "program" in this paper. "M" indicates the metastable liquidus. The metastable phase dissolves above this temperature, which is measured later by the in-situ method.

power supply. By this devitrification, anorthite started crystallization immediately from the glass surface (heterogeneous nucleation). The product prepared at this devitrification (1250°C, 1 hour) was powdered and used as anorthite seeds in the in-situ experiments. The seeds were sprinkled on a tip of thin Pt wire before the run. For "An seeding", the tip was dipped in the liquid with a manipulator.

The liquidus of the hexagonal $CaAl_2Si_2O_8$ was directly measured by the in-situ method, reported (Abe *et al.* 1991), with a slight modification. The hexagonal crystal was prepared by the program (II) procedure. Thereafter, the morphological change from a polyhedral to a rounded form was traced in-situ by changing the temperature. Thus measured liquidus was ensured by EPMA on the ex-situ products. These analyses were made on the glasses around the hexagonal crystals grown at 1100°C for 30 hours and at 1200°C for 20 hours. The former was nucleated and grown under the isothermal condition, and the latter was growth by the program method. For comparison, the product containing anorthite was also analyzed. It was prepared by the devitrification at 1360°C and the quench in oil.

The change of the hexagonal phase in the presence of anorthite was examined in combination with in-situ and ex-situ runs. In the in-situ experiments, we tried to observe the change directly. For this purpose, the hexagonal phase was grown by the program procedure, then the anorthite was crystallized by the An seeding. The change was also traced by detailed observations on a series of quenched samples, which were prepared by the ex-situ runs. This preparation was used since the sample was heated at more controlled and homogeneous temperature. At first, we prepared the products containing hexagonal crystals by the program method. After they were quenched and checked, anorthite was crystallized by the devitrification. Thus reheated products were examined by XRD, polarizing microscope, backscattered electron image (BEI) and Mg distribution image using Mg-Kα radiation. The latter two images were observed by the EPMA instrument, operated 15kV and 2.5nA. The BEI observations were made in the mode named as "super backscattered electron image". In addition, etching technique was applied for detailed texture observations. It would reveal defects and grain boundaries even if there was no compositional difference. A polished surface of the sliced specimen was etched in a mixed solution of 2% HF and 1% HCl for 1 minute, followed by observation with a differential interference contrast microscope (Nikon, Microphoto-SA) and SEM (JEOL, JSM-T100).

Results

Nucleation and Growth under Isothermal Conditions

The studied composition lies on the join An_{100} and the ternary eutectic point and in the primary field of anorthite (Andersen, 1915). On the basis of this diagram, only anorthite should appear at temperatures from 1400°C (liquidus) to 1220°C (solidus), and below 1220°C enstatite and tridymite become stable concurrently besides anorthite. The phase observed in-situ, however, was different from the equilibrium assemblage. Even when the molten liquid was cooled to 1000°C, triclinic phase, anorthite, was not observed, but hexagonal phase was observed within a few hours. It took a dendritic morphology in a hexagonal shape. As an exceptional case, triclinic $CaAl_2Si_2O_8$ was detected depending on the holder. Anorthite growth was always started from the same spot of the same holder and in a short incubation, within 1 hour, indicating that the anorthite was formed heterogeneously.

In the ex-situ runs using the ring holder, such an anomalous crystallization of anorthite from the particular spot was observed when the sample was in contact with the pins. These were excluded from the results. This is the reason why we ensured the holding manner before the runs. Although the different atmosphere from that of the in-situ runs was used, the hexagonal phase was also observed dominantly in the ex-situ runs at lower temperatures. The ex-situ isothermal runs were made at temperatures ranging from 1250°C to 1000°C and at duration up

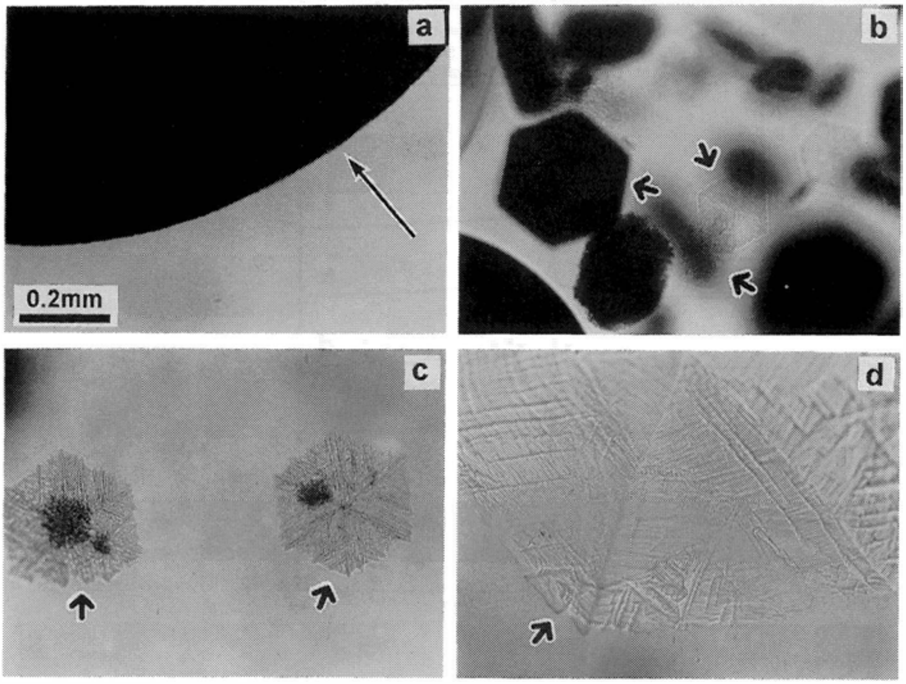


FIG. 3. Photomicrographs of crystals encountered in the isothermal experiments. Anorthite grows as a spherulite, indicated by a long arrow, at 1000°C in 3 hours (a), whereas the hexagonal crystals appear as a dendritic to platy form, by short arrows, at 1000°C in 20 hours (b), at 1050°C in 10 hours (c), and at 1100°C in 20 hours (d). All the products were observed in a bulk specimen, not in sections. Note also that the smooth and rounded object seen in the corner of (b) is a bubble, not anorthite.

to 60 hours. At 1000°C, anorthite was observed as a rare case. It grew as a spherulite from the holder surface (Fig. 3a). Its XRD (Fig. 4a) showed only a few peaks due to the presence of glass. Among them, the obvious peaks matched with characteristic peaks of anorthite. This product also contained tiny dendritic crystals in a hexagonal form. They were present sparsely in the glass. Due to a small volume, this phase was not detected by XRD. The same hexagonal crystals, judged from the morphology, were observed commonly in the 1.5 to 20 hours' run products at 1000°C. They were recognized both on the holder and in the glass. They nucleated and grew not only from the holder wall but also in the glass. The glass phase was still present in quantity in all the products. In a prolonged run, the crystals became bigger but lost transparency. Such translucent crystals were common in the products longer than 10 hours, although smaller crystals showing a similar shape were still transparent. One example after 20

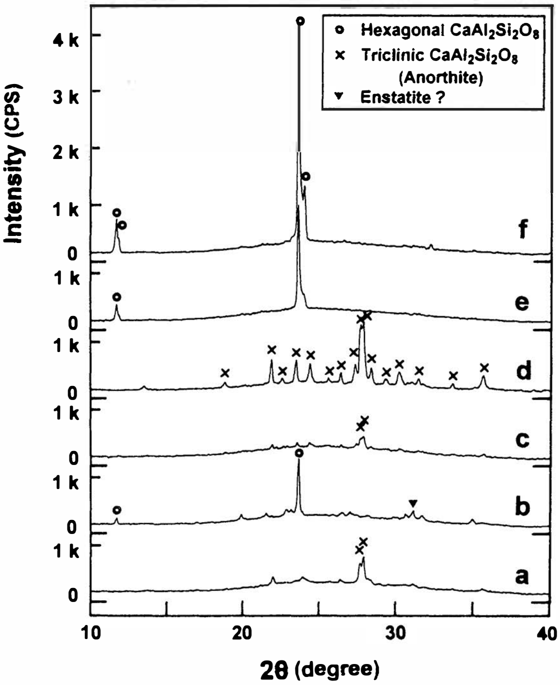


FIG. 4. XRD patterns of the quenched products. (a) Anorthite grown by the ex-situ isothermal run (1000°C, 3 hours). (b) Hexagonal phase by the ex-situ isothermal run (1000°C, 20 hours). (c) Anorthite by the devitrification (1200°C, 5 minutes). (d) Anorthite by the in-situ seeding (1150°C, 1 hour). (e) Hexagonal phase by the ex-situ program run (1200°C, 15 hours). (f) Hexagonal phase by the in-situ program run (1150°C, 20 hours). The crystals corresponding to the XRD patterns are shown in Figs. 3 and 6.

hours is shown in Fig. 3b. XRD on this product (Fig. 4b) shows a characteristic peak near 24° (2θ), which corresponds to the strongest peak of hexagonal $CaAl_2Si_2O_8$. Other diffractions, weak and diffuse ones, were also noticeable but failed to identify. They are different from peaks from any $CaAl_2Si_2O_8$ phases. One at about 31° indicated by an inverted triangle in the figure corresponded to the strongest peak of enstatite. These phases were not detected as an isolated crystal by microscopy. So we judged that they precipitated among the dendritic arms of the hexagonal phases and the latter became translucent. Such a precipitation is related to a high viscosity. Hexagonal crystals were also dominant at 1050°C. They also exhibited a dendritic form, whose arms were long (Fig. 3c). At 1100°C, transparent hexagonal crystals in a platy form (Fig. 3d) were detected in 6 to 30 hours. Morphological changes from dendritic to platy forms of this phase were ascertained later by in-situ observations. At 1150, 1200, and 1250°C, the hexagonal crystals were not observed. Whereas, anorthite was observed in cases above 1100°C. Its incubation time was very much scattered, and it was observed that some were spherulitic aggregates radiating from the holder wall. Orthorhombic $CaAl_2Si_2O_8$, which was also found to nucleate metastably in pure anorthite melt (Abe *et al.* 1991), was not observed in the $An_{70}Fo_{10}Silica_{20}$ solution under isothermal conditions. The observed $CaAl_2Si_2O_8$ phases in the isothermal experiments were plotted in Fig. 5, TTT (Temperature-Time-Transformation) diagram. As the temperature decreases below 1100°C, the hexagonal phase becomes dominant. The incubation time becomes shorter as decreasing temperature, i.e., increasing ΔT.

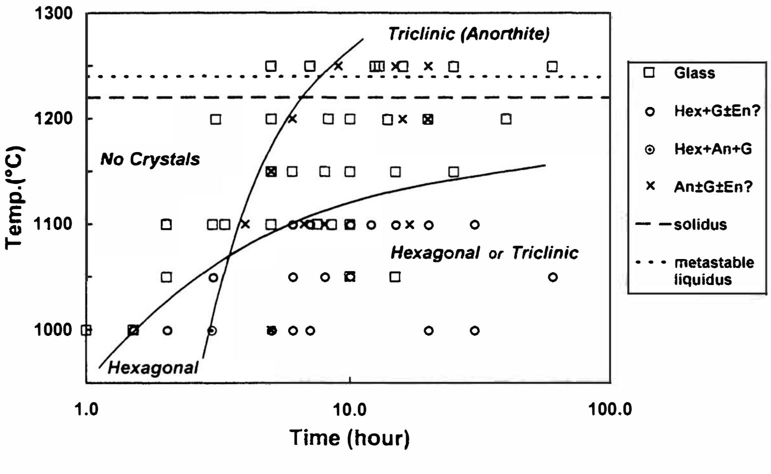


FIG. 5. TTT diagram showing the $CaAl_2Si_2O_8$ phases identified in ex-situ experiments on $An_{70}Fo_{10}Silica_{20}$. There is a lot of glass in all the products containing the hexagonal crystals. The metastable liquidus of hexagonal $CaAl_2Si_2O_8$ (dotted line) and the ternary solidus of anorthite, enstatite and tridymite (dashed line) are indicated.

This is in accordance with a general tendency in nucleation. It is also noted that the supercooling at 1000°C for 2 hours is suitable to prepare the small hexagonal crystals. This condition was used to secure the hexagonal seed crystals in the later experiments. Whereas, the region of anorthite was still in vague due to the scattered nucleations, which might include the heterogeneous nucleation from the holder. Provided not all the anorthite nucleations were of heterogeneous, the scattered incubation would be due to a statistical deviation. The region of anorthite was drawn tentatively based on their shortest incubation. With the decrease of temperature, the anorthite region becomes gradually wider but intersects with that of the hexagonal phase.

Characteristics of Hexagonal and Triclinic $CaAl_2Si_2O_8$

We used the seeding methods and grew the desired polymorph. Thus observed phases in the present solution have the growth rates different distinctly, similarly as in the case of melt. For example, at 1230°C the growth rate of anorthite in the fastest growth direction is about 1.5 μm/sec, while that of hexagonal $CaAl_2Si_2O_8$ 3.5×10^{-4} μm/sec, order of four difference. Also, both polymorphs take distinctly different morphologies. This is also noticed above 1100°C, as seen in Figs. 4 and 6. Anorthite grows as a radiating aggregate of elongated thin plates at 1150 and 1200°C. In thin sections they appears as a bundle of needle crystals (Fig. 6b). This figure also shows how anorthite was formed by the devitrification. The anorthite plates become thicker and more isolated as increasing temperature, decreasing ΔT. Above 1300°C, $\Delta T < 100$°C, anorthite grows in a platy form (Fig. 6c). The hexagonal crystals, taking a dendritic form at 1000–1050°C, becomes platy above 1100°C. Dendritic features are not observable any more above 1200°C (Figs. 6e and f), although in cases they had some grain boundaries and defects inherited from the seed. The crystal becomes more polyhedral as increasing temperature and the run duration. The polyhedral morphology is observable in a wider temperature range in the present solution than that in the melt. This is in good agreement with the general tendency argued by Sunagawa (1982). In the ex-situ program runs above 1200°C, most of the crystals were often oriented horizontally to the sample surface. This is the reason why we prepared the thin section cut vertically to the ring holder. So, the hexagonal phase is often seen as an elongated tabular form in thin sections (cf. Fig. 11).

By XRD on quenched specimens, hexagonal $CaAl_2Si_2O_8$ is easily distinguished from the triclinic phase, anorthite (cf. Figs. 4 and 10). Two sets of paired peaks are observable at 12° (d=7.48 and 7.36Å) and 24° (d=3.74 and 3.68Å), where there is no peaks for anorthite. Judging from their pairing, the observed phase is closer to the pseudo-hexagonal phase, *C*2 (Ito, 1973), than to the hexagonal, $P6_3$/mcm (Takéuchi and Donnay, 1959). In this study, we treated this phase simply as "hexagonal". The d-values and the XRD pattern are almost the same with those observed in our previous study on the An_{100}, except for the relative intensity. In both pairs, the intensities at the side of lower angle are stronger for the crystals grown in the solution, whereas they are opposite for the crystals grown in the An_{100} melt, in spite that they were annealed at

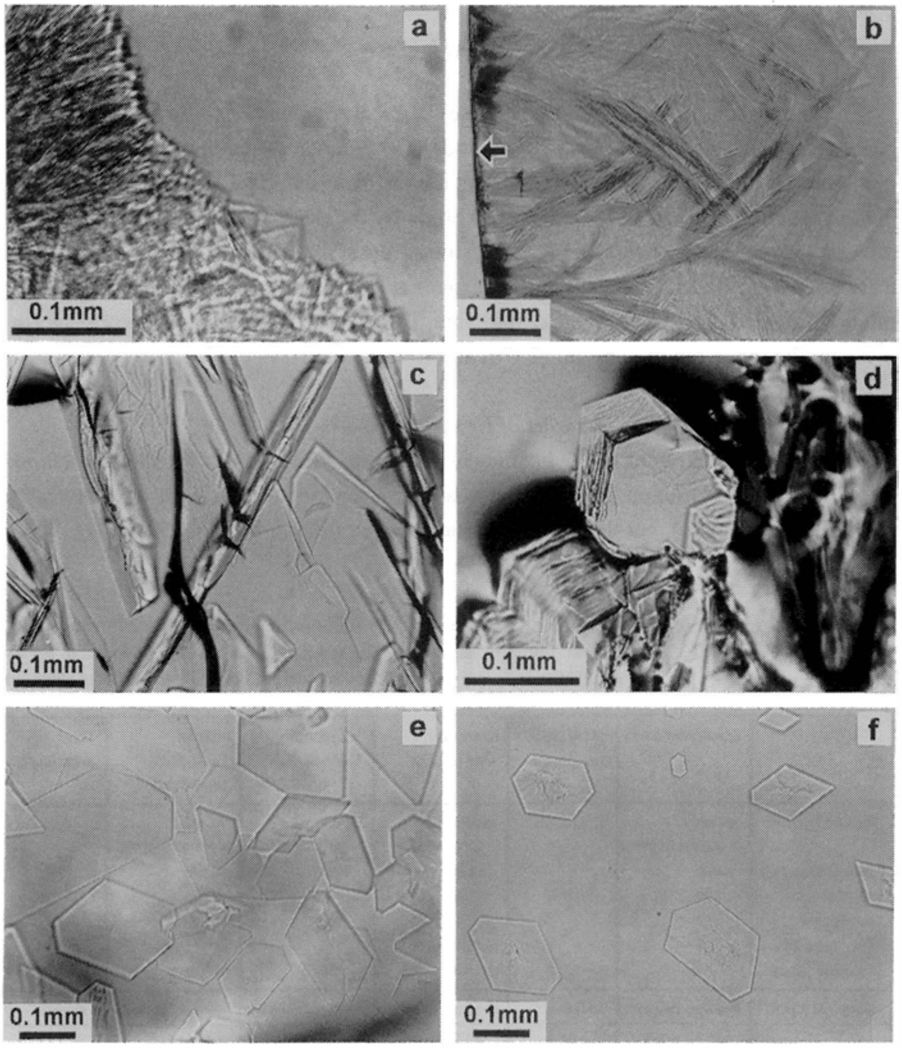


FIG. 6. Photomicrographs showing the characteristic morphologies. (a) Growing anorthite at 1150°C, after 7 minutes from the in-situ seeding. This phase was quenched after 1 hour and examined by XRD (Fig. 4d). (b, c) Anorthite in thin sections. They were grown by the ex-situ devitrification at 1200°C for 5 minutes and at 1360°C for 1 hour, respectively. Anorthite crystallization was started from the glass surface indicated by the arrow in (b). (d) Growing hexagonal phase by the in-situ run (1150°C, 20 hours). This phase was quenched and examined by XRD (Fig. 4f). (e, f) Hexagonal phase in bulk specimen. They were grown by the ex-situ program method, at 1200°C for 15 hours and 1220°C for 10 hours, respectively.

the same temperature and considered to have the same crystal composition. This may indicate the detailed structure of "hexagonal" $CaAl_2Si_2O_8$ varies depending on how they grow, slowly or rapidly.

The two polymorphs have almost the same chemical compositions with small differences. The hexagonal crystals grown at 1200°C and 1150°C have the compositions close to the stoichiometric one (Table 1). Only small deviations from the ideal formula are noticeable. Whereas, anorthite grown at 1360°C for 20 hours by the devitrification shows much larger deviation than the hexagonal phase, although they grew at the same ΔT. The anorthite crystals take nearly twice the MgO content of the hexagonal crystals. In addition, excess of SiO_2 and depletions of Al_2O_3 and CaO are also remarkable. The excess SiO_2 and the vacancy in anorthite are within the range reported by Ito (1976) and Longhi and Hays (1979).

Determination of Metastable Liquidus of Hexagonal $CaAl_2Si_2O_8$.

The metastable liquidus of the hexagonal phase was measured by the in-situ method. It is seen that three polyhedral hexagonal crystals are growing steadily with straight edges at 1230°C (Figs. 7a and b), but the edges become rounded (dissolved) at 1250°C (Fig. 7c). By

TABLE 1. Averaged compositions of glass, hexagonal crystals and anorthite crystals, together with the ideal glass in $An_{70}Fo_{10}Silica_{20}$ and the stoichiometric anorthite. The methods and the conditions used for the crystal preparations are also noted. The terms "program" and "devitrification" indicate the seeding methods.

	quenched glass		ideal glass (An_{70}·Fo_{10}·$Silica_{20}$)	hexagonal $CaAl_2Si_2O_8$		hexagonal $CaAl_2Si_2O_8$		triclinic $CaAl_2Si_2O_8$ (anorthite)		ideal anorthite
method	ex-situ (simple heating)		——	ex-situ (program)		in-situ (program)		ex-situ (devitrification)		——
Temperature (°C)	1480			1200		1150		1360		
ΔT (°C)	-80			40		90		40		
duration (hr)	2			20		50		20		
prepared products	3			2		1		1		
analyzed points	40			43		53		26		
oxide (wt%)	average	deviation	nominal	average	deviation	average	deviation	average	deviation	nominal
SiO_2	52.7	0.8	54.5	43.2	0.5	43.4	0.4	45.2	0.4	43.2
MgO	7.7	0.1	5.7	0.2	0.0	0.2	0.0	0.3	0.0	0.0
CaO	13.8	0.2	14.1	20.0	0.2	20.0	0.2	18.9	0.3	20.2
Al_2O_3	25.7	0.6	25.7	36.6	0.4	36.0	0.4	35.7	0.4	36.6
total	100.0	0.5	100.0	99.9	0.6	99.5	0.4	100.2	0.4	100.0
cation (O=8)	average	deviation	nominal	average	deviation	average	deviation	average	deviation	nominal
Si	2.38	0.03	2.51	2.00	0.01	2.02	0.01	2.08	0.01	2.00
Mg	0.52	0.01	0.39	0.01	0.00	0.01	0.00	0.02	0.00	0.00
Ca	0.67	0.01	0.70	0.99	0.01	0.99	0.01	0.93	0.02	1.00
Al	1.37	0.03	1.39	2.00	0.02	1.97	0.02	1.93	0.02	2.00
total	4.94	0.02	5.00	5.00	0.01	5.00	0.01	4.96	0.01	5.00

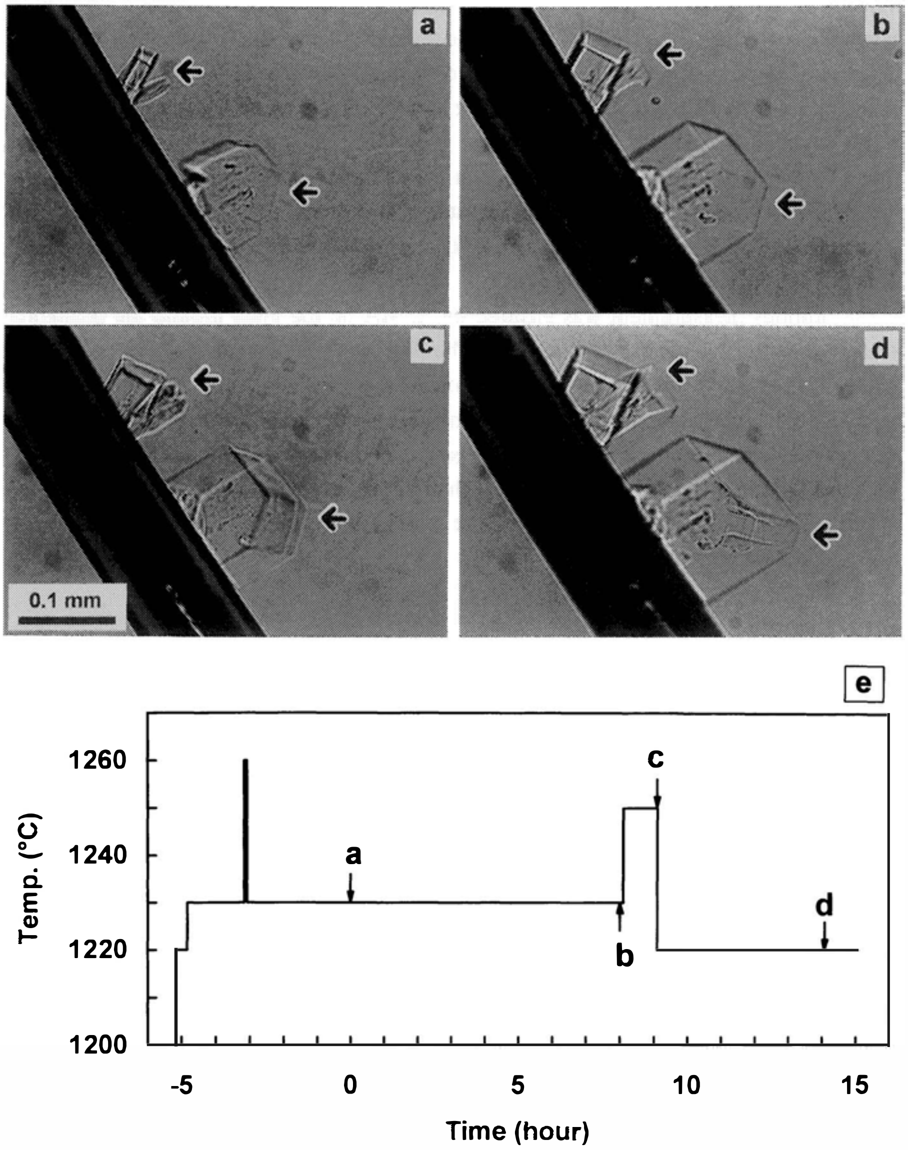


FIG. 7. Successive photomicrographs showing growth and dissolution of hexagonal crystals in the absence of anorthite, by changing temperatures. The outline indicated by arrows changes from straight (a and b) to rounded (c), and again straight (d). (e) shows the temperature and time conditions corresponding to photomicrographs (a)–(d). The time mark 0 corresponds to the moment of (a).

decreasing the temperature again down to 1220°C, the crystals again transform to polyhedral with straight edges (Fig. 7d). Thus the growth and dissolution process is reversible with change of temperature, and the metastable liquidus is determinable about 1240±10°C in this liquid composition. This is about 20°C higher than the ternary eutectic point and about 160°C lower than the liquidus of anorthite. This difference is almost comparable with that in the An_{100} composition where the metastable liquidus is at 1400°C and the stable one at 1553°C (Abe *et al.*, 1991). It is also worthwhile to note that crystals of hexagonal $CaAl_2Si_2O_8$ dissolve slowly near the liquidus, but they disappear more quickly by rapid dissolution at higher temperature, such as at 1300°C.

The liquidus measurement was ensured by EPMA on the glass around the hexagonal crystals, compared with those of anorthite. The data were converted into the contents of $CaAl_2Si_2O_8$, SiO_2 and Mg_2SiO_4, and projected on the section along An_{100} – eutectic point. As seen in Fig. 8, the glass compositions around the hexagonal crystals are quite different from those expected from the anorthite liquidus. These are concordant with the metastable liquidus on the presumption that it exists 150°C lower than the anorthite liquidus. It is also noted that most of the plots at 1100°C are still around the initial composition. This is due to the lower diffusion and the higher viscosity.

Disappearance of Hexagonal $CaAl_2Si_2O_8$

It was expected from the liquidus relation (Fig. 8) that the hexagonal phase would dissolve with the crystallization of anorthite. Such a dissolution must be observed if the direct transformation is not operative. In the actual experiments, however, the dissolution was not obviously observed, as seen in Figs. 9, corresponding photomicrographs and a temperature-time diagram. In Fig. 9a, three hexagonal crystals are growing with distinct polyhedral morphology on the wire at 1230°C in the absence of anorthite crystals. Then anorthite crystallization was started by the seeding. Anorthite grew much faster than the hexagonal crystals since it was subjected to a much larger supercooling than the hexagonal phase. Fig. 9b indicates the moment when anorthite (labelled "An" on the right) got in contact with the hexagonal crystals, after 8 minutes from the seeding. The temperature is the same as in Fig. 9a, and the hexagonal crystals do not show any change in their morphology. In keeping at this temperature for further 5 minutes, needle crystals of anorthite continued to grow and completely covered the hexagonal $CaAl_2Si_2O_8$ crystals. Temperature was then increased up to above 1400°C, the anorthite liquidus, in a stepwise manner. By keeping the sample at about 1410°C for more than 10 minutes, anorthite seen on the right of Fig. 9b was dissolved away. Fig. 9c shows the feature immediately after this event. It should be noted in Fig. 9c that the original outline of hexagonal crystals was still preserved as a whole, although it became shaggy. When the temperature was further increased up to 1430°C, the shaggy appearance was enhanced while keeping the general outline of the crystals unchanged, although the sizes became smaller and the outline became rounded. Such a slight modification of the outline is

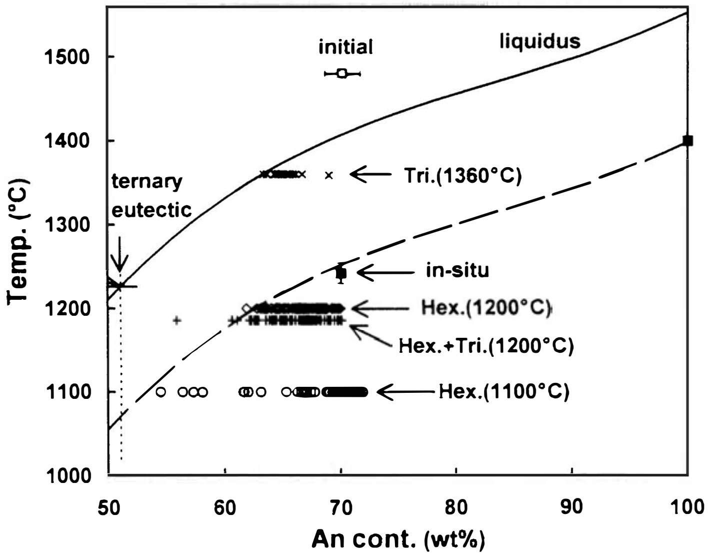
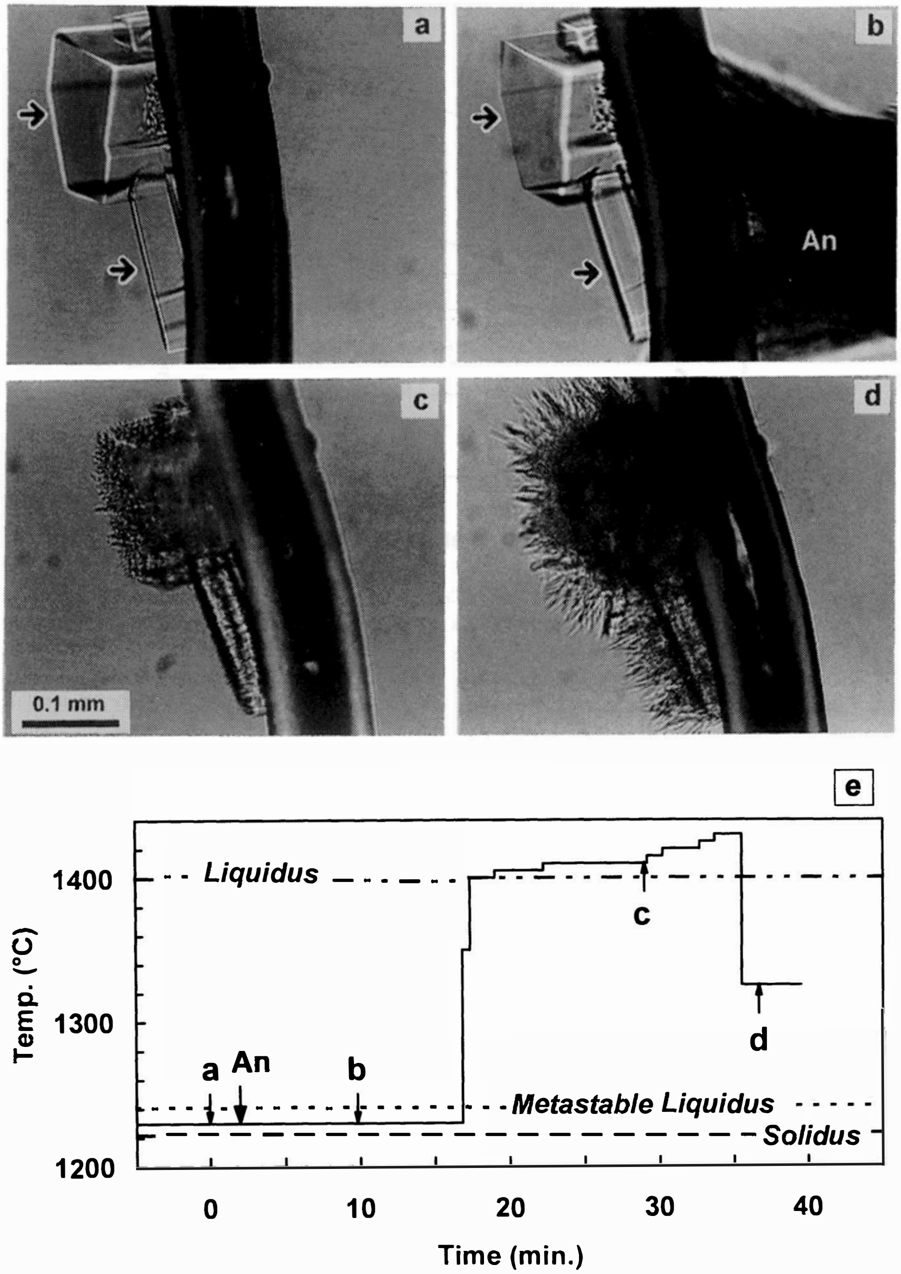


FIG. 8. Metastable liquidus (dashed line) in the section including anorthite and the starting composition, which is drawn by the shift to 150°C lower temperature from the anorthite liquidus (Andersen, 1915). The in-situ measurement is also imposed in the diagram (solid square). The open square with an deviation bar at 1480°C indicates the averaged composition of the starting materials. Other plots indicate glass compositions, measured by EPMA, around the hexagonal crystals grown at 1200°C for 20 hours and 1100°C for 30 hours, and the anorthite crystals at 1360°C for 20 hours. For the product with the hexagonal phase and anorthite (at 1200°C, after 1 hour's seeding), the plots are shifted downward to avoid the overlap.

probably due to a slow dissolution at this temperature, and is not explainable if the crystals were still hexagonal. They must have changed to anorthite. This is proved by the growth of anorthite when the temperature is decreased to 1320°C (Fig. 9d).

We made another in-situ experiment at 1150°C, in which the hexagonal crystals were grown large for 20 hours and anorthite was crystallized by the seeding. Also in this case, the dissolution form was never observed. The preexistent hexagonal crystals were not dissolved but simply covered with anorthite, whose growth rate was smaller than in the former case since the liquid was more diluted. Yet, XRD on the sample quenched in 5 hours after the seeding indicated that hexagonal phase disappeared completely and anorthite was present dominantly.

By a series of ex-situ experiments, the above behavior was traced systematically and in detail. In Figs. 10 and 11, representative examples are shown by XRD charts and corresponding photomicrographs. Figs. 10a and 11a show the sample before the reheating. It consisted of hexagonal crystals and glass. Higher background around 25° (CuKα) is due to the presence of


a
b
An
c
d
0.1 mm
e
Temp. (°C)
1400
1300
1200
Liquidus
Metastable Liquidus
Solidus
a
An
b
c
d
0
10
20
30
40
Time (min.)

glass. The sample was heated again at 1200°C. By this reheating, anorthite crystallization was started from the glass surface, similarly as observed in the devitrification of the glass. The change owing to the quench and reheat was never observed on the hexagonal crystals, except for the cracking. After 0.5 hour of reheating, anorthite crystallizes partially and gets in contact with hexagonal crystals. A part of hexagonal crystals transformed to anorthite during this duration (cf. etched features in Fig. 12c and d), but glass and unchanged hexagonal crystals are

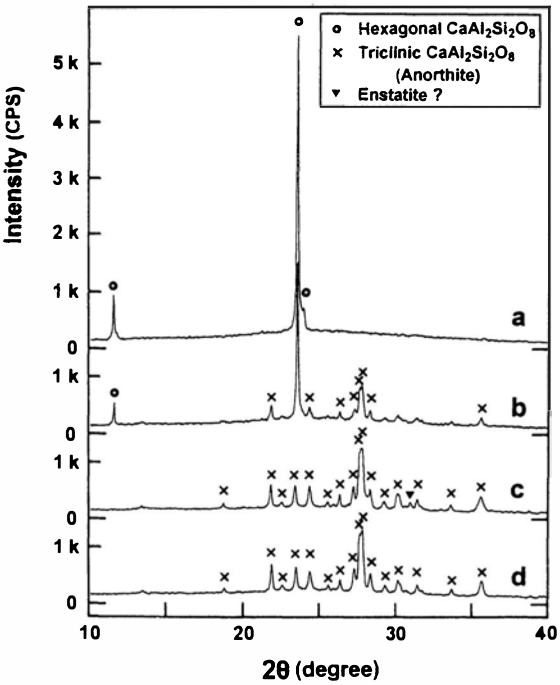


FIG. 10. XRD patterns of quenched ex-situ specimens. (a) The product before the reheating. It consists of the glass and hexagonal CaAl$_2$Si$_2$O$_8$. The hexagonal crystals were prepared by the program method, nucleation at 1000°C, and were grown large for 20 hours at 1200°C. (b, c) The products after 1 and 2 hours' reheating, respectively, at 1200°C. Note that the peaks from the pre-existent phase becomes weak and diminishes. (d) The reference product, prepared by reheating a glass, which did not contain hexagonal phase, at 1200°C for 1 hour.

FIG. 9. Photomicrographs showing how hexagonal CaAl$_2$Si$_2$O$_8$ crystals (arrows) change to anorthite, when anorthite is present. Needles in (c) and (d) are anorthite crystals formed by "An" in (b) whose crystallization was triggered by seeding. (e) shows the temperature and time conditions corresponding to respective photomicrographs (a)–(d). An with an arow indicates the onset of seeding of anorthite (start of the anorthite crystallization). The time mark 0 corresponds to the moment of (a).

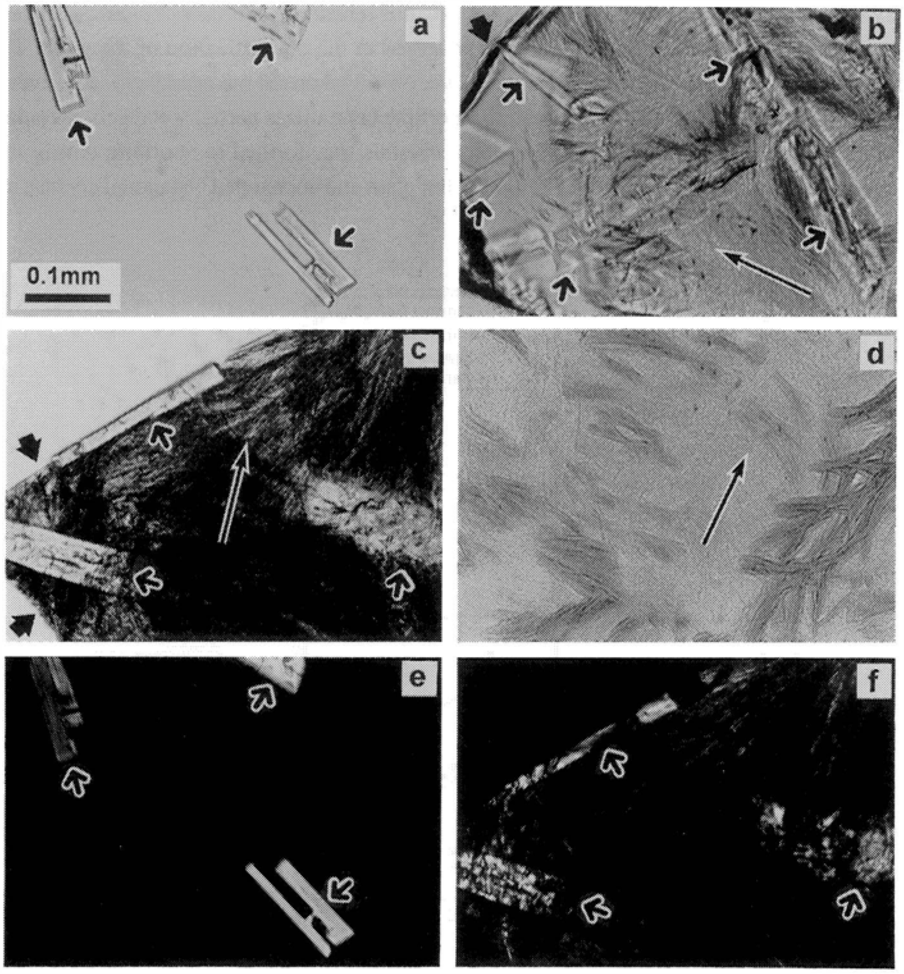


FIG. 11. Photomicrographs of thin sections corresponding to (a)–(d) in Fig. 10. Short arrows are hexagonal crystals, long arrows anorthite, and thick bold arrows the boundary between mounting resin and the specimen, which corresponds to the free surface of the bulk specimen. With crossed nicols, sections (a) and (c) are seen as (e) and (f), respectively.

still present. The slow rate of anorthite crystallization is consistent with the in-situ observation. This is due to the presence of the hexagonal crystals. As time elapses, anorthite becomes dominant and hexagonal phase entirely disappears, mostly within a few hours. The intensities of hexagonal phase diminish markedly in less than 1 hour (Fig. 10b). In the thin section (Fig.

11b), feather-like needle anorthite crystals (long arrows) cover the pre-existing hexagonal crystals (thick arrows), but straight outlines of unchanged hexagonal crystals are still clearly seen in the residual glass, indicating that dissolution did not take place even in the presence of

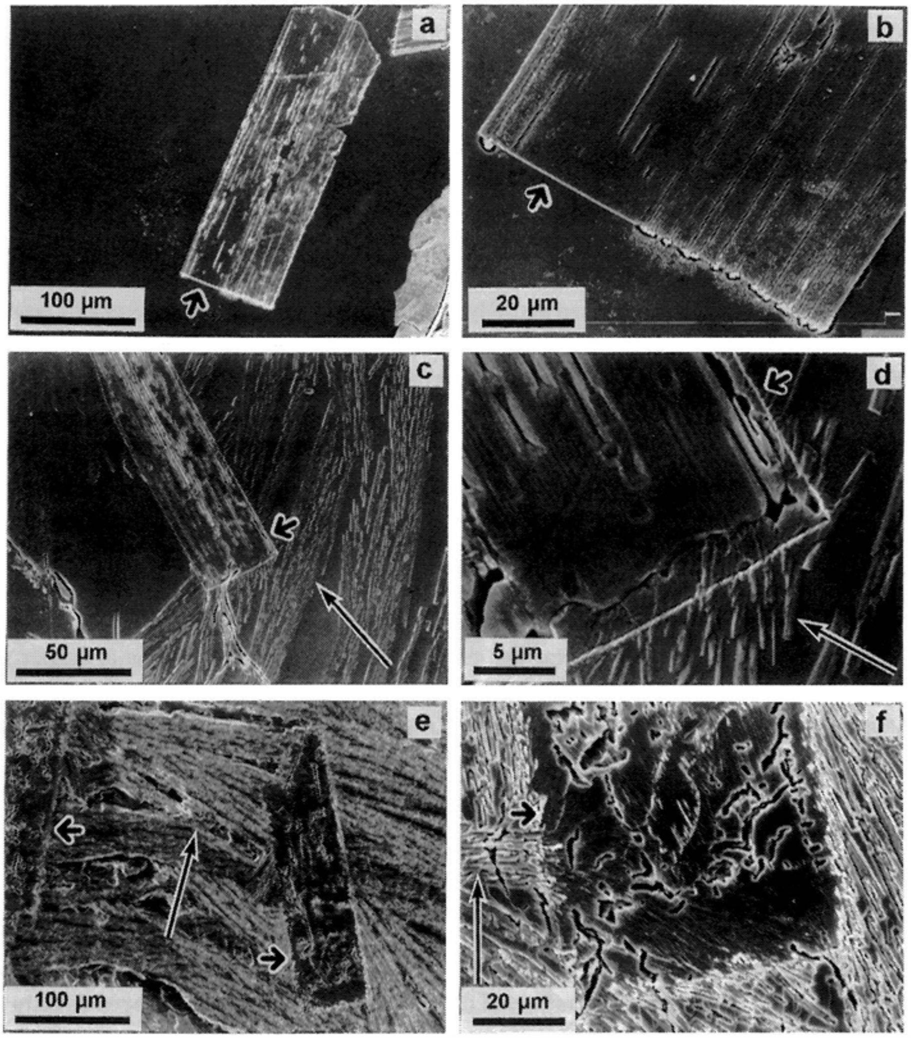


FIG. 12. Etched surfaces of sliced and polished specimens at different magnifications. (a, b) Before the reheating. The hexagonal crystals were grown by the same procedure in Figs. 10a and 11a. (c, d) After 30 minutes' reheating. (e, f) After 2 hours' reheating. Short arrows indicate the outline of hexagonal crystals. The surrounding needle crystals (long arrows) are anorthite.

anorthite. Actually, as seen in Fig. 8, the composition of the residual glass was changed slightly from that in the absence of anorthite. In the XRD after 2 hours' reheating (Fig. 10c), no peak from the hexagonal phase is detectable. It shows the similar pattern with the reference, the devitrified glass (Fig. 10d). In the section (Fig. 11c), however, the hexagonal crystals is still seen in a quantity to be detectable by XRD, together with anorthite crystals. Therefore, the pre-existent hexagonal crystals must have transformed into anorthite while preserving their characteristic forms. Actually, it is noted in the detail observations that the outline of hexagonal crystals became rugged and the crystal perfection diminished. The extinction under a polarizing light became diffused, wavy and patched, and was related at portions to that of anorthite (Fig. 11f).

By etching the polished section, the transformation process from hexagonal phase to anorthite is more clearly discerned. The etched surface of a hexagonal crystal before reheating shows many faint but clear grooves parallel to the basal plane (Fig. 12a and b). After 0.5 hour reheating, hexagonal phase changed partially to anorthite. The change started from the points on the periphery of the hexagonal crystal where needle crystals of anorthite were in touch with the former, and proceeded inward. The inner part of the hexagonal crystal was still unchanged, as exemplified by the presence of parallel grooves (Fig. 12c and d). It should be noted that the outline of the hexagonal crystal remained sharp and straight, in spite of that the inner texture changed to consist of needles, resembling the surrounding anorthite needles. Such a texture cannot be observed if the hexagonal phase was simply dissolved by the crystallization of anorthite. In addition, the SEM shows clearly that the crystallites of anorthite are in a needle shape and isolated by the glass. This is the reason why the liquid composition was not changed much even around the anorthite aggregate and why anorthite got in contact with the hexagonal crystal. After 2 hours, original hexagonal crystals changed completely to an aggregate of needle crystals whose elongation is related to that of the surrounding anorthite needles. The outline of hexagonal crystals became diffuse and rugged (Fig. 12e and f), owing to later growth, coarsening.

The SEM observations were proved further by BEI and X-ray images. If the dissolution process operated essentially in the phase change, the Mg-rich interface between the hexagonal and triclinic crystals should be observed. We observed the polished surfaces of the samples before reheating and after 1 hour' reheating (Fig. 13). From the condition and the presence of the grooves, the observed crystals (Fig. 13c) were judged to have changed partly to the triclinic phase. Nevertheless, the Mg-rich layer is never detectable between the two phase (Figs. 13c and d). Thus, all the observations indicated that the hexagonal phase has changed directly to the triclinic one.

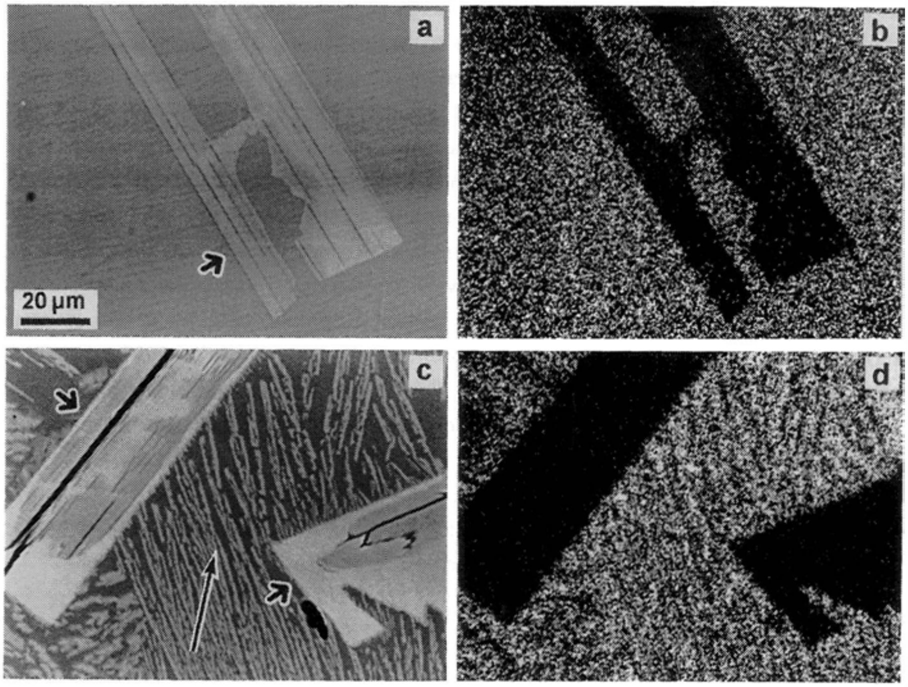


FIG. 13. Two sets of BEI and X-ray images (Mg-Kα radiation). The portion enriched in light elements, such as Mg, appears dark in the BEI, and that enriched in Mg appears bright in the X-ray images. (a, b) Before the reheating, and (c, d) after 1 hour's reheating. Short arrows indicate the outline of hexagonal crystals. The surrounding needle crystals (long arrow) are anorthite. In (c), the characteristic grooves are seen in the inner, but not at the outer contacted with the needle anorthite. This indicates that the hexagonal crystals have changed from the contact. Yet, the Mg-rich layer is not noticed between them.

Discussion

Nucleation and Growth

Hexagonal $CaAl_2Si_2O_8$ nucleates prior to triclinic one at 1050 and 1000°C, in spite of 160°C larger ΔT being subjected to anorthite than to the hexagonal. Whereas, anorthite appears first at higher temperatures. This inverse occurrence is not explained by the growth rates, since the growth rate of anorthite is always larger than that of the hexagonal at any temperatures. So the earlier appearance of the hexagonal phase at lower temperatures arises from the faster nucleation rate. This is explainable qualitatively by the same argument as in our previous study on An_{100} melt (Abe *et al.*, 1991). As a first approximation, we analyze the nucleation rate taking only the activation energy for nucleation into consideration. The nucleation rate is proportional to exp(−ΔGa/kT), where ΔGa is the activation energy barrier, k the Boltzmann's constant, and T the absolute temperature. ΔGa is proportional to the third power of the interfacial energy, γ^3, and inversely to the second powder of the free energy change, μ^2. Although the studied system is not a pure melt, we estimate $\mu \approx -\Delta H \bullet \Delta T/T_e$ similarly as in the case of melt, where ΔH is the enthalpy of fusion and T_e the liquidus temperature. In this estimation, we presume that the heat capacities of two polymorphs change greatly with the temperature change. This is not so implausible for the crystalline phase whose structure does not change with temperature. Anyway, the former estimation is an oversimplification for the solution system, but still valuable for understanding the nucleation behavior qualitatively as a function of respective ΔT. Consequently, the activation energy for nucleation is proportional to γ^3 and inversely $(\Delta H)^2(\Delta T)^2$. At any temperatures, ΔT for anorthite is 160°C larger than that for hexagonal phase, so anorthite should always appear first if γ and ΔH values are nearly the same for the two phases. This conflicts obviously with the observation, namely, intersecting curves show a higher slope for anorthite than for hexagonal phase. Such a relation results when γ^3 is larger or ΔH^2 is smaller enough for anorthite than that for the hexagonal. The smaller ΔH for anorthite, which is stable and grows much faster, is implausible. Therefore, we conclude the earlier nucleation of the hexagonal is due to the smaller interface energy. As understood from the extreme case at 1240°C, where the hexagonal phase can not obtain any ΔT but anorthite obtains 160°C, the degree of ΔT determines the phase to nucleate as the temperature increases. This is the reason why anorthite appears at higher temperatures. At lower temperatures, anorthite should appear as the secondary phase. However, once the hexagonal phase nucleates and grows large enough, the liquid composition is diluted for $CaAl_2Si_2O_8$, which delays the other nucleation, so that anorthite rarely appears.

As seen in Fig. 5, the incubation time should decrease with the decrease of temperature, and the hexagonal should appear easily. However, it is rather dangerous to further extend them to lower temperatures, since the atoms lose mobility with the decrease of temperature and the nucleation is delayed significantly. Below the glass transition temperature the nucleation and the growth is not expected anymore. The glass transition temperature in this solution and other dry silicates is presumably in the range from 700 to 800°C, judged from the temperatures of 753°C for $CaMgSi_2O_6$ melt, (Briggs, 1975) and 812°C for $CaAl_2Si_2O_8$ melt (Arndt and Häberle, 1973). Therefore, the minimum incubation is present at the temperature between 1000 and 700°C. This temperature practically confines the lowest limit of temperature for the hexagonal phase to appear. We have to consider this effect in order to judge whether the hexagonal $CaAl_2Si_2O_8$ appears in other silicate systems. For $An_{70}Fo_{10}Silica_{20}$, the hexagonal phase needs ΔT>200°C, which corresponds to ΔT>360°C for anorthite. If a silicate solution, which has a lower liquidus temperature, is supercooled largely enough for the hexagonal phase to attain large ΔT, the temperature might be already below the minimum incubation temperature and in cases below the glass transition temperature. If so, the crystal phase is rarely or never expected to appear. Therefore, the metastable nucleation of hexagonal $CaAl_2Si_2O_8$ is observable in the systems whose the liquidus is high enough.

Disappearance of Hexagonal $CaAl_2Si_2O_8$

When anorthite is absent, hexagonal crystals behave as if they were crystals of a stable phase, although the phase does not have its stability field of temperature. This is quite in contrast for the case of hexagonal $BaAl_2Si_2O_8$, which is more stable at high temperature than celsian, monoclinic phase (Lin *et al.*, 1968). The metastable liquidus temperature of hexagonal $CaAl_2Si_2O_8$ changes depending on the composition; 1240°C for $An_{70}Fo_{10}Silica_{20}$, 1360°C for $An_{80}Wo_{20}$ and 1400°C for An_{100}. The difference from the corresponding liquidus temperature of anorthite is 160, 140, and 150°C, respectively and is almost constant within the experimental error. Therefore, the average difference, 150°C, is useful in practical estimation of a metastable liquidus in another silicate system, unless the system contains substitution elements.

In the presence of anorthite, however, hexagonal crystals disappears quickly. Two different processes have to be considered for this change: (1) concurrent growth of anorthite and dissolution of hexagonal phase, and (2) reconstructive transition triggered by anorthite. As reported previously (Abe *et al.*, 1991), the process (1) was directly confirmed by in-situ observation in the An_{100} composition. The temperature increase, which is caused by the anorthite crystallization, is considered as the only driving force for this melting. However, the temperature increase is not expected to be large enough to account for all the changes observed at lower temperatures. Actually, the melting in the presence of anorthite was observable only when the metastable phase was growing just below the metastable liquidus. We, therefore, assumed in the previous study that the direct transformation should have taken place in the change from hexagonal $CaAl_2Si_2O_8$ to anorthite at extensive temperatures.

From the liquidus relation of the polymorphs (Fig. 8), we can expect that the process (1) should be detected more easily in a solution than in the melt. This is true even if two other stable phases, enstatite and/or tridymite, crystallize together with anorthite at subsolidus temperatures. However, in the solution of $An_{70}Fo_{10}Silica_{20}$, process (1) was not observed. This suggests that the process (2) is more likely operating than the process (1). As seen in Fig. 9, hexagonal phase transforms to anorthite, while preserving its original polyhedral outline sharp. Only at a later stage after complete transformation of hexagonal phase to anorthite, the straight outline of original polyhedral crystals becomes rounded. All these observations indicate that the change should have been brought by direct transformation. We, therefore, conclude that the reconstructive type transition from hexagonal phase to anorthite (process 2) is a more likely process even in solution systems than dissolution and growth (process 1). It starts as soon as crystals of both phases are in contact with each other, and the points of contact act as nucleation sites of transition. The transition proceeds more quickly and easily than the dissolution proceeds in which diffusion process is required. The process (1) is not significant and may be operative only slightly, even if any. The dissolution of this type might be observed when a crystal small enough to be dissolved out in a short time is present in a temperature range close to the metastable liquidus.

In nature, heterogeneous nucleation of anorthite occurs more likely than in the laboratory. Even if the hexagonal phase nucleates, the transition proceeds easily in the presence of anorthite. Therefore, it should be very difficult to find hexagonal phase in nature. Exceptionally, there is a little probability in the case of highly heated and rapidly cooled materials enriched in pure anorthite. Small droplets ejected from an impact melt of anorthosite on the moon may correspond to such an exceptional case, where we may expect that metastable nucleation of hexagonal phase took place one time, as yoshiokaite crystallized metastably (Vaniman and Bish, 1990).

Conclusions

When a liquid with composition of $An_{70}Fo_{10}Silica_{20}$ is supercooled largely down to 1100–1000°C, hexagonal $CaAl_2Si_2O_8$ nucleates dominantly instead of anorthite in an incubation time from 10 to 1.5 hours, similarly as in the case of An_{100} melt and $An_{80}Wo_{20}$ solution. The incubation time, however, is much longer than that observed in the latter. The nucleation of anorthite was rarely observed at 1000–1050°C in spite of the larger ΔT, 350–400°C, being realized for anorthite, but it was observed more at 1100–1250°C, smaller ΔT. This is because the hexagonal phase is not subjected to ΔT large enough to nucleate soon. Thus, the appearance of two polymorphs can be understood as a competition between the two factors, the degree of ΔT and interfacial energy. In the present solution, the orthorhombic phase was not observed.

The chemical composition of hexagonal phase is practically the same as its ideal composition. The deviation from the ideal formula is slight and not characteristic. The XRD's pattern and morphology are distinctly different from those of anorthite. Crystals of hexagonal phase take a thick platy habit to a thin dendritic form with hexagonal symmetry, depending on growth conditions.

The metastable liquidus of hexagonal phase was measured by the morphology observations and EPMA and is 140–160°C lower than that of anorthite. This difference is almost independent on the liquid composition. At a temperature below this metastable liquidus, hexagonal crystals can grow steadily. When anorthite crystals are crystallized in the liquid by seeding technique, anorthite grows four orders of magnitude faster than hexagonal crystals, due to much larger ΔT of anorthite.

Hexagonal $CaAl_2Si_2O_8$ cannot coexist with anorthite. Once anorthite appears in the system and comes into contact with a hexagonal crystal, the latter easily disappears. All the examinations by the in-situ and ex-situ methods support that the hexagonal phase changes to anorthite through the transition process, not through the dissolution process. Owing to this change, it would be difficult to find hexagonal crystals in nature, even if they were once formed.

Acknowledgments–The authors are grateful to Dr. K. Tsukamoto of the Tohoku

University for his advice and help. They are also indebted to Dr. Y. Isozaki of the Yamaguchi University for his help with SEM. Thanks also to the instrumental analysis center of Yamaguchi University for the usage of EPMA.

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Received November 29, 1994; accepted March 30, 1995.