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Effect of Water on Crystallization Process of Coesite

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The effect of water on crystallization process of coesite was studied at 450 to 700 °C under 30 kbars by using different starting materials. The presence of water under compression and heating was found to have remarkable effects not only on the kinetics of crystallization of coesite also on the morphology of metastable quartz, consequently of coesite crystals. Under anhydrous condition, from amorphous silica and silica glass, the spherulitic aggregates of metastable quartz appeared. The coesite crystals were developed in the spherulites of quartz as elongated crystals with different sizes and appeared to be defective. When synthetic quartz was used as a starting material, however, no formation of spherulitic aggregates of quartz was observed and granular coesite crystals were obtained. Under hydrous condition, granular coesite crystals with homogeneous size were developed rapidly at 450 °C from both amorphous silica and silica glass through the discrete particles of metastable quartz.

Water plays a very important role in the crystallization and phase transformation of silica.[1–7] Previously,[8] the effect of water on the crystal growth of coesite under 30 kbars at 900 °C has been discussed from crystal morphology and size of coesite formed; in anhydrous condition the coesite grains are sintered and appeared to be defective, whereas in hydrous condition the coesite crystals are euhedral and less defective. It has also been pointed out that the transformation of amorphous silica to coesite is a consecutive process through the metastable phase of quartz and that water accelerates both steps in the consecutive process.[9,10] The formation of spherulitic aggregates of metastable quartz has been briefly reported under anhydrous condition.[11]

In the present paper, the effect of water on the crystallization process of coesite was studied in detail, particularly paying attention to morphology and aggregation state of metastable quartz, by using various starting materials between 450 and 700 °C under 30 kbars.

Experimental

Materials. The starting materials used were noncrystalline silicas, so-called amorphous silica and silica glass, and synthetic quartz. Amorphous silica with particle size of 0.1—10 μm was prepared by hydrolysis of silicon ethoxide and then heating at 1200 °C for 2 h. Silica glass with particle size of 0.5—1.0 μm was prepared by mechanical grinding of the commercial silica glass rods and by means of elutriation. The silica glass was heated at 800 °C for 2 h in order to remove the strain and the adsorbed water. The quartz powder with particle size of 0.5—1.0 μm was prepared by the method similar to the preparation of silica glass. Heating at 800 °C for 48 h was necessary for removing water adsorbed.

High Pressure Treatment. The crystallization of coesite was performed at the temperature range of 450 °C to 700 °C under 30 kbars for various durations up to 96 hr, with a girdle type high pressure apparatus,[10] either with or without water. Amount of water added into the sample was 4, 10, or 16 wt%. The samples were heated with the heating rate of 200 °C/min and after the programmed duration at a desired temperature quenched in the cell under compression.

Characterization of Specimen. The phases formed were identified with the X-ray powder technique and optical microscopy. The proportions of the phases were determined from the relative peak intensities of diffraction lines.[10] The crystallite size of metastable quartz was evaluated from the half widths of X-ray diffraction lines according to Hall's equation. The crystals of metastable quartz and coesite were examined by optical and scanning electron microscopes.

Results and Discussion

Crystallization from Amorphous Silica. In Fig. 1, the variations of proportion of the original amorphous silica, metastable phase of quartz and coesite with heating time are shown in both cases, without water and with 10 wt% water, at 450 °C. The kinetic process of the transformation changes by the addition of water.[9] The effect of water addition was seen not only from kinetics also from morphology of metastable quartz and coesite. Under anhydrous condition, metastable phase of quartz crystallized into spherulitic aggregates with the apparent size up to 50 μm after 4 h heating. These spherulites of quartz were formed in the matrix of unchanged amorphous matrix. The aggregate consisted of fine quartz crystals with the size of 0.5—1.0 μm, of which c-axes oriented radially. The size of the aggragates increased with the increase of heating time. It became up to 300 μm after 48 h. In the center of the spherulitic aggragates, where the radial orientation of crystals of quartz collapsed, needle-like crystals of coesite with the size of 20—50 μm were often found (Fig. 2-A). After 96 h quartz completely transformed to coesite, but the size of coesite crystals did not show any detectable increase. With 10 wt% water, on the other hand,

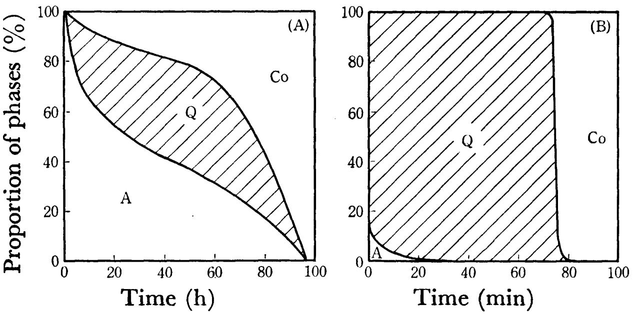

Fig. 1. Variations in proportions for phases obtained from amorphous silica at 450 °C under 30 kb.
A: Without water, B: with 10 wt % water.
Abbreviations; A: amorphous phase, Q: quartz, Co: coesite.

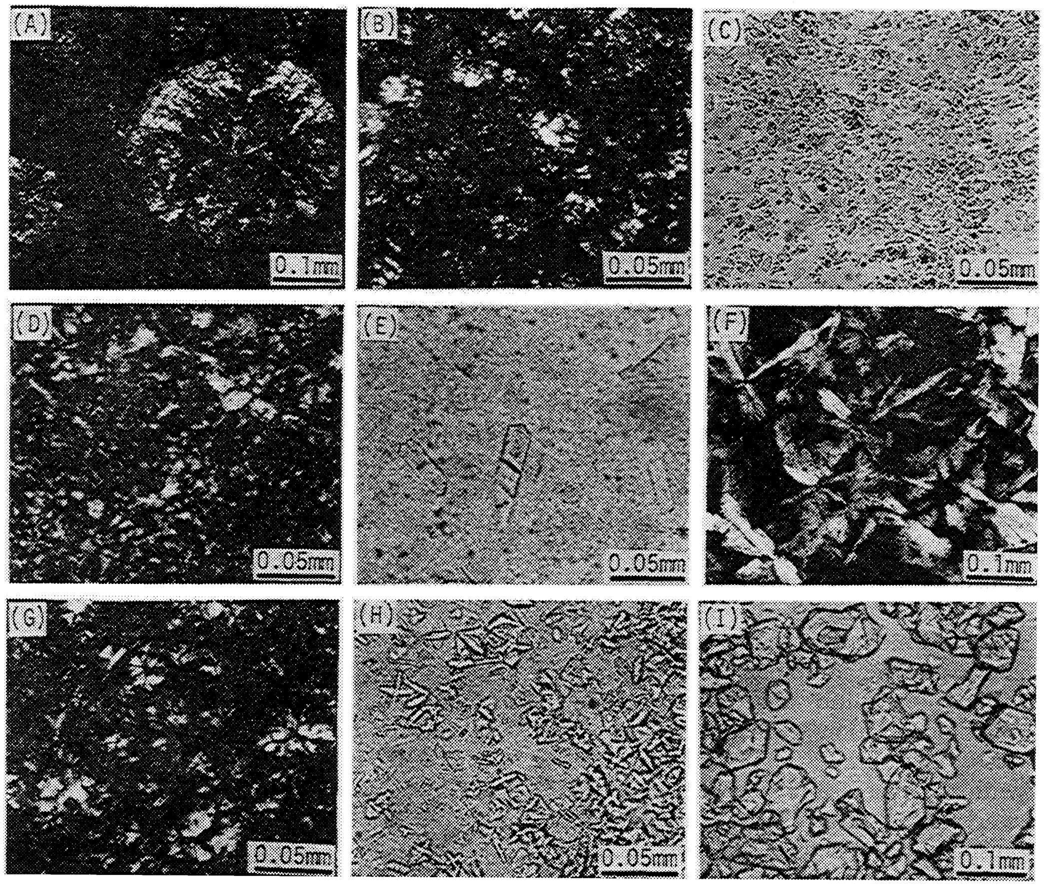

Fig. 2. Microphotographs of crystallization process of coesite from amorphous silica under 30 kb.

A: Spherulitic aggregates of metastable quartz in amorphous silica and radial growth of coesite at the center of the spherulite after heating at 450 °C for 48 h without water (under crossed nicols).

B: Small quartz aggregates in amorphous silica matrix heated at 450 °C for 1 h in the presence of 10 wt % water (under crossed nicols).

C: Granular coesite crystals formed after heating at 450 °C for 80 min in the presence of 10 wt % water (under open nicol).

D: Quartz aggregates in sintered state after heating for 10 min at 600 °C without water (under crossed nicols).

E: Lath-shaped and needle-like coesite crystals developed in quartz matrix of sintered state after heating for 60 min at 600 °C without water (under open nicol).

F: Penetration twins and lath-shaped coesite crystals grown after heating for 3 h at 600 °C without water (under crossed nicols).

G: Quartz spherulitic aggregates in amorphous silica matrix heated at 600 °C for 3 min in the presence of 4 wt % water (under crossed nicols).

H: Tiny penetration twins and granular crystals of coesite developed in quartz matrix after heating for 10 min at 600 °C in the presence of 4 wt % water (under open nicol).

I: Granular and euhedral coesite crystals grown after heating for 3 h at 600 °C in the presence of 16 wt % water (under open nicol).

most of the original amorphous silica was converted, within a few minutes, to quartz of discrete particles with the size of 0.02—0.03 μm. Many quartz aggregates were also observed in the fine particles of quartz. After 60 minutes, single phase of quartz was obtained and its crystal size increased up to 0.05—0.06 μm (Fig. 2-B). After 80 minutes metastable quartz transformed rapidly to coesite, of which crystal grew to 2—5 μm (Fig. 2-C).

The similar effect of water on crystal morphology was observed during the crystallization process at 600 °C. Some micrographs are shown in Figs. 2-D~I. Under the anhydrous condition (Fig. 2-D~F), amorphous silica completely transformed within 10 minutes to sintered quartz and the size of single crystal region was 1—3 μm (Fig. 2-D). In this case, the crystallization of metastable quartz is rather fast and the crystals sintered each other. This may be why we could not recognize the spherulitic aggregates of quartz crystals. After 60 minutes, the lath-shaped and needle-like crystals of coesite with the size of about 70 μm were developed in quartz matrix, as shown in Fig. 2-F. The coesite crystals occurred mostly at grain boundaries of quartz crystals, and they grew along the c-axis. After 3 h, single phase of coesite was obtained. Most of the crystals were in lath-shape and 100—300 μm in size. They showed wavy extinction under microscope. The penetration twins of coesite crystals were often observed[12] (Fig. 2-F). With 4 wt% water, amorphous silica crystallized completely to quartz after 3 minutes. In this case, many spherulitic aggregates of quartz crystals were also observed in the matrix of the fine quartz crystals with the size of 0.5—1.0 μm (Fig. 2-G). After 10 minutes, however, the spherulitic aggregates disappeared. The granular crystals and penetration twins of coesite were formed in the matrix of fine quartz crystals (Fig. 2-H). After 60 minutes, the number of twins decreased and the granular coesite crystals with the size of 20—50 μm were formed. In the crystallization with 16 wt% of water, both steps of the consecutive process were so accelerated that only the morphology of coesite crystals could be discussed. The metastable quartz which was formed from amorphous silica in very short time transformed completely to coesite within 10 minutes. The spherulitic aggregates of quartz crystals and also penetration twins of coesite were hardly observed (Fig. 2-I). The granular coesite crystals grew with the increase in heating time. After 3 h, the coesite crystals as large as 100 μm were found, which were transparent and showed clear extinction.

The observation by electron scanning microscope agreed in the sizes and morphology of crystals with the results mentioned above.

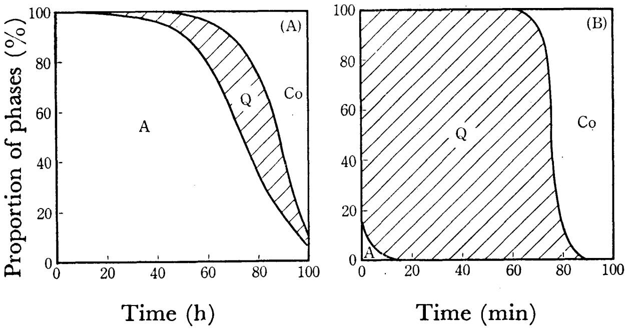

Fig. 3. Variations in proportions of phases obtained from silica glass under 30 kb;
A: without water at 600 °C.
B: with 10 wt % water at 450 °C.

Crystallization from Silica Glass. Under anhydrous condition, silica glass remained in amorphous state even after 96 h at 450 °C. At 600 °C, the crystallization of silica glass to coesite through metastable quartz was observed (Fig. 3-A). This kinetics is rather similar to that from amorphous silica to coesite at 450 °C (Fig. 1-A). The morphological changes during crystallization were found to be also similar to those which were observed at 450 °C on amorphous silica. After 48 h, the spherulitic aggregates of quartz crystals with the size of 20—200 μm were found to be scattered in amosphous matrix (Fig. 4-A). In the spherulite, the c-axes of quartz crystals oriented mostly to the radial direction. The coesite crystals were also developed radially from the center of the quartz spherulites (Fig. 4-B). It seemed likely that before the transformation to coesite the radial arrangement of quartz crystals were destroyed to be random. After 96 h, lath-shaped and needle-like coesite were developed, but the spherulitic texture remained even after the complete transformation to coesite (Fig. 4-C). With 10 wt% water at 450 °C, however, the kinetics and morphological changes to coesite from silica glass was found to be similar to the case from amorphous silica under the same condition, that is, at 450 °C with 10 wt% water (Fig. 3-B).

Crystallization from Quartz. Under anhydrous condition at 450 °C, the starting quartz remained

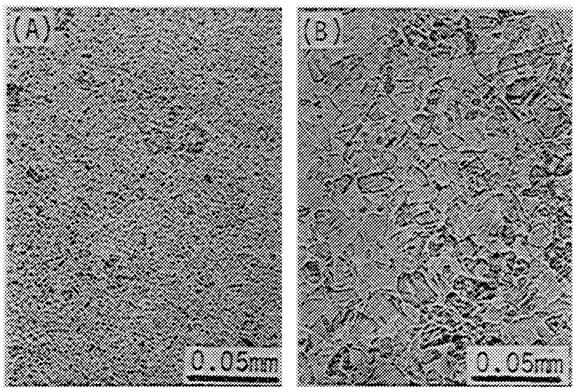

Fig. 5. Microphotographs of coesite prepared from quartz;
A: heated at 700 °C for 24 h without water (under open nicol).
B: heated at 450 °C for 4 h with 10 wt % water (under open nicol).

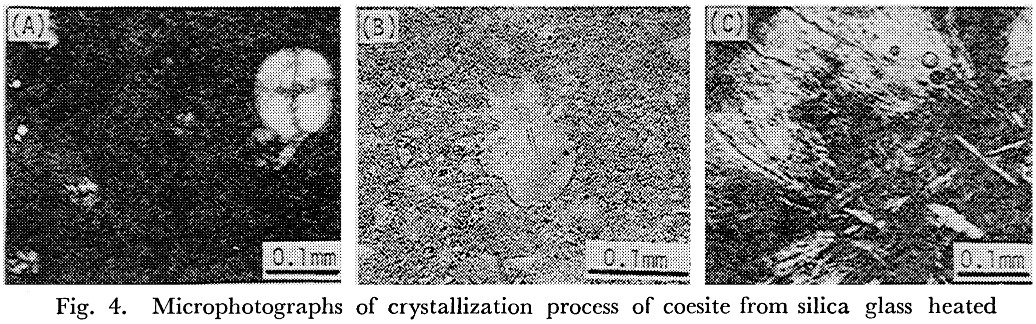

Fig. 4. Microphotographs of crystallization process of coesite from silica glass heated at 600 °C under 30 kb without water;
A, B: for 48 h (under crossed nicols).
C: for 96 h (under crossed nicols).

TABLE 1. CRYSTALLIZATION OF COESITE PREPARED FROM VARIOUS STARTING MATERIALS AT 450°C UNDER 30 kb WITH 10 wt% WATER

Starting materials	Crystallite size of metastable quartz (Å)	Nucleation period (min)	Nucleation rate (s^{-1})	Growth rate (s^{-1})
Amorphous silica, silica glass	200~500	60	2.8×10^{-4}	7.5×10^{-2}
Quartz	5000	80	9.3×10^{-5}	2.8×10^{-2}

unaltered in a powdered state even after 96 h, although the broadening of X-ray diffraction profiles and the undulatory extinction under optical microscope were observed. The single phase of coesite was obtained from the quartz only after 2 h at 700 °C. The coesite crystals formed are in granular shape with the size of 2—5 μm (Fig. 5-A). With 10 wt% water at 450 °C, coesite crystallized after an induction period of about 3 h. After 4 h, 90% of the starting quartz was converted into the granular coesite crystals with the size of 20—40 μm (Fig. 5-B).

Effect of Water on Crystallization of Coesite. Under anhydrous condition, the crystallization rate of coesite is different from the starting materials; amorphous silica changes completely to coesite at 450 °C after 96 hr, but silica glass needs 600 °C and quartz 700 °C for complete transformation to coestite. During the crystallization from amorphous silica and silica glass, the formation of spherulitic aggregates of metastable quartz was observed. The spherulites formed in the silica glass appeared to have better orientation (Fig. 4-A) and are less in number than those in amorphous silica, probably due to the slow rate of transformation of glass to metastable quartz. The formation of spherulitic aggregates may be explained by the surface tension developed in amorphous state, similar to the devitrification of glass.[13] Mostly from the center of the spherulites, the growth of coesite crystals is found to start. Therefore, the formation of spherulites and also orientation of quartz crystals in spherulites restrict the morphology and size of coesite crystals.

Under hydrous condition, no difference in the crystallization rate of coesite is observed between amorphous silica and silica glass. They transform to coesite much faster than quartz. The process of transformation of metastable quartz to coesite seems to be the rate determining step. Since the formation curve of coesite could not be refered to a paraboric law, no long range diffusion process should be involved in the crystallization process of coesite. Thus, the crystallization rate of coesite was analyzed by adopting the linear law,[14] which had been commonly used for the rate determining process of interfacial reaction. The nucleation period of coesite from metastable quartz, the nucleation rate, and the growth rate evaluated from the slope of the formation curve are summarized in Table 1. The crystallite size of metastable quartz is also shown in Table 1. Both the nucleation rate and the growth rate of coesite crystals are found to be larger for amorphous silica and silica glass than for quartz. This difference in the rates may be due to the smaller particle size of metastable quartz formed from amorphous silica and silica glass than that from quartz. It has been well known that the dimension and the microstructure of the starting crystal affect both speed and temperature of its phase transformation.[15]

The coesite crystals prepared from the amorphous phases under anhydrous condition have an elongated form with heterogeneous size and appears to be defective, but well sintered. The crystals prepared under hydrous condition, however, are granular in shape, homogeneous in size and also less defective. With more than 10 wt% of water, the granular crystals of metastable quartz and also of coesite are obtained from any starting materials. Water may prevent the aggragation of metastable quartz. Even in the presence of water the elongated crystals and penetration twins of coesite were often observed at the beginning of crystallization, but they disappeared after prolonged heating. These experimental results may suggest the growth mechanism of coesite as the dissolution and precipitation through a solvent of water. This mechanism may be understood from the fact that water of even 4 wt% is largely enough to cover the surface of quartz and coesite grains by water layer of few tens molecular thickness.

When quartz was used as a starting material, the penetration twins and needle-like crystals of coesite were hardly observed even under anhydrous condition. Random orientation and rigid boundaries of the original quartz particles may prevent the aggregation of quartz and the preferential growth of coesite.

Conclusively, the crystallization process of coesite is found to depend strongly on the morphological characteristics of metastable quartz as well as on the significant roles of water. The granular coesite having homogeneous size could be obtained under hydrous condition through the discrete crystals of metastable quartz. The crystal size of coesite could also be controlled by the selection of heating temperature and time.

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