AN ELECTRON MICROSCOPIC STUDY OF GAS CONDENSATES IN THE SYSTEM Mg-Si-O-H

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Abstract: Condensates of $MgSiO_3$ and SiO_2 from a gas formed by evaporation of enstatite at an H_2 pressure of 4.4×10^{-10} bar and a temperature of 1525°C by B.O. Mysen and I. Kushiro (Am. Mineral. (in press), 1988) and I. Kushiro and B.O. Mysen (Advances in Physical Geochemistry, New York, Springer (in press), 1988) were investigated with an analytical transmission electron microscope (ATEM), a scanning electron microscope (SEM) and an electron probe micro-analyzer (EPMA). With decreasing temperature at an approximately constant total pressure the $Mg/(Mg+Si)$ atomic ratio of the condensate (mixture of $MgSiO_3$ and SiO_2 polymorphs) decreases first, then increases, and finally reaches a constant value. This compositional change of the condensate is inconsistent with the equilibrium condensation model.

The TEM studies suggest that metastable condensation of coesite and probably of protoenstatite and cristobalite took place. Coesite probably condensed by heterogeneous nucleation on protoenstatite. Fibrous quartz was also formed by heterogeneous nucleation on molybdenum fibers which condensed from a molybdenum vapor by a partial evaporation of a Knudsen cell used in the experiment. Heterogeneous nucleation might have played an important role in condensation process in the solar nebula. The texture of the experimental clinopyroxene condensate is different from that in interplanetary dust particles (J.P. Bradley *et al.*, Nature, **301**, 473, 1983).

1. Introduction

It has been proposed that condensation of minerals played an important role in chemical and mineralogical processes in the primodial solar nebula (*e.g.*, Grossman and Larimer, 1974). The planets and parent bodies of meteorites were postulated to have been formed by accretion of the condensation products.

If the nebula had cooled very slowly, the condensation must have taken place under nearly equilibrium conditions. The equilibrium condensation process has been examined theoretically (*e.g.*, Grossman and Larimer, 1974). Experimental studies to determine the equilibrium phase relations have also recently been conducted (Mysen *et al.*, 1985; Mysen and Kushiro, 1988; Kushiro and Mysen, 1988). In contrast, if the nebula had cooled rapidly, kinetic effects on condensation must be taken into ac-

count. Yamamoto and Hasegawa (1977) and Kozasa and Hasegawa (1987) studied some kinetic effects theoretically, and concluded that a homogeneous nucleation dominates at the cooling rates proposed for the nebular (Yamamoto and Hasegawa, 1977). However, an experimental approach to the kinetic problem is still in an early stage, and only a little work has been done (Nagahara et al., 1987).

Mysen and Kushiro (1988) and Kushiro and Mysen (1988) have carried out evaporation experiments in the system Mg_2SiO_4-SiO_2-H_2 in the pressure range form 10^{-2} to 10^{-10} bar and in the temperature range from $1350°$ to $1650°C$ to determine phase relations of the system. In these experiments, condensation of $MgSiO_3$ and SiO_2 phases took place from the Si-rich vapor which was formed by incongruent vaporization of enstatite. In the present study, these condensates were examined with an analytical transmission electron microscope (ATEM) and a scanning electron microscope (SEM) to compare the experimental condensates with interplanetary dust particles (IPDP's) (Bradley et al., 1983), and to examine the crystallization process of the condensation, especially its kinetic effects. The transmission electron microscopy was very useful to determine phases and microtextures of the condensates which are too small to be characterized by an optical microscope and SEM.

2. Experiments

A specimen used in the present study is the product of 4-day experiment at evaporation temperature of $1525°C$ and H_2 pressure of 4.4×10^{-10} bar (run #2664 of Mysen and Kushiro, 1988). In the experiments, a synthetic enstatite powder was placed in a molybdenum Knudsen cell which was hooked with a molybdenum wire and suspended inside a tube furnace. The vapor which effused through an orifice of the cell condensed on the wire, from about 12 to 22 mm above the top of the cell (Fig. 1). Condensation temperatures roughly estimated ($\pm 50°C$ uncertainty) from a thermal gradient of the furnace decrease from bottom ($\sim 1000°C$) to top ($\sim 500°C$) of the condensation zone; the zone being distinguished into four sub-zones A, B, C and D on the basis of mineralogical and chemical differences.

Chemical analyses were made on the condensates with a SEM (HITACHI-S530 equipped with a HORIBA-EMAX2200 EDX analytical system) by scanning an electron beam (specimen current 1.5 nA and accelerating voltage 20 kV) over areas of about 20×30 to $70 \times 100 \, \mu m^2$. X-ray intensities were corrected by the ZAF method with standards using a focused beam. The analytical sums were less than 100% due to rough surfaces of the specimens. We assume that the atomic ratios in the analyses were not largely affected by this deficit and use them in later discussions.

After the SEM studies, the condensates were removed from the wire and mounted on copper grids. During this process only those from zones A and B were successfully recovered. A TEM (HITACHI-H700 equipped with a HORIBA-EMAX3000 EDX analytical system) was used to study crystal structures and chemical compositions of the condensates. As a by-product of the recovering process, portions of the condensates separated into individual grains. These allowed identification of individual phases with TEM; a special computer program (Tsuchiyama, in preparation) was additionally used to distinguish SiO_2 polymorphs.
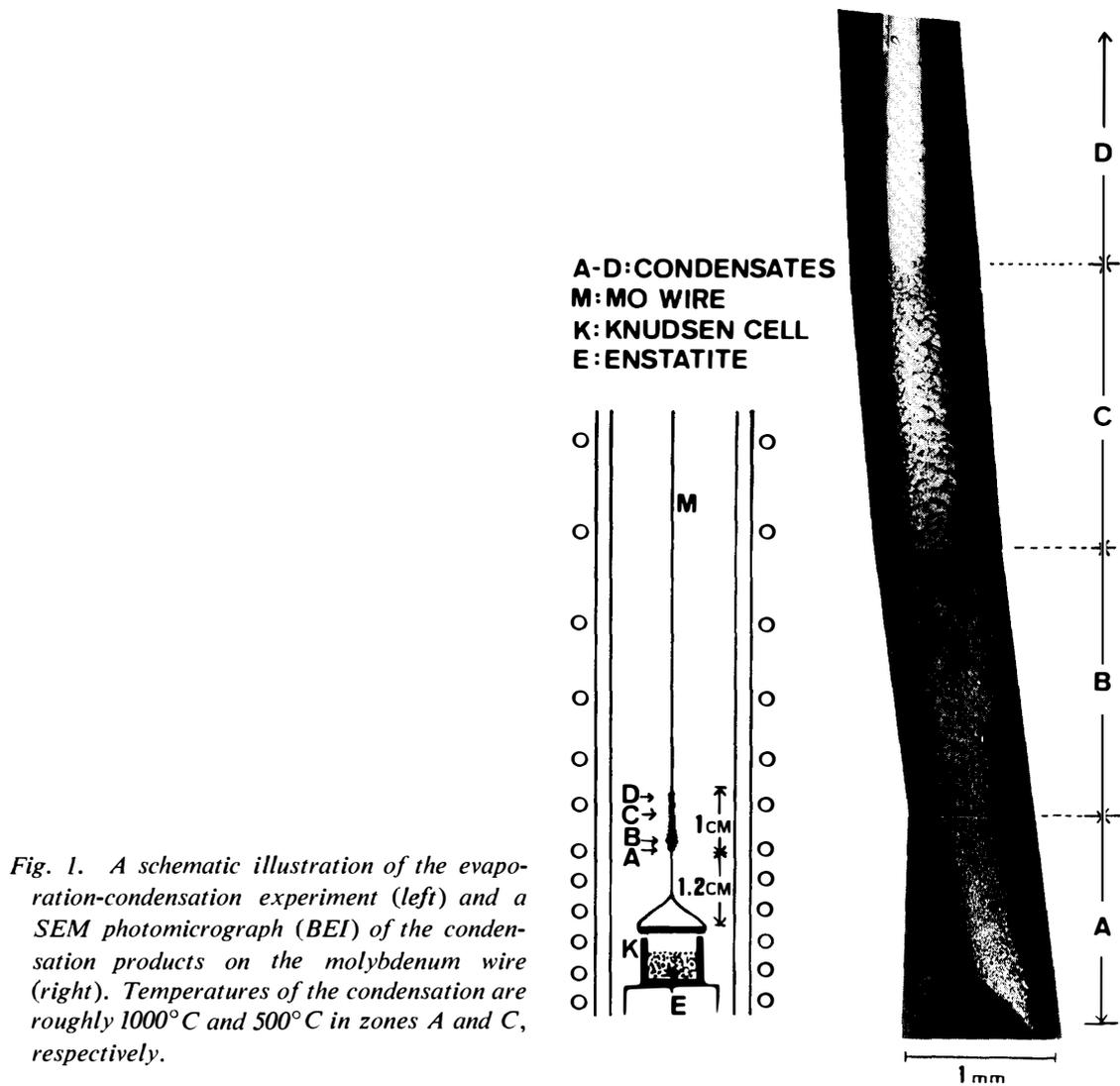
Fig. 1. A schematic illustration of the evaporation-condensation experiment (left) and a SEM photomicrograph (BEI) of the condensation products on the molybdenum wire (right). Temperatures of the condensation are roughly 1000°C and 500°C in zones A and C, respectively.

3. Results

3.1. SEM study

KUSHIRO and MYSEN (1988) reported a preliminary SEM observation of the specimen. In the present study, a more detailed SEM observation was made on the same specimen using back-scattered electron images (BEI's) and secondary electron images (SEI's).

In zone A (where the condensation took place at the highest temperature) SiO_2 and $MgSiO_3$ phases coexist (Figs. 2a and 2b). The SiO_2 phases are prismatic, platy or fibrous, while all the $MgSiO_3$ phases are prismatic. Most of the grains are less than a few μm in width, except for the fibrous SiO_2 which usually elongates to more than a few tens of μm. In zone B, the relative proportion of the fibrous SiO_2 to the other SiO_2 and $MgSiO_3$ phases is larger than that in zone A (Figs. 2c and 2d). The SiO_2 fibers show various morphologies; some are whiskers, and the others are rootlike. With
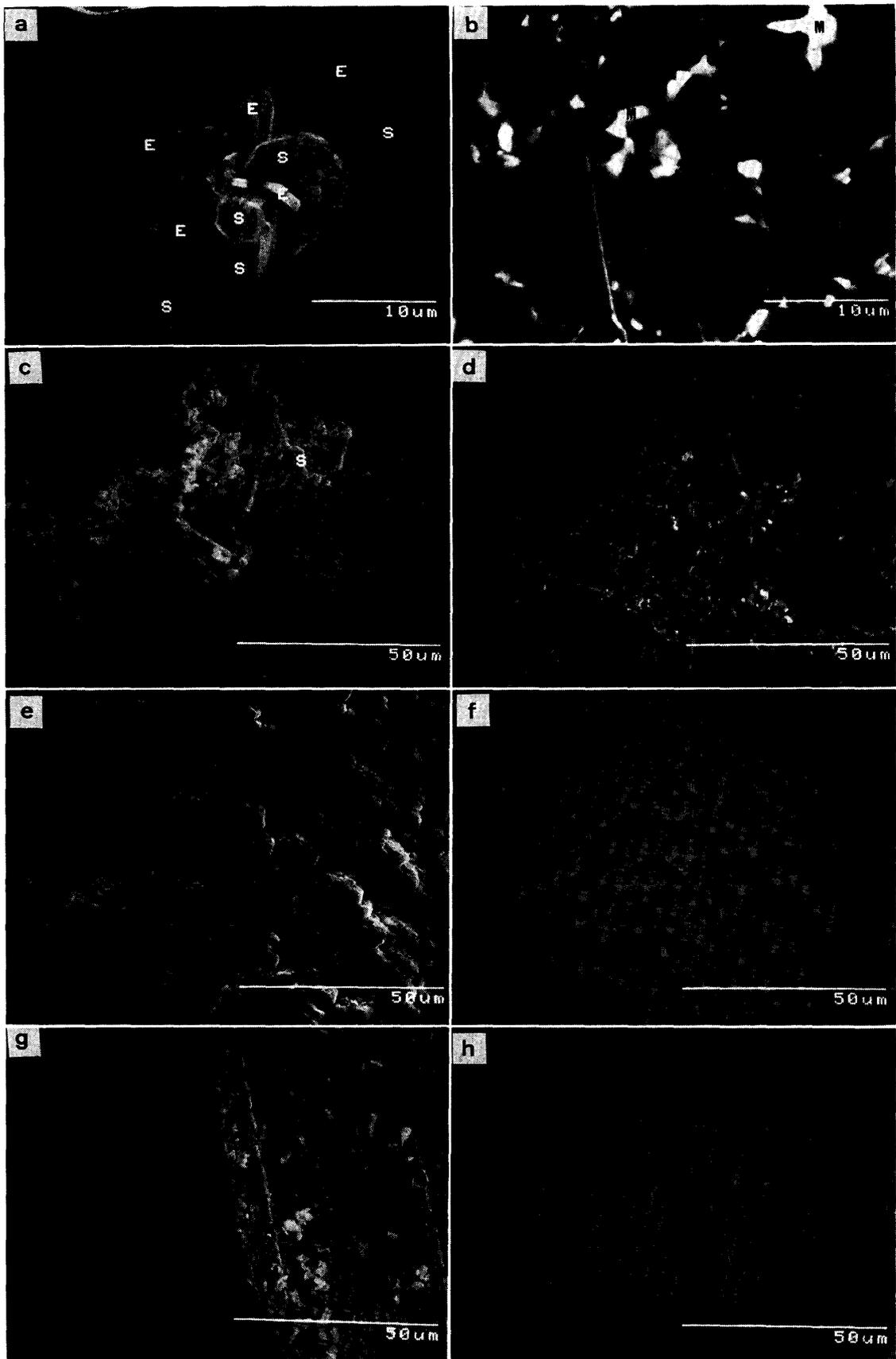
decreasing condensation temperature from zone B to C the SiO_2 fibers become thinner, and reniform textures consisting of fine fibers are formed in zone C (Figs. 2e and 2f). In the lowest temperature zone D, condensate grains are too small to be identified with the SEM (Figs. 2g and 2h).

Molybdenum metal with a small amount of tungsten frequently coexists with the SiO_2 fibers. The source of the molybdenum is probably the sample container, whereas tungsten most likely was derived from the W97Re3-W75Re25 thermocouples used in the experiment. No molybdenum was found adjacent to the $MgSiO_3$ phases.

Figure 3 shows chemical compositions of the condensate mixtures determined by scanning electron beams as a function of the location of the wire, X ($X = 0$ at the highest temperature part). The Mg/(Mg+Si) ratio at $X = 0$ is close to that of enstatite composition, 0.5. With increasing X, and thus with decreasing temperature, the ratio decreases to naerly zero at about $X = 3$ mm (low temperature part of zone B), and increases to 0.2 at $X > 5$ mm (zone D). The W/(W+Mo) ratio decreases slightly with X.
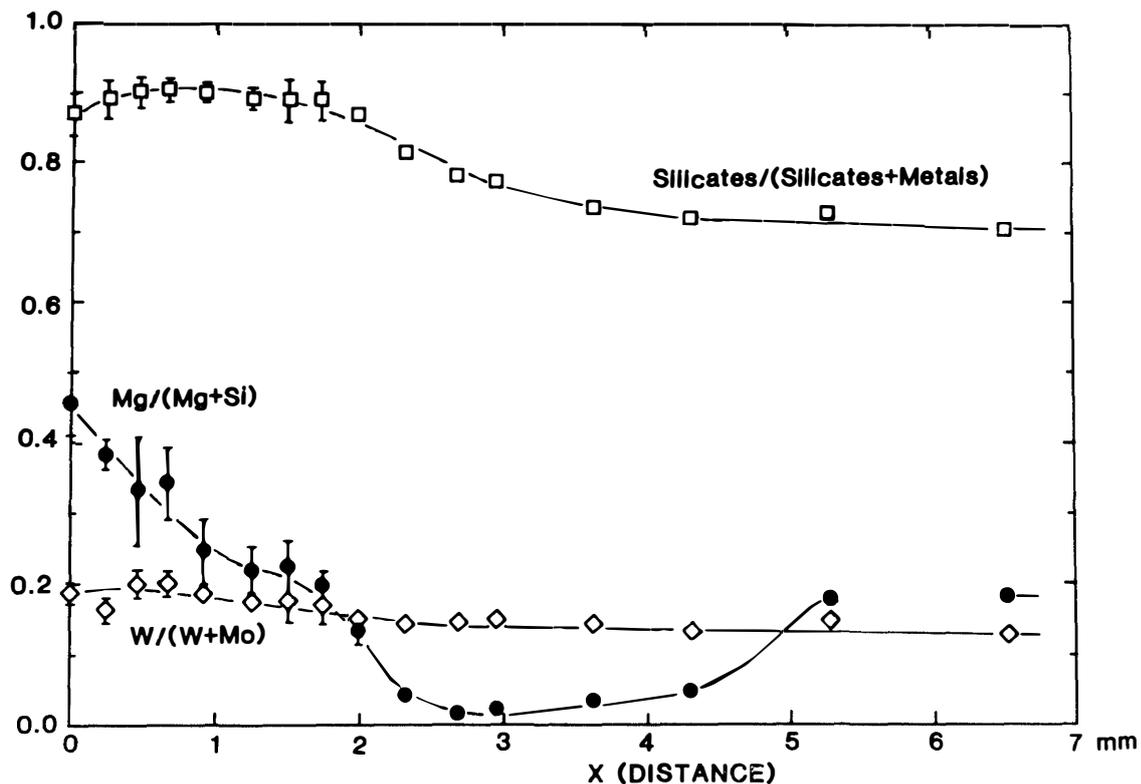

Fig. 3. Average chemical compositions of the condensate mixtures as a function of X: the location of condensation along the molybdenum wire measured from the lowermost border of the condensate. The condensation temperature is a monotonously decreasing functoin of X as a result of the temperature gradient established inside the furnace.

Fig. 2 (opposite). SEM photomicrographs of the condensates. (a) Zone A, secondary electron image (SEI). (b) Zone A, back-scattered electron image (BEI). (c) Zone B, SEI. (d) Zone B, BEI. (e) Zone C, SEI. (f) Zone C, BEI. (g) Zone D, SEI. (h) Zone D, BEI. E=enstatite, S=silica, and M=molybdenum (bright materials seen in BEI's).
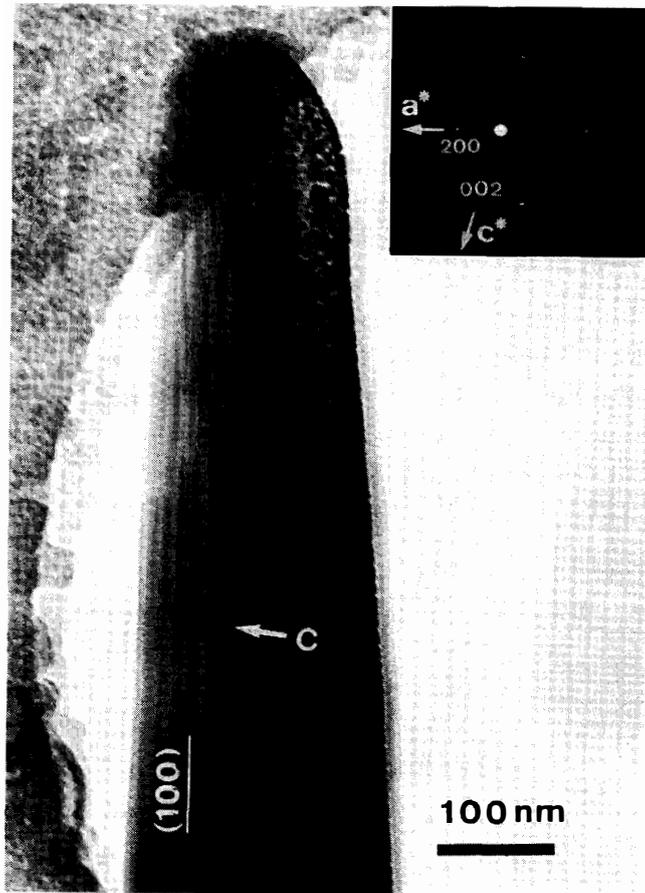
Fig. 4. A TEM photomicrograph of low-clinoenstatite elongated to the c-axis. Polysynthetic (100) twins, and cracks nearly parallel to (001) (C in the figure) are seen.

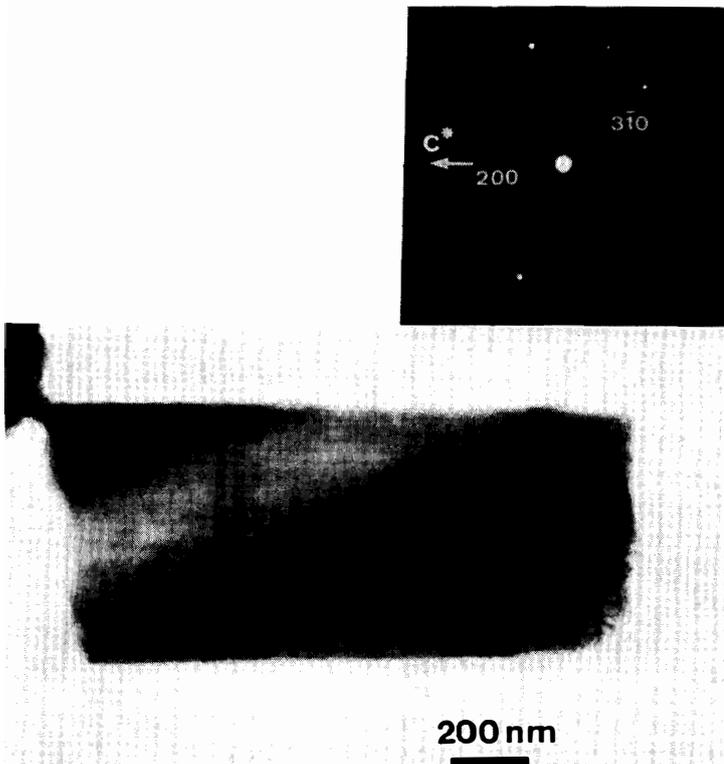Fig. 5. A TEM photomicrograph of orthoenstatite which elongates in the direction of the c-axis.
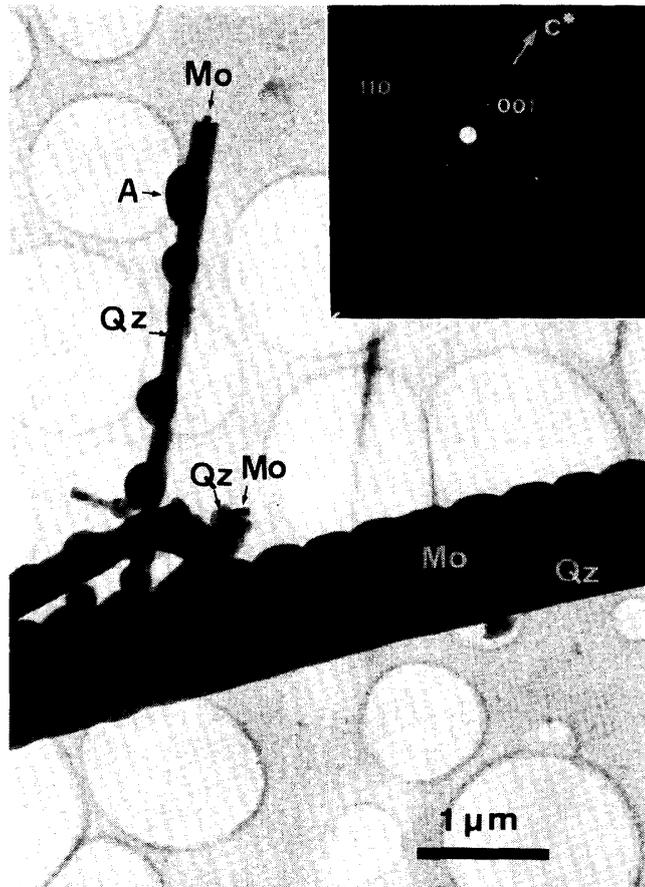
Fig. 6. A TEM photomicrograph of quartz fibers (Qz) with molybdenum cores (Mo) and amorphous silica beads (A). An electron diffraction pattern of quartz in the thickest fiber is also shown.
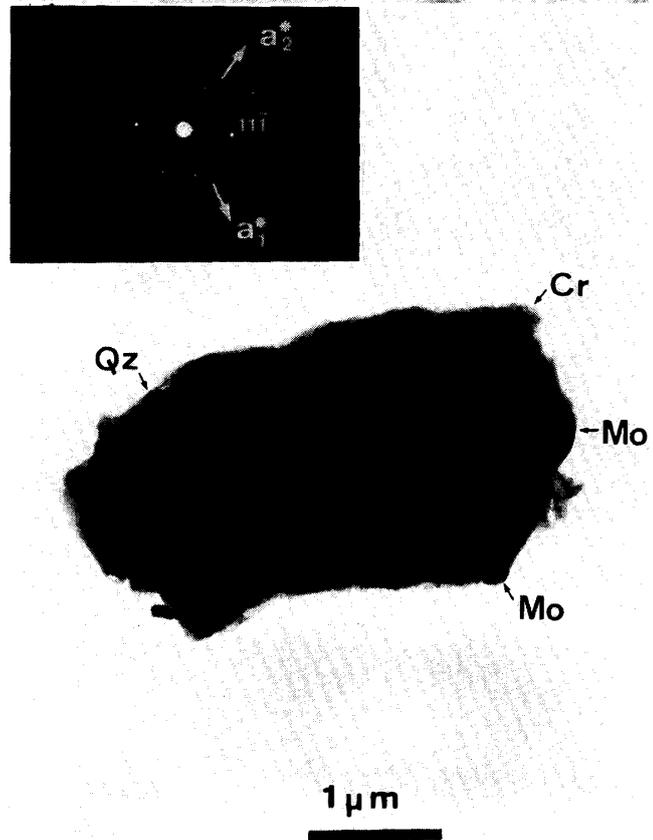
Fig. 7. A TEM photomicrograph of an aggregate of quartz (Qz) and high-cristobalite (Cr). An electron diffraction pattern of the cristobalite is also shown. Mo = molybdenum (black spots).
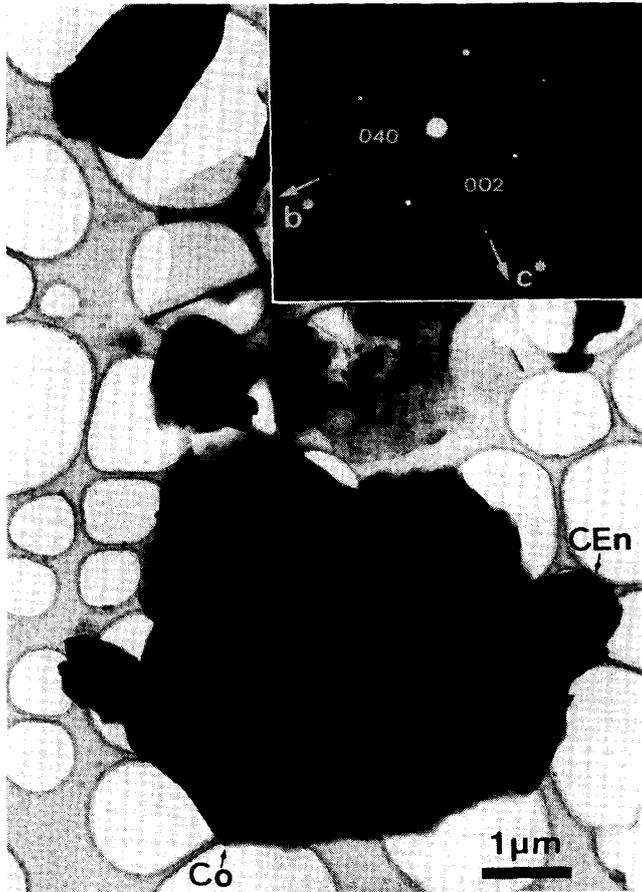
Fig. 8. A TEM photomicrograph of an aggregate of low-clinoenstatite (CEn) and coesite (Co). An electron diffraction pattern of the coesite is also shown.
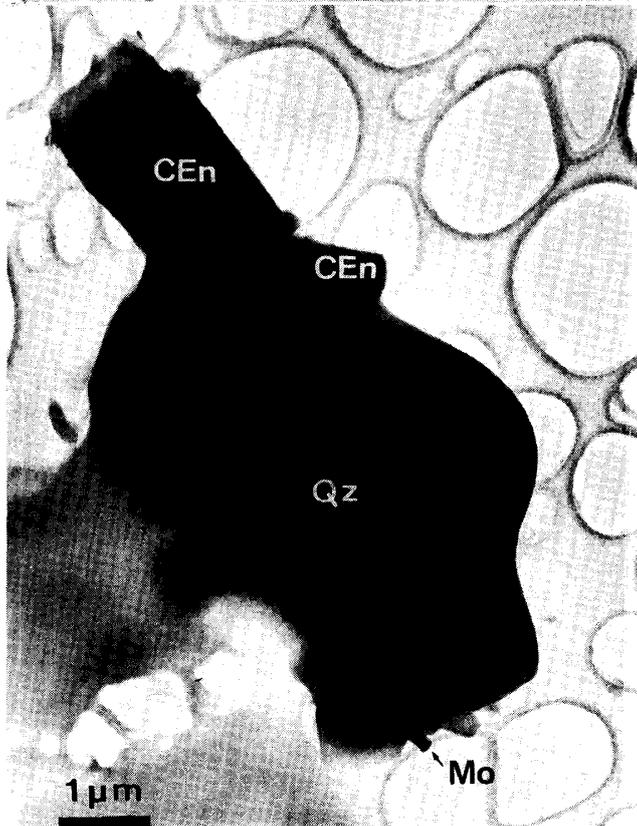
Fig. 9. A TEM photomicrograph of an aggregate of low-clinoenstatite (CEn) and quartz (Qz). Mo=molybdenum (a small fiber).

3.2. TEM study

With TEM the following phases were identified in the condensates; low-clinoenstatite (Fig. 4), orthoenstatite (Fig. 5), quartz (Fig. 6), high-cristobalite (Fig. 7), coesite (Fig. 8), amorphous silica (Fig. 6), and molybdenum metal (bcc structure). Single crystals of clinoenstatite and quartz fibers with molybdenum cores are most abundant. The prismatic-platy SiO_2 phases are aggregates of finer crystals of various sizes, in which combinations of clinoenstatite-quartz, clinoenstatite-coesite, and quartz-cristobalite are found. Clinoenstatite is in contact with quartz (Fig. 9). Precise contacts between the last two assemblages were not observed (Figs. 7 and 8). Both low-clinoenstatite and orthoenstatite crystals elongate along the c-axis. The clinoenstatite crystals have (100) polysynthetic twins and cracks nearly parallel to the (001) face (Fig. 4), while which were not observed in the orthoenstatite (Fig. 5). The fibrous SiO_2 phase is quartz (Fig. 6). No specific crystallographic orientation was recognized. The quartz crystals always enclose molybdenum fibers in their cores. A crystal orientation of molybdenum metal could not be determined. Small beads, less than $0.5 \mu m$ in diameter, are usually attached to quartz fibers (Fig. 6). They are probably amorphous SiO_2 based on the electron diffraction and EDX analysis.

4. Discussion

4.1. Primary condensation phases in the experiment

The phases observed in TEM are considered to be primary condensates from the vapor and are not secondary ones formed by transition from other phases except for clinoenstatite because any textures due to the transitions were not observed. In fact, possible transitions, such as from tridymite to quartz, are too slow to take place during the experiment. Crystallization of silica from its own melt is also very slow (origin of amorphous silica will be discussed in the next section). The fact that any quenched melts containing Mg and Si were not found with TEM suggests that they did not crystallize either from a metastable melt which condensed from the vapor. Transition of clinoenstatite is discussed in the next section.

4.2. Fine textures of clinoenstatite and fibrous quartz

The (100) polysynthetic twins and (001) cracks of low-clinoenstatite indicate that the pyroxene was crystallized as protoenstatite at high temperatures and inverted to low-clinoenstatite (YASUDA et al., 1983) during cooling. BRADLEY et al. (1983) found clinoenstatite crystals elongated along the a-axis in interplanetary dust particles. Based on their unique morphology and microstructures, it was proposed that they were primary vapor phase condensates which could have formed either in the solar nebula or in presolar environments. In the present experiment, however, only pyroxene with usual morphology was formed.

The quartz crystals with molybdenum fibers in their cores suggest that they nucleated heterogeneously on the molybdenum substrate. Accordingly, the morphology of the quartz was probably determined by that of the molybdenum fibers. The molybdenum fibers are also considered as condensates from vapor by a partial evaporation of the Knudsen cell which was used as a sample container. Amorphous silica beads on the

quartz fiber may be a product of the Vapor-Liquid-Solid (VLS) growth mechanism (e.g., GIVARGIZOV, 1975), in which a crystal grows from an eutectic melt formed by a vapor-substrate reaction. However, this is unlikely because there is no eutectic point between amorphous silica and quartz (since both of them are pure SiO_2). The amorphous silica are probably condensation products by quenching the vapor during the cooling of the furnace.

4.3. Metastable condensation of minerals

An important factor in the present study is that the temperature distribution inside the furnace was kept constant through the experiments. This implies that condensates at the same position on the molybdenum wire should have nearly the same condensation temperatures. Then, the coexistence of some minerals observed in the experiments (protoenstatite-quartz, quartz-cristobalite, and coesite-protoenstatite) conflicts with ordinary phase stability relations.

Protoenstatite is stable at temperatures above 985°C (HUEBNER, 1980), and quartz below 867°C (KRACEK, 1939). It is generally true that the low temperature phase, that is, a low entropy phase (quartz in this case), rarely crystallizes above its stability field. Therefore, quartz might have grown in its stability field while protoenstatite grown metastably at temperatures lower than 867°C. However, the estimated highest condensation temperatures (~1100°C) at which both phases condensed suggest that protoenstatite grew in its stability field while quartz grew metastably. If this is the case, metastable crystallization of quartz, a low entropy phase, is probably caused by the heterogeneous nucleation on molybdenum fibers. The quartz-cristobalite assemblage also suggests metastable crystallization of either phase. Cristobalite might be a metastable phase as a high temperature phase crystallizes below its stable temperature rather easily than a low temperature phase does over its stability limit.

Coesite is a high pressure phase and is not expected to grow at any temperatures at such low pressures as in the present experiment. In fact, coesite is a low entropy phase compared with quartz. However, it is known that a heterogeneous nucleation of diamond, a high pressure phase (and a low temperature phase compared with graphite), can take place metastably at low pressures by means of its overgrowth on diamond seeds or its epitaxial growth on other materials (Si, Mo, W, Cu and Au) (SPITSYN et al., 1981). Although special crystallographic relations were not determined, the fact that the coesite coexisted only with clinoenstatite may suggest an epitaxial growth of coesite on protoenstatite.

As already mentioned, quartz also nucleated heterogeneously on molybdenum fibers. FUKUNAGA et al. (1987) proposed vapor-growth diamonds in meteorites, and this requires a heterogeneous nucleation of diamond. According to the equilibrium condensation model (e.g., GROSSMAN and LARIMER, 1974) condensation of refractory metals and oxides took place before condensation of major phases, such as olivine, pyroxene, and metallic iron. It is not known whether or not the refractory phases act as heterogeneous nucleation sites for the major phases, but if it were the case, the condensation sequence might differ from the equilibrium condensation model and even from the model with homogeneous nucleation (YAMAMOTO and HASEGAWA, 1977; KOZASA and HASEGAWA, 1987).

4.4.   Compositional change of the condensates as a function of temperature

In the experiment the condensation did not take place in a closed system but in an open system.   However, if a local equilibrium is maintained between solid and vapor even in this open system, it is expected from the phase relations of the system MgO-SiO$_2$-H$_2$ (MYSEN and KUSHIRO, 1988) that only enstatite grows at higher temperatures and silica mineral grows together with enstatite below the eutectic temperature of the two minerals.   However, the compositional change of the condensates at higher temperatures (zones A and B) is very different from the equilibrium condensation sequence probably because (1) the composition of the vapor might be changed during the experiment due to the incongruent vaporization of enstatite, (2) the vapor might be fractionated in the furnace due to difference of the evacuation velocities of different gas molecule species, such as SiO, Mg, and (3) condensation of the minerals was largely affected by heterogeneous nucleation.   It is uncertain which factor is most effective.

At the lower temperatures (zones C and D), the Mg/(Mg+ Si) ratio increases and becomes constant with decreasing temperature.   Although phases in this region were not determined, the constant composition might be explained by condensation of a quenched product which is probably amorphous Mg and Si oxide.

5.   Concluding Remarks

(1)   Characteristic textures of clinoenstatite found in the IPDP's (BRADLEY *et al.*, 1983) were not reproduced in the evaporation-condensation experiments of KUSHIRO and MYSEN (1988).

(2)   In the condensation, metastable crystallization of minerals, coesite and probably protoenstatite and cristobalite, took place.

(3)   Metastable growth of coesite is probably due to heterogeneous nucleation on protoenstatite.   Quartz also nucleated heterogeneously on molybdenum.   This suggests that a heterogeneous nucleation should be taken into consideration in a future study of the condensation of the solar nebula.,

(4)   Change of the chemical compositions of condensate mixtures is inconsistent with the equilibrium condensation model.

Acknowledgments

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