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Coesite and Stishovite: Stepwise Reversal Transformations

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Abstract. *Very marked differences in the metastable persistence of coesite and stishovite have been demonstrated; the former possibly persists indefinitely below 1000°C at 1 atmosphere "dry," and the latter completely decomposes in minutes above 500° to an amorphous or short range order phase. Quartz was grown (metastably) at temperatures well above its stability field from both coesite and stishovite, possibly by way of a short range order phase. The absence of stishovite in meteor-impact craters cannot be taken as evidence that it was not formed. If it has "reversed" in normal natural environments the product would almost certainly be a short range order phase or derivative.*

In all the reconstructive transformations which the silica minerals undergo, it has long been assumed that an amorphous or short range order (SRO) intermediate phase is formed as the first step. Recent data (1) substantiate this idea. Specifically, short range order is the most general term that can be used to describe phases which are not crystalline (that is, they do not have periodicity over distances greater than about 100 Å). The extent of structural order in SRO phases is therefore limited to the first sphere of coordination and possibly up to a few unit cells.

The SRO phase of a one-component system may have properties dependent on the conditions of treatment, while in a multi-component system the composition of the SRO phase also may vary.

In spite of the existence of the SRO as an intermediate in such transformations it is clear, however, that structural control derived from the parent or original modification is still a reality. While Ostwald's step rule (2) may have constituted an overgeneralization, its fundamental validity is rooted in the transmission of inherent structure in a direct manner through epitaxy or topotaxy, or in a more indirect manner through an SRO intermediate.

With the increasing use of coesite and stishovite (3, 4), which are the high pressure modifications of SiO₂ as indicators of meteorite impact, it is essential to know the conditions under which these forms would revert to other forms of SiO₂, and the structural controls and kinetics of the various reactions that occur.

Quenching experiments and high-temperature x-ray measurements were used to follow the reversal of the high-pressure phases, coesite and stishovite, to the various forms of SiO₂ which are stable at 1 atmosphere.

The quartz-coesite equilibrium (5) focused our attention on the kinetics of this reaction. In an effort to determine the activation volume for the coesite-

quartz reaction, an attempt was made to determine how long the metastable coesite would persist at atmospheric pressure in air at various temperatures. Such data would also give information on the possible ceramic use of coesite. Coes (6), in his original paper, stated that at 1700°C coesite was transformed to cristobalite and silica glass. In the present work, samples from two "large" batches of synthetic coesite were heated at different temperatures for varying lengths of time, and examined optically and by x-ray diffraction.

At temperatures from 1100° to 1350°C, coesite apparently changes to quartz, and the quartz so-formed then undergoes transformation to cristobalite; intermediate amorphous forms precede the emergence of each crystal modification. Typical runs are summarized in Fig. 1 and a few optical data are given in Table 1. Tridymite was obtained only once from among several similar runs.

Heating the coesite at these temperatures (1100° to 1350°C) did not form an amorphous phase with the refractive index of silica glass (1.458). At least no grains were observed with this low index. However, the refractive index of all the coesite grains was lowered variably and decreased further at higher temperature and with longer time. When coesite alone is present, as determined by x-ray diffraction, the lower refractive index of the grains probably

signifies the presence of SRO silica. When coesite or cristobalite or both are present, the minimum index is below those of cristobalite but it is not as low as 1.458.

We have here evidence for the metastable formation of quartz in the stability field of a less dense polymorph. In the case of the LiO₂-Al₂O₃-SiO₂ system (7), the formation of quartz, in a few seconds, below 870°C and its subsequent persistence above this temperature apparently gives rise to a similar phenomenon. This sequence does not apply in the present work since the coesite does not become transformed at all below 870°C, nor are solid solutions of quartz a factor. This transformation constitutes to date the only synthesis of quartz, at atmospheric pressure, in the absence of any mineralizing agent. The only other way to form quartz from other forms of silica without such agents other than small amounts of water is at pressures of about 20 kb at about 500°C.

With the use of a high-temperature x-ray furnace (8), the growth of quartz, as the coesite was heated at 1150°C, was detected easily by the development of the quartz (101) diffraction peak during the first 15 minutes at this temperature. At this time the integrated intensities of quartz (101), β-cristobalite (111), and coesite (130) were about ½, 2½, and ½ times, respectively, that of the initial coesite (130). Periodic scanning of these maxima through a period of 5 hours showed that the intensity of β-cristobalite (111) increased further (about five times); both the coesite and quartz essentially disappeared, but the coesite did so more rapidly.

This rapid growth of cristobalite is noteworthy whether it arises from an SRO phase directly from the coesite or from an intermediate quartz phase. Under dry conditions, cristobalite crystallized from silica glass powder only after heating ½ to 1 hour at 1300°C (9). We observed no growth of cristobalite from quartz (-325 mesh) by these high-temperature x-ray methods after exposure for 10 hours at 1200°C, and only 5 percent after an additional 6 hours at 1250°C.

All the experiments on stishovite were conducted with a natural stishovite (3) supply that weighed 20 mg (10). The individual experiments, on 1- to 2-mg samples which were contained in platinum envelopes, were limited to static runs at different temperatures followed by rapid quenching.

Table 1. Results of heating coesite. The pressure was one atmosphere.

Temp (deg)	Time (hr)	Ratio† cristobalite/coesite	R.I.		
			Aggregate	Min.	Max.
1165	20	0:1	1.555	1.483	1.585
1155	24	2:1	1.485	1.476	1.560
1160	42	1:0	1.476	1.470	1.496
1340	1	0:1‡	1.553	1.500	1.573
1345	2	0:1‡	1.517	1.480	1.557
1340	5	1:1‡	1.480	1.466	1.553
1070	550	0:1	1.585	1.580	1.587

* ±0.002. † The ratio of cristobalite to coesite is based on x-ray diffraction intensities. ‡ Both the microscope and x-ray diffraction show traces of quartz. For comparison, the normal refractive indices are cristobalite (1.487, 1.483); quartz, (1.544, 1.553); coesite (1.598, average). Data for 17 μ coesite.

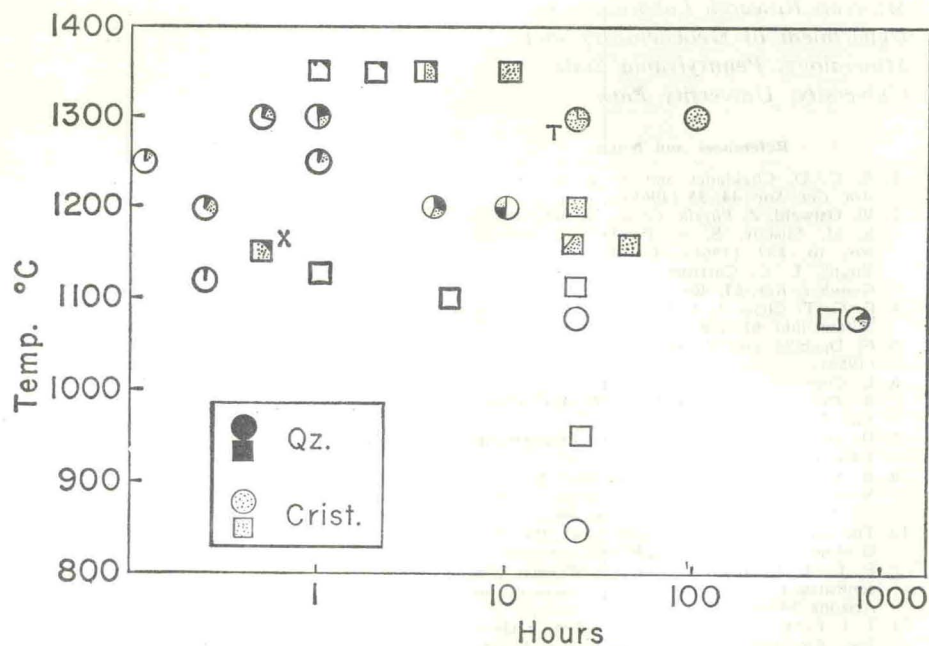


Fig. 1. Influence of time and temperature on the alteration of coesite. Time is plotted on a logarithmic scale. Solid and dotted filling indicate relative amounts of quartz, cristobalite, and tridymite modifications determined by x-ray diffraction. Circle and square points are for separate lots of concentrated coesite in which grain sizes averaged 8 and 17 microns respectively. The square marked X represents the average observations during a 5-hour x-ray study at high temperature.

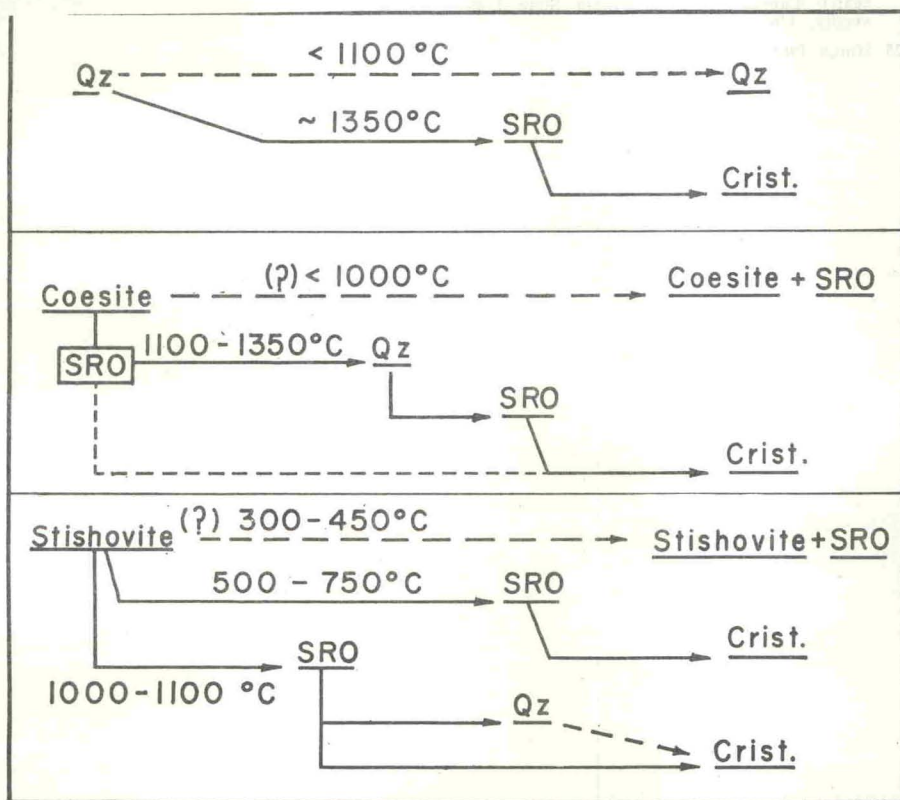


Fig. 2. Scheme of the most likely inversion paths of coesite and stishovite. Lower temperature limits are strongly dependent on time.

The data in Table 2 show that the stishovite differs markedly from the coesite in metastable persistence. It withstands exposure at 425°C for a few hours, but becomes completely amorphous to x-ray diffraction methods after heating less than 5 minutes be-

tween 650° and 750°C. Judging from the change of the aggregate refractive index, stishovite breaks down slowly at 350°C and much faster at 425°C. At lower temperatures the stishovite should be more resistant to change, obvious in its persistence in the crushed sandstone

of the Arizona Meteor Crater formed thousands of years ago. At higher temperatures and longer heating times (½ to 18 hours) crystallization of quartz (in the stability field of tridymite) in the presence of the SRO phase is again observed. Although cristobalite is the first to be observed by x-ray diffraction it is barely evident microscopically after 18 hours at 1100°C whereas quartz can be detected microscopically after 2 hours. No evidence of a transient formation of coesite from the much denser stishovite has as yet been found.

In Fig. 2, we attempt to summarize schematically some of the results obtained and to offer a probable interpretation. Coesite apparently forms a "dense," fine grained SRO phase, which then is converted to quartz. In the case of stishovite it is inconceivable that the rutile-type structure (where the coordination number is 6) could avoid the SRO stage and indeed there is direct evidence for the formation of the SRO and subsequent conversion at low temperatures. That the refractive index of the SRO phase rapidly approaches that of silica glass, may be a manifestation of a high disordering tendency of the coordination change, not involved in the case of coesite. The relative amounts of the various phases formed in any particular run might be explained on the basis of the competing reactions stishovite (or coesite) → SRO, SRO → quartz, quartz → SRO, and SRO → cristobalite with widely differing activation energies (12).

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Table 2. Heat treatment of stishovite at 1 atm pressure. The bulk color of the samples changed from grey to white with the presence of a large amount of amorphous material. A, amorphous, C, cristobalite, Q, quartz, S, stishovite, W, weak. For comparison, data from the literature is included. a. Synthetic stishovite of Stishov and Popova [Geokhimiya No. 10, 837 (1961)]. b. Natural stishovite, Fahey (11).

Temp. (°C)	Time (hr)	Results		
		X-ray	Microscopy	R.I. aggregate*
1100	18	C + Q	Q + A + C	—
1100	2	C + Q	Q + A + C	—
1060	0.5	C	A	1.456
1040	0.1	A	A	1.456
750	0.1	A	A	1.480
750	0.2	A	A	—
650	0.2	W S	S	1.500
500	0.2	S	S	—
425	3.5	S	S	1.740
350	70.	S	S	1.783
350	0.2	S	S	—
130	0.5	S	S	—
900 (a)	6.0	C + A	—	—
498 (b)	165.	A + S	—	1.557

* R.I. of starting stishovite aggregate (1.793 average).

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12. This work is part of a program of high pressure crystal chemical studies supported by the Metallurgy Branch of the Office of Naval Research. We are indebted to N. Raimondo who performed many of the coesite experiments. This report is contribution No. 62-47, College of Mineral Industries, Materials Research Laboratory, Pennsylvania State University, University Park.

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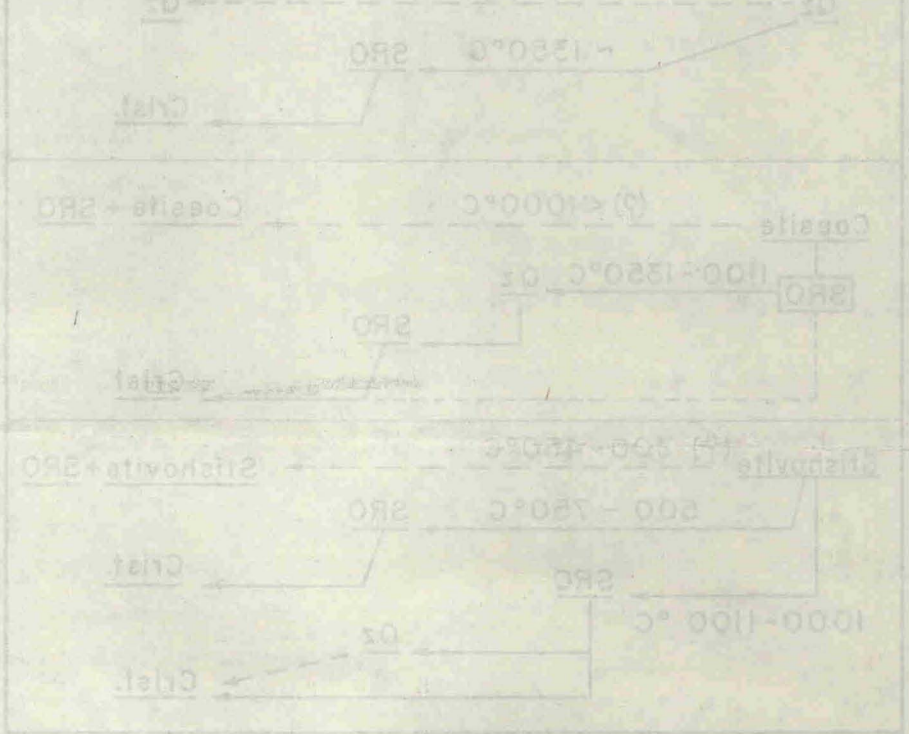


Fig. 2. Scheme of the most likely evolution path of coesite and stishovite. Lower temperature limits are roughly dependent on time.

The data in Table 1 show that the coesite differs markedly from the stishovite in its resistance to disintegration. The coesite is more resistant to disintegration than the stishovite, especially at lower temperatures. The stishovite is more resistant to disintegration than the coesite, especially at higher temperatures. The coesite is more resistant to disintegration than the stishovite, especially at lower temperatures. The stishovite is more resistant to disintegration than the coesite, especially at higher temperatures.

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