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Effect of Pressure and Temperature on the Reversal Transitions of Stishovite

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INTRODUCTION

Stishovite (SiO_2) was first synthesized by Stishov and Popova (1961) in the region of 1200-1400°C and approximately 160-180 kbars. Following this accomplishment, Chao, Fahey, Littler, and Milton (1962) detected stishovite in the coesite extracted from the impacted sandstone at Meteor Crater, Arizona. The latter authors, taking note of the conditions for synthesis, indicated that the presence of stishovite in the sandstone could only have been the result of meteoritic impact.

The synthesis has since been repeated by other researchers and the crystal system has been determined to be tetragonal (Chao, et al. 1962) with a rutile structure (Stishov and Belov 1962). This is the only known example of a structure with silicon in 6-fold coordination with oxygen. As expected, it is the densest form of silica with a specific gravity of 4.28 (Chao, et al. 1962) and a correspondingly high mean refractive index of 1.806 (Skinner and Fahey 1963).

The other polymorphs of interest in this study are coesite, quartz, and a short range order (SRO) transitional phase, all of which have Si in 4-fold coordination with oxygen and appear in the phase diagram as indicated in Figure 1. The SRO phase is not included because it is a metastable disordered material that may be formed during transitions. It has properties similar to those of silica glass (Dachille and Roy 1962 a; Skinner and Fahey 1963).

The temperature dependence of the reversal transitions of stishovite to the lower pressure polymorphs has been recorded by various authors. Stishov and Popova (1961) reported the conversion of synthetic stishovite to cristobalite at 900°C and 1 atm. Dachille, Zeto and Roy (1963) noted the formation of a SRO phase as low as 350°C at 1 atm. and of cristobalite and quartz above 1100°C at 1 atm. A study of the effect of temperature on natural stishovite was also made

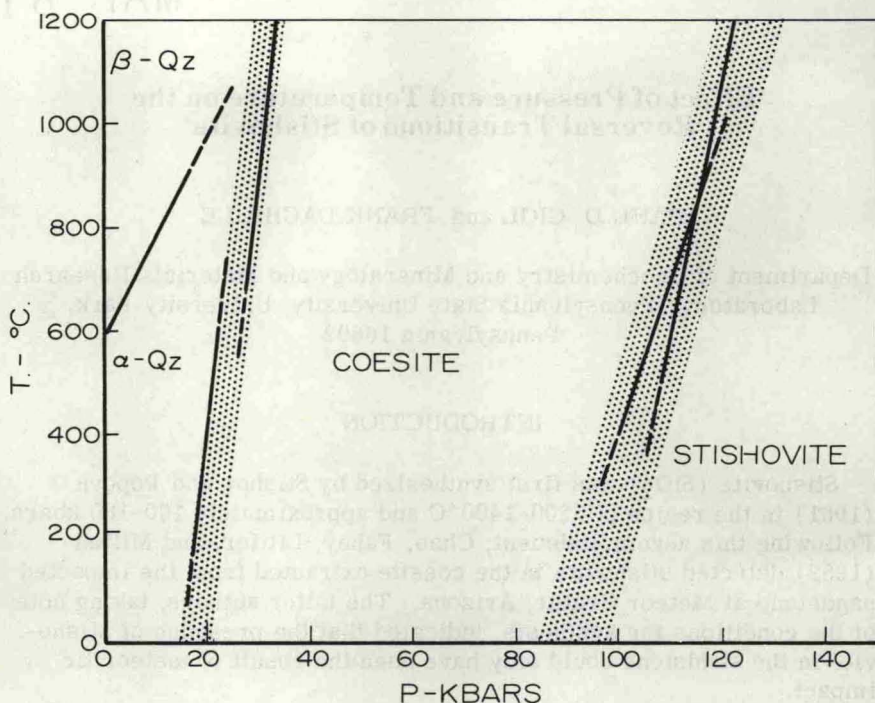


FIGURE 1—P-t diagram of silica system with representative phase boundaries. α - β quartz boundary by Yoder (1950). Quartz-Coesite boundary (lower temperature) by Dache and Roy (1959a) and the other by Boyd and England (1960). Coesite-stishovite boundary (lower temperature) by Ostrovsky (1966) and the other by Stishov and Popova (1963).

by Skinner and Fahey (1963). The inversion rate to silica glass (SRO phase as used in this paper) was determined at various temperatures and a model for nucleation and growth was postulated by them.

When considered with regard to theoretical temperature and pressure gradients in the earth, the work concerning the persistence of stishovite gives support to the hypothesis that its presence at the earth's surface could only have been the result of meteoritic impact. This paper explores this thesis further by studying the influence of various pressure-temperature (p-t) conditions on the reversal transitions of stishovite. The parameters of shear stresses and mineralizers were also utilized in a number of experiments.

MATERIALS AND PROCEDURES

Natural stishovite was the starting material. It was concentrated from Coconino sandstone from Meteor Crater by Fahey (1964) and most generously supplied by him. Stishovite was the only mineral detectable by x-ray diffractometry. The initial mean refractive index was 1.778 ± 0.003 and corresponds to the presence of about 4% SRO phase by weight as calculated by the method of Skinner and Fahey (1963).

Ninety runs were made in which about three mgs of stishovite were held at various p-t conditions for periods of 6 hours to 25 days. These runs can be divided into three groups. First, stishovite held over anhydrous CaSO_4 served as the "dry" starting material. Second, a mineralizer of water or a dilute aqueous solution of ammonium chloride was added to the starting material. Third, continuously oscillating shear stresses were superimposed on the opposed anvil apparatus (Dachille and Roy 1962 b) while using the "dry" starting material.

Hydrostatic and opposed anvil devices were employed to obtain a range of pressure from 1 to 110 kbars. Steel "test tube" or "cold seal" bombs (Roy and Tuttle 1956) with a water pressure medium and samples sealed in welded gold capsules were used for conditions of up to 2 kbars and 680°C . The opposed anvil apparatus provided conditions from 9 to 110 kbars and temperature to 450°C . For these runs, the sample was pelleted in a nickel ring (3/16 in. O.D.X. 0.125 in. I.D.) and sandwiched between Pt-10% Rh foil disks. The samples were "quenched" from p-t conditions by air-blast cooling of the bomb or anvils, then releasing the pressure.

Samples were analyzed for the various components by means of optical, infrared, and x-ray techniques. X-ray diffractometry was used to detect and estimate the proportions of the crystalline phases. The method described by Klug and Alexander (1954) was employed to determine the proportions of crystalline phases present in mixtures of two polymorphs.

The starting material was a powder consisting of aggregate grains. The individual crystallites in the grains of both products and reactants could not be adequately resolved with a petrographic microscope. Consequently, only the mean refractive index (n) of the grains could be determined by the Becke line method.

The infrared absorption spectra of the samples were obtained by using the KBr pellet technique for solids in conjunction with a Perkin Elmer 621 Spectrometer. A quantitative measure of the reactants was hoped for but could not be satisfactorily accomplished on account of broadness and overlap of the absorption bands. This technique was used to detect and characterize the SRO phase.

RESULTS

P-t phase boundaries of the silica system have been reported by a number of authors employing a variety of methods. Representative boundaries of interest here are plotted in Figure 1. It is obvious that agreement is not perfect; thus the transition boundaries are approximated by an area. The stippled areas are reduced to average lines in the succeeding diagrams in order to provide a background for presenting experimental results.

"Dry" System. Stishovite held over a desiccant was the starting material for these experiments. Zones based on the products of the reversal reaction of three-day duration define areas in p-t phase space and are plotted in Figure 2. Representative runs are given in Table I.

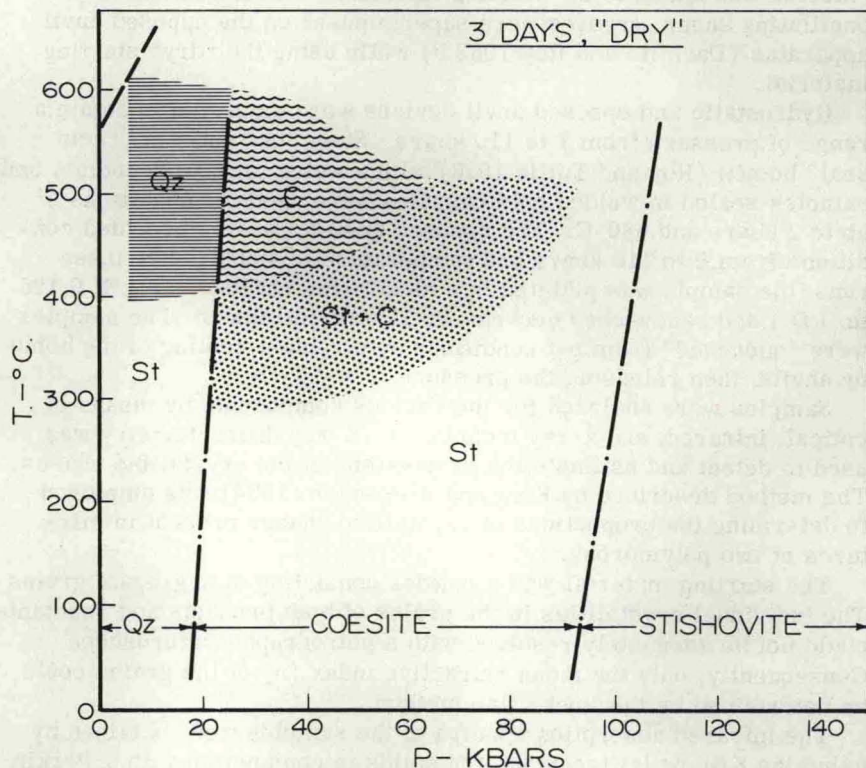


FIGURE 2—"Dry" system. Three zones which are based on the products of the reversal reactions define areas in p-t phase space. Further details are in text. The zones are: 1) complete conversion to quartz (Qz) or coesite (C), 2) partial conversion to coesite (St+C), and 3) partial conversion to SRO phase only (St). The dot-dash lines represent average phase boundaries and the equilibrium phases are indicated along the bottom of the diagram.

TABLE I. Crystalline Phases Obtained from Pressure-Temperature Treatment of Stishovite.

Pressure (kbars)	Temperature (°C±5 °C)	Time (days)	Products
"Dry" System			
1.5	668	3.5	SRO
10	309	3	st
10	359	3.5	st
15	410	3	qtz
23	347	3	st, qtz, coe
40	454	3	coe
40	362	3.5	st, qtz, coe
40	306	3	70% st, 30% qtz
40	242	4	st
60	449	3	80% st, 20% coe
70	406	3	90% st, 10% coe
70	295	3	st
80	449	3	90% st, 10% coe
100	396	3	st
"Wet" System			
2	678	4	qtz
10	405	3	st, coe, qtz
10	296	3	60% st, 40% qtz
10	252	3	95% st, 5% qtz
10	106	3	st
20	207	4	st
25	198	4	st
30	449	3	75% coe, 25% qtz
30	357	3	st, coe, qtz
40	453	3	coe
60	446	3	75% st, 25% coe
60	305	3	st, coe, qtz
80	444	3	95% st, 5% coe
80	400	3	st
100	400	3.5	st
Shear System			
65-75	365	6	80% st, 20% coe
70-80	351	7	st
50-60	295	3	st

The zones show 1) Complete conversion of stishovite to another polymorph, 2) Partial conversion to a crystalline phase, 3) Partial conversion to the SRO phase only.

The zone of complete conversion is bounded by a curve beginning at 400°C and greater than 2 kbars. As the pressure is increased, the lower temperature limit increases until a sharp upsweep occurs above 40 kbars in the coesite phase region. Below this curve, partial conversion occurs. The amount of conversion to other crystalline phases decreases with a reduction in temperature until conditions are reached where such conversion stops. The boundary is roughly parallel to the zone of complete conversion except in the quartz phase region where no conversion to quartz was observed in the three day interval. The last zone occupies the remaining area in Figure 2 and is defined by reactions which have the SRO phase as a product, detectable by the lowering of the index n . In other words, stishovite does not recrystallize to other polymorphs readily in this low temperature area, but does become disordered.

Kinetics determines the general form of the reaction zone boundaries of Figure 2. If equilibrium were easily achievable in this system, the zone boundaries would drop to lower and lower temperatures with increasing time at conditions, until they would move off the diagram. The presence of stishovite in known craters shows, however, that its reversal transitions are indeed sluggish at low pressures and temperatures. Equilibrium is clearly obtained with great difficulty at moderate conditions so that Figure 2 probably provides a reasonable picture of the behavior of this mineral under these conditions. In a general manner, this figure also demonstrates the increase in reactivity commonly observed at higher temperatures and also provides an example of the inhibiting effect of pressure on some reactions. Figure 3 shows both these effects in a more quantitative manner.

Figure 4 also demonstrates the change of reaction products as pressure is increased isothermally. Clearly the transition rate decreases as the stishovite is brought closer to its stability area. This may be expected because the free energy difference between the metastable stishovite and the stable phase should become less as the stishovite stability area is approached.

"Wet" System. When mineralizers were added to the starting material, the rate of conversion of stishovite to the other polymorphs was noticeably increased. The results are summarized by Figure 5 and Table I.

The complete conversion zone is essentially the same as that for the "dry" system except that now the zone extends into the pressure region of less than two kilobars. Similarly, the zone of partial conversion to other crystalline forms has now been extended at least

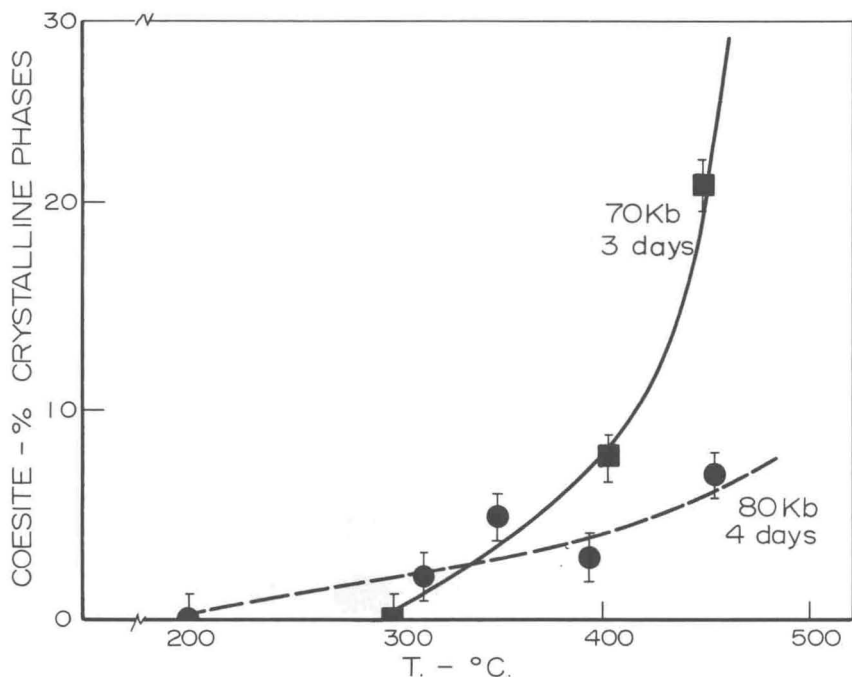


FIGURE 3—Trend with temperature at 70 and 80 kbars of the stishovite-coesite reaction.

150°C downward in the quartz phase region. The SRO zone again lies below the partial conversion zone and is somewhat reduced.

The effect of mineralizers is negligible at pressures above 70 kbars, so that the zone boundaries are essentially the same whether the material is "wet" or "dry." Mineralizers therefore have their greatest effect on the reversal reactions at lower pressures.

Shear System. Incorporating shear stresses in a number of experiments did not produce any detectable difference with respect to the "dry" system. Representative examples are given in Table I. In this technique, wafers were made without the nickel ring. Under shear, the extreme toughness of stishovite became apparent in that a number of the tungsten carbide anvil faces were pitted or indented by the sample which, at times, would "ball up" under the oscillation. The applied pressure was recalculated in accordance with the projected area of the pellet when removed; thus the pressures were not as accurately known in comparison with the non-shear experiments.

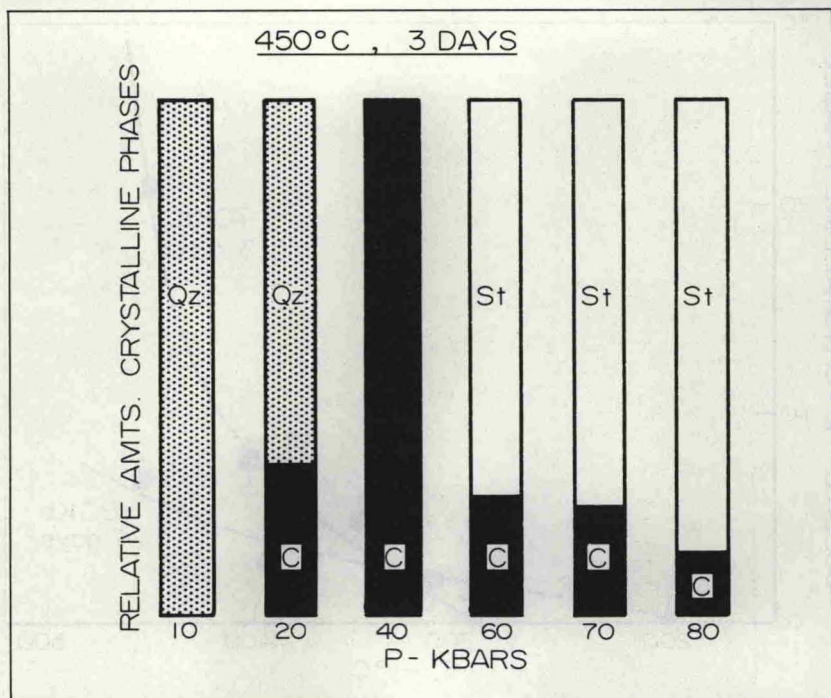


FIGURE 4—Effects of pressure on the reversal reaction of stishovite at 450°C. The products are quartz (Qz), coesite (C), and stishovite (St), respectively.

GENERAL

The infrared spectrum of SRO derived from stishovite under pressure was of interest because it might reveal a second form of silica having Si in 6 coordination. Such a form, of course, would have value in studies of shock metamorphism. Tracings of representative spectra are shown in Figure 6. The first is of stishovite and the last two are of silica glass and quartz, respectively. The mean cation-anion stretching frequency of the latter occurs between 1050-1150 cm^{-1} and is characteristic of Si in 4 coordination. For stishovite with Si in 6 coordination, the absorption is between 950-850 cm^{-1} , as could be predicted by the method of Dacheille and Roy (1959 b). The second, third, and fourth correspond to spectra of reaction products (Stishovite + SRO) containing increasing concentrations of SRO. Comparison of the spectra shows a rapid shift from the stishovite to the glass-quartz type pattern. The conclusion is that Si is clearly in 4 coordination in the SRO phase and the SRO phase must be very similar to silica glass with respect to structure.

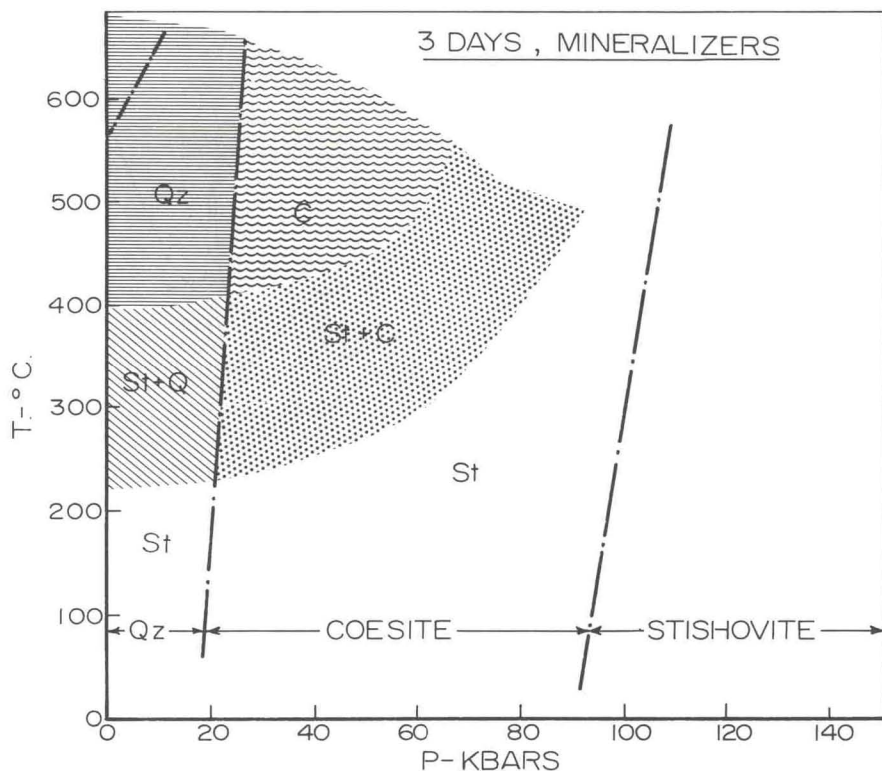


FIGURE 5—"Wet" system. The diagram is similar to Figure 2. Mineralizers were added to the system in this case. Note the crystallization of quartz from stishovite both at lower pressures and lower temperatures than those of the dry system.

An unexpected result was observed in the SRO phase at extreme pressures (Figure 7). The index n of the samples was found to increase when exposed to increasing temperature. This would indicate an unlikely decrease in the rate of reaction as the temperature was increased. This phenomenon can be attributed to the competition between two simultaneous reactions producing opposite effects on n : 1) the conversion of stishovite to the SRO phase, and 2) the densification of the SRO phase.

Since the SRO phase and silica glass are similar in structure and other characteristics, they might be expected to behave in a similar manner under similar conditions. Cohen and Roy (1961) have shown that silica glass can be permanently densified above a threshold pressure of 20 kbars with a corresponding increase of index n . They also found that increase of temperature at a given pressure increases

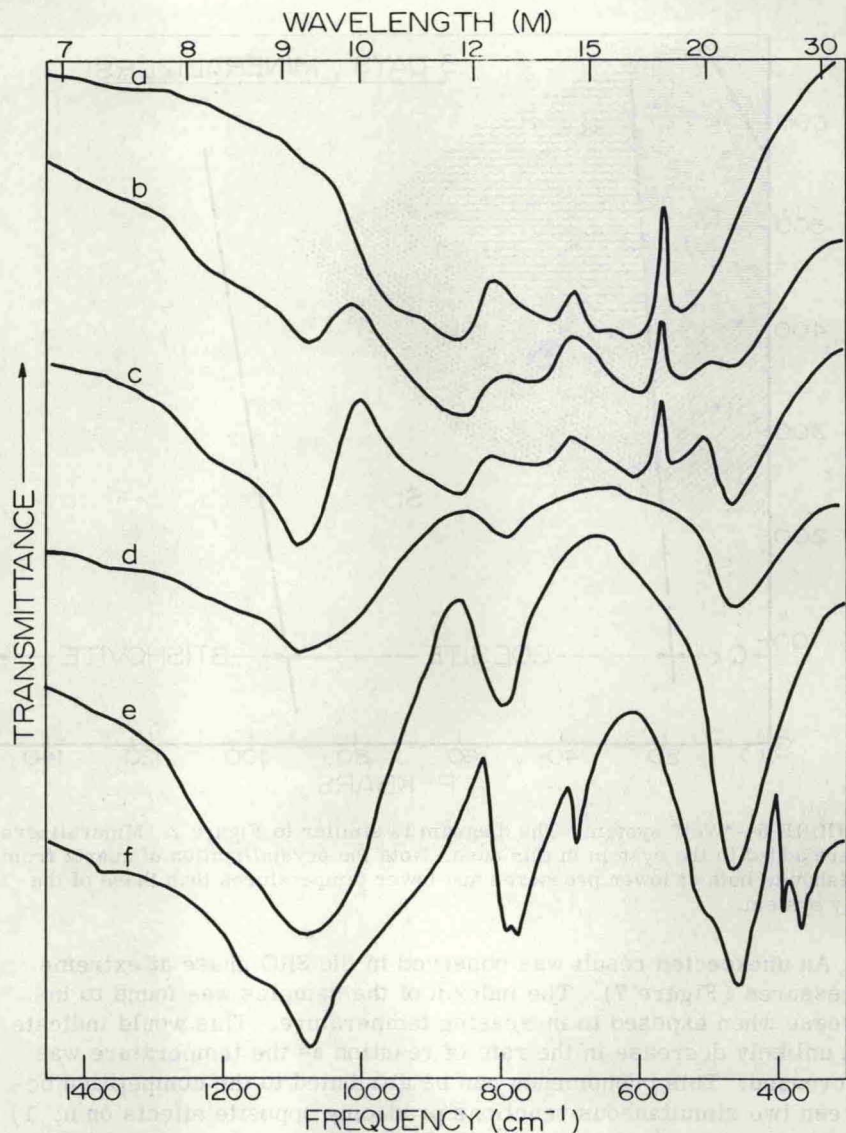


FIGURE 6—Infrared absorption spectra for the interval of $500\text{--}1500\text{ cm}^{-1}$. a) stishovite; b), c), and d) are spectra of reaction products containing increasing concentrations of SRO phase, respectively; e) silica glass; f) α -quartz. The Si-O stretching frequency at $1050\text{--}1150\text{ cm}^{-1}$ is characteristic of Si in 4 coordination and that of $850\text{--}950\text{ cm}^{-1}$ is of Si in 6 coordination.

densification. We have found that the SRO phase derived from stishovite behaves in the same manner. For example, stishovite heated at

855°C at atmospheric pressure for 45 minutes yielded a product with n of 1.466 ± 0.003 (silica glass, $n = 1.458$). After this product was held for one hour at 90 kbars and room temperature, n was 1.540 ± 0.004 . In another run but at 185°C, resultant n was 1.554 ± 0.003 . At 15 kbars and for one hour, the corresponding change of n was negligible (1.468 ± 0.004). When combined with the observation that the reversal transitions of stishovite are slowed with increasing pressure, the densification behavior of the derivative SRO phase helps explain the opposite trends of n with temperature at high and low pressures (Figure 7). It also complicates any relationship between the index n and amount of SRO phase in aggregate products of the experiments. The index n therefore was not used for the quantitative determination of conversion to SRO phase at pressure.

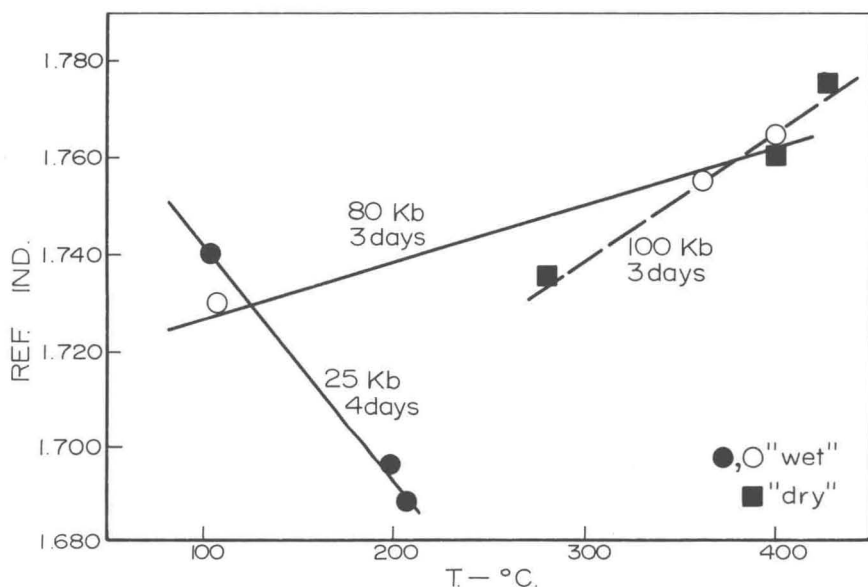
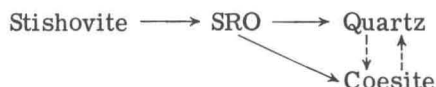


FIGURE 7—Trend of refractive index of products containing stishovite and SRO phase.

The growth of quartz metastably in the coesite phase area was observed at pressures as great as 60 kbars at 300°C. The growth of coesite as low as 10 kbars at 400°C was also observed. Such growth could be the result of 1) a sequence of transitions toward equilibrium, as for example:



with the quartz-coesite reaction being quite slow. Similar metastable transitions were observed by Dachille, et al. (1963) and by Skinner and Fahey (1963).

2) Undetectable quartz or coesite nuclei may have been present in the starting material (concentrated from an impacted sandstone). This would eliminate a nucleation barrier, and tend to favor metastable growth.

CONCLUSION

When the silica phase diagram is related to model p-t curves of the earth (Figure 8), it is clear that the p-t area of accessible geological depth is in the quartz phase region. This is also the region of the highest reversal rate of stishovite. In addition to this, one should note that stishovite would have to be located at least 350 km below the surface in order to remain as a stable phase according to the Turner and Verhoogen model and at even greater depth on the Daly model. It

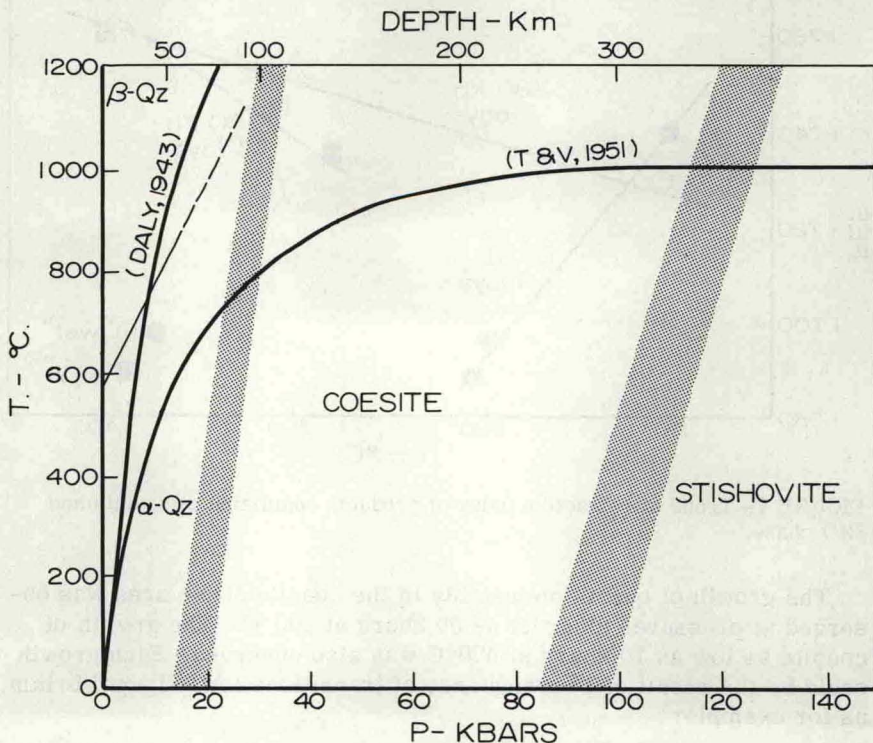


FIGURE 8—The p-t curves of the earth as given by Daly (1943) and Turner and Verhoogen (1951) are superimposed on the generalized silica phase diagram of Figure 1.

has been shown that only a few days at above 400°C and up to about 20 kbars are sufficient to cause complete conversion of stishovite to quartz; at slightly higher pressures complete conversion to coesite would result. It has also been shown that at temperatures below 225°C stishovite is resistant to conversion to other crystalline phases despite the use of shearing forces, mineralizers, and pressure. It is inconceivable that any known geological process could bring material from such depths without subjecting it to long dwell times in p-t regions that would bring about the complete alteration of any stishovite being so transported.

All these facts support the hypothesis that naturally occurring stishovite can only be formed by impacts of great magnitude and consequently is a very good index mineral for identifying astroblemes.

ACKNOWLEDGMENTS

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