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Comparison between thermochemical and phase stability data for the quartz–coesite–stishovite transformations[1]

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Abstract

Phase stability and elasticity data have been used to calculate the Gibbs free energy, enthalpy, and entropy changes at 298 K and 1 bar associated with the quartz–coesite and coesite–stishovite transformations in the system SiO_2. For the quartz–coesite transformation, these changes disagree by a factor of two or three with those obtained by calorimetric techniques. The phase boundary for this transformation appears to be well determined by experiment; the discrepancy, therefore, suggests that the calorimetric data for coesite are in error. Although the calorimetric and phase stability data for the coesite–stishovite transformation yield the same transition pressure at 298 K, the phase-boundary slopes disagree by a factor of two. At present, it is not possible to determine which of the data are in error. Thus serious inconsistencies exist in the thermodynamic data for the polymorphic transformations of silica.

Introduction

Since silica is a fundamental building block for the rock-forming minerals, the physical and chemical properties of its polymorphs have been the subjects of investigation for many years. In particular, the elastic properties of quartz and two high-pressure polymorphs, coesite and stishovite, and the pressure–temperature phase stability boundaries for these phases have been studied repeatedly because of their geological and geophysical significance. However, only a single study of the thermochemical properties of coesite and stishovite has been reported (Holm *et al.*, 1967).

The Gibbs free energy difference between two polymorphs at a standard condition of 1 bar and 25°C can be computed if the volume and bulk modulus (or compressibility) for each of those phases and the pressure of transformation are known. In addition, if the slope of the thermodynamic equilibrium boundary is known, the changes in enthalpy and entropy at the transformation pressure can be obtained from the Clausius–Clapeyron equation. On the other hand, thermochemical measurements for such quantities as the heat of solution and heat capacity would also yield these quantities at 1 bar pressure. Thus, the changes in the thermodynamic quantities associated with a phase transformation can be obtained from two entirely independent sets of measurements, which can then be compared to test the degree of consistency.

In this paper the available phase stability data for both the quartz–coesite and coesite–stishovite transformations are reviewed critically, and the published $P–V$ and bulk modulus data for these three phases are summarized. On the basis of those data, the changes in free energy, enthalpy, and entropy associated with the quartz–coesite transformation are computed, and compared to the respective calorimetric values obtained by Holm *et al.* (1967) for a test of consistency. It is demonstrated that the values obtained from those two approaches are not consistent. A similar test for the coesite–stishovite transformation also suggests a lack of consistency.

The effect of pressure and temperature on thermodynamic quantities

Theory

The Murnaghan equation (Murnaghan, 1949, p. 167) provides a simple and adequate approximation

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to the pressure–volume relation for quartz, coesite, and stishovite since the compression is small (<10 percent) in the pressure range of present interest. The Murnaghan equation can be written in the form

$$V = V_0[1 + K_0'P/K_0]^{-1/K_0'} \tag{1}$$

where V is the molar volume, P is the pressure, $K = -V(\partial P/\partial V)_T$ and $K' = (\partial K/\partial P)_T$, the isothermal bulk modulus and its pressure derivative, respectively; the subscript zero denotes quantities evaluated at 1 bar pressure. The free energy change due to compression can be calculated by integration of the identity $(\partial G/\partial P)_T = V$ which yields

$$G(P, T) - G(0, T) = K_0V_0(K_0' - 1)^{-1} [(1 + K_0'P/K_0)^{(K_0' - 1)/K_0'} - 1] \tag{2}$$

The effect of the compression on the entropy can be estimated from the identities $(\partial S/\partial V)_T = (\partial P/\partial T)_V = \alpha K$, where $\alpha = V^{-1}(\partial V/\partial T)_P$, the thermal expansion coefficient. A linear approximation (*i.e.*, αK = constant) yields

$$S(P, T) - S(0, T) = \alpha_0 K_0(V - V_0) \tag{3}$$

An improved approximation for the entropy can be obtained since the Murnaghan equation assumes K' to be constant and hence $K = K_0(V/V_0)^{-K_0'}$. A similar expression for the volume dependence of α is obtained by assuming that the dimensionless anharmonic parameter $\delta_t = -(\alpha K)^{-1}(\partial K/\partial T)_P$ is also constant, implying that $\alpha = \alpha_0(V/V_0)^{\delta_{t0}}$ (Anderson, 1967). Use of these approximations for α and K then yields

$$S(P, T) - S(0, T) = \frac{\alpha_0 K_0 V_0}{(\delta_{t0} - K_0' + 1)} [(V/V_0)^{\delta_{t0} - K_0' + 1} - 1] \tag{4}$$

Equation 4 reduces to equation 3 if $\delta_{t0} = K_0'$.

The anharmonic parameter δ_t needed in equation 4 can be estimated from the temperature derivative of the adiabatic bulk modulus K_s. The approximation $\delta_t \approx \delta_S + \gamma$ where $\delta_S = -(\alpha K_S)^{-1}(\partial K_S/\partial T)_P$ and $\gamma = V\alpha K_S/C_p$, where C_p is the specific heat, may be expected to hold both at high temperatures (for example, see Anderson *et al.*, 1968) as well as at low temperatures. For quartz, the values $\delta_{S0} = 7.3$ and $\gamma_0 = 0.7$ (Anderson *et al.*, 1968) result in the estimate $\delta_{t0} = 8.0$. Since the temperature derivative of the bulk modulus has not been measured for either coesite or stishovite, it is not possible to apply equation 4 to these materials. However, since the compressions are relatively small, the difference between equations 3 and 4 will be less important for coesite and stishovite than for quartz.

The effect of pressure on the molar volume, free energy, and entropy differences for a phase transition can be calculated by applying equations 1 to 4 to each phase separately and then taking the difference. In the following, the notation

$$\Delta V_P = V(P, T, \text{phase } 2) - V(P, T, \text{phase } 1)$$

is used, where Δ denotes differences between phases, the subscript P indicates the pressure, and phases 1 and 2 denote the low- and high-pressure phases, respectively. Equations 1 to 3 then yield ΔV_P, $\Delta G_P - \Delta G_0$, and $\Delta S_P - \Delta S_0$, respectively. Unless otherwise stated, all quantities are evaluated at 298 K.

Molar volume, elasticity, and thermal expansivity data

The molar volume, bulk modulus (K_0), pressure derivative of bulk modulus (K_0'), and thermal expansivity data are summarized in Table 1. The vol-

Table 1. Summary of the molar volume, bulk modulus, pressure derivative of bulk modulus, and thermal expansivity for quartz, coesite, and stishovite at room temperature

	Measured value	Reference
	V_o (cm^3/mole)	
Quartz	22.690	Frondel and Hurlbut (1955)
Coesite	20.64	Robie et al. (1966)
Stishovite	14.016	Chao et al. (1962)
	K_o (Mbar)*	
Quartz	0.371 (t)	McSkimmin et al. (1965)
	0.374 (s)	Soga (1968)
Coesite	0.972 (s)	Akimoto (1972)
	1.05 (s)	Liebermann (personal communication)
	1.137 (s)	Weidner and Carleton (1977)
	1.19 (t)	Bassett and Barnett (1970)
Stishovite	2.49 (s)	Liebermann et al. (1976)
	2.69 (t)	Bassett and Barnett (1970)
	2.81 (t)	Sato (1977)
	3.33 (t)	Liu et al. (1974)
	3.43 (s)	Akimoto (1972)
	K_o' $(=(\partial K/\partial P)_T)$	
Quartz	6.3	McSkimmin et al. (1965)
	6.4	Soga (1968)
Coesite	(6.0)	Estimated
Stishovite	(6.0)	Estimated
	α_o (10^{-6}°C^{-1})	
Quartz	36.6	McSkimmin et al. (1965)
Coesite	6.9	Skinner (1962)
Stishovite	8.9 ± 1.5	Weaver et al. (1973)
	17.1 ± 1.0	Ito et al. (1974)

* (t) and (s) denote the isothermal and adiabatic bulk modulus, respectively.

ume compression data to 100 kbar for α-quartz obtained by McWhan (1967) using X-ray diffraction methods are consistent with the K_0 and K_0' values listed in Table 1. The values for K_0 and K_0' obtained by Soga (1968) are based on a reanalysis of the data reported by McSkimmin *et al.* (1965). Since reported K_0 values for coesite and stishovite vary from 0.97 Mbar to 1.19 Mbar and from 2.49 Mbar to 3.43 Mbar, respectively, these ranges of values are used as bounds for the calculations. Because of this wide range of values, the difference between the adiabatic and isothermal bulk moduli, which amounts to less than 1 percent, has been ignored. The K_0' values for coesite and stishovite are assumed to be 6.0, as they are not available for either mineral.

The results of applying equations 1 to 4 to the quartz–coesite transition are shown in Figure 1. Separate curves were calculated for the values $K_0 = 0.97$ Mbar (curves 1, 2, 3, and 4) and $K_0 = 1.19$ Mbar (curves 1′ and 2′) in order to show the effect of the range of reported values for the bulk modulus of coesite. This range of values of K_0 for coesite results in an uncertainty of 4 percent in ΔV_P and 2 percent in ΔG_P at $P = 20$ kbar. The range of values for ΔS_P was found to be 0.3 percent, and was too small to be shown on the scale of the figure. The effects resulting from changes in K_0 for quartz were far smaller than those due to the range of values for coesite and are not shown. The difference between curves 3 and 4 (6 percent at 20 kbar) indicates that the effect of the assumptions concerning the volume-dependence of the entropy of quartz is small but not negligible. Since most of the pressure effect on ΔS results from the compression of quartz, the results are insensitive to the value of α_0 for coesite, and a ± 50 percent change in α_0 yields a change of only ± 0.05 e.u. in $\Delta S_P - \Delta S_0$. Note that the volume change of transition decreases rapidly with pressure, due to the large difference in the compressibilities of quartz and coesite. Hence, both the free energy change and the entropy change of transition are non-linear functions of pressure.

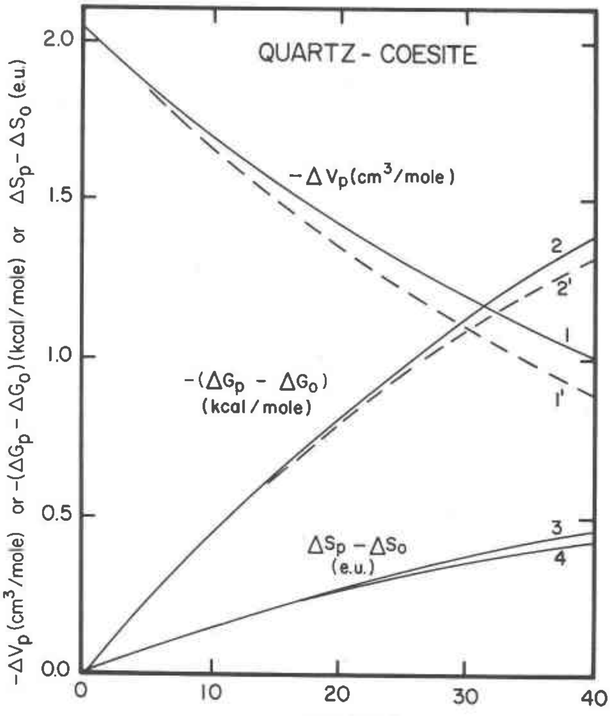

Fig. 1. The effect of pressure on the molar volume (V), Gibbs free energy (G), and entropy (S) changes for the quartz–coesite transition calculated using equations 1–4. The notation ΔV_p, *etc.*, denotes the difference (coesite minus quartz) evaluated at pressure P. Curves 1 and 2 were calculated using $K_0 = 0.97$ Mbar for coesite, and curves 1′ and 2′ were calculated using $K_0 = 1.19$ Mbar. The values of ΔG and ΔS are expressed as changes from the zero-pressure values.

The calculated results for the coesite–stishovite transition are shown in Figure 2. The net effect of the range of reported values of K_0 for both coesite and stishovite was determined by calculating: (1) with $K_0 = 1.19$ Mbar for coesite and $K_0 = 2.49$ Mbar for stishovite (curves 1 and 2); and (2) with values of 0.97 and 3.43 Mbar (curves 1′ and 2′). The two cases correspond to the minimum and maximum differences in the bulk moduli. At 80 kbar, the range of values considered leads to an uncertainty of 5 percent in the volume of transition and 3 percent in the free

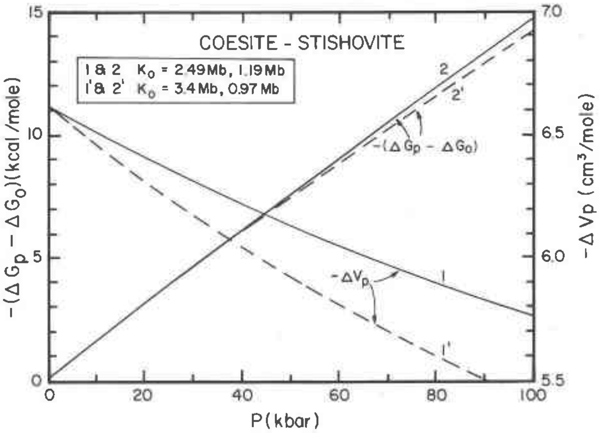

Fig. 2. The effect of pressure on the molar volume (V) and Gibbs free energy (G) changes for the coesite–stishovite transition. The notation ΔV_p denotes the difference (stishovite minus coesite) at pressure P. The free energy is expressed as the change from the value at $P = 0$.

energy. When the value for α_0 for stishovite reported by Weaver *et al.* (1973) is used, quantity $\Delta S_P - \Delta S_0$ was calculated to be less than 0.01 e.u. for pressures up to 80 kbar. The value of α_0 for stishovite reported by Ito *et al.* (1974) yields $\Delta S_p - \Delta S_0 = -0.20 \pm 0.01$ e.u. at $P = 80$ kbar. The difference in those values is not large enough to change any of the conclusions of this work. A ± 50 percent change in the value of α_0 for coesite results in a ± 0.1 e.u. change in $\Delta S_p - \Delta S_0$ at 80 kbar.

The calculated results shown in Figures 1 and 2 can be used to estimate the transition pressure P_t and its temperature derivative dP/dT when values of ΔH_0 and ΔS_0 are given. The values $\Delta H_0 = 1.21 \pm 0.15$ kcal/mole and $\Delta S_0 = -0.23$ e.u. reported for the quartz–coesite transition (Holm *et al.*, 1967) lead to values of the transition pressure ranging from 35.5 to 38 kbar at 298 K. The corresponding values for the temperature derivative range from -0.0074 to -0.0096 kbar/°C. The range of values of P_t and dP/dT results from the range of values of $K_0 = 0.97$ to 1.19 Mbar considered for coesite. An additional uncertainty of ± 6 kbar due to the uncertainty in ΔH_0 must be included in P_t. The values for the transition pressure and its temperature derivative calculated here differ substantially from those calculated by Holm *et al.* (1967), who obtained $P_t = 28 \pm 3$ kbar; and $dP/dT = 0.005$ kbar/°C. The differences arise from the use of different values for the bulk modulus of coesite (Holm *et al.* used an estimated value near 470 kbar) and from including the effect of pressure on the entropy, which was neglected by Holm *et al.*

For the coesite–stishovite transition, the values $\Delta H_0 = 10.58 \pm 0.3$ kcal/mole and $\Delta S_0 = -3.01$ e.u. (Holm *et al.*, 1967) yield P_t from 77 to 79 kbar and dP/dT from 0.021 to 0.023 kbar/°C, depending on the values assumed for K_0, with an additional uncertainty of ± 2 kbar in P_t resulting from the uncertainty in ΔH_0. The linear approximations to the phase boundary calculated from thermochemical data are compared with experimental results in Figures 3 and 4.

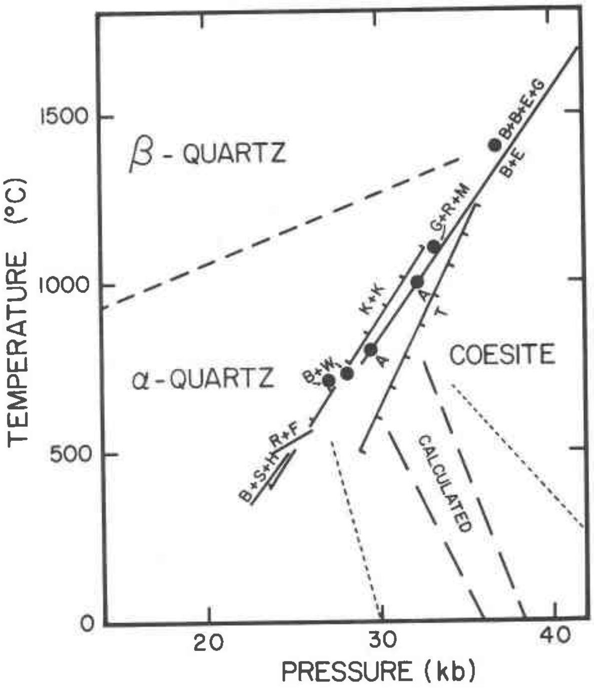

Fig. 3. Selected experimental determinations of the quartz–coesite boundary, compared to the boundary calculated from the thermodynamic values of Holm *et al.* (1967). Piston–cylinder data have been corrected using the correction curve of Boettcher and Wyllie (1968). Boundaries with tick marks represent lower (Kitahara and Kennedy, 1964) and upper (Takahashi, 1963) bounds to the pressure of the transformation. See Fig. 5 for references. The limits on the calculated transition pressure and slope at 25°C are shown by the dashed lines. The central range (heavy dashed lines) includes the uncertainty in the calculated values, while the outer range (light dashed lines) includes also the uncertainty in the thermodynamic values of Holm *et al.* (1967).

Phase stability studies of the quartz–coesite–stishovite transformations

Quartz–coesite transformation

Since the announcement of the first synthesis of coesite (Coes, 1953), there have been repeated attempts to determine the thermodynamic equilibrium phase relations between coesite and quartz. Table 2 summarizes these studies, while the boundary curves or points on the curves, as reported in these studies, are shown in Figure 5. Clearly there is no single curve which will satisfy the data of all of the investigators. In attempting to select the curve which represents the thermodynamic equilibrium curve, the following criteria are utilized. Only runs in which quartz was transformed (at least in part) into coesite, or the reversal of this reaction, will be considered to be definitive in demonstrating that the phase boundary has been crossed. Synthesis runs starting with some other more reactive material, such as silicic acid, and runs showing no change in the starting material cannot be considered to rigorously demonstrate equilibrium, even though they may give consistent and reproducible results. A series of runs in which the transformation was run in only one direction can provide only an upper or lower bound to the pressure of the reaction curve.

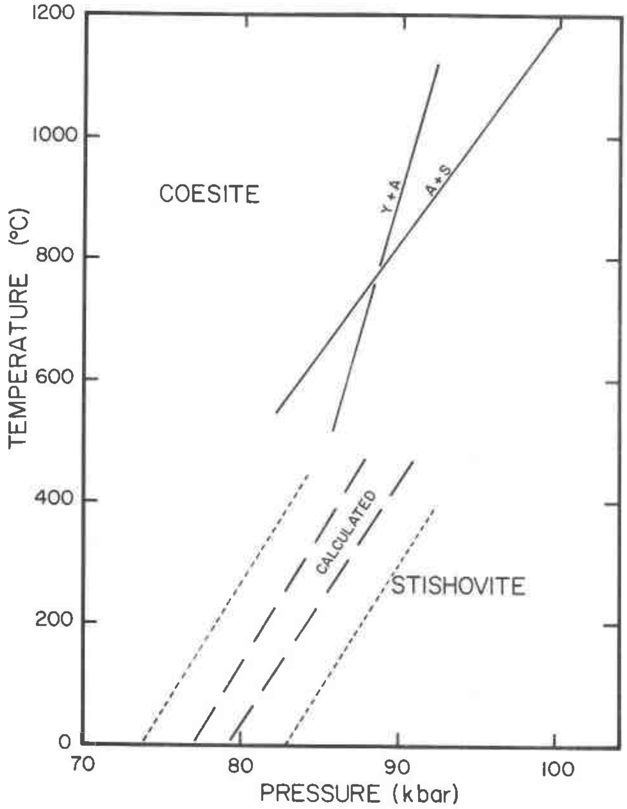

Fig. 4. Coesite–stishovite boundary curves as experimentally determined by Akimoto and Syono (1969) and by Yagi and Akimoto (1976) compared with the boundary calculated from the thermodynamic values of Holm *et al.* (1967). The uncertainties in the calculated transition pressure and slope at 25°C are shown by the heavy dashed lines. The light dashed lines include also the uncertainty in the thermodynamic values of Holm *et al.* (1967).

Of the five studies which used the opposed anvil device, the earliest two (MacDonald, 1956; Griggs and Kennedy, 1956) were synthesis studies and can be rejected on that basis alone. The third study (Dachille and Roy, 1959) included two runs in which coesite transformed into quartz; these two points possibly define a lower pressure bound to the reaction curve. However, the opposed-anvil device has subsequently been found to produce excessive pressures across part of the anvil faces over those calculated from the applied force and anvil area (Boyd and England, 1960; Kitahara and Kennedy, 1964), which casts doubts on the accuracy of the results reported in these early studies. Later modifications have been made to improve the accuracy of the opposed-anvil device by introducing a shearing motion to the anvils (Bell *et al.*, 1965) and by increasing the diameters of the anvil faces (Roy and Frushour, 1971). The considerable reduction in the hysteresis of the reaction observed using these modified devices and the observation that the new phase appeared evenly distributed across the anvil faces suggest that the pressure gradients across the anvil faces have been greatly reduced. If so, the calculated pressure must be close to the true pressure applied to the sample. It is noteworthy that the results of these two studies are in close agreement with the piston–cylinder determinations.

Investigations using the piston–cylinder device have resulted in fairly narrow brackets of the equilibrium curve, but there is some uncertainty as to the magnitude of the friction correction that must be applied to the calculated pressures. Actually the data agree better before than after being corrected by the various investigators. While several methods of pressure calibration have been applied, the best would be one which compared the results of studies of reactions at pressures and temperatures close to those of the equilibrium phase boundary with results of the same reactions investigated using a high-pressure gas apparatus. Boettcher and Wyllie (1968) found a room-temperature correction of −13 percent (applied to piston-in run pressures) on the basis of the I–II transformation in bismuth, and a correction of −7 percent at 850°C using the melting of LiCl as a standard. Subsequent studies of the reaction albite ⇄ jadeite + quartz in piston–cylinder devices (Johannes *et al.*, 1971) and in the high-pressure gas apparatus (Hays and Bell, 1973), using the same starting material, suggest a correction of −8±3 percent at 600°C, in good agreement with the correction curve of Boettcher and Wyllie.

Of the several studies in which the piston–cylinder device was used, that of Boyd and England (1960) is perhaps the most useful for determining the position of the quartz–coesite equilibrium boundary. In this investigation the reaction was reversed at several temperatures between 705° and 1710°C. Kitahara and Kennedy (1964), working at lower temperatures with various "mineralizers" to increase the reaction rate, converted coesite to quartz in several runs, but did not run the reaction in the reverse direction; their curve thus serves as a lower bound to the pressure of the equilibrium boundary. This bound, if uncorrected for friction and anvil effects, is compatible with all of the other uncorrected piston-cylinder determinations. Most of the experimental runs reported by Boettcher and Wyllie (1968) were synthesis runs; in only two cases were quartz or coesite in the starting material converted into the other polymorph in the product. These two runs bracket the reaction at 800°C and are

Table 2. Summary of experimental studies of quartz–coesite equilibrium

Investigators	Apparatus	Starting material	Equation of boundary or point of boundary
MacDonald (1956)	Opposed anvil	Silicic acid	P(kbar)=9.5+0.0225T(°C)
Griggs & Kennedy (1956)	Opposed anvil	Silicic acid	P=6.3+0.0286T
Dachille & Roy (1959)	Opposed anvil	Tridymite, Cristobalite, Silicic acid, Coesite	P=12.9+0.0155T
Boyd & England (1960)	Piston-cylinder	Quartz, Coesite, Cristobalite, Silicic acid	P=19.5+0.0112T
Takahashi (1963)	Tetrahedral press	Quartz, Silicic acid	P=24+0.0096T
Kitahara & Kennedy (1964)	Piston-cylinder	Quartz, Coesite, Amorphous silica	P=21+0.010T
Boyd (1964)	(Revision of friction correction of Boyd and England, 1960)		P=21.2+0.0112T
Bell et al. (1965)	Opposed anvil (with shearing)	Quartz, Coesite	P=17.8+0.0134T
Green et al. (1965)	Piston-cylinder	Quartz, Coesite, Silicic acid	P=34.3kbar @ 1100°C (talc) P=31.8kbar @ 1100°C (AgCl)
Boettcher & Wyllie (1968)	Piston-cylinder	Albite glass (±qtz), Jadeite+quartz	P=28kbar @ 735°C P=27kbar @ 710°C
Roy & Frushour (1971)	Opposed anvil (1/2" diam. faces)	Quartz, Coesite, Silicic acid	P=15.1+0.0173T
Naka et al. (1972)	Girdle	Quartz, Coesite	P=13+0.0137T (wet) P=14+0.010T (dry, above 1100°C) P=15.3+0.037T (dry, below 1100°C)
Böhler & Arndt (1974)	Belt (with in situ x-ray)	Quartz, Silica gel, Coesite	P=31+0.0075T
Akella (1978)	Piston-cylinder	Quartz, Coesite	P=21+0.012T (talc) P=21.8+0.009T (NaCl)

consistent with Boyd and England's curve at this temperature. Green *et al.* (1966) and Boyd *et al.* (1967) carefully studied the reaction at temperatures of 1100°C and 1400°C, respectively. The pressure-uncorrected brackets determined in runs using talc as the pressure medium are in complete agreement with the uncorrected curve of Boyd and England. When Green *et al.* used AgCl pressure cells, the apparent pressure of the reaction was 2.5 kbar lower than with talc. It is likely that the lower pressure found in the AgCl cell was caused by an anvil effect, as the central column of pyrophyllite and ceramic would be expected to bear a disproportionately large share of the load. Recently Akella (1978; also personal communication) has re-examined the pressure of transition at 800° and 1000°C, using a fairly standard talc–glass–alsimag pressure cell and a low-friction NaCl pressure cell similar to that described by Mirwald *et al.* (1975). While the nominal pressures found using the talc–glass–alsimag cell are in close agreement with the curve (pressure uncorrected) of Boyd and England (1960), the NaCl cell gave nominal pressures which were lower by 1.2 and 1.7 kbar at 800° and 1000°C, respectively. As this cell does not contain a less compressible central column, there should be no appreciable anvil effect; the pressure difference between the two types of cells cannot be explained at the present time.

Takahashi (1963) used the tetrahedral press to convert quartz to coesite in several runs, but did not study the reverse reaction. His curve could serve as a fairly accurate upper bound to the pressure of the reaction, as the tetrahedral device was calibrated against Yoder's (1950) gas-apparatus determination of the α–β quartz transition at temperatures up to approximately 800°C and pressures up to 10 kbar. Naka *et al.* (1972) converted quartz into coesite in a series of anhydrous runs in a girdle apparatus and ran the reaction in both directions in the presence of water. While their "dry" curve should provide an *upper* bound to the pressure of the reaction, it is located several kbar *below* their own "wet" reaction curve. Apparently their room-temperature pressure calibration of the device was insufficient to describe the actual pressures at temperatures between 900° and 1500°C. Until high-temperature calibrations against well-known reactions are carried out, the accuracy of both of their curves will remain in doubt.

Böhler and Arndt (1974) were able to observe the quartz–coesite reaction by use of an *in situ* X-ray method. Hays (1975) has pointed out that only six of their runs successfully converted one polymorph into the other, and these runs result in a bracket which is 14 kbar wide, encompassing all of the previously-determined curves and points.

In attempting to select a "best" curve (Fig. 3) to represent the equilibrium phase boundary, the results of the most thorough of the piston–cylinder determinations, that of Boyd and England, are used. As the authors indicated in their later work (Boyd, 1964; Boyd *et al.*, 1967), their early pressure calibration was based on room-temperature transformations and should not be used at higher temperatures. Boettcher and Wyllie's (1968) temperature-dependent pressure correction curve is preferable. Although this correction curve is uncertain above 850°C, it is well determined at lower temperatures and will be assumed to be linear through the entire range of temperatures represented by the quartz–coesite equilibrium studies. The corrected stability boundary curve appears to be linear throughout the entire range of temperatures over which it was studied in the piston–cylinder device, and if extrapolated linearly would agree well with the brackets determined by Bell *et al.* (1965) at temperatures as low as 350°C. The equation of this "best" curve is:

$$P(\text{kbar}) = 18.3 + 0.013\ T(°\text{C})$$

The selected data are summarized in Figure 3.

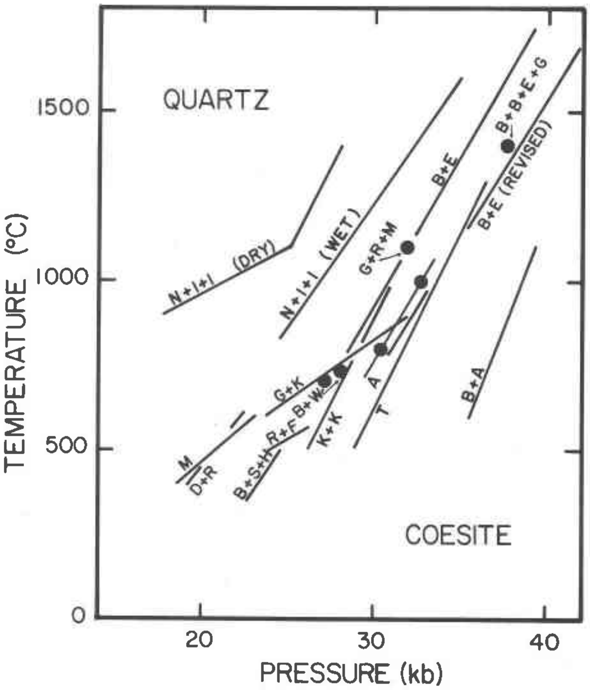

Fig. 5. Experimentally-determined boundary curves for the quartz–coesite transformation. References: M, MacDonald (1956); G + K, Griggs and Kennedy (1956); D + R, Dachille and Roy (1959); B + E, Boyd and England (1960); T, Takahashi (1963); K + K, Kitahara and Kennedy (1964); B + S + H, Bell *et al.* (1965); G + R + M, Green *et al.* (1966); B + B + E + G, Boyd *et al.* (1967); B + W, Boettcher and Wyllie (1968); R + F, Roy and Frushour (1971); N + I + I, Naka *et al.* (1972); B + A, Böhler and Arndt (1974); A, Akella (1978).

Coesite–stishovite transformation

All earlier studies of the relative stabilities of coesite and stishovite suffer from serious inadequacies; they were all synthesis rather than equilibrium studies, and the pressure calibrations were made only at room temperature (Stishov and Popova, 1961; Sclar *et al.*, 1962; Ryabinin, 1964; Ostrovsky, 1965, 1967). Two more recent investigations (Akimoto and Syono, 1969; Yagi and Akimoto, 1976) may have located the boundary curve with more certainty and will be discussed in greater detail.

Akimoto and Syono, using a tetrahedral press and several different starting materials, carried out a series of quenching experiments between 550° and 1200°C. In most of the runs coesite and/or stishovite were synthesized from either anhydrous amorphous silica or quartz. In seven runs, however, the starting material was either coesite or stishovite and in five of these seven runs the other polymorph appeared in the final product. These five runs appear to bracket the equilibrium boundary curve between 930° and 1200°C. All these runs, however, approached their final pressures and temperatures through the stishovite stability field. In the three runs in which coesite was the starting material, it is possible that the transformation of coesite to stishovite occurred while the temperature was being raised, and thus these runs may not accurately specify the conditions of equilibrium between the two polymorphs. The two runs in which stishovite transformed into coesite indicate that the equilibrium curve had been crossed by the time the final run conditions were reached, and thus these two runs establish only a lower bound to the pressure of the transition at 1050° and 1200°C.

A more serious objection to the validity of the results of their study originates in the uncertainty of the accuracy of the pressure calibration used by Akimoto and Syono. Yagi (1976) and Yagi and Akimoto (1976) have reported that pressure calibrations made at room temperature are not correct at elevated temperatures in multi-anvil devices. In their cubic press at temperatures below approximately 600°C, increasing temperature was found to cause an increase in the pressure due to the thermal expansion of the sample and surrounding materials. At higher temperatures, creep in the gasketing material and disproportionation of the pyrophyllite parts of the pressure cell become more significant, and further heating results in a decrease in the pressure applied to the sample. Presumably similar behavior occurred but was not recognized in the tetrahedral press of Akimoto and Syono.

In an effort to avoid the need for the application of such uncertain pressure calibrations, Yagi and Akimoto (1976) studied the equilibrium between coesite and stishovite by means of a cubic press equipped for *in situ* X-ray diffraction of the sample. NaCl was mixed with the sample to serve as both a pressure standard and a low-strength pressure-transmitting medium. The final pressure of each run was calculated from the temperature, measured using chromel/alumel thermocouples, and the measured lattice parameter of NaCl, using Decker's (1971) equation-of-state pressure scale. The growth or disappearance of coesite in the sample as it was brought up to its final temperature and pressure was also identified by monitoring the most intense X-ray diffraction peak of coesite continuously during heating. Once the final temperature of the run was reached, the nature of the phase of SiO_2 present in the sample and the lattice parameter of NaCl were determined by scanning a limited range of 2θ. The identity of the polymorph or polymorphs in the sample was confirmed by X-ray diffraction after the sample was quenched and unloaded.

If this study were considered to be merely another quenching experiment, with improved knowledge of the run pressures, the results would be questionable on the basis of the use of silicic acid as the starting material. However, if Yagi and Akimoto's interpretation of the changing intensity of the coesite X-ray peak during each run is correct, the reaction curve must have been crossed in several of the experimental runs. The initial growth of coesite observed in all runs was a synthesis and as such was correctly considered by the authors to be possibly metastable. The growth of stishovite from coesite observed in several of the runs demonstrated that the sample was within the stishovite stability field when the stishovite formed. The partial reversion of this stishovite to coesite in three runs indicated that the phase boundary was crossed as these runs were being brought to their final temperatures. Unfortunately, these results do not unambiguously determine the position of the boundary curve. Since the initial pressure increase due to increasing temperature was essentially the same as the slope of the reported equilibrium boundary curve (approximately 7 kbar increase during the first 700° rise of temperature; Yagi, personal communication, 1977), none of the runs below 800°C can have crossed the curve, and hence none can be used with confidence to establish its location. At best, the runs in which stishovite formed from coesite below 800°C provide an upper bound to the transition pressure. Of the higher-temperature runs, only the three which were observed to cross the boundary can be used to locate it, and these only place a lower bound on the pressure of the transition. Given the observed slow reaction rate and short run times (10 to 15 minutes at the highest temperatures; Yagi, personal communication, 1977), it is quite probable that the true phase boundary is actually located at higher pressures than those reported. Note also that the NaCl pressure scale has not been verified at elevated temperatures. Since the temperature-dependent part of the NaCl pressure scale is large at the conditions of Yagi and Akimoto's experiment, a significant error in transition pressure and its temperature derivative may have been introduced.

Discussion

As can be seen in Figure 3, the phase boundary calculated for the quartz–coesite transition does not appear to be consistent with the experimentally-determined phase relations. The source of the discrepancy appears to lie in the calorimetric values for ΔH_0 and ΔS_0 reported by Holm *et al.* (1967) rather than the compression data or the equation of state used to calculate the effect of pressure. In particular, it does not appear to be possible to reduce the calculated transition pressure below 30 kbar at 25°C without requiring excessively small values for the bulk modulus of coesite. It is possible to draw a phase boundary starting with the calculated transition pressure and slope at room temperature and then change the slope from negative to positive so as to join the trend of the experimental values at higher temperature. However, such a phase boundary would require a large change in the entropy of transition within a narrow pressure and temperature range. Such a change appears to be improbable. Since the results of the quench experiments appear to be internally consistent, it seems necessary to question the calorimetric values for ΔH_0 and ΔS_0.

If the results of the phase stability experiments are accepted as describing the equilibrium phase boundary for the quartz–coesite transition, the transition pressure and slope can be combined with the compression calculations presented in Figure 1 to yield values $\Delta H_0 = 0.56$ kcal/mole and $\Delta S_0 = -0.70$ e.u. These results can be compared with the values $\Delta H_0 = 1.21 \pm 0.15$ kcal/mole and $\Delta S_0 = -0.23$ e.u. reported by Holm *et al.* (1967). In making this comparison, note that the uncertainty reported by Holm *et al.* is an "estimated limit of error" which includes systematic as well as random components. The phase equilibrium calculations yield a value for ΔH_0 which is less than one half of the calorimetric value, while the values for ΔS_0 differ by a factor of three. Since these discrepancies are large compared with the possible sources of error in the phase equilibrium calculations, we propose that the calorimetric values may be in error.

In attempting to find possible sources of error in the calorimetric values, note that Holm *et al.* performed three separate sets of measurements in order to determine ΔS_0 and ΔH_0 for the quartz–coesite transition: (1) A calorimetric determination of the low temperature heat capacity (C_p) of coesite was used to estimate the entropy of coesite and hence ΔS_0. (2) The heats of solution of quartz and coesite were determined for a lead–cadmium–borate solvent. This experiment yielded values for the enthalpy of transition ΔH_t^{970} at 970 K. (3) The increment in enthalpy of coesite from 298 to 970 K $(H^{970} - H^{298})_{\text{coes}}$ was determined by a transposed-temperature drop calorimetric technique. The results from 2 and 3 then determine ΔH_0 for the transition at 298 K, as $\Delta H_0 = \Delta H_t^{970} - (H^{970} - H^{298})_{\text{coes}} + (H^{970} - H^{298})_{\text{qtz}}$. Since both ΔS_0 and ΔH_0 disagree with the phase equilibrium values, it seems likely that some effect associated with the coesite samples used might be responsible for the discrepancy. The specific heat and enthalpy increment experiments were performed on samples of natural coesite from Meteor Crater, Arizona, whereas the heat of solution calorimetry was done with synthetic coesite samples. Holm *et al.* note that the natural coesite was extremely fine-grained (95 percent of the grains having diameters less than 0.5 microns) and suggest that the entropy of coesite might be too large by "several tenths" e.u. due to surface contributions to the heat capacity. Reducing the calorimetric entropy of coesite would tend to remove the discrepancy in ΔS_0. However, the surface contribution to the heat capacity would also be reflected in a reduction of the enthalpy increment $(H^{970} - H^{298})_{\text{coes}}$ and would lead to an increase in ΔH_0, resulting in a larger discrepancy. Since the surface effect cannot account for the discrepancies in both ΔS_0 and ΔH_0, a second problem associated with the solution calorimetry must also be present.

The transition pressure $P_t = 80 \pm 2$ kbar for the coesite–stishovite transformation reported by Yagi and Akimoto (1976) yields a free energy difference $\Delta G_0 = 11.7 \pm 0.5$ kcal/mole, where the uncertainty includes the uncertainties in P_t and $\Delta G_p - \Delta G_0$. This value agrees with either the value $\Delta G_0 = 11.5 \pm 0.4$ kcal/mole reported by Holm *et al.* (1967) or the value $\Delta G_0 = 11.9 \pm 0.3$ kcal/mole calculated using the revised value for the quartz–coesite transformation found above. The slope of the phase boundary $dP_t/dT = 0.011 \pm 0.003$ kbar/°C (Yagi and Akimoto, 1976) yields calculated values $\Delta S_0 = -1.5 \pm 0.4$ e.u. and $\Delta S_0 = -1.3 \pm 0.4$ e.u., using the values of α_0 reported by Weaver *et al.* (1973) and Ito *et al.* (1974), respectively. These values disagree with the value $\Delta S_0 = -3.01$ e.u. reported by Holm *et al.* (1967) and the value $\Delta S_0 = -2.54$ e.u. obtained using the revised values for coesite found here. The value for the entropy of stishovite estimated from the phase stability boundary, $S_0 = 7.7 \pm 0.4$ e.u., is about one e.u. larger than the calorimetric value 6.64 e.u. However, since the calorimetric value is based on measurements of the low-temperature heat capacity of a sample of very fine-grained stishovite from Meteor Crater, it would be expected that the surface contribution to the entropy would lead to an error of the opposite sign. Hence, the sample grain size cannot be used to explain the discrepancy in the entropy values for stishovite, as was suggested earlier for coesite. However, because of the sluggish rate for the formation of stishovite, the value of dP_t/dT determined by Yagi and Akimoto may actually be somewhat less than that for the equilibrium boundary, and hence the equilibrium transition pressure at room temperature may be less than the reported value. Such a change in slope would increase ΔS_0. This would tend to reduce the discrepancy with the calorimetric values.

Summary and conclusions

The experimental determinations of the phase boundaries for the quartz–coesite and coesite–stishovite transformations have been reviewed. With few exceptions the experimental determinations of the quartz–coesite equilibrium boundary are consistent with the curve $P(\text{kbar}) = 18.3 + 0.13\,T\,(°\text{C})$. All the piston–cylinder determinations and the later opposed-anvil determinations agree with this boundary to within 1 kbar over the temperature range 350° to 1750°C. For the coesite–stishovite transformation, there appears to be only a single determination of the equilibrium phase boundary, that reported by Yagi and Akimoto (1976).

The effect of pressure at 298 K on the molar volume, free energy, and entropy of quartz, coesite, and stishovite has been calculated using the Murnaghan equation of state. The uncertainty in the values of bulk modulus and thermal expansivity and the approximations inherent in the equation of state used in the calculations result in uncertainties in the free energy difference of less than 3 percent for both quartz–coesite and coesite–stishovite transformations. The error in the entropy change at the transition probably does not exceed ±0.05 e.u. for the quartz–coesite transformation and ±0.1 e.u. for the coesite–stishovite transformation.

The calorimetric values of entropy and enthalpy change reported by Holm *et al.* (1967) have been combined with the calculated results to estimate the transition pressures and phase boundary slopes at 298 K. For the quartz–coesite transformation, the transition pressure was estimated to lie in the range $P_t = 30$ to 44 kbar and the slope dP_t/dT to be from -0.007 to -0.010 kbar/°C. These calculated values are in serious disagreement with the experimentally measured values $P_t = 18.6$ kbar and $dP_t/dT = 0.013$ kbar/°C. The discrepancy is large compared with the uncertainties in the equation of state and the bulk modulus and thermal expansivity data as well as the estimated limits of error in the calorimetric data reported by Holm *et al.* (1967). It seems likely that the calorimetric data for coesite are in error. The discrepancy in slope may result from an error in the calorimetrically-determined entropy of coesite, due to the surface contributions to the heat capacity resulting from the extreme fineness of the natural coesite samples studied by Holm *et al.* However, an additional source of error must be present in their solution calorimetry experiment in order to explain the discrepancy in the transition pressure.

The transition pressure $P_t = 75$ to 81 kbar at 298 K calculated for the coesite–stishovite transformation is in agreement with the value $P_t = 80 \pm 2$ kbar reported by Yagi and Akimoto (1976). However, the calculated slope of the phase boundary $dP_t/dT = 0.021$ to 0.023 kbar/°C does not agree with the measured slope 0.011 ± 0.003 kbar/°C. The discrepancy cannot be accounted for by a surface contribution to the entropy of stishovite. Part of the discrepancy in slope may result from a potential error in the values reported by Yagi and Akimoto (1976). A consideration of the P–T paths followed in their experiment indicates that they may have determined an upper bound on the transition pressure at low temperature and a lower bound at high temperature, resulting in a lower bound on the value of dP_t/dT.

Based on the foregoing discussion, the following conclusions can be drawn:

(1) Although the quartz–coesite transformation appears to be experimentally well determined, the thermochemical data for coesite (Holm *et al.*, 1967) may be seriously in error, and a redetermination is highly desirable.

(2) The discrepancy in the slope for the coesite–stishovite transformation may indicate errors in the thermochemical data or the experimental determination of the phase boundary.

(3) The quartz–coesite transformation is sufficiently well determined to provide a good basis for pressure calibration at high temperature. The coesite–stishovite transformation cannot provide a reliable means of pressure calibration without further study. It should also be noted that the NaCl pressure scale has not been verified at elevated temperature. Hence, any proposed phase boundary based on the NaCl scale must be viewed as tentative.

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