coesite, respectively) and ΔH_0 and ΔS_0 are defined similarly, (14) gives

$$\Delta G_0 = \Delta H_0 - T_0 \Delta S_0 \qquad (18)$$

The values of ΔH_0 and ΔS_0 can be found from the results of *Holm et al.* [1967]. At 298°K $\Delta H_0 = 10.58$ kcal/mole $= 7.36 \times 10^9$ ergs/g and $\Delta S_0 = -3.01$ cal/mole°K $= -2.09 \times 10^8$ ergs/g°K.

Now from (16), using (18), we obtain

$$G^s(V_0{}^s, T) - G^c(V_0{}^c, T) = P_0(T)(V_0{}^s - V_0{}^c)$$
$$+ U^s(V_0{}^s, T) - U^c(V_0{}^c, T)$$
$$- T[S^s(V_0{}^s, T) - S^c(V_0{}^c, T)] \qquad (19)$$

To evaluate this expression we need U and S as functions of T for both stishovite and coesite. These functions are known accurately [*Holm et al.*, 1967] only up to 350°K. However, the difference $U^s(V_0{}^s, T) - U^c(V_0{}^c, T)$ and the analogous difference for S can be approximated as being constant above about 350°K for the following reasons. The specific heats C_p of stishovite and coesite given by *Holm et al.* [1967] converge toward each other above about 150°K. Also, at 300°K, C_p differs from C_v by about 0.6% for stishovite and by about 0.1% for coesite. Thus the C_v will also converge at higher temperatures. Because U and S are integrals of C_v, $U^s - U^c$ will approach a constant value at higher temperatures, as will $S^s - S^c$. Thus the differences in U and S in (19) can be replaced by their values at 298°K. When it is noted, finally, that $\Delta U_0 \approx \Delta H_0$, (19) becomes

$$G^s(V_0{}^s, T) - G^c(V_0{}^c, T)$$
$$= P_0(V_0{}^s - V_0{}^c) + \Delta H_0 - T\Delta S_0 \qquad (20)$$

The integral in (17) is more easily evaluated here by noting that

$$\int_{P_0}^{P} V \, dP' = \int_{V}^{V_0} P(V', T) \, dV'$$
$$+ VP - V_0 P_0 \qquad (21)$$

Equations 17, 20, and 21 and equation 3 for an isotherm allow the Gibbs free energies of 'coesite' and stishovite to be compared.

The phase line resulting from these calculations is shown in Figure 8. The error bars represent variations due to the use of the alter-native equations of state given in the previous sections. The uncertainty due to the approximations used for $U^s - U^c$ and $S^s - S^c$ is difficult to estimate, but it should not be greater than a few per cent. Errors of 5% in $U^s - U^c$ and $S^s - S^c$ would cause errors of about 1 and 3%, respectively, in the calculated transition pressure at 10,000°K.

As can be seen in Figure 8, the calculated phase line deviates considerably from the line separating the 'coesite' and stishovite Hugoniot fields. The difference is about a factor of 2 in temperature, which would seem to be well outside the range of uncertainties of the calculations. If this result is correct, the phase obtained in the shock-wave experiments is outside the coesite stability field. It would be surprising if this phase were coesite, since it would be expected that the high temperatures involved would promote the transition to stishovite.

An alternative interpretation of the data is suggested by re-examining Figure 8, in which the lower-pressure quartz-liquid-gas region of the phase diagram is also shown [*Levin et al.*, 1969; *JANAF Tables*, 1965]. The 'coesite'-stishovite Hugoniot boundary intersects the calculated phase line at about 2500°K, which is comparable to the melting temperature of quartz. Is it possible that the 'coesite' is the liquid phase?

The plausibility of this hypothesis can be tested by using the Clausius-Clapeyron relation for the slope of a phase line:

$$dP/dT = \Delta S / \Delta V \qquad (22)$$

where Δ denotes the change through the phase transition. Let us apply this at the hypothetical coesite-stishovite-liquid triple point at 125 kb and 2500°K. We know that the volumes of the coesite and the liquid must be very similar at this pressure because of the agreement between the coesite static-compression data and the 'coesite' Hugoniot data (Figure 6). If the difference in their volumes is zero, (22) shows that the coesite-liquid phase line is horizontal in Figure 8 (also shown by line 1 in Figure 9, which illustrates the relevant region of the phase diagram in more detail). If the difference in volumes is not zero, the slope of the phase line can be estimated as follows. The coesite-stishovite phase line is still fairly well determined below the triple point. The coesite-

stishovite volume difference is about 0.09 cm³/g. The entropy difference is, then, from either the slope of the phase line (0.02 kb/°K) and (22) or the approximation made in the previous section, about 2×10^6 ergs/g°K. When the liquid-stishovite volume difference is assumed to be also about 0.09 cm³/g, the slope of the liquid-stishovite phase line (0.06 kb/°K) and (22) give the liquid-stishovite entropy difference as about 5×10^6 ergs/g°K. When these results are combined, the liquid-coesite entropy difference is about 3×10^6 ergs/g°K. From Figure 6 we can estimate a reasonable maximum volume difference between the coesite and the liquid to be about 0.01 cm³/g. Equation 22 then gives a slope of about 0.3 kb/°K (line 2 in Figure 9). Line 3, which has the same slope as the stishovite-liquid phase line, would imply that coesite has a volume similar to that of stishovite, which is clearly unreasonable.

Lines 1 and 2 both extrapolate to the range of melting temperatures of quartz. There is a difficulty, though, since a similar set of relationships would hold at the quartz-coesite-liquid triple point, and thus we would be led to predict a slope of the quartz-liquid phase line rather different from the one shown. However, we may observe that the liquid would have to vary continuously from a density of about 2.2 g/cm³ at zero pressure (the density of fused quartz) to about 3.1 g/cm³ at 100 kb. This variation would cause the phase lines to be concave downwards (Figure 9) in this range and

might allow these relationships to hold without contradiction.

The preceding discussion is intended as a plausibility argument. It must be considered a serious possibility that a coesitelike liquid phase was produced in the shock-wave experiments.

To return, finally, to the coesite-stishovite phase line below the hypothetical triple point, the calculated transition pressure at 300°K is 78 kb. This value is in reasonable agreement with that of 69 kb estimated by *Akimoto and Syono* [1969] from their experimental results. It may also be compared with their values of 85–95 kb calculated by using a rough estimate of the coesite compressibility.

The average slope of the phase line is about 0.023 kb/°K, which compares very well with the value of 0.024 kb/°K found by *Akimoto and Syono* [1969].

Note added in proof. An analysis by E. K. Graham (unpublished manuscript, 1972) of some of the stishovite Hugoniot data analyzed here yielded the values $K_0 = 3.35$ Mb, $K_0' = 5.5$, and $\gamma_0 = 1.64$. A high value of K_0' was also obtained by *Ahrens et al.* [1970] ($K_0 = 3.0$, $K_0' = 6.9$, $\gamma_0 = 1.58$). Although some differences between these analyses and the present analysis are due to the different equations used, a critical difference is that cases 2 and 3 of the present analysis rely on the Hugoniot data of the more porous samples to constrain γ, whereas those in the other analyses rely on *Weaver*'s [1971] coefficient of thermal expansion. The effect of these different approaches can be seen by comparing case 1 with cases 2 and 3 above. Case 1 also relies on Weaver's data. The preference for case 2 rests on the critical assumption that the Grüneisen parameter does not vary greatly with temperature at very high temperatures.
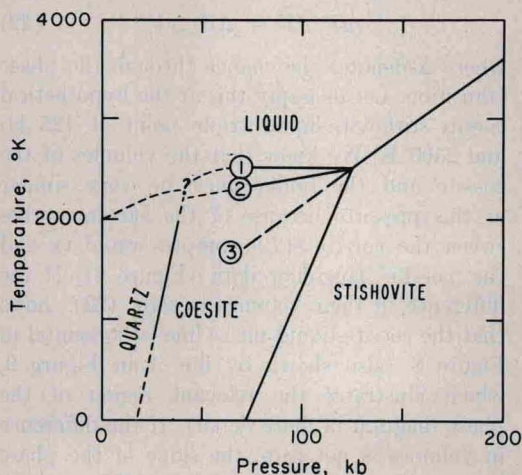
Fig. 9. Hypothetical silica phase diagram. Lines 1, 2, and 3 correspond to different assumptions about the relative densities of the coesite and the liquid (see text).

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