

CALCULATIONS FOR SiO₂ GLASS

The refractive indices were calculated at 25° and 600°C for compression to 100 kb, for comparison with the measurements of *Cohen and Roy* [1961, 1965] and *Roy and Cohen* [1961], which were made along these two isotherms. The resulting n - P curves are shown in Figure 3 together with the measured data; additional measurements reported by *Cohen and Roy* [1961, Figure 2] at a few temperatures between their two isotherms are also plotted. The 25°C curve is based on the direct 0- to 100-kb volume compression measurements of *Bridgman* [1948], and the 600°C curve is based on the high-temperature quadratic parameters as described earlier, extrapolated above 10 kb by means of the Murnaghan equation. The quadratic equation gives essentially identical results. In both cases the high-pressure index is calculated from the index of the uncompressed glass, $n_0 = 1.458$ given by *Cohen and Roy*, by using equation 2 with $\beta = 1.37$. It should be noted that the SiO₂ glass compressibility decreases with increasing temperature, so that the 600°C curve falls below the 25°C curve, in contrast to the relationship in normal glasses. At the glass point, however, κ must increase markedly with temperature, and so there is a minimum compressibility at something like 800°–900°C and above 1200°C the curves will lie above the 25° curve in Figure 3.

Calculations were also made for the limiting equations (equations 3 and 4). An indication of the maximum range can be seen from the values at 50 kb, 600°C; $n_{LL} = 1.521$, $n_D = 1.502$, whereas $n = 1.508$ for $\beta = 1.37$ and is thus intermediate with a value proportional to the ratio of β to the maximum value $4\pi/3$.

The SiO₂ results show several marked features: (1) samples compressed at 500°–700°C plot generally in the range of the two isothermal curves; (2) samples compressed at 25°C have indices far lower than expected from the compressibility data; (3) samples compressed at intermediate temperatures have indices between the 25° and 600°C data and are considerably lower than the predicted values (which would lie between the 25° and 600°C isotherms).

The low-temperature data in Figure 3 are consistent with the observation of *Bridgman and Simon* [1953] that SiO₂ glass has a thresh-

old pressure or elastic limit that must be exceeded for permanent compression; the data of *Cohen and Roy* indicate this limit is about 20 kb at room temperature, and, as they noted, it disappears at temperatures of 500°C or higher. *Anderson* [1956] studied the compression of borosilicate glass in the range 4–7 kb, 100°–300°C, and showed that both reversible and irreversible volume changes, which he called densification and compaction, occur at these temperatures. SiO₂ glass showed no permanent compression at these pressures and temperatures. The data in Figure 3 are quite consistent with his results and indicate that at temperatures of 200°C and less SiO₂ glass is almost totally elastic at all pressures, so that even above the threshold pressure the permanent compression obtained is only a fraction of the actual volume change given by the compressibility. At 300°–400°C, the glass is partly elastic, so that at 40 kb the permanent compression is about half the total volume change corresponding to the compressibility. Both the elastic limit and the fraction of the deformation that is elastic or reversible decrease with increasing temperature and vanish at about 500°C. Accordingly, the discussion of the temperature-refractive index relationship is limited to temperatures above 500°C in the range in which the elasticity effects have vanished.

HIGH-TEMPERATURE SiO₂ DATA (500–700°C)

All data points in Figure 3 were picked off the plots of *Cohen and Roy* [1961] and *Roy and Cohen* [1961] and Figure 1 of *Cohen and Roy* [1965] as no tabulations have been published; the indicated precision is about ± 0.005 in the index and is estimated to be ± 10 kb in pressure [*Cohen and Roy*, 1965]. Some of the scatter in the index data is evidently due to their use of powdered glass samples with subsequent inhomogeneity. The large uncertainties in the data, coupled with the relatively close spacing of the two isotherms, makes it impossible to match the data to one or the other of the two isotherms, and, in fact, it appears that a scatter of points between the two isotherms should be expected because of variations in the quenching procedures. The quenching techniques used by *Cohen and Roy* [1961] are not described in their paper, but *Mackenzie* [1963, footnote 5] refers to a preprint of *Cohen and*

amples quenched from a series of will, in a P - V diagram, plot on a origin corresponding to V_0 (25°, a slope proportional to the constant 25°. The pressure effect is predicted in when the glass cools through; below this temperature the longer an equilibrium phase, but to configurational equilibrium is volume effects can be discussed in usual parameters. However, small variations of α and κ rate should occur, so that the cannot be expected to be as exact equilibrium phase.

Noting that the fit observed requires that not only the compressibility also its pressure dependence, be correct. In fact, one sees that the curves fit the points with very deviations, the slope in the diopside quite correct, especially at high. With the same assumptions used the calculation could be reversed to the compressibility parameters from indices. Carrying this through a plot of $[f(n) - f(n_0)] / f(n)P$ where $f(n)$ is the Lorentz-Lorenz index $(n^2 - 1)/(n^2 + 2)$, is linear except deviation of the point at 10.8 kb. The point and slope of the plot give effective $10^6 a = 1.08$, $10^{12} b = 7.4$, and a curve with a mean deviation of only 0.1, which indicates an effective compressibility very similar to that of the crystal somewhat higher initial value and pressure dependence. Both these differences in the direction expected, but, more; the improved fit shows that the indices are very consistent with the pressure dependence shown by normal glasses, i.e. compressibility decreasing with pressure.²

ded in press. F. R. Boyd has pointed out that in his experiments the quench is nearly isobaric; the actual load pressure at the point is somewhat lower than the pressure because of the rapid thermal expansion. He suggests that a fluid liquid, such as water at 1700°C, might record this pressure which would also account for the slight deviations of the 40- to 50-kb diopside points in