brought to pressure and temperature through both the solid and the liquid fields, and diopside samples were brought up to temperature at pressure through the crystalline field. All samples were temperature-quenched at pressures; with their apparatus, which has water cooling, the furnace temperature can be dropped to less than 500°C within 5 seconds [Boyd and England, 1960]. The glasses are quenched under pressure from above the liquidus (temperatures of 1100°–1850°C in their experiments), and the uniform relationships obtained from glasses of different history show that a highly reproducible effect is being observed.

If we assume that the agreement of calculated and measured effects shown in Figure 2 is not a coincidence, we must then ask why the quenched glasses are matched by the curve calculated for 25°C. The straightforward answer is that the total pressure effect is 'locked' into the glass, but the thermal effect is relieved during temperature release at load pressure. We know from equation 1 that $(\partial\alpha/\partial P) = -(\partial\kappa/\partial T)$, so that the volume change in taking an equilibrium phase from temperature and pressure T, P, to 25°, P, is the same as that along the path (T, P), $(T, 1 \text{ bar})$, $(25°, 1 \text{ bar})$, $(25°, P)$. This means that, if the pressure effect at T, P, is locked in, the pressure dependence of α is

such that samples quenched from a series of T, P, states will, in a P-V diagram, plot on a curve with an origin corresponding to V_o (25°, 1 bar) and a slope proportional to the compressibility at 25°. The pressure effect is presumably locked in when the glass cools through the glass point; below this temperature the glass is no longer an equilibrium phase, but the approach to configurational equilibrium is so slow that volume effects can be discussed in terms of the usual parameters. However, small deviations due to slight variations of α and κ with cooling rate should occur, so that the relationship cannot be expected to be as exact as for an equilibrium phase.

It is worth noting that the fit observed in Figure 2 requires that not only the compressibility, but also its pressure dependence, be approximately correct. In fact, one sees that, although the curves fit the points with very small mean deviations, the slope in the diopside curve is not quite correct, especially at high pressures. With the same assumptions used previously, the calculation could be reversed to calculate the compressibility parameters from the observed indices. Carrying this through shows that a plot of $[f(n) - f(n_o)] / f(n)P$ versus P, where $f(n)$ is the Lorentz-Lorenz index function $(n^2 - 1)/(n^2 + 2)$, is linear except for a large deviation of the point at 10.8 kb. The intercept and slope of the plot give effective values of $10^6 a = 1.08$, $10^{12} b = 7.4$, and a calculated curve with a mean deviation of only 0.0005 in n, which indicates an effective compressibility very similar to that of the crystal but with a somewhat higher initial value and a greater pressure dependence. Both these differences are in the direction expected, but, more importantly, the improved fit shows that the observed indices are very consistent with the type of pressure dependence shown by normal substances, i.e. compressibility decreasing with increasing pressure.[2]

Fig. 3. Refractive indices of SiO₂ glass compressed at the indicated temperatures and pressures.

---

[2] Note added in press. F. R. Boyd has pointed out to me that in his experiments the quench is not absolutely isobaric; the actual load pressure at the glass point is somewhat lower than the nominal run pressure because of the rapid thermal contraction. He suggests that a fluid liquid, such as diopside at 1700°C, might record this pressure change, which would also account for the slight deviations o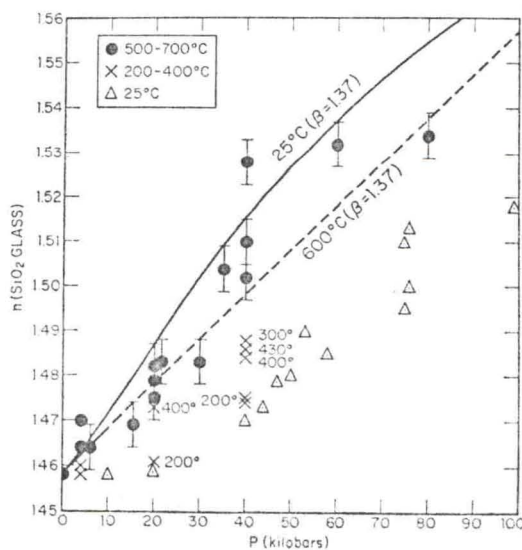f the 40- to 50-kb diopside points in Figure 2.