tional anion disorder for the production of calcite polymorphs. He sites experimental evidence to show that such disorder results in c-axis expansion, not contraction, and hence is doubtful that anion rotation can be the mechanism of transformation of calcite I to calcite II.

Recalling that Schock and Katz found their pressure induced v_1 fundamental irreversible, a plot of carbonate v_1 absorbance vs. central pressure of the cell was provided by them to show that the effect of a calcite I—II or II—III transition is inconsistent with the above interpreted reversibility of this transformation. In that the v_1 mode in our study is not preserved when pressure is released, we cannot comment on the validity of this conclusion but only suggest the remote possibility that the irreversible aragonite polymorph may have been produced even though their X-ray data show no evidence of aragonite. In this study, and that of Weir, *et al.*, a shift in the v_1 band to a higher wavenumber as pressure is increased is observed suggesting a change in the orientation or center of gravity of the carbonate ion. Weir, *et al.*, go on to interpret this shift as a result of a decrease in the C—O bond distance in the carbonate ion under pressure. This is not to say that the C—O bond is easily compressed but only that the calculated parameter of compressibility compares favorably with that of Bridgman. $[(-1/R)(\Delta R/\Delta P)]$ $= 2.8 \times 10^{-7}$ atm.; calculated by use of the internuclear potential function (Lippincott and Schroeder, 1956). The increase of the 740 cm^{-1} band with pressure, previously interpreted as a repulsion between oxygen atoms in the plane of the carbonate ion, further confirms a change in the ion orientation. The change in the v_4 (740 cm^{-1}) mode, however, does not appear to be due entirely to repulsion of oxygen atoms in the plane of the carbonate ion. If the 740 cm^{-1} band is due entirely to repulsion of the oxygen atoms resulting from a decrease of the carbon-oxygen bond distance, the v_1 mode (symmetric stretching) should also shift to a much larger wavenumber. This is not observed to be the case. At a pressure of 61 kbar the v_1 mode has shifted from 1087 cm^{-1} to 1105 cm^{-1}, whereas the v_4 mode has shifted from 715 cm^{-1} to 747 cm^{-1}. The v_4 mode (an in-plane bend) may interact with the calcium by intraionic bonding with the oxygen of the carbonate, resulting in a change of only the in-plane bending constant. The v_1 mode will be essentially unaffected by this bond. It is, therefore, necessary to consider the position of the calcium atoms in the crystal lattice and their effect on the carbonate ion. Investigation of these lattice modes under pressure in the region below 400 cm^{-1} will be attempted later. At the present, the mid-infrared data suggests ample evidence of a change in the ion orientation for our purposes.

The above observations have shown themselves to be reversible below

approximately 20 kbar of pressure. On the basis of the infrared evidence an irreversible aragonite structure or C_s symmetry is not produced until pressures above 20 kbar are attained. It is our belief that pressure induced spectral changes below this pressure are calcite I→II or II→III transitions. Interpretation of the spectral data suggests anion-disorder and the reversibility of this transition is consistent with the findings of Bridgman and Jamieson.

As the pressure exerted is increased above 20 kbar (Fig. 1), the 690 cm^{-1} band becomes stable and does not increase in intensity or shift. The v_1 mode shifts to a higher wavenumber as expected when pressure is increased. The striking feature produced by pressures above 25 kbar is the change resulting in the 740 cm^{-1} band relative to the 715 cm^{-1} fundamental. The 740 cm^{-1} band increases in intensity, indicative of a higher concentration of the polymorph producing this band, and shifts to a higher wavenumber with increasing pressure. The 715 cm^{-1} fundamental decreases with increasing pressure; at the end point of our experiment, 60 kbar, it is the weakest band in the spectrum (Fig. 1).

Recalling the stability of 690 cm^{-1} band, we have interpreted this band to be indicative of a constant volume of aragonite since it is unique to only the aragonite structure. The increasing ratio of the 740 cm^{-1} to 690 cm^{-1} band has been interpreted as being indicative of an increasingly higher concentration of the polymorph that produces the 740 cm^{-1} band. This unknown polymorph has been observed by its infrared spectrum to be reversible to the aragonite structure upon release of the pressure.

This is not to imply that the new polymorph is derived from aragonite although this is a possibility. It seems more likely that all the calcite has not been converted to aragonite, that which has not is converted to an unstable polymorph. The detection of calcite in aragonite would be difficult due to overlap of concurrent bands. The above results perhaps can be more easily visualized by the graph in Figure 2.

The observed forward reflection (transmission) powdered diffraction pattern of the compressed calcium carbonate is consistent with the high pressure infrared data. A "vateritelike" structure is the principal polymorph at 61 kbar; calcite and aragonite are also present but in lesser quantities. Table 2 lists the observed d Å of the pattern for the high pressure polymorph, giving their assignments and appropriate ASTM powder data file value correlation for calcite, aragonite and vaterite.

Conclusion

It is obvious that the frequency trends observed in this study are attributable to changes in the carbonate ion; specifically, arising from