# General Disclaimer

## One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

# PYROXENES AND OLIVINES:

## STRUCTURAL IMPLICATIONS OF SHOCK-WAVE DATA FOR HIGH PRESSURE PHASES[*]

Raymond Jeanloz and Thomas J. Ahrens

Seismological Laboratory, Division of Geological and Planetary Sciences

California Institute of Technology

Pasadena, CA    91125

## ABSTRACT

A reexamination of Hugoniot equation of state data and three new release adiabat points indicates that results for enstatite-bronzite composition pyroxene are compatible with its transforming to a perovskite phase at high pressure (for $En_{90}$: $\rho_0 = 4.20$ gm/cm$^3$, $K_0 \sim 260 \pm 35$ GPa, $K'_0 \sim 3.5 \pm .65$). The release adiabat data as well as results from porous samples imply that the shock-wave data do not define an equilibrium, high pressure phase Hugoniot below about 100 GPa. These also suggest a further transformation to a phase (or assemblage) with density about 5% (or more) greater than that of orthorhombic perovskite. The data would allow such a transformation to occur at pressures as low as $\sim 60$ GPa under shock, representing an upper bound for the equilibrium transition pressure.

Hugoniot data on magnesian olivines also appear to represent states of thermodynamic disequilibrium or a mixed phase region below about 80–100 GPa. However, Hugoniot points for Mg-pyroxene and Mg-olivine coincide at pressures above 70 GPa suggesting that these minerals transform to high pressure phases or phase assemblages of comparable density. Since MgO (presumably as periclase or in a closely related structure) attains relatively low densities at these pressures, the shock-wave data are in strong disagreement with the disproportionation of $Mg_2SiO_4$ to a $MgSiO_3$ (perovskite) + MgO assemblage above 80–100 GPa. Conversely, the shock-wave data do not preclude a transformation of the type, $Mg_2Si_2O_6 \rightarrow Mg_2SiO_4$ ("post-perovskite" phase) + $SiO_2$ (rutile or fluorite structure). Again, these results would imply polymorphism to very dense, "post-perovskite" phases. Based on the arguments made for pyroxene, this could occur at pressures as low as 60 GPa under equilibrium conditions.

We note that the combined results of high-pressure experiments allow Mg-pyroxene compositions to be as likely candidates for the lower mantle as olivine.

## INTRODUCTION

Upon recognition that the features associated with plate tectonic processes on the earth (subduction zones, ridges and plumes) are either minor surficial expressions, or alternatively reflect an integral sampling of the mantle convective flow field, and with the perspectives attained from the last decade of terrestrial planetary exploration, experimental high-pressure geophysics has focussed increasingly on studying candidate materials of the earth's lower mantle and core.

Current ideas [e.g., Schubert and Anderson, 1975] suggest that active convection in the earth takes place to depths of at least ∼750 km. However, it is important to discern whether the upper mantle above ∼350 km depth, and possibly the phase transition region extending to depths of at least ∼670 km, represents a differentiate of the lower mantle and is thus atypical of the silicate zone of the earth as proposed by D. L. Anderson et al. [1972] and D. L. Anderson [1976], in contradistinction to the views of Ringwood [1975] which have emphasized the essential homogeneity of the mantle.

Clear-cut data specifying the composition of the upper mantle stems largely from inclusions in kimberlites [e.g., Boyd, 1973] and nodules from volcanic rocks of deep-seated origin [MacGregor, 1975 and Basu, 1975, for example] which demonstrate the upper mantle to be largely garnet lherzolite with minor amounts of eclogite. This composition is not unlike the "pyrolite" model originally proposed by Clark and Ringwood [1964] which, by means of variations in temperature, pressure, and degree of partial melting, accounts for the genesis of a large class of effusive and plutonic rocks which penetrate the crust [Green, 1972].

The lower mantle, extending from depths of 670 to 2900 km, represents 49% of the mass of the earth. What can be learned of its mineralogy and thermal state must, at present, be inferred from comparison of shock-wave

and seismological data [Al'tschuler and Sharpidzhanov, 1971a, b; Anderson et al., 1972; and Anderson 1976], and by extrapolation of results based on quench products from static high pressure, petrological experimentation [e.g. Ringwood, 1975; Akimoto et al., 1976; Liu, 1975a, b, 1976] using largely ultrasonic and static compression equations of state.

Not unrelated to the questions of the properties of pyroxenes and olivines at high pressures and hence, of mantle compositions, has been an increasing awareness among earth scientists, that the composition, structure, and thermal history of the earth must ultimately be related to the composition of the sun, the moon, meteorites and other terrestrial planets, and the processes of planetary accretion [e.g. Lewis, 1972; Ringwood, 1975; Hanks and Anderson, 1969].

In the present study the nature of the shock-induced, high-pressure phases of olivine and pyroxene rocks is examined in the light of data for the densities of a new class of perovskite-related silicate structures synthesized by Liu [1975a, b, and 1976], and some new Hugoniot and release adiabat data for bronzite. Previous data for olivine-rich samples in the range Fo100 to Fo85 and for enstatitic samples (over a similar range of Fe contents) are reported by Trunin et al. [1965] and McQueen et al. [1967]. Trunin et al. [1965] and recently Simakov and Trunin [1973] have reported single datum points for four different compositons, extending our knowledge of Hugoniot states for ferromagnesian silicates to pressures in excess of 240 GPa.

## EXPERIMENTAL METHODS

Discs (1 cm-diameter) of Bamle bronzite $(Mg_{.86}, Fe_{.14})SiO_3$ were cored from the same aliquot previously studied to shock pressures of 48 GPa [Ahrens and Gaffney, 1971] and machined to thickness tolerances of $\sim\pm0.05$ mm. The density of each disc was determined at least twice by weighing in air and in reagent grade toluene (temperature corrections from Berman, 1939). The samples were mounted on 0.5 mm thick Cu or Ta driver plates and impacted by flyer-plate bearing projectiles at speeds ranging from 5.4 to 6.1 km/sec with a light-gas apparatus qualitatively similar to that described by Jones et al. [1966]. Pure (commercial-grade) Cu and Ta flyer plates, 2.5 mm thick, with a minimum diameter of 17 mm (Fig. 1) are hot-press welded into lexan projectile blanks using techniques developed by A. Mitchell (private communication, Lawrence Livermore Laboratory). After molding and stress relieving, a polyethylene, gas sealing rear portion of the projectile was press fit onto the 6 mm long lexan flyer plate (front) portion of the projectile. The final projectile diameter was machined so as to provide a $\sim0.03$ mm interference fit with the light-gas gun launch tube. The resulting projectiles had masses of 14 and 20 gm for Cu and Ta flyer plates, respectively. The light-gas gun used to accelerate these projectiles employs a 20 m-long, 16 cm diameter pump tube in which a $\sim20$ Kg high-density polyethylene piston is used to compress the propelling gas, $H_2$, initially at a pressure of 0.1 MPa. The polyethylene piston achieves speeds of $\sim0.4$ km/sec using approximately 3 Kg of double-based propellant. The projectile is launched upon bursting of a diaphram (at a gas pressure of $\sim0.07$ GPa) at the breech of the 25 mm diameter - 7 mm long launch tube. The total flight of the projectile from the muzzle of the launch tube to the target is $\sim500$ mm and occurs in a vacuum of 10 to 30 mtorr. Projectile velocities are measured using the flash X-ray method

of Jones et al. [1966], except that interruption of a continuous X-ray beam
[Long and Mitchell, 1972] is used to trigger the first flash X-ray unit
(∿15 ns exposure), and the breakage of a 0.05 mm diameter copper wire inter-
cepting the outer edge of the projectile is used to trigger the second
flash X-ray unit. The center lines of the two flash X-ray units are ∿350 mm
apart and the time interval between X-ray flashes is measured to within an
uncertainty of ±0.01 µsec. Since triggering in our initial experiments was
not reliable, we have had to rely on the redundancy provided by measuring
the electronic delays of both flash X-ray units, and the time interval between
the second X-ray flash and the closure of the redundant pin switch(es)
mounted on the sample assembly (Fig. 1) to infer impact velocity. The ∿3°
projectile tilt observed in Fig. 1, is highly reproducible and the sample
assembly was thus pre-oriented to achieve nearly normal impact.

As in the experiments of Ahrens et al. [1971] an electronically triggered,
image-converter streak camera was used to record shock transit-time through
the sample. However, in the present experiments the onset of illumination
on shock arrival at the mirrors (presumably arising from the high temperatures
behind the shock in the glass) was used to record shock arrivals with the
streak camera, and the arrival of the shock at the mirror free-surface was
observed to result in the immediate loss of illumination (Fig. 2). We infer
this effect is caused by the disintegration of the specular mirror surface,
probably upon incongruent vaporization of the glass, and the accompanying
sudden adiabatic expansion of the vaporized species. In the present experi-
ments the streak camera was writing at a speed of 25 mm/µsec for a duration
of ∿2 µsec on 20 X 22.5 cm (4 X 5 inch) Tri-X film. Developing procedures
were used to force the film to a sensitivity of ASA 3000. Time calibration
was obtained using a Pockel-cell modulated Ar-ion laser beam modulated at 20

Mhz, thus providing time marks at 50 μsec intervals. The writing rate at any point on the streak camera trace was measurable to within ±0.25%, and a practical time resolution of ∿2 nsec was achieved.

Hugoniot states are determined using the impedance match method Rice et al. [1958] and release adiabat data employ the buffer technique described by Ahrens et al. [1969]. The equations of state for Ta and Cu employed in the impedance match solutions are those given by McQueen et al. [1970].

## EXPERIMENTAL RESULTS FOR GLASS AND BAMLE BRONZITE

The unexpected self-illumination and prompt light decay upon passage of strong shocks through the soda-lime glass mirrors (microscope slide quality, plate glass) provided consistent, and we believe reliable measurements of shock-wave velocities in this material. The resulting data are given in Table 1 and plotted in Figures 3 and 4. The shock wave velocity ($U_s$) - particle velocity ($U_p$) relation in Fig. 3 is concordant with data reported by Dremin and Adadurov [1964] to pressures of 41 GPa for a glass of similar zero-pressure density (2.48 gm/cm$^3$) but of slightly different composition. The linear $U_s$-$U_p$ relation indicated in Fig. 3 fits the present four data points, and Dremin and Adadurov's data points at 33 and 41 GPa with a co-efficient of correlation $r^2 = 0.997$. This fit was used to obtain the release adiabat points for the Bamle bronzite (Figure 5, Table 2).

Qualitatively, the behavior of Na-Ca glass is observed to be similar to that first reported by Wackerle [1962] for fused quartz. It appears that above ∼15 GPa, the $Si^{+4}$ ion begins to transform from tetrahedral to octahedral coordinations with the $O^{2-}$ ion, as in the case of the quartz to stishovite transition [McQueen et al., 1963]. This, and possible coordination increases of the $Na^+$ an and $Ca^{++}$ ions, account for the imcompressible behavior indicated above 50 GPa. The zero-pressure ($P_0$) density shown in Fig. 4 is calculated using our microprobe analyses, standard oxide molar volumes [Robie and Waldbaum, 1962], and assuming a stishovite molar volume of 14.014 cm$^3$ for $SiO_2$.

Although the uncertainties in the measurement of projectile and shock velocity can be obtained from scatter of redundant projectile time-interval measurements and uncertainties in discerning shock arrival-times on the streak records, the calculation of uncertainties in the pressure-density plane shown in Figures 4 and 5 are less straightforward. The non-orthoganality

of the uncertainty brackets shown in both figures for the Hugoniot data arise from the fact that the particle velocity, and hence pressure and density, are not independently related to uncertainties in projectile and shock velocity via the impedance match solution. The uncertainty arising from both the density and pressure are calculated from the uncertainty in projectile velocity holding the shock velocity fixed (at its average value) and vice versa. The uncertainty in the three release points take into account only the uncertainty in shock velocity through the buffer (1 mm-thick glass).

## DISCUSSION

Shock-wave data for magnesian pyroxenes are summarized in Figure 5, including results for porous (synthetic aggregate) samples, non-porous samples, and our new data on Bamle bronzite (cf. Table 2). At pressures below about 70-100 GPa it is clear that the porous Hugoniot data bear an anomalous relation with respect to the non-porous data since the former should lie on "hot compression" curves, systematically displaced to lower densities (at a given pressure) from the principal Hugoniot presumably defined by non-porous data. The energy associated with irreversible compaction of porosity represents a thermal pressure as a function of initial density, via Grüneisen's $\gamma$ (V,T), which defines this displacement. For this reason, the porous data have, in general, been very scantily discussed, considered uninterpretable, or outright dismissed as wrong [McQueen, Marsh, and Fritz, 1967; McQueen, 1968; Ahrens, Anderson, and Ringwood, 1969; Davies and Gaffney, 1973; Simakov and Trunin, 1973].

The relatively high density attained by the porous materials on shocking can, nevertheless, be explained as a kinetic effect [c.f. McQueen et al., 1967, and 1970]. Assuming that pyroxene transforms to a dense phase or assemblage above a given pressure, this transformation, even once initiated under shock, may not have time to go to completion without substantial overdriving. Because porous samples become much hotter on shocking, their rate of transformation is expected to be significantly enhanced, thus yielding a larger proportion of high pressure phase material for a given pressure compared with non-porous samples. Assuming this model applies, it is easy to explain the distribution of Hugoniot data in the figure.

The pressure-release points shown in Figure 5 provide independent support for such a model. Since the release path is adiabatic (isentropic to within

The approximation of reversibility) while entropy increases monotonically up a material's Hugoniot, the P-V slope of the release path should be no steeper than the Hugoniot slope at a given pressure [see Duvall and Fowles, 1966, for example]. Because the measured release adiabat points lie below the Hugoniot data, this indicates that a mixed phase region extends to pressures around 70-100 GPa with transformation to a high density assemblage complete at pressures no lower than these. This high pressure assemblage must have a metastable Hugoniot with a P-V slope at least as great as the release paths, and thus supports the hypothesis of an extended mixed phase (or disequilibrium) region probably associated with the rate of phase transformations under shock.

At pressures above about 100 GPa, the non-porous samples achieve densities that are generally (and consistently) higher than the porous points. So we believe that the shock-wave data begin to define an equilibrium, high-pressure assemblage Hugoniot at these pressures, below which one or more phase transformations result in a wide mixed-phase region.

Similarly, Hugoniot data for magnesian olivines are summarized in Figure 6. These show the same anomalous relations between porous and non-porous samples, implying transformation to a high density phase or assemblage subject to kinetic effects (though release adiabat data for such compositions are not yet available). This conclusion fits in with the discussion of Ahrens and Petersen [1969].

Aside from these results with porous data and steep measured release paths [c.f. Ahrens et al., 1969; Grady, 1975 and this volume, as well], a comparison of shock-recovery and static high-pressure experiments [Ahrens and Graham, 1972; Liu, 1974, 1975c; Schneider and Hornemann, 1976] also indicate that overdriving beyond equilibrium transition pressures is commonly needed in silicates to achieve a given phase transformation under shock, clearly implying control by kinetics of nucleation and growth of high pressure phases [but note Podurets and Trunin, 1974]. Thus, porous samples may well

indicate the presence and nature of high pressure phases (or assemblages) more readily than non-porous samples under shock. Also, high pressure phase Hugoniots will tend to be significantly steeper (and therefore centered at higher $P_0$ densities) than would be apparent from the distribution of the data.

Zero-pressure densities for high-pressure phases interpreted from pyroxene and olivine shock-wave data by several workers are summarized in Figure 7. The tendancy has been to assign higher densities (for a given composition) to olivine ($A_2BO_4$) than to pyroxene ($ABO_3$) stoichiometries. One problem is apparent near the magnesian end, however, in that interpreted densities seem to actually decrease with increasing Fe-content. Barring very complex phase relations, this is highly unlikely due to the enormous difference in the atomic masses of Fe and Mg. Rather, it appears that the density estimates for the magnesian endmembers have been biased upwards relative to the Fe-bearing compositons by the high densities implied by the porous data (which only exist for the endmembers, forsterite and enstatite). Based on the arguments developed above, it is not appropriate to directly compare the porous data with the data for (non-porous) Fe-bearing compositions.

Liu's recent [1975a, b, 1976; Liu and Ringwood, 1975] static high pressure experiments have confirmed the previously suspected occurrence and significance of perovskite-related structures in silicates [Reid and Ringwood, 1975, 1974, 1969; Ringwood and Major, 1971; Shimizu et al., 1970]. Distorted (non-cubic), perovskite-like structures have been quenched from diamond-anvil experiments on both magnesian olivines and pyroxenes. These structures, apparently of the orthorhombic rare-earth orthoferrite type [Marezio et al., 1970] will be loosely termed perovskites. Densities versus compositon for the perovskite phases and assemblages of pyroxene ($ABO_3$) and olivine ($ABO_3$ + AO) derived from Liu's [1975a, b] X-ray parameters are also shown in Figure 7. It is interesting to note that an olivine stoichiometry actually results in a lower

density perovskite assemblage than a pyroxene stoichiometry. This is a direct consequence of the low density of (Mg, Fe)O in the $ABO_3$ + AO assemblage. The densities of such (Mg, Fe)O recovered from high pressure lie directly between the densities of MgO (periclase) and FeO (stoichiometric wüstite) as can be seen in Figure 7. This is compatible with the shock-wave data on MgO which shows no evidence for phase transformations to pressures over 100 GPa [Carter et al., 1971; McQueen and Marsh, in Birch, 1966; McQueen, 1968].

In order to compare the static results with the shock wave data, theoretical metastable Hugoniots were constructed for perovskite of appropriate composition $(Mg_{.9}Fe_{.1}SiO_3)$ based on Birch-Murnaghan principal adiabats. This approach is philosophically and computationally similar to that of Davies & Gaffney [1973]. Necessary parameters are shown in Table 3 along with the values used here. Density and the energy of the pyroxene-perovskite transformation (at $P_0$) were derived from Liu's work via Figure 7 and by using $\Delta E_{tr} \leq (-P\Delta V + T\Delta S)_{tr}$. Since the last term is not known it is assumed to be negligibly small (i.e., $\frac{dP}{dT} = 0$ for the phase boundary). Because the experimental data upper bound the equilibrium pressure of transition, and most likely $T\Delta S \leq 0$, the resulting estimate for $\Delta E_{tr}$ is probably a strict upper bound (and rather high). Incidentally, though we discuss the direct transformation from pyroxene to perovskite structures under shock, this obviously represents a metastable phase boundary (based on our current knowledge from Liu's work). Intermediate structures may well be involved.

Estimates of the bulk modulus $K_0$ and $K_0' = \left(\frac{dK}{dP}\right)_{P=0}$ were based on their empirical correlation with density, with particular emphasis given to data for perovskite-structured compounds [Davies, 1976; Beattie and Samara, 1971]. The wide range in values given easily overlap estimates based on the various K-$\rho$ relations that have been proposed [O. L. Anderson, 1972; D. L. Anderson, 1969, 1967; D. L. Anderson and O. L. Anderson, 1970; O. L. Anderson et al., 1968].

Similarly, Grüneisen's (bulk or thermodynamic) $\gamma$ was estimated from typical values for various compounds, with a volume dependence that has been found to be not unreasonable for those cases where it has been studied. Temperature dependence was assumed to have a negligible effect and, again, rather wide bounds were given for reasonable values. Finally, a family of theoretical perovskite Hugoniots was constructed for the best estimate values given in Table 3 and by varying each of the parameters within the stated bounds. An envelope containing this family of curves along with the Hugoniot based on the best values are shown in Figure 5.

It is immediately clear that the shock-wave data is compatible with Mg-pyroxene transforming to a perovskite structure at pressures above approximately 80 GPa. This is contrary to the conclusions of Simakov and Trunin [1973]. In fact, by cnsidering the most porous data (which achieve high densities at relatively low pressures) and the arguments presented above, it seems that perovskite-like densities can be achieved by about 50 GPa. If anything, the left half of the envelope in Figure 5 agrees with the data as well as the best estimate, which could be consistent with an even lower pressure, for transformation to the perovskite structure. This, then, is an upper bound for the pressure of transformation based solely on Hugoniot data, yet still represents a significant overdriving compared to the static experiments [Liu, 1975b, 1976].

Compared with the theoretical Hugoniots, the release paths still appear to have very steep slopes, and the most porous data cross over to yet higher densities. These latter data may be erroneous [Simakov and Trunin, 1973], but assuming that they are not they suggest, along with the release adiabats, the possibility of a phase (or assemblage) with a zero-pressure density even higher than perovskite. Transformation to such a "post-perovskite" phase could occur at pressures as low as about 60 GPa, according to the shock data;

this would therefore be an upper limit for the equilibrium transition pressure. An initial density of 5% or so greater than for orthorhombic perovskite could be consistent with the data.

In similar fashion, a theoretical Hugoniot (Figure 6) was constructed for a perovskite assemblage corresponding to olivine stoichiometry ($MgSiO_3$ (perovskite) + MgO (periclase)) based on the best-estimate Hugoniot in Figure 5 and the rather well determined Hugoniot of MgO [Carter et al., 1971; McQueen, 1968; McQueen and Marsh, in Birch, 1966] shown in Figure 8. Because the left half of the envelope in Figure 5 appeared most consistent with the pyroxene points a corresponding band is shown in Figure 6.

In this case, perovskite-like densities are achieved in the 60-80 GPa range. Once more, the shock wave data are consistent with the static results which demonstrate olivine transferring to perovskite at high pressures (but again at pressures significantly lower than under shock). On the other hand, the olivine points are clearly shifted to higher densities than the perovskite-assemblage Hugoniot at pressures above about 70 GPa. Because the theoretical curve for the perovskite assemblage cannot be shifted without causing a sig-nificant deviation from the pyroxene points, the olivine data are in strong disagreement with a perovskite assemblage at high pressure.

If the olivine points did not deviate so systematically from the theoretical Hugoniot which is consistent with the pyroxene shock data, this divergence might well be ascribed to be within experimental error. However, the same discrepancy emerges from Figure 8, quite apart from any theoretical curves. The point here is that above about 70 GPa, the olivine and pyroxene data overlap, whereas a perovskite model would predict olivine densities to be lower than pyroxene densities (i.e., shifted towards the MgO Hugoniot) as was mentioned above and can be inferred from Figure 7. Granted that we have discussed kinetic effects and a mixed phase region to the 100 GPa range, but

the overlap continues to much higher pressures.  Furthermore, the nature of

the perovskite-forming transformations would suggest that pyroxene (which

involves no disproportionation) would form perovskite at least as readily as

olivine, whereas in the high-pressure data of Figure 8 one must either con-

sider the olivine too dense or the pyroxene not dense enough to agree with

a self-consistent perovskite model.

## CONCLUSIONS

After reviewing experimental techniques, we presented new Hugoniot data for Bamle bronzite including simultaneously measured release paths, based on the mirror-buffer technique. Calculation of Hugoniot states for the mirror glass provides a satisfactory internal check, with the soda-lime glass behaving in a fashion similar to fused quartz under shock.

Reexamining available shock data for magnesian pyroxenes and olivines leads to the conclusion that they define a mixed phase (or disequilibrium) region to about the 100 GPa range, related to the kinetics of phase transformation in these silicates. By recognizing this point, certain discrepancies in previous interpretations of shock data can be explained. A set of theoretical Hugoniots for pyroxene and olivine stoichiometry, perovskite-bearing assemblages was constructed based on their properties deduced from high-pressure work, showing that the shock data is compatible with transformations to perovskites in the 45-70 GPa region (decidedly above the equilibrium pressure of transformation).

A perovskite model implies different densities for pyroxene and olivine stoichiometries, however. We note that considering an extremely simplistic assemblage for the lower mantle, consisting of high-pressure phases of only olivine and pyroxene, varying the proportions of these components results in a significant variation in the overall density of the assemblage. In other words, any compelling evidence for density variations within the lower mantle (based, say, on seismological data) can be readily explained without resorting, for example, to variations in Mg:Fe ratios. This degree of freedom is likely to exist whatever the pertinent, multi-phase assemblage may be for the lower mantle. In fact, we consider our two-phase model simplistic if for no other reason than that we have ignored (for lack of data) the effects on phase relations of other likely components such as Al or Ca.

In addition, the high-pressure shock data suggest the presence of a yet higher density phase (or assemblage) than perovskite. In particular, the results on olivine diverge from predicted estimates and from densities consistent with pyroxene Hugoniot points. Taken together, the data do not preclude transformations involving a "post-perovskite" phase of $Mg_2SiO_4$ at pressures above 80-100 GPa, and including a reaction of the type: $Mg_2Si_2O_6 \rightarrow Mg_2SiO_4$ ("post-perovskite" phase) + $SiO_2$ (rutile, $\alpha$-$PbO_2$, or fluorite structure: c.f., German et al., 1974; Jamieson, this volume).

We reiterate that the static high-pressure results (and thus our analysis) involve an orthorhombic (i.e., non-ideal) modification of perovskite. Since this class of structures includes a wide variety of related modifications [succinctly summarized by Salje, 1976], it is quite possible that the higher-pressure phase suggested by the shock data in fact is a perovskite such as the ideal cubic form. Indeed, it is quite possible that the phase quenched from high pressure is a modification of the actual structure attained under pressure. Bearing in mind the well known difficulties of recovering these high-pressure polymorphs on quenching [e.g., Liu and Ringwood, 1975] and the important effects of environmental conditons on the perovskite modifications [see Sis et al., 1973, for example] it is not unlikely that they are involved in higher density assemblages than have yet been described. Recently discussed hexagonal forms, may be an example of this [compare Burbank and Evans, 1948]. However, there are other structure-types which could also be likely, some of which have only begun to be discussed as possible high-pressure polymorphs [e.g., Moore, 1976; also, Reid and Ringwood, 1970, and as reviewed by Ringwood, 1975].

Finally, the shock data indicate very similar properties for olivine and pyroxene at high pressures making them both equally likely candidates for the lower mantle.

## ACKNOWLEDGEMENTS

# REFERENCES

Ahrens, T. J., Shock-wave equations of state of minerals, in Mantle and Core in Planetary Physics, edited by L. Corso, Academic Press, New York, pp. 157-187, 1971.

Ahrens, T. J. and E. S. Gaffney, Dynamic compression of enstatite, J. Geophys. Res., 76, 5504-5513, 1971.

Ahrens, T. J. and E. K. Graham, Shock-induced phase change in iron-silicate garnet, Earth Planet. Sci. Letters, 14, 87-90, 1972.

Ahrens, T. J. and C. F. Petersen, Shock wave data and the study of the Earth, in The Application of Modern Physics to the Earth and Planetary Interiors, edited by S. K. Runcorn, Wiley-Interscience, New York, pp. 449-461, 1969.

Ahrens, T. J., D. L. Anderson, and A. E. Ringwood, Equations of state and crystal structures of high-pressure phases of shocked silicates and oxides, Rev. Geophys., 7, 667-707, 1969.

Ahrens, T. J., J. H. Lower and P. L. Lagus, Equation of state of forsterite, J. Geophys. Res., 76, 518-528, 1971.

Ahrens, T. J., C. F. Petersen, and J. T. Rosenberg, Shock compression of feldspars, J. Geophys. Res., 74, 2727-2746, 1969.

Akimoto, S., M. Akuaogi, K. Kawada, and O. Nishizawa, Mineralogic distribution of iron in the upper half of the Transition Zone in the Earth's mantle, in The Geophysics of the Pacific Ocean Basin and Its Margin, edited by G. H. Sutton, M. H. Manghnani, and R. Moberly, Am. Geophys. Union Monograph 19, pp. 399-405, 1976.

Al'tschuler, L. and I. Sharpidzhanov, Additive equation of state of silicates at high pressure, Izv. Earth Physics, 3, 11-21, 1971a.

Al'tschuler, L. and I. Sharpidzhanov, Distribution of iron in the Earth and its chemical differentiations, Izv. Earth Physics, 4, 3-16, 1971b.

Anderson, D. L., A seismic equation of state, Geophys. J. R. Astr. Soc., 13, 9-30, 1967.

Anderson, D. L., Bulk modulus-density systematics, J. Geophys. Res., 74, 3857-3864, 1969.

Anderson, D. L., Composition of the mantle and core, submitted to Annual Review of Earth and Planetary Sciences, 1976.

Anderson, D. L. and O. L. Anderson, The bulk modulus-volume relationship for oxides, J. Geophys. Res., 75, 3494-3500, 1970.

Anderson, D. L., C. Sammis, and T. Jordan, Composition of the mantle and core, in The Nature of the Solid Earth, edited by E. C. Robertson, McGraw-Hill Co., New York, pp. 41-66, 1972.

Anderson, O. L., Patterns in elastic constants of minerals important to geophysics, in The Nature of the Solid Earth, edited by E. C. Robertson, McGraw-Hill Co., New York, pp. 557-613, 1972.

Anderson, O. L., E. Schreiber, R. C. Liebermann, and N. Soga, Some elastic constant data on minerals relevant to geophysics, Rev. Geophys., 6, 491-524, 1968.

Basu, A. R., Hot-spots, mantle plumes and a model for the origin of ultramafic xenoliths in alkali basalts, Earth Planet. Sci. Letters, 28, 261-274, 1975.

Beattie, A. G. and G. A. Samara, Pressure dependence of the elastic constants of $SrTiO_3$, J. Appl. Phys., 42, 2376-2381, 1971.

Bénard, J., Sur les paramètres limites de la phase FeO, Acta Cryst., 7, 214, 1954.

Berman, H., A torsion microbalance for the determination of specific gravities of minerals, Am. Mineralogist, 24, 434-440, 1939.

Birch, F., Compressibility; elastic constants, in Handbook of Physical Constants, edited by S. P. Clark, Jr., Geol. Soc. Am. Mem. 97, pp. 97-173, 1966.

Boyd, F. R., A pyroxene geotherm, Geochim. Cosmochim. Acta, 37, 2533-2546, 1973.

Burbank, R. D. and H. T. Evans, Jr., The crystal structure of hexagonal barium titanate, Acta Cryst., 1, 330-336, 1948.

Carter, W. J., S. P. Marsh, J. N. Fritz, and R. G. McQueen, The equation of state of selected materials for high-pressure reference, in Accurate Characterization of the High-Pressure Environment, edited by E. C. Lloyd, Nat. Bur. Stds. Pub. 326, pp. 147-158, 1971.

Clark, S. P., Jr. and A. E. Ringwood, Density distribution and constitution of the mantle, Rev. Geophys., 2, 35-88, 1964.

Davies, G. F., The estimation of elastic properties from analogue compounds, Geophys. J. R. Astr. Soc., 44, 625-647, 1976.

Davies, G. F. and D. L. Anderson, Revised shock-wave equations of state for high-pressure phases of rocks and minerals, J. Geophys. Res., 76, 2617-2627, 1971.

Davies, G. F. and E. S. Gaffney, Identification of high-pressure phases of rocks and minerals from Hugoniot data, Geophys. J. R. Astr. Soc., 33, 165-183, 1973.

Dremin, A. N. and G. A. Adadurov, The behavior of glass under dynamic loading, Soviet Physics - Solid State, 6, 1379-1384, 1964.

Duvall, G. E. and G. R. Fowles, Shock waves, in High Pressure Physics and Chemistry, 2, edited by R. S. Bradley, Academic Press, New York, pp. 209-299, 1966.

German, V. N., N. N. Orlova, L. A. Tarasova, and R. F. Trunin, Synthesis of the orthorhombic phase of silica in dynamic compression, Izv. Earth Physics, 7, 50-56.

Grady, D. E., W. J. Murri, and G. R. Fowles, Quartz to stishovite: wave propagation in the mixed phase region, J. Geophys. Res., 79, 332-338, 1974.

Green, D. H., Magmatic activity as the major process in the chemical evolution of the Earth's crust and mantle, Tectonophys., 13, 47-71, 1972.

Hanks, T. C. and D. L. Anderson, The early thermal history of the Earth, Phys. Earth Planet. Interiors, 2, 19-29, 1969.

Jones, A. H., W. M. Isbell, and C. J. Maiden, Measurement of the very high pressure properties of materials using a light-gas gun, J. Appl. Phys., 37, 3493-3499, 1966.

Kalinin, V. A. and V. L. Pan'kov, Equations of state of rocks, Izv. Earth Physics, 7, 10-20, 1974.

Katsura, T., B. Iwasaki, S. Kimura, and S. Akimoto, High-pressure synthesis of the stoichiometric compound FeO, J. Chem. Phys., 47, 4559-4560, 1967.

Lewis, J. S., Metal/silicate fractionation in the solar system, Earth Planet. Sci. Letters, 15, 286-290, 1972.

Liu, L., Disproportionation of kyanite to corundum plus stishovite at high pressure and temperature, Earth Planet. Sci. Letters, 24, 224-228, 1974.

Liu, L., Post-oxide phases of forsterite and enstatite, Geophys. Res. Letters, 2, 417-419, 1975a.

Liu, L., Post-oxide phases of olivine and pyroxene and mineralogy of the mantle, Nature, 258, 510-512, 1975b.

Liu, L., High-pressure reconnaissance investigation in the system $Mg_3Al_2Si_3O_{12}$-$Fe_3Al_2Si_3O_{12}$, Earth Planet. Sci. Letters. 26, 425-433, 1975c.

Liu, L., The high pressure phases of $MgSiO_3$, Earth Planet. Sci. Letters, 31, 200-208, 1976.

Liu, L. and A. E. Ringwood, Synthesis of a perovskite-type polymorph of $CaSiO_3$, Earth Planet. Sci. Letters, 28, 209-211, 1975.

Long, J. R. and A. C. Mitchell, A dc X-ray fiducial pulse generator for light-gas gun work, Rev. Scient. Instr., 43, 914-917, 1972.

MacGregor, I. D., Petrologic and geophysical significance of mantle xenoliths in basalts, Rev. Geophys. Space Phys., 13, 90-93.

Marezio, M., J. P. Remeika, and P. D. Dernier, The crystal chemistry of the rare earth orthoferrites, Acta Cryst., B26, 2008-2022, 1970.

McQueen, R. G., Shock-wave data and equations of state, in Seismic Coupling, edited by G. Simmons, Advanced Research Projects Agency Meeting, 1968.

McQueen, R. G., J. N. Fritz, and S. P. Marsh, On the equation of state of stishovite, J. Geophys. Res., 68, 2319-2322, 1963.

McQueen, R. G., S. P. Marsh, and J. N. Fritz, Hugoniot equation of state of twelve rocks, J. Geophys. Res., 72, 4999-5036, 1967.

McQueen, R. G., S. P. Marsh, J. W. Taylor, J. N. Fritz, and W. J. Carter, The equation of state of solids from shock wave studies, in High Velocity Impact Phenomena, edited by R. Kinslow, Academic Press, New York, pp. 294-419.

Moore, P. B., The glaserite, $K_3Na[SO_4]_2$, structure type as a "super" dense-packed oxide: evidence for icosahedral geometry and cation-anion mixed layer packings, N. Jb. Miner. Abh., 127, 187-196, 1976.

Pan'kov, V. L. and V. A. Kalinin, Thermodynamic characteristics of rocks and minerals under the conditions obtaining in the Earth's mantle, Izv. Earth Physics, 3, 3-15, 1975.

Podurets, M. A. and R. F. Trunin, On the microstructure of the dense phase of shock-compressed quartz, Izv. Earth Physics, 7, 21-24, 1974.

Reid, A. F. and A. E. Ringwood, New dense phases of geophysical significance, Nature, 252, 681, 1974.

Reid, A. F. and A. E. Ringwood, High-pressure modification of $ScAlO_3$ and some geophysical implications, J. Geophys. Res., 80, 3363-3370, 1975.

Reid, A. F. and A. E. Ringwood, The crystal structure of dense $M_3O_4$ polymorphs: high pressure $Ca_2GeO_4$ of $K_2NiF_4$ structure type, J. Solid State Chem., 1, 557-565, 1970.

Reid, A. F. and A. E. Ringwood, High-pressure scandium oxide and its place in the molar volume relationships of dense structures of $M_2X_3$ and $ABX_3$ type, J. Geophys. Res., 74, 3238-3252, 1969.

Rice, M. H., R. G. McQueen, and J. M. Walsh, Compression of solids by strong shock waves, in Solid State Physics. 6, edited by F. Seitz and D. Turnbull, Academic Press, New York, pp. 1-63, 1958.

Ringwood, A. E., _Composition and Petrology of the Earth's Mantle_, McGraw-Hill
Co., New York, 1975.

Ringwood, A. E. and A. Major, Synthesis of majorite and other high pressure
garnets and perovskites, _Earth Planet. Sci. Letters_, 12, 411–418, 1971.

Robie, R. A. and D. R. Waldbaum, Thermodynamic properties of minerals and
related substances at $2918.15^{\circ}K$ $(25.0^{\circ}C)$ and one atmosphere (1.013 bars)
pressure and at high temperatures, _U.S. Geol. Survey Bull. 1259_, 256 pp.,
1968.

Robie, R. A., P. M. Bethke, M. S. Toulmin, and J. L. Edwards, X-ray crystal-
lographic data, densities, and molar volumes of minerals, in _Handbook of
Physical Constants_, edited by S. P. Clark, Jr., _Geol. Soc. Am. Mem. 97_,
pp. 27–73, 1966.

Salje, E., Symmetry and lattice dynamics of oxides with perovskite-like
structures, _Acta Cryst._, A32, 233–238, 1976.

Schneider, H. and U. Hornemann, Disproportionation of andalusite ($Al_2SiO_5$)
into $Al_2O_3$ and $SiO_2$ at very high dynamic pressures, _Am. J. Sci._, in press,
1976.

Schubert, G. and O. L. Anderson, The Earth's thermal gradient, _Physics Today_,
27, 28–34, 1974.

Shimizu, Y., Y. Syono, and S. Akimoto, High-pressure transformations in
$SrGeO_3$, $SrSiO_3$, $BaGeO_3$, and $BaSiO_3$, _High Temp. - High Press._, 2, 113–120,
1970.

Simakov, G. V. and R. F. Trunin, On the existence of overdense perovskite
structures in magnesium silicates under conditions of high pressure,
_Izv. Earth Physics_, 9, 80–81, 1973.

Sis, L. B., G. P. Wirtz, and S. C. Sorensen, Structure and properties of
reduced $LaCoO_3$, _J. Appl. Phys._, 44, 5553–5559, 1973.

Trunin, R. F., V. I. Gon'shakova, G. V. Simakov, and N. E. Galdin, A study of rocks under the high pressures and temperatures created by shock compression, _Izv. Earth Physics_, 9, 1-12, 1965.

Wackerle, J., Shock-wave compression of quartz, _J. Appl. Phys._, 33, 922-932, 1962.

## Table 1. Hugoniot Data, Soda-Lime Glass[a]

| Shot No. | Flyer Plate | Projectile Velocity (km/sec) | Shock Velocity (km/sec) | Pressure (GPa) | Density (gm/cm$^3$) |
|---|---|---|---|---|---|
| LGG9 | Cu | $5.76 \pm 0.18$[b] | $8.90 \pm 0.13$ | 91.9 | 4.66 |
| LGG11 | Cu | $5.85 \pm 0.02$[b] | $8.91 \pm 0.12$ | 93.4 | 4.72 |
| LGG14 | Ta | $5.541 \pm 0.010$[c] | $9.094 \pm 0.013$ | 98.1 | 4.756 |
| LGG12 | Ta | $5.66 \pm 0.10$[c] | $9.11 \pm 0.02$ | 100.5 | 4.85 |

a)  $Na_2O$, 0.1; MgO, 0.02; $SiO_2$, 0.75; CaO, 0.13

   Initial Density, $3.49 \pm 0.01$ gm/cm$^3$

b)  1 mm-thick sample

c)  2 mm-thick sample

Table 2. Hugoniot and Release Adiabat Data, Bamle Bronzite

| Shot No. | Flyer Plate | Initial Density (gm/cm$^3$) | Flyer Plate Velocity (km/sec) | Shock Velocity (km/sec) | Pressure (GPa) | Shock Density (gm/cm$^3$) | Buffer Shock Velocity (km/sec) | Release Pressure (GPa) | Release Density (gm/cm$^3$) |
|---|---|---|---|---|---|---|---|---|---|
| LGG6 | Cu | 3.2923 ± 0.0003 | 5.375[a] | 10.08 ± 0.13 | 112.6 | 4.963 | 9.14 ± 0.11 | 80.3 | 4.950 |
| LGG8 | Cu | 3.2943 ± 0.0012 | 6.09 ± 0.13 | 10.37 ± 0.05 | 132.4 | 5.261 | 9.62 ± 0.16 | 92.3 | 5.260 |
| LGG14 | Ta | 3.3021 ± 0.0007 | 5.54 ± 0.01 | 10.07 ± 0.03 | 133.5 | 5.491 | 8.83 ± 0.15 | 73.0 | 5.258 |

a) Projectile velocity inferred from shock velocity through arrival mirrors.

Table 3. Parameters for Theoretical Hugoniot of (Mg, Fe) $SiO_3$ Perovskite

Composition: $(Mg_{.9}Fe_{.1})SiO_3$

$$\rho_0 = 4.20 \text{ gm/cm}^3 \tag{1}$$

$$K_0 = \sim 260 \ (\pm 35) \text{ GPa} \tag{2}$$

$$K_0' = \sim 3.5 \ (\pm 1.0) \tag{2}$$

$$\Delta E_{tr} < \sim 166 \text{ KJ/mol} \tag{1}$$

$$\gamma_0 \simeq 1.5 \ (\pm 0.5)$$

$$\gamma = \gamma_0 (V/V_0)^n$$

$$n \simeq 1.0 \ (\pm 0.5)$$

(1) From data of Liu [1975a, b].

(2) See Davies [1976], for example.

Figure 1.   Flash radiographs of projectile taken at stations 390 mm (upper)

and 33 mm (lower) from target.  Nominal exposure times are ~15 nsec.

Projectile speed is 5.5 km/sec.  Shot LGG14.

Figure 2.   Static (a) and dynamic (b) streak camera photograph of bronzite

Hugoniot and release adiabat experiment.  Shot LGG14.

Figure 3.   Shock velocity versus particle velocity data for soda-lime glass.

Figure 4.   Shock pressure versus density for soda-lime glass.

Figure 5.   Compilation of shock data of Mg-rich pyroxenes.  Hugoniot points

for samples of varying porosities (synthetic, polycrystalline

aggregates) and pyroxene-rich (>90%) rocks are included, as are

newly determined release paths (arrows).  Theoretical Hugoniot

(solid curve) and envelope (dashed) are discussed in the text and

Table 3.  McQueen and Marsh [1966] are quoted in Birch [1966].

Figure 6.   Compilation of shock data for Mg-rich olivines including results

on porous samples (synthetic, polycrystalline aggregates) and

olivine-rich (>90%) rocks.  Theoretical Hugoniot (solid curve)

for a Mg-endmember, high-pressure assemblage are discussed in the

text.  Dashed curve corresponds to the left side of the envelope

in Figure 5.  McQueen and Marsh [1966] are quoted in Birch [1966].

Figure 7.   Summary of zero-pressure densities for high-pressure phases of

olivines and pyroxenes as a function of composition based on

interpretation of shock-wave data (symbols), and calculated from

X-ray parameters for $ABO_3$ (perovskite) and AO quenched from high-

pressure diamond-anvil experiments (lines through points).  MgO

(periclase) and FeO (stoichiometric wüstite) values are from:  Bénard

[1954], Katsura et al. [1967], Robie et al. [1966], and Robie

and Waldbaum [1968], with error bars showing variations in measure-

ment and estimate, while error bars on the remaining points are

based on Liu's [1975a, b] estimates of error in the X-ray parameters.

Figure 7.    The dashed line ($ABO_3$ + AO) corresponds to the density of a
(Cont'd)
            perovskite assemblage with olivine stoichiometry (assuming

            $K_D^{Mg-Fe}$ ol-perov. =1).  Symbols are keyed as follows:

            A      Ahrens [1971]

            AAR    Ahrens, Anderson, and Ringwood [1969]

            AG     Ahrens and Gaffney [1971]

            AS     Al'tschuler and Sharpidzhanov [1971a]

            DA     Davies and Anderson [1971]

            DG     Davies and Gaffney [1973]

            KP     Kalinin and Pan'kov [1974]

            MHF    McQueen, Marsh, and Fritz [1967]

            PK     Pan'kov and Kalinin [1975]

Figure 8.    Representative Hugoniot data from Figures 5 and 6 compared with

            the Hugoniot for MgO [Carter et al., 1970; McQueen, 1968; McQueen

            and Marsh, quoted in Birch, 1966].