A SHOCK-INDUCED PHASE CHANGE IN IRON-SILICATE GARNET

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Hugoniot measurements on iron-silicate garnet [(FeO)_{0.5}, MgO_{0.5}, CaO_{0.38}, MnO_{0.057}, Al_{2}Si_{5}O_{12}] initial density 4.15 g/cm^{3}. Demonstrates that above a shock pressure of 205 ± 20 kbar transition to a high-pressure phase(s), having an apparent zero-pressure density and bulk modulus of 4.44 ± 0.06 g/cm^{3} and 3.3 ± 0.3 Mbar, occurs. Crystal chemical systematics and Debye-Scherrer X-ray patterns of a recovered phase(s), which may be the shock-induced high-pressure form, suggest possible formation of a phase with a density of 4.48 g/cm^{3}. Occurrence of such a poly- morph of garnet in the mantle would give rise to an increase in density and seismic velocity below ~600 km in the earth.

By measuring the Hugoniot equation of state to ~660 kbar and carrying out shock recovery experiments we have discovered that above 205 ± 20 kbar silicate garnet (almandine) undergoes a transition to a high-pressure form having a zero-pressure density and bulk modulus of 4.44 ± 0.06 g/cm^{3} and 3.3 ± 0.3 Mbar, which is ~6% greater than that of the initial material. Nineteen Hugoniot experiments were carried out on 4-mm thick, 18-mm diameter, disc-shaped samples taken from a ~15-cm diameter almandine-rich garnet crystal from Salida, Colorado. The samples were purchased from Ward's National Science Establishment, Rochester, N. Y. Bulk densities varied from 4.175 to 4.186 g/cm^{3} except for one sample, shocked to 283 kbar, which had an initial density of 4.158 g/cm^{3}. Microprobe analyses (carried out by A. Chodas, California Institute of Technology) of the crystal gave an average composition of (FeO)_{0.5}, MgO_{0.5}, CaO_{0.38}, MnO_{0.057}, Al_{2}Si_{5}O_{12}. In deriving this formula, we have assumed that all of the iron occurs as Fe^{2+} as no variation in Al^{3+} is observed. Debye-Scherrer patterns yielded an average initial lattice parameter of ~11.519 ± 0.001 Å, implying single crystal density of 4.19 g/cm^{3}. The garnet had an index of refraction of 1.802 ± 0.003 at 24°C.

Slight compositional crenetic zoning of the Fe, Mg, Ca and Mn in the crystal was observed qualitatively by radiography and quantitatively by electron microprobe scans. The samples were chosen to minimize this effect as is the case for the very slight density variation.

The planar sample surfaces were cut to within ± 3° of (001). The specimens were mounted with flat and inclined mirrors on 1.5 mm thick driver plates of polycrystalline tungsten or 2024 aluminum and impacted with 3.5 mm thick flyer plates at speeds of 0.8 to 2.5 km/sec. The use of reflected light techniques for measuring shock and free-surface velocity is described by Doran [1] and Ahrens et al. [2]. The flyer plates were the same material as the driver plates and were launched in plastic sabot to appropriate impact velocity using the Caltech high performance propellant gun [3]. In each experiment, the flyer plate velocity prior to impact, and the resulting shock and free-surface velocities associated with the final shock state ... and in most shots ... the elastic shock state, were measured using a series of time interval counters and a streak camera. By measuring distances and angles on the streak film, and application of the Rankine-
Murnaghan equation [6] from the ultrasonic data of Soga [7]. We infer that garnet remains stable under shock compression at these pressures.

Between 205 ± 20 kbar and approximately 320 kbar, our data display both anomalously high compression, and sharply diverge from the garnet isotherms. We assume that for shock states in this range a mixture of the compressed garnet, and a new, high-pressure phase (hph), or phases, with an intrinsically greater density is being formed. We also assume that above 320 kbar and extending to 662 kbar, the series of ten Hugoniot states shown in fig. 1 represent the compression of the hph of garnet. With these assumptions the raw data suggest that the hph has a zero-pressure density (zpd) which is from 5 to 8% (4.39 to 4.51 g/cm³) greater than the initial garnet. If, however, it is assumed that all the shock data above ~205 kbar represent a metastable mixed-phase state, then the formation of a much denser phase (of presently undeterminable equation of state) is implied. Although we do not subscribe to this latter possibility, it nevertheless is difficult to completely rule out.

To further clarify the nature of the hph we fired a series of shock recovery experiments with samples of Salida and Brazil, (FMg₃.ₐ₁, Mn₀.ₕ₂, Cu0.ₐ₃) by Al₂Si₂O₅·7· garnet. The Brazil garnet was purchased from Shales, Los Angeles, California. The samples were encapsulated in stainless steel holders and subjected to flyer-plate impact induced shocks of ~400 kbar using the techniques described by Horz and Ahrens [13] and Gibbons and Ahrens [14].

In two experiments (table 1), material which under microscopic examination appeared only to be deformed garnet, yielded Debye-Scherrer (FvK, reflection Mo filter) patterns containing lines which are distinctly different from the starting garnet. These lines could also not be indexed as any combination of quartz (α and β), clinop, whitmowite, fayalite, ringwoodite, Fe₃O₄ (orthohom clino.), A1₂O₃, FeO and Fe₂O₃. We conclude that these lines probably result from a small quantity (< 1%) based on intensity of the hph of the garnet which remained embedded in the sample, upon pressure release, however, we cannot rule out the possibility that the hph produced has not partially reversed to still another phase(s). Although the limited X-ray data cannot yield a unique structural determination, the data could not be fit with the hypothetical undistorted ilmenite structure. Since the
Table 1. X-ray data for presumed hpp recovered from garnet shocked to ~ 400 kbar.

<table>
<thead>
<tr>
<th>Salidus garnet-hpp</th>
<th>Brazil garnet-hpp</th>
<th>Brazil garnet-hpp (^a)</th>
<th>Combined values</th>
<th>(d)</th>
<th>Residuals (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Å]</td>
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</tr>
<tr>
<td>2.95</td>
<td>3.52</td>
<td>3.52</td>
<td>3.52 ± 0.01</td>
<td>0.02</td>
<td>0.077</td>
</tr>
<tr>
<td>2.41</td>
<td>2.95 ± 0.02</td>
<td>2.95 ± 0.02</td>
<td>2.95 ± 0.02</td>
<td>0.02</td>
<td>0.016</td>
</tr>
<tr>
<td>2.31</td>
<td>2.19</td>
<td>2.19</td>
<td>2.19 ± 0.01</td>
<td>0.01</td>
<td>-0.015</td>
</tr>
<tr>
<td>2.23</td>
<td>2.07</td>
<td>2.07</td>
<td>2.07 ± 0.01</td>
<td>0.02</td>
<td>0.008</td>
</tr>
</tbody>
</table>

\(^a\) Corrected by ratio of lattice parameters to composition of Salidus garnet.
\(^b\) From orthorhombic indexing.
\(^c\) Not observed.

The data require a crystal with lower symmetry, we have tentatively indexed them in an orthorhombic structure, and obtained residuals within experimental error for the lattice parameters \(a = 4.94 ± 0.06 \text{ Å}, b = 4.47 ± 0.04 \text{ Å}, c = 0.74 ± 0.11 \text{ Å}\). Assigning six \(\text{ABO}_6\) molecules to a unit cell, which is somewhat arbitrary, yields a density of 4.4 ± 0.06 g/cm\(^3\).

Taking into account both known zero-pressure structures, and pressure-induced polymorphs of crystal-chemically analogous compounds, we infer that the high-pressure regime observed in the Hugoniot experiments could represent the properties of the following crystal structures: (1) breakdown to the oxides, 

\(\text{Waistite, Pervoskite, Corundum, and Stishovite; (2) disproportionation to corundum plus pyroxene (\(c\)), ilmenite (\(b\)), or perovskite (\(c\)); (3) perovskite structure; or (4) ilmenite structure. The products of (1) infer a zpd of ~ 4.66 g/cm\(^3\). This would imply an impossibly low, probably negative, value of \((\text{d}Kg/\text{d}p)P\) (\(Kg\) is isentropic bulk modulus, \(P\) is pressure). Case 2a will yield a zpd of ~ 4.33 g/cm\(^3\). This is difficult to discount, a priori, but is lower than expected from the Hugoniot data. Case 2b would yield a zpd of ~ 4.48 g/cm\(^3\), slightly higher than expected from the Hugoniot results although it is difficult to discount this case alone.

Gopher, no corundum or pyroxene is observed in the recovery experiments. Although case 2c has been observed in the case of yttrium-iron and yttrium-aluminum garnets by Mareci et al. [9], it is not a likely hhp. Ringwood [10] has pointed out that in perovskites formed from oxides which individually crystallize in the halite and rutile structure the zpd’s are 5 to 10\% greater than those of the oxides. Hence, both cases 2c and 3 may also be excluded. The systematic relations of the molar volume and ionic radii [1] of ilmenite-structures compounds indicated in fig. 2, yield an expected zpd, for the Salidus garnet composition, of ~ 4.41 g/cm\(^3\). On the basis of both ilmenite density systematics and the observation by Ringwood and Major [12] of the transformation under pressure of \(\text{Mg}_2\text{Al}_2\text{O}_4\) to the ilmenite structure in the range (\(\text{Fe}_2\text{Al}_2\text{O}_4\)) to (\(\text{Mg}_2\text{Al}_2\text{O}_4\)), it appears to us that an ilmenite, or ilmenite-like, structure is most likely to be the phase which is shock-induced in the Hugoniot experiments. Reducing the high-pressure regime Hugoniot data to a Birch–Murnaghan isentropic equation of state, using the method outlined by Ahrens et al. [15], with a phase-transformation energy of \(2.5 \times 10^8\) erg/g and a zpd of 4.45 g/cm\(^3\) yields values of \(Kg\) and \((\text{d}Kg/\text{d}p)P\) of 7.5 Mbar and 3. It may be that the low value of \((\text{d}Kg/\text{d}p)P\) above ~ 305 kb results from the partial shock-induced electronic transition in the ilmenite structure from unpaired to paired d-electron spins in octahedrally coordinated Fe\(^2+\).

Stenn [16] has calculated that in Fe\(_{30}\)O this will occur when the mean Fe–O distance is 2.05 Å. This Fe–O distance will occur at ~ 300 kbar in the proposed hhp ilmenite structure.

If the observed shock-induced transformation in garnet represents the formation of a phase which is stable at pressures above ~ 205 kbar, we expect that this phase will be present at depths below 650 km in the earth’s mantle. Distribution coefficients for Fe\(^{3+}\)/(Mg\(^{2+}\) + Fe\(^{3+}\)) in coexisting chloroanortite and
Fig. 2. Relation of molar volume to ionic radii for isomorhic

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