

Shock Wave Compression of Iron-Silicate Garnet¹EARL K. GRAHAM² AND THOMAS J. AHRENS*Seismological Laboratory, California Institute of Technology
Pasadena, California 91109*

Shock wave Hugoniot data have been obtained for almandine-garnet of composition (Fe_{0.70}, Mg_{0.14}, Ca_{0.04}, Mn_{0.03}) Al₂Si₃O₁₂ to pressures of >650 kb. The Hugoniot data indicate the onset of a high-pressure phase at 195 ± 20 kb. Equation-of-state systematics and crystal chemical data (stemming largely from analog compounds) suggest that the high-pressure phase occurs in an 'ilmenitelike' structure with an initial density of 4.44 ± 0.04 g/cm³. This value represents an increase of about 6% over the initial garnet density of 4.180 ± 0.005 g/cm³. The adiabatic bulk modulus K_0^s and its first pressure derivative $(\partial K_0^s/\partial P)_T$ were calculated for the high-pressure phase and found to be 3.19 ± 0.39 Mb and 2.6 ± 0.7, respectively. The major source of probable error in these values results from the indicated uncertainty in the initial density of the high-pressure phase. These results strongly suggest that upper mantle minerals are likely to occur in the ilmenite structure over a substantial part of the lower mantle.

It is generally accepted that the upper mantle of the earth is composed predominantly of some combination of the minerals olivine, pyroxene, and garnet. In particular, it has been shown by *Graham* [1970] that a pyrolite composition derived from a mixture of 75% alpine peridotite and 25% Hawaiian basalt [*Ringwood*, 1966] satisfies the density and elasticity requirements of the upper mantle within present experimental uncertainties, as well as petrological and geochemical considerations. Data on the elastic properties and the high-pressure behavior of these minerals are essential to our understanding of the constitution and the structure of the earth's mantle.

The proportion of garnet in petrological models suggested for the upper mantle varies from about 14 wt % in the pyrolite model to over 50 wt % for eclogitic compositions. In addition, work by *Ringwood and Major* [1966] suggests that, in the presence of dissolved Al₂O₃, pyroxene is capable of transforming into a garnetlike structure. *Smith and Mason's* [1970] observation of this new garnet (majorite), which is close to the stoichiometry of

pyroxene and presumably shock induced, in the Cooraro meteorite confirms the existence of this phase. More recently, a high-pressure phase induced in Bamle enstatite by shock wave compression has been interpreted by *Ahrens and Gaffney* [1971] as probably representing this same garnet structure. When the foregoing is considered, it is apparent that a significant fraction of the upper mantle could be in the garnet structure. The importance of understanding the high-pressure characteristics of garnet is thus considerably amplified.

Of primary importance, in addition to an understanding of the pressure and temperature dependence of the elastic properties of garnet per se, is the possibility of transformation to a high-pressure phase. It is instructive to consider a Goldschmidt diagram indicating the structural fields of some ABO₃ compounds in relation to the ionic radii of the constituent A and B cations. Figure 1 shows the central and transitional positions of the garnet field in relation to the pyroxene, ilmenite, and perovskite structural fields. In addition to suggesting the garnet-pyroxene transformation discussed previously, the diagram also suggests the possibility of a garnet transformation into an ilmenite or perovskite structure under very high pressure and temperature conditions. It has been suggested by *Boyd* [1964] that, at sufficiently high pressure, pyrope (Mg₃Al₂Si₃O₁₂) would invert to a solid solution between MgSiO₃

¹ Contribution 2093, Division of Geological Sciences, California Institute of Technology.

² Now at Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802.

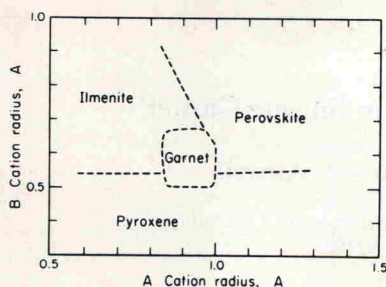


Fig. 1. Schematic diagram of the fields of pyroxene, ilmenite, perovskite, and garnet structures based on a plot of A and B ionic radii for $A^{2+}B^{4+}O_3$ compounds possessing the indicated structures [after Ringwood, 1970].

(ilmenite) and Al_2O_3 (corundum). Partial confirmation of this supposition has been provided by Ringwood and Major's [1967a] studies of the system $Mg_3Al_2Si_3O_{12}$ - $Mg_3Al_2Ge_3O_{12}$ at high pressure and temperature. Their data indicate a homogeneous series of ilmenite solid solutions near the germanate end of the system above 70 kb at about 900°C. Although the data were inconclusive on the silicate end, Ringwood and Major projected a transformation pressure of about 200–300 kb for the phase transition of pyrope-garnet to an ilmenite structure. The density increase of this transformation was determined to be about 7.5%. In addition to suggesting the garnet-ilmenite possibility, Figure 1 also suggests considering the perovskite structure as a high-pressure garnet phase. This supposition has also been verified experimentally by Ringwood and Major [1967b], who transformed $CaGeO_3$ (wollastonite structure) under very high pressure into a distorted garnet structure and finally into a perovskite structure. Moreover, Marezio *et al.* [1966] were able to transform yttrium-iron and yttrium-aluminum garnets into a perovskite structure by using a conventional piston cylinder apparatus. The density increase of the garnet-perovskite transformation indicated by these studies is about 18%. Therefore, although a high-pressure phase has not been experimentally verified as yet for an earth-forming silicate-garnet, the possibility of such a transformation is suggested strongly by the foregoing studies on analog structures and crystal chemical systematics.

The use of shock wave techniques has already revealed a number of important phase trans-

formations in rocks and minerals [Wackerle, 1962; Ahrens and Gregson, 1964; Ahrens and Gaffney, 1971; McQueen *et al.*, 1967] and has provided valuable information on the equations of state of the high-pressure phases [Anderson and Kanamori, 1968; Ahrens *et al.*, 1969]. The characterization of the properties of such high-pressure phases by shock techniques has provided important information concerning compositional aspects of the earth's mantle and core [Anderson and Jordan, 1970; Ringwood, 1970].

In this study shock wave compression data to over 650 kb are presented for single-crystal almandine-garnet. The data indicate the initiation of a phase transformation near 200 kb; total transition to the high-pressure polymorph occurs at approximately 300 kb. The zero pressure density of the high-pressure phase is determined by crystal chemical arguments and supported by preliminary shock recovery experiments. When the calculated zero pressure density is used, the metastable Hugoniot of the high-pressure phase centered at room conditions is determined by assuming a form for the Grüneisen parameter consistent with the linear bulk modulus approximation. Lastly, the elastic properties of the high-pressure phase are calculated from the metastable Hugoniot data by using the linear shock velocity-particle velocity relationship.

SPECIMEN DESCRIPTION

The specimen material selected for this study consisted of a single-crystal sample of almandine-garnet from Salida, Colorado. Almandine-garnet crystals from this locality were first described by Penfield and Sperry [1886]. The crystal used in the present work was a large well-formed rhombic dodecahedron of almandine lightly coated with a chloritic alteration product. Examination of the interior revealed negligible fracturing and alteration minerals. Consistency among the measured lattice parameters, the composition, and the density verify the foregoing observation; therefore the individual specimen blanks have been regarded as pore free. A schematic representation of the initial sample and the relation of the external morphology to the chosen shock propagation direction, the [100] axis, are indicated in Figure 2.

The large single crystal was initially cut into