# HIGH-PRESSURE STUDIES OF THE SYSTEMS $Mg_2GeO_4$-$Mg_2SiO_4$ AND $GeO_2$-$SiO_2$ WITH SPECIAL REFERENCE TO THE OLIVINE-SPINEL TRANSITION

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# HIGH-PRESSURE STUDIES OF THE SYSTEMS $Mg_2GeO_4$-$Mg_2SiO_4$ AND $GeO_2$-$SiO_2$ WITH SPECIAL REFERENCE TO THE OLIVINE-SPINEL TRANSITION

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Phase equilibrium studies have been extended by more than one order of magnitude beyond pressures attainable in hydrothermal systems. Pressures close to 900,000 psi have been obtained by the use of relatively simple uniaxial devices in which a large force is applied to a sample for tens of hours by means of very hard tool steel or cemented carbide pistons with small bearing surfaces. The sample is pressed into a thin nickel ring and isolated from the piston faces by platinum foils. Temperatures of 550-600°C are the practical upper limits at the extreme pressure range. Tests have been made which show that the pressure is uniform across the sample assembly, and further, that the results are comparable to those obtained with hydrostatic pressure.

The system $Mg_2GeO_4$-$Mg_2SiO_4$ above 500°C has been studied to the limits of the hydrothermal and uniaxial methods. It has been determined that the olivine-spinel phase transition is reversible and reproducible. The univariant p-t curve for this transition for $Mg_2GeO_4$ passes through 823°C at 10,000 psi and increases at the rate of 24.6 ± 1.2°C to 80,000 pai. The $\Delta V$ of the two phases at room temperature and pressure is 3.5cc per mol. The $\Delta H$ of the transition calculated via the Clapeyron relation is 3.7 Kcal/mol. The maximum silicate content of the spinel solid solution obtained is 53 mol percent at 65 kilobars and 542°C. Extrapolation of the phase fields shows that $Mg_2SiO_4$ should convert to the spinel form at 100 ± 15 kilobars at 542°C. Other considerations suggest that the transition temperatures should rise 13°C per kilobar.

Assuming linear variation of x-ray "d-spacing" data with composition for the spinel solid solutions, the spinel phase of $Mg_2SiO_4$ will have a cell edge of 8.22Å. Thus the $\Delta V$ of transition for $Mg_2SiO_4$ would be only 2.0 cc per mol.

The geophysical implication of these results is that an olivine-spinel transition in the mantle of the earth does appear to be a likely explanation of the seismic and density discontinuities at the 400 km depth as suggested by Jeffreys and Bernal provided that the mantle composition is in fact olivine, and that the temperatures in the mantle are in the range proposed by Daly or Turner and Verhoogen.

Uniaxial high pressure studies in the system $GeO_2$ $SiO_2$ at 500°C locate the quartz-coesite transition for $SiO_2$ at 20.4 ± 0.4 kilobars. The quartz solid solution field is reduced from 33 mol percent $GeO_2$ at low pressures to es-

sentially nothing at the eutectoid pressure of 32 kilobars and 13 mol percent $GeO_2$, leaving $SiO_2$ (coesite) and $GeO_2$ (rutile).

A beginning has been made in the use of infra-red data for diagnostic purposes in the solid state. An empirical relation has been worked out which allows comparison of coordination polyhedra about major cations in simple compounds. The infra-red data lead to the conclusion that the $4^+$ cations of silicates and germanates with the olivine structure are situated in distorted tetrahedra characterized by two pairs of oxygens in different equivalent coordinations to the cation. It also leads to the proposal that the $Mg_2SiO_4$ spinel will have the normal structure, and that $Mg_2GeO_4$ spinel has the inverse structure. Some x-ray corroboration of this fact has been found in relative intensities of the (422) and (400) reflections. According to earlier calculations for $Mg_2GeO_4$ spinel, the type may be distinguished by the I422/I400 ratio and would be normal, disordered or inverse if the ratio were 1.67, 3.3 or 6.6 respectively. In the present work the ratio found was always above 3.8 and as high as 6.5 for $Mg_2GeO_4$.

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