

phase changes

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### The Spinel-Olivine Inversion in $Mg_2GeO_4$ \*

DURING the past few years there has been active interest in the problem of alternative explanations other than layers of different composition in the Earth to explain seismic data. The most important of these arises from an early suggestion by Bernal<sup>1</sup> regarding the possible inversion of the orthorhombic mineral olivine to a dense form with the spinel structure. An actual example of this inversion from the spinel to the olivine had been reported by Goldschmidt<sup>2</sup> for the compound  $Mg_2GeO_4$ . However, there have always been some doubts regarding this observation, since it was mentioned only in a footnote and could not be repeated.

With the revived interest, there have apparently been several attempts<sup>3</sup> to synthesize the spinel form of  $Mg_2GeO_4$ . But the general conclusion was that this form probably does not exist. However, in 1954, Roy and Roy<sup>4</sup> reported the reproducible synthesis and reversible inversion to olivine of a spinel form of  $Mg_2GeO_4$ . This work has been generally missed, since the paper describing it was concerned with the morphology of synthetic serpentines. In 1955, a quantitative equilibrium study of the whole problem was started with the view of determining the pressure-temperature conditions for the inversion of natural olivines into spinel structures. The problem was tackled in stages by determining a series of  $t-x$  sections of the  $Mg_2SiO_4$ - $Mg_2GeO_4$  system; the study of  $t-x$  sections with 10 and 20 mol. per cent  $Fe^{2+}$  replacing  $Mg^{2+}$ , and finally a  $p-x$  section of the  $Mg_2GeO_4$ - $Mg_2SiO_4$  system at 542° C. up to the experimental limit of 65,000 atm. Many of these results were presented orally at the 1956 annual meeting of the Geological Society of America<sup>5</sup>. While the results of this extensive experimental study will be published later elsewhere, it is considered worth while to summarize here the new data on the spinel-olivine inversion obtained from some four hundred runs in hydrostatic or uniaxial pressure devices.

The work utilized high-pressure water as a catalyst, and under such conditions there is no problem with reproducible synthesis of the spinel phase. The inversion temperature for the  $Mg_2GeO_4$  (spinel)  $\rightleftharpoons$   $Mg_2GeO_4$  (olivine) equilibrium (obtained by extrapolation from runs as low as 1,000 lb./sq. in.) is 810° C. at atmospheric pressure. The  $\Delta V$  of inversion

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from X-ray data is  $3.5 \text{ cm.}^3/\text{mol.}$ ;  $\Delta H$  (calculated from the pressure-dependence slope) is  $3,690 \text{ cal./mol.}$  The entropy of inversion is thus a reasonable  $3.4 \text{ E.U.}$  The inversion temperature is raised by  $0.025 \text{ deg. C./bar}$  for the first  $5,500 \text{ bars.}$  X-ray intensities and infra-red absorption spectra clearly show that  $\text{Mg}_2\text{GeO}_4$  is an inverse spinel. It may be of interest to record that the inversion in  $\text{Mg}_2\text{SiO}_4$  as determined by extrapolation of experimental points up to  $60 \text{ mol. per cent Mg}_2\text{SiO}_4$  in the  $p-x$  section is set at  $100 \pm 15 \text{ kilobars at } 542^\circ \text{ C.}$  Further, the change in lattice spacings of the spinel solid solutions of  $\text{Mg}_2\text{GeO}_4$ .  $\text{Mg}_2\text{SiO}_4$  shows that the spinel form of  $\text{Mg}_2\text{SiO}_4$  will have a cell edge of  $8.22 \text{ \AA.}$  Therefore, the  $\Delta V$  of this transition is  $2.0 \text{ cm.}^3/\text{mol.}$  The dependence of the  $\text{Mg}_2\text{SiO}_4$  transition upon pressure is beyond direct experimental study at present, but from a consideration of various sections in the  $p-t-x$  volume constructed with the data for the system  $\text{Mg}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$ , one would expect that it will be only  $0.013 \text{ deg. C./bar.}$

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<sup>1</sup> Bernal, J. D., *Geophys. Dis. Roy. Astro. Soc.*, No. 748, 267 (1936).

<sup>2</sup> Goldschmidt, V. M., *Nacht. Gesell. Wissensch. Göttingen, Math. Phys. Kl., Fachgr. IV*, Bd. 1, 184, 190 (1931).

<sup>3</sup> Urey, H. C., "The Planets", 69 (Yale University Press, New Haven, 1952). Romeijn, F. C., *Phillips Res. Rep.*, 8, 321 (1953). Bertaut, E. F., Durif-Varambon, A., and Pauthenet, E., "Propriétés Cristallographiques et Magnétique de Quelques Nouvelles Séries de Spinelles Mistes", Third Int. Cong. Cryst., Paris (1954). Ringwood, A. E., *Amer. J. Sci.*, 254, No. 11, 707 (1956).

<sup>4</sup> Roy, D. M., and Roy, R., *Amer. Min.*, 39, 957 (1954).

<sup>5</sup> Dacheille, F., and Roy, R., *Bull. Geol. Soc. Amer.*, 67, 1682 (1956) (Abstract).