phase changes H. T. Hall

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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[1] 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[2] 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[3] 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[4] 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[5]. 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) $\rightleftarrows$ 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 ΔV of inversion

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from X-ray data is 3·5 cm.³/mol.; ΔH (calculated from the pressure-dependence slope) is 3,690 cal./mol. The entropy of inversion is thus a reasonable 3·4 E.U. The inversion temperature is raised by 0·025 deg. C./bar for the first 5,500 bars. X-ray intensities and infra-red absorption spectra clearly show that Mg_2GeO_4 is an inverse spinel. It may be of interest to record that the inversion in Mg_2SiO_4 as determined by extrapolation of experimental points up to 60 mol. per cent Mg_2SiO_4 in the p–x section is set at 100 ± 15 kilobars at 542° C. Further, the change in lattice spacings of the spinel solid solutions of $Mg_2GeO_4 \cdot Mg_2SiO_4$ shows that the spinel form of Mg_2SiO_4 will have a cell edge of 8·22 A. Therefore, the ΔV of this transition is 2·0 cm.³/mol. The dependence of the Mg_2SiO_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 Mg_2GeO_4–Mg_2SiO_4, one would expect that it will be only 0·013 deg. C./bar.

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