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¹ Ramdohr, P., "Die Erzminerale und Ihre Verwachsungen", 718 (1955).

² Uytendogaardt, W., "Tables for Microscopic Identification of Ore Minerals", 173 (Princeton Univ. Press, 1951).

³ Mason, B., *Geol. Foren. Forhandl.*, **65**, 146 (1943).

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 Bernal¹ 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 Goldschmidt² 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 attempts³ 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 Roy⁴ 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 America⁵. 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 ΔV of inversion 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 - Mg_2SiO_4 shows that the spinel form of Mg_2SiO_4 will have a cell edge of 8.22 Å. 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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¹ Bernal, J. D., *Geophys. Dis. Roy. Astro. Soc.*, No. 748, 267 (1936).

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

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

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

⁵ Dachille, F., and Roy, R., *Bull. Geol. Soc. Amer.*, **67**, 1682 (1956) (Abstract).

BIOCHEMISTRY

Chlorination of Proteins as a Method of increasing their Opacity in the Electron Microscope

THE basic difficulty in devising a method for selectively increasing the density of protein in a tissue section, in order to increase its contrast under the electron microscope, is to choose some atom or group of atoms unique to the protein, and which may be replaced or substituted by some heavier atom or group. The amide group occurs in all proteins as the peptide link, while it is absent in all other macromolecular cell constituents. N-chlorination ($\cdot NH \cdot CO \rightarrow \cdot NCl \cdot CO \cdot$) is a well-known reaction with simple amides, and it therefore seemed that chlorination might offer a simple means of increasing the density of the protein. Although chlorination of other cell constituents (and other structures in the protein) would undoubtedly also occur, it was considered that the background increase in density produced in this way would be small compared with the increase in density of the protein, for theoretically 1 gm. atom of chlorine can react with each 100-150 gm. of protein, depending upon its amino-acid composition. Vandeveld¹ has shown that many proteins, both fibrous and globular, react with chlorine to give materials which contain about 15 per cent chlorine, a content which corresponds to substitution at most of the peptide links. Most of the chlorine is lost from the modified protein by treatment with water, giving hydrochloric acid, which probably arises by hydrolysis of the N-Cl bond followed by oxidation of the protein by the hypochlorous acid which is formed. Exposure to chlorine gas, followed by spraying with iodine and starch solutions, has been used as a delicate test for amino-acid, peptide and protein spots on paper chromatograms².