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GEOLOGY

Olivine-Spinel Transition on Nickel Orthosilicate

THE pressure-induced transition of olivine to a denser spinel structure is probably of considerable importance in the Earth's mantle¹. Olivine-spinel transitions are known in Mg_2GeO_4 (refs. 2 and 3) and Fe_2SiO_4 (ref. 1), while a variety of evidence indicates that Mg_2SiO_4 will undergo a similar transition around 125,000 atmospheres and 600°C. (refs. 1 and 3). These results suggested the desirability of exploring for olivine-spinel transitions in other substances which normally crystallize with an olivine structure.

Such a substance is nickel orthosilicate— Ni_2SiO_4 . From preliminary¹ and recent (Ringwood, A. E., unpublished results) data on the solid solubility of Ni_2SiO_4 in Ni_2GeO_4 (spinel) and vice versa, I have calculated that Ni_2SiO_4 should undergo an olivine-spinel transition around 54,000 atmospheres at 1,500°C. However, Wentorf⁴ has recently reported unsuccessful attempts to synthesize a spinel modification of Ni_2SiO_4 at pressures up to 110,000 atmospheres. I have carried out further high-pressure experiments using a uniaxial pressure apparatus (squeezer), in an attempt to resolve the conflict, and provide further information on olivine-spinel transitions.

Intimate mixtures of $Ni(OH)_2$ and silicic acid in orthosilicate ratios were prepared, and subjected to pressures between 0 and 50,000 atmospheres, at 650°C., for periods between 1 and 6 hr. Fourteen runs were made. After completion of a run, the pressure was rapidly released, while the sample was quenched and then examined by X-ray diffraction.

At pressures below 15,000 atmospheres the phases observed were Ni_2SiO_4 olivine, NiO , and nickel talc. It may be shown that the last two products constitute a metastable assemblage, due to incomplete reaction. Above 20,000 atmospheres, olivine disappeared and in its place a spinel phase appeared, together with NiO and talc. Between 15,000 and 20,000 atmospheres, spinel, olivine, talc and NiO appeared simultaneously. A run at 50,000 atmospheres, using a mix containing 20 per cent excess $Ni(OH)_2$ over that required to form the normal orthosilicate, produced spinel and NiO . Talc was absent.

A sample of Ni_2SiO_4 olivine was prepared by sintering a tablet of intimately mixed NiO and SiO_2 at 1,400°C. for 6 hr. The tablet was then crushed, reformed and resintered, this procedure being repeated twice. A sample thus prepared was subjected to 50,000 atmospheres and 700°C. for 2½ hr. About 80 per cent conversion to the spinel form was observed. Similar runs were carried out at 30,000 and 20,000 atmospheres. A small amount of spinel

formed at 20,000 atmospheres, but curiously, no spinel formed at 30,000 atmospheres.

Mixtures of silicic acid, hydrous germanium dioxide, and nickel hydroxide were prepared at intervals in the composition range between Ni_2GeO_4 and Ni_2SiO_4 . These were run at 33,000 atmospheres and 650°C. A complete series of spinel solid solutions was found to exist between Ni_2GeO_4 (normally a spinel) and Ni_2SiO_4 . The solid solutions obeyed Vegard's law.

It is concluded that the new phase is the spinel modification of Ni_2SiO_4 and that the equilibrium pressure for the olivine-spinel transition in Ni_2SiO_4 at 650°C. is about 18,000 atmospheres. Ni_2SiO_4 spinel is green, transparent, and has a lattice parameter of 8.044 Å. The calculated density is 5.34 gm./c.c., which is about 9 per cent higher than that of the olivine modification.

The experimental transition pressure is in good agreement with the value calculated (54,000 atm.) from zero pressure equilibria at 1,500°C. in the system $Ni_2GeO_4 - Ni_2SiO_4$ if a reasonable allowance is made for the effect of temperature on transition pressure. A detailed description of equilibria in this system, and the calculations based upon it, will be published elsewhere.

Wentorf's failure to synthesize Ni_2SiO_4 spinel at much higher pressures than I used may be due to the different type of apparatus employed⁵. We both used mixtures of $Ni(OH)_2$ and silicic acid as starting materials, and operated at temperatures sufficiently high to cause the components to react and form Ni_2SiO_4 . However, the uniaxial device which I used permits rapid quenching—in particular, the water vapour pressure can be instantaneously released. Published descriptions⁵ suggest that Wentorf's apparatus may not have been able to quench the reaction products as quickly; furthermore, the quenching may be carried out in the presence of a high pressure of water vapour (from the pyrophyllite pressure medium). Thus it is possible that any spinel formed at high pressures afterwards became inverted to olivine during the quench.

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Potassium-Argon Ages of Some Rocks from the South Atlantic

THE ages of micas separated from a number of rocks from the South Orkney Islands have been determined using the potassium-argon method.

In these particular measurements, the total volume of argon evolved on fusion of the samples was measured by means of a McLeod gauge, and a correction applied for atmospheric contamination using a mass spectrometer to resolve the argon isotopes. Potassium analyses were made with a flame photometer.