HIGH-PRESSURE RECONNAISSANCE INVESTIGATIONS
IN THE SYSTEM Mg_2SiO_4 - MgO - H_2O

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1. INTRODUCTION

This investigation was commenced with the objective of testing suggestions [1,2] that close-packed compounds of the type x MgO.SiO_2, where $x > 2$, might be stable under very high pressures and might therefore be present in the earth's mantle. About 40 runs at pressures between 100 and 180 kilobars and temperatures of 600-1100°C have been made on oxide mixtures and gels possessing widely varying ratios of MgO to SiO_2, the reaction products being examined by optical and X-ray diffraction techniques. Results have not been as definitive as had been hoped. It has become clear that this particular problem might be approached more successfully with a different type of high-pressure temperature apparatus, and no further work on this system is planned in the near future. Nevertheless, in view of the synthesis of some new dense phases, and the possible bearing of our work upon recently reported results by others [3], a brief description appeared warranted.

2. EXPERIMENTAL

Gels and oxide mixtures with compositions x MgO.SiO_2, where x = 1, 2, 2.5, 3, 4, 5, were prepared. The oxide mixtures were made from silicic acid ($\sim 10\%$ H_2O) and MgO, whilst the gels were prepared by mixing alcoholic and aqueous solutions of ethyl-orthosilicate and magnesium nitrate, respectively, evaporating and drying. Separate portions of the gels were then ignited for 1 hr at 700°C, 900°C, 1100°C, 1200°C, and the water contents of the resultant oxide mixtures were determined. They were found to be 7%, 5%, 2% and < 0.5% respectively. Samples so prepared were subjected to pressures in the range 100-180 kb (NaCl pressure

scale) [4] and temperatures of 600-1100°C in a high-pressure, high-temperature device. This device [5] consisted essentially of a pair of Bridgman anvils with a heater placed between them. After completion of a run, the sample was quenched under pressure, retrieved and examined by optical and X-ray techniques.

Although this apparatus has been used very successfully with crystalline starting materials [5,6], the use of partially dehydrated gels as starting materials posed some problems which were not satisfactorily solved. The gels tended to extrude unevenly between the heater faces when pressure was applied. This resulted in a highly non-uniform distribution of temperature, and also prevented runs being carried out for more than 5 min because of the development of hot spots. Accordingly, when samples were retrieved (often with considerable difficulty) they usually consisted of unevenly heated material, some portions of which had reached equilibrium, whereas other portions consisted of unreacted oxides or intermediate phases. This caused considerable difficulty in the interpretation of X-ray diffraction photographs, which usually consisted of a mixture of phases, mostly unknown, but also including MgO, stishovite and sometimes forsterite, all of which had to be distinguished and identified. Also, it proved very difficult to correlate optical mounts (usually of very small samples from restricted regions) with X-ray diffraction pictures which tended to "average" the phases from a much larger volume.

Despite these difficulties, some progress was made. The system proved much more complex than anticipated. Three new phases, A, B and C, were distinguished on X-ray diffraction photographs, and there were clear indications of the presence of other new phases in addition to those which could be specified. Optical examination of mounts proved difficult owing to small grain size

and heterogeneity. However, three and perhaps four phases in addition to MgO were distinguished. Mean refractive indices could only be estimated approximately. The three defined birefringent phases had mean refractive indices in the vicinity of 1.65, 1.71 and 1.77, respectively. In addition there appeared to be a fourth birefringent phase, with a refractive index close to 1.74. However, because of the presence of MgO (RI also 1.74), recognition of this phase was uncertain.

Identification of A, B and C was accomplished by careful comparison of X-ray diffraction photographs from a large number of runs on materials with different initial compositions. d spacings for these phases are given in table 1. Familiar phases such as talc, serpentine, chondrodite-humite group brucite and the 10Å phase of Sclar and Carrison [7] was not recognized. Apparently these phases are unstable under the P-T conditions used. Our information is insufficient to infer the composition or stability fields of these new phases. However, from a consideration of their synthesis fields, some useful limitations can be assembled.

3. RESULTS

Observed synthesis fields of phases in the system Mg_2SiO_4 - MgO - H_2O are as follows.

3.1. *Phase A*
This phase has a mean refractive index of about 1.65, and a low to medium birefringence. Interplanar d spacings are given in table 1. It is formed readily from mixtures of MgO and silicic acid in the 2:1 (mol) ratio in the pressure range 100-150 kb. At lower pressures, forsterite is often formed from the mixture. In some runs at about 100 kb, forsterite predominated in the hot central regions of the metal strip furnace, whereas phase A predominated in the cooler outer regions. We suspect that phase A is hydrated, and that the temperature in the centre of the furnace was too high to permit it to remain stable. Phase A was not synthesized in any runs on a mixture with an MgO silicic acid ratio of 1:1. Clino-enstatite was always formed instead between 100 and 200 kb. In gels and mixtures with MgO/SiO_2 ratios ranging between 2.5 and 5, only one other probable synthesis of phase A was observed (in a 4/1 gel at 120 kb). This result was anomalous in comparison to other runs. From the preferred synthesis field it appears possible that phase A may have an MgO/SiO_2 ratio in the

Table 1
Interplanar d spacings (Å) of phases A, B and C.

A		B		C	
d	I	d ‡	I	d ‡	I
3.94	5	3.035	1	7.4	1
3.65	3	2.476	3 *	7.0	1
2.99	2	2.230	8	4.79	3 *
2.90	1	2.059	10	4.40	1
2.79	7	1.886	6	2.99	5
2.27	10	1.748	< 1	2.72	8 overlap
2.01	4	1.699	< 1	1.604	2
1.76	3	1.578	2	1.571	5
1.61	1	1.468	2 *	1.440	10
1.54	4	1.448	8 *	1.375	3
1.49	8	1.410	< 1		
		1.376	< 1		
		1.335	< 1		
		1.029	1		
		0.916	1		
		0.845 α_1	1		
		0.840 α_1	1		

Identification of the characteristic reflections of A, B and C was impeded by the presence of other phases. This applies particularly to reflections marked by an asterisk *. These reflections may not belong to the phases specified.
‡ Last figure may not be significant.
I = Estimated relative visual intensity.

vicinity of 3/2 or 2. The mean refractive index indicates a density of about 3.2 g/cm^3 which is substantially higher than other hydrated magnesium silicates.

3.2. *Phase B*
This phase occurred in nearly all runs at pressures above 110 kb. The best yields were from partially dehydrated 3/1 gels, where in some runs it was the most abundant phase (as indicated by X-ray diffraction). Interplanar d spacings for this phase are given in table 1. Phase B was formed in only one run from 2/1 gel (2% H_2O) at a pressure of about 140 kb. Below this pressure forsterite was formed. In the 5/2 and 3/1 gels, phase B sometimes formed at pressures as low as 110 kb. At lower pressures the observed assemblage was forsterite + periclase. In all runs on compositions with MgO/SiO_2 ratios > 2.5 MgO was present together with B. From the preferred synthesis fields it appears that the MgO/SiO_2 ratio of phase B is between 2 and 3.

The state of hydration of phase B is not yet established. It forms readily from gels or oxide mixtures containing from 2-10% of H_2O. However, it was not formed under otherwise similar conditions from a dehydrated gel which contained < 0.5% of H_2O. This could indicate that phase B

is hydrated. On the other hand, reaction rates in the absence of water may have been too slow to permit the formation of B from MgO and Mg_2SiO_4 in the short time available.

The mean refractive index of phase B is higher than 1.70, but it is not clear which of the optically observed high RI phases it corresponds to. There appear to be two possibilities: 1) phase B may be identical with the low birefringent phase having a mean refractive index of about 1.71, or 2) it may be identical with the medium birefringent phase having a mean refractive index of about 1.77. The observational evidence tends to favour the second alternative. It is possible, however, that the high refractive index phase is stishovite which has grown under non-equilibrium conditions, and that phase B corresponds to the lower RI phase. Whichever of these alternatives is correct, the range of refractive indices (1.71-1.77) indicates that phase B has a high density, probably between 3.5 and 3.8 g/cm^3.

3.3. *Phase C*

This phase has been recognized only in runs on gels and oxide mixtures containing $\geqslant 5\%$ H_2O, and with MgO/SiO_2 ratios between 3 and 5. It occurs always as a relatively minor phase and has not been identified optically. Interplanar d spacings are given in table 1C. The low angle reflections suggest it may be a layer lattice mineral, perhaps related to the chondrodite-humite series. The fact that it has only been synthesized from compositions such as water support this inference.

4. DISCUSSION

The possibility that phases of the type x $MgO.SiO_2$ $(x > 2)$ might exist was suggested by the existence of the phase $4MgO.GeO_2$ [8] and by some high P-T experiments by Ringwood and Seabrook [1] on a mixture of MgO with hydrous germania ($MgO/GeO_2 = 2$). These authors found that at 600°C and at pressures up to 90 kb, the mixture crystallized to Mg_2GeO_4 spinel. However, above this pressure the reaction products were found to be $MgGeO_3$ (ilmenite) plus a new phase, believed to be approximately $5MgO.GeO_2$. Accordingly it was inferred that Mg_2GeO_4 spinel was unstable at high pressure and transformed into a denser mixture of phases. We have since checked this interpretation by subjecting a sample of the phase $4MgO.GeO_2$ [8] to a pressure of 170 kb and 1000°C under *dry* conditions. Com-

plete conversion into Mg_2GeO_4 (spinel) + MgO was observed. This indicates that the new phase formed by Ringwood and Seabrook above 90 kb was probably hydrated, and that Mg_2GeO_4 spinel is stable under dry conditions at least to 170 kb. Comparison with the corresponding germanate system accordingly does not support the interpretation of phase B as an anhydrous phase x $MgO.SiO_2$ with $2 < x < 3$. It suggests on the contrary that phases B and C may be hydrated. Nevertheless, the germanate-silicate analogy is not decisive in the present case since phases B and C do not correspond structurally to the germanate phase referred to above. The nature of the new silicate phases can only be finally established with a different type of high P-T apparatus capable of maintaining much higher temperatures for sustained periods than our present apparatus. The existence of phase B with its high density provides an incentive for further investigation. If it should turn out to be anhydrous, then it could be of major importance as a constituent of the earth's mantle. If, on the other hand, it proves to be hydrated, then it could also be of significance in the deep mantle as a high-density host mineral for OH^{-1} ions.

Phase A is also of some significance in connection with research on the olivine-spinel transition. We found previously that whereas forsterite could be readily synthesized by reacting mixtures of MgO and silicic acid at pressures up to about 120 kb at 900°C, neither forsterite nor the new spinel-like phase [5] Mg_2SiO_4 could be formed in this manner at pressures of 150-200 kb (900°C). Bundy (personal communication) has had similar experience. In our experiments, phase A is nearly always synthesized from the 2/1 oxide mixture at pressures greater than about 120 kb. Recently Kawai et al. [3] have reported some high-pressure experiments on mixtures of MgO and SiO_2 at 800°C. At pressures below 150 kb, they synthesized forsterite whereas above 150 kb they claimed to have synthesized Mg_2SiO_4 spinel with a lattice parameter of 8.19Å. From the X-ray diffraction chart which they published we are very doubtful whether their new phase is a spinel. Furthermore the lattice parameter of their "spinel" is in serious disagreement with the concordant results obtained by other workers [3, 9, 10].

We do not know whether the oxide mixture used by Kawai et al. contained any water, but we suspect it might. In our experience, dry mixtures of MgO and SiO_2 at 800°C and under high pressures do not readily react to completion in short runs, but yield principally periclase +

stishovite. If the mixture used by Kawai et al. contained some water then an explanation of their results may be at hand, since the diffraction pattern of their "spinel" bears a strong resemblance to our hydrated phase A.

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