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THE SYSTEM MgF_2–MgO–H_2O

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ABSTRACT. The phase relations in the system MgF_2–MgO–H_2O and the stability field of the compound Mg(OH)F were determined. Limited solid solution of Mg(OH)F in both MgF_2 and $Mg(OH)_2$ exists.

INTRODUCTION

Investigation of the system MgF_2–MgO–H_2O was begun initially as part of a larger study on the stability relations of the humite mineral group. The humites, having the general formula $nMg_2SiO_4 \cdot Mg(F,OH)_2$ where n is 1, 2, 3, or 4, fall within the quaternary system MgF_2–MgO–SiO_2–H_2O. The present system comprises one side of the compositional tetrahedron. This study has demonstrated the existence of an intermediate compound having the composition Mg(OH)F. This compound was postulated by Buckner, Hafner, and Kreidl (1962) from the infrared spectra of hot-pressed MgF_2 and by Messier (ms) as an intermediate phase in the hydrolysis of MgF_2. The limits of solid solution of Mg(OH)F in both MgF_2 and $Mg(OH)_2$ were determined.

EXPERIMENTAL METHODS

The starting materials used in this study were chemically-pure MgO, $Mg(OH)_2$, or MgF_2, or appropriate mixtures of these. Charges of a particular composition (with or without excess water) were placed within either gold, platinum, or silver tubes and sealed with an oxygen-natural gas flame. These capsules were placed within cold-seal rod bombs and held at the required temperature and pressure for periods of time ranging from a few days to several weeks.

The bomb temperatures were recorded and controlled with chromel-alumel thermocouples, which had been calibrated against a standard thermocouple, and are accurate to $\pm$ 10°C. The water pressure was read with Bourdon gauges which had been calibrated against a Heise-Bourdon tube gauge; the pressures stated are accurate to $\pm$ 20 bars. At the end of a run the bombs were quenched in an air blast for about one minute, followed by immersion in water.

The phase assemblages were usually determined with a Norelco X-ray high angle diffractometer using Cu radiation and a Ni filter. Routine phase determination was made at 2° per minute, and precise measurements at 1/4° per minute.

Solid solutions limits were determined by means of shifts of interplanar spacings. Intermediate mixtures between Mg(OH)F and both MgF_2 and $Mg(OH)_2$ were run. The maximum extent of solid solution of Mg(OH)F in MgF_2, at a particular temperature, was determined by noting the composition that showed the maximum displacement of the (220) peak of MgF_2. In a similar manner the displacement of the (110) peak of $Mg(OH)_2$ was used to determine the maximum amount of Mg(OH)F

TABLE 1

Runs within the ternary system MgF_2–MgO–H_2O

Composition in mole % MgF_2	$Mg(OH)_2$	MgO	Excess water	Temperature, °C	Pressure, bars	Time, hrs	Products*
The binary systems MgF_2–H_2O, MgF_2–MgO, and MgO–H_2O							
100	0	0	Yes	400	1000	121.5	S, H
100	0	0	Yes	600	1000	115.5	S, H
100	0	0	Yes	800	1000	88.5	S, H
95	0	5	No	602	1000	101.0	S, P
95	0	5	No	780	1000	101.0	S, P
0	50	50	No	600	1000	96.0	B, P
0	100	0	Yes	600	1000	96.0	B, H
The pseudo-binary join MgF_2–$Mg(OH)_2$							
80	20	0	No	400	1000	200	S(s.s.), SB
60	40	0	No	400	1000	200	S(s.s.), SB
50	50	0	No	400	1000	200	1:1, some B
40	60	0	No	400	1000	200	B(s.s.), SB
20	80	0	No	400	1000	200	B(s.s.), SB
80	20	0	No	600	1000	72	S(s.s.), SB
60	40	0	No	600	1000	72	S(s.s.), SB
40	60	0	No	600	1000	72	B(s.s.), SB
20	80	0	No	600	1000	72	B(s.s.), SB
80	20	0	No	800	1000	96	S(s.s.), P, H
60	40	0	No	800	1000	96	S(s.s.), P, H
40	60	0	No	800	1000	96	S(s.s.), P, H
20	80	0	No	800	1000	96	S(s.s.), P, H
The solid solution relations in the pseudo-binary join MgF_2–$Mg(OH)_2$							
90	10	0	No	500	1000	168	S(s.s.)
80	20	0	No	500	1000	168	S(s.s.), SB
70	30	0	No	500	1000	168	S(s.s.), SB
60	40	0	No	500	1000	168	S(s.s.), SB
95	5	0	No	790	1000	250	S(s.s.)
90	10	0	No	790	1000	250	S(s.s.)
85	15	0	No	790	1000	250	S(s.s.)
80	20	0	No	790	1000	250	S(s.s.)
75	25	0	No	790	1000	250	S(s.s.)
80	20	0	No	790	1000	250	S(s.s.), SB
75	25	0	No	790	1000	250	S(s.s.), SB
5	95	0	No	390	1000	420	B(s.s.)
10	90	0	No	390	1000	420	B(s.s.), SB
20	80	0	No	390	1000	420	B(s.s.), SB
5	95	0	No	606	1000	72	B(s.s.)
10	90	0	No	606	1000	72	B(s.s.)
15	85	0	No	606	1000	72	B(s.s.)
20	80	0	No	606	1000	72	B(s.s.), SB
25	75	0	No	606	1000	72	B(s.s.), SB
The phase relations in the system MgF_2–MgO–H_2O							
35	15	50	No	600	1000	123	S(s.s.), P, S
70	30	0	Yes	600	1000	150	S(s.s.), SB
15	35	50	No	600	1000	124	B(s.s.), P, SB
30	70	0	Yes	600	1000	132	B(s.s.), SB

TABLE 1 (Continued)

Composition in mole % MgF_2	$M(gOH)_2$	MgO	Excess water	Tempera-ture, °C	Pressure, bars	Time, hrs	Products*
The univariant stability curve for Mg(OH)F							
Starting material							
Mg(OH)F			No	775	1000	72	S(s.s.), P, H
Mg(OH)F			No	755	1000	204	SB
Mg(OH)F			No	740	500	114	S(s.s.), P, H
Mg(OH)F			No	725	510	114	SB
Mg(OH)F			No	667	110	120	S(s.s.), P, H
Mg(OH)F			No	646	100	102	SB
Mg(OH)F			No	510	1	24	S(s.s.), P, H
Mg(OH)F			No	493	1	68	SB

* Definition of symbols: S = sellaite, MgF_2; S(s.s.) = sellaite (solid solution), $Mg(F, OH)_2$; P = periclase, MgO; B = brucite, $Mg(OH)_2$; B(s.s.) = brucite (solid solution), $Mg(OH, F)_2$; SB = Mg(OH)F; H = water vapor.

substitution in $Mg(OH)_2$. The limits of solid solution were determined to ± 5 mole percent.

EXPERIMENTAL RESULTS

The various runs and their products are listed in table 1. The results are summarized in the three isothermal ternary sections shown in figures 1, 2, and 3. The pseudo-binary system MgF_2–$Mg(OH)_2$ is presented in figure 4.

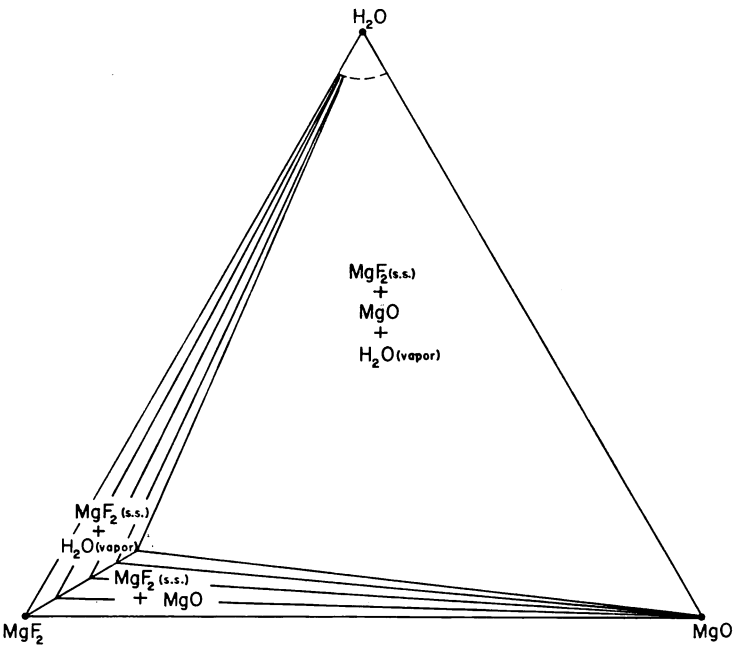

Fig. 1. The system MgF_2–MgO–H_2O at 800°C and 1 kb pressure.

Figure 1 shows an isothermal section at 800°C and 1 kb pressure. It is seen that MgF_2 has a moderately broad compositional range as a result of hydroxyl substitution; this was determined to be about 20 mole percent at this temperature. There appears to be no substitution of either MgO or H_2O in the sellaite structure at this or lower temperatures.

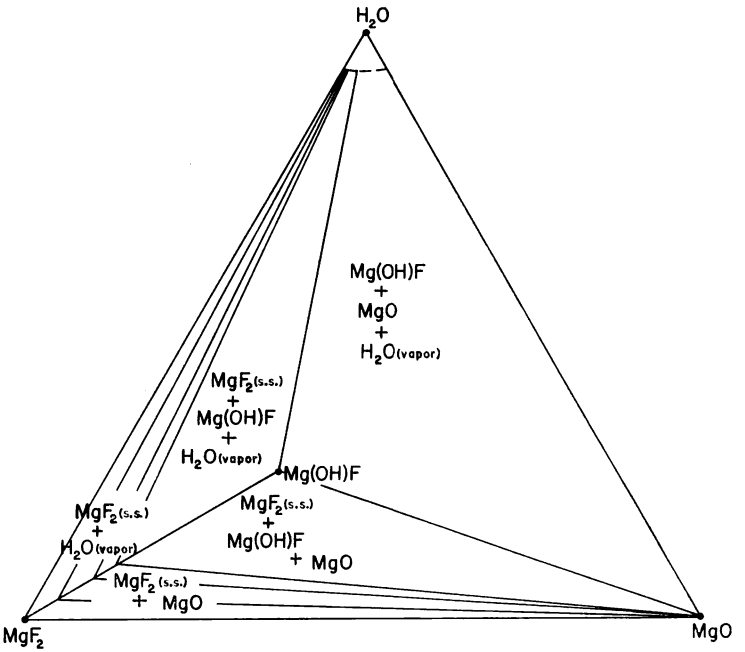

Fig. 2. The system MgF_2–MgO–H_2O at 700°C and 1 kb pressure.

At a temperature of 700°C and 1 kb (fig. 2) the extent of substitution of $Mg(OH)_2$ in the MgF_2 structure is about 17 mole percent. In this section the compound Mg(OH)F is present. This phase was demonstrated to decompose to MgO, H_2O, and MgF_2 (solid solution, s.s.). The reversibility of this reaction was demonstrated at 1 kb; at lower pressures reaction rates were insufficient. The reaction $MgF_2 + H_2O \rightarrow MgO + 2HF$ which occurs at 1 atm, as described by Meisser (ms), is suppressed by pressure.

At 600°C and 1 kb (fig. 3) the amount of solid solution of Mg(OH)F in MgF_2 is decreased to about 15 mole percent. The compound Mg(OH)F remains stable. Brucite, $Mg(OH)_2$, is present; substitution of Mg(OH)F in the $Mg(OH)_2$ structure is possible up to 15 mole percent under these conditions.

The limits of substitution within the MgF_2 and $Mg(OH)_2$ structures are best shown on the 1 kb pseudo-binary join between MgF_2 and $Mg(OH)_2$, figure 4. These limits are indicated by lines with blocks

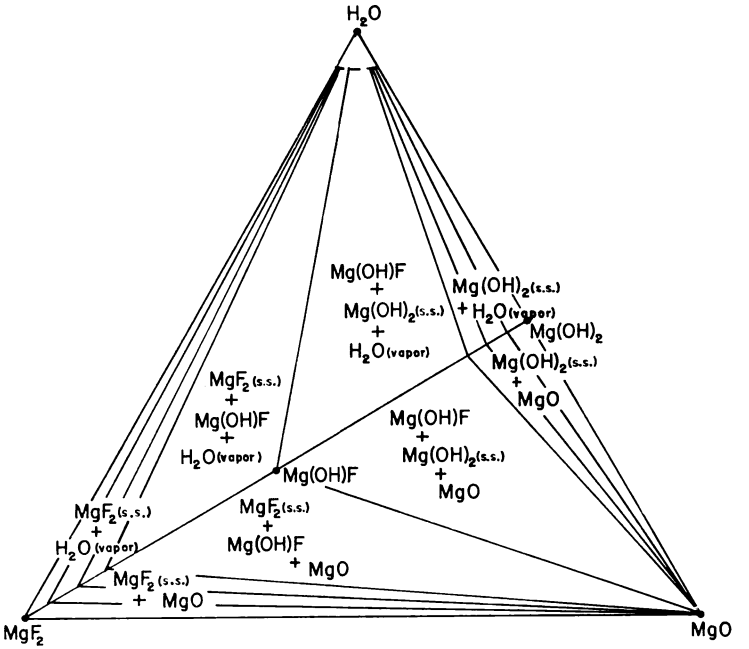

Fig. 3. The system MgF_2–MgO–H_2O at 600°C and 1 kb pressure.

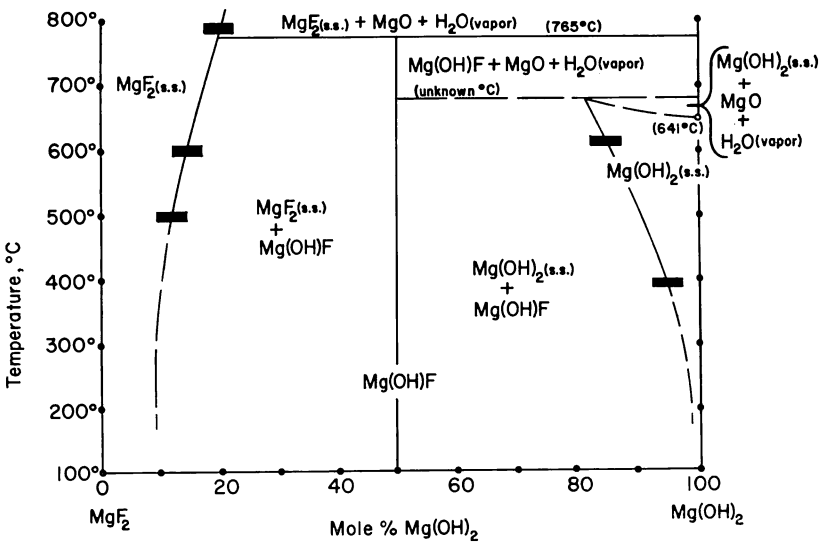

Fig. 4. The pseudo-binary system MgF_2–$Mg(OH)_2$ at 1 kb.

indicating the accuracy of the determined substitutions. The peak shifts for the solid solution of Mg(OH)F in both $Mg(OH)_2$ and MgF_2 is approximately 0.02° 2θ/mole percent of Mg(OH)F. It may be presumed that substitution of Mg(OH)F within the $Mg(OH)_2$ structure will increase its thermal stability over the 641°C dehydration temperature which was determined by Roy and Roy (1957); therefore, although not experimentally determined, the stability of brucite is shown to increase slightly with increasing substitution.

The decomposition curve of the compound Mg(OH)F was determined in some detail and is shown in figure 5. Upon heating this compound decomposes to form MgF_2 (s.s.), MgO, and H_2O. The X-ray diffraction data for Mg(OH)F are shown in table 2. Indexing was unsuccessful, probably because of an insufficient number of reflections. Optical examination revealed that Mg(OH)F is biaxial, with a 2V of 60°. The indices of refraction are $\alpha = 1.465$, $\beta = 1.467$, and $\gamma = 1.473$; all measurements are accurate to $\pm$ 0.001. Dispersion is strong, with v > r. The habit is somewhat platy, parallel to X and Y. Twinning is either polysynthetic (with a maximum angle of Z to the composition plane of 30°) or sector (with alternate 30° and 60° angles between intersecting com-

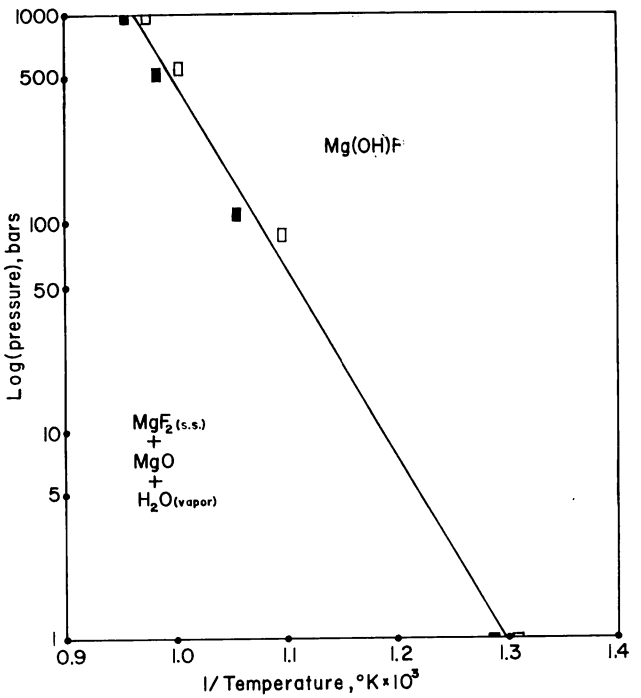

Fig. 5. The univariant stability curve for Mg(OH)F plotted as log (pressure) as a function of 10^3/temperature. All black squares indicate that the reaction products were MgF(s.s.), MgO, and H_2O. All white squares indicate the reaction product was Mg(OH)F.

position planes). The crystal system could not be determined by either X-ray diffraction or optical techniques. Infrared analyses of the compound were performed on a Perkin-Elmer no. 225 Grating Spectrophotometer. The sample was prepared by mixing in KBr and CsI pellets. Absorption peaks were present at 2.80, 2.94, 10.6, and 13.8 μ. The lower two values correspond to characteristic OH stretching vibrations.

TABLE 2

X-ray diffraction data for Mg(OH)F

d(Å)	I/Io
4.25	100
2.736	24
2.494	24
2.293	40
2.226	28
2.046	6
1.750	35
1.719	27
1.591	13
1.540	8
1.480	13
1.448	6
1.418	7
1.382	8
1.343	6
1.330	1
1.288	2
1.266	2

Radiation used was CuK_{α_1}

CONCLUSIONS

This study demonstrates the existence of limited amounts of substitution of hydroxyl ions in MgF_2 and fluorine ions in $Mg(OH)_2$. The appearance of the new compound Mg(OH)F is surprising in light of the fairly common occurrence of the other phases of this system in both natural and synthetic environments. The chemically analogous compound Mg(OH)Cl has been known for many years in the hydrolysis of $MgCl_2$ (Glasner and Mayer, 1961) and the chlorination of periclase in the presence of water (Pechkovskii and Kostin, 1964).

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