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THE SYSTEM $MgO\text{-}GeO_2\text{-}H_2O$

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ABSTRACT

Compatibility relations within the system $MgO\text{-}GeO_2\text{-}H_2O$ have been investigated by hydrothermal synthesis. While no germanium-hydroxyl analogs of the humite minerals were found, a new compound, $Mg_4GeO_6 \cdot Mg(OH)_2$, alters previously reported tie-lines in the system.

The system $MgO\text{-}GeO_2\text{-}H_2O$ was examined as part of a larger study involving stability relations of the humite minerals in the systems $MgO\text{-}GeO_2\text{-}MgF_2$ and $MgO\text{-}SiO_2\text{-}MgF_2$. This system was briefly examined by Roy and Roy (1954) as part of a study on synthetic serpentines. They found the system $MgO\text{-}GeO_2\text{-}H_2O$ to be somewhat analogous to the system $MgO\text{-}SiO_2\text{-}H_2O$, studied earlier by Bowen and Tuttle (1949), Roy, Roy and Osborn (1953) and more recently by Greenwood (1963).

The boundary system $MgO\text{-}GeO_2$ was examined by Robbins and Levin (1959), who found it to be partially analogous to the system $MgO\text{-}SiO_2$,having definite areas of immiscibility, and two intermediate compounds Mg_2GeO_4 and $MgGeO_3$. The compound Mg_2GeO_4 was reported to have a congruent melting point at 1855±30°C, and $MgGeO_3$ a congruent melting point at 1700±20°C. The 1:1 germanate was found to exist in two modifications. The low temperature orthorhombic form stable below 1555°C, is isostructural with entsatite, and the higher temperature monoclinic polymorph probably is isostructural with clinoenstatite. Unlike $MgSiO_3$, which melts incongruently at 1557°C, (Bowen and Anderson, 1914), $MgGeO_3$ melts congruently at 1700±20°C. The compound Mg_4GeO_6, synthesized by Robbins and Levin (1959), dissociates at 1495±10°C to periclase and germanium forsterite and has no analogous compound in the silicates.[2] Conversely, no protoenstatite phase of the 1:1 germanate was observed. Koelmans and Verhagen (1959) synthesized what might be an additional polymorph of $MgGeO_3$; their diffraction pattern did not correspond to the metagermanates of Robbins and Levin.

The 2:1 orthogermanate exists in two crystalline modifications having

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[2] Attempts by the present authors to synthesize this compound in the silicate system, utilizing a Belt apparatus at 600°C and 50 kbars, and a shear squeezer at 500°C and 30 kbars produced only MgO and Mg_2SiO_4.

spinel and forsterite structures (Goldschmidt 1931). Dachille and Roy (1960) have determined the P-T curve relating germanium spinel to germanium forsterite. The olivine structure is converted to the denser spinel at about 806°C at atmospheric pressure and at 840°C at 20,000 psi.

Roy and Roy (1954) performed the only experimental work on the ternary system MgO-GeO$_2$-H$_2$O. They reported the synthesis of three ternary compounds—germanium serpentine ($Mg_3Ge_2O_5(OH)_4$), germanium talc ($Mg_3Ge_4O_{10}(OH)_4$) and germanium anthophyllite ($Mg_7Ge_8O_{22}(OH)_2$). Phase equilibrium relations in the system were presented as a series of compatibility triangles from about 450 to 600°C at 10,000 psi. Their data shows germanium serpentine decomposing at 520±15°C to germanium spinel, germanium anthophyllite, and H$_2$O. Germanium talc is reported to decompose at about 600°C to germanium anthophyllite, "x", and H$_2$O. The compound "x" is reported as an unknown phase in the border system MgO-GeO$_2$.

Procedure

Most of the experiments performed in this study used standard Stellite cold seal reactor vessels (Tuttle, 1949) and either a Tem-Press Model HR-11304 four-unit pressure-temperature system, or equivalent. The samples, either with or without an excess of water, were sealed in Pt or Au tubes, which were placed within the reactor vessels. The vessels were brought to temperature in a nichrome-wound furnace; the desired water pressure

Table 1. Compositions in the System MgO-GeO$_2$-H$_2$O

No.	Mixed Crystalline Phases	Mole percent		
		MgO	GeO$_2$	H$_2$O
1	$6MgO+8GeO_2+3Mg(OH)_2$	45.00	40.00	15.00
2	$3Mg_4GeO_6+Mg(OH)_2$	76.47	17.65	5.88
3	$Mg_4GeO_6+Mg(OH)_2$	71.43	14.29	14.29
4	$Mg_4GeO_6+4Mg(OH)_2$	61.54	7.96	30.77
5	$12MgO+2GeO_2+Mg(OH)_2$	81.25	12.50	6.25
6	$6MgO+2GeO_2+Mg(OH)_2$	70.00	20.00	10.00
7	$2Mg_2GeO_4+Mg(OH)_2$	62.50	25.00	12.50
8	$Mg_2GeO_4+Mg(OH)_2$	60.00	20.00	20.00
9	$3GeO_2+Mg_4GeO_6+2Mg(OH)_2$	50.00	33.33	16.67
10	$4MgGeO_3+2GeO_2+Mg(OH)_2$	41.67	50.00	8.33
11a	$2MgO+4GeO_2+Mg(OH)_2$	37.50	50.00	12.50
11b	$2MgGeO_3+2GeO_2+Mg(OH)_2$	37.50	50.00	12.50
12	$6MgO+8GeO_2+Mg(OH)_2$	43.75	50.00	6.25
13	$MgGeO_3$	50.00	50.00	—
14	$2GeO_2+Mg(OH)_2$	25.00	50.00	25.00
15	$6MgO+12GeO_2+Mg(OH)_2$	38.00	60.00	5.00
16	$2MgO+8GeO_2+5Mg(OH)_2$	35.00	40.00	25.00

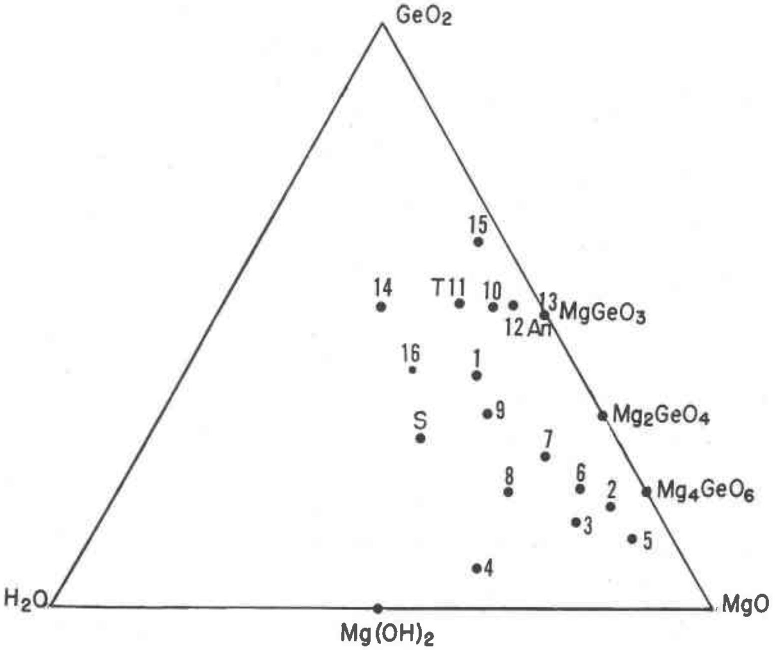

FIG. 1. Compositions in the system MgO-GeO_2-H_2O (S = serpentine; T = talc; An = anthophyllite).

for the reactor vessels was achieved by a small air pressure pump. The sealed sample tubes collapsed until the fluid pressure within was equivalent to the water pressure applied to the reactor.

Sample temperatures were measured by placing either a Pt-Pt 10 percent rhodium, or chromel-alumel thermocouple in a small well in the reactor vessel about $\frac{1}{10}$ of an inch from the sample. The precision is ±15°C.

Compositions used in this study are given in Table 1 by number, mole percent of MgO, GeO_2 and H_2O, and by the crystalline phases present in the mixture. Attainment of equilibrium is difficult in many silicate and germanate systems; this may result from the very rapid formation and presistence of metastable phases from highly reactive starting materials (Fyfe, 1960); or alternatively, other synthesis reactions may involve such low free energy changes that reactions do not take place in experimentally reasonable lengths of time. A compromise between these two extremes must be reached in the selection of the starting materials. In this system, mixtures of fine-grained, crystalline phases were employed. As indicated in Table 1, Mg_4GeO_6, Mg_2GeO_4 (germanium forsterite), $Mg(OH)_2$ and $MgGeO_3$ (germanium enstatie) are components of many mixtures. Although the reaction rates of these materials are slower than the more commonly-used unstable gels and glasses, a closer approach to equilibrium can be demonstrated. The reactant compositions are plotted in Figure 1, the composition triangle MgO-GeO_2-H_2O.

The products were identified by X-ray diffraction, as the phases were almost always too fine-grained for optical examination. The sample mounts for routine examination were prepared by packing the powder into a depression on a glass slide. Samples were examined with a Norelco high-angle X-ray diffractometer using Cu radiation and a Ni filter. For ordinary determinations, the scanning speed was 1° 2θ per minute, and for precise work $\frac{1}{8}$° 2θ per minute with a chart speed of four inches per minute.

EXPERIMENTS

More than forty hydrothermal runs were made at three temperatures —470, 570 and 670°C at about 689.5 bars (10,000 psi). Reactions in this study were examined initially in order to determine whether hydroxyl-germanium members of the humite group could be synthesized. It was soon apparent that humites cannot be synthesized under these experimental conditions. Reaction products included a new compound in the system in addition to the expected germanium analogs. Reaction data are tabulated in Table 2.[1] Products and equilibrium relations are summarized in the two compatibility triangles shown in Figure 2.

Reactions at 670°C indicate the presence of an unreported compound $Mg_4GeO_6 \cdot Mg(OH)_2$. This compound forms easily when spinel and brucite, or Mg_4GeO_6 and brucite mixtures are reacted. Compositions in the vicinity of $Mg_4GeO_6 \cdot Mg(OH)_2$, when reacted, indicated the presence of compatibility lines between this compound and H_2O, Mg_2GeO_4 (spinel), Mg_4GeO_6 and MgO.

The compound $Mg_4GeO_6 \cdot Mg(OH)_2$ is usually too fine-grained for optical characterization. Electron micrographs show most particles considerably less than 1μ in diameter, sometimes having hexagonal outlines. Particles large enough for optical examination have low first-order birefringence with indices that fall between 1.725 and 1.731 (white light). The particles have a high density of anhedral to subhedral inclusions, with polysynthetic twinning occasionally observed. Uniaxial optical-character could not be demonstrated.

X-ray diffraction data is presented in Table 3. The pattern was corrected with a high-purity silicon internal standard. Electron diffraction of hexagonal or pseudo-hexagonal platlets gave an apparent (0001) centered pattern but graphical indexing on both hexagonal and tetragonal cells was unsuccessful. After 1000 hours, at 670°C (10,000 psi), particles were still too fine for single crystal methods. Attempts to synthesize larger crystals are continuing.

Other runs at 670°C produced no other ternary compounds, and indicated that $MgGeO_3$ (enstatite) and Mg_2GeO_4 (spinel) are stable in the presence of excess water. Roy and Roy (1954), at temperatures above

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[1] To obtain a copy of Table 2, order NAPS Document #00711 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $1.00 for microfiche or $3.00 for photocopies, in advance, payable to ASIS-NAPS.

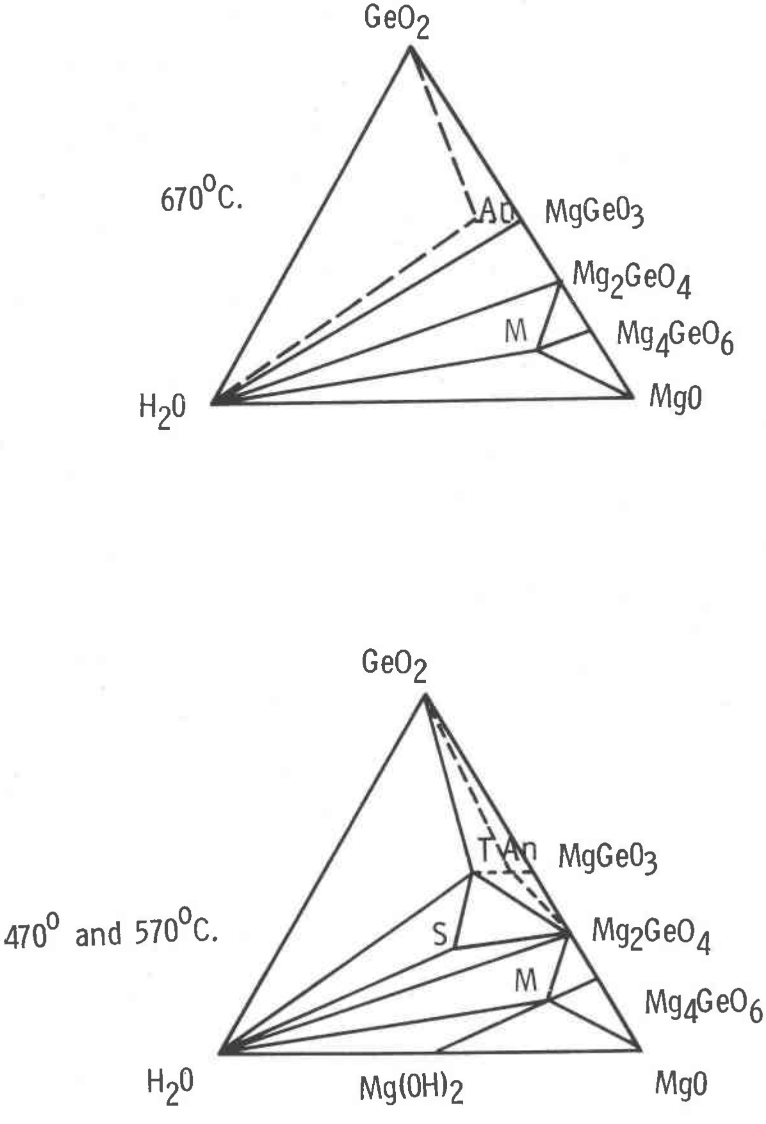

FIG. 2. Equilibrium relations in the system MgO-GeO_2-H_2O.
($M = Mg_4GeO_6 \cdot Mg(OH)_2$)

600°C, synthesized spinel, anthophyllite and the compound "x" (lying in composition between $MgGeO_3$ and GeO_2). Neither anthophyllite not "x" were synthesized under any *P-T* conditions in this study. The lack of synthesis of anthophyllite is not surprising in view of the difficulty in

TABLE 3. X-RAY DIFFRACTION DATA FOR $Mg_4GeO_6 \cdot Mg(OH)_2$

d(obs)	I[a]	d(obs)	I[a]
7.085	100	2.081	27
4.470	61	2.049	5
4.175	31	2.033	3
3.777	6	2.018	2
3.490	33	1.905	22
3.275	6	1.872	16
3.041	11	1.799	11
2.925	2	1.775	6
2.899	3	1.740	3
2.777	41	1.656	3
2.743	80	1.649	17
2.705	83	1.6176	5
2.581	11	1.6048	8
2.567	36	1.5917	13
2.508	25	1.5532	8
2.489	33	1.5050	8
2.443	8	1.4786	24
2.414	6	1.4599	64
2.341	6	1.4207	3
2.266	13	1.3974	16
2.257	33	1.2320	8
2.218	5	1.1960	22

[a] Height above baseline relative to the strongest peak.

nucleation and growth of the silicon anthophylilte, as seen by the studies of Bowen and Tuttle (1949) and Greenwood (1963). If anthophyllite exists stably in this system at 670°C, its compatibility relations with other phases in the system may be as indicated by the dashed lines in Figure 2.

At 550°C, $Mg_4GeO_6 \cdot Mg(OH)_2$ is stable. Similar compatibility relations are present, with the addition of a tie line to brucite, which exists stably at this pressure and temperature. Roy and Roy (1954) indicate coexistence of spinel and brucite, whereas in this study, crystalline forsterite and brucite held at 600°C at 15,000 psi, and 610°C at 19,000 psi, react to form spinel, $Mg_4GeO_6 \cdot Mg(OH)_2$ and H_2O. No tie line is present between Mg_2GeO_4 and brucite.

The talc composition at 570°C produces talc, $MgGeO_3$, and tetragonal GeO_2 from mixtures of $Mg(OH)_2$, GeO_2 and MgO, or mixtures utilizing $Mg(OH)_2$, GeO_2 and $MgGeO_3$ as reactants. Talc is indicated as stable in study of Roy and Roy.

It appears that at and below 570°C, $MgGeO_3$ may not be stable.

Mixtures near the composition $MgGeO_3$ crystallize other phase assemblages in preference to $MgGeO_3$; $MgGeO_3$ is not indicated on the diagram of Roy and Roy (1954) as their runs were all made with excess water, and the possible stable area of $MgGeO_3$ was covered by more hydrated phases up to at least 600°C. As $MgGeO_3$ has not been demonstrated to decompose at these temperatures and pressures, the inferred lack of stability of $MgGeO_3$ is necessarily conjectural.

Also found at and below 570°C is serpentine. Roy and Roy (1954) state a dissociation temperature of 520 ± 15°C for the Ge serpentine. As the temperatures in this system are read and calibrated to ±15°C or better, no comparison with their data is possible. It should be noted that neither formation nor non-formation of a phase from a batch of unstable reactants proves equilibrium. The dissociation temperature of the serpentine should be further examined.

Examination of the system at 470°C yielded the same compatibility relations as observed at 570°C. No additional phases were observed.

CONCLUSIONS

The system MgO-GeO_2-H_2O is analogous to the system MgO-SiO_2-H_2O in having structures analogous to serpentine, talc, enstatite, olivine, stishovite and quartz. In addition, both systems do not contain any of the humite-type minerals; apparently some MgF_2 is necessary in place of $Mg(OH)_2$ for successful synthesis. Anthophyllite is difficult to synthesize in both systems. The phases Mg_4GeO_6 and $Mg_4GeO_6 \cdot Mg(OH)_2$ have no known silicate analogs.

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