

Stability Relations of $K_2Mg_5Si_{12}O_{30}$, and End Member of the Merrihueite-Roedderite Group of Meteoritic Minerals

F. SEIFERT and W. SCHREYER

Institut für Mineralogie der Ruhr-Universität, Bochum, Germany

Received February 24, 1969

Abstract. The phase $K_2Mg_5Si_{12}O_{30}$ was synthesized both hydrothermally and dry under a variety of pressures and temperatures, and its stability relations were determined. Under hydrothermal conditions it exhibits a lower stability limit lying at 595°C, 1 kb, and 650°C, 2 kb, due to its breakdown into the hydrous assemblage quartz + $KMg_{2.5}Si_4O_{10}(OH)_2$ (a mica phase). Its upper temperature stability under hydrothermal conditions is given by its incongruent melting to $MgSiO_3$ + liquid. Near 820°C at a fluid pressure of approximately 6.5 kb the two univariant curves for these breakdown reactions intersect thus limiting the stability field to lower fluid pressures. — Under anhydrous conditions $K_2Mg_5Si_{12}O_{30}$ becomes unstable at pressures between approximately 7 and 32.5 kb due to its incongruent melting to the assemblage $MgSiO_3$ + quartz (or coesite) + liquid; this melting curve has a pronounced negative slope. No subsolidus breakdown assemblage was encountered at 32.5 kb down to temperatures as low as 750°C. This behavior is probably due to the instability of other ternary compounds in the system K_2O - MgO - SiO_2 at high pressures and thus to the existence of very low-temperature eutectics involving only binary and unary solid phases plus liquid. It is likely that these stability relations provide a model for those of the natural minerals merrihueite and roedderite which contain Na and Fe^{+2} partly substituting for K and Mg and which were encountered in several meteorites. Therefore, the cosmic events leading to the formation of these minerals must have taken place at relatively low pressures and high temperatures, especially when water was present. The bulk compositions of these minerals appear to be incompatible with average chondritic matter under equilibrium conditions. Hence merrihueite and roedderite are not likely to be found in equilibrated chondrites which contain feldspars instead.

Previous Work

The minerals of the merrihueite-roedderite group have only recently been discovered in nature as rare silicate phases of meteorites. Whereas merrihueite (DODD, VAN SCHMUS and MARVIN, 1965) with an overall composition of $(K, Na)_2(Fe, Mg)_5Si_{12}O_{30}$ is rich in potassium and ferrous iron, sodium and magnesium predominate in roedderite, $(Na, K)_2(Mg, Fe)_5Si_{12}O_{30}$ (FUCHS, FRONDEL and KLEIN, 1966). Thus the general formula of the whole group may be given as $R_2^{+1}R_5^{+2}Si_{12}O_{30}$, in which $R^{+1} = K, Na$ and $R^{+2} = Mg, Fe$.

With these cations four possible end members may be distinguished, at least two of which have already been synthesized in earlier experimental investigations of the requisite silicate systems: The pioneering work was done in the system K_2O - MgO - SiO_2 by ROEDDER (1951) who first synthesized $K_2Mg_5Si_{12}O_{30}$ and clarified the unusual oxide ratio 1:5:12 of this compound on the basis of its liquidus relationships. In a subsequent study of the system Na_2O - MgO - SiO_2 the synthesis of an analogous phase $Na_2Mg_5Si_{12}O_{30}$ was reported by SCHAIRER, YODER and KEENE (1954). On the other hand ROEDDER (1952) did not succeed in synthesizing the KFe end member in the system K_2O - FeO - SiO_2 , and there

are not enough experimental data available for the system $Na_2O-FeO-SiO_2$ to state the presence or absence of a phase $Na_2Fe_5Si_{12}O_{30}$. A preliminary liquidus diagram of that system (SCHAIRER, YODER and KEENE, 1954) shows only "several fields" in the area where the primary liquidus field of such compound would be expected. Synthetic solid solutions between the NaFe and NaMg end members were, however, described by ERNST (1960) as breakdown products of magnesioriebeckite, $Na_2Mg_3Fe_2^{+3}Si_8O_{22}(OH)_2$ at high temperatures and low water pressures.

In the present investigation the stability of the end member $K_2Mg_5Si_{12}O_{30}$ was studied for the first time both dry and hydrothermally under high confining pressures. It will be shown that the shape of the stability field of this compound under hydrothermal conditions is probably characteristic for all phases of this mineral group.

Structural Relationships

A close structural relationship of the synthetic 1:5:12 phases with osumilite, $(K, Na, Ca)(Mg, Fe^{+2})_2(Al, Fe^{+3}, Fe^{+2})_3(Si, Al)_{12}O_{30} \cdot H_2O$, (MIYASHIRO, 1956) was recognized by SCHREYER and SCHAIRER (1962). Recently SCHREYER and SEIFERT (1967) synthesized an end member osumilite with the composition $KMg_2Al_3[Si_{10}Al_2O_{30}] \cdot xH_2O$. Thus the main compositional differences between osumilites and the merrihueite-roedderite minerals are the lack of alumina and the higher alkali contents of the latter, although most recently even a slightly aluminous roedderite was described by OLSEN (1967a).

According to MIYASHIRO (1956) the structure of osumilite is built of hexagonal $(Si, Al)_{12}O_{30}$ double rings that are linked to each other by the small cations in fourfold and sixfold coordination as well as by the large 12-coordinated cations that are situated within the stacks of double rings. The space inside the double rings is apparently occupied by molecular water. The osumilite structure is related to the cordierite structure through the fact that the latter contains six-membered single rings rather than double rings.

Simple comparison of the cation contents of osumilite and merrihueite-roedderite indicates that the two minerals cannot be strictly isostructural. There is an additional large alkali atom per formula unit in merrihueite-roedderite, which according to a suggestion of SCHREYER and SCHAIRER (1962) might take the place of water in osumilite, i.e. occupy the space inside the double rings. However, there are indications from natural material (OLSEN, 1967a) as well as from synthetic work (unpublished data of the authors in the system $Na_2O-MgO-SiO_2$), that the structure can accommodate even more than two large cations. It is suspected, therefore, that the basic osumilite framework may contain additional positions that are so far unrecognized.

Experimental Methods

The starting material for the synthesis of $K_2Mg_5Si_{12}O_{30}$ was a powder mix of the requisite composition consisting of crystallized glass of the composition $K_2O \cdot 12SiO_2$, and MgO . The glass had previously been prepared from K_2CO_3 and natural quartz following the directions given by SCHAIRER and BOWEN (1956). In addition to the powder mix glass of the composition $K_2O \cdot 5MgO \cdot 12SiO_2$ was also available, but no difference in the behavior of the two starting

materials were recognized. For breakdown experiments previously crystallized $K_2Mg_5Si_{12}O_{30}$ was used.

Most hydrothermal runs were performed in standard cold-seal bombs. However, for the determination of the upper stability limit the internally heated pressure vessel of Dr. H. S. YODER, Jr., at the Geophysical Laboratory, Washington, D.C., was used.

High pressure runs in excess of 10 kb were made in a solid media piston-cylinder-type apparatus available at Ruhr-Universität, Bochum. Pressure was calibrated by the Bi I—II transition using a value of 25,499 kb (HEYDEMANN, 1967). Piston-out runs were made exclusively. No corrections for friction or for emf-changes in the thermocouple (Pt-Pt₁₀Rh) under pressure were applied.

Description of Synthetic $K_2Mg_5Si_{12}O_{30}$

In hydrothermal runs a dependence of the crystal morphology of $K_2Mg_5Si_{12}O_{30}$ on the experimental conditions was observed. At the lowest pressures (< 1 kb) and temperatures (< 650°C) at which the phase was synthesized it usually formed long, essentially prismatic crystals with irregular terminations. In the range 1—2 kb and 600—900°C predominantly lens-shaped crystals were encountered, which frequently contained voids aligned and elongated in well-defined crystallographic planes such as the prism faces. Mostly short prisms with well-developed terminal faces appeared at still higher pressures. Runs under anhydrous conditions yielded intimately intergrown aggregates of anhedral crystals typical of devitrification products.

The crystals synthesized are uniaxial positive with $\omega = 1.545 \pm 0.002$ and $\varepsilon = 1.550 \pm 0.002$. These refractive indices are identical, within experimental error, with those determined by ROEDDER (1951) on $K_2Mg_5Si_{12}O_{30}$ synthesized in the anhydrous system. In contrast to the structurally similar phase Mg-cordierite (SCHREYER and YODER, 1964) no variations of the refractive indices with pressure and temperature conditions of hydrothermal synthesis could be observed. It is thus expected that molecular water does not, as in the case of Mg-cordierite, enter the structure of $K_2Mg_5Si_{12}O_{30}$. The most likely explanation for this behavior is that the channels parallel to *c*, possibly including the space inside the double rings, are occupied by the large K ions.

The x-ray powder diffraction data of the hydrothermally synthesized $K_2Mg_5Si_{12}O_{30}$ (Table 1) do not differ appreciably from those given by ROEDDER (1951) for the phase obtained in the anhydrous system. However, in addition to the lines already tabulated by ROEDDER (1951) 24 new ones could be identified in the present study. All these reflections can be fitted to a hexagonal unit cell. Its cell dimensions calculated from the measured d-values and refined by the least-squares method are

$$\begin{aligned} a_0 &= 10.220 \pm 0.001 \text{ \AA} \\ c_0 &= 14.149 \pm 0.002 \text{ \AA} \end{aligned}$$

A lattice constants refinement on the basis of the d-values given by ROEDDER (1951) for the phase made in the dry system yielded these same values within the limits of error.

Systematic extinctions of h0l- and hhl reflections with $l = 2n + 1$ are indicative — as in all minerals with osumilite-type structure — of the two possible space groups P6/mcc and P6cc (MIYASHIRO, 1956).

An attempt was made to use the intensities of the basal reflections (001) in order to determine whether or not the site inside the double rings with the

Table 1. X-ray powder diffraction data of $K_2Mg_5Si_{12}O_{30}$ prepared from glass at 800° C, $P_{H_2O} = 1000$ bars, 15 hours. The cut-off was at $6^\circ 2\theta$. For comparison, the data of ROEDDER (1951) for $K_2Mg_5Si_{12}O_{30}$ prepared in the anhydrous system are given

hkl	$2\theta_{obs}$	λ	d_{obs}	d_{calc}	I/I ₀	d_{obs} (ROEDDER)
002	12.500	CuK α	7.082	7.0743	89	7.12
102	16.015		5.533	5.5260	2	5.54
110	17.330		5.116	5.1100	18	5.13
200	20.045		4.429	4.4254	39	4.43
112	21.440		4.145	4.1424	18	4.14
202	23.700		3.754	3.7518	48	3.74
004	25.140		3.542	3.5371	100	3.53
210	26.625		3.348	3.3453	4	—
104	27.145		3.285	3.2846	31	—
211	27.385		3.257	3.2555	81	3.25
212	29.530		3.025	3.0242	2	—
300	30.285		2.951	2.9503	3	—
114	30.730		2.910	2.9084	84	2.90
204	32.390		2.764	2.7630	50	2.76
213	32.810		2.730	2.7286	14	—
220	35.110		2.556	2.5550	20	2.55
310	36.610		2.454	2.4547	6	2.456
214	36.960		2.432	2.4305	1	—
311	37.155	2.420	2.4186	6	2.415	
006	38.145	2.359	2.3581	6	—	
312	38.800	2.321	2.3191	1	—	
106	39.525	CuK α_1	2.278	2.2786	3	—
304	39.760		2.265	2.2656	4	2.266
313	41.445		2.177	2.1775	11	2.175
402	42.790		2.111	2.1118	7	2.113
206	43.450		2.081	2.0811	4	—
224	43.650		2.072	2.0712	4 B	2.072
320	44.590		2.030	2.0305	3	—
314	44.920		2.016	2.0167	12	2.016
322	46.495		1.9515	1.9517	1	—
410	47.015		1.9311	1.9314	3	—
411	47.475		1.9135	1.9137	8	1.914
404	48.490		1.8758	1.8759	1	—
412	48.850		1.8628	1.8632	2	—
315	49.100		1.8539	1.8543	19	1.852
306	49.435		1.8421	1.8420	2	—
413	51.055		1.7874	1.7873	1	—
008	51.655		1.7681	1.7686	41	1.765
226	52.790		1.7326	1.7329	14	1.731
330	53.775		1.7031	1.7033	2	—
414	54.050		1.6952	1.6952	3	1.696
118	54.885		1.6713	1.6713	2	1.669
421	55.245		1.6613	1.6611	1 B	—
208	55.950		1.6420	1.6423	3	1.640
422	56.480		1.6272	1.6278	1 B	—
406	57.020	1.6137	1.6136	1 B	—	
415	57.750	1.5951	1.5952	1 B	—	
511	58.375	1.5795	1.5797	6	1.578	
317	59.180	1.5599	1.5604	1	—	
512	59.570	1.5506	1.5510	1	—	

B = broad reflection.

coordinates 0,0,0 may be filled with K. Unfortunately this attempt failed due to the impossibility of measuring enough basal reflections using the powder method. Thus a clarification of this problem can only be expected from a structure determination on single crystals.

In Table 2 the unit cell dimensions of some natural and synthetic minerals of the merrihueite-roedderite group are compiled. The phase $K_2Mg_5Si_{12}O_{30}$

Table 2. Comparison of lattice constants of natural and synthetic phases within the roedderite — merrihueite group

	a_0	c_0
Merrihueite (DODD, VAN SCHMUS and MARVIN, 1965)	10.16 Å	14.32 Å
Roedderite (FUCHS, FRONDEL and KLEIN, 1966)	10.14	14.28
$K_2Mg_5Si_{12}O_{30}$ (this paper)	10.22	14.15
$Na_2Mg_5Si_{12}O_{30}$ (SEIFERT, 1966, unpublished)	10.15	14.26

differs from the other members of the group in its relatively large a_0 and small c_0 values. From a comparison of the pure synthetic phases $K_2Mg_5Si_{12}O_{30}$ and $Na_2Mg_5Si_{12}O_{30}$ it seems to follow that this extension in a and contraction in c is due to the large K ions whatever their sites. However, the fact that the mineral merrihueite (DODD, VAN SCHMUS and MARVIN, 1965) with $K > Na$ also has a small a_0 and large c_0 value indicates further complexities that can only be approached after the crystal structure of these phases is known more accurately than at present.

In some high pressure experiments under anhydrous conditions outside the stability field of $K_2Mg_5Si_{12}O_{30}$ an observation was made that may be of some crystal chemical interest. When crystalline $K_2Mg_5Si_{12}O_{30}$ was used as a starting material, short runs yielded an optically isotropic phase with a normal osumilite-type powder X-ray pattern in addition to the stable breakdown assemblage enstatite, quartz, and liquid (see later). This isotropic phase is likely to represent a metastable intermediate breakdown product with a composition other than $K_2Mg_5Si_{12}O_{30}$. It is of interest to note that several osumilite-type phases of different bulk compositions were synthesized by the authors (unpublished work) in the related system Na_2O -MgO-SiO₂.

Stability Relations

The crystalline phases encountered in the system K_2O -MgO-SiO₂-H₂O are shown in Fig. 1 in a projection onto the water-free base plane. The miscibility range originating from the composition $K_2O \cdot 5MgO \cdot 8SiO_2 \cdot 2H_2O$ and leading towards more Mg-rich bulk compositions represents a series of solid solutions of a new type of micas first described by SEIFERT and SCHREYER (1965) and, in more detail, by these authors (1969). The three anhydrous phases $K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, and $K_2O \cdot MgO \cdot SiO_2$ already synthesized by ROEDDER (1951) do not exhibit osumilite-type structures but are structural derivatives of leucite, kalsilite, and $K_2O \cdot Al_2O_3$ (carnegieite-type), respectively, to which they are related chemically through simple $MgSi \rightleftharpoons AlAl$ substitutions in each case.

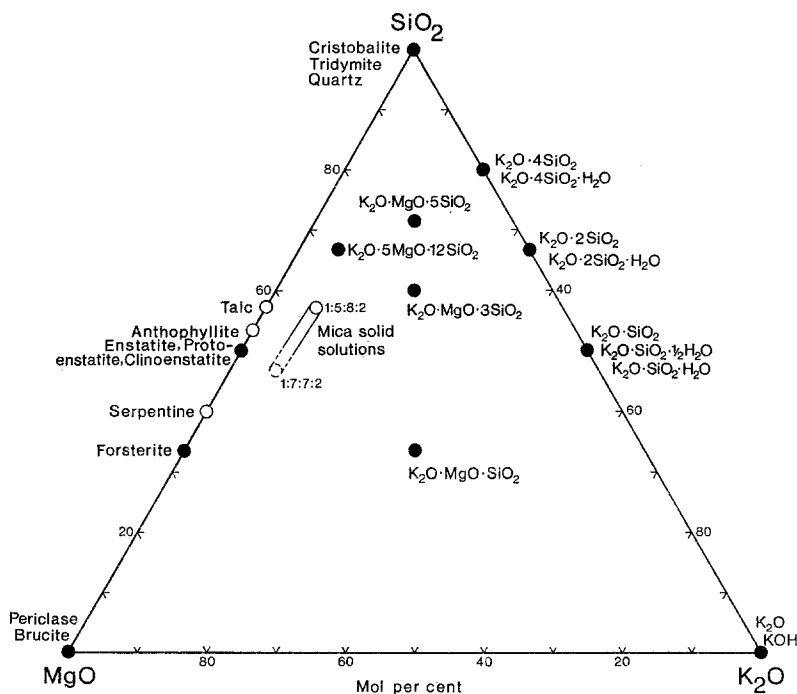


Fig. 1. Projection of important phases in the system K_2O - MgO - SiO_2 - H_2O onto the water-free base plane. Anhydrous phases are indicated by solid dots, hydrated phases by open circles. Compositions of anhydrous ternary phases were taken from ROEDDER (1951), those of the mica solid solution from SEIFERT and SCHREYER (1969). Symbols 1:5:8:2 etc. indicate oxide proportions in the order K_2O : MgO : SiO_2 : H_2O

1. Investigations under Hydrothermal Conditions

The results of some significant hydrothermal experiments are compiled in Table 3. They were used for the construction of the PT diagram of Fig. 2 which displays the stability field of the phase $K_2Mg_5Si_{12}O_{30}$ under the conditions $P_{fluid} = P_{total}$. The lower temperature stability limit is given by the reaction



The hydrous phase on the left side of this equation is the most siliceous end member of the series of mica solid solutions mentioned earlier. The above reaction also marks the upper temperature compatibility limit of this mica with quartz. Reactions in the vicinity of the univariant breakdown curve are relatively sluggish, and metastable assemblages are obtained in short runs over a considerable temperature range. Thus at temperatures above the reaction curve quartz and the mica phase were synthesized first from the glass. Only in longer runs did these two metastable products react further to form $K_2Mg_5Si_{12}O_{30}$. The equilibrium position of the univariant curve was determined on the basis of long runs utilizing also previously crystallized $K_2Mg_5Si_{12}O_{30}$ as a starting material. The breakdown of this phase yielded characteristic pseudomorphs which although

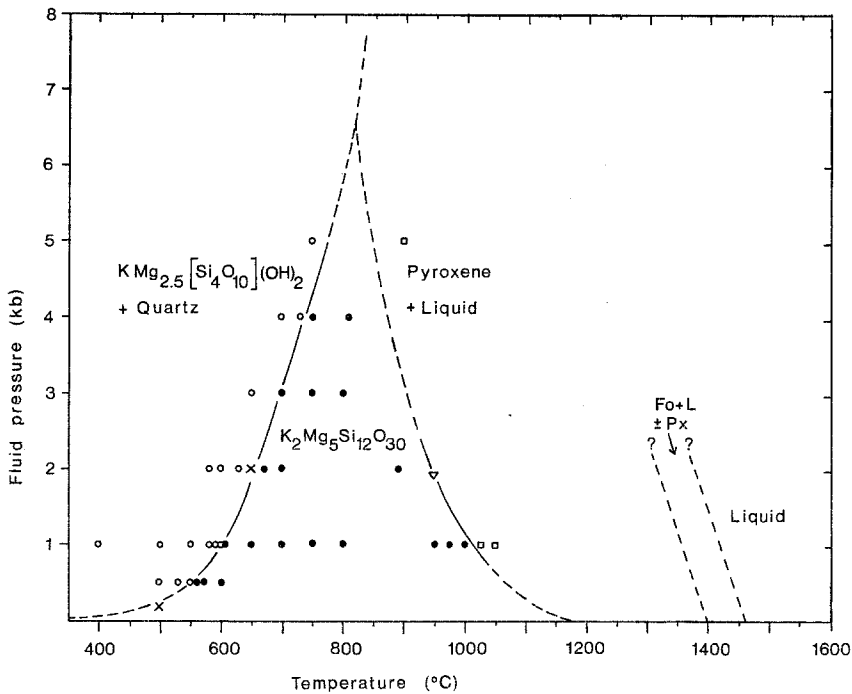


Fig. 2. Pressure-temperature diagram for the composition $K_2O \cdot 5MgO \cdot 12SiO_2 + \text{excess } H_2O$. Each point represents one or several runs. Symbols: open circles = formation of quartz + mica; solid dots = growth of $K_2Mg_5Si_{12}O_{30}$; crosses = no reaction observed; triangle = $K_2Mg_5Si_{12}O_{30} + \text{pyroxene} + \text{liquid}$; open squares = pyroxene + liquid. In all these assemblages a hydrous gas phase or fluid was present in addition. Data at 1 atm. were taken from ROEDDER (1951)

retaining the initial hexagonal shape of the roedderite phase consist solely of an extremely finegrained intergrowth of quartz and mica.

Extrapolation of the low-temperature breakdown curve by means of the integrated Clausius-Clapeyron equation resulted in an equilibrium temperature value of $300 \pm 50^\circ C$ for a water pressure of one bar.

The upper temperature stability limit of $K_2Mg_5Si_{12}O_{30}$ at water pressures at least up to 2 kb is given by its melting curve which shows the negative slope typical for anhydrous silicate phases. Similarly to the melting behavior at 1 atmosphere (ROEDDER, 1951) $K_2Mg_5Si_{12}O_{30}$ was found to melt incongruently to a $MgSiO_3$ pyroxene plus liquid at least up to 2 kb. A further similarity to the anhydrous system is displayed by the crystallization behavior of $K_2Mg_5Si_{12}O_{30}$ glass under hydrothermal conditions. As much as $100^\circ C$ below the incongruent melting curve metastable clinenstatite appears which reacts only slowly with the remaining metastable liquid to form $K_2Mg_5Si_{12}O_{30}$. This observation seems to be of some significance when compared with the stable phase relations of anhydrous $K_2Mg_5Si_{12}O_{30}$ at high pressures (see below). Because of this metastable behavior of glassy starting materials the equilibrium melting curve shown in Fig. 2 is also based on runs using previously crystallized $K_2Mg_5Si_{12}O_{30}$. The run

Table 3. Results of some significant hydrothermal runs on the composition $K_2O \cdot 5 MgO \cdot 12 SiO_2$. Abbreviations. a) Starting materials. Mix = $K_2O \cdot 12 SiO_2$ -glass + MgO, Glass = $K_2O \cdot 5 MgO \cdot 12 SiO_2$ glass, Cryst = crystalline $K_2Mg_5Si_{12}O_{30}$, made from glass at 750° C, $P_{H_2O} = 1$ kb, 20 hours. b) Phases. Q = quartz, mica = mica of composition $KMg_{2.5}Si_4O_{10}(OH)_2$, 1:5:12 = $K_2Mg_5Si_{12}O_{30}$, CE = clinoenstatite, PE = protoenstatite, OE = orthoenstatite, $MgSiO_3$ = undefined pyroxene, L = liquid.

Starting material	Temperature (°C)	Pressure (bars)	Duration (h)	Condensed phases
Mix	500	200	402	Q, mica
Cryst	500	200	402	1:5:12
Glass	550	500	652	Q, mica
Cryst	550	500	652	Q, mica
Glass	560	500	671	1:5:12, trace Q + mica
Glass	570	500	558	1:5:12
Cryst	570	500	558	1:5:12
Mix	550	1,000	408	Q, mica
Cryst	550	1,000	408	Q, mica
Glass	600	1,000	423	Q, mica
Cryst	600	1,000	423	Q, mica, 1:5:12, Q,
Glass	610	1,000	171	1:5:12, Q, mica
Cryst	610	1,000	171	1:5:12
Mix	650	1,000	524	1:5:12
Mix	950	1,000	0.5	CE, L
Mix	950	1,000	4	1:5:12, CE, L
Cryst	975	1,000	2	1:5:12
Mix	1,000	1,000	1	1:5:12, CE, L
Cryst	1,000	1,000	1	1:5:12
Glass	1,025	1,013	1	CE, PE, L
Cryst	1,025	1,013	1	CE, L, trace 1:5:12
Glass	1,050	1,026	1	CE, PE, L
Cryst	1,050	1,026	1	CE, L
Mix	550	2,000	350	Q, mica
Cryst	580	2,000	350	Q, mica
Mix	630	2,000	401	Q, mica
Cryst	630	2,000	401	Q, mica
Glass	650	2,000	355	Q, mica
Cryst	650	2,000	355	1:5:12
Glass	670	2,000	168	1:5:12
Mix	890	2,000	15	1:5:12
Glass	950	1,903	1	1:5:12, trace CE, L
Cryst	950	1,903	1	1:5:12, CE, PE or OE, L
Glass	650	3,000	287	Q, mica
Cryst	650	3,000	287	Q, mica
Mix	700	3,000	262	1:5:12, Q, mica
Cryst	700	3,000	262	1:5:12
Glass	800	3,000	100	1:5:12, Q, mica
Glass	730	4,000	236	Q, mica
Cryst	730	4,000	236	Q, mica, trace 1:5:12
Mix	750	4,000	439	Q, mica, trace 1:5:12 ?
Cryst	750	4,000	439	1:5:12
Glass	770	4,000	73	1:5:12, Q, mica
Mix	810	4,000	5	1:5:12, Q, mica
Cryst	810	4,000	5	1:5:12
Mix	750	5,000	73	Q, mica
Cryst	750	5,000	73	Q, mica
Glass	900	5,000	2	$MgSiO_3$, mica, Q, L
Cryst	900	5,000	2	$MgSiO_3$, mica, Q, L

performed at 1903 bars and 950°C has apparently fallen on the curve within experimental error.

At higher water pressures the interpretation of the experimental results becomes more difficult due to the appearance of quench products. In the run made at 5 kb, 900°C, $K_2Mg_5Si_{12}O_{30}$ broke down completely to mica, quartz, and very coarse, long (> 1 cm) prisms of a pyroxene similar to protoenstatite but with obvious displacement of X-ray diffraction peaks. It is possible that not only quartz and the mica but also this pyroxene represent a quench product of a hydrous liquid, or, perhaps, of a supercritical fluid. The work of SEIFERT and SCHREYER (1966) shows that critical phenomena seem to appear in the Mg-rich portion of the system at relatively low fluid pressures. It is equally possible, however, that the coarse pyroxene has been in stable coexistence with a fluid under the conditions of the run. In Fig. 2 these uncertainties were ignored, and the dashed portion of the stability curve shown at higher pressures is a Claudius-Clapeyron extrapolation of the low-pressure data.

It can be seen from Fig. 2 that the stability field of the phase $K_2Mg_5Si_{12}O_{30}$ in the presence of excess water ends at a pressure of about 6.5 ± 1 kb due to the intersection of the lower and upper stability curves. Thus an invariant point is created at this pressure and about 820°C, at which the phases $K_2Mg_5Si_{12}O_{30}$, quartz, mica, pyroxene, liquid, and vapor may coexist. Possibly only one fluid phase may exist instead of liquid and vapor the system thus gaining one degree of freedom. At fluid pressures in excess of this pressure the low-temperature assemblage quartz + mica should react with increasing temperature directly to pyroxene and liquid (or fluid).

It is likely that the principal stability relations as outlined above are also characteristic for other members of the roedderite-merrhueite-group. According to preliminary experimental results of the authors the lower stability limit of $Na_2Mg_5Si_{12}O_{30}$ lies near 800°C at 1 kb water pressure and exhibits a positive slope. This temperature is appreciably higher than that for the lower stability limit of $K_2Mg_5Si_{12}O_{30}$ as shown in Fig. 2. On the other hand, the melting temperature of $Na_2Mg_5Si_{12}O_{30}$ at 1 atm is given by SCHAIRER, YODER, and KEENE as 1250°C, which is only slightly higher than that of $K_2Mg_5Si_{12}O_{30}$. Assuming similar slopes for the lower and upper stability curves of the two compounds with increasing fluid pressures, it would appear that the intersection of the lower stability curve and the melting curve for $Na_2Mg_5Si_{12}O_{30}$ occurs at a fluid pressure near 4 kb. Therefore, the stability field of the Na-compound is likely to be still smaller and even more confined to low fluid pressures.

2. Investigations under Anhydrous Conditions at High Confining Pressures

Because of the general similarity of the crystal structure of $K_2Mg_5Si_{12}O_{30}$ to that of the low-pressure mineral cordierite (SCHREYER and YODER, 1960) it was expected that the phase might break down at high pressures into denser phases even in the absence of water. For this reason the various starting materials including crystalline $K_2Mg_5Si_{12}O_{30}$ were run dry at pressures between 13 and 32.5 kb over the temperature range 750–1600°C. To make sure that no water was present the furnace assemblies for the solid-media apparatus, without the

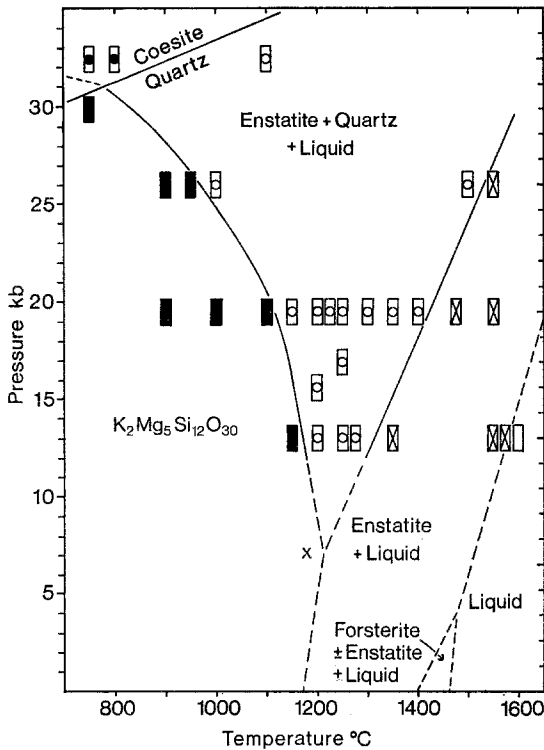


Fig. 3. Pressure-temperature diagram for the composition $K_2O \cdot 5MgO \cdot 12SiO_2$ under anhydrous conditions. Data at 1 atm were taken from ROEDDER (1951). The size of the boxes indicates the approximate errors in temperature and pressure measurements. Symbols: Solid boxes = growth of $K_2Mg_5Si_{12}O_{30}$; boxes with open circles = orthoenstatite + quartz + liquid; boxes with solid circles = orthoenstatite + coesite + liquid; boxes with crosses = orthoenstatite + liquid; open box = liquid. For the significance of point X see text. The quartz-coesite transition curve corresponds to that given by BOYD (1964), which was generally confirmed by the present work

talc sleeve but including the open Pt-capsule containing the sample, were dried over P_2O_5 under vacuum at $150^\circ C$ prior to each run.

The results of characteristic runs are listed in Table 4 and plotted in the PT-diagram of Fig. 3. It can be seen readily that the stability field of $K_2Mg_5Si_{12}O_{30}$, which may expand slightly with increasing pressure up to some 7 kb, is terminated towards still higher pressures by a curve exhibiting a pronounced negative slope. This curve was located through runs using seeded starting materials. Surprisingly enough it marks the incongruent melting of $K_2Mg_5Si_{12}O_{30}$ to an assemblage $MgSiO_3$ (enstatite) + SiO_2 + liquid which differs from the low-pressure assemblage of incongruent melting (ROEDDER, 1951) by the additional presence of a silica phase, i.e. quartz, or, above 30 kb, coesite. By virtue of the negative slope of this curve the temperatures of incongruent melting for the bulk composition $K_2O \cdot 5MgO \cdot 12SiO_2$ are lowered drastically from a maximum of about $1200^\circ C$ at 7 kb to a value below $750^\circ C$ at 32.5 kb. Because of the low reaction rates at low temperatures no effort was made to determine the stability relations at still higher pressures and thus at still lower temperatures, at which a subsolidus breakdown should occur.

The explanation of this unusual behavior is, of course, hampered by the fact that no other ternary bulk compositions in the system K_2O - MgO - SiO_2 were investigated under these same pressures and temperatures. Thus the following discussion must be considered as preliminary, and the conclusions are tentative.

Table 4. Results of some significant anhydrous runs on the composition $K_2O \cdot 5 MgO \cdot 12 SiO_2$
 Abbreviations. a) Starting materials. Glass = $K_2O \cdot 5 MgO \cdot 12 SiO_2$ glass, Cryst = $K_2Mg_5Si_{12}O_{30}$
 prepared hydrothermally and heated to $1100^\circ C$, G + Cr = $K_2O \cdot 5 MgO \cdot 12 SiO_2$ glass, partly
 crystallized to $K_2Mg_5Si_{12}O_{30}$ + enstatite + relic glass. b) Phases. 1:5:12 = $K_2Mg_5Si_{12}O_{30}$,
 OE = orthoenstatite, Q = quartz, COE = coesite, L = liquid. In seeded runs (starting material
 G + Cr) changes in relative amounts of individual phases are indicated by (+) and (-),
 respectively, when the reaction was not complete.

Starting material	Temperature ($^\circ C$)	Pressure (kb)	Duration (h)	Phases
G + Cr	1,150	13	18	1:5:12 (+), OE (-), L
G + Cr	1,200	13	19	OE, Q, L
Cryst	1,250	13	2	1:5:12, OE, Q, L
Cryst	1,275	13	3	OE, Q, L
G + Cr	1,350	13	1	OE, L
G + Cr	1,575	13	1	OE, L
G + Cr	1,600	13	1	L
Cryst	1,000	19.5	20	1:5:12
Cryst	1,100	19.5	5	1:5:12
Glass	1,100	19.5	3	1:5:12
G + Cr	1,150	19.5	27	OE, Q, L
Cryst	1,225	19.5	1	OE, Q, L
G + Cr	1,400	19.5	1	OE, Q, L
G + Cr	1,475	19.5	2	OE, L
G + Cr	1,550	19.5	0.5	OE, L
Cryst	900	26	24	1:5:12
Glass	900	26	39	1:5:12
G + Cr	900	26	17	1:5:12
Cryst	1,000	26	16	OE, Q, L
G + Cr	1,500	26	1	OE, Q, L
G + Cr	1,550	26	0.5	OE, L
G + Cr	750	30	21	1:5:12 (+), OE (-), Q, L
G + Cr	750	32.5	14	1:5:12 (-), OE (+), Q, COE, L
G + Cr	800	32.5	24	1:5:12 (-), OE (+), Q, COE, L
Cryst	1,100	32.5	11	OE, Q, L

It is apparent, however, that after the breakdown of the osumilite-type phase $K_2Mg_5Si_{12}O_{30}$ at high pressures no other crystalline phases exist that can accommodate the potassium of this bulk composition. Because of their loosely packed crystal structures the other known ternary phases of the system (Fig. 1) are not likely to withstand these pressures either. Therefore, the beginning of melting in the system should, probably for all ternary compositions, be governed by ternary eutectics at which only binary and unary phases coexist with liquids. To the silica-rich bulk composition of $K_2Mg_5Si_{12}O_{30}$ an eutectic involving the solid phases enstatite, SiO_2 , and $K_2O \cdot 4SiO_2$ would apply, provided the phase $K_2O \cdot MgO \cdot 5SiO_2$ were unstable but $K_2O \cdot 4SiO_2$ were stable under these conditions. However, GORANSON and KRACEK (1932) have calculated, on the basis of thermochemical data, that above about 1250 bars $K_2O \cdot 4SiO_2$ should break down to $K_2O \cdot 2SiO_2$ and quartz, and that the melting of the bulk composition $K_2O \cdot 4SiO_2$ should be controlled by that of the assemblage quartz + $K_2O \cdot 2SiO_2$ which takes place near $680^\circ C$ at 1250 bars. Therefore, the ternary eutectic

governing the melting of the bulk composition $K_2Mg_5Si_{12}O_{30}$ for all pressures above the stability of the osumilite-type phase is likely to be that at which the phases coesite + enstatite + $K_2O \cdot 2SiO_2$ + liquid may coexist. Its temperature is estimated to lie in the order of 700°C for a pressure near 32 kb. With these provisions the low-temperature end of the discussed incongruent melting curve of $K_2Mg_5Si_{12}O_{30}$ (Fig. 3) should be marked by an invariant point in the PT-diagram involving the phases $K_2Mg_5Si_{12}O_{30}$, enstatite, coesite, $K_2O \cdot 2SiO_2$, and liquid. Considerably more experimental work on a variety of other bulk compositions would be necessary to confirm these phase relations that apply, however, to pressure-temperature conditions of little direct interest to earth scientists.

The melting relations of $K_2Mg_5Si_{12}O_{30}$ as determined experimentally at high pressures and temperatures allow further deductions concerning the changing path of crystallization on the liquidus surface of the system for this bulk composition as a function of pressure. Neglecting the small temperature interval at which forsterite and liquid coexist stably near the liquidus temperature of the composition $K_2O \cdot 5MgO \cdot 12SiO_2$, the main feature of the crystallization of this composition at one atmosphere (ROEDDER, 1951) is the coexistence of $MgSiO_3$ and liquid until the temperature of 1174°C, the incongruent melting point of $K_2Mg_5Si_{12}O_{30}$, is attained (Fig. 4a). This point represents a temperature maximum on the peritectical boundary curve enstatite — $K_2Mg_5Si_{12}O_{30}$. With increasing pressure the liquidus field of $K_2Mg_5Si_{12}O_{30}$ is gradually shifted towards less siliceous compositions whereas the liquidus field of quartz expands considerably. Therefore, at a pressure of about 7 kb the crystallization path of the 1:5:12 composition hits the ternary reaction point at the junction of the three liquidus fields of $K_2Mg_5Si_{12}O_{30}$, $MgSiO_3$, and quartz (Fig. 4b). This reaction point projects onto the PT-diagram for the bulk composition studied (Fig. 3) as point X for the isobar 7 kb. At higher pressures the gradual temperature and pressure changes of this reaction point are marked in Fig. 3 by the univariant curve $K_2Mg_5Si_{12}O_{30}$ + enstatite + quartz (or coesite) + liquid, which also represents the upper stability limit of the phase $K_2Mg_5Si_{12}O_{30}$. At pressures above about 7 kb the quartz liquidus field expands further so that the crystallization path now hits the quartz liquidus field first (Fig. 4c). At the same time, due to the negative slope of the upper pressure breakdown curve of $K_2Mg_5Si_{12}O_{30}$ (Fig. 3), the assemblage SiO_2 + enstatite + liquid becomes stable over an increasingly wide temperature interval. Yet, even at 26 kb, the expanding quartz liquidus field has not yet reached the bulk composition $K_2Mg_5Si_{12}O_{30}$ itself, which still lies in the enstatite field (Fig. 4d).

In summary, it may be concluded that the phase $K_2Mg_5Si_{12}O_{30}$ is indeed confined to relatively low pressures. Its breakdown at higher pressures reduces drastically the overall melting temperatures, at least in this portion of the system.

Application to Petrology and Meteoritics

The minerals of the roedderite-merrihueite group have thus far only been found as rare constituents of some meteorites making up not more than 0.1% of the whole meteorite and generally much less. In Table 5 the occurrences known up to the present are compiled. It is of interest to note that these minerals occur

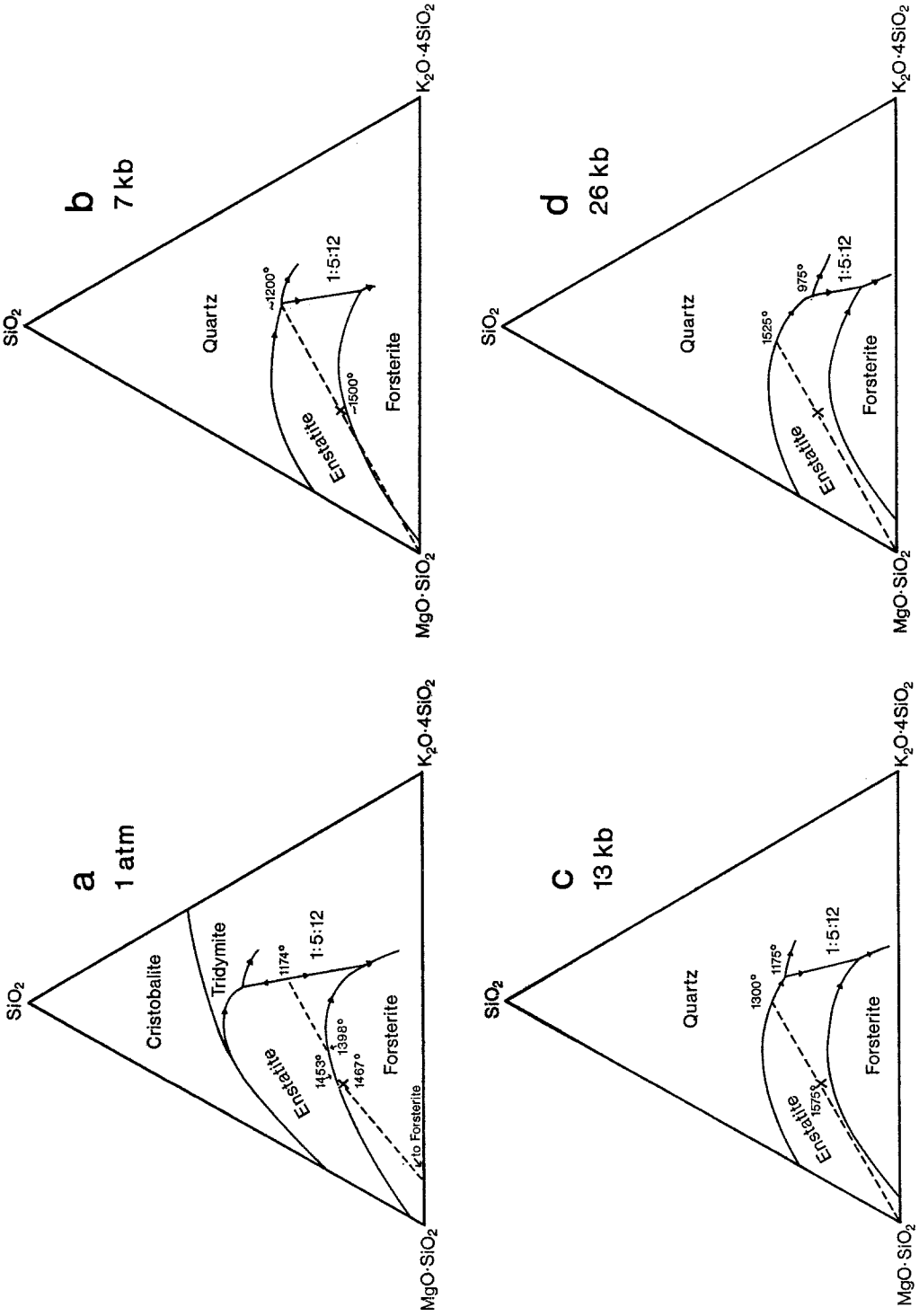


Fig. 4 a.—d

Table 5. Occurrences of roedderite-merrihueite minerals in meteorites

Mineral	Paragenesis	Meteorite		Reference
		Name	Type	
Roedderite	enstatite, clino-enstatite, troilite, nickel-iron, schreibersite, high albite, tridymite, oldhamite, organic matter, glass	Indarch	enstatite chondrite E 4 ^a	FUCHS <i>et al.</i> (1966)
Roedderite	albite etc.	Kota-Kota	enstatite chondrite E 4	BINNS and DAVIS in FUCHS <i>et al.</i> (1966)
Merrihueite	clinoenstatite, fayalitic olivine, nickel-iron	Mező-Madaras	ordinary chondrite probably L 3	DODD <i>et al.</i> (1965)
Roedderite	forsterite, albite, whitlockite, graphite, richterite	Wichita County	iron	OLSEN (1967 a)
Roedderite	ureyite, richterite, chromite, sphalerite, troilite, graphite, krinovite (OLSEN and FUCHS (1968)	Canyon Diablo	iron	OLSEN and FUCHS (pers. comm. 1968)

^a Indicates classification symbol taken from VAN SCHMUS and WOOD (1967).

in chondrites as well as in iron meteorites, for which in the past grossly different modes of origin had been assumed.

On the basis of the present study it is concluded that the minerals of the roedderite-merrihueite group are low-pressure phases, the more so the higher the partial pressure of water (cf. Figs. 2 and 3). This is in general agreement with current opinions (e.g. WOOD, 1963) concerning the maximum size and, thus, the highest possible load pressures of meteorite parent bodies. If one assumes the largest bodies to be some 250 km in radius, their central rock pressures may be estimated as 3 or 13 kb for all-chondritic or all-iron materials making up these bodies, respectively. Because of the common presence of graphite and metals strongly reducing conditions must have prevailed in most meteorite materials. Therefore, the partial pressures of water in these environments were determined by the gas equilibria in the system C-H-O (FRENCH and EUGSTER, 1965), which, under these reducing conditions, show in general a preponderance of methane over water and other gases. Hence, it is concluded that water pressures will only amount to fractions of the total pressures prevailing in meteorite parent bodies.

Fig. 4a—d. Liquidus relationships in part of the system $MgO \cdot SiO_2 - K_2O \cdot 4SiO_2 - SiO_2$ at four different pressures. The subdivision of the triangles is in approximate weight per cent. Data at 1 atm were taken from ROEDDER (1951), those at higher pressures from Fig. 3. The locations and shapes of boundary curves for these pressures are inferred. The possible existence of cristobalite in (b) has been neglected. The location of the compound $K_2Mg_5Si_{12}O_{30}$ is indicated by the cross

Chondrites, which are the most common meteorites, may, as a first approximation, be divided into three main categories: carbonaceous chondrites, ordinary chondrites, and enstatite chondrites. WICK (1956) noted that their main chemical distinction was the ubiquity of water in carbonaceous chondrites versus essential lack of water in the other two varieties and an apparently stepwise decrease in oxygen content of these chondrites following the above sequence. Thus, if the carbonaceous chondrites were considered as a parental cosmic material (MASON, 1962), a process of dehydration and reduction might have produced the other two chondrite varieties. However, more recent work by AHRENS (1964, 1965) has shown other significant differences in their bulk compositions, which seem to preclude any derivation of other chondrite varieties from carbonaceous chondrites (see also UREY, 1961).

Minerals of the roedderite-merrihueite group have thus far only been encountered in *ordinary* and *enstatite chondrites* (Table 5). This indicates that temperatures prevailing during the evolution of these two chondrite varieties were high enough to allow the formation of these rare mineral phases, which at least in one chondrite (DODD *et al.*, 1965) were found to occur within the chondrules themselves. It is impossible, however, to deduce any precise temperature limits for their formation because neither the magnitude of the fluid pressure nor the influence of Na and Fe⁺² substitutions on the lower stability limit of roedderite-merrihueite phases is known.

Because of the occurrence of badly crystallized serpentine-like material in *carbonaceous chondrites* it is likely that this group of meteorites has formed at generally lower temperatures than the ordinary and enstatite chondrites. However, except for the Type I carbonaceous chondrites (VAN SCHMUS and WOOD, 1967), high-temperature mineral phases are also found in chondrules occurring in these meteorites. This coexistence may represent a state of disequilibrium or a condition in which partial pressure of water is less than total pressure. The apparent absence of minerals of the roedderite-merrihueite group from any type of carbonaceous chondrites may have several different reasons: It may be due to different bulk compositions of these chondrites as compared with ordinary and enstatite chondrites (see above), or, it may even be that these rare minerals were just not recognized in the studies made thus far. However, their absence, if true, may also be caused by different conditions of crystallization, at least with respect to the serpentine-like material making up all of the Type I carbonaceous chondrites. Because of the coexistence of magnetite rather than metal with carbon in these chondrites, water pressures might have been as high as 300 to 500 bars. Under these pressures pure Mg-serpentine is only stable at temperatures below about 400°C (SCARFE and WYLLIE, 1967). If the "serpentine" in carbonaceous chondrites is a ferric septechlorite (BOSTRÖM and FREDRIKSSON, 1966), this temperature limit will probably not be much different. On the other hand, pure $K_2Mg_5Si_{12}O_{30}$ requires a minimum temperature of 560°C at 500 bars fluid pressure to become stable (Fig. 2). Therefore, the absence of roedderite-merrihueite minerals, at least in Type I carbonaceous chondrites, may already be explained on the basis of their stability relations as discussed in the present paper. If the silicate portion of these chondrites should indeed comprise bulk compositions requisite for the formation of

roedderite-type phases, only the low-temperature breakdown products of these phases, for example a mica similar to the one obtained in the present experiments (see also SEIFERT and SCHREYER, 1965, 1969) would be expected to occur. It is doubtful, however, whether a mica phase of this type, if present in very small amounts among other phyllosilicates, would be detected.

The classification of chondritic meteorites, previously based mainly on chemical grounds, has recently been extended by VAN SCHMUS and WOOD (1967) to include various petrologic criteria. Perhaps the most interesting property that can be defined on the basis of this new classification is the varying degree of equilibration of chondrites. Although admittedly the three roedderite- or merrihueite-bearing chondrites found to date are by no means a representative basis for statistics, it may not be fortuitous that they are unequilibrated or poorly equilibrated chondrites which show considerable inhomogeneity in their mineral compositions. The symbols of the VAN SCHMUS-WOOD nomenclature pertaining to these three chondrites are also given in Table 5. If this relationship were generally valid, the absence of roedderite-merrihueite in the equilibrated chondrites could only mean that these minerals are not stable in the overall bulk composition of these chondrites. Their appearance in the more primitive unequilibrated chondrites would, in this case, only be due to local equilibria in alumina-deficient chondrules, for which the roedderite-merrihueite minerals are, of course, stable phases.

In *iron meteorites* roedderite occurs in silicate inclusions within graphite nodules (OLSEN, 1967a). Of particular interest is the coexistence of roedderite with the amphibole richterite. Although these richterites are predominantly fluorine-amphiboles, they undoubtedly also contain water (OLSEN, 1967b and pers. communication 1968). Therefore, it is likely that the roedderites even of the iron meteorites grew in a somewhat hydrous atmosphere and thus the model equilibrium diagram of Fig. 2 with the variables temperature and fluid pressure should apply. This provides a limitation of the water pressure prevailing during the formation of these roedderites. Hence the present experimental data are consistent with the results of recent studies of the Widmannstätten pattern in iron meteorites (e.g. GOLDSTEIN and SHORT, 1967) which indicate that the iron meteorites formed under low pressures, thus adding to the demise of the old classical model of iron meteorites representing fragments of deep, high pressure zones of large celestial bodies.

In view of the fact that chondritic meteorites also provide a *model for the primitive earth* it may not seem too far-fetched to speculate about the behavior of the roedderite and merrihueite *compositions* in deeper zones of our globe. Especially, the evolutionary aspects may be of some significance. If primitive, unequilibrated, chondritic matter locally containing roedderite-merrihueite phases as important alkali-carriers were subjected — during or after the agglomerative origin of the earth — in depths of the present upper mantle to pressures in excess of some 25–30 kb, these mineral phases would have to break down and liberate their alkalis to form siliceous liquids. Such liquids, however, seem to be incompatible with the total bulk chemistry of the chondritic matter and would, therefore, react with more aluminous portions to form feldspars. Thus the net result of these reactions would be identical to an equilibration under subsolidus conditions as demonstrated by the equilibrated chondrites.

The apparent absence of roedderites and merrihueites in terrestrial rocks can be explained in the light of the present experimental data: Rocks containing these minerals can only be formed in special chemical environments rich in alkalis and Mg, Fe, but poor in Al, which are, however, hardly available in the strongly alumina-enriched present-day crust of the earth. Such environments may possibly exist in some rare alkaline igneous rocks of deep-seated origin like mica peridotites and kimberlites. These rocks, however, have at least partly crystallized under relatively high confining pressures that may preclude the formation of roedderite and merrihueite. Furthermore such rocks are commonly rich in water which might, during the cooling of the magma, react with some possibly earlier-formed merrihueite-roedderites to form their hydrous mica breakdown products. It is of interest to note that several phlogopites from kimberlites were found that exhibit an Al-deficiency in the direction towards these breakdown products (SEIFERT and SCHREYER, 1969).

Acknowledgements. The experimental equipment used in this study was partly provided by Deutsche Forschungsgemeinschaft, Bad Godesberg. In addition, Dr. H. S. YODER, JR., Washington D.C., and Dr. S. W. RICHARDSON, now at Edinburgh, are to be thanked for their cooperation in making available a Geophysical Laboratory gas apparatus and performing some high-temperature runs in it. The X-ray data were refined at Deutsches Rechenzentrum, Darmstadt, using a least-squares program kindly provided by Prof. C. W. BURNHAM, Harvard University. The manuscript has been reviewed by Drs. EDWARD OLSEN, Chicago, E. ROEDDER, Washington, D.C., and W. R. VAN SCHMUS, Lawrence, Kansas. Their critical comments have materially improved this paper.

References

- AHRENS, L. H.: Si-Mg fractionation in chondrites. *Geochim. Cosmochim. Acta* **28**, 411—423 (1964).
- Observations on the Fe-Si-Mg relationships in chondrites. *Geochim. Cosmochim. Acta* **29**, 801—806 (1965).
- BOSTRÖM, K., and K. FREDRIKSSON: Surface conditions of the Orgueil meteorite parent body as indicated by mineral associations. *Smithsonian Misc. Coll.* **151**, No. 3, 1—39 (1966).
- BOYD, F. R.: Geological aspects of high-pressure research. *Science* **145**, 13—20 (1964).
- DODD, R. T., R. W. VAN SCHMUS, and U. B. MARVIN: Merrihueite, a new alkali-ferromagnesium silicate from the Mezö-Madaras chondrite. *Science* **149**, 972—974 (1965).
- ERNST, W. G.: The stability relations of magnesioriebeckite. *Geochim. Cosmochim. Acta* **19**, 10—40 (1960).
- FRENCH, B. M., and H. P. EUGSTER: Experimental control of oxygen fugacities by graphite-gas equilibrium. *J. Geophys. Res.* **70**, 1529—1539 (1965).
- FUCHS, L., C. FRONDEL, and C. KLEIN: Roedderite, a new mineral from the Indarch meteorite. *Am. Mineralogist* **51**, 949—955 (1966).
- GOLDSTEIN, J. L., and J. M. SHORT: The iron meteorites, their thermal history and parent bodies. *Geochim. Cosmochim. Acta* **31**, 1733—1770 (1967).
- GORANSON, R. W., and F. C. KRACEK: An experimental investigation of the phase relations of $K_2Si_4O_9$ under pressure. *J. Phys. Chem.* **34**, 913—926 (1932).
- HEYDEMANN, P. L.: The Bi I—II transition pressure measured with a dead-weight piston gauge. *J. Appl. Phys.* **38**, 2640—2644 (1967).
- KRACEK, F. C., N. L. BOWEN, and G. W. MOREY: The system potassium metasilicate-silica. *J. Phys. Chem.* **33**, 1857—1879 (1937).
- MASON, B.: *Meteorites*. New York: Wiley & Sons 1962.
- MIYASHIRO, A.: Osumilite, a new silicate mineral and its crystal structure. *Am. Mineralogist* **41**, 104—116 (1956).

- OLSEN, E.: A new occurrence of roedderite and its bearing on osumilite-type minerals. *Am. Mineralogist* **52**, 1519—1523 (1967a).
- Amphibole: First occurrence in a meteorite. *Science* **156**, 61—62 (1967b).
- , and L. FUCHS: Krinovite, $NaMg_2CrSi_3O_{10}$: A new meteorite mineral. *Science* **161**, 786—787 (1968).
- ROEDDER, E. W.: The system K_2O - MgO - SiO_2 . *Am. J. Sci.* **249**, 81—130, 224—248 (1951).
- A reconnaissance of liquidus relations in the system $K_2O \cdot 2SiO_2$ - FeO - SiO_2 . *Am. J. Sci.*, Bowen Vol., 435—456 (1952).
- SCARFE, C. M., and P. J. WYLLIE: Serpentine dehydration curves and their bearing on serpentinite deformation in orogenesis. *Nature* **215**, 945—946 (1967).
- SCHAIERER, J. F., and N. L. BOWEN: The system K_2O - Al_2O_3 - SiO_2 . *Am. J. Sci.* **253**, 681—746 (1956).
- H. S. YODER, and A. G. KEENE: The systems Na_2O - MgO - SiO_2 and Na_2O - FeO - SiO_2 . *Carnegie Inst. Washington Year Book* **53**, 123—125 (1954).
- SCHMUS, W. R. VAN, and J. A. WOOD: A chemical-petrologic classification for the chondritic meteorites. *Geochim. Cosmochim. Acta* **31**, 747—765 (1967).
- SCHREYER, W., and J. F. SCHAIERER: Metastable osumilite- and petalite-type phases in the system MgO - Al_2O_3 - SiO_2 . *Am. Mineralogist* **47**, 90—104 (1962).
- , and F. SEIFERT: Metastability of an osumilite end member in the system K_2O - MgO - Al_2O_3 - SiO_2 - H_2O and its possible bearing on the rarity of natural osumilites. *Contr. Mineral. and Petrol.* **14**, 343—358 (1967).
- , and H. S. YODER: Instability of anhydrous Mg -cordierite at high pressures. *Carnegie Inst. Washington Year Book* **59**, 90—91 (1960).
- — The system Mg -cordierite — H_2O and related rocks. *Neues Jahrb. Mineral. Abhandl.* **101**, 271—342 (1964).
- SEIFERT, F., and W. SCHREYER: Synthesis of a new mica, $KMg_{2.5}Si_4O_{10}(OH)_2$. *Am. Mineralogist* **50**, 1114—1118 (1965).
- — Fluide Phasen im System K_2O - MgO - SiO_2 - H_2O und ihre mögliche Bedeutung für die Entstehung ultrabasischer Gesteine. *Ber. Bunsenges.* **70**, 1045—1050 (1966).
- — Synthesis and stability of micas in the system K_2O - MgO - SiO_2 - H_2O and their relations to phlogopite. In manuscript (1969).
- UREY, H. C.: Criticism of Dr. Mason's paper on "The origin of meteorites". *J. Geophys. Res.* **66**, 1988—1991 (1961).
- WILK, H. B.: The chemical composition of some stony meteorites. *Geochim. Cosmochim. Acta* **9**, 279—289 (1956).
- WOOD, J. A.: Physics and chemistry of meteorites. In: *The moon, meteorites, and comets*, chap. 12, p. 337—401. Chicago: University Chicago Press 1963.

F. SEIFERT, W. SCHREYER
Institut für Mineralogie der Ruhr-Universität
4630 Bochum, Buscheystraße