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## Synthetic gedrite: a stable phase in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (MASH) at 800 °C and 10 kbar water pressure, and the influence of FeNaCa impurities

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**Abstract** Seeded, solid-media piston-cylinder runs of unusually long duration up to 31 days indicate growth or persistence of synthetic gedrite of the composition  $\square\text{Mg}_6\text{Al}[\text{AlSi}_7\text{O}_{22}](\text{OH})_2 (=6:1:7)$ , prepared from the purest chemicals available, at 10 kbar water pressure and 800 °C. Conversely, breakdown was observed at 11 kbar and 850 °C to aluminous enstatite,  $\text{Al}_2\text{SiO}_5$ , and a melt of the composition  $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{SiO}_2$ . Thus, pure gedrite free of iron, sodium, and calcium is likely to have only a small *PT* stability field in the MASH system, estimated as  $10 \pm 1$  kbar,  $800 \pm 20$  °C, even though metastable growth of gedrite can be observed over a larger *PT* range. A second starting material with the anhydrous composition  $5\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$  also yielded gedrite of the composition 6:1:7, together with more aluminous phases such as kyanite, corundum or sapphirine, thus suggesting that the end-member gedrite defined as  $\square\text{Mg}_5\text{Al}_2[\text{Al}_2\text{Si}_6\text{O}_{22}](\text{OH})_2 (=5:2:6)$  by the IMA Commission on New Minerals and Mineral Names probably does not exist. With the use of this second starting material, which contains FeNaCa impurities, growth of 6:1:7-gedrite was observed over a still wider *PT*-range. Seeded runs indicate that the true stability field of such slightly impure 6:1:7-gedrites may also be larger than that of the pure MASH phase and extend at least to 15 kbar, 800 °C. There is, thus, a remarkable stabilization effect on the orthoamphibole structure by impurities amounting only to a total of less than one weight percent of oxides in the starting material. The gedrites synthesized are structurally well ordered amphiboles nearly free of chain multiplicity faults, as revealed by HRTEM. The X-ray diffraction work on the gedrites synthesized yielded the smallest cell volume yet reported for this phase. The small stability field of the

pure MASH gedrite is intersected by the upper pressure stability limit of hydrous cordierite for excess- $\text{H}_2\text{O}$  conditions, thus leading to complicated phase relations for both gedrite and cordierite involving the additional phases aluminous enstatite, talc, quartz,  $\text{Al}_2\text{SiO}_5$ , melt and perhaps boron-free kornerupine.

### Introduction

The gedrite series comprises orthorhombic Li-poor aluminous amphiboles that in nature cover the entire range of  $\text{Mg} \leftrightarrow \text{Fe}^{2+}$  substitution, and – with very few exceptions – contain appreciable amounts of sodium in the A-position of the structure. The general formula is  $\text{Na}_x\text{Li}_z(\text{Mg}, \text{Fe}^{2+}, \text{Mn})_{7-y-z}\text{Al}_y[\text{Al}_{x+y-z}\text{Si}_{8-x-y+z}\text{O}_{22}](\text{OH}, \text{F}, \text{Cl})_2$  (Leake et al. 1997). Experimentally, Na- and Li-free magnesium gedrite has been synthesized over a considerable *PT*-range (10–20 kbar, 850–900 °C; Schreyer 1968; Schreyer and Seifert 1969a; Yoder 1971), but it was not clear as to whether or not this phase is truly stable. Moreover, as rather impure starting materials had been used for most of these synthesis experiments, there was also the possibility that such impurities might have favoured its growth, or even stabilized it relative to other phases in the pure MASH system.

In this contribution we report the main results of an experimental study conducted by the first author for a Diploma Thesis (Fischer 1991), in which new insights were gained into the question of gedrite stability in the MASH system, both with and without impurities.

### Experimental apparatus

Synthesis runs were carried out in solid-media piston-cylinder apparatus of the Boyd and England (1960) type with NaCl as pressure medium. Pressure uncertainties can be estimated to be less than approximately  $\pm 0.5$  kbar. Such precision in runs of up to 31 days was made possible by a sensitive automatic pressure control system. Temperature uncertainties are within  $\pm 10$  °C (Fischer 1991).

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Synthetic products were routinely examined in immersion mounts under the polarizing microscope and with a Cambridge 250 Mk 3 scanning electron microscope at the Ruhr-Universität Bochum. Precise determination of refractive indices was achieved by phase contrast techniques. Phase characterization by high-resolution transmission electron microscopy (HRTEM) was carried out on a number of samples with a Philips EM400 T, 100 kV instrument at 100 kV at the University of Kiel, in accord with the optimum defocus conditions discussed by Buseck and Iijima (1974). The synthetic samples were ground and deposited onto a perforated carbon grid from a slurry.

Lattice parameters of synthetic gedrites were refined from data collected on an automated Siemens D500 diffractometer with the data reduction system supplied with the instrument (Maresch and Czank 1985). Silicon powder was used as an internal standard. Reflections were indexed on the basis of calculated X-ray diffraction patterns (Borg and Smith 1969). For routine phase analysis and peak-height comparisons in bracketing experiments, a non-automated Philips PW 1710 instrument was also employed.

## Starting materials

Although it seemed likely from the earlier study of Schreyer and Seifert (1969a) that MASH gedrites have compositions close to or identical with the anhydrous oxide ratio  $6\text{MgO} \cdot 1\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ , hydrous starting materials both with this ratio, corresponding to the formula  $\text{Mg}_6\text{Al}[\text{AlSi}_7\text{O}_{22}](\text{OH})_2 (=6:1:7)$ , and a more aluminous one (5:2:6) corresponding to  $\text{Mg}_5\text{Al}_2[\text{Al}_2\text{Si}_6\text{O}_{22}](\text{OH})_2$ , the theoretical end-member formula of gedrite (Leake et al. 1997), were employed (Fig. 1). It should be noted that the 6:1:7 composition corresponds exactly to the boundary between the anthophyllite and gedrite compositional fields, according to the new IMA nomenclature (Leake et al. 1997). In anticipation of the results to be reported we will refer here to the 6:1:7 phase as gedrite.

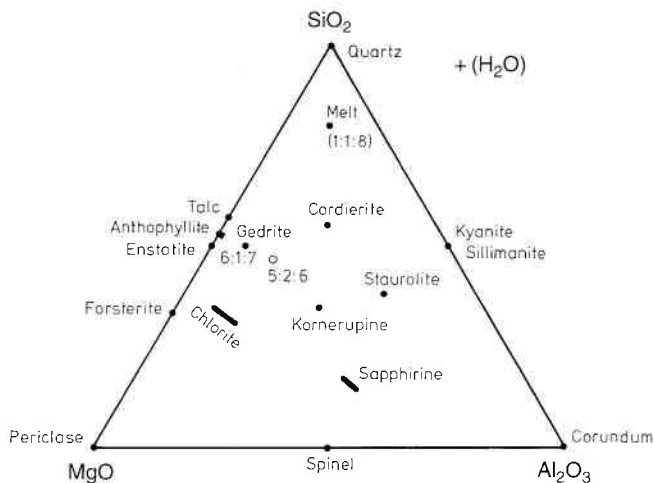
In accordance with successful earlier synthesis experiments (Schreyer 1968), the two starting mixtures consisted of the crystalline phases talc, kyanite and periclase. However, whereas the 5:2:6 mixture contained impure natural talc (1.39 wt%  $\text{Fe}_2\text{O}_3$  as total iron; 0.12 wt% CaO; 0.34 wt%  $\text{Na}_2\text{O}$ ) and kyanite (0.11 wt%  $\text{Fe}_2\text{O}_3$ ; 0.01 wt%  $\text{Na}_2\text{O}$ ; 0.01 wt%  $\text{K}_2\text{O}$ ), synthetic talc and kyanite were especially prepared from the purest possible chemicals avail-

able for the 6:1:7 mixture: MgO p.A. (Ventron GmbH), aluminium band (E. Merk AG) and TEOS (Fluka). Talc was obtained by running a gel (Hamilton and Henderson 1968) of appropriate composition in a solid-media piston-cylinder apparatus at 700 °C and 30 kbar for 48 hours, and kyanite in an analogous manner at 800 °C, 50 kbar, 24 hours. In view of its 5:2:6 stoichiometry the impure mixture contained a total of 0.72 wt%  $\text{Fe}_2\text{O}_3$ , 0.17 wt%  $\text{Na}_2\text{O}$ , 0.06 wt% CaO and 0.01 wt%  $\text{K}_2\text{O}$ .

## Synthesis runs

The chemically pure 6:1:7 and the impure 5:2:6 mixtures (Fig. 1), plus 10 wt% excess water, were reacted in solid-media piston-cylinder runs in the range of 10–20 kbar water pressure and 800–900 °C. The results summarized in Table 1(A, B) indicate that despite long durations of up to 21 days single-phase gedrite was never obtained; the orthoamphibole synthesized always coexisted with other phases such as talc, chlorite, enstatite, kyanite, corundum, sapphirine and boron-free kornorupine (compare Fig. 1). Interestingly, the *PT* range of successful amphibole syntheses differs appreciably between the pure and impure starting materials (Fig. 2). The impure 5:2:6 mixture yielded a gedrite phase between 10 and 15 kbar, 800–870 °C, whereas from the pure 6:1:7 mixture gedrite was obtained only between 10 and 12 kbar, 800–850 °C. At 20 kbar, 850–900 °C no gedrite formed, but enstatite, kyanite, and/or Mg-staurolite crystallized from both mixtures. These results are in contrast to those of Schreyer and Seifert (1969a) in which a gedrite phase grew or persisted up to a pressure of 31.5 kbar.

Time studies at given *PT* conditions (Table 1) yielded insight into the sequence of the – in part metastable – phase crystallization and thus gave first indications of possible equilibrium relationships. At 10 kbar, 800 °C, both mixtures showed only talc + chlorite as the dominant phases after 27 hours, but yielded considerable amounts of the gedrite phase after 21 days. At 11 kbar, 850 °C, the pure 6:1:7 mixture (Table 1A) gave increasing amounts of gedrite in runs up to 27 hours duration, but gedrite decreased in amount after 5 days and reacted out after 21 days, leaving only enstatite + kyanite + B-free kornorupine. As reported by Wegge and Schreyer (1994), kornorupine is a stable phase under these conditions. For the impure 5:2:6 mixture (Table 1B) no runs of similarly long duration were performed, so that the possible influence of the bulk chemical composition on amphibole crystallization cannot be discussed at this stage.



**Fig. 1** Relevant phases of the MASH system projected onto the anhydrous base plane (solid circles and bars). 6:1:7 and 5:2:6 (open circle) indicate the anhydrous oxide ratios of the two starting materials used in the present study. 6:1:7 is also the oxide ratio of the gedrites synthesized. 1:1:8 is the oxide ratio of the melt encountered. Al-incorporation into enstatite is ignored. Solid solubility between gedrite and anthophyllite was not studied

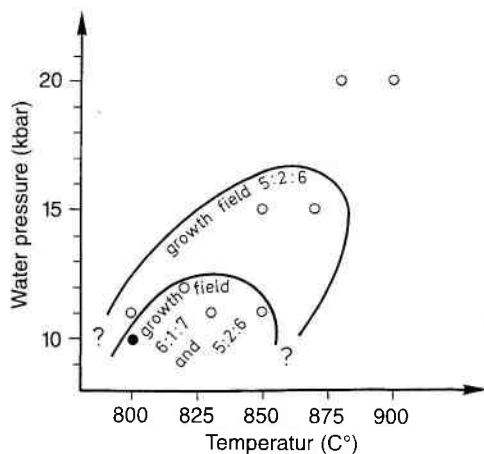
## Bracketing runs

For the determination of relative phase stabilities, the seeding technique has generally been successful in experimental petrology. In the present work the products of incomplete synthesis runs, as described above, could be used directly, as they presumably represent mixtures

**Table 1A, B** Results of hydrothermal synthesis runs for gedrite using two different starting mixtures. (*C* corundum, *Chl* chlorite, *En* orthoenstatite, *Ge* gedrite, *Ko* boron-free kornerupine, *Ky* kyanite, *MSt* magnesiostauroilite, *Sa* sapphirine, *Tc* talc; < small amounts, « trace amounts, without prefix major phase, ↑ amount of phase increased relative to that observed in run of previous line, ↓ amount of phase decreased relative to that observed in run of previous line).

Pressure (kbar)	Temperature (°C)	Duration (h)	Crystalline run products
<b>A</b> Mixture of composition $6\text{MgO} \cdot 1\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ (chemically pure)			
10	800	27	Tc, Chl, < Ky, «C
10	800	504	Ge, En, «?
11	800	64	Tc, Chl, < Ky
11	830	20	En, Ge, Tc, < Ky
11	850	5	En, Ge, < C, «Sa
11	850	19	En↓, Ge↑, < Ky, «C
11	850	27	En↓, Ge↑, < Ky, «C, «Sa
11	850	120	En↑, Ge↓, < Ky, «C, «Sa
11	850	504	En, Ko, < Ky
12	820	27	En, Ge, < Ky
12	820	192	En, Ge↑, < Ky, «C
15	850	27	En, Ky
15	870	27	En, Ky
20	880	27	En, Ky
20	900	27	En, Ky
<b>B</b> Mixture of composition $5\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (chemically impure, for details see text)			
10	800	27	Tc, Chl, < C
10	800	504	Ge, ?
11	800	68	Ge, En, Tc, Ky
11	830	20	En, Ge, Ky, < C
11	850	3	Tc, Sa, Ky, < G
11	850	5	Ge = En, Sa, C
11	850	27	Ge↑, En, Ky, Sa
11	850	72	Ge, Sa, Ky↓, Tc
12	820	27	Tc, Chl, < Ky, «C
12	820	192	Ge, En, C
15	850	27	En, Ge, Ky, < C
15	870	27	En, Ge, Ky, C
20	880	27	En, < MSt, < Ky
20	900	27	En, MSt, < Ky

of gedrite and its potential breakdown products. As starting material for our bracketing attempts we first used the product of the run with the 6:1:7 gel at 11 kbar,



**Fig. 2** Approximate limits of the pressure-temperature fields of growth of gedrite from the chemically pure 6:1:7 starting material as well as from the impure 5:2:6 mixture. *Solid* and *open circles* indicate run conditions (Table 1). At the condition of the *solid circle*, chemically pure gedrite with the oxide ratio 6:1:7 is a stable phase (Fig. 4), whereas it is metastable over the remaining growth field 6:1:7. The gedrite synthesized from the impure 5:2:6 mixture exhibits both a larger growth field and a larger stability field. For details see text and Tables 1 and 2

850 °C, 19 hours, which consisted of enstatite, gedrite, kyanite and traces of corundum (Table 1A). This material was rerun, again with excess water between 10 and 20 kbar, 800–900 °C. The results are listed in Table 2A. At 15–20 kbar, 850–900 °C, gedrite broke down completely or was reduced to traces, while enstatite + kyanite grew and corundum disappeared. At 12 kbar, 820 °C, gedrite decreased strongly after 8 days; at 11 kbar, 850 °C it disappeared after 21 days. Because this *PT* combination represents the initial condition of the gedrite synthesis, it is clear that this phase had grown only metastably, and is, in fact, thermodynamically unstable at this *P* and *T*. On the other hand, at 10 kbar, 800 °C, gedrite persisted after 27 hours and clearly grew in runs of 9 and 31 days. Only in a 21-day run was gedrite found to decrease slightly relative to enstatite.

We interpret the above results of bracketing runs with the 6:1:7 mixture as an indication that a chemically pure magnesium gedrite is a stable phase of the MASH system at 10 kbar, 800 °C, but not at any other *PT* conditions investigated, the nearest ones being 12 kbar, 820 °C, and 11 kbar, 850 °C (Fig. 2). The decrease in the amount of gedrite in the 21-day run at 10 kbar, 800 °C, may suggest that this *PT* coordinate lies very close to the upper limit of the presumed stability field of gedrite. Thus, unavoidable *PT* fluctuations within the limits of error given earlier may have caused cyclic fluctuations in growth or breakdown of gedrite.

**Table 2A, B** Results of bracketing runs bearing on the stability of gedrite

Pressure (kbar)	Temperature (°C)	Duration (h)	Crystalline run products (for abbreviations see Table 1)
<b>A Starting material: 6:1:7 run product (11 kbar, 850 °C, 19 h; Table 1A)</b>			
10	800	27	<sup>a</sup> En, Ge, Ky, «Tc, «C
10	800	216	Ge↑, En↓, <C, <Ky
10	800	504	Ge↓, En↑, <C, <Ky, «Tc
10	800	744	Ge↑, En↓, <Ky
12	820	27	En↑, Ky, <Ge↓
12	820	192	En↑, Ge↓, «C
15	850	27	En↑, Ky↑, «Ge
15	870	27	En↑, Ky↑, «Ge
20	880	27	En↑, Ky↑
20	900	27	En↑, Ky↑
<b>B Starting material: 5:2:6 run product (11 kbar, 850 °C, 5 hours; Table 1B)</b>			
10	800	27	<sup>b</sup> Ge↑, C↑, «Tc
10	800	216	Ge↑, <C, «Tc, ?
10	800	504	Ge↑, Tc, <C, «Ky
10	800	744	Ge↑, C↑
11	800	27	Ge↑, <Tc, <C
11	850	27	Ge↑, C, En↓, Sa
11	850	168	Ge↑, Ko, «En, «Tc
11	850	312	Ge↑, Ko, <C, «Ky
12	820	27	Ge↑, En↓, C↓
12	820	192	Ge↑, C
15	850	27	Ge↑, En↓, C↓, «Ky
15	870	27	Ge↑, En↓, C
20	880	27	En↑, MSt, <Ky
20	900	27	En↑, MSt, <Ky

<sup>a</sup> ↑ amount of phase increased relative to that in 6:1:7 starting material (En, Ge, <Ky, «C), ↓ amount of phase decreased relative to starting material

<sup>b</sup> ↑ amount of phase increased relative to that in 5:2:6 starting material (En=Ge, Sa, C), ↓ amount of phase decreased relative to starting material

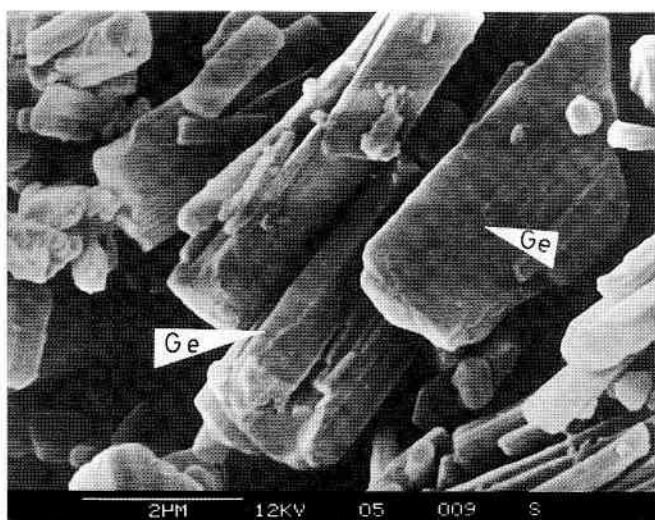
For comparison, bracketing runs were also performed with the impure 5:2:6 mixture. In this case, the starting material was the product of the synthesis run at 11 kbar, 850 °C, 5 hours, consisting of about equal amounts of a gedrite phase and enstatite with additional sapphirine and corundum (Table 1B). Runs with this material (Table 2B) between 10 and 20 kbar, 800–900 °C, for various lengths of time showed gedrite breakdown at 20 kbar, 880–900 °C, to form enstatite + kyanite with some Mg-stauroilite. At 15 kbar, 850–870 °C gedrite increased after 27 hours, and at 10–12 kbar, 800–850 °C gedrite grew so strongly that in the longest run of 31 days at 10 kbar, 800 °C it is the only magnesian phase present together with corundum. At 11 kbar, 850 °C, B-free kornerupine makes its appearance after 5–13 days, substituting for corundum. The presence of the more aluminous phases kornerupine and corundum in addition to gedrite in the 5:2:6 composition indicates that gedrite itself is less aluminous than 5:2:6 and may be close to or identical with 6:1:7, as already deduced by Schreyer and Seifert (1969a). Importantly, these bracketing runs on the impure 5:2:6 mixture result in a considerably larger *PT* stability field for this kind of gedrite. It may extend from 10 kbar, 800 °C to at least 15 kbar, 850 °C, so that a possible stability field for the gedrite grown from the impure 5:2:6 mixture may coincide more or less with its growth field as outlined in Fig. 2. On the other hand, for gedrite grown from the chemically pure 6:1:7 mixture, the condition 10 kbar,

800 °C, is the only one investigated at which a gedrite phase appears to be stable (solid circle in Fig. 2). Thus it is difficult to escape the conclusion that the FeNaCa impurities present in the 5:2:6 mixture stabilize the gedrite phase over a larger *PT* area relative to the pure MASH gedrite. This conclusion is also supported by the observation (Tables 1B and 2B) that the impure 5:2:6 mixture gave the largest yields of gedrite, although the bulk chemistry of this starting material is considerably more aluminous than that of the orthoamphibole synthesized (see above).

### Physical and chemical properties of synthetic gedrites

The synthetic gedrite forms small needles and prisms only 1–10 micrometres in length, even after long run durations (Fig. 3). The refractive indices are  $n_x \cong 1.617 \pm 0.002$  and  $n_z = 1.629 \pm 0.002$  giving a birefringence of about 0.012. These values apply to a gedrite produced from the 5:2:6 mixture, which therefore probably contains minor impurities.

The X-ray powder diffraction patterns of the synthetic gedrites closely resemble the one given by Schreyer and Seifert (1969a). In Table 3 the cell dimensions of two synthetic gedrites prepared from the 6:1:7 and 5:2:6 starting mixtures are listed and compared with those calculated from the data of Schreyer and Seifert (1969a) for a gedrite also obtained from a 5:2:6 starting material.



**Fig. 3** SEM picture of synthetic gedrite (*Ge*) produced from the 5:2:6 starting material at 12 kbar, 820 °C after 192 hours. Scale bar = 2 micrometres

It can be seen that – within a  $2\sigma$  uncertainty range – there are no significant differences in the X-ray properties of the two new gedrites synthesized here, thus supporting the earlier conclusion that the composition of the gedrites prepared from the two different starting materials is virtually the same, that is near 6:1:7. It is also clear that possible traces of Fe, Na and Ca in the gedrite introduced from the impure 5:2:6 starting mixture do not have any significant effect on the X-ray properties. The cell volumes of the two new synthetic gedrites in Table 3 are somewhat smaller than that obtained from the data given by Schreyer and Seifert (1969a) and represent the lowest ones ever measured for a gedrite.

Recent studies of synthetic amphiboles with high-resolution transmission electron microscopy (HRTEM) indicate that macroscopic variations in chemical composition may be due to a “Realbau” that differs considerably from the ideal amphibole structure (e.g. Maresch et al. 1994, and references therein). Therefore, some of the synthetic gedrites reported on here were subjected to HRTEM studies at the University of Kiel with the help of Dr. M. Czank. An important result is that most of the crystals studied show an ideal double-chain amphibole structure. Only in about 10 per cent of

the gedrites grown from the 6:1:7 mixture at 10 kbar, 800 °C, after 9 days, were very few chain multiplicity faults (CMF) detected, although a\* still gave sharp reflections with no streaking. In gedrites grown from the impure 5:2:6 mixture under identical conditions no CMFs could be identified, which again suggests that the amphibole structure is stabilized by certain impurities.

The synthetic gedrites studied by HRTEM were also analysed chemically with the aid of an attached energy-dispersive system. Although this analytical method must be regarded as semiquantitative only – the crystals are too small for analysis by electron microprobe – the results show that all the crystals analysed gave compositions clustering uniformly about the ideal proportion 6:1:7. The deviations may amount to  $\pm 4$  mol% oxides, but they are identical for the products of four runs on both the 6:1:7 and the 5:2:6 mixtures. On this basis we suggest again that the gedrites synthesized in this study are essentially and invariably of the composition  $\text{Mg}_6\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$ , independent of starting material and run conditions, but neglecting the impurities discussed before.

#### HRTEM analyses of coexisting phases

In conjunction with the HRTEM studies of gedrite, the various run products were also inspected carefully for other phases, some of which were analysed. This procedure led to the discovery of both an additional phase not identifiable by X-ray methods and of aberrant compositions of the synthetic enstatites.

The prismatic enstatite crystals, again ranging in size from about 1 to 8 micrometres, invariably, and independently of the starting material employed, show compositions which plot off the general Tschermak substitution line enstatite-corundum (Fig. 1) in a direction towards higher  $\text{SiO}_2$ -contents. These deviations may be so extensive that the cluster of enstatite analyses obtained overlaps that of the gedrite analyses discussed above, although the Al-contents of enstatites tend to be lower than those of the gedrites. The problem of ternary solid solutions of aluminous enstatites not following solely the accepted Tschermak substitution trend  $\text{AlAl}$  for  $\text{MgSi}$  was recently investigated by Fockenberg and Schreyer (1997) on the basis of synthesis experiments. These authors obtained aluminous enstatites similar to

**Table 3** Cell dimensions of synthetic gedrite prepared in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ . (Uncertainties quoted represent  $1\sigma$  values from the refinement.)

Starting mixture	Synthesis conditions			No. of reflections	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	Source
	<i>P</i> (kbar)	<i>T</i> (°C)	Hours						
6:1:7	10	800	216	15	18.416(4)	17.817(6)	5.258(2)	1725.3(7)	This work
5:2:6	11	850	27	17	18.410(5)	17.796(8)	5.259(2)	1723.0(8)	This work
5:2:6	11	850	27	22	18.417(4)	17.800(6)	5.269(2)	1727.2(7)	Schreyer and Seifert (1969) <sup>a</sup>

<sup>a</sup> Reflections reindexed on the basis of calculated X-ray powder diffraction patterns (Borg and Smith 1969)

those of the present study, i.e. invariably too rich in  $\text{SiO}_2$ . They suggest that this ternary enstatite miscibility can be explained by an additional substitution of Si for Al<sup>[4]</sup> plus 0.5 Mg, leading to a theoretical end member  $(\square_{0.5}\text{Mg}_{0.5}\text{Al})[\text{Si}_2\text{O}_6]$ , which they named "Mg-Eskola-molecule" and which contains vacancies in the 6–7 coordinated structural site. In the present context, the enstatites analysed semiquantitatively have compositions clustering more or less along the line between anthophyllite and 6:1:7 (Fig. 1). A possible structural formula for such aluminous enstatite could be calculated as  $(\square_{0.09}\text{Mg}_{1.67}\text{Al}_{0.24})[\text{Al}_{0.07}\text{Si}_{1.93}\text{O}_6]$ , which would show even more vacancies than deduced by Fockenberg and Schreyer (1997); note however the large analytical uncertainty. At any rate, the aberrant compositions of aluminous enstatites are significant in terms of the nature of alternative breakdown assemblages of gedrite.

The HRTEM investigations also showed that in all studied run products obtained at 11 kbar, 850 °C, glass with a composition near the oxide ratio  $1\text{MgO}\cdot 1\text{Al}_2\text{O}_3\cdot 8\text{SiO}_2$  (Fig. 1) appears among the reaction products. Thus, the solidus temperature has been exceeded for both starting mixtures, and a siliceous melt formed that is part of the breakdown assemblage of gedrite. For the product obtained from the impure 5:2:6 mixture, this indicates that gedrite is a liquidus phase coexisting with melt under these conditions. Unfortunately, the HRTEM work necessary for identification of melt in the runs could not be extended to other *PT* conditions, so that the detailed melting relations and variations of melt composition in the MASH system at these pressures remain unclear.

The appearance of melt at 11 kbar, 850 °C, is in agreement with the results of Yoder (1971), who showed a small field of liquid in the MASH system at 10 kbar water pressure, 850 °C. His liquid composition is very similar to that analysed here. Yoder (1971) found what he called aluminous anthophyllite coexisting with cordierite and this liquid in runs of 3 to 10 days duration at these *PT* conditions. In comparison to our results on the 6:1:7 mixture, showing orthoamphibole breakdown in long runs at 11 kbar, 850 °C (Table 1A), this may indicate metastability of his orthoamphibole. Because synthetic glasses of high purity prepared by J.F. Schairer were used as starting materials by Yoder (personal communication 1998), a stabilizing influence by impurities as found for the 5:2:6 mixture used in the present study (Table 2B) seems less likely for his experiments. The finding of melt at 11 kbar, 850 °C, also supports the result of Newton (1972), who reported the assemblage enstatite + sillimanite + melt at 11–12 kbar, 830 °C.

It is important to note that HRTEM work always showed a second type of glass phase consisting entirely of  $\text{SiO}_2$ . This represents the product of the quenched vapour phase which, therefore, shifts the reacting solid bulk compositions away from 6:1:7 and 5:2:6 towards less siliceous compositions (cf. Fig. 1). It is for this reason that single-phase gedrite of the composition  $\text{Mg}_6\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$  could not be obtained during the

hydrothermal runs, even after very long durations at 10 kbar, 800 °C, with the 6:1:7 starting mixture (see above). The additional presence of aluminous enstatite and kyanite is believed to be the result of this silica loss from the solid to the fluid phase (leaching).

## Discussion

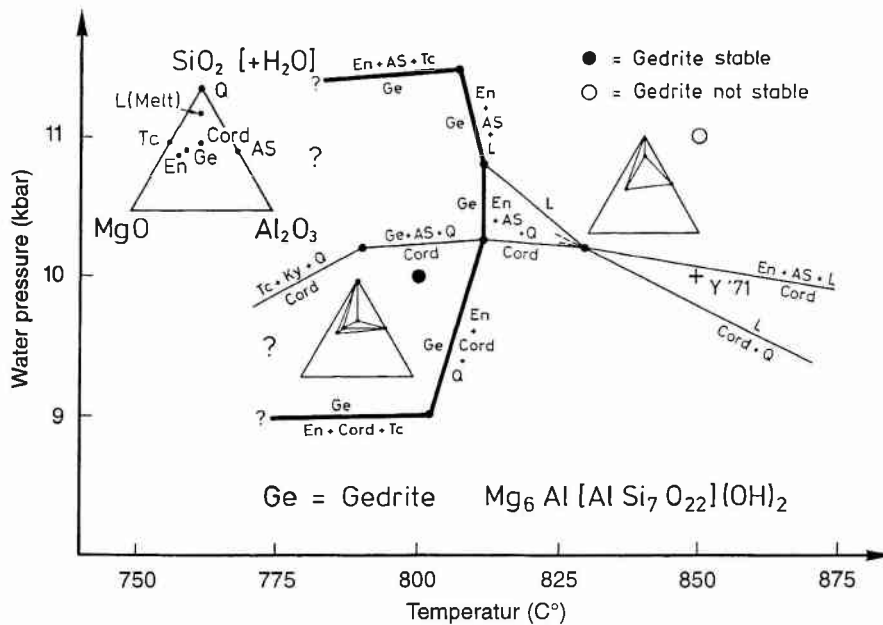
Although the experimental results obtained in this study are of limited scope, both regarding compositions and *PT* conditions studied, some cautious but very important deductions can be made on the phase relations in the MASH system in a particularly critical area of overlapping stability limits of various solid phases. The solid-media piston-cylinder runs of unusually long durations have resulted in the correct interpretation of metastable growth encountered in shorter experiments.

If the discussion is confined to the purest possible MASH chemistry first, the phase gedrite is shown to be stable at 10 kbar fluid pressure and 800 °C (Fig. 4) with a composition close to or identical with  $\square\text{Mg}_6\text{Al}[\text{AlSi}_7\text{O}_{22}](\text{OH})_2$ . Unfortunately, no direct comparison to natural Mg-rich gedrites is possible, because these always contain additional elements, mainly sodium and iron (e.g. Schreyer and Abraham 1976; Deer et al. 1997). In fact, from the view point of complex natural systems, a pure Na-free magnesium gedrite end member could actually have been regarded as non-existent or at least metastable, even after the synthesis of "aluminous anthophyllite" by Yoder (1971). Based on the present results, this is no longer true.

Lower pressures and temperatures outside the stability range of pure MASH gedrite (Fig. 4) were not investigated here, but it can be assumed from earlier synthesis experiments (Schreyer and Seifert 1969a) that no gedrite phase is stable there. Thus, its true stability field indicated in Fig. 4 seems to be very small ( $10 \pm 1$  kbar,  $800 \pm 20$  °C?). Future long-duration studies at lower pressures and temperatures may lead to modifications of this assumption.

It is important to note that the only gedrite composition found to be stable in the pure MASH system corresponds to  $\square\text{Mg}_6\text{Al}[\text{AlSi}_7\text{O}_{22}](\text{OH})_2$ , a composition representing the boundary between the anthophyllite and gedrite fields according to IMA nomenclature (Leake et al. 1997). End-member gedrite, defined by Leake et al. (1997) as  $\square\text{Mg}_5\text{Al}_2[\text{Al}_2\text{Si}_6\text{O}_{22}](\text{OH})_2$ , could not be synthesized, even on its own bulk composition, and does not seem to exist even as a metastable phase. Nevertheless, it may remain valid as a theoretical end member in the nomenclature scheme.

A crucial point for MASH phase relations is that at 10 kbar water pressure, 800 °C, hydrous end-member cordierite (Fig. 1) has been shown to be a stable phase as well (Schreyer and Yoder 1964), but that these conditions are also close to its upper pressure limit (Schreyer 1968; Newton 1972, 1995). The present experiments on the 6:1:7 and 5:2:6 compositions cannot contribute di-



**Fig. 4** Tentative stability field of the gedrite synthesized from the chemically pure 6:1:7 starting material (*heavy lines*) relative to the upper pressure stability limit of hydrous Mg-cordierite with a selection of resulting phase relationships (*thin lines*). *Inset* in the upper left shows the phases involved with enstatite containing Al in solid solution but ignoring its Si-excess (see previous section). The other *two insets* depict selected compatibility relations for portions of the divariant fields in which they are placed. Two run conditions investigated here and the results concerning gedrite stability are shown by *solid* and *open circles*. The + sign marks the *PT* condition investigated by Yoder (1971). (Abbreviations as in Table 1, except for: *AS*  $\text{Al}_2\text{SiO}_5$  (kyanite or/and sillimanite), *Cord* hydrous cordierite, *L* melt, *Q* quartz). The chemical formula of the gedrite is given at the *bottom*. Note that the gedrite stability outlined here does not apply to the gedrite synthesized from the 5:2:6 starting material that contains FeNaCa impurities

rectly to this topic, especially as their solid bulk chemistry is shifted due to  $\text{SiO}_2$ -leaching (see above). Nevertheless, based on the results at 10 kbar, 800 °C and 11 kbar, 850 °C, a revised, but still tentative *PT* grid is constructed in Fig. 4, observing the rules of Schreinemakers, for the relations between the phases gedrite, aluminous enstatite, cordierite, talc,  $\text{Al}_2\text{SiO}_5$ , quartz, and a melt near 1:1:8 composition. Although B-free kornerupine is also stable under both of these *PT* conditions (Wegge and Schreyer 1994), and although this phase was obtained here in long runs on both 6:1:7 and 5:2:6 mixtures at 11 kbar, 850 °C (Tables 1A and 2B), it is disregarded in Fig. 4, mainly because its role cannot be ascertained with the limited data at hand. The presence of melt in the pure 6:1:7 composition at 11 kbar, 850 °C after 504 hours together with enstatite, kyanite, and additional kornerupine (Table 1A) could indicate a univariant assemblage occurring along a reaction or melting curve such as Al-enstatite +  $\text{Al}_2\text{SiO}_5$  = kornerupine + melt (see Fig. 1). As the 1:1:8 melt was also found to occur, however, in run products not containing kornerupine, the appearance of

the four phases may also be due to disequilibrium. Therefore, it is assumed in Fig. 4 that the enstatite- $\text{Al}_2\text{SiO}_5$  tie line is stable within the small *PT* range under discussion.

The *PT* plot of Fig. 4 delineates the possible stability field of pure gedrite, which is intersected by the upper pressure stability limit of pure Mg-cordierite as deduced by Schreyer and Seifert (1969b, Fig. 2). Therefore, the breakdown reactions of gedrite are expected to lead to cordierite-bearing assemblages at pressures below about 10 kbar. Above this pressure, only the phases talc, enstatite,  $\text{Al}_2\text{SiO}_5$  (kyanite, sillimanite), quartz, and melt are involved. Over a limited pressure range, the 6:1:7 gedrite is a liquidus phase melting incongruently to Al-enstatite +  $\text{Al}_2\text{SiO}_5$  + liquid.

Cordierite shows, in agreement with preliminary data of Schreyer (1968) and with the grid of Schreyer and Seifert (1969b), subsolidus breakdown into the assemblages talc + kyanite + quartz, gedrite + kyanite/sillimanite + quartz, and enstatite + sillimanite + quartz, as a function of increasing temperature (Fig. 4). When the solidus temperature for  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  is surpassed, cordierite melts incongruently to enstatite + sillimanite + liquid. Because this eutectic liquid has its composition close to the oxide ratio 1:1:8, it should be formed, at somewhat lower water pressures and temperatures, by melting of the assemblage cordierite + quartz. The nature and *PT* locations of these melting curves, which are drawn here, respecting the instability of cordierite + quartz at 10 kbar, 850 °C (Yoder 1971), are decisive for the breakdown relationships of Mg-cordierite. They agree in a general way with the schematic configuration envisaged by Newton (1972, Fig. 8), who, however, ignored the phase gedrite.

The nature of the two gedrite breakdown reactions within the cordierite field (Fig. 4) are speculative at this stage and require future work below 10 kbar. The



difference in phase relations compared with the hypothetical grid of Schreyer and Seifert (1969b) results from the fact that in Fig. 4, contrary to the earlier work, an Al-content of enstatite has been taken into account, so that corundum no longer appears as a phase.

An important open problem remains in regard to the role of boron-free kornerupine (Fig. 1) in the phase relationships. According to Wegge and Schreyer (1994), this phase is stable throughout the *PT* range of Fig. 4, but no longer at pressures beyond about 12 kbar. Tables 1 and 2 confirm that in the present experiments the kornerupine phase only appears within its stability field. Long-term experiments with boron-free kornerupine as seed crystals and techniques appropriate to identify the appearance of melt will be necessary to show as to whether or not the stability fields of pure MASH gedrite and hydrous cordierite are affected by reactions involving the kornerupine phase.

Finally, it is clear from this study that small amounts of impurities have a considerable effect on gedrite stability. The results obtained on the 5:2:6 starting material show that FeCaNa contamination of less than one weight percent total oxides extends the stability field of gedrite from 10 kbar, 800 °C (Fig. 4) at least to the range 10–15 kbar, 800–850 °C. Thus, in impure natural systems of appropriate compositions Mg-rich gedrites can be expected as rather common high-pressure, high-temperature minerals.

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