

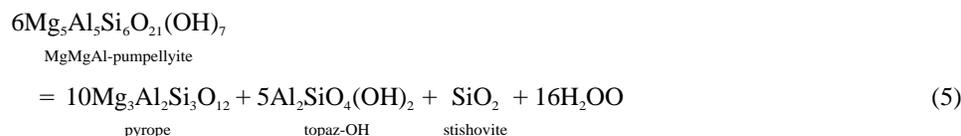
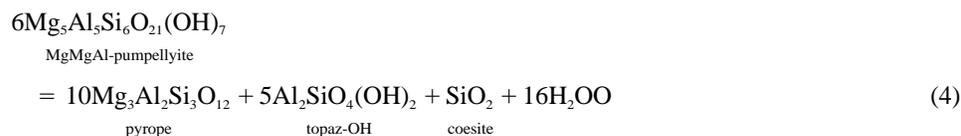
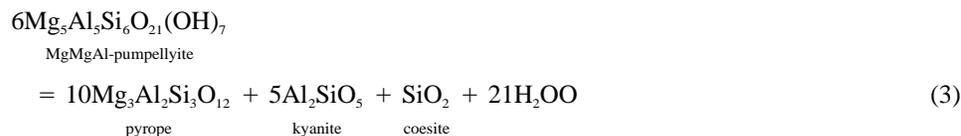
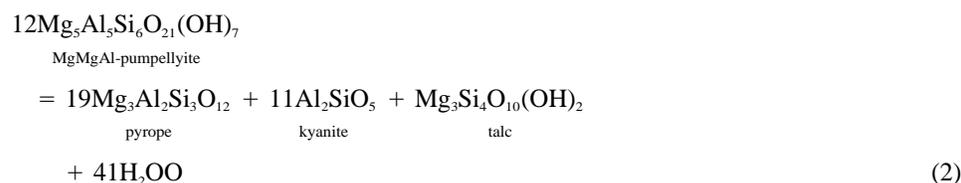
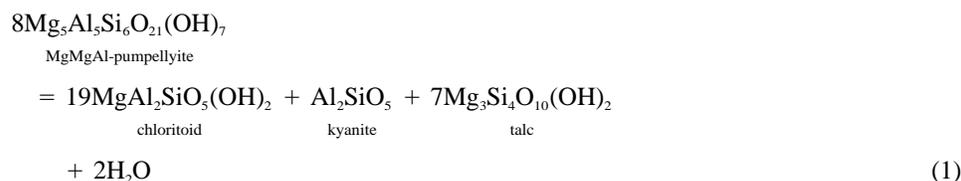
An experimental study of the pressure-temperature stability of MgMgAl-pumpellyite in the system MgO-Al₂O₃-SiO₂-H₂O

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ABSTRACT

The stability field of MgMgAl-pumpellyite, Mg₅Al₅Si₆O₂₁(OH)₇, was determined in the system MgO-Al₂O₃-SiO₂-H₂O in reversal experiments at pressures between 34 and 100 kbar and temperatures in the range of 597 to 1050 °C. Brackets were obtained on five breakdown reactions (in order of increasing pressure):



This phase becomes stable only at pressures of more than 34 kbar and temperatures up to 820 °C. Thus, MgMgAl-pumpellyite may be an H₂O-containing phase at depths greater than 100 km in the coldest parts of subduction zones.

INTRODUCTION

MgMgAl-pumpellyite, Mg₅Al₅Si₆O₂₁(OH)₇ (Fig. 1), was identified in experiments on a hypothetical (Ti,Zr,P)-free end-member of ellenbergerite in the simple chemical system MgO-Al₂O₃-SiO₂-H₂O by Schreyer et al. (1986; see also 1987, 1991). This Mg analogue of CaMg-pumpellyite was synthesized from a gel of the ideal composition 5MgO:2.5Al₂O₃:6SiO₂ at 50 kbar and 700 °C in the presence of excess H₂O. Preliminary *P-T* stability rela-

tions presented by Schreyer (1988) indicated that MgMgAl-pumpellyite is a high-pressure phase, stable at pressures above 37 kbar and temperatures between about 400° and 800 °C. Its low-*T* limit is marked by a breakdown reaction to talc + Mg-carpholite + chlorite, which has been bracketed by reversal experiments (Schreyer et al. 1991). Schreyer also determined that the high-*T* stability limit of MgMgAl-pumpellyite, as defined by a dehydration reaction to pyrope + kyanite + coesite + H₂O,

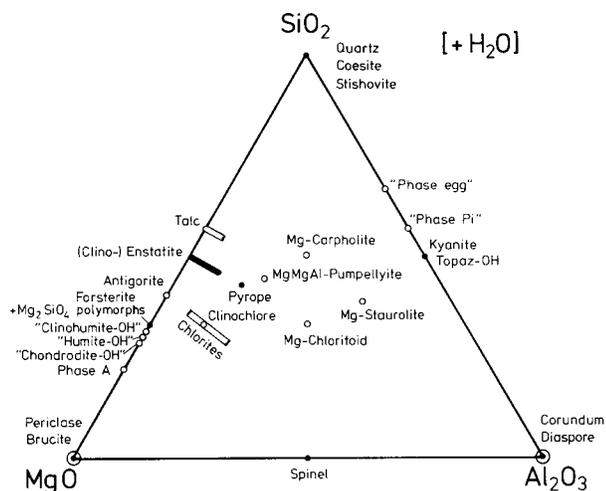


FIGURE 1. Selected phases in the system MgO-Al₂O₃-SiO₂-H₂O stable at high pressure in a projection from H₂O. Open symbols = hydrous phases, solid symbols = anhydrous phases. "Phase egg" describes an ultrahigh pressure phase synthesized by Eggleton et al. (1978) having a molar ratio of 5 Al₂O₃:10 SiO₂:1 H₂O.

occurred at 50 kbar and 775 °C. Three additional breakdown reactions, connecting the two reactions mentioned above, are in order of rising temperature: MgMgAl-pumpellyite = Mg-chloritoid + talc + Mg-carpholite; MgMgAl-pumpellyite = Mg-chloritoid + talc + kyanite + H₂O; and MgMgAl-pumpellyite = talc + kyanite + pyrope + H₂O. The first reaction represents the lower pressure limit of the pumpellyite phase, whereas the other two are dehydration reactions that should have positive slopes (Schreyer 1988). Liu (1989) determined that the upper pressure stability of MgMgAl-pumpellyite, is represented by breakdown reaction to pyrope + kyanite + stishovite + H₂O at *P* < 160 kbar and pyrope + stishovite + corundum + H₂O at *P* > 160 kbar. However, these curves do not reflect the stable compatibility relations at these ultra-high pressures, because the *P-T* conditions (80–220 kbar; 800–1000 °C) of all experiments chosen by Liu lie within the stability field of topaz-OH (Wunder et al. 1993a).

A calculated *P-T* grid for the system MASH up to pressures of 70 kbar was presented by Massonne (1995) based on the thermochemical data (Berman 1988) and experimental data of those MASH-phases lacking in the Berman data set. Massonne computed a stability field for MgMgAl-pumpellyite with a minimum pressure of 40 kbar. He was able to reproduce the breakdown reactions toward high temperatures given by Schreyer et al. (1991) but found different phase relations for the formation of the pumpellyite phase at temperatures below 700 °C. According to the data of Massonne (1995), MgMgAl-pumpellyite forms from the assemblages talc + Mg-chloritoid + topaz-OH and talc + Mg-chloritoid + coesite, whereas those reactions involving Mg-carpholite (see above) should be metastable.

The topic of this experimental study is the determination of the upper thermal stability of MgMgAl-pumpellyite at pressures up to 100 kbar. The results yield a better insight into the possible role of this pumpellyite phase as an H₂O-containing mineral within subducting slabs at convergent plate boundaries.

EXPERIMENTAL TECHNIQUES

Gels were used as starting materials for synthesis of the phases MgMgAl-pumpellyite, talc, pyrope, kyanite, and Mg-chloritoid. These gels were prepared following the method of Hamilton and Henderson (1968) using Si(OC₂H₅)₄ (tetraethylorthosilicate, TEOS, >99%, Merck, Darmstadt, Germany), Mg powder (>99.8%, Fluka, Buchs, Switzerland), Al powder (>99.5%, Schuchardt, Munich, Germany), and nitric acid and ammonium hydroxide 25% (both p.a. quality). The compositions of the gels and the *P-T* conditions for synthesis experiments are given in Table 1. Coesite was prepared by R. Wirth using SiO₂ gel (99.999% purity). Starting materials for reversal experiments consisted of approximately equal amounts of MgMgAl-pumpellyite and intimately mixed stoichiometric mixtures of the respective breakdown phases in the presence of excess H₂O.

Synthesis and reversal experiments were carried out at pressures up to 65 kbar in a piston-cylinder apparatus constructed after the design of Boyd and England (1960). The pressure cell (diameter 12.7 mm) used up to 50 kbar

TABLE 1. Starting materials, conditions, and results of synthesis experiments

Experiment	Starting material	<i>T</i> (°C)	<i>P</i> (kbar)	<i>T</i> (h)	Product phases (for more details see text)
Pu 10	gel Pu2	650	50	16	MgMgAl-pmp
Pu 25	gel Pu2	650	50	16	MgMgAl-pmp
Ctd 27	gel 111 + synth. Mg-cld	650	40	38	Mg-cld + dsp (about 5%)
Ky 10	gel 011	800	40	48	ky
Tc 8	gel 304	600	2	48	tic
Py 114	gel 313	800	35	23	prp
Py 110	gel 313	800	40	18	prp

Note: Abbreviations used in this paper: coe = coesite; cld = chloritoid; dsp = diaspore; ky = kyanite; pmp = pumpellyite; prp = pyrope; stish = stishovite; tic = talc; top-OH = topaz-OH. gel Pu2 = 10 MgO:5 Al₂O₃:12 SiO₂, gel 011 = 1 Al₂O₃:1 SiO₂, gel 111 = 1 MgO:1 Al₂O₃:1 SiO₂, gel 313 = 3 MgO:1 Al₂O₃:3 SiO₂, gel 304 = 3 MgO:4 SiO₂.

consisted of NaCl and fired pyrophyllite causing negligible friction. This cell is similar to type III described by Massonne and Schreyer (1986). Quoted experimental pressures are based on a simple force per area calibration of the oil pressure and piston area. The overall 2σ pressure uncertainty was assumed to be 2%. Temperature measurement and control were achieved using mantled chromel-alumel thermocouples. Combining all the uncertainties in the thermocouple, the wires, and the control instruments, the 2σ uncertainty in T is estimated to be 2%. Correction of the emf of the thermocouple followed the data of Getting and Kennedy (1970); about 3–5 °C (depending on P and T) have to be subtracted from the measured temperature. A second correction to the temperature was applied according to the temperature distribution within a salt pressure cell as investigated by Leister (1979), because the thermocouple junction was placed about 0.5 mm away from the capsule in the axial direction. Because the capsule is placed in the hot spot of the salt cell 2 °C must be added to the measured temperature.

Synthesis experiments were carried out using large gold capsules (length = 16 mm, diameter = 6.1 mm, wall thickness = 0.25 mm); smaller gold capsules served for reversal experiments (length = 4 mm, diameter = 2.3 mm, wall thickness = 0.25 mm). Experiments at 60 and 65 kbar were carried out using pressure cells composed of natural CaF₂ instead of rock salt. The diameter of these cells is 8 mm. Ultrahigh-pressure experiments at 80 and 100 kbar were carried out in the 1200 ton uniaxial split sphere multianvil press at the Bayerisches Geoinstitut, Bayreuth. This type of multianvil press is described by Ito et al. (1984); detailed information on pressure calibration, anvils, and sample assemblies are given by Wunder et al. (1993b). Temperature uncertainty is assumed to be about ± 50 °C (D. Canil, personal communications) and pressure uncertainty is as much as ± 5 kbar (Wunder et al. 1993b). Experimental charges were enclosed in gold capsules with a length of 4 mm, an outer diameter of 2 mm, and a wall thickness of 0.25 mm.

All experiments were carried out under excess H₂O conditions; all cold-sealed capsules were tested for leakage after the experiments. Direction of the reaction of reversal experiments was determined by comparing the intensities of the X-ray diffractograms of the experimental products with those of the starting mixtures.

Chemical analyses of synthetic MgMgAl-pumpellyite were carried out using the electron microprobe at Ruhr-University (CAMECA SX 50) with a PAP correction (Pouchou and Pichoir 1984). The beam current was 10 nA, the accelerating voltage was 15 kV, and the counting time was 20 s. Pyrope served as the standard (MgK α , AlK α , SiK α).

SYNTHESES OF PURE MASH PHASES

Synthesis conditions, starting materials, and results are summarized in Table 1. Details of the experiments are given below.

TABLE 2. Chemical formulae of synthetic MgMgAl-pumpellyite as determined by electron microprobe analysis

Experimental conditions	Mg	Al	Si	Number of analyses
Pu 25 50 kbar/650° C	9.75(15)	10.35(14)	11.87(4)	14
Pu 37-G 37 kbar/640° C	9.55(33)	10.17(28)	12.10(33)	12
Pu 35-G 45 kbar/700° C	9.54(23)	10.21(34)	12.08(18)	17
Pu 18-G 50 kbar/700° C	9.33(25)	10.29(18)	12.12(6)	22
Pu 16-G 80 kbar/800° C	9.22(69)	10.26(49)	12.20(20)	18
Pu 17-G 100 kbar/800° C	9.67(48)	10.10(54)	12.09(35)	15

Note: Formula proportions calculated on the basis of 49 O atoms. Numbers in parentheses indicate 2σ uncertainty.

MgMgAl-pumpellyite

Single-phase pumpellyite was synthesized from the original gel Pu2 used by Schreyer et al. (1991) at 50 kbar and 700 °C for 16 h. Crystals are euhedral with lengths up to 30 μ m. Lattice parameters for the monoclinic cell were determined as: $a = 8.544(3)$ Å; $b = 5.717(2)$ Å; $c = 18.502(6)$ Å; $\beta = 97.71(3)^\circ$. These values are identical (within 2σ error) to those reported by Schreyer et al. (1991). The chemical composition of the crystals was determined by electron microprobe analysis, yielding a mean H₂O-free formula of Mg_{9.75}Al_{10.35}Si_{11.87}O₄₉ (average of 14 grains, see Table 2). Although this composition deviates by $\sim 3\%$ from the initial stoichiometric oxide ratio of the gel, no additional phases were identified in the X-ray patterns of the experimental products nor during electron microprobe analysis. Nevertheless, because the composition of the synthetic pumpellyite plots away from the ideal ratio toward Al-richer compositions, small amounts of additional phases such as enstatite or pyrope + coesite must be present in the products.

Talc

Synthetic talc was obtained by reacting a gel of the ideal oxide ratio 3MgO:4SiO₂ in the presence of excess water at 2 kbar and 600 °C. Lattice parameters of this phase were determined as: $a = 5.34(8)$ Å; $b = 9.12(2)$ Å; $c = 9.40(2)$ Å; $\alpha = 90.6(3)^\circ$; $\beta = 97.4(6)^\circ$; $\gamma = 89.9(2)^\circ$. With the exception of the a parameter, these values are somewhat lower than those determined by Wunder (1993), who presented values of: $a = 5.288(5)$ Å; $b = 9.149(4)$ Å; $c = 9.455(4)$ Å; $\alpha = 90.8(1)^\circ$; $\beta = 98.6(1)^\circ$; $\gamma = 90.0(1)^\circ$. This discrepancy may result from stacking faults in the talc lattice. Wunder (1993) demonstrated that talc synthesized from starting materials having the ideal oxide ratio of 3:4 (see above) contains variable amounts of Mg(OH)₂-layers, which can directly influence the lattice parameters.

TABLE 3. Results of bracketing experiments for reactions 1, 2, and 3

Experiment	<i>P</i> kbar	<i>T</i> (nom.) °C	<i>T</i> (corr.) °C	Dura- tion (h)	Growth of:	Reaction extent
Reaction 1 mix PP-C1						
Pu 39-G	34	600	596	46	cld, ky, tlc	(+)
Pu 40-G	34	640	638	70	cld, ky, tlc	(+)
Pu 41-G	35	600	597	44	no reaction	
Pu 42-G	35	640	637	23	pmp	(+)
Pu 31-G	36	600	599	93	pmp	(++)
Pu 38-G	36	640	638	46	pmp	(+)
Pu 37-G	37	640	639	69	pmp	(+++)
Pu 36-G	38	600	602	46	pmp	(+++)
Reaction 2 mix PP-B1						
Pu 22-G	40	640	642	119	pmp	(+)
Pu 30-G	40	660	658	93	no reaction	
Pu 20-G	40	680	679	115	prp, ky, tlc	(++)
Pu 35-G	45	700	702	42	pmp	(++)
Pu 32-G	45	720	719	70	prp, ky, tlc	(+)
Reaction 3 mix PP-A1						
Pu 18-G	50	700	698	47	pmp	(++)
Pu 27-G	50	730	728	70	pmp	(+)
Pu 12-G	50	750	753	68	no reaction	
Pu 19-G	50	780	787	47	prp, ky, coe	(++)
Pu 26-G	60	730	732	70	pmp	(+)
Pu 34-G	60	760	762	22	prp, ky, coe	(+)
Pu 24-G	60	780	782	40	prp, ky, coe	(+)
Pu 23-G	65	850	852	21	prp, ky, coe	(++)

Note: Starting materials: mix PP-A1 from experiment PU 10 (Mg-pmp), Py 110 (prp), Ky 9 (ky), coe, mix PP-B1 from experiment Pu 25 (Mg-pmp), Py 114 (prp), Ky 10 (ky), and Tc 8 (tlc), mix PP-C1 from experiment Pu 25 (Mg-pmp), Ctd 27 (Mg-cld), Ky 10 (ky), and Tc 8 (tlc). Symbols: (+) small (10%), (++) intermediate (40%), (+++) large (60%) amount of reaction. *T*(nom.) = Measured temperature at the thermocouple junction. *T*(corr.) = Temperature corrected for axial thermal gradient and pressure effect on the emf. Abbreviations: See Table 1. (1) 8Mg-pumpellyite = 19Mg-chloritoid + 1kyanite + 7talc + 2H₂O. (2) 12Mg-pumpellyite = 19pyrope + 11kyanite + 1talc + 41H₂O. (3) 6Mg-pumpellyite = 10pyrope + 5kyanite + 1coesite + 21H₂O.

Kyanite

A gel of the oxide ratio 1Al₂O₃:1SiO₂ was run at 40 kbar and 800 °C and yielded only kyanite. The euhedral crystals show low birefringence and have a length of 10 μm. Lattice parameters of this phase are: *a* = 7.12(4) Å; *b* = 7.89(4) Å; *c* = 5.58(4) Å; α = 89.9(6)°; β = 100.8(6)°; γ = 106.3(6)°. These agree well with those determined by Massonne (1989), which were *a* = 7.1217(3) Å; *b* = 7.8476(4) Å; *c* = 5.5730(3) Å; α = 89.945(7)°; β = 101.192(5)°; γ = 106.006(3)°.

Pyrope

Single-phase pyrope was synthesized from a gel having the oxide ratio 3 MgO:1 Al₂O₃:3 SiO₂ at 50 kbar/900 °C. The euhedral crystals are about 50 μm in diameter. The cubic cell edge was determined to be 11.4578(9) Å, which is in good agreement with that given by Geiger et al. (1991) as 11.457(2) Å.

Coesite

Pure coesite was prepared by R. Wirth from an SiO₂ gel at 30 kbar and 700 °C. Crystals are up to 50 μm in

TABLE 4. Results of bracketing experiments for reactions 4 and 5

Experiment	<i>P</i> (kbar)	<i>T</i> (nom.) °C	Dura- tion (h)	Growth of:	Reaction extent
Reaction 4					
Pu 16-G	80	800	13	pmp	(+)
Pu 28-G	80	850	12	prp, top-OH, coe	(++)
Pu 8-G	80	900	13	prp, top-OH, coe	(++)
Pu 4-G	80	950	13	prp, top-OH, coe	(++)
Pu 7-G	80	1000	13	prp, top-OH, coe	(++)
Reaction 5					
Pu 17-G	100	800	13	pmp	(+)
Pu 29-G	100	850	12	prp, top-OH, stish(?)	(+)
Pu 14-G	100	900	13	prp, top-OH, stish(?)	(++)
Pu 9-G	100	940	13	prp, top-OH, stish(?)	(++)
Pu 5-G	100	980	14	prp, top-OH, stish(?)	(++)
Pu 6-G	100	1050	14	prp, top-OH, stish(?)	(++)

Note: Starting material: mix PP-A2 from experiment Pu 25 (Mg-pmp), Py 100 (prp), Ky 9 (ky), coe. Symbols: See Table 2. Abbreviations: See Table 1.

length, and lattice parameters are: *a* = 7.139(25) Å; *b* = 12.423(35) Å; *c* = 7.121(26) Å; β = 120.0(4)°.

Mg-chloritoid

A gel of the oxide ratio 1MgO:1Al₂O₃:1SiO₂ along with precrystallized Mg-chloritoid as seeds was reacted at 650 °C and 35 kbar to yield Mg-chloritoid plus small traces of corundum. Lattice parameters are: *a* = 9.45(5) Å; *b* = 5.48(2) Å; *c* = 18.10(8) Å; β = 101.5(7)°, which are similar to those of Chopin et al. (1992).

RESULTS OF REVERSAL EXPERIMENTS

The present determination of the *P-T* stability field of MgMgAl-pumpellyite is in general agreement with the grid constructed by Schreyer et al. (1991) from theoretical and experimental work. Conditions and results of the reversal experiments are given in Tables 3 and 4 and Figure 2.

Reaction 1: MgMgAl-Pumpellyite ↔ Mg-Chloritoid + Kyanite + Talc + H₂O

This reaction was bracketed between 34 and 36 kbar at ~600 °C, and between 34 and 35 kbar at ~640 °C (Table 3). Though Massonne (1995) calculated this curve with a negative slope (−19.6 K/kbar), in Figure 2 the univariant boundary is shown schematically to have a small positive slope due to the fact that H₂O is released in most other reactions toward higher temperatures. In fact, the experimental results do not constrain the sign of the slope of the curve, but they do imply that it is shallower than the calculated reaction curve. The breakdown of pumpellyite at pressures below 35 kbar indicates that this phase is stable toward lower pressures than estimated by Schreyer et al. (1991, lower *P* limit at 37 kbar) and computed by Massonne (1995, lower *P* limit at 40 kbar).

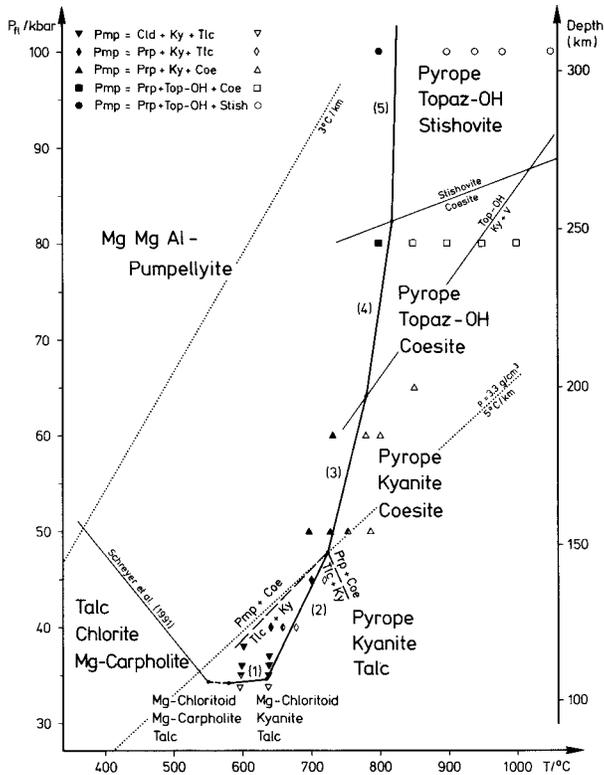
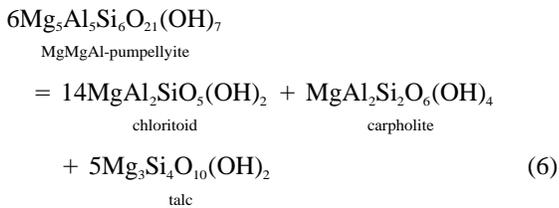
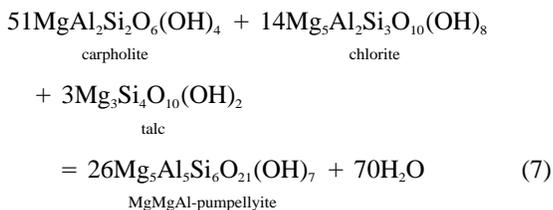


FIGURE 2. *P-T* diagram showing the stability field of MgMgAl-pumpellyite. Solid and open symbols refer to growth or breakdown, respectively, of MgMgAl-pumpellyite; half-closed symbols indicate no reaction (see Tables 2 and 3). The reaction curve carpholite + chloritoid + chlorite = pumpellyite was adopted from Schreyer et al. (1991), reaction curve carpholite + chloritoid + talc = pumpellyite (broken line) was not determined experimentally. The breakdown of topaz-OH to kyanite + vapor was reversed by Wunder et al. (1993a) and the transition coesite = stishovite by Zhang et al. (1996). Broken lines define the upper pressure limit of the assemblage talc + kyanite as given by Schreyer (1988). Linear geotherms were calculated for a mean rock density of 3.3 g/cm³.

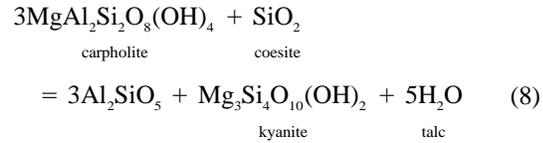
The breakdown reaction



connecting reaction 1 and the reaction



investigated by Schreyer et al. (1991) was not studied in this work. As an H₂O-absent reaction, 6 is assumed to have a shallow Clapeyron slope. Assuming that the positions of reactions 1 and 2 given in Figure 2 are correct, reaction 6 likely lies at a pressure of ~34 kbar and temperatures between 540 and 570 °C. The high temperature limit is defined by the intersection with the reaction



The position of reaction 8 is taken from Schreyer et al. (1991).

Reaction 2: MgMgAl-Pumpellyite ↔ Talc + Pyrope + Kyanite + H₂O

Brackets of this reaction were obtained at 40 kbar between ~640 and ~680 °C and at 45 kbar between ~700 and ~720 °C (Table 3). A range of Clapeyron slopes is permitted by the reversals. If a slope of +5 K/kbar (calculated +6.4 K/kbar; Massonne 1995) is assumed, the invariant point connecting curves 1 and 2 would be located at 34.2 kbar and 637 °C (Fig. 2) and reaction 1 would be stable. However, taking into account the uncertainties in *P* and *T* of the experiments and the width of the reversals, the invariant point may occur at slightly higher or substantially lower temperatures. The current experiments permit a sufficiently shallow Clapeyron slope that reaction 1 may be metastable. Regardless of its relative stability, however, the invariant point defined by the intersection of reactions 1 and 2 must lie at ~35 kbar and <650 °C, as opposed to ~41 kbar and 740 °C proposed by Schreyer et al. (1991).

Reaction 3: MgMgAl-Pumpellyite ↔ 10 Pyrope + Coesite + Kyanite + H₂O

Reaction 3 was bracketed between ~730 and ~780 °C at 50 kbar (Table 3). No significant change in the intensities of the X-ray reflections was detected at 50 kbar and 753 °C. Another bracket was obtained between ~730 and ~760 °C at 60 kbar (Table 2). The location of this reaction curve with a steep positive slope of +3 K/kbar (Fig. 2) agrees both with the position proposed by Schreyer et al. (1991) and calculated by Massonne (1995; slope +3.8 K/kbar).

The invariant point defined by the intersection of reactions 2 and 3 is located at 48 kbar and 715 °C (Fig. 2); Schreyer (1988) assumed its position to lie at 44 kbar and 760 °C. Massonne (1995) calculated this point to lie at 44 kbar and 710 °C, which is in fairly good agreement with the experimental data. This invariant point also represents the maximum pressure for the stable coexistence of the whiteschist assemblage talc + kyanite (Fig. 2).

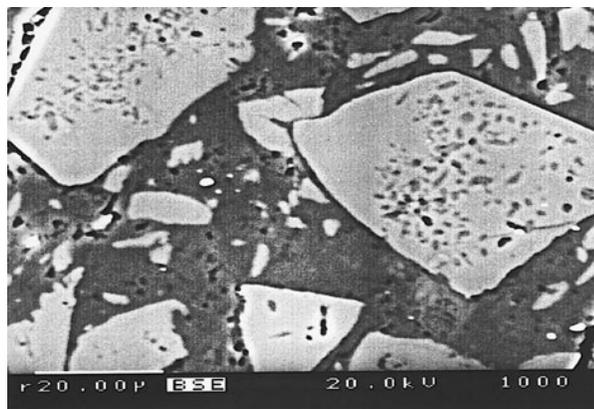


FIGURE 3. Backscattered-electron (BSE) image of the products of experiment PU 17-G, reaction 5, 6Pumpellyite = 10Pyrope + 5Topaz-OH + 1Stishovite + 16H₂O, 100 kbar and 800 °C). The light gray crystals are pyrope. The matrix (dark gray) consists of MgMgAl-pumpellyite. Note the intergrowth of pumpellyite with pyrope (small dark gray crystals within the large pyrope grains).

Reactions 4 and 5: MgMgAl-Pumpellyite ↔ Pyrope + Topaz-OH + Coesite or Stishovite + H₂O

Because insufficient amounts of either stishovite and topaz-OH were available for use in the present experiments, the starting material of the reversal experiments at ultrahigh pressure conditions is identical to that of reaction 3. Nevertheless, in all experiments within the stability field of topaz-OH (see Wunder et al. 1993a), kyanite was observed to disappear completely at the expense of topaz-OH. Presumably, because of the very small amount of the SiO₂-phase produced, no reflections of coesite or stishovite were observed in the X-ray patterns. Direction of reaction was detected by the growth or decrease of the reflections of pumpellyite, pyrope, and topaz-OH.

Reactions 4 and 5 are constrained to lie between ~800 and ~850 °C at both 80 and 100 kbar (Table 4), indicating that their Clapeyron slopes are steep. Because no new phase was identified in the X-ray patterns of the experiment products, the maximum pressure of MgMgAl-pumpellyite stability should exceed 100 kbar.

PETROGRAPHY AND CHEMICAL COMPOSITION OF MgMgAl-PUMPELLYITE

A backscattered-electron (BSE) image (Fig. 3) of the products of experiment Pu 17-G (Table 3) shows large grains of pyrope (light gray) in a matrix of pumpellyite (dark gray), in which individual crystals cannot be distinguished because of their fine grain size (<10 μm). Thus, textural relationships between pyrope and pumpellyite indicating the growth of pumpellyite on a pyrope surface cannot be observed. However, small grains of pumpellyite are intergrown with pyrope (dark spots on the surface of pyrope crystals, Fig. 3), which may reflect the breakdown of pyrope and the formation of new grains MgMgAl-pumpellyite.

The MgMgAl-pumpellyite produced in selected bracketing experiments was analyzed by the electron microprobe. Mean compositions of pumpellyites calculated on an H₂O-free base (normalized on 49 O atoms) are presented in Table 2. The mean pumpellyite compositions after reversal experiments are distinguished from those of the starting material (Table 2, experiment Pu 25) by their higher Si and lower Mg and Al contents. However, the large 2σ uncertainties indicate that there is wide chemical variability of the pumpellyite grains in each sample (Table 4), and no statistical significance should be ascribed to the differences. The heterogeneity in the chemical compositions may result from the relatively short experiment times employed in this study. Deviations from stoichiometric MgMgAl-pumpellyite of at least several percent appear to be common to all experiments. The reason for this is not known.

DISCUSSION

Reversal experiments on five breakdown reactions of MgMgAl-pumpellyite indicate that this phase is stable only at ultra high-pressure (UHP) conditions. Figure 2 shows the pumpellyite stability field and linear geotherms calculated on the basis of a rock density of 3.3 g/cm³, which may be close to the average density of the Earth's lithosphere. According to the results of this work, MgMgAl-pumpellyite requires a minimum pressure of 35 kbar, or about 115 km depth, to become a stable phase. The largest part of the pumpellyite field falls into a *P-T* realm characterized by geotherms lower than 5 °C/km. Although this geotherm has been regarded as the lowest one realized on Earth (see Schreyer 1988), new simulations on the temperature distribution within subduction zones (e.g., Peacock 1990) indicate that rocks could be subducted along geotherms as low as 3 °C/km. These geotherms are realized in the inner parts of rapidly buried continental or oceanic crust in long-lasting subduction zones (Peacock 1990). MgMgAl-pumpellyite, as a H₂O-containing mineral (7.1 wt% H₂O; Schreyer et al. 1991), may therefore transport H₂O to great depths provided that the bulk composition is appropriate for its formation under these geotherms (see below).

Assuming a linear geotherm of 5 °C/km, metamorphic rocks containing MgMgAl-pumpellyite as the only hydrous phase will dehydrate completely at depths greater than 150 km due to formation of pyrope-rich garnet + kyanite + coesite. At 3 °C/km, MgMgAl-pumpellyite becomes unstable at ~300 km (Fig. 2) and produces pyrope + topaz-OH + stishovite + H₂O. In metamorphic rocks buried along geotherms higher than 5 °C/km, pumpellyite can grow with no H₂O loss from the assemblage Mg-carpholite + Mg-chloritoid + talc. Alternatively, the formation of the pumpellyite phase from Mg-chloritoid + kyanite + talc (reaction 1) requires only small amounts of H₂O, which may be available in a subducting slab from dehydration reactions involving other minerals. Because these two reactions are located within the realm of geotherms higher than 5 °C/km, the pumpellyite phase may

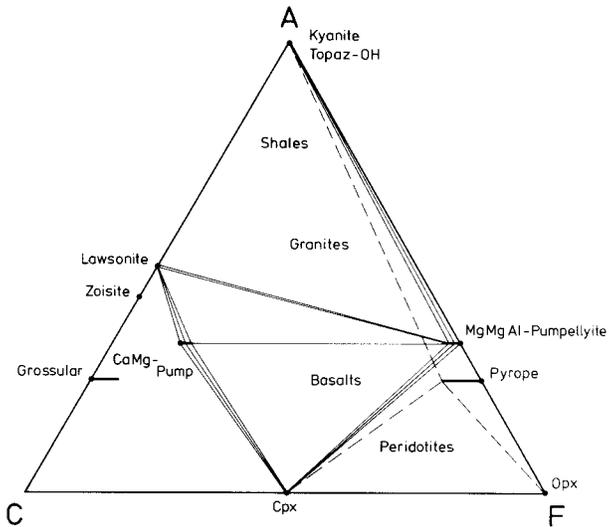


FIGURE 4. ACF-diagram showing the locations of high-pressure minerals together with fields of four typical rock types (from Winkler 1979). Also shown are assumed tie-lines for geotherms lower than 5 °C/km. Solid lines represent coexistence of MgMgAl-pumpellyite with high-pressure phases outside the stability field of pyrope. Broken lines represent coexistence of pyrope especially with kyanite, which cuts off MgMgAl-pumpellyite from the compositional fields of the four rock types.

occur as a rock-forming mineral in subducted continental slabs. Figure 2 also shows the reaction curve talc + kyanite = MgMgAl-pumpellyite + coesite (Schreyer 1988), which represents the lower pressure limit of the pumpellyite phase in an assemblage with an SiO₂-phase (coesite). Because this curve is nearly identical with the 5 °C/km geotherm, the pumpellyite-silica assemblage is restricted to the coldest parts of a subducted coesite-bearing rocks, whereas pumpellyite may occur in SiO₂-depleted rocks at somewhat higher geotherms.

The experimental data on reactions 2 and 3 agree well with the calculated curves given by Massonne (1995) as to their positions within the *P-T* field and Clapeyron slopes, but large deviations occur concerning the *P-T* position of reaction 1. The experiments carried out on this reaction could not reproduce the large negative Clapeyron slope of the calculated curve given by Massonne (1995) indicating that MgMgAl-pumpellyite is more stable to lower pressures than computed. Because chloritoid does not appear as a reactant in reactions 2 and 3, this discrepancy may be caused by the provisional thermodynamic data of this phase given by Massonne.

In which kind of rocks may the pumpellyite phase occur in nature? Figure 4 is an ACF diagram that shows the location of high-pressure minerals that are expected to be stable at geotherms lower than 5 °C/km; also shown are broad compositional fields for four different rock types (Winkler 1979). In addition, tie-lines are drawn for *P-T* conditions outside the stability field of pyrope (solid lines) and for those *P-T* condition lying within the pyrope field (broken

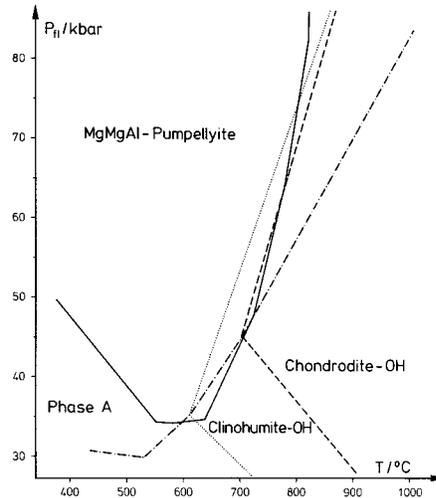


FIGURE 5. *P-T* diagram showing the stability fields of the synthetic phases MgMgAl-pumpellyite (solid line; this work), phase A (dot-dashed), clinohumite-OH (dotted), and chondrodite-OH (dashed; all taken from Wunder 1996).

lines). Outside the stability field of pyrope, the pumpellyite phase may coexist with CaMgAl-pumpellyite and a Ca-bearing clinopyroxene in basaltic rocks, whereas it will occur with clinopyroxene and orthopyroxene in ultramafic rocks. In more felsic rocks (granites, pelites) coexistence with lawsonite plus kyanite or topaz-OH can be predicted. Thus, MgMgAl-pumpellyite is a possible phase in rocks having a diversity of bulk compositions. It should therefore be an important H₂O-bearing phase in rocks subducted along low geotherms. Its maximum temperature will be limited by its breakdown to form pyrope-bearing assemblages in nearly every kind of rock. Only Ca-free and Al-rich rocks (whose compositional fields lie close to the line MgMgAl-pumpellyite-kyanite in the ACF-diagram) that were metamorphosed under high-pressure conditions are possible candidates for rocks that may preserve the pumpellyite phase to higher *P-T* conditions.

On the other hand, it is doubtful whether MgMgAl-pumpellyite can be retained in any rocks brought to the Earth's surface from these depths because any subsequent heating during retrograde metamorphism would cause it to break down into the assemblages indicated in Figure 2. The only way to preserve the pumpellyite phase during exhumation of a rock unit may be as an inclusion in a high-strength mineral such as garnet or zircon (Schertl and Schreyer 1996), in a fashion similar to the coesite inclusions found in pyrope from the Dora-Maira Massif, Italy (Chopin 1984).

Following Schreyer et al. (1991), who discussed the compatibility of MgMgAl-pumpellyite with dense hydrous magnesium silicates of the system MSH, it is of interest to determine which MSH phases are candidates for the inclusion in breakdown assemblages of MgMgAl-pumpellyite. The pumpellyite field overlaps with the stability fields of clinohumite-OH, chondrodite-OH, and Phase A (Fig. 5). The

overlapping region with chondrodite-OH is very small and the one with clinohumite-OH extends over a maximum temperature interval of about 50 °C. Thus, compatibility relations with these two phases are unlikely to be significant in natural rocks. On the other hand, the stability fields of pumpellyite and Phase A overlap each other almost completely, and it is therefore likely that there are compatibility relations of these phases. However, more experimental work must be done concerning an up-to-now hypothetical stability field of the two-phase assemblage pumpellyite plus phase A. As dense hydrous magnesium silicates were not observed among the experimental products in this study, as well as in the former ones by Schreyer et al. (1991) and Liu (1989), it is likely that they can be neglected for the low-pressure and high-temperature phase relations of MgMgAl-pumpellyite.

Future work should be done on the possible solid-solution between MgMgAl-pumpellyite and CaMg-pumpellyite and the *P-T* stability fields of this solid-solution. Replacement of Mg by Ca will certainly stabilize this phase toward lower pressures and lower temperatures (see Schreyer 1988). Another unexplored problem is the influence of Fe-Mg substitution. As a result the pumpellyite phase may be stable in subduction zones that had undergone metamorphism at higher gradients than 4 °C/km and may occur in this regime as an important rock-forming mineral, even though there is no record yet for the presence of FeMg-pumpellyite phases in natural rocks.

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REFERENCES CITED

- Berman, R.G. (1988) Internally consistent thermodynamic data for minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. *Journal of Petrology*, 29, 445–522.
- Boyd, F.R. and England, J.L. (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C. *Journal of Geophysical Research*, 65, 741–748.
- Chopin, C. (1984) Coesite and pure pyrope in high-grade blueschists of the Western Alps: A first record and some consequences. *Contributions to Mineralogy and Petrology*, 86, 107–118.
- Chopin, C., Seidel, E., Theye, T., Ferraris, G., Ivaldi, G., and Catti, M. (1992) Magnesiochloritoid, and the Fe-Mg series in the chloritoid group. *European Journal of Mineralogy*, 4, 67–76.
- Eggerton, R.A., Boland, J.N., and Ringwood, A.E. (1978) High pressure synthesis of a new aluminium silicate: Al₃Si₃O₁₇(OH). *Geochemical Journal*, 12, 191–194.
- Fockenber, T. (1995) New experimental results up to 100 kbar in the system MgO-Al₂O₃-SiO₂-H₂O (MASH): Preliminary stability fields of chlorite, chloritoid, staurolite, MgMgAl-pumpellyite, and pyrope. *Bochumer geologische und geotechnische Arbeiten*, 44, 39–44.
- Geiger, C.A., Langer, K., Bell, D.R., Rossman, G.R., and Winkler, B. (1991) The hydroxide component in synthetic pyrope. *American Mineralogist*, 76, 49–59.
- Getting, I.C. and Kennedy, G.C. (1970) Effect of pressure on the emf of chromel-alumel and platinum-platinum 10% rhodium thermocouples. *Journal of Applied Physics*, 41, 4552–4562.
- Hamilton, D.L. and Henderson, C.M.B. (1968) The preparation of silicate composition by a gelling method. *Mineralogical Magazine*, 36, 832–838.
- Ito, E., Takahashi, E., and Matsui, Y. (1984) The mineralogy and chemistry of the lower mantle: An implication of the ultra-high pressure phase relations in the system MgO-FeO-SiO₂. *Earth and Planetary Science Letters*, 67, 238–248.
- Leistner, H. (1979) Temperaturgradienten-messungen in piston-zylinderpressen. *Fortschritte der Mineralogie*, 57, 81–82.
- Liu, L.-G. (1989) Stability fields of Mg-pumpellyite composition at high pressures and temperatures. *Geophysical Research Letters*, 16, 847–849.
- Massonne, H.-J. (1989) The upper thermal stability of chlorite + quartz: An experimental study in the system MgO-Al₂O₃-SiO₂-H₂O. *Journal of Metamorphic Geology*, 7, 567–581.
- (1995) Experimental and petrogenetic study of UHPM. In R.G. Coleman and X. Wang, Eds., *Ultrahigh Pressure Metamorphism*, p. 33–95. Cambridge University Press, U.K.
- Massonne, H.-J. and Schreyer, W. (1986) High-pressure synthesis and X-ray properties of white micas in the system K₂O-MgO-Al₂O₃-SiO₂-H₂O. *Neues Jahrbuch für Mineralogie Abhandlungen*, 153, 177–215.
- Peacock, S.D. (1990) Numerical simulation of metamorphic pressure-temperature-time paths and fluid production in subducting slabs. *Tectonics*, 9, 1197–1211.
- Schertl, H.-P. and Schreyer, W. (1996) Mineral inclusions in heavy minerals of the ultrahigh-pressure metamorphic rocks of the Dora-Maira massif and their bearing on the relative timing of the petrological events. *Geophysical Monograph* 95, 331–342.
- Schreyer, W. (1988) Experimental studies on metamorphism of crustal rocks under mantle pressures. *Mineralogical Magazine*, 52, 1–26.
- Schreyer, W., Maresch, W.V., Medenbach, O., and Baller, T. (1986) Calcium-free pumpellyite, a new synthetic hydrous Mg-Al-silicate formed at high pressures. *Nature*, 321, 510–511.
- Schreyer, W., Maresch, W.V., and Baller, T. (1987) MgMgAl-pumpellyite: A new hydrous, high-pressure, synthetic silicate resulting from Mg-Ca substitution. *Terra Cognita*, 7, 385.
- (1991) A new hydrous, high-pressure phase with a pumpellyite structure in the system MgO-Al₂O₃-SiO₂-H₂O. In L.L. Perchuk, Ed., *Progress in Metamorphic and Magmatic Petrology*, p. 47–64. Cambridge University Press, U.K.
- Winkler, H.G.F. (1979) *Petrogenesis of metamorphic rocks* (5th edition), 348 p. Springer, Berlin.
- Wunder, B. (1993) Hochdruckuntersuchungen in den systemen Al₂O₃-SiO₂-H₂O und MgO-SiO₂-H₂O mit synthese, eigenschaften und stabilität zweier neuer hochdruck-aluminiumsilikate, 146 p. Ph.D. thesis, Ruhr-Universität, Bochum.
- (1996) Gleichgewichtsexperimente im system MgO-SiO₂-H₂O: Vorläufige stabilitätsfelder von klinohumit (Mg₉Si₄O₁₆(OH)₂), chondroit (Mg₅Si₂O₈(OH)₂) und phase A (Mg₇Si₂O₈(OH)₆). *Berichte der deutschen Mineralogischen Gesellschaft, Beiheft 1 zum European Journal of Mineralogy*, 8, 321.
- Wunder, B., Rubie, D.C., Ross, C.R., II, Medenbach, O., Seifert, F., and Schreyer, W. (1993a) Synthesis, stability and properties of Al₂SiO₄(OH)₂: A fully hydrated analog of topaz. *American Mineralogist*, 78, 285–297.
- Wunder, B., Medenbach, O., Krause, W., and Schreyer, W. (1993b) Synthesis, properties and stability of Al₂Si₂O₇(OH)₃ (phase Pi), a hydrous high-pressure phase in the system Al₂O₃-SiO₂-H₂O (ASH). *European Journal of Mineralogy*, 5, 637–649.
- Zhang, J., Li, B., Utsumi, W., and Liebermann, R.C. (1996) In situ X-ray observations of the coesite-stishovite transition: Reversed phase boundary and kinetics. *Physics and Chemistry of Minerals*, 23, 1–10.

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