

Lawsonite: Upper pressure stability and formation of higher density hydrous phases

MAX W. SCHMIDT

Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

ABSTRACT

The high-pressure phase relationships in a H_2O -saturated synthetic $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (CASH) system were studied by multi-anvil experiments. The most extreme pressure condition under which pure lawsonite [$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$] exists is 120 kbar at 960 °C. This maximum stability is located at the intersection of the lawsonite breakdown reaction with the topaz-OH + stishovite = phase “egg” reaction. At lower pressures and higher temperatures lawsonite decomposes to grossular + topaz-OH + stishovite + H_2O , whereas at lower pressures and lower temperatures lawsonite first reacts to grossular + phase egg + topaz-OH + H_2O and at still lower temperatures to grossular + phase egg + diaspore + H_2O . The two latter reactions have positive dP/dT slopes, with lawsonite on the low-pressure side, and thus delimit the occurrence of lawsonite toward higher pressures. The occurrence of topaz-OH (10.7 wt% H_2O) is limited through a reaction to phase egg (7.5 wt% H_2O) + diaspore; the phase boundary extends from 110 kbar and 720 °C to 130 kbar and 920 °C. Phase egg is inferred to have a composition of $\text{AlSiO}_3(\text{OH})$ and a monoclinic unit cell similar to that proposed by Eggleton et al. (1978).

The high-pressure breakdown of lawsonite in CASH does not result in an anhydrous assemblage. Lawsonite is known to occur experimentally in basaltic and andesitic compositions to at least 77 kbar; however, it is unknown whether topaz-OH and phase egg appear in natural multicomponent systems, in particular those saturated in kyanite and H_2O .

INTRODUCTION

Lawsonite [$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$] is a relatively dense, hydrous mineral with a wide P - T stability field in synthetic [$\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (CASH)] and natural systems. In addition to two OH groups, the lawsonite structure hosts an H_2O molecule, and Al is completely in octahedral coordination (Rumanova and Skipetrova, 1959). This results in a density of 3.09 g/cm^3 , which is higher than the 2.76 g/cm^3 density of its anhydrous chemical equivalent, plagioclase. In the CASH system, lawsonite forms from laumontite at approximately 3 kbar (Nitsch, 1968) and persists to more than 92 kbar (Schmidt and Poli, 1994). Pawley (1994) found lawsonite to be stable at 120 kbar and extrapolated the stability limit to higher pressures. The maximum thermal stability of lawsonite is 1040 °C at a pressure of 92 kbar (Schmidt and Poli, 1994). Pawley (1994) determined the maximum thermal stability to ca. 1080 °C at 94 kbar. The reasons for this small difference will be discussed below.

In natural rocks subducted to high-pressure, low-temperature conditions, lawsonite is common in blueschist terrains (mostly 3–15 kbar, see Evans and Brown, 1986, and references therein) but also occurs in basaltic xenoliths in kimberlites (Watson and Morton, 1969) that originated from a depth equivalent of more than 25 kbar (Helmstedt and Schulze, 1988). Poli and Schmidt (1995) have shown experimentally that lawsonite occurs in ba-

saltic and andesitic compositions to pressures of more than 77 kbar; relatively cold thermal regimes in subduction zones permit lawsonite, formed at blueschist-facies conditions, to persist in subducted crust to a depth of more than 240 km. Lawsonite does not commonly occur in eclogites from depths equivalent to > 15 kbar. This is probably the result of thermal relaxation during the exhumation process. Steep geothermal gradients are common during the descent of oceanic crust, however. When the descent comes to a halt and exhumation begins, thermal relaxation of the anomalous cold thermal structures also begins. Consequently, most exhumation paths commence with a prograde temperature evolution (e.g., England and Thompson, 1984). The occurrence of lawsonite in eclogitic xenoliths in a kimberlite pipe (Watson and Morton, 1969), i.e., in a locality where extremely fast exhumation occurred, proves that eclogites that ascended through relatively slow tectonic processes do not necessarily preserve the most extreme high-pressure, low-temperature conditions. During the exhumation process, cold eclogites are likely to follow initially prograde temperature paths, and consequently lawsonite reacts to form zoisite. The latter reaction is documented in many eclogitic terrains (Newton, 1986, and references therein).

In this study two hydrous phases were encountered, which are known from experimental studies but not from the Earth's surface. Topaz-OH was first described by Wunder et al. (1993a) and is a phase with topaz structure

in which F is completely replaced by OH. Phase egg was first synthesized by Eggleton et al. (1978) at approximately 1000 °C and at pressures greater than 100 kbar. Eggleton et al. (1978) did not name this phase. The name phase egg is assigned in this study to give credit to Eggleton et al. (1978). Although the H₂O content of phase egg as inferred from this study is different from the original study, X-ray diffraction shows that both phases are otherwise identical.

This contribution is intended to examine the upper stability of lawsonite in a synthetic CASH system and to clarify whether other hydrous phases are formed from lawsonite at its pressure breakdown.

EXPERIMENTAL CONDITIONS

The experiments were performed in a split sphere and a split-cylinder-type multi-anvil equipped with WC cubes of 32 mm edge length. Mg-octahedra (95 wt% MgO, 5 wt% Cr₂O₃) of an edge length (M) of 14 mm were used on a truncation edge length (TEL) of 8 mm. Pyrophyllite gaskets with a 2.5 × 5.0 mm cross section, cardboard of 0.4 mm thickness, and Teflon tape of 0.13 mm thickness were directly glued onto the WC cubes. The 14 M/8 TEL setup was calibrated against coesite-stishovite (Yagi and Akimoto, 1976) and α - β spinel (Katsura and Ito, 1989) and can be used at pressures ranging from 90 to 160 kbar. The octahedra were drilled and furnished with a zirconia sleeve for thermal insulation and a stepped LaCrO₃ heater with a wall thickness of 0.3 mm in the upper and lower 3.1 mm and with a wall thickness of 0.5 mm in the central 2.7 mm. A MgO spacer separated the capsule from the furnace, and Mo disks or rings were placed between the LaCrO₃ heater and the WC cube (for details see Rubie et al., 1993). Capsules were made from 1.6 mm outer diameter Pt tubing. The starting material was composed of synthetic lawsonite + zoisite + grossular + cristobalite + Al(OH)₃, and of natural kyanite. Syntheses were performed as described in Schmidt and Poli (1994). Fe and other trace elements in the natural kyanite were below the detection limit of an electron microprobe. The bulk composition of the starting material is located in the quadrangle lawsonite-topaz-OH-phase egg-H₂O (Fig. 1). Precisely 12 wt% H₂O was present in the starting material bound in lawsonite, zoisite, and mostly in stoichiometric Al(OH)₃. The starting material was filled into half capsules, which were then welded and pressed into cylinders with lengths varying from 1.4 to 2.6 mm. Temperatures were measured with welded Pt-Pt₉₀Rh₁₀ thermocouples (S-type). No pressure correction for the emf was applied. The standard assembly includes only one axial thermocouple, however a few experiments were performed with a second axial thermocouple in the geometrical center of the stepped heater. At 700–950 °C, temperature gradients over the length of the capsule were between 20 and 40 °C, the highest temperature always being located in the geometric center of the furnace. The pressure precision is estimated to \pm 4% (Walker, 1991), however the accuracy is probably significantly better because *P* spacings of 5

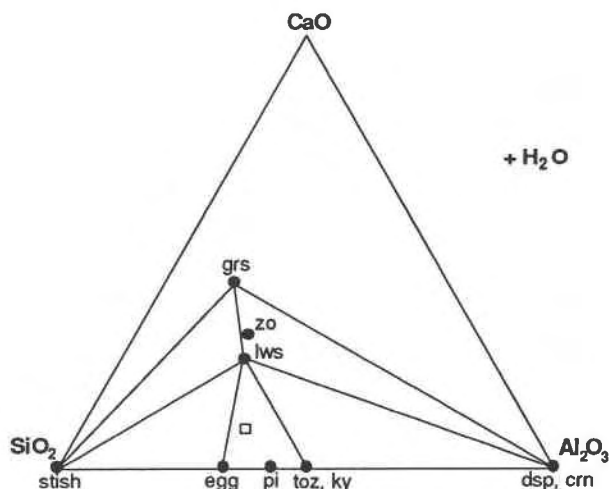


Fig. 1. Starting material composition. Square = bulk composition. Abbreviations for Figs. 1–3 are as follows: and = andalusite, coes = coesite, crn = corundum, dsp = diaspore, egg = phase egg, grs = grossular, ky = kyanite, lws = lawsonite, pi = phase "pi," sil = sillimanite, stish = stishovite, toz = topaz-OH, v = H₂O, zo = zoisite.

kbar yielded consistent results. The experimental products were measured with a STOE powder diffractometer, equipped with a Co tube and a monochromator.

After the experiment, the amount of free fluid phase in the capsule was not determined. In a sample weighing approximately 4 mg, a total of 0.5 mg H₂O was present in the capsule at the beginning of an experiment. At the end of the experiments, depending on the resulting assemblage, 0.1–0.4 mg of the H₂O was bound in hydrous phases, thus the remaining amount of free fluid phase was too small to measure by weight difference because puncturing of a capsule generally results in small losses of material from the capsule. Samples that obviously failed because the thermocouple ceramics penetrated the capsule resulted in the anhydrous assemblages grossular + stishovite + corundum or grossular + stishovite + kyanite. In some samples, compositions of the experimental products were determined by a Cameca SX50 microprobe operated at 12 kV and 20 nA.

In all samples except experiment lwma21, reaction was always complete, resulting in a three-phase + H₂O assemblage. Lwma21, which was first analyzed in a longitudinal section by electron microprobe, showed minor grossular instead of lawsonite in the outer portion from the middle of the capsule. This is interpreted as an overstepping of the phase boundary as a result of the thermal gradient present in the capsule. The experiments contained lawsonite and grossular in the starting material. However, they do not represent true reversals because the starting material did not contain topaz-OH or phase egg and SiO₂ was not present as stishovite. However, because reaction was always complete, the results are believed to represent equilibrium. The lack of apparent kinetic problems is probably due to the high reactivity of the fluid-

TABLE 1. Experimental conditions and results of H₂O-saturated experiments

Expt.	<i>P</i> (kbar)	<i>T</i> (°C)	<i>t</i> (min)	Expt. products
lwma20	150	850	65	grs, egg, dsp
lwma23	140	700	340	grs, egg, dsp
lwma26	133	875	210	grs, egg, dsp
lwma27	125	800	270	grs, egg, dsp
lwma32	125	900	120	grs, egg, toz
lwma30	120	720	99	grs, egg, dsp
lwma28	120	800	175	grs, egg, dsp
lwma21	120	950	720	lws, toz, stish, grs(-)*
lwma24	120	985	260	grs, toz, stish
lwma36	110	675	66	lws, dsp, stish
lwma35	110	750	64	lws, toz, stish
lwma29	110	800	188	lws, toz, stish
lwma31	105	700	120	lws, toz, stish

Note: Abbreviations of experimental products are as follows: grs = grossular, egg = phase egg, dsp = diasporite, toz = topaz-OH, lws = lawsonite, stish = stishovite.

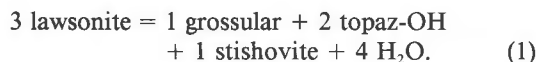
* The minus sign indicates that a very minor amount was present.

saturated CASH system at the *P-T* conditions investigated. By contrast, the low nucleation energy of this system at high pressures is a problem for the synthesis of large crystals. Experimental products have an equilibrium texture with 120° phase angles, but the average grain size of the experimental products is typically between 0.5 and 2 μm, and only a few crystals have significantly larger sizes, up to 10 μm. This average grain size did not increase with the duration of experiments, indicating that after initial nucleation and formation of a texturally equilibrated assemblage, growth processes did not play an important role.

EXPERIMENTAL RESULTS

The experiments resulted in phase assemblages containing lawsonite, diasporite, grossular, phase egg, stishovite, topaz-OH, and H₂O. Experimental results are given in Table 1 and Figure 2. The reaction positions in Figure 2 are constrained by the experiments and drawn in accordance with Schreinemakers rules.

Between 95 and 120 kbar the lawsonite breakdown reaction in a H₂O-saturated CASH system is



This reaction has a negative *P-T* slope of approximately -3 °C/kbar. The highest temperature stability of chemically pure lawsonite is 1040 °C (Schmidt and Poli, 1994), located at the low-pressure end of Reaction 1 where Reaction 1 intersects the kyanite + H₂O = topaz-OH (Wunder et al., 1993a) and coesite = stishovite (Yagi and Akimoto, 1976) phase boundaries (invariant points 4 and 3, Fig. 2). Whether the lawsonite breakdown reaction intersects the kyanite + H₂O = topaz-OH hydration reaction slightly above, at, or below the coesite = stishovite transition is beyond the experimental resolution of a multi-anvil apparatus. The two possible topologies are shown in Figure 3.

Topaz-OH [Al₂SiO₄(OH)₂, 10.7 wt% H₂O] forms from

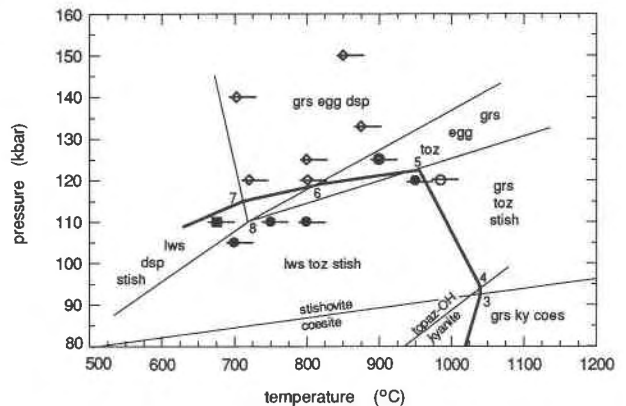


Fig. 2. Experimentally determined phase diagram for the lawsonite-out reactions in the H₂O-saturated system from 90 to 150 kbar. The shading (solid/open) refers to the presence of lawsonite, the symbol shape to the appearance of topaz-OH (circles), phase egg (diamonds), and diasporite + stishovite (square). Lawsonite-out reaction at 90 kbar as determined by Schmidt and Poli (1994). The numbers are described in the text. Abbreviations as in Fig. 1.

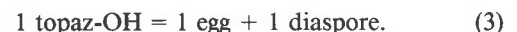
kyanite + H₂O, as determined experimentally by Wunder et al. (1993a). At higher pressures topaz-OH reacts to form AlSiO₃(OH), a phase denoted here as phase egg that was first synthesized by Eggleton et al. (1978).

Eggleton et al. (1978) estimated the H₂O content in their formula Al₃Si₅O₁₇(OH) by X-ray diffraction. Microprobe measurements in several samples resulted in totals of 92–93 wt% (the same samples yielded totals of 99.1–100.5 wt% for grossular) implying an H₂O content of roughly 7–8 wt%, which is consistent with the most simple formula AlSiO₃(OH) (7.5 wt% H₂O). The X-ray powder diffraction of this study resulted in almost identical peak positions of phase egg as determined by Eggleton et al. (1978). From the best quality diffractogram (experiment lwma27), 14 reflections were selected that fulfill the criteria of Orville (1967). Cell parameters obtained by fitting a monoclinic unit cell as proposed by Eggleton et al. (1978) are as follows: *a* = 9.820(7), *b* = 18.236(7), and *c* = 5.372(4) Å, β = 103.84(7)°, and *V* = 934.0 ± 1.0 Å³. Eggleton et al. (1978) determined a unit cell having 72 O atoms, thus for the composition AlSiO₃(OH) *Z* would be 18, resulting in a density of 3.84 g/cm³.

The breakdown of topaz-OH to phase egg occurs by two reactions. With increasing pressure, these are



and



At *P-T* conditions lying between Reactions 2 and 3 (Fig. 2), topaz-OH and phase egg coexist. Both reactions have positive *P-T* slopes and intersect at approximately 700 °C, 110 kbar. At 900 °C they differ in pressure by < 10 kbar.

The most extreme pressure condition under which pure lawsonite exists is 120 kbar, 960 °C, at the intersection

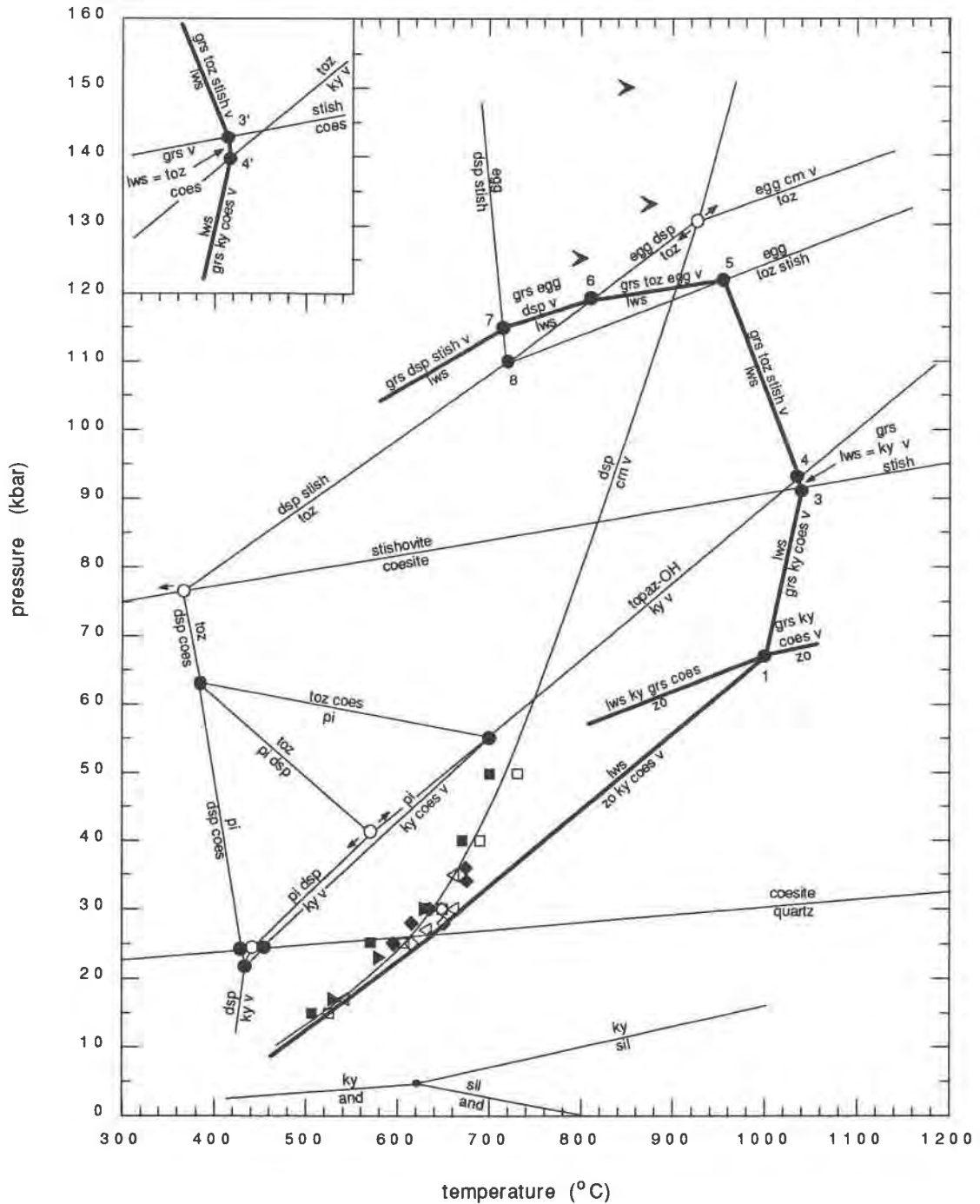
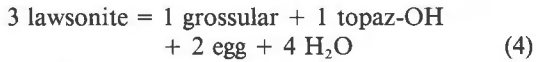


Fig. 3. Topology of the CASH system to 150 kbar with reactions delimiting the stability fields of lawsonite and zoisite in CASH and of diaspore, phase "pi," topaz-OH, and phase egg in ASH. Thick lines delineate the lawsonite and zoisite stability fields as experimentally determined by Schmidt and Poli (1994) and in this study. Quartz = coesite from Bohlen and Boettcher (1982), coesite = stishovite from Yagi and Akimoto (1976), topaz-OH = kyanite + H₂O from Wunder et al. (1993a), and reactions involving phase "pi" from Wunder et al. (1993b). Experimental brackets for the equilibrium diaspore-corundum from Grevel et al. (1994, squares), Schmidt and Poli (1994, triangles), and Vidal et al. (1994, diamonds); open symbols = diaspore,

solid symbols = corundum. The arrowheads at 120–150 kbar indicate diaspore stability; the phase boundary is extrapolated because a high-temperature constraint at these pressures is not available. Solid circles are invariant points with *P-T* locations well defined by experiments; exact *P-T* locations of invariant points represented by open circles remain uncertain. Arrows indicate in which direction(s) the latter invariant points might be displaced. Note that the high-pressure lawsonite delimiting reactions are hydration reactions with increasing temperature. The inset shows the second possible topology at conditions around 90 kbar, 1040 °C. Abbreviations as in Fig. 1.

of the lawsonite breakdown reaction with phase egg forming Reaction 2 (invariant point 5, Fig. 2). At pressures above Equilibrium 2 the lawsonite breakdown reaction is



and transforms at temperatures below Reaction 3 into



Reactions 4 and 5 have positive slopes of approximately 40 and 25 °C/kbar, respectively, with lawsonite on the high-temperature–low-pressure side. Thus, these reactions delimit the stability of lawsonite toward higher pressures and lower temperatures.

Diaspore is an experimental product in all experiments performed at pressures above the topaz-OH destabilization. As a result, the maximum pressure stability of diaspore exceeds 150 kbar (at 700–900 °C). Experiments conducted at temperatures above 900 °C resulted in topaz-OH and thus are not suitable to examine the thermal stability of diaspore because the bulk composition is located between topaz-OH and the SiO₂-apex (Fig. 1).

TOPOLOGY

The topology of a H₂O-saturated CaO-Al₂O₃-SiO₂-H₂O system (Fig. 3) is constructed from the present experiments and from those of Schmidt and Poli (1994) and Wunder et al. (1993a, 1993b). The breakdown reactions of lawsonite depend mostly on phase relationships in the Al₂O₃-SiO₂-H₂O (ASH) subsystem. It is only at the intersection of the lawsonite-out reactions with the pressure-sensitive breakdown reaction of zoisite to grossular + kyanite + coesite + H₂O that an invariant point (1, Fig. 3) is defined by three reactions between Ca-bearing phases. All other invariant points are defined by ASH phase relationships, which determine the lawsonite-out reactions and the topology of the CASH system at pressures above 67 kbar. All lawsonite-out reactions at these conditions are of the type lawsonite = grossular + 2 ASH phases + H₂O. As the densities of the ASH phases increase, lawsonite changes from the high-pressure side to the low-pressure side of its breakdown reactions. Very unexpectedly, Reactions 4 and 5 are hydration reactions with increasing temperature, i.e., H₂O is situated on the low-temperature side of Reactions 4 and 5 (Figs. 2 and 3). This indicates that phase egg has, besides a relatively high density, also a relatively low third-law entropy. Another hydration reaction with increasing temperature is constituted by the low-temperature (<700 °C), high-pressure formation reaction of lawsonite (Fig. 3).

The principal features of the ASH topology (Fig. 3) are as follows: At relatively low pressures of 20–60 kbar and relatively low temperatures from 450 to 600 °C, phase “pi” [Al₃Si₂O₇(OH)₃, ρ = 3.23 g/cm³] appears (Wunder et al., 1993b); the stability field of this phase entirely overlaps that of lawsonite. At intermediate pressures of

50–120 kbar topaz-OH (ρ = 3.37 g/cm³) forms (Wunder et al., 1993a). At pressures higher than 90–120 kbar phase egg (ρ = 3.84 g/cm³) forms instead of topaz-OH. At temperatures below 430–690 °C stishovite or coesite coexists with diaspore. The high-temperature behavior of phase egg and topaz-OH remain unknown; they could either melt or decompose to stishovite + corundum + H₂O.

DISCUSSION OF PREVIOUS EXPERIMENTAL WORK

Pawley (1994) also determined the position of Reaction 1 and estimated the maximum temperature stability of lawsonite. Considering the relatively large uncertainties of Pawley’s experiments, her experimental results are in fair agreement with the present study. The results obtained in this study are considered to be more accurate because of the following differences in the experimental setup: (1) Pawley (1994) did not calibrate pressure above 90 kbar for the octahedra used on a 4 mm truncation (TEL). Only a half-bracket at 140 kbar is reported. Thus, Pawley’s pressures have a larger error than the present study, in which a complete calibration was undertaken and a much larger octahedra was used for the same pressure range (14 mm octahedra on 8 mm truncation edge length). (2) Pawley (1994) used an inconel furnace, i.e., a metal heater with a positive correlation between electrical resistancy and temperature. Such heaters always result in sharp hot spots, and consequently Pawley (1994) found temperature gradients in excess of 100 °C (at 1000 °C) for a capsule length of about 3 mm. Pawley points out that the “autoamplification” effect on the thermal gradient is less pronounced for inconel furnaces than for rhenium furnaces, the latter resulting in the largest thermal gradients of all furnace materials commonly used in multi-anvil experiments. However, such large thermal gradients are not inherent to multi-anvil experiments. LaCrO₃ is one of the rare materials suitable for furnaces in which electrical resistivity decreases with temperature. This behavior causes warm zones to heat less than cold zones, and consequently the hot spot is spread out. In addition, the LaCrO₃ furnaces in the present experiments were stepped heaters, i.e., the electrical resistancy is lower in the central, thicker part of the furnace. This resulted in temperature gradients on the order of 20–40 °C over the capsule length of 2.6 mm (both experimental setups using 8 mm TEL).

Eggleton et al. (1978) synthesized phase egg in a Bridgmann-anvil apparatus at “pressures greater than 100 kbar and at about 1000 °C.” Because precise synthesis conditions are not given and pressures and temperatures were not as well calibrated as can be presently achieved, this first synthesis appears to be in agreement with the lower pressure stability limit defined in this study. Phase egg was also synthesized by Fockenberget al. (1994) at 150 kbar, 1000 °C, and by Pawley (1994) at 140 kbar, 740–840 °C. Pawley (1994) recognized that the estimated H₂O content of 1.6 wt% (Eggleton et al., 1978) is probably too low. The difference of Al₂O₃ + SiO₂ totals from 100 wt% in microprobe analyses led her to conclude that the for-

mula is probably $\text{AlSiO}_3(\text{OH})$. This is confirmed by the present study. However, a direct measurement of the H_2O -content of phase egg is necessary to obtain a precise determination of its stoichiometry.

A high-pressure topology for the ASH system was also presented by Pawley (1994, her Fig. 6). Invariant point 8 (Fig. 3) [her invariant point (ky, coes, v)] is similar in that arrangement, and stabilities of reactions around this invariant point are identical except that reaction slopes are now constrained experimentally. The high-temperature parts of the topologies are different because the reaction diaspore = corundum + H_2O was not considered by Pawley (1994). The low-pressure part of the topologies are different because the formation of phase "pi" from topaz-OH (Wunder et al., 1993b) was intentionally not considered by Pawley (1994, p. 105).

THE OCCURRENCE OF LAWSONITE, TOPAZ-OH, AND PHASE EGG IN NATURE

The present study also indicates conditions of maximum persistence of lawsonite in natural rock compositions. Lawsonite has been shown experimentally to be present in basalts, andesites, and probably greywackes to pressures of at least 77 kbar. Once formed at blueschist conditions, lawsonite remains stable in natural rocks to temperatures about 100–150 °C lower than in the synthetic CASH system (i.e., to 780 °C at 60 kbar in basalt and to 900 °C at 77 kbar in andesite: Poli and Schmidt, 1995). Poli and Schmidt (1995) also showed that in natural rock compositions lawsonite has only minor impurities (1–2 wt%), whereas grossular contents in garnet increase with pressure from 15 to 45 mol%. The maximum stability of pure lawsonite is reached at 120 kbar (950 °C), equivalent to a depth of 350 km. In natural rocks, impure lawsonite is expected to decompose at somewhat lower pressures.

Thermal models predict that relatively cold structures are common in subduction zones with fast subduction rates where relatively old crust is subducted: For the top of the slab, Hsui and Toksöz (1980) predict 650–800 °C at 400 km depth, Davies and Stevenson (1992) 600–800 °C at 400 km depth, Ito and Sato (1992) 600–900 °C at 400 km depth, Furukawa (1993) ca. 650 °C at 200 km depth, and Peacock (1993) ca. 800 °C at 250 km depth. These calculations show that temperatures are low enough in cold subduction zones to permit the occurrence of lawsonite up to its maximum pressure stability. Nevertheless, a precise determination of lawsonite occurrence in natural rock compositions is necessary to elucidate this point further.

In the synthetic system, hydrous breakdown products of lawsonite are topaz-OH, phase egg, or both. Topaz-OH is expected to appear in natural bulk compositions saturated in kyanite at relatively low-pressure conditions, i.e., metapelites and some greywackes. In such compositions, the dehydration of lawsonite (11 wt% H_2O) would result directly in the formation of topaz-OH (10.7 wt% H_2O) at pressures between 90 and 120 kbar. Direct ex-

perimental evidence for such a reaction is not available; nevertheless, at pressures above 35 kbar, lawsonite decomposes in andesites (which have bulk compositions similar to greywackes) to garnet + omphacite + kyanite + H_2O . Thus, similar or more aluminous bulk compositions (e.g., metapelites, greywackes, or metagranitoids) potentially could bear topaz-OH. However, it remains uncertain if topaz-OH occurs in the complex multisystems that constitute natural rocks.

Phase egg, having a composition located between kyanite (topaz-OH) and stishovite, could appear in compositions that are less aluminous than those necessary for the formation of topaz-OH. Because phase egg has not been reported from systems more complex than CASH, its appearance in nature remains speculative. However, the pressure destabilization of lawsonite in natural rocks is expected to result in a high-density phase, which could be the hydrous phase egg or another new phase. The significance of the high-density, hydrous phases topaz-OH and phase egg for natural systems (if any) needs to be clarified by additional experiments.

ACKNOWLEDGMENTS

This project follows a previous study conducted in collaboration with Stefano Poli, to whom I am grateful. I thank my colleagues at the Bayerisches Geoinstitut, especially Ross Angel, Bob Linnen, Brent Poe, and Dave Rubie, for their help and support. I also thank A. Pawley and J.G. Liou for reviewing the paper.

REFERENCES CITED

- Bohlen, S.R., and Boettcher, A.L. (1982) The quartz = coesite transformation: A precise determination and the effects of other components. *Journal of Geophysical Research* B, 87, 7073–7078.
- Davies, J.H., and Stevenson, D.J. (1992) Physical model of source region of subduction zone volcanics. *Journal of Geophysical Research*, 97, 2037–2070.
- Eggleton, R.A., Boland, J.N., and Ringwood, A.E. (1978) High pressure synthesis of a new aluminium silicate: $\text{Al}_3\text{Si}_2\text{O}_{17}(\text{OH})$. *Geochemical Journal*, 12, 191–194.
- England, P.C., and Thompson, A.B. (1984) Pressure-temperature-time path of regional metamorphism: I. Heat transfer during the evolution of regions of thickened continental crust. *Journal of Petrology*, 25, 894–928.
- Evans, B.W., and Brown, E.H. (1986) Blueschists and eclogites. *Geological Society of America Memoir*, 164, 423 p.
- Fockenbergh, T., Schreyer, W., Skrok, V., and Wunder, B. (1994) Experimental studies relevant to ultrahigh-pressure metamorphism (abs.), p. 121. International Mineralogical Association, 16th General Meeting, Pisa, Italy.
- Furukawa, Y. (1993) Depth of the decoupling plate interface and thermal structure under arcs. *Journal of Geophysical Research*, 98, 20005–20013.
- Grevel, K.D., Fockenbergh, T., Wunder, B., and Burchard, M. (1994) Experimental determination of the equilibrium curve 2 diaspore = corundum + H_2O to high pressures and modified thermodynamic data for diaspore. *Terra Abstracts*, 6, supplement 1, 20.
- Helmstedt, H., and Schulze, D.J. (1988) Eclogite-facies ultramafic xenoliths from Colorado Plateau diatreme breccias: Comparison with eclogites in crustal environments, evaluation of the subduction hypothesis, and implications for eclogite xenoliths from diamondiferous kimberlites. In D.C. Smith, Ed., *Eclogites and eclogite facies rocks*, p. 387–450. Elsevier Science, Amsterdam.
- Hsui, A.T., and Toksöz, M.N. (1980) The evolution of thermal structures beneath subduction zones. In *Development in Geotectonics*, 14, 325–342.
- Ito, E., and Sato, H. (1992) Effect of phase transformations on the dy-

- namics of the descending slab. In Y. Syono and M.H. Manghni, Eds., *High-pressure research: Application to earth and planetary sciences*, p. 257–262. Terra Scientific, Tokyo.
- Katsura, T., and Ito, E. (1989) The system Mg_2SiO_4 - Fe_2SiO_4 at high pressures and temperatures: Precise determination of the stabilities of olivine, modified spinel and spinel. *Journal of Geophysical Research*, 94, 15663–15670.
- Newton, R.C. (1986) Metamorphic temperatures and pressures of group B and C eclogites. *Geological Society of America Memoir*, 164, 17–30.
- Nitsch, K.H. (1968) Die Stabilität von Lawsonit. *Naturwissenschaften*, 55, 388.
- Orville, P.M. (1967) Unit-cell parameters of the microcline-low albite and the sanidine-high albite solid solution series. *American Mineralogist*, 52, 55–86.
- Pawley, A. (1994) The pressure and temperature stability limits of lawsonite: Implications for H_2O recycling in subduction zones. *Contributions to Mineralogy and Petrology*, 118, 99–108.
- Peacock, S.M. (1993) Large-scale hydration of the lithosphere above subducting slabs. *Chemical Geology*, 108, 49–59.
- Poli, S., and Schmidt, M.W. (1995) H_2O transport and release in subduction zones: Experimental constraints on basaltic and andesitic systems. *Journal of Geophysical Research*, in press.
- Rubie, D.C., Karato, S., Yan, H., and O'Neill, H.St.C. (1993) Low differential stress and controlled chemical environment in multianvil high-pressure experiments. *Physics and Chemistry of Minerals*, 20, 315–322.
- Rumanova, I.M., and Skipetrova, T.I. (1959) The crystal structure of lawsonite. *Soviet Physics Doklady*, 4, 20–23.
- Schmidt, M.W., and Poli, S. (1994) The stability of lawsonite and zoisite at high pressures: Experiments in CASH to 92 kbar and implications for the presence of hydrous phases in subducted lithosphere. *Earth and Planetary Science Letters*, 124, 105–118.
- Vidal, O., Theye, T., and Chopin, C. (1994) Experimental study of the reactions between chloritoid and almandine at high pressure and various f_{O_2} conditions. *Contributions to Mineralogy and Petrology*, 118, 256–270.
- Walker, D. (1991) Lubrication, gasketing, and precision in multianvil experiments. *American Mineralogist*, 76, 1092–1100.
- Watson, K.D., and Morton, D.M. (1969) Eclogite inclusions in kimberlite pipes at Garnet Ridge, northeastern Arizona. *American Mineralogist*, 54, 267–285.
- Wunder, B., Rubie, D.C., Ross, C.R., II, Medenbach, O., Seifert, F., and Schreyer, W. (1993a) Synthesis, stability, and properties of $Al_2SiO_4(OH)_2$: A fully hydrated analogue of topaz. *American Mineralogist*, 78, 285–297.
- Wunder, B., Medenbach, O., Krause, W., and Schreyer, W. (1993b) Synthesis, properties and stability of $Al_3Si_2O_7(OH)_3$ (phase Pi), a hydrous high-pressure phase in the system Al_2O_3 - SiO_2 - H_2O (ASH). *European Journal of Mineralogy*, 5, 637–649.
- Yagi, T., and Akimoto, S.I. (1976) Direct determination of coesite-stishovite transition by in-situ X-ray measurements. *Tectonophysics*, 35, 259–270.

MANUSCRIPT RECEIVED MARCH 15, 1995

MANUSCRIPT ACCEPTED JULY 7, 1995