

Hydrous Phases and Water Transport in the Subducting Slab

Tatsuhiko Kawamoto

*Institute for Geothermal Sciences
Graduate School of Science
Kyoto University
Beppu 874-0903, Japan
e-mail: kawamoto@bep.vgs.kyoto-u.ac.jp*

INTRODUCTION

Arc volcanoes are typically located 90-180 km above the surface of downgoing slabs, as shown by Wadati-Benioff deep seismic foci (Gill 1981; Tatsumi 1989). The intimate relationship between the dip angles of the subducting slab and the locations of volcanic arcs indicates that subduction zone magmatism is triggered by material input from the subducting slab (Tatsumi and Eggins 1995). The slab-derived components are thought to be aqueous fluids or H₂O-rich partial melts of subducted oceanic crust. Therefore, knowledge of the stability of hydrous phases and the chemical and physical properties of aqueous fluids in downgoing slabs is essential to understand the material transport in subduction zones. In this section, I will review the stability of hydrous phases in downgoing peridotite, basalt and sediment systems, and the chemical and the wetting properties of aqueous fluids.

Recent experimental studies indicate that 3-4 GPa, equivalent to 90-120 km depth, is a key pressure, where (1) the chemical compositions of silicate components dissolved in aqueous fluids equilibrated with mantle minerals approach the composition of mantle peridotite itself (Stalder et al. 2001; Mibe et al. 2002; Kawamoto et al. 2004), (2) the dihedral angle between olivine and aqueous fluids starts becoming smaller than 60° (Watson et al. 1990; Mibe et al. 1998, 1999), and (3) the immiscibility gap between peridotitic melts and aqueous fluids disappears and consequently hydrous minerals liberate supercritical aqueous fluids (Mibe et al. 2004a, 2006). The similarity between these pressures and the depths of downgoing slab underneath volcanic fronts, where the maximum numbers of volcanoes are formed, 124 ± 38 km (Gill 1981) or 112 ± 19 km (Tatsumi 1986), suggests that subduction zone magmatism can be triggered by the input of supercritical fluids from the downgoing peridotite and basalt.

LOW-PRESSURE HYDROUS MINERALS AND HIGH-PRESSURE HYDROUS PHASES

Many hydrous crystalline phases are stable in peridotite, basalt and sediment systems over a wide range of pressure. Their chemical formulae and H₂O contents are summarized together with those of nominally anhydrous minerals in Table 1. Some hydrous phases have been found only in high-pressure and high-temperature experimental products and have not yet been found in nature: dense hydrous magnesium silicates (DHMS) or alphabet phases (Ringwood and Major 1967), phase Egg (Eggleton et al. 1978), phase Pi (Wunder et al. 1993a), topaz-OH (Wunder et al. 1993b), and δ-AlOOH (Suzuki et al. 2000). Although phase D, F, and G were originally suggested as different phases, these phases seem to be identical (Frost 1999; Ohtani et al. 2001). The chemical compositions of DHMS are plotted in Figure 1 with the estimated

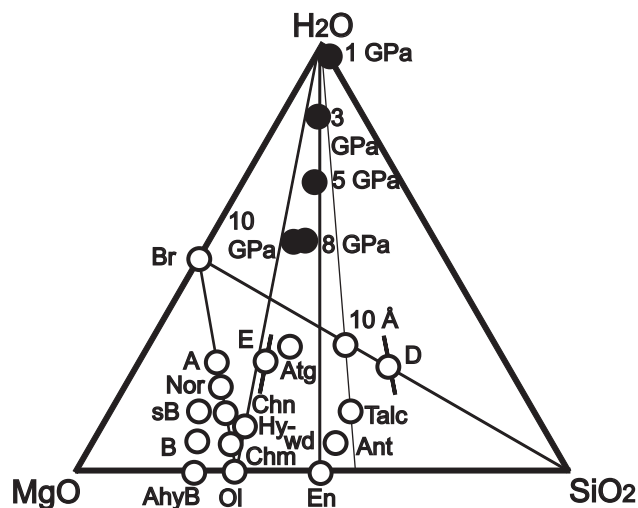


Figure 1. Compositions of hydrous minerals and dense magnesium hydrous silicates stable in peridotite system plotted with compositions of silicates dissolved into aqueous fluids coexisting with forsterite and enstatite at 1100 °C at 1-10 GPa estimated by Zhang and Frantz (2000) and Mibe et al. (2002) in the MgO-SiO₂-H₂O system. Phase D, E, antigorite, and 10 Å phase are non-stoichiometric phases. Humite is located between chondrodite and clinohumite. Abbreviations are in Table 1.

chemistry of aqueous fluids equilibrated with forsterite + enstatite in the MgO-SiO₂-H₂O system (Mibe et al. 2002).

The hydrous crystalline phases can be divided into three major groups with respect to their stability range (Fig. 2): (1) low-pressure hydrous minerals such as chlorite (clinochlore), talc, and amphibole (the relevant end members are listed in Table 1), which are commonly observed in metamorphic rocks, (2) high-pressure hydrous phases such as DHMS (Fig. 1), K-richterite, topaz-OH, and phase Egg, and (3) middle-pressure hydrous minerals such as phlogopite, antigorite, Mg-sursassite and 10 Å phase in peridotite, lawsonite in basalt, and phengite in sediment. The last group is stable between 5 and 7 GPa, and may be important for delivering H₂O from low-pressure hydrous minerals to high-pressure hydrous phases (Fig. 2).

Liu (1987) recognized that phase A, a DHMS, can accommodate much more water than amphibole or phlogopite. Therefore he emphasized the important reaction forsterite + H₂O = phase A + enstatite, and he described this reaction boundary as a “water-line,” implying that a region deeper than the water-line can be a H₂O reservoir in the mantle. In Figure 2, the water-line is shown by the low-pressure stability of DHMS. Kawamoto et al. (1996) identified the presence of a “choke point” in a down going slab. A choke point represents a pressure and temperature condition along a *PT* path where low-pressure and middle-pressure hydrous minerals get dehydrated at certain pressure conditions and cannot deliver H₂O to high-pressure hydrous phases (Fig. 2). The choke point curve, the curve connecting the array of choke points, represents the high-pressure and high-temperature stability limit of the low-pressure and middle-pressure hydrous minerals. In the MgO-SiO₂-H₂O system, the invariant point composed of antigorite, phase A, enstatite, forsterite and H₂O represents the lowest temperature and highest pressure of the choke point. In recent literature, this point is at around 6.2 GPa and 620 °C (Iwamori 2004), and at 5.1 GPa and 550 °C (Komabayashi et al. 2005). In Figure 2, based on the KLB-1 peridotite data, TiO₂ stabilizes chondrodite and clinohumite. Therefore, in the peridotite systems, the *PT* conditions where antigorite meets chondrodite and clinohumite represent the lowest temperature and highest pressure choke point. In the MgO-

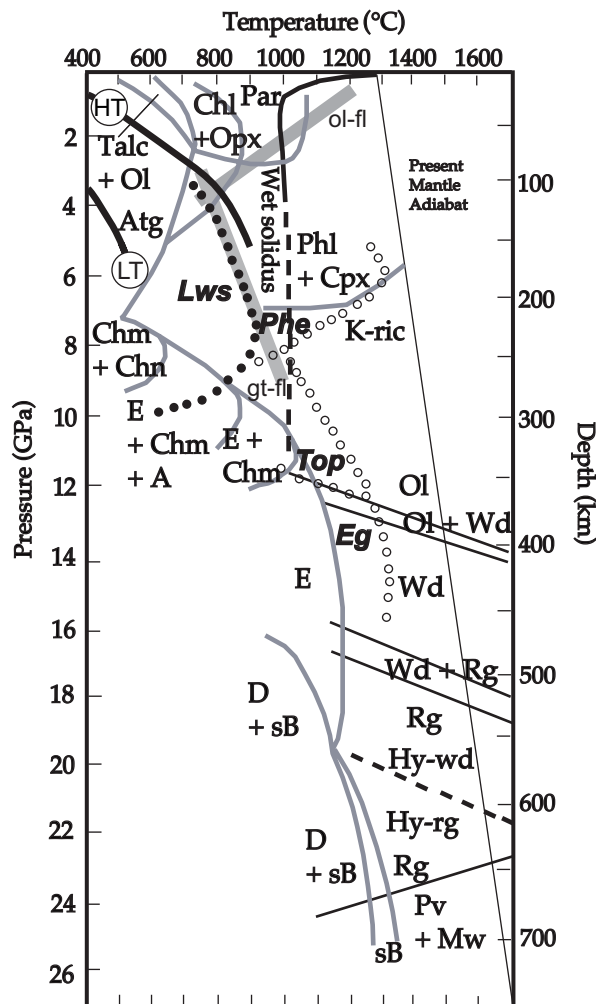


Figure 2. Pressure and temperature diagram showing stability of hydrous minerals/phases in peridotite (Kawamoto 2004a) with some hydrous phases in basalt/sediment systems. The wet solidus is from Kawamoto and Holloway (1997). Since a second critical endpoint between peridotite melt and aqueous fluids is located at around 3.8 GPa (Mibe et al. 2004a; 2006), the wet solidus is drawn by dashed line at pressures higher than 4 GPa. Stability of lawsonite in basalt is indicated by solid dots and stability boundaries among phengite, topaz-OH, and phase Egg is drawn by open dots, respectively. The stabilities of Par, Chl, Talc, Atg, Phl, K-rich, Lws, Top, Eg are after Schmidt and Poli (1998), Pawley (2003), Ulmer and Trommsdorff (1995), Sudo and Tatsumi (1990), and Ono (1998); phase boundaries among Ol, Ol + Wd, Wd, and Wd + Rg - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ and Rg - $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ and Mg-perovskite (Mg-Pv) + magnesium wüstite (Mw) in dry conditions are after Katsura and Ito (1989), and Ito and Takahashi (1989), respectively. The phase boundary of Hy-wd and Hy-rg (dashed line) is at higher pressure than under dry conditions. The 60° isopleths of the dihedral angle in garnet-garnet-fluid (gt-fl) and olivine-olivine-fluid (ol-fl) are also shown (thick gray line). The data of the dihedral angle are compiled in Figure 5. HT and LT represent *PT* paths of high-temperature and low-temperature subducting slab surface, respectively (Peacock and Wang 1999). Abbreviations are in Table 1.

Table 1. Formula of hydrous minerals/phases and nominally anhydrous minerals in metamorphic basalts, metamorphic sediments, and peridotite (after Wunder and Schreyer 1992, Pawley and Wood 1995, Mysen et al. 1998, Ono 1999, Forneris and Holloway 2003).

Name	Symbols	Formula	wt% H ₂ O
<i>(Amphibole groups)</i>			
Tremolite	Trm	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	2.2
Pargasite	Par	Na ₂ Ca ₃ Mg ₈ FeAl ₃ Si ₁₃ O ₄₄ (OH) ₄	2.2
Barroisite	Bar	NaCaMg ₃ Al ₂ Si ₇ AlO ₂₂ (OH) ₂	2.3
Glaucofanite	Gln	Na ₂ Mg ₃ Al ₂ Si ₈ O ₂₂ (OH) ₂	2.3
K-richterite	K-ric	K _{1,9} Ca _{1,1} Mg ₅ Si _{7,9} Al _{0,1} O ₂₂ (OH) ₂	2.1
<i>(Peridotite system)</i>			
Chlorite	Chl	(Mg ₅ Al)(AlSi ₃)O ₁₀ (OH) ₈	13
Talc	Tlc	Mg ₆ Si ₈ O ₂₀ (OH) ₄	4.8
Serpentine	Serp	Mg ₃ Si ₂ O ₅ (OH) ₄	13
Antigorite	Atg	Mg ₄₈ Si ₃₄ O ₈₅ (OH) ₆₂	12.3
Clinohumite	Chm	Mg ₉ Si ₄ O ₁₆ (OH) ₂ , Ti _{0,5} Mg _{8,5} Si ₄ O ₁₇ (OH)	2.9 - 1.4
Humite	Hm	Mg ₇ Si ₃ O ₁₂ (OH) ₂	3.75
Chondrodite	Chn	Mg ₅ Si ₂ O ₈ (OH) ₂ , Ti _{0,5} Mg _{4,5} Si ₂ O ₉ (OH)	5.3 - 2.6
Norbergite	Nor	Mg ₃ SiO ₄ (OH) ₂	9.0
Phase A	A	Mg ₇ Si ₂ O ₈ (OH) ₆	11.8
Brucite	Br	Mg(OH) ₂	30.9
Phase B	B	Mg ₂₄ Si ₈ O ₃₈ (OH) ₄	2.4
Superhydrous B	sB	Mg ₁₀ Si ₃ O ₁₄ (OH) ₄	1.6
Anhydrous B	AhyB	Mg ₁₄ Si ₅ O ₂₄	
Phase E	E	Mg _{2,27} Si _{1,26} H _{2,4} O ₆	11.4
Phase D/F/G	D	MgSi ₂ H ₂ O ₆	10.1
Anthophyllite	Ant	Mg ₇ Si ₈ O ₂₂ (OH) ₂	2.3
Talc	Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	4.75
10 Å phase	10 Å	Mg ₃ Si ₄ O ₁₀ (OH) ₂ · xH ₂ O	7.6 - 13
Mg-sursassite	MgS	Mg ₅ Al ₅ Si ₆ O ₂₁ (OH) ₇	7.2
Hydrous wadsleyite	Hy-wd	Mg _{1,75} SiO ₄ (OH) _{0,5}	3.3
Hydrous ringwoodite	Hy-rg	Mg _{1,75} SiO ₄ (OH) _{0,5}	3.3
<i>(Basalt and sediment systems)</i>			
Zoisite/clinozoisite	Zo / Czo	Ca ₂ Al ₂ Si ₂ O ₁₂ (OH)	2
Staurolite	Sta	(Mg,Fe) ₂ (Al,Fe) ₉ Si ₄ O ₂₂ (O,OH) ₂	2
Apatite	Ap	Ca ₅ (PO ₄) ₃ (OH,F,Cl)	1.8
Sphene	Spn	CaTiSiO ₄ (O,OH,F)	1.5
Phlogopite	Phl	KMg ₂ Si ₃ AlO ₁₀ (OH) ₂	4.8
Phase Egg	Eg	AlSiO ₃ (OH)	7.5
Topaz-OH	Top	Al ₂ SiO ₄ (OH) ₂	10.0
Phase Pi	Pi	Al ₃ Si ₂ O ₇ (OH) ₃	9.0
Lawsonite	Lws	CaAl ₂ Si ₂ O ₇ (OH) ₂ · H ₂ O	11.5
Chloritoid	Cld	(Mg, Fe) ₂ (Al,Fe) ₄ Si ₂ O ₁₀ (OH) ₄	8
Phengite	Phe	K(Al _{2-x} Mg _x)(Si _{3+x} Al _{1-x})O ₁₀ (OH,F) ₂	4.6
δ-AIOOH	δ-Al	AIOOH	15
<i>(Nominally anhydrous minerals)</i>			
Olivine/Wadsleyite/Ringwoodite	Ol / Wd / Rg	Mg ₂ SiO ₄	
Clinopyroxene	Cpx	(Na,Ca)(Mg,Al)Si ₂ O ₆	
Ca-perovskite	Ca-pv	CaSiO ₃	
Orthopyroxene/ Majorite/ Akimotoite/ Perovskite	Op _x / Mj / Ak / Pv	MgSiO ₃	
Quartz/ Coesite/ Stishovite	Qz / Coe / St	SiO ₂	
Spinel	Sp	MgAl ₂ O ₄	
Garnet	Gt	(Fe,Mg,Ca) ₃ Al ₂ Si ₃ O ₁₂	

Al₂O₃-SiO₂-H₂O system, Mg-sursassite (Gottschalk et al. 2000), which was previously called MgMgAl-pumpellyite (for example, Domanik and Holloway 1996), is stabilized at higher temperature than this invariant point (Fig. 3; Bromiley and Pawley 2003), and its presence therefore increases the temperature of the choke point.

The transition zone (410-660 km depth) is also characterized by the high H₂O storage capacity of hydrous wadsleyite and hydrous ringwoodite (Fig. 3; Smyth 1987; Inoue et al. 1995; Kawamoto et al. 1996; Kohlstedt et al. 1996; Kudoh et al. 1996; Smyth and Kawamoto 1997; Smyth et al. 1997; Demouchy et al. 2005). Therefore, the transition zone could play a significant role as a large H₂O -reservoir formed by crystallization of hydrous wadsleyite and ringwoodite from a hydrous magma ocean. Kawamoto and Holloway (1997) measured the partition coefficient of H₂O between hydrous wadsleyite/ringwoodite and hydrous partial melts of peridotite, and suggested the possible existence of a hydrous transition zone in the early history of the Earth. Upwelling from such a hydrous reservoir could generate partial melting at 410 km and produce komatiitic magmas. Through partial melting of a hydrous transition zone, in this hypothesis, the transition zone has been getting drier during the geological time, because the choke point prevents H₂O from subducting into the transition zone. Therefore the present transition zone has much less ability to produce komatiite magmas. This hypothesis thus explains why komatiites were produced mainly in the Archean period.

STABILITY OF HYDROUS PHASES IN DOWNGOING PERIDOTITE

There are two potentially-hydrated peridotite layers in subduction zones. One is the harzburgite/lherzolite of the subducting lithospheric mantle, which is overlain by oceanic basaltic crust and sediments. The other is downdragged mantle at the base of the mantle wedge. To what extent the peridotite layers are hydrated remains uncertain. Along transform faults, serpentine minerals (antigorite, lizardite, chrysotile) can be formed by seawater alteration. However, the rest of the subducting lithospheric mantle may not be hydrated. The downdragged mantle peridotite at the base of the mantle wedge should be hydrated by aqueous fluids liberated by dehydration reactions of hydrous minerals in downgoing sediment and basalt layers. Nicholls and Ringwood (1973) suggested that subducting basalt will be almost dry beneath the fore-arc region. Sakuyama and Nesbitt (1986), therefore, suggested that downdragged peridotite in the mantle wedge will be hydrated through H₂O released by dehydration of the hydrous minerals in the basaltic layer and may carry H₂O beneath the volcanic arc.

Iwamori (2004) compiled the stability of hydrous phases in the MgO-SiO₂-H₂O, the MgO-Al₂O₃-SiO₂-H₂O, and KLB-1 peridotite systems, and presented the distribution of maximum H₂O contents bound in mantle peridotite (Fig. 3). Komabayashi et al. (2004) also presented a similar stability diagram of hydrous phases based on Schreinemaker's net analysis. They noticed two main differences of hydrous phase stability between the peridotite system and simple systems: (1) the addition of Al₂O₃ expands the stability field of phase E to the lower pressures and (2) the addition of TiO₂ enhances the stability field of clinohumite and chondrodite (Fig. 2). The addition of fluorine is also found to expand the stability of clinohumite into a lower pressure range (Stalder and Ulmer 2001). According to Fumagalli et al. (2001), the 10 Å phase (Table 1) is reported to be stable in the peridotite system at 5.2 GPa and 680 °C. Fumagalli and Poli (2005) found that the 10 Å phase has high Al₂O₃ contents (about 10 wt%) and suggested that this phase is a mixed layer of chlorite and pure 10 Å phase formed in the MgO-SiO₂-H₂O system. The stability field of this Al-rich 10 Å phase is close to the stability of Mg-sursassite (Bromiley and Pawley 2002). These phases cover some regions of the choke point (Fig. 3), though the H₂O content contributed by Mg-sursassite and Al-rich 10 Å phase to peridotite is limited to 0.7 (Iwamori 2004; Fig. 3) and 1 wt% (Fumagalli and Poli 2005), respectively.

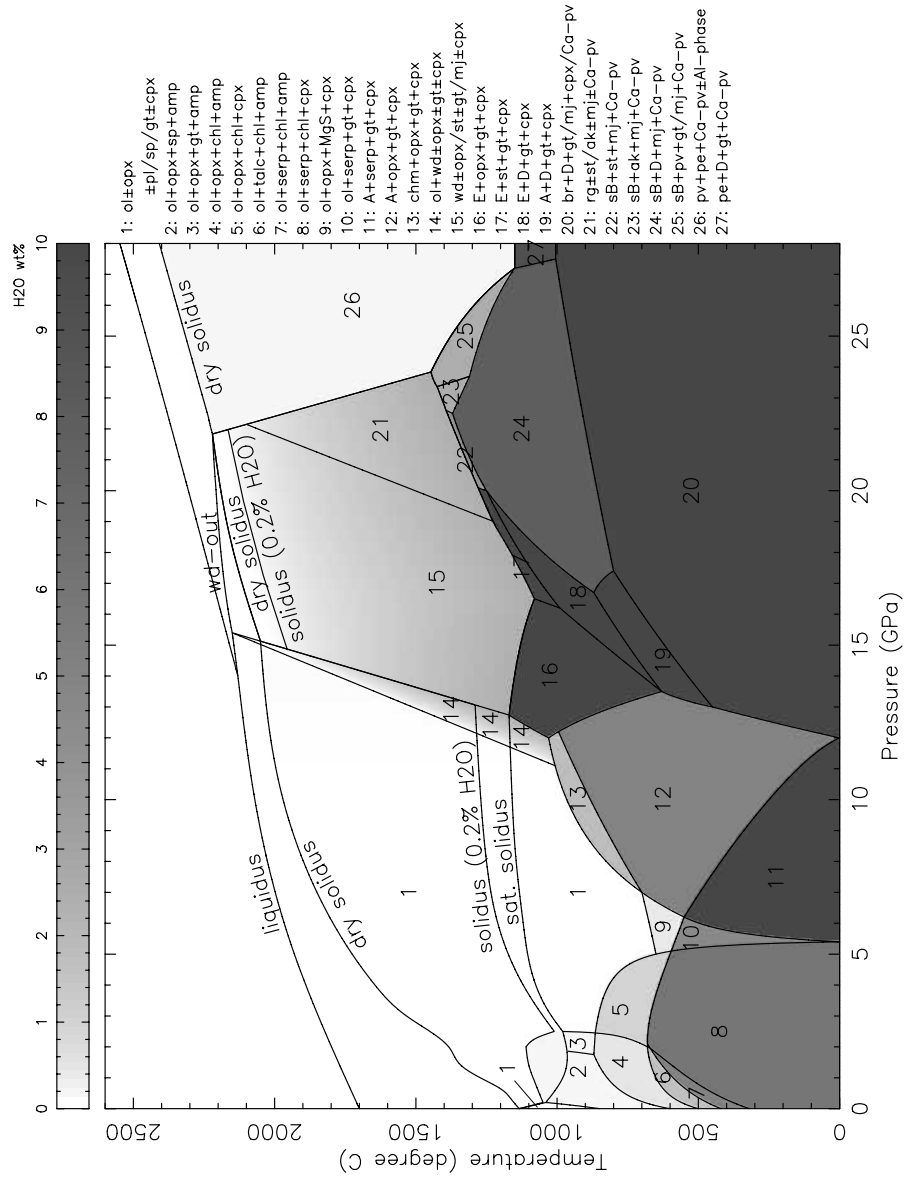


Figure 3. Phase diagram showing maximum H₂O contents bound in hydrous minerals/phases in the peridotite system. The phase assemblages of fields numbered are shown on the right hand side. Abbreviations are in Table 1. This gray figure was made by the courtesy of Hikaru Iwamori. The original diagram is in full color with better resolution (Iwamori 2004).

Amphibole was historically thought to be the most important phase to deliver H₂O beneath the volcanic arc (fields 2, 3, 4, 6, and 7 in Fig. 3; Tatsumi 1986; Schmidt and Poli 1998; Niida and Green 1999). According to the compilation by Schmidt and Poli (1998), pargasite can be stable up to between 2.2 GPa and 3.0 GPa depending on the bulk rock chemistry of the system. Although Schmidt and Poli (1998) adopted the lowest pressure (2.2 GPa) for pargasite in harzburgite, it is important to realize that pargasite can be stable up to 3 GPa in more enriched peridotite such as enriched pyrolite (Niida and Green 1999). The 3.5 GPa for the high-pressure stability limit of pargasite adopted by Tatsumi (1986) seems overestimated as Schmidt and Poli (1998) suggested. In Figure 2, 2.8 GPa was adopted as a pressure limit for pargasite according to the recent experimental study by Fumagalli and Poli (2005). The stability of antigorite (line between fields 5 and 8 in Fig. 3) also depends on bulk composition and the effect of Al was evaluated by Bromiley and Pawley (2003). The stability of antigorite in Figure 2 is drawn with the data reported by Ulmer and Trommsdorff (1995).

STABILITY OF HYDROUS PHASES IN DOWNGOING BASALT AND SEDIMENT

There are many hydrous minerals observed in metamorphic basalt and sediments. Several experimental studies have explored their high *PT* stabilities. Concerning the stability of amphibole in the basalt system (Fig. 4), there is a discrepancy between Schmidt and Poli (1998) and Forneris and Holloway (2003). According to Schmidt and Poli (1998), in subducting basalt, amphibole and zoisite dehydrate first, then along a colder path, zoisite and chloritoid dehydrate, and finally lawsonite with or without chloritoid can retain H₂O to the deep mantle (Fig. 4B). Along a warmer path, instead of lawsonite, zoisite becomes the only hydrous phase to possess H₂O after amphibole dehydration, and then zoisite dehydrates liberating H₂O (Fig. 4B). In contrast, according to Forneris and Holloway (2003), amphibole and zoisite at higher temperatures and amphibole with lawsonite at lower temperatures are stable up to 2.5-3.2 GPa (Fig. 4A). Then amphibole and zoisite dehydrate and lawsonite

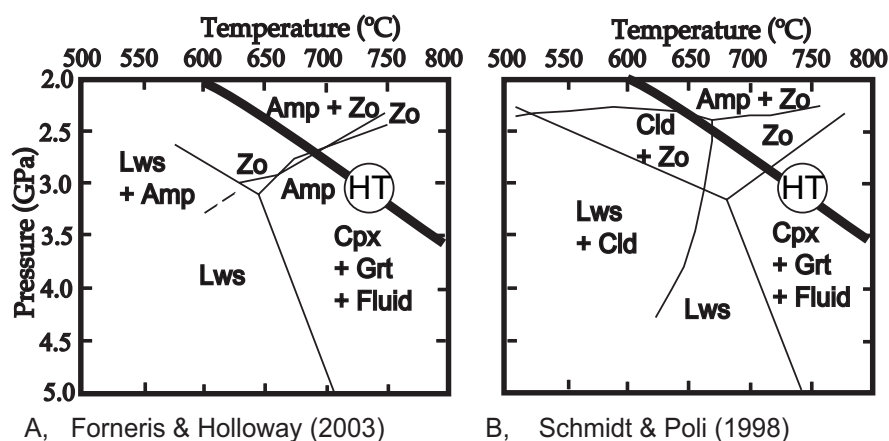


Figure 4. Phase diagrams showing stability of hydrous minerals in the MORB system. (A) Forneris and Holloway (2003), Amp represents barroisite at high temperatures and glaucophane at low temperatures, (B) Schmidt and Poli (1998). This figure is after Forneris and Holloway (2003). According to Forneris and Holloway (2003), the chloritoid in B is likely to be formed by metastable crystallization, see text. HT represent a *PT* path of high-temperature subducting slab surface, and a *PT* path of low-temperature one (LT in Figure 2) is outside of this *PT* diagram (Peacock and Wang 1999).

becomes the only hydrous phase (Fig. 4A). Forneris and Holloway (2003) suggested that a possible explanation for the discrepancy was the crystallization of metastable chloritoid (Fig. 4B) during short experimental run durations in the former experiments, perhaps due to the chemical difference between their starting materials: bulk compositions studied by Forneris and Holloway (2003) contained more MgO and Al₂O₃ than the starting materials of Schmidt and Poli (1998). The appearance of metastable chloritoid depresses the stability of amphibole. According to Schmidt and Poli (1998) and Forneris and Holloway (2003), basalt can possess 0.5-0.8 and 0.3 wt% H₂O at 650 °C and 3 GPa.

Lawsonite is the most important hydrous phase in subducting basalt because it is stable at relatively high temperature (Pawley and Holloway 1993; Pawley 1994; Poli and Schmidt 1995; Schmidt and Poli 1998; Ono 1998; Forneris and Holloway 2003; Schmidt et al. 2004). In particular, its stability covers the choke points in the stability of hydrous minerals of the peridotite system from 3 to 9 GPa (Fig. 2), and therefore lawsonite could re-hydrate the downdragged peridotite layer under those pressures when it dehydrates. At a temperature region higher than the lawsonite stability field, Schmidt and Poli (1998) observed phengite in basalt. The modal proportion of phengite is, however, limited in basalt because MORB has a low concentration of K and also if K is available in the system, K is partitioned preferentially into fluid.

In the system relevant to sediments, Domanik and Holloway (1996) and Ono (1998) reported the stability of phengite, Mg-sursassite, topaz-OH, and phase Egg. These hydrous phases are characterized by their higher temperature stability than hydrous phases in peridotite and basalt systems as seen in Figure 2. Phengite has dehydration conditions similar to that of phlogopite (Fig. 2). The reaction boundary between topaz-OH and phase Egg is identical to the olivine - wadsleyite boundary (Fig. 2). Ono (1998) demonstrated that subducting sediment can bring 2 wt% H₂O in phengite to 7 GPa, 0.7 wt% H₂O in topaz-OH to 9 GPa, and 0.4 wt% H₂O in phase Egg up to 15 GPa, and that subducting basalt can bring about 1 wt% H₂O in lawsonite to 6 GPa and 800 °C. Phase Egg could be stable at least up to the transition zone, while lawsonite could dehydrate at around 10 GPa. This means that phase Egg could be formed in the sediment layer by H₂O coming from dehydration of lawsonite in the basaltic layer. In addition to these phases, the δ-AlOOH phase, a high-pressure polymorph of diasporite, was proposed to be an important H₂O host in sediment or basalt systems (Suzuki et al. 2000). However, it is still uncertain whether this phase is stable in sedimentary or basaltic systems (Litasov and Ohtani 2005).

PRESSURE - TEMPERATURE CONDITIONS AND DEHYDRATION REACTIONS IN THE SUBDUCTING SLAB

Obviously the *PT* conditions of the downgoing slab are critical to determine the dehydration processes of hydrous phases in the slab. Furukawa (1993), Peacock (1993) and Peacock and Wang (1999) suggested several *PT* paths for subducting slabs (Fig. 2). These calculations have large uncertainties of 100-200 °C in the temperature at 90 km (3 GPa), because steep temperature gradients exist near to slab surfaces. Iwamori (2004) suggested that a kinematic critical parameter comprising the product of subduction angle, potential temperature, slab velocity and slab age, must be exceeded for *PT* paths to pass below the choke point at 6.2 GPa and 620 °C.

When the downgoing hydrous peridotite follows relatively warm *PT* paths, antigorite breaks down, followed by talc and chlorite (HT path in Fig. 2). Beyond the chlorite-out reaction the subducting peridotite will be almost free of H₂O bound in crystals except for a small amount in phlogopite at around 2.5 – 6.5 GPa. This means that when downgoing hydrous peridotite goes on paths like this, the hydrous minerals should encounter a “choke point” at 2.5 GPa (Fig. 2). If there is enough K₂O to stabilize phlogopite in the mantle, the downgoing hydrous peridotite will carry a small amount of H into the deeper mantle. At 6.5-11 GPa, the

phlogopite breaks down into K-richterite, which has an equal H/K atomic ratio and is stable at least up to 13 GPa (Sudo and Tatsumi 1990) and then dehydrates again into another hydrous phase containing lower H/K (Trønnes et al. 1988; Inoue et al. 1998). The crystal structure of this phase remains to be investigated. When the downgoing hydrous peridotite follows relatively cold *PT* paths, antigorite breaks down at 6 GPa (LT path in Fig. 2) and beyond which small amounts of H₂O may retain in phlogopite.

Lawsonite in subducting basaltic crust contains ~11 wt% H₂O and is stable beyond the choke point (Figs. 2, 4). Therefore, since the lower pressure stability of DHMS overlaps with the high-pressure stability of lawsonite, DHMS such as chondrodite, clinohumite, phase A and phase E in the downdragged base of the mantle wedge could absorb H₂O from decomposing lawsonite in the basaltic layer and become H₂O carriers in a cold subduction zone (LT path in Fig. 2) to the deeper mantle beyond the choke point. Phengite, topaz-OH and phase Egg in downgoing sediment could also pass H₂O into DHMS because of their high-temperature stability (Fig. 2).

COMPOSITION AND DIHEDRAL ANGLES OF AQUEOUS FLUIDS IN MANTLE PERIDOTITE

Since the pioneering work by Nakamura and Kushiro (1974), the chemical compositions of silicates dissolved in aqueous fluids have been assumed to be characterized by an SiO₂-rich component at relatively shallow depths corresponding to pressures between 1 and 3 GPa (Ryabchikov et al. 1982; Zhang and Frantz 2000). In contrast, recent experimental data above 3 GPa suggest that aqueous fluids coexisting with enstatite (MgSiO₃) and forsterite (Mg₂SiO₄) exhibit higher Mg/Si ratios as the pressure increases from 3 GPa up to 10 GPa (Fig. 1; Stalder et al. 2001; Mibe et al. 2002).

When the dihedral angles between crystals and fluids are smaller than 60°, permeable flow is allowed even if the porosity is small. The dihedral angles at triple junctions between forsterite crystals and aqueous fluid change from >60° to <60° from 1 to 3 GPa at 1000 °C (Fig. 5A; Watson and Brenan 1987; Watson et al. 1990; Mibe et al. 1998, 1999). This finding is coincident with (1) the chemical change in the aqueous fluids from an SiO₂-rich regime to an enstatite-rich regime and (2) the increase in silicate solubility at around 3 GPa (Fig. 1). The dihedral angle of H₂O fluid in forsterite continues to decrease in the pressure range 3-5 GPa (Mibe et al. 1998; 1999). This may be due to an increasing amount of silicate in the aqueous fluids (Takei and Shimizu 2002) and/or a chemical change from an enstatite-rich to a more MgO-rich constitution (Fig. 1).

Ono et al. (2002) reported that the dihedral angles of aqueous fluids in pyrope garnet (Mg/Si = 1) increase with increasing pressure from 4 to 9 GPa. Mibe et al. (2003) measured the dihedral angles of aqueous fluids in pyrope garnet and clinopyroxene, which are major constituents of eclogite (Fig. 5B). The *PT* conditions at which the dihedral angles of olivine - olivine - fluid (ol - fl), and garnet - garnet - fluid (gt - fl) are equal to 60°, are plotted in Figure 5C. Comparison of the *PT* conditions of the 60° isopleths and the stability of hydrous phases (Fig. 2) suggests the following: (1) The *PT* conditions of the 60° isopleths between garnet and fluids lie along the stability limit of lawsonite. The fluid liberated from lawsonite can readily migrate upward in the eclogite (basalt) system. (2) The *PT* conditions of the 60° isopleths between olivine and fluid looks similar to the stability limits of pargasite and chlorite. This means that the fluids liberated by their dehydration reactions in peridotite may readily migrate upward. (3) The liberated fluids in peridotite system re-enter into the stability fields of chlorite or pargasite when they migrate upward, and again they are trapped in these hydrous minerals. The aqueous fluid will be released again when chlorite/pargasite re-dehydrate in the downgoing flow beyond their stability fields. Davies and Stevenson (1992) called this process the lateral

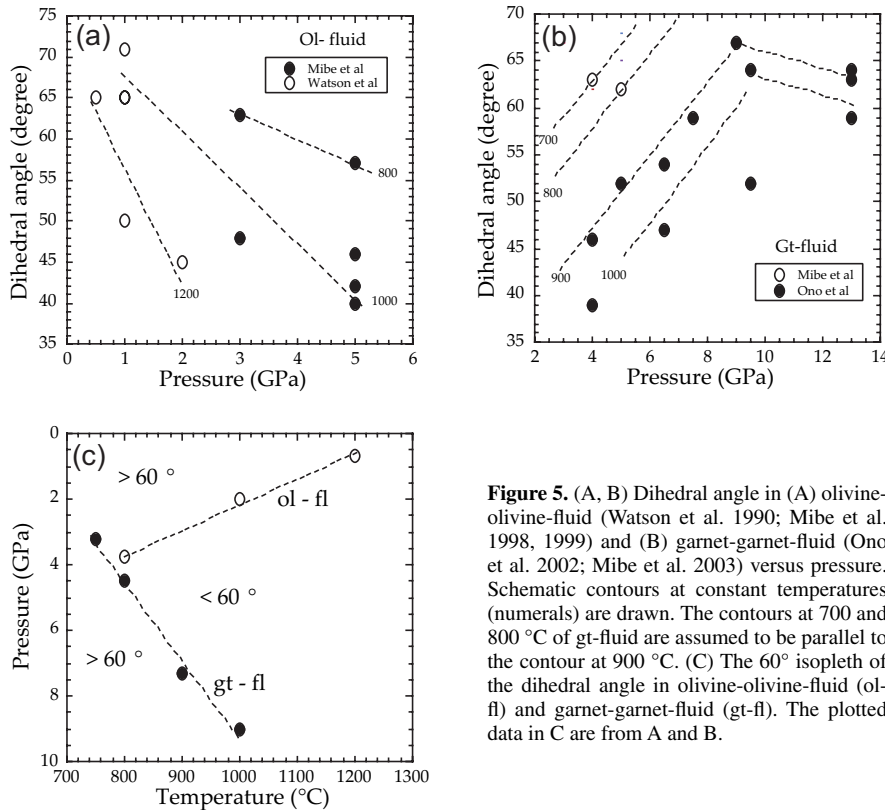


Figure 5. (A, B) Dihedral angle in (A) olivine-olivine-fluid (Watson et al. 1990; Mibe et al. 1998, 1999) and (B) garnet-garnet-fluid (Ono et al. 2002; Mibe et al. 2003) versus pressure. Schematic contours at constant temperatures (numerals) are drawn. The contours at 700 and 800 °C of gt-fluid are assumed to be parallel to the contour at 900 °C. (C) The 60° isopleth of the dihedral angle in olivine-olivine-fluid (ol-fl) and garnet-garnet-fluid (gt-fl). The plotted data in C are from A and B.

H₂O transport and suggested that this mechanism delivers H₂O laterally to the partial melting zone. Such a process was also considered in numerical calculations by Iwamori (1998). A hydrous mineral is carried deeper by induced mantle flow until the stability limit of the hydrous mineral is reached. H₂O is then liberated and fluids are trapped as structural H₂O in the hydrous minerals and as immobile fluids due to their dihedral angle >60°. These would get dragged down in the induced flow, and this process would be repeated until the fluid reaches the zone of partial melting.

SECOND CRITICAL ENDPOINT BETWEEN MAGMAS AND AQUEOUS FLUID: IMPLICATIONS FOR SLAB-DERIVED COMPONENT

Simple silicate melts and aqueous fluids can mix completely under certain *PT* conditions (Fig. 6A,B). At pressure conditions equivalent to the Earth's upper mantle, silicate melts and aqueous fluids cannot be distinguished from each other at the temperature-pressure conditions beyond a second critical endpoint, where a critical temperature meets its wet solidus (Kennedy et al. 1962; Paillat et al. 1992; Shen and Keppeler 1997; Bureau and Keppeler 1999). Following the visual demonstration of the complete mixing between albite melt and H₂O (Shen and Keppeler 1997), Bureau and Keppeler (1999) reported complete miscibility between aqueous fluids and K₂O-bearing nepheline melt, pure jadeite melt, haplogranitic melt, Ca-bearing haplogranitic melt and dacite in the SiO₂-Al₂O₃-Na₂O-K₂O-CaO-MgO system. Sowerby and Keppeler (2002) demonstrated complete miscibility between B₂O₃ - F enriched albite melt or pegmatite and H₂O

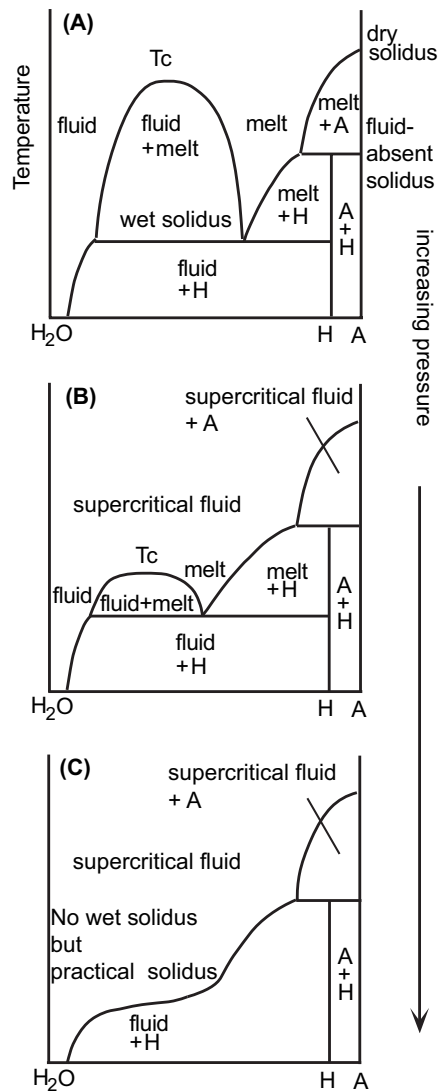


Figure 6. Schematic phase diagrams in the system of mineral A and H₂O (Kawamoto et al. 2004). H is a hydrous mineral. (A, B) As pressure increases, a critical temperature (T_c) between H₂O-bearing silicate melt and silicate-bearing H₂O fluid decreases. (C) The T_c meets the H₂O-saturated solidus temperature in the system at a second critical endpoint. At pressures beyond that of the second critical endpoint, there is no difference between melts and fluids. In this case there is no H₂O-saturated solidus temperature. The practical solidus represents a temperature above which a detectable amount (more than a few percent) of silicate melt is formed (Iwamori 1998).

(Sowerby and Keppeler 2002). Kawamoto (2004b) reported similar observations of mixing relationships between aqueous fluids and natural andesitic/dacitic melt (Fig. 7). The critical PT conditions observed in the andesite/dacite- H₂O system are similar to those observed in the other simple silicate-H₂O systems (Fig. 8; Shen and Keppeler 1997; Bureau and Keppeler 1999).

Experiments to determine H₂O-saturated solidus temperatures often identify them from abrupt changes in chemical composition of the minerals and/or the appearance of dendritic textures with increasing temperature at a given pressure (Inoue 1994; Kawamoto and Holloway 1997; Irifune et al. 1998; Stalder et al. 2001; Mibe et al. 2002). Some workers have distinguished two types of dendritic texture, one quenched from partial melt and the other from aqueous fluids (Irifune et al. 1998; Litasov and Ohtani 2002). However, they mentioned that it is difficult to distinguish between these types of texture at pressures greater than 10-13 GPa. As the critical temperature between aqueous fluids and silicate melts decreases with increasing pressure (Paillat et al. 1992; Shen and Keppeler 1997; Bureau and Keppeler 1999), it should meet an H₂O-saturated solidus temperature with increasing pressure (Fig. 6C).

It is difficult to melt basaltic compositions in a Bassett-type diamond anvil cell due to its temperature limitation of 1100 °C (Bureau and Keppeler 1999). Therefore, a supercritical behavior between aqueous fluids and mafic magmas equilibrated with mantle peridotite had remained to be investigated for years. Recently Mibe and his coworkers experimentally determined the PT conditions of a second critical endpoint between peridotite/basalt melts and aqueous fluids by the use of a Kawai-type large volume press and synchrotron X-ray radiography (Kanzaki et al. 1987; Mibe et al. 2004a). They reported that a second critical endpoint between peridotite/basalt melts and aqueous fluids may be located at 3.8 and 3 GPa, respectively (Mibe et al. 2004b, 2005, 2006). This pressure range is lower than that estimated by Kessel et al. (2005). Although

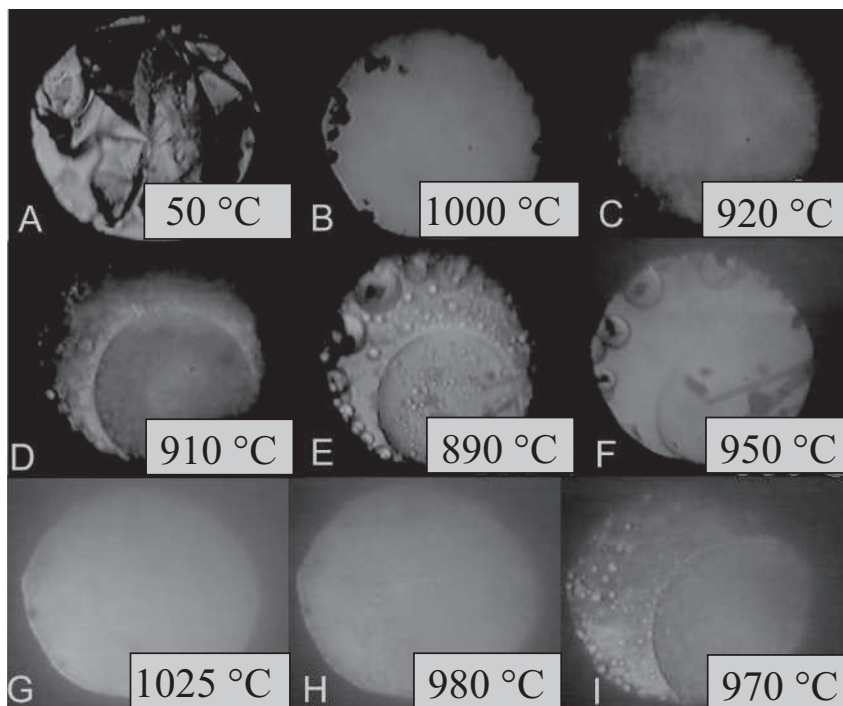


Figure 7. Microphotographs showing supercritical behavior between Fuji 1707 andesite and H₂O using Bassett-type externally heated diamond anvil cell (Kawamoto 2004b). (A) Chips of the andesitic glass and water are in the rhenium gasket (gasket hole is 0.5 mm) with a small bubble (right) at 50 °C. (B) At 1000 °C and about 1 GPa, a homogeneous fluid, with several grains of unidentified crystals. (C) On cooling to 920 °C, a milky appearance due to tiny droplets of andesite melt in aqueous fluid is seen. (D, E) At 910-890 °C, melt globules are growing in the aqueous fluid. (F) Then during re-heating to 950 °C, the boundary disappears the fluid homogenizes. The crystals are also melting. (G) After heating at 1025 °C, there are no crystals left, and (H, I) during the subsequent cooling, the sample turns milky and separates into andesite globules and aqueous fluid. The difference among the critical temperatures on the first cooling (920 °C, in C, D), the heating (950 °C, in F), and the second cooling (980 °C, in H) could be due to a pressure decrease during the experiment.

Kessel et al. (2005) suggested that there is still a melt-fluid solvus at 4 and 5 GPa, they did not show the coexistence of two phases at 4 or 5 GPa. Therefore, the data shown in Figure 5 of Kessel et al. (2005) can be interpreted as evidence that the fluid compositions observed at 4 and 5 GPa vary continuously with temperature as in Figure 6C and these pressures are already beyond the second critical endpoint. In contrast, Mibe et al. (2004b, 2005, 2006) observed melts and fluids up to 3.8 and 3 GPa in peridotite- H₂O and basalt- H₂O systems, respectively, and found no coexisting two phases at higher pressures. Although X-ray radiography method is not able to detect a small difference between fluids and melts under certain conditions, Mibe et al. (2004a, 2006) tightly constrain the second critical endpoint between peridotite melt and aqueous fluids at 3.8 GPa, 1000 °C and with 55 wt% H₂O. The pressure of 3.8 GPa is equivalent to the depth of the Wadati-Benioff zone beneath the volcanic front.

If supercritical fluids are common at the base of the mantle wedge beneath volcanic arcs, the traditional H₂O-saturated solidus temperature may represent a temperature where the concentration of silicate components dissolved into aqueous fluids increases drastically and should therefore be described as a practical solidus (Fig. 6C; Iwamori 1998). If supercritical

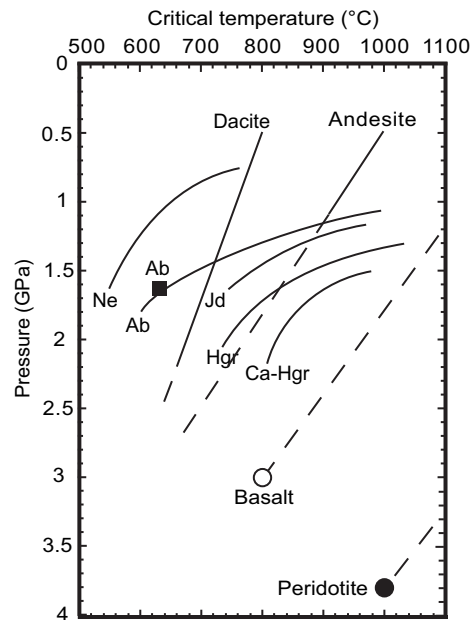


Figure 8. Critical temperatures observed between aqueous fluids and albite (Ab, Shen and Keppler 1997), nepheline (Ne), jadeite (Jd), and haplogranitic (Hgr) melts, Ca bearing haplogranitic melts (Ca-Hgr) and dacite (Bureau and Keppler 1999), and natural calc-alkaline andesite/dacite (Kawamoto 2004b). The estimated second critical endpoints between albite (Stalder et al. 2000), basalt (Mibe et al. 2005), and peridotite (Mibe et al. 2004a, 2006) and aqueous fluids are also plotted.

fluids commonly exist in the mantle wedge in subduction zones, such a supercritical fluid could separate into a silicate melt and an aqueous fluid when PT conditions become below the second critical endpoint along its migration to the surface (Fig. 8; Bureau and Keppler 1999). In this case, partitioning of elements between aqueous fluids and silicate melts should occur (Bureau et al. 2004). Such elemental fractionation may affect the chemical characteristics of the volcanic rocks. The existence of a second critical endpoint underneath the volcanic arcs suggests that dense supercritical fluids can come from the slab and separate into the aqueous fluid and melt in the mantle wedge. Otherwise, the slab component would be an aqueous fluid in cold subduction zones or a partial melt in warm subduction zones. Detailed studies of the critical curvatures in the peridotite, basalt, sediment systems will shed light on establishing a quantitative model for the magma generation and H_2O transport in subduction zones (Manning 2004).

CONCLUDING REMARKS

Our knowledge of the stability of hydrous phases in the downgoing slab has increased dramatically in the last decade (Figs. 2, 3, 4). Recently we have also learned much about the chemical features of aqueous fluids under upper mantle conditions. First, the chemical compositions of silicate components dissolved into aqueous fluids coexisting with mantle peridotite change from silica-rich at pressures lower than 3 GPa to magnesium-rich at pressures greater than 3 GPa (Fig. 1; Stalder et al. 2001; Mibe et al. 2002; Kawamoto et al. 2004). This means that the aqueous fluids in the mantle have peridotitic compositions beneath volcanic arcs. Second, dihedral angles formed between olivine and aqueous fluids change from $>60^\circ$ to $<60^\circ$ at 1000 °C and 3 GPa (Fig. 5; Mibe et al. 1998). This change was suggested to control the location of volcanic arcs (Mibe et al. 1999). Both the change of chemical composition and of wetting properties of mantle fluids with pressure may be related to the onset of complete miscibility between silicate melt and aqueous fluids as the pressure and temperature conditions approach the critical endpoint (Fig. 8).

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