

Subduction of ophicarbonates and recycling of CO₂ and H₂O

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ABSTRACT

Because subducted serpentinites may release significant quantities of volatiles, high-pressure phase equilibria were computed for two end-member hydrothermally altered mantle harzburgite protoliths (ophicarbonates): calcite + antigorite + brucite and calcite + antigorite + talc. For both bulk compositions, most of the H₂O released by metamorphic dehydration occurs at subarc depths; thus dehydration of serpentinites could be a major source for H₂O in arc magmas. In contrast, for both model compositions a significant fraction of the original carbonate is retained to depths exceeding 200 km. Consequently, deep subduction of ophicarbonate rocks of the oceanic lithosphere and/or downward drag of mantle wedge ophicarbonates provide a mechanism for carbonating the mantle and thus a potentially significant CO₂ source for deep mantle melts. The probable CO₂ sources for arc magmas are metamorphic decarbonation of marine sediments and/or carbonated mafic volcanics in the subducted slab.

INTRODUCTION

Metamorphic decarbonation in subduction zones has long been considered a source for mantle CO₂. However, in spite of considerable quantitative treatment of phase equilibria involving the release of H₂O via metamorphic dehydration in subduction zones (e.g., Liu et al., 1996), treatments of CO₂ release by metamorphic decarbonation reactions in subducted carbonate-bearing lithologies have been largely qualitative.

Chemical signatures imply that CO₂ in arc magmas is largely derived from carbonate of marine origin (Sano and Marty, 1995). This supports modeling the global carbon cycle assuming that CO₂ sequestered in marine sediments or hydrothermally altered oceanic crust is returned to the atmosphere by arc magmatism (Berner and Lasaga, 1989). However, global-scale estimates of CO₂ fluxes suggest that the amount of subducted CO₂ exceeds that released by arc magmatism (Bebout, 1995). Accordingly, the fate of the CO₂ not returned to the atmosphere by magmatism is relevant to the global carbon cycle and to the origin, transport, and residence of volatiles in the crust and mantle.

Selverstone and Gutzler (1993) hypothesized that cooling during the Cenozoic was produced by removal of CO₂ from the ocean-atmosphere system into subduction zones. Although their specific arguments regarding paleoclimate are controversial (Kerrick and Caldeira, 1994, 1998), Selverstone and Gutzler's (1993) study emphasizes that carbonate is present in deeply subducted slabs.

PROTOLITH

Primary carbonate-bearing lithologies in subducted slabs include marine sediments and mafic and ultramafic lithologies of the oceanic crust that were carbonated by hydrothermal reactions asso-

ciated with mid-ocean ridge systems. In this study we focused on carbonate-bearing ultramafic rocks (ophicarbonate) that are common in some mid-ocean ridge systems (Bonatti et al., 1974) and in ophiolites (Trommsdorff et al., 1993, O'Hanley, 1996). There are two primary reasons for confining our attention to ophicarbonates. First, metamorphic dehydration of subducted serpentinites may be a dominant H₂O source for arc magmatism (Ulmer and Trommsdorff, 1995; Scambelluri et al., 1995; Tatsumi and Kogiso, 1997). Accordingly, we evaluated ophicarbonates as a CO₂ source for arc magmas. Second, phase equilibria in ophicarbonate systems are relatively simple compared to other carbonate-bearing CO₂ source rocks (metabasalts or calcareous sediments). Furthermore, ultramafic assemblages are comparatively uncomplicated by crystalline solution. In contrast, the other primary CO₂ source rocks in subducted slabs (metamorphosed mafic volcanics and marls) have relatively complex mineral solutions. Uncertainties in the activity-composition relations for these solutions could introduce significant error in calculated phase equilibria.

Ophicarbonate breccias, consisting of clasts of serpentinite enclosed in a carbonate matrix, are exposed on the sea floor of the Mid-Atlantic Ridge (Bonatti et al., 1974). Ophicarbonates are also common in ophiolites. As with Mid-Ocean Ridge ophicarbonates (Bonatti et al., 1974), isotopic compositions of the carbonates in ophiolites suggest a marine origin (Trommsdorff et al., 1993). Significant quantities of carbonate are present in some ophicarbonates (Ferry, 1995).

Calcite is the most common carbonate mineral in ophicarbonates of the ocean floor and ophiolites (Evans, 1977). Lizardite and chrysotile are the primary serpentine group minerals formed from low-temperature hydrothermal alteration of oceanic ultramafic rocks (Evans, 1977). How-

ever, these minerals are replaced by antigorite upon incipient metamorphism (Bucher and Frey, 1994). Accordingly, in our computations we consider a model "protolith" containing antigorite as the sole serpentine group mineral. For the ultramafic component, we assumed a fully hydrated harzburgite, and thus confined our analysis to protoliths containing only the hydrous minerals: brucite, antigorite, and talc. From the range of mantle bulk rock compositions (harzburgites) depicted by Bucher and Frey (1994, Fig. 5.2), we chose two limiting assemblages: (1) a Mg-rich assemblage: 80% antigorite + 20% brucite, and (2) a Mg-poor assemblage: 80% antigorite + 20% talc (proportions in mol%). No data exist on the average carbonate content of subducted ophicarbonate rocks; thus, we arbitrarily assumed a CO₂ content of ~5 wt%. The model compositions were obtained by adding calcite (10–12 vol%) to the fully hydrated model "protoliths" (antigorite + brucite and antigorite + talc). Our starting compositions consisted of a mixture of 12 vol% calcite and 88% of assemblage (1) and another with 10.8 vol% calcite and 89.2% of assemblage (2).

OPHICARBONATE PHASE EQUILIBRIA

The devolatilization behavior of CO₂-H₂O-bearing rock is determined by pressure-temperature conditions and the composition and amount of fluid present at the onset of devolatilization. Such a fluid might be generated by the surrounding rocks. In this case, it is impossible to predict the evolution of a system without simultaneous consideration of the processes in its environment. For this reason, we have adopted a closed-system model for devolatilization in which we assume that fluid is generated solely by devolatilization of the ophicarbonate rock. Although a closed system model may seem unrealistic, fluid flow in rocks where pore connectivity is unstable must occur by

propagation of isolated domains of fluid-filled porosity (Connolly and Podladchikov, 1998). Moreover, reaction-generated fluid production has the capacity to overwhelm external fluid sources (Connolly, 1997). These considerations justify either closed or batch devolatilization models.

The compositions and amounts of the stable phases can be calculated as functions of pressure and temperature for a closed system, provided that thermodynamic data are available for the phases of interest. These calculations are straightforward; however, the uncertainties introduced in extrapolating thermodynamic data to high pressures, and possible effects of nonvolatile components dissolved in high-pressure H₂O-CO₂ fluids (Ulmer and Trommsdorff, 1995), are such that at pressures of 4–8 GPa there are discrepancies approaching 200 °C in the computed conditions of equilibria, depending on the choice of thermodynamic data and equations of state. Rather than attempting a critique of existing data, we have taken a semiempirical approach and chosen thermodynamic data (Berman, 1988, with modifications as described by Trommsdorff and Connolly, 1990, and Bose and Ganguly, 1995) and fluid equations of state (Haar et al., 1984, for pure H₂O, and Holland and Powell, 1991, for pure CO₂ and H₂O and for CO₂ activities in CO₂-H₂O mixtures) that reproduce the experi-

mental determinations of the antigorite and talc dehydration equilibria (Ulmer and Trommsdorff, 1995; Bose and Ganguly, 1995). With this approach, decarbonation equilibria are constrained by the experimentally calibrated dehydration equilibria. For the two model ophicarbonates bulk compositions, calculations were carried out with the PERPLEX computer program (Connolly, 1990), taking into consideration the phases shown in Figure 1. More complex calculations of phase equilibria for a lherzolitic bulk composition have shown that the crystalline solutions involving Fe-Mg and the Al₂O₃ component are minor in light of the uncertainties in our calculations (Trommsdorff and Connolly, 1996).

As illustrated in Figure 1, carbonate breakdown occurs at univariant reactions or over divariant regions marked by the progressive increase in X_{CO₂} of the fluid phase. For example, starting with the assemblage diopside - enstatite - forsterite - magnesite (Fig. 1), the prograde reaction: enstatite + magnesite → forsterite + CO₂ yields an increase in X_{CO₂} and results in complete decarbonation at X_{CO₂} = 0.15. Through this divariant region, the CO₂ content is reduced from the initial value of the model rock compositions (i.e., 5.5 and 4.9 wt%) to zero.

Varying the CO₂ content from that of the model rock compositions (~5 wt%) affects the

pressure-temperature location of the carbonate-out equilibrium. Decreasing the proportion of initial carbonate (i.e., more conservative initial carbonate contents of the model rocks) causes carbonate to be consumed at X_{CO₂} < 0.15. Thus, for example, half of the initial carbonate content yields complete decarbonation at X_{CO₂} ≅ 0.07.

DISCUSSION

For subduction zone pressure-temperature conditions (Fig. 1), dehydration is complete at 600–650 °C; in contrast, decarbonation is confined to higher temperature conditions. The contrasting pressure-temperature regimes of dehydration versus decarbonation have important implications regarding the devolatilization of subducted ophicarbonates.

Ophicarbonates in a subducted slab would release most of the initial H₂O (~11 wt%) in the range 550–650 °C (Fig. 1). Ulmer and Trommsdorff (1995) considered that serpentinites dehydrate by a single reaction: Atg = Fo + En + H₂O. In contrast, for the two model compositions considered in our study, dehydration would be stepwise, occurring by several reactions. Although we propose a different dehydration reaction scheme, we concur with Ulmer and Trommsdorff (1995) that substantial dehydration of serpentinites occurs in subduction zones beneath vol-

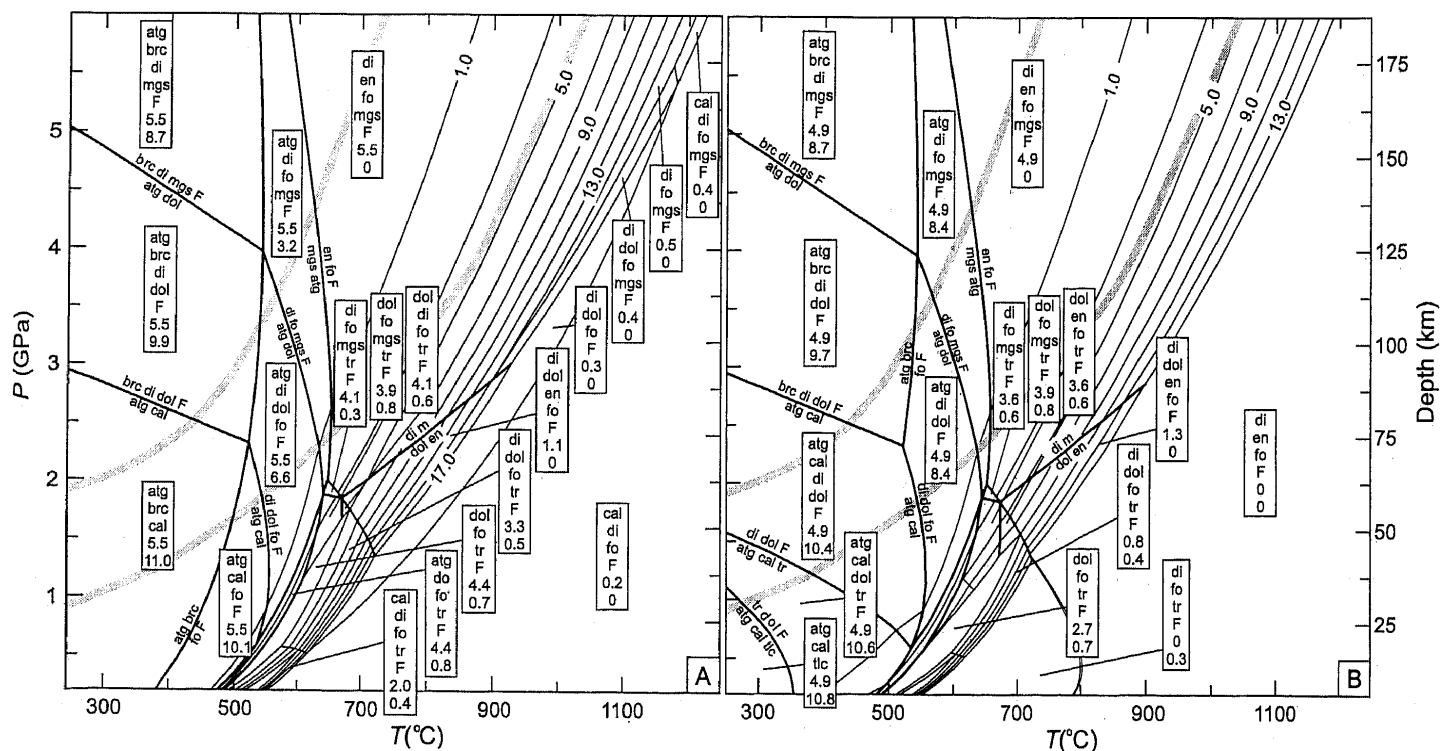


Figure 1. Phase equilibria for two model ophicarbonates bulk compositions. Mineral assemblages in divariant fields are listed in boxes. Phase abbreviations (from Kretz, 1983) are: atg—antigorite, brc—brucite, cal—calcite, di—diopside, dol—dolomite, en—enstatite, F—fluid (H₂O-CO₂), fo—forsterite, mgs—magnesite, tlc—talc, tr—tremolite. Initial volume percents of solid phases in two model rock compositions are: (A) 86.77% atg + 1.23% brc + 12.00% cal; (B) 86.94% atg + 2.26% tlc + 10.80% cal. Pair of numbers in each box denotes rock volatile content; wt% CO₂ is listed above wt% H₂O. As given in assemblage in the lower left part of each diagram, the respective initial wt% CO₂ and H₂O contents are 5.5 and 11.0 (A) and 4.9 and 10.8 (B). Univariant equilibria are depicted with thicker lines. Thin lines depict multivariant equilibria—numbers (1, 5, 9, and 13) are mol% CO₂ contents in fluid phase for selected isopleths. Adjacent isopleths correspond to differences in fluid composition of 2 mol% CO₂ and rock CO₂ content of about 0.7 wt%. Subduction zone pressure-temperature paths (from Peacock, 1990) are depicted with shaded bands. In both diagrams, higher temperature shaded band corresponds to top of subducted slab, whereas lower temperature band represents lower limit for “cold” subduction.

canic arcs. Release of water into the overlying mantle wedge and consequent production of anatectic melts is compatible with the top of the subducted slab at 100–150 km (~3–4.5 GPa) beneath volcanic arcs (Pawley and Holloway, 1993).

Along colder pressure-temperature paths of subducted slabs (Fig. 1), less than 1 wt% CO₂ would be lost from the solid portion of the rock. Taking the hottest pressure-temperature path shown in Figure 1, the maximum CO₂ loss would be ~1.5 wt% (i.e., along the 5 mol% CO₂ isopleth in Fig. 1). Because hydrothermal alteration is primarily confined to the upper kilometer of oceanic crust (Alt, 1995), the pressure-temperature conditions of the top of the subducted slab (Fig. 1) are most relevant to ophicarbonates. Following a down-dip path along the top of the slab (Fig. 1), ophicarbonates should release about 1.5 wt% CO₂ in the 2–4 GPa range followed by negligible CO₂ loss between 4 and 6 GPa. Significant amounts of CO₂ would remain in both model rock compositions (~4 wt% for the atg-brc-cal starting composition and ~3.5 wt% for the atg-tlc-cal model assemblage). Accordingly, in subducting ophicarbonate rocks, the remaining carbonate would be preserved to depths exceeding the base of the asthenosphere (~200 km). This provides a mechanism for carbonating the subasthenospheric mantle.

The pressure-temperature path for the top of the subducted slab (Fig. 1) passes through the pressure-temperature conditions (2.8–4 GPa and 700–900 °C) estimated for ultrahigh-pressure metamorphic rocks (Ernst and Peacock, 1996). Ernst and Peacock (1996) suggest that ultrahigh-pressure complexes were decoupled from the subducting lithosphere and subsequently heated. If so, for the top of coherent (nondetached) subducted slabs the pressure-temperature trajectory may be to the left of the curve shown in Figure 1. This conclusion is in concert with Peacock's (1995) modeling of the pressure-temperature conditions of subduction. Accordingly, the prograde pressure-temperature path of the top of the subducted slab would result in relatively little (<1 wt%) CO₂ loss during subduction to subasthenospheric pressures.

Our results are in agreement with the conclusions of previous studies (e.g., Liou et al., 1995) that deep burial of carbonates would be maximized with "cold" subduction (depicted in Fig. 1). These conditions would be met with rapid subduction of old oceanic crust.

Thermobarometric data suggest that ultrahigh-pressure terranes had a clockwise pressure-temperature path during burial and subsequent exhumation. Although ultrahigh-pressure complexes represent metamorphosed sialic crust, the exhumed tectonic "sheet" of Ernst and Peacock's (1996) model could include ultramafic rocks of the oceanic lithosphere. Superimposing Ernst and Peacock's (1996, Fig. 2) adiabatic retrograde pressure-temperature path for ultrahigh-pressure

terrane onto Figure 1, complete decarbonation of ophicarbonates would occur upon reaching pressures of ~1 GPa. Thus, while not a significant CO₂ source upon prograde metamorphism, deeply subducted ophicarbonates could degas significant quantities of CO₂ upon exhumation.

Mid-ocean ridge ophicarbonates consist of clasts of serpentinite enclosed in a carbonate matrix (Bonatti et al., 1974), and carbonate veins are abundant in ophicarbonates of ophiolites (O'Hanley, 1996). During metamorphism, limited exchange of components between the serpentinite and carbonate would impede consumption of carbonate, and thus limit decarbonation. However, petrologic evidence suggests that silicate-carbonate reactions readily proceed in ophicarbonate breccias subjected to amphibolite facies metamorphism (Driesner, 1993).

Ulmer and Trommsdorff (1995) and Scambelluri et al. (1995) provided no quantitative data supporting their contention that large volumes of serpentinitized oceanic mantle are subducted. Serpentinitized ultramafic rocks are commonly exposed on the sea floor of slow-spreading systems such as the Mid-Atlantic Ridge and the Atlantic-India Ridge (Cannat, 1993). The emplacement of mantle-derived ultramafic rocks is considered to reflect the low rate of magma supply that forms typical oceanic crust (i.e., gabbro-dike complex-pillow basalt sequences). In the well-studied area of the Kane Fracture Zone of the Mid-Atlantic Ridge, ultramafics occupy about half of the oceanic crust (Cannat, 1993). Taking the Atlantic oceanic crust as a baseline, and assuming that serpentinitization of the mantle ultramafics is confined to the upper 0.5 km of the oceanic crust, we provisionally assume a model oceanic crust with 5 vol% serpentinites. Accordingly, if ca. 6×10^{16} g of oceanic crust is subducted each year (Bebout, 1995), dehydration of subducted oceanic slab serpentinites at sub-arc depths could release $\sim 2 \times 10^{13}$ moles/yr of H₂O. As this flux is 3–4 times larger than the estimated annual flux of H₂O from subaerial volcanism (Bebout, 1995), this would support Ulmer and Trommsdorff's (1995) contention that dehydration of subducted serpentinites of the oceanic slab may be a dominant H₂O source for arc magmas. Because serpentinites are abundant in Alpine ophiolites, they may have been important fluid sources in subduction associated with the Tethyan orogen (Scambelluri et al., 1995). However, serpentinites are rare in the medium-to-fast spreading centers within the Pacific Ocean (Cannat, 1993). Because Pacific Ocean spreading centers have undergone medium-to-fast spreading since the Cretaceous (Kominz, 1984), it is likely that mantle peridotites are rare in the Pacific oceanic crust. Accordingly, serpentinites in the subducted oceanic slab may play a minor role in the volatile budget of circum-Pacific subduction zones. However, metamorphic dehydration and decarbonation of sediments and altered basaltic crust

in the oceanic slab underneath forearcs would hydrate and carbonate peridotites of the overlying mantle wedge (Peacock, 1993). Cogent evidence for this process is the presence of serpentinite seamounts in the Mariana subduction zone in the western Pacific (Fryer et al., 1995). Here, the compositions of vent fluids, and carbonate chimneys at hydrothermal vents, attest to active decarbonation of the forearc slab. Blueschist facies mafic clasts in the serpentinites (Maekawa et al., 1993) suggest that hydrothermally altered basalts of the subducted oceanic plate could be a major source (protolith) for the volatiles. The serpentinite diapirs are considered to have formed by water released by dehydration of the subducted slab (Fryer et al., 1995). This conclusion is compatible with phase equilibria of metabasic rocks, which imply that most of the H₂O is released in the first 70–80 km of subduction (Tatsumi and Kogiso, 1997). However, disequilibrium overstepping of reactions in subducting mafic rocks of the oceanic crust could retard dehydration of metamafic rocks to subarc depths (Liu et al., 1996). Subsequent downward drag of the hydrothermally-altered mantle wedge would result in devolatilization at greater depths (Bose and Ganguly, 1995; Tatsumi and Kogiso, 1997). Thus, the altered mantle wedge could provide a significant H₂O source for circum-Pacific arc magmatism and, through subduction beyond the sub-arc depths, a source of CO₂ to the deeper mantle.

In island arcs, magmatic volatiles are released from arc volcanoes and back arc basins. Using the computed CO₂ released by intrusive magmas in the back arc basin of the Taupo Volcanic Zone as a baseline, Seward and Kerrick (1996) concluded that the amount of CO₂ released from the western Pacific back arc basins could be globally significant ($\sim 10^{12}$ moles/yr). While this rough estimate needs to be refined, it suggests that substantial decarbonation occurs in the subducted oceanic slab below volcanic arcs and adjacent back-arc basins (Giggenbach et al., 1993). Tatsumi and Kogiso (1997) suggested that dehydration in the mantle wedge is a significant source of H₂O for back arc basin magmas. Whether mantle wedge ophicarbonates could be a CO₂ source for Western Pacific back arc basin magmas requires further thermal modeling of the pressure-temperature conditions of subduction zones beneath back arc basins.

In light of our conclusion that ophicarbonates undergo little or no decarbonation at or before subarc depths, we conclude that the probable CO₂ sources for arc magmas are metamorphic decarbonation of marine sediments and/or carbonated mafic volcanics in the subducted slab.

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