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Subduction zone metamorphic pathway for deep carbon cycling: II. Evidence from HP/UHP metabasaltic rocks and ophicarbonates

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ABSTRACT

Exposures of low-grade metabasalts and ophicarbonates in the Northern Apennines, and their high- and ultrahigh-pressure metamorphic equivalents in the Western and Ligurian Alps and Tianshan (representing an overall peak *P–T* range of ~0.2–3.0 GPa, 200–610 °C), allow investigation of the effects of prograde metamorphic devolatilization, and other fluid–rock interactions, on degrees of retention and isotopic evolution of C in subducting oceanic crust and associated mantle rocks. Such work can inform models of C cycling at convergent margins, helping to constrain the efficiency of return of initially subducted C via arc volcanism and the fraction of this subducted C entering the deeper mantle beyond arcs.

In the metabasaltic rocks, the preservation of finely disseminated carbonate with $\delta^{13}C$ overlapping that of seafloor-altered protoliths, and the minimal mineralogical evidence of decarbonation, indicates large degrees of carbonate retention in this suite extending to UHP conditions similar to those beneath modern volcanic fronts. For many of the metabasalts, the $\delta^{18}O$ of this carbonate can be explained by closed-system equilibration with silicate phases (e.g., garnet, clinopyroxene) during HP/UHP metamorphism. Larger volumes of carbonate preserved in interpillow regions and as breccia-filling largely escaped decarbonation, showing little or no evidence for reaction with adjacent metabasalt. Calculated devolatilization histories demonstrate that, in a closed-system model, carbonate in metabasaltic rocks can largely be preserved to depths approaching those beneath volcanic fronts (80–90 km). Modeling of open-system behavior indicates that episodic infiltration of such rocks by H_2O-rich fluids would have greatly enhanced decarbonation. Trends in O–C isotope composition of carbonate in some metabasaltic suites likely reflect effects of infiltration by externally-derived fluid with or without resulting decarbonation. Most carbonated ultramafic rocks similarly show little mineralogical evidence for decarbonation, consistent with calculated reaction histories, and have $\delta^{13}C$ largely overlapping that of seafloor equivalents. However, the high-grade ophicarbonates show more restricted ranges in $\delta^{18}O$ consistent with some control by infiltrating fluids, likely during subduction.

This combination of field, petrographic, and isotopic evidence, together with calculated decarbonation histories, is consistent with minimal loss of CO_2 from these rocks via decarbonation during forearc metamorphism. Combining our results with those of Cook-Kollars et al. (2014; *Chemical Geology*) for associated W. Alps metasedimentary rocks, we suggest that the majority of the CO_2 (perhaps 80–90%, considering the full range of rock types) could be retained through forearcs in more intact volumes of subducting sediment, basalt, and ophicarbonate experiencing closed- or limited open-system conditions. Deep in forearcs and beneath arcs, decarbonation (and also carbonate dissolution) could be enhanced in shear zones and highly fractured volumes experiencing larger fluid flux in part from dehydrating sub-crustal ultramafic rocks in slabs. Degrees of C loss by decarbonation, carbonate dissolution, and partial melting should be particularly significant as the subducting sections experience heating to >600 °C at depths of 80–120 km (i.e., approximately at depths beneath arcs).

1. Introduction

Understanding of deep-Earth C flux in subducting oceanic lithosphere and sediments is crucial to modeling volatile contributions to

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volcanic arcs, evolution of the atmosphere, and long-term degassing or regassing of the mantle (Berner et al., 1983; Zhang and Zindler, 1993; Marty and Tolstikhin, 1998; Berner, 1999; Dasgupta and Hirschmann, 2010; Van Der Meer et al., 2014). Current understanding of the degrees of C retention to great depths in subduction zones is largely based on studies of volcanic gas output in comparison with subduction zone inputs, the latter based on knowledge of seafloor lithologies (see Hilton et al., 2002). Additional understanding has come from theoretical and experimental studies of phase stabilities in subducting oceanic lithologies (e.g., Kerrick and Connolly, 1998, 2001a,b; Molina and Poli, 2000; Gorman et al., 2006; Poli et al., 2009; Tsuno and Dasgupta, 2011; Cook-Kollars et al., 2014; Schmidt and Poli, 2014). There is general agreement that the behavior of C (and other major volatiles) along the subduction-zone metamorphic pathway must be taken into account when assessing long-term Earth degassing and atmosphere evolution (Bebout, 1995, 2007b, 2014; Javoy, 1998; Kerrick, 2001; Dasgupta and Hirschmann, 2010; Dasgupta, 2013; Cook-Kollars et al., 2014). However, there has been relatively little petrologic and geochemical study of decarbonation, and other mechanisms of C mobilization, in high-pressure (HP) and ultrahigh-pressure (UHP) metamorphic suites representing the pathway taken by appropriate rock types subducting through forearcs and to beneath arcs.

A number of studies have considered global C subduction flux through comparison of subduction zone inputs in sediments, altered oceanic crust, and hydrated ultramafic rocks and subduction outputs in volcanic gases (e.g., Bebout, 1995, 2007b, 2014; Hilton et al., 2002; Jarrard, 2003; Dasgupta and Hirschmann, 2010; Dasgupta, 2013). The complexity and related uncertainty of these estimates are evident in the large ranges of published input flux estimates presented in Table 1 (also see Cook-Kollars et al., 2014). The combination of the uncertainties in the inputs and outputs results in a wide range in the estimates of volcanic arc return efficiency (16–80% arc return of the C entering trenches; Table 1). Some studies of arc volcanic CO_2 emissions have estimated the efficiencies of volcanic return of deeply subducted C for individual margins (e.g., Hilton et al., 2002; Shaw et al., 2003; Zimmer et al., 2004; de Leeuw et al., 2007; Marin-Ceron et al., 2010; Halldorsson et al., 2013). To examine the sourcing of C flux measured in volcanic gases, de Leeuw et al. (2007) compared C inputs measured by Li and Bebout (2005) for sediments outboard of the Central America trench. They suggested that contributions of sedimentary C alone could account for the measured output of gases and estimated a C return of 12–18% in Costa Rica and ~29% in El Salvador. The lack of a contribution of volatiles from subducting oceanic crust to arc volcanic gases was also suggested by Sano et al. (2001; Sano and Williams, 1996), Hilton et al. (2002), and Zimmer et al. (2004). However, it could be difficult to distinguish the contributions of CO_2 from carbonate sediment and from carbonate in altered oceanic crust based on the $CO_2/^3He$ and $\delta^{13}C$ of the volcanic gases (see House et al., 2014).

Table 1
Estimates of C subduction input and output fluxes from the recent literature.

Input ($\times 10^{12}$ mol C/year)	Sediments	Basalts	Ultramafics	Total
Bebout (2007a, b, 2014)[a]	0.9–4.8	3.1–4.0	0.4–0.8[b]	4.4–9.6
Dasgupta (2013)	1.1–1.4	3.0–5.1	0.4–0.8	4.5–7.3
Hilton et al. (2002)	1.34	2.12	0.4–0.8[b]	3.86–4.26
Jarrard (2003)	1.2	2.27		3.87–4.27
Output ($\times 10^{12}$ mol C/year)		**Arc gas**		**Return efficiency**
Varekamp et al. (1992)		1.5		16–80%
Marty and Tolstikhin (1998)		2.5		
Sano and Williams (1996)		3.1		

[a] The methods for calculating these fluxes are presented in Sadofsky and Bebout (2003).
[b] From Dasgupta (2013); this flux is added to the sediments and basalts estimates by the other authors.

Theoretical studies have calculated phase stabilities for sediments, oceanic crust, and ultramafic lithologies associated with inputs into subduction zones (Kerrick and Connolly, 1998, 2001a,b; Molina and Poli, 2000; Proyer, 2003; Wei and Powell, 2003; Wei et al., 2003; Connolly, 2005; Gorman et al., 2006; Cook-Kollars et al., 2014). Kerrick and Connolly (2001a) calculated mineral assemblages and volatiles concentrations for a wide range of sediment compositions, along subduction-zone *P*–*T* paths for modern margins, examining a closed-system model where decarbonation in subducting sediments allows CO_2 to be expelled from sediments without the influence of infiltrating, externally-derived H_2O fluids. In contrast, Gorman et al. (2006) investigated "open" system behavior in which crustal material, and sub-crustal slab ultramafic rocks, can contribute H_2O-rich fluids to overlying sediments and basalts, thus driving decarbonation reactions. It is conceivable that the H_2O-rich fluids emanating from the upper mantle in subducting slabs contain small amounts of CO_2 (or other C fluid species), depending on the C content of the hydrated ultramafic rocks (see Kerrick and Connolly, 1998; discussion by Alt et al., 2013). The coupling of external fluid-ingress and decarbonation within subducting slabs has been described in some studies of HP rocks (e.g., John et al., 2008; Ague and Nicolescu, 2014), and the opposite has also been described, with carbonation occurring along major intra-slab fluid conduits (Beinlich et al., 2010; John et al., 2012). Closed- and open-system scenarios can produce drastically differing degrees of forearc devolatilization (Gorman et al., 2006; see the discussion by Cook-Kollars et al., 2014), pointing to the need for "ground-truthing" by detailed study of devolatilization and fluid mobility in exposures of HP/UHP-metamorphosed oceanic lithologies.

Few studies have investigated the degrees of deep retention of C, as carbonate or reduced C (the latter largely metamorphosed organic matter), in appropriate lithologies (sediment, oceanic crust, and carbonated ultramafic rocks) and over the wide range of *P*–*T* conditions representative of trench to subarc metamorphism in subduction zones. The studies to date, mostly focusing on metasedimentary suites, have indicated substantial retention of C and other volatiles during the relatively cool metamorphic conditions experienced at <40 km depths in most forearcs (see Bebout and Fogel, 1992; Bebout, 1995; Sadofsky and Bebout, 2003) and extending to depths approaching those beneath volcanic fronts (e.g., in the HP/UHP units in the Italian Alps; Cook-Kollars et al., 2014; also see Busigny et al., 2003; Bebout et al., 2013). Greater degrees of devolatilization and associated volatiles losses, including C isotope shifts in reduced C, occur in metasedimentary rocks along relatively warm subduction-zone *P*–*T* paths, such as those represented by the higher-grade units of the Catalina Schist (see Bebout and Fogel, 1992; Bebout, 1995). Other field and petrologic studies provide descriptions for UHP carbonate rocks at individual localities without detailed work evaluating extents of decarbonation and related isotopic shifts (e.g., Becker and Altherr, 1992; Kato et al., 1997; Zheng et al., 2003; Castelli et al., 2007; van der Straaten et al., 2008, 2012; Lu et al., 2014; Proyer et al., 2014). The smaller number of studies of HP/UHP metabasaltic rocks conducted at single localities, or over small ranges in grade (prehnite–pumpellyite to blueschist facies), have similarly indicated retention of C in subducting oceanic crust, with little or no isotopic shift, across metamorphic grades (Cartwright and Barnicoat, 1999, 2003; Miller et al., 2001). This points to the need for more thorough study of C loss from altered oceanic crust (AOC) and ultramafic rocks, the latter representing either peridotite hydrated and carbonated on the seafloor or sub-crustal slab ultramafic rocks hydrated and carbonated during slab bending and associated faulting and deep infiltration by seawater (see discussion of faulting and infiltration process by Ranero et al., 2005). The decarbonation and overall C loss history of deeply subducting AOC is particularly key to understanding subduction C cycling as this lithology could convey one-half to two-thirds of the subduction C input inventory into trenches (Table 1; see Dasgupta