



Carbonation of subduction-zone serpentinite (high-pressure ophicarbonates; Ligurian Western Alps) and implications for the deep carbon cycling



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ABSTRACT

Much of the long-term carbon cycle in solid earth occurs in subduction zones, where processes of devolatilization, partial melting of carbonated rocks, and dissolution of carbonate minerals lead to the return of CO₂ to the atmosphere via volcanic degassing. Release of COH fluids from hydrous and carbonate minerals influences C recycling and magmatism at subduction zones. Contradictory interpretations exist regarding the retention/storage of C in subducting plates and in the forearc to subarc mantle. Several lines of evidence indicate mobility of C, of uncertain magnitude, in forearcs. A poorly constrained fraction of the 40–115 Mt/yr of C initially subducted is released into fluids (by decarbonation and/or carbonate dissolution) and 18–43 Mt/yr is returned at arc volcanoes. Current estimates suggest the amount of C released into subduction fluids is greater than that degassed at arc volcanoes: the imbalance could reflect C subduction into the deeper mantle, beyond subarc regions, or storage of C in forearc/subarc reservoirs.

We examine the fate of C in plate-interface ultramafic rocks, and by analogy serpentinitized mantle wedge, via study of fluid–rock evolution of marble and variably carbonated serpentinite in the Ligurian Alps. Based on petrography, major and trace element concentrations, and carbonate C and O isotope compositions, we demonstrate that serpentinite dehydration at 2–2.5 GPa, 550 °C released aqueous fluids triggering breakdown of dolomite in nearby marbles, thus releasing C into fluids. Carbonate + olivine veins document flow of COH fluids and that the interaction of these COH fluids with serpentinite led to the formation of high-*P* carbonated ultramafic-rock domains (high-*P* ophicarbonates). We estimate that this could result in the retention of ~0.5–2.0 Mt C/yr in such rocks along subduction interfaces. As another means of C storage, 1 to 3 km-thick layers of serpentinitized forearc mantle wedge containing 50 modal % dolomite could sequester 1.62 to 4.85 Mt C/yr.

We stress that lithologically complex interfaces could contain sites of both C release and C addition, further confounding estimates of net C loss at forearc and subarc depths. Sites of C retention, also including carbonate veins and graphite as reduced carbonate, could influence the transfer of slab C to at least the depths beneath volcanic fronts.

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1. Introduction

In part due to the anthropogenic buildup of CO₂ in the atmosphere, geoscientists have devoted considerable attention to understanding not only CO₂ release by burning of fossil fuels, and natural and human-induced sequestration of atmospheric CO₂ storage

in minerals, but also the full set of geologic processes governing long-term (up to 10⁹ yr) change in atmospheric CO₂ levels (Kerrick and Connolly, 1998; Jarrard, 2003; Kelemen and Matter, 2008; Dasgupta and Hirschmann, 2010; Reusch, 2011; Tumiati et al., 2013; Stagno et al., 2013; Dasgupta, 2013; Bebout, 2014). Much of the long-term cycling of C in the solid Earth occurs at subduction zones, where carbonated rocks (and rocks containing organic C; Bebout, 2014) are transported into the mantle and where devolatilization, melting, and dissolution of subducted rocks leads

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to return of CO₂ to the atmosphere in arc volcanic gases (Berner et al., 1983; recent discussion in Dasgupta, 2013; Collins et al., 2015; Kelemen and Manning, 2015). In such environments, the interplay of carbonation and decarbonation of rocks exerts a major, if not absolute, control on surface C emission and thus atmosphere evolution.

The deep C subduction cycle is still poorly understood, and a broad range of possibilities exists regarding the residency of C in subducting plates and in the supra-subduction mantle over wide ranges in pressure, temperature and fluid composition. The available experiments and closed-system thermodynamic modeling of carbonated rocks (metasediments, altered oceanic crust) document that carbonate minerals can remain stable to the very high pressures and temperatures experienced in subduction zones, resulting in minimal C release to subduction fluids in forearcs (Molina and Poli, 2000; Thomsen and Schmidt, 2008; Kerrick and Connolly, 1998, 2001a, 2001b; Poli et al., 2009; Cook-Collars et al., 2014; Collins et al., 2015). Reduction of carbonate to graphite, related to fluid–rock interaction, also can affect the degree of C retention to great depths in subducting rocks (Galvez et al., 2013). On the other hand, much higher C solubility at subarc conditions (>700 °C; 2.5 GPa) has been proposed (Caciagli and Manning, 2003; Gorman et al., 2006; Kelemen and Manning, 2015). Several observations indicate significant C release from slabs at deep forearc and subarc depths, and transport of this C into forearc mantle wedges (and overlying crust) where it can be stored. These observations include (i) high CO₂ output from arc volcanoes, (ii) carbonic and diamond-bearing fluid/melt inclusions in high- and ultrahigh-*P* rocks, (iii) hydrated–carbonated assemblages in metasomatized peridotites from subducting plates and mantle wedges (McInness and Cameron, 1994; Van Roermund et al., 2002; Stöckhert et al., 2001; Sapienza et al., 2009; Scambelluri et al., 2008, 2015; Frezzotti et al., 2011; Malaspina et al., 2009; Kelemen and Manning, 2015). Thermodynamic modeling indicates release of C as CO₂ via decarbonation of hydrated–carbonated rocks, in particular in situations where these rocks are infiltrated by externally-derived H₂O-rich fluids (Gorman et al., 2006; Dolejs and Manning, 2010; Cook-Collars et al., 2014; Collins et al., 2015; Kelemen and Manning, 2015). Also, experimental work and studies of natural high- and ultrahigh-*P* rocks demonstrate that carbonate can dissolve in aqueous fluids at forearc-to-subarc *P*–*T* conditions (Caciagli and Manning, 2003; Dolejs and Manning, 2010; Sanchez-Valle et al., 2003; Frezzotti et al., 2011; Ague and Nicolescu, 2014). Thus, there are multiple lines of evidence for the mobility of C in forearc and subarc slab sections, but the magnitude of C loss by each of these mechanisms remains highly uncertain (Poli et al., 2009; Ague and Nicolescu, 2014; Cook-Collars et al., 2014; Collins et al., 2015; Kelemen and Manning, 2015). A poorly constrained fraction of the 40–115 Mt/yr C initially subducted is released into fluids and melts (by decarbonation, carbonate dissolution, and partial melting) and 18–43 Mt/yr is returned at arc volcanoes (see the recent estimates by Collins et al., 2015; Kelemen and Manning, 2015). The apparent imbalance between the amounts of C delivered to subduction fluids and the smaller C return to the atmosphere at arcs could reflect the subduction of C into the deeper mantle, or the storage of (hidden) C in the forearc and subarc mantle, and in deep crustal reservoirs (see Sapienza et al., 2009; Collins et al., 2015; Kelemen and Manning, 2015).

A key open issue regards the fate of carbonic fluids when they interact with rocks other than their sources (i.e., downstream from their sites of generation), particularly in slabs and in supra-subduction serpentinitized mantle and depending on their *P*–*T* flow trajectories. For example, abundant calcite/aragonite-bearing veins, and carbonated rocks in melange zones, attest to the ability of C-bearing fluids to deposit carbonate along some fluid flow paths

(see Bebout, 1991; Kelemen and Manning, 2015; Bebout and Penniston-Dorland, 2016). Here we examine the subduction-zone evolution of eclogitic serpentinite, marble and carbonated serpentinite in the Voltri Massif (W. Alps, Italy). We show that the H₂O-rich fluid released by dehydration of serpentinite triggers decarbonation of nearby dolomitic marble, leading to C release into fluids. Abundant magnesite + olivine veins at this locality indicate the transport of an aqueous–carbonic fluid and we suggest that the interaction of this COH fluid with some of the serpentinite layers resulted in carbonation of silicate mineral assemblages and formation of a new class of rocks, identified here as high-*P* ophicarbonates. We discuss this finding in terms of fluid/rock interactions controlling the fate of C in the slab and in serpentinitized supra-subduction mantle. We conclude that C fixed by such a mechanism into carbonate in slab and mantle wedge serpentinite would not be released from the subduction interface at the *P*–*T* conditions recorded in these rocks, and instead would remain at the base of the mantle wedge unless later released as a result of heating and/or decompression.

2. Geological background

The outcrops studied are in the Ligurian Voltri Massif, a high-*P*, blueschist- to eclogite-facies ophiolite at the SE end of the Italian W. Alps (Fig. 1A). The Voltri Massif largely consists of high-*P* serpentinite hosting eclogitic metagabbro, metarodingite and metabasalt, associated with high-*P* carbonate-bearing oceanic metasedimentary rocks (referred to as the Schistes Lustrés) inter-layered with metabasalt and chert (Capponi and Crispini, 2002). The Erro-Tobbio (meta)peridotite Unit, recording pre-Alpine rifting and oceanization, followed by Alpine subduction, is tectonically coupled with the above rock units (Hoogerduijn Strating et al., 1993; Scambelluri et al., 1995).

Several petrologic studies have considered the Alpine subduction-zone evolution of the Voltri Massif; most relevant to the present study are the *P*–*T* estimates of eclogites and associated serpentinite. The first rock-type develops garnet, omphacite and rutile at 450–500 °C and 1.3–1.7 GPa (Messiga and Scambelluri, 1991; Federico et al., 2004). The Voltri serpentinite records a polyphase evolution, with initial low-grade chrysotile–lizardite replaced by antigorite and then by olivine-bearing assemblages (Cimmino et al., 1979; Scambelluri and Rampone, 1999). This evolution is comparable to that documented for the Erro-Tobbio metaperidotite and, further North in the Alps, for the Lanzo Massif, recording transition from chrysotile/lizardite to antigorite serpentine, followed by eclogite-facies dehydration to olivine + antigorite + Ti-clinohumite-bearing assemblages (Scambelluri et al., 1995; Debret et al., 2013). This peak assemblage also occurs in vein systems, collecting the aqueous subduction fluid released by serpentinite during eclogitization (Scambelluri et al., 1995). Ages of peak metamorphism ranging from 45 to 34 Myr were estimated with ⁴⁰Ar/³⁹Ar and in-situ U/Pb isotopic systems, respectively (Federico et al., 2005; Rubatto and Scambelluri, 2003). Prograde subduction evolution was followed by retrograde blueschist- to greenschist-metamorphism related to exhumation (Messiga and Scambelluri, 1991; Hermann et al., 2000). This evolution was accompanied by superposed deformation episodes producing composite tectonic fabrics and isoclinal folding (Capponi and Crispini, 2002). An evolution of the Voltri Massif along plate interface domains, where rock slices of different provenance (slab and overlying mantle) and age are tectonically stacked together, was recently proposed according to field, geochemical and numerical modeling studies (Federico et al., 2007; Scambelluri and Tonarini, 2012; Malatesta et al., 2012).

All of the above studies focus on hydrated mafic–ultramafic systems, with little attention paid to C-bearing lithologies, notably ophicarbonates. For decades (Cortesogno et al., 1980, 1981) these

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