



An experimental investigation of C–O–H fluid-driven carbonation of serpentinites under forearc conditions

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ABSTRACT

The carbonation of serpentinites in the forearc region of the mantle wedge in subduction zones and of serpentinites within the subducting slab by fluids derived from prograde dehydration and decarbonation has important implications for the deep Earth carbon cycle. This study shows that the carbonation of serpentinites under the forearc can establish, over time, a significant reservoir for carbon within a partially hydrated mantle wedge and that carbonation of (ultra-) mafic rocks within the subducting slab contributes to C-transfer to greater depths and might supply carbon for arc volcanism or the deep mantle. We report a new high pressure experimental investigation of the interactions between oxidised C–O–H fluids and serpentinite and model the reaction progress with time series experiments. The CO₂, H₂O and alkane (C_nH_{2n+2}, n = 1–6; e.g. methane, ethane) contents in the fluid phase from quenched experimental run products have been analysed by gas chromatography and the results are compared with thermodynamic calculations. With progressive carbonation, the formation of magnesite + chlorite together with quartz, quartz + talc or talc at 1–2 GPa and 500–650 °C was observed. At temperatures above antigorite stability ($T \gtrsim 700$ °C and 2 GPa) magnesite + chlorite is stable together with talc, talc + enstatite, enstatite or enstatite + forsterite for decreasing CO₂-content in the fluid. Carbonation of serpentinite is a rapid process where magnesite forms within the first hour of the experiments, filtering CO₂ from the fluid effectively and equilibrium is approached within 48 h. The CO₂-sequestration and magnesite production are less pronounced at higher temperatures. Therefore, C–O–H fluids released under subarc conditions might migrate through the mantle with only minor changes in their carbon budget whereas significant carbonation likely occurs under the forearc. Furthermore, partition coefficients for Ca, Ba, Sr and Pb between magnesite and a C-poor aqueous fluid have been established to demonstrate the potential of newly formed magnesite to sequester fluid mobile elements.

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1. Introduction

A key aspect of the deep carbon cycle is how exogene carbon may be fixed in oceanic lithosphere via hydrothermal alteration of oceanic crust, subducted into the mantle and then recycled within subduction zones (Berner, 1999; Hayes and Waldbauer, 2006; Kelemen and Manning, 2015). Large amounts of carbon stored in marine sediments and altered oceanic crust are transported into the Earth's mantle at subduction zones. Through decarbonation, carbonate dissolution and partial melting, a poorly constrained fraction of carbon is released into fluids and melts during subduction

(Poli, 2015) and some carbon is returned to shallower reservoirs (e.g. crust, biosphere and atmosphere), but some carbon is subducted deeper and may be sequestered in the deep mantle (Yaxley and Green, 1994). The magnitudes of the various carbon fluxes and reservoirs have been investigated in several studies (see discussions in Collins et al., 2015; Dasgupta and Hirschmann, 2010; Kelemen and Manning, 2015) but remain controversial.

In the absence of fluids and for typical subducting slab geotherms, carbonates are stable and refractory. The stability of carbonates at high pressures has been demonstrated in experimental studies on carbonated peridotites and eclogites (Brey et al., 2008; Yaxley and Brey, 2004; Yaxley and Green, 1994). The transport of carbon to greater depths has further been evidenced by stable isotope and mineral inclusions data in some diamonds (Stachel and Harris, 2008).

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Table 1

Four starting mixes (SP1–4) with various serpentinite/fluid ratios have been used in this study. Oxalic acid dihydrate (OAD) is the main fluid source. Ba-, Sr-, Pb-, Ca-carbonate were added to the starting mix and are assumed to be present in the fluid in the beginning of the experiment in the listed concentrations.

Start mix			SP1	2*stdev	SP2	2*stdev	SP3	2*stdev	SP4	2*stdev
	Serpentinite	wt%	80.0	0.3	66.4	0.4	74.3	0.4	87.8	0.2
	OAD	wt%	19.3	0.3	33.0	0.4	25.1	0.3	11.5	0.2
Conc. in fluid	Ba	ppm	2118	21	1050	11	1528	11	3803	38
	Ca	wt%	1.32	0.01	0.65	0.01	0.95	0.01	2.33	0.02
	Pb	ppm	2118	21	1050	11	1528	15	3803	38
	Sr	ppm	2101	21	1042	10	1516	15	3772	38
	X _{CO₂} bulk*		0.27	0.004	0.35	0.005	0.31	0.005	0.2	0.004

* The listed bulk X_{CO₂} takes the water content of antigorite and the CO₂ content of added carbonates into account.

However, carbonates can dissolve into aqueous fluids (Caciagli and Manning, 2003; Dolejs and Manning, 2010), released during subduction. The capacity of the slab to produce such aqueous fluids is pronounced at an early stage of subduction, because prograde metamorphism leads to dehydration reactions. Thermodynamic models have shown that carbon is released as CO₂ from carbonated rocks especially when externally derived hydrous fluids infiltrate them (Gorman et al., 2006; Kerrick and Connolly, 2001a, 2001b). The amount of CO₂ in fluids is higher under forearc (X_{CO₂} ≤ 0.7) compared to subarc (X_{CO₂} ≤ 0.21) conditions as shown in experimental studies (X_{CO₂} = $\frac{n_{\text{CO}_2}[\text{mol}]}{n_{\text{CO}_2}[\text{mol}] + n_{\text{H}_2\text{O}}[\text{mol}]}$; Molina and Poli, 2000; Poli, 2015; Poli et al., 2009). Such C–O–H fluids might interact with the surrounding slab lithologies and (ultra-) mafic rocks in the overlying mantle wedge causing carbonation. Field observations demonstrate the importance of C–O–H fluid driven carbonation in the slab and overlying mantle wedge (Ague and Nicolescu, 2014; Beinlich et al., 2012; Bjerga et al., 2015; Piccoli et al., 2016; Scambelluri et al., 2016).

This study focuses on the potential capacity of serpentinites to store carbon as carbonates when C–O–H bearing fluids released from the slab migrate into and interact with the partially serpentinitized mantle and serpentinites in the slab (Hyndman and Peacock, 2003; Kerrick and Connolly, 1998; Tumiati et al., 2013). Carbon concentrations in fluids are poorly constrained, because earlier experimental studies were often inhibited by the inability to precisely measure the volatile compositions in equilibrium with the solid phases. To analyse the volatile species in C–O–H fluids from experimental capsules Tiraboschi et al. (2016) used a mass spectrometer based technique and computed the obtained mass/charge signal into volatile concentrations.

In this study, we measured directly the C–O–H fluid species in quenched experimental fluids by gas chromatography using an inlet system, that allows the experimental capsule to be pierced under vacuum and the gas phase to be extracted (Martin and Hermann, 2018). We compare the measured volatile fluid compositions with thermodynamic calculations and show to what extent the behaviour of real fluids containing dissolved species like CO₃²⁻, Si⁴⁺ and Mg²⁺ can be approximated by pure CO₂–H₂O fluids assumed in the model. We demonstrate how fast the formation of carbonates reduces the amount of CO₂ in the fluids by investigating the kinetics of the carbonation reaction through time series experiments. We further show the potential of newly formed magnesite to sequester Ca and fluid mobile trace elements such as Ba, Sr and Pb and show to what extent they may become enriched in carbonated ultramafic rocks. Our results are important to constrain carbon fluxes in subducted ultramafic rocks and the mantle wedge as we demonstrate that the forearc mantle may, over time, become an important and previously unrecognised reservoir for carbon, whereas carbonation in the subarc is less pronounced.

2. Methods

2.1. Experimental methods

Piston cylinder experiments were performed using powdered natural serpentinite (>98% antigorite, traces of magnetite and no sulfides according to XRD) mixed with various amounts of oxalic acid dihydrate (OAD; abbreviations are listed in the supplementary information) as the main source of H₂O and CO₂. Four starting mixes (SP1–4) with various serpentinite/fluid ratios were used (Table 1). Ba, Pb, Sr and Ca-carbonate were added in trace and minor abundances (Table 1). See supplementary information for details of preparation and performance of the piston cylinder experiments.

Experiments were run at 1 and 2 GPa, between 500–750 °C for 48 h. Two sets of time series experiments, both using SP1, were performed at 600 °C, 2 GPa for 24, 48 and 72 h and at 550 °C, 1 GPa for 0.1, 0.42, 0.85, 1, 48 and 192 h.

2.2. Analytical methods

After the piston cylinder experiments, the composition of the fluid in the recovered capsules was analysed by gas chromatography (GC-TCD). Then the capsules were mounted, polished and C-coated for electron microscopy (SEM and EPMA). Afterwards, LA-ICP-MS was used to determine the trace element composition of the solid assemblage on selected runs. The presence of particular mineral phases was verified by powder X-ray diffraction (XRD) for selected samples. The details of these techniques are reported in the supplementary information.

2.2.1. Gas chromatography – thermal conductivity detector (GC-TCD)

Gas-chromatography was applied to identify and quantify the amount and composition of the volatile species in post-run fluids. A sample-inlet system connected to a gas-chromatograph allows capsules recovered after piston cylinder experiments to be pierced under vacuum and the released gas can be analysed (Fig. S1 in the supplementary information). For analysing the gas composition of post-run fluids, the sample holder is first heated to ~150 °C for ~10 min and then pierced under vacuum. Heating is necessary to guarantee that all volatiles can escape from the sample. The pressure is sensed at constant temperature (ΔT ~2 °C per analytical session; temperature range over all analyses ~130–160 °C) and volume. This pressure is proportional to the amount of the released sample gas according to the ideal gas law. The sample gas is then topped up with pure He gas to above atmospheric pressure (~140 kPa). The gas mixture (sample plus He) is homogenised after waiting ~60 min at constant temperature. Aliquots of this gas mixture are then progressively introduced into, and analysed with the connected GC-TCD 5–7 times showing a reproducibility of ~19%. This routine was used for measuring both standards and samples.

CO₂ was calibrated using pure CO₂ as a standard and alkanes were calibrated using a certificated standard containing 1000 ppm

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