



# Tracing olivine carbonation and serpentinization in CO<sub>2</sub>-rich fluids via magnesium exchange and isotopic fractionation

Jan Prikryl<sup>a,\*</sup>, Andri Stefánsson<sup>a</sup>, Christopher R. Pearce<sup>b</sup>

<sup>a</sup> Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavík, Iceland

<sup>b</sup> National Oceanography Centre Southampton, University of Southampton Waterfront Campus, European Way, Southampton SO14 3ZH, UK

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## Abstract

Chemical exchange between seawater and the oceanic crust is thought to play a significant role in the regulation of the global magnesium (Mg) cycle, yet relatively little is known about the rates and mechanisms of Mg exchange in these crustal environments. In this study we experimentally characterize the extent, and nature, of Mg isotope fractionation during the carbonation and serpentinization of olivine (one of the principal minerals found in ultramafic rocks) under hydrothermal conditions. Olivine alteration was found to be incongruent, with the reactant fluid composition varying according to the extent of olivine dissolution and the precipitation of secondary minerals. In mildly acid water (pH ~ 6.5), olivine dissolved to form Mg-Fe carbonate solid solutions and minor chrysotile. Upon carbonation and a decrease of CO<sub>2</sub> in the water, the pH increased to >8, with chrysotile and brucite becoming the dominant alteration minerals. The Mg-rich carbonates preferentially incorporated lighter Mg isotopes, resulting in a ~0.5‰ increase of the δ<sup>26</sup>Mg composition of the fluid relative to olivine during the initial carbonation and serpentinization reactions. This was followed by a decrease in δ<sup>26</sup>Mg under higher pH conditions associated with the formation of brucite. Our experimental and modeling results therefore demonstrate that the δ<sup>26</sup>Mg composition of fluids involved in olivine alteration reflect the type and quantity of secondary Mg minerals formed, which in turn depend on the pH and CO<sub>2</sub> concentration of the water. Comparison of these results with natural groundwaters and geothermal waters from basaltic terrains indicate that the δ<sup>26</sup>Mg composition of natural waters are likely to also be controlled by mafic rock dissolution and the preferential incorporation of isotopically light Mg into carbonates and isotopically heavy Mg into Mg-Si minerals. Together, these findings improve our understanding of Mg isotope systematics during water-rock interaction, and suggest that δ<sup>26</sup>Mg may be a useful tool for tracing reactions that are critical to geological CO<sub>2</sub> sequestration. Crown Copyright © 2018 Published by Elsevier Ltd. All rights reserved.

**Keywords:** Kinetic model; Mg isotope fractionation; Hydrothermal; Carbonation; CO<sub>2</sub>; Serpentinization; Tracing reaction progress

## 1. INTRODUCTION

Earth's hydrosphere, continental crust and oceanic crust contain <0.1% of the total Mg in the bulk Earth yet show the largest extent of Mg isotopic variation (e.g. Galy

et al., 2003; Huang, 2013; Teng, 2017). Characterising the mechanisms and processes that control Mg isotopic fractionation and the isotopic balance of the bulk Earth can therefore improve our understanding of the global Mg cycle. The oceanic crust plays a significant role in global Mg budgets as it mainly consists of Mg-rich ultramafic and mafic rocks, with olivine one of the major primary minerals (e.g. McDonough and Sun, 1995). Furthermore, the alteration of olivine near and at the Earth's surface is fast

\* Corresponding author.

E-mail address: [jap5@hi.is](mailto:jap5@hi.is) (J. Prikryl).

relative to many other igneous minerals (e.g., Palandri and Kharaka, 2004) and involves the dissolution of olivine followed by precipitation of Mg-rich secondary minerals such as carbonates, chrysotile, talc and brucite (e.g., Janecky and Seyfried, 1986; Berndt et al., 1996). The serpentinization of mafic rocks also results in the generation of H<sub>2</sub> by water reduction through oxidation of ferrous iron (Fe<sup>II</sup>) dissolved from the primary rocks like olivine. The H<sub>2</sub> formed may further lead to formation of inorganic hydrocarbons from reduction of inorganic carbon like CO<sub>2</sub> (e.g., McCollom and Seewald, 2001; Etiopie and Sherwood Lollar, 2013). These reactions within mafic and ultramafic rocks have received growing interest from the scientific community as they represent a potential method for reducing atmospheric CO<sub>2</sub> concentrations by long-term CO<sub>2</sub> storage, as such rock types are a primary source of the principal cations (Mg<sup>2+</sup>, Fe<sup>2+</sup> and Ca<sup>2+</sup>) needed for carbonate formation (e.g., McGrail et al., 2006; Gíslason et al., 2010; Matter et al., 2016).

Previous studies on the carbonation and serpentinization of mafic and ultramafic rocks have focused on characterizing water-rock interaction with seawater and meteoric water under various pressures and temperatures (e.g., James et al., 2003; Giammar et al., 2005; Béarat et al., 2006; Seyfried et al., 2007; Andreani et al., 2009; McCollom and Bach, 2009; King et al., 2010; Jones et al., 2010; Stefánsson, 2010; Daval et al., 2011; Hövelmann et al., 2011; Gysi and Stefánsson, 2011, 2012a; Klein and Garrido, 2011; Marcaillou et al., 2011; Lafay et al., 2012; Marieni et al., 2013; Neubeck et al., 2014). Alteration under these conditions has been observed to result in the formation of various carbonate minerals at elevated CO<sub>2</sub> concentrations and pH < 7, whereas at low CO<sub>2</sub> concentrations the fluid pH becomes more alkaline, resulting in the formation of clays and serpentine minerals. Unfortunately, attempts to quantify the rate of carbonation and serpentinization within these reactions (and hence the processes that influence them) is complicated by the fact that many of the alteration minerals contain the same major elements as the primary phases. This means that, in the absence of mineralogical evidence, any changes observed in Mg concentrations can only be used to speculate on the extent of Mg-carbonate or silicate minerals being precipitated. In contrast, the extent of isotopic fractionation varies between mineral phases and reaction pathways, thus quantifying variations in the Mg isotope ( $\delta^{26}\text{Mg}$ ) composition of the reacting fluids may help quantify the extent of carbonation and CO<sub>2</sub> mineral sequestration associated with the alteration of mafic and ultramafic rocks.

Ultramafic and mafic oceanic rocks and mantle xenoliths show a relatively small  $\delta^{26}\text{Mg}$  range of  $-0.35$  to  $-0.18\text{‰}$  (e.g., Wiechert and Halliday, 2007; Teng et al., 2007, 2010, 2015; Liu et al., 2017). In contrast, continental basalts display more negative  $\delta^{26}\text{Mg}$  values of  $-0.60$  to  $-0.35\text{‰}$  as a result of incongruent partial melting of an isotopically light carbonated mantle (e.g., Huang et al., 2015), while altered oceanic basalts show significant  $\delta^{26}\text{Mg}$  variations ranging from  $-2.76$  to  $+0.21\text{‰}$ , suggesting significant Mg isotope fractionation upon water-rock interaction (Huang, 2013). The lowest  $\delta^{26}\text{Mg}$  ratios in these altered

basalts are typically associated with carbonation reactions, while the higher values are generally associated with serpentinization reactions. The fluids associated with these alteration reactions also have varying  $\delta^{26}\text{Mg}$  compositions, with seawater having a uniform composition of  $-0.83 \pm 0.09\text{‰}$  (e.g. Ling et al., 2011), while thermal and non-thermal groundwaters range between  $-0.96$  and  $+0.64\text{‰}$  (Pogge von Strandmann et al., 2008). Carbonate minerals formed in the altered rocks are typically enriched in <sup>24</sup>Mg relative to original silicate phases (Beinlich et al., 2014; Wimpenny et al., 2014). The variations observed in fluid  $\delta^{26}\text{Mg}$  may result from Mg isotope fractionation upon water-rock interaction with different fractionation factors for different secondary minerals (Wimpenny et al., 2014; Voigt et al., 2016; Liu et al., 2017). Once they have been properly quantified, such differences may be used to trace the degree of water-rock interaction, including the carbonation and serpentinization of mafic and ultramafic rocks.

In this study, we conducted reaction path experiments and geochemical and isotope modeling of olivine alteration in CO<sub>2</sub>-rich hydrothermal fluids as a function of reaction time and CO<sub>2</sub> concentration. Our kinetic reaction path model was prioritized to a mass balance approach in order to include a time dimension that enables us to extrapolate the geochemical reaction networks during reaction progress to natural systems. The reaction process was traced through time by solution chemistry, alteration mineralogy and Mg isotope systematics in order to define the major factors controlling water-olivine (mafic rock) alteration. Particular focus was placed on characterising the extent of  $\delta^{26}\text{Mg}$  fractionation during the formation of secondary phases, and its potential for use as a mechanism of tracing CO<sub>2</sub> sequestration in mafic and ultramafic rocks.

## 2. EXPERIMENTAL METHODS

### 2.1. Material and experimental design

The olivine used in the experiments was collected from Almklovdalen peridotite massif, Western Gneiss Region, Norway (Brueckner et al., 2010). The source dunite samples contained over 90% olivine, which was handpicked, crushed in a jaw crusher and agate mortar and pestle then dry sieved. The 45–125  $\mu\text{m}$  size fraction was used in all of the experiments. The grains were unzoned, and have a composition determined by EMPA ( $n = 23$ ) of  $\text{Mg}_{1.81-1.88}\text{Fe}_{0.13-0.15}\text{Si}_{0.97-1.01}\text{O}_4$ . The sum of other elements was  $\leq 0.36$  wt %. Hereafter, the olivine composition is referred to as 93% forsterite (Fo<sub>93</sub>). Prior to the experiments it was cleaned using deionized water, acetone and a magnet to separate any magnetic particles present, followed by drying at 40 °C. The specific geometric surface area ( $A_{\text{geo}}$ ) was determined according to the method of Tester et al. (1994) to be 226.3 cm<sup>2</sup>/g.

The batch (closed-system) experiments of olivine alteration in CO<sub>2</sub>-rich aqueous solutions were carried out at 5–21 mmol/kg initial total dissolved inorganic carbon ( $\Sigma\text{CO}_2$ ) in a Parr stirring reactor made of titanium (Fig. 1). Prior to each experiment the 600 ml reactor was filled with  $\sim 53$  g Fo<sub>93</sub> and  $\sim 400$  g of degassed CO<sub>2</sub>-rich

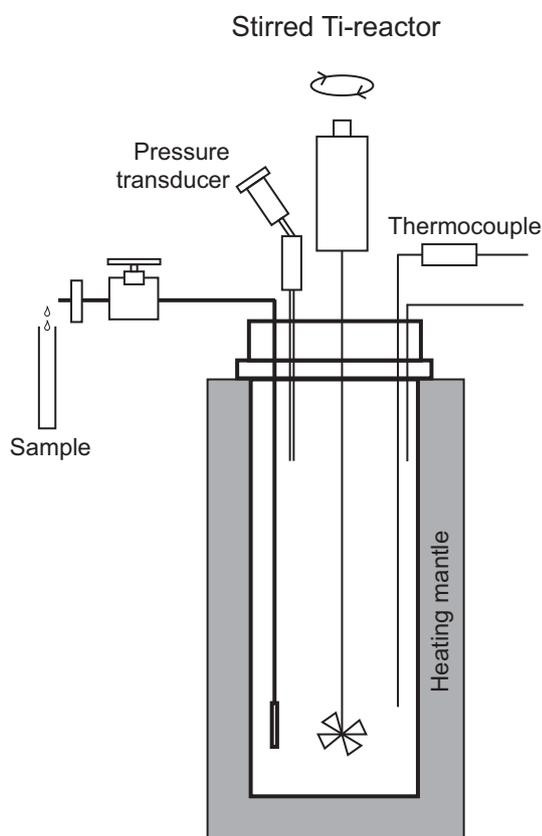


Fig. 1. A schematic picture of the experimental setup.

fluid under  $N_2$  atmosphere, giving an initial fluid/rock ratio of  $\sim 8$ . The reactor was heated to  $150\text{ }^\circ\text{C}$  with the pressure controlled by the solution vapor saturation pressure. The solutions were prepared from deionized water, NaCl (ACS, Sigma-Aldrich),  $NaHCO_3$  (ACS, Sigma-Aldrich) and 37% HCl (pro. anal. Merck). The starting conditions of the experiments are summarized in Table 1.

## 2.2. Sampling and analysis

Solution samples were collected regularly throughout the experiments. Samples for pH determination were analyzed immediately using a combination pH electrode (Cole-Parmer) calibrated with commercial buffer solutions. Samples for  $CO_2$  analyses were collected into 0.01–0.1 M NaOH solutions to prevent degassing and analyzed immediately

using a modified alkalinity titration (Stefánsson et al., 2007). Samples for Cl concentration determination were filtered through a  $0.2\text{ }\mu\text{m}$  filter (cellulose acetate) followed by analysis using ion chromatography (Dionex-2000). Samples for Na, Mg, Si, Fe concentrations and Mg isotopic analyses were also filtered through a  $0.2\text{ }\mu\text{m}$  filter, acidified to 1%  $HNO_3$  (Merck Suprapur<sup>®</sup>) followed by analysis by ion chromatography for Na and Mg (Dionex-1000) and spectrophotometrically for Si and Fe (Dougan and Wilson, 1973; Fishman and Friedman, 1989). The analytical precision based on repeated analysis of an internal standard (GYG13) at the 95% confidence level was 4.4% for Na, 3.0% for Mg, 2.8% for Cl, 6.5% for Fe and 8.7% for Si.

Samples of the reacted solid were collected at the end of each experiment. These were dried at room temperature prior to analysis. The chemical composition of the material was determined using an electron microprobe (JEOL JXA-8200 Superprobe) with an accelerating voltage of 15 kV, a beam current of 15 nA, and a beam size of 5–1  $\mu\text{m}$ . Unfortunately, most of the secondary phases (with the exception of magnesite) were too fine for point analysis, even with a beam size of 1  $\mu\text{m}$ , and were too small to be visible on polished samples. The surface morphology of the olivine grains and secondary phases were also studied by scanning electron microscope (SEM) equipped with EDS (HITACHI TM-3000) at an accelerating voltage of 15 kV with a working distance of 6.8 mm. Finally, the samples were analyzed using powder x-ray diffraction (XRD) with scans collected for 9 hours with a Bruker D8 Advanced ( $CuK\alpha_1$ , 1.5406  $\text{\AA}$ ;  $2\theta$  range 3–90;  $0.01^\circ/\text{step}$  and 768 s/step). Patterns were compared to standard mineral files compiled in the PDF2 database (ICDD PDF-2 Powder Diffraction File Database) using the software code EVA.

## 2.3. Magnesium isotope analyses

Solution samples were prepared for Mg isotopic ( $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$ ) analysis by evaporating between 0.4 ml and 1.9 ml of solution in order to process  $\sim 2\text{ }\mu\text{g}$  Mg per sample. Once dry each sample was dissolved in concentrated  $HNO_3$ , followed by drying and dissolution in 0.2 ml 0.8 M  $HNO_3$ . For olivine, 5 mg of fresh sample was digested in HF- $HNO_3$  at  $130\text{ }^\circ\text{C}$ . Once dissolved the samples were dried down, dissolved in concentrated HCl, dried again, dissolved in concentrated  $HNO_3$ , dried down and then finally dissolved in 0.8 M  $HNO_3$ . The solution and olivine samples were loaded onto acid-cleaned Teflon columns filled with

Table 1  
Summary of the experimental conditions.

Exp. #	Sample #	t ( $^\circ\text{C}$ )	Duration (days)	pH <sub>T</sub> <sup>a</sup>	CO <sub>2</sub> (mmol/kg) <sup>a</sup>	r/w ratio <sup>b</sup>
e	1e–9e	150	25.3	6.48	20.9	0.130
f	1f–8f	150	12.7	6.59	5.17	0.134
g	1g–8g	150	6.8	6.96	6.36	0.137
h	1h–8h	150	28.8	6.63	5.72	0.151
k	1k–5k	150	6.8	6.82	13.7	0.133

<sup>a</sup> The initial CO<sub>2</sub> and pH corresponds to the values measured in the first sample of each experimental run.

<sup>b</sup> The initial experimental rock to water ratio.

a AG50W-X12 cation exchange resin to a height of 8.5 cm in 0.8 M HNO<sub>3</sub>. Magnesium separation followed the technique described by [Pogge von Strandmann et al. \(2011\)](#), with the sample being loaded and washed in 0.8 M HNO<sub>3</sub> before the Mg fraction was eluted in 2 M HNO<sub>3</sub>. All samples were passed through the ion exchange columns twice to ensure complete separation from the other matrix elements, which was verified by ICP-MS analysis prior to isotopic analysis.

Isotopic analyses were performed on a ThermoFisher Scientific ‘Neptune’ Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). Samples were introduced to the Ar Plasma in 2% aqueous HNO<sub>3</sub> using a standard sample induction system (SIS) attached to a PFA Teflon nebuliser. <sup>24</sup>Mg, <sup>25</sup>Mg, and <sup>26</sup>Mg were measured in low-resolution mode, with each analysis consisting of 1 block of 30 measurements per analysis. Solution concentrations of 600 ppb typically gave beam intensities of ~12 V for <sup>24</sup>Mg, with total procedural blanks having a negligible contribution of <12 mV. Isotopic compositions were determined via sample-standard bracketing, and are reported as δ<sup>26</sup>Mg with respect to the DSM-3 standard ([Galy et al., 2003](#)). All sample analyses were run in duplicate, with the mean value and associated 2 standard error (se) reported ([Table 4](#)). Total procedural reproducibility was assessed by the analysis of the DSM, BCR, IAPSO and JDol standards during the same measurement session, with the corresponding δ<sup>26</sup>Mg values of +0.01 ± 0.02‰, −0.26 ± 0.10‰, −0.83 ± 0.02‰ and −2.32 ± 0.01‰ being identical to, or within error, of those previously reported by [Pearce et al. \(2012\)](#). The long-term reproducibility (2σ) of the δ<sup>26</sup>Mg analytical protocol at the University of Southampton, determined by repeat analyses of the DSM-3 Mg standard, is 0.07‰.

The δ<sup>25</sup>Mg and δ<sup>26</sup>Mg systematics of the dataset show mass dependent behavior. It follows that δ<sup>25</sup>Mg ratios do not provide additional information of magnesium isotope systematics beyond that of δ<sup>26</sup>Mg, thus although the δ<sup>25</sup>Mg data are reported in this study ([Table 4](#)) only the δ<sup>26</sup>Mg results are used in the models and discussion.

### 3. NUMERICAL SIMULATIONS

#### 3.1. Geochemical reaction path modeling

Reaction path simulations were carried out using the PHREEQC geochemical program ([Parkhurst and Appelo, 2013](#)). The Wateq.dat database used in these simulations was updated for dominant aqueous species, mineral solubilities and reaction kinetics of interest ([Appendix A](#)).

The general rate expression used to simulate the progress of olivine dissolution, formation of secondary minerals and the associated solution chemistry was;

$$r_{\pm,T,i} = \pm \zeta_i A_i \sum_j \left( k_{T,j} \prod_j a_j^x \right) (1 - SI_i^n) \quad (1)$$

where  $\zeta$  is the fraction of the surface area that is reactive having a value between 0 and 1 ([Přikryl et al., 2017](#)),  $A$  is the surface area,  $k_T$  is the rate constant at given tempera-

ture and  $\prod_j a_j^x$  is an activity expression for the  $j$ -th dissolved aqueous or surface species in solution. The saturation index to the power of  $n$  standing for order of reaction, SI, is defined as;

$$SI = Q/K \quad (2)$$

where  $Q$  is the activity product of the mineral reaction and  $K$  is the respective equilibrium solubility constant.

The surface area of the dissolved phase was expressed as decreasing upon dissolution or loss of moles, assuming the grains to be spherical, i.e.

$$A = A^0 \left( \frac{m_t}{m_0} \right)^{2/3} \quad (3)$$

where  $m$  is number of moles. The secondary minerals were also allowed to dissolve with the principle of microscopic reversibility. The rate expressions for secondary mineral formation represent crystal growth rates of a given mineral surface. However, the initial formation of minerals and mineral surfaces involves nucleation with  $A = A_n$  whereas  $A_n$  is the total surface area of the nuclei formed for a given mineral. In this study nucleation was not included into the rate expression. Instead, the initial surface area of the secondary minerals was assigned with  $A_n$  representing 0.1–10% of the initial olivine surface area. The surface area of growing phases was 1% in the presented models. The purpose of varying the  $A_n$  value was to study the effect of this initial surface area of secondary minerals on the model results. For the mineral formation, the value of  $\zeta$  was taken to be 1.

#### 3.2. Isotope modeling

The variations in δ<sup>26</sup>Mg were simulated as a part of the reaction path model in a similar manner as described previously (e.g., [Stefánsson and Barnes, 2016](#); [Stefánsson et al., 2016](#); [Stefánsson et al., 2017](#); [Gunnarsson-Robin et al., 2017](#)). In this context, the isotopic composition of the system (water-rock reaction in the reactor) can be defined as;

$$\delta^{26}Mg^{system} = \sum_s x_s \delta^{26}Mg_s = \sum_i x_i \delta^{26}Mg_i \quad (4)$$

where  $s$  denotes the various sources and their isotope values. As olivine is the only source of Mg in the system, the δ<sup>26</sup>Mg composition of the system becomes equal to that of olivine (δ<sup>26</sup>Mg<sup>system</sup> = δ<sup>26</sup>Mg<sub>olivine</sub>).  $i$  denotes the  $i$ -th aqueous species and mineral being formed, and  $x_i$  is the mole fraction defined by:

$$x_i = \frac{n_i}{\sum_i n_i} \quad (5)$$

where  $n$  is the number of moles of Mg in the  $i$ -th aqueous species and/or minerals. Isotopic fractionation due to chemical reactions including the formation of secondary minerals can be calculated as a function of reaction progress ( $\xi$ ), where

$$n_i = n_i^0 + v_i \Delta \xi \quad (6)$$

where  $n_i^0$  and  $v_i$  are the initial mole number and stoichiometry coefficient of the  $i$ -th aqueous species and minerals.

The isotope values of aqueous species and minerals is subsequently calculated from,

$$\delta^{26}\text{Mg}^{\text{system}} = x_k \delta^{26}\text{Mg}_k + \sum_i x_i (\alpha_{i-k} (1000 + \delta^{26}\text{Mg}_k) - 1000) \quad (7)$$

$$\delta^{26}\text{Mg}_i = \alpha_{i-k} (1000 + \delta^{26}\text{Mg}_k) - 1000 \quad (8)$$

where  $k$  is the key aqueous species or mineral, here taken to be  $\text{Mg}^{2+}$ .  $\alpha_{i-k}$  is the equilibrium isotope fractionation factor between the  $i$ -th and  $k$ -th phases defined by;

$$\alpha_{i-k} = \frac{1000 + \alpha^{26}\text{Mg}_i}{1000 + \alpha^{26}\text{Mg}_k} \quad (9)$$

The values for the fractionation factors between  $\text{Mg}^{2+}$  and various secondary minerals, and their associated sources, are listed in Table 2 and shown in Fig. 2. The min-

erals included Mg-carbonates (magnesite and Mg-Fe carbonate solid solutions), talc, brucite and chrysotile (which was taken to be equivalent to that of chlorite). In order to obtain the fractionation factors under the experimental conditions of 150 °C, the reported fractionation factors were fitted assuming a linear relationship between  $10^3 \ln \alpha$  and  $1/T^2$  with a zero intercept at infinite temperature ( $\alpha \rightarrow 1$  at  $1/T^2 \rightarrow 0$ ) (Fig. 2), similar to Huang et al. (2013).

## 4. RESULTS

### 4.1. Solution composition

Two types of experiments were conducted at 150 °C: (1) low  $\text{CO}_2$  concentrations of 5.17–6.36 mmol/kg (Experiments F, G and H), and (2) elevated  $\text{CO}_2$  concentrations of 13.7–20.9 mmol/kg (Experiments K and E). The changes

Table 2  
 $\delta^{26}\text{Mg}$  fractionation factors between minerals and  $\text{Mg}^{2+}$  in aqueous solutions.

Reaction	$10^3 \ln \alpha$ (150 °C)	fit (T in Kelvin)	Source
Talc- $\text{Mg}^{2+}$ (aq)	0.431	$10^3 \ln \alpha = 0.0771 (10^6/T^2)$	Beinlich et al. (2014), extrapolated
Chrysotile- $\text{Mg}^{2+}$ (aq)	-0.25	$10^3 \ln \alpha = -0.046 (10^6/T^2)$	Beinlich et al. (2014), extrapolated
Brucite- $\text{Mg}^{2+}$ (aq)	0.36	$10^3 \ln \alpha = 0.064 (10^6/T^2)$	Wimpenny et al. (2014), extrapolated
Magnesite- $\text{Mg}^{2+}$ (aq)	-1.19	$10^3 \ln \alpha = -0.207 (10^6/T^2)$	Pearce et al. (2012), Beinlich et al. (2014)

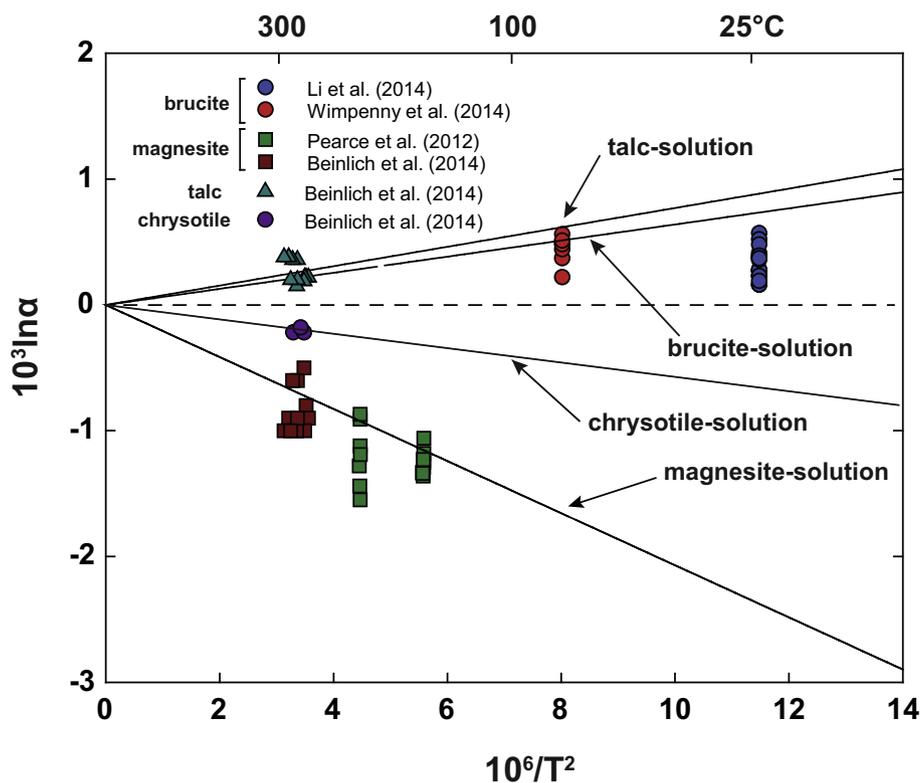


Fig. 2. Summary of previously reported  $\delta^{26}\text{Mg}$  fractionation factors between Mg-rich minerals and dissolved  $\text{Mg}^{2+}$ . The lines represent regressions through the data points assuming  $\alpha \rightarrow 1$  when  $1/T^2 \rightarrow 0$ . The data are based on results reported by Brucite from Wimpenny et al. (2014), Li et al. (2014), Pearce et al. (2012) and Beinlich et al. (2014) and the regression lines are consistent with the interpretations of Rustad et al. (2010) and Schauble (2011).

in solution chemistry as a function of reaction time are given in Table 3. Initially the pH of the solutions was  $\sim 6.5$  and increased to between  $\sim 6.7$  and  $\sim 7.5$  with reaction time. The pH increased with decreasing aqueous  $\text{CO}_2$  concentration. The dissolved concentrations of Si and Mg increased rapidly during the first hours, reaching values of Si  $\sim 0.4$ – $1.2$  and Mg  $\sim 0.7$ – $1.1$  mmol/kg after  $\sim 30$  minutes followed by a decrease with experimental duration after  $\sim 1$ – $10$  days. An increase in Si concentration observed in experiment E from day 2 was significant compared to runs with lower  $\text{CO}_2$  concentration. The high  $\text{CO}_2$  experiments resulted in greater mass of dissolved olivine, and a corresponding faster intake of Mg ions by secondary phases from solution, relative to the low  $\text{CO}_2$  experiments. Very low concentrations (generally less than  $\sim 1$   $\mu\text{mol/kg}$ ) were also initially observed for Fe.

Variations in the  $\delta^{26}\text{Mg}$  composition of the reacting fluid were determined together with the composition of

the reacting olivine in experiment E, which showed the greatest change in Mg concentration (Table 4). The  $\delta^{26}\text{Mg}$  ratio determined for the olivine sample was  $-0.22 \pm 0.07\text{‰}$ , and no variation between the initial and reacted material was observed. This is similar to the previously observed  $\delta^{26}\text{Mg}$  ratio of unaltered oceanic crust and mantle xenolites of  $-0.35$  to  $-0.18\text{‰}$  (e.g., Wiechert and Halliday, 2007; Teng et al., 2007, 2010, 2015; Liu et al., 2017). The  $\delta^{26}\text{Mg}$  ratios of the experimental solutions ranged from  $-0.27$  to  $+0.35\text{‰}$ , was low initially, increased during the first five days followed by a relatively steady value.

#### 4.2. Secondary mineralogy

The identified secondary minerals were magnesite, chrysotile/lizardite, amorphous silica and halite. Halite was considered to form upon quenching of the experimental systems. SEM images of the alteration products with

Table 3  
Experimental solution composition.

Exp. #	Time days	pH/22 °C	$\text{CO}_2$ mmol/kg	Si mmol/kg	Mg mmol/kg	$\text{Fe}_{\text{tot}}$ $\mu\text{mol/kg}$	Na mmol/kg	Cl mmol/kg
1e	0.02	6.48	20.9	1.27	1.12	0.64	31.1	27.9
2e	0.71	6.90	18.6	0.841	1.33	0.37	30.6	26.7
3e	2.60	6.73	17.2	1.15	1.24	2.8	31.0	28.5
4e	4.60	6.80	15.8	1.33	1.09	0.61	31.3	28.5
5e	6.79	6.87	13.7	1.63	0.783	0.69	31.0	29.0
6e	8.63	6.84	13.2	2.06	0.640	0.74	31.4	29.1
7e	10.56	6.93	11.3	1.33	0.519	1.3	31.2	29.0
8e	21.48	6.91	9.41	1.22	0.338	1.4	30.9	28.4
9e	25.31	7.07	8.15	0.982	0.298	1.7	31.3	28.7
1f	0.03	6.59	5.17	n.a.	0.822	0.8	10.3	11.0
2f	0.71	7.22	4.76	0.494	1.01	1.1	10.7	10.6
3f	2.69	7.41	5.28	0.297	0.879	0.44	10.0	10.8
4f	4.81	7.29	4.77	0.261	0.860	1.7	10.4	10.7
5f	6.69	7.32	4.96	0.228	0.821	1.0	10.4	10.9
6f	8.79	7.26	3.97	0.227	0.782	0.91	10.3	11.0
7f	10.75	7.31	4.45	0.172	0.669	0.53	10.3	10.9
8f	12.67	7.36	4.14	0.184	0.597	0.96	10.4	11.2
1g	0.04	6.96	6.36	0.493	0.688	0.75	10.5	10.5
2g	0.77	7.29	5.24	0.287	0.783	0.53	10.7	10.5
3g	1.90	7.37	5.24	0.244	0.720	0.31	10.4	10.5
4g	2.81	7.33	5.19	0.210	0.683	0.34	10.6	10.3
5g	3.94	7.44	4.71	0.236	0.610	0.54	10.6	10.5
6g	5.00	7.45	4.67	0.142	0.572	0.51	10.7	10.5
7g	5.79	7.43	4.44	0.221	0.520	0.88	10.6	10.4
8g	6.81	7.41	4.44	0.299	0.475	0.81	10.6	10.3
1h	0.04	6.63	5.72	0.773	0.718	0.17	10.7	10.8
2h	2.00	6.76	5.64	0.324	0.775	79	10.4	10.9
3h	5.06	6.87	5.92	0.910	0.748	33	10.3	10.9
4h	9.85	7.16	4.99	1.032	0.613	20	10.3	10.8
5h	14.94	6.91	5.36	0.179	0.493	16	10.6	10.7
6h	19.83	7.09	5.26	0.216	0.405	17	10.6	10.8
7h	23.83	7.07	5.03	0.134	0.374	12	10.4	12.2
8h	28.81	7.20	2.61	0.146	0.314	9.3	10.4	10.7
1k	0.17	6.82	13.7	0.425	0.977	3.5	28.1	26.0
2k	0.90	7.04	12.4	0.443	0.912	3.8	28.3	25.9
3k	2.75	7.01	11.9	0.513	0.679	6.2	28.3	26.2
4k	4.77	7.13	9.96	0.531	0.441	10	28.0	26.0
5k	6.81	7.35	8.64	0.549	0.394	14	28.2	26.1

Table 4

Isotopic composition of forsterite and experimental fluid in the run E. Long-term analytical reproducibility ( $2\sigma$ ) is 0.07‰.

Sample /Exp.	$\delta^{25}\text{Mg}\text{‰}$		$\delta^{26}\text{Mg}\text{‰}$	
	Mean	2 s.e.	Mean	2 s.e.
Fo <sub>93</sub> – Unreacted	−0.121	0.006	−0.224	0.009
Fo <sub>93</sub> – Altered	−0.108	0.007	−0.221	0.010
e1	−0.070	0.010	−0.136	0.018
e2	−0.154	0.009	−0.266	0.018
e3	0.058	0.008	0.105	0.015
e4	0.150	0.008	0.317	0.016
e5	0.168	0.009	0.354	0.016
e6	0.155	0.007	0.317	0.014
e7	0.149	0.011	0.292	0.019
e8	0.112	0.006	0.255	0.011
e9	0.158	0.007	0.319	0.012

altered olivine surfaces are shown in Fig. 3. The unaltered olivine surfaces showed pristine and smooth surfaces with sharp mineral edges. Upon dissolution, conical or funnel-shaped etch pits were observed to form along the mineral edges and within the previously smoothed surfaces. The composition of the chrysotile/lizardite was determined to be  $\text{Mg}_{2.87}\text{Fe}_{0.19}\text{Si}_{1.96}\text{O}_5(\text{OH})_4$  and the composition of magnesite was  $\text{Mg}_{(0.92-0.95)}\text{Fe}_{(0.08-0.05)}\text{CO}_3$ . No precipitating iron oxides were observed, Fe released from the dissolving olivine was mostly incorporated into the magnesite and/or chrysotile/lizardite solid solutions.

The changes in mineralogy as a function of reaction time at constant initial  $\text{CO}_2$  ( $\sim 6$  mmol/kg; Experiments G and H) are shown in Fig. 3 (d and e). Small single euhedral crystals of magnesite formed up to 1  $\mu\text{m}$ . Randomly distributed needle shaped formations, up to 0.5  $\mu\text{m}$  in length, are chrysotile/lizardite. No major dissolution features on the olivine surfaces were observed after 7 days (Fig. 3d). After two weeks, no large changes were observed except magnesite crystals grew and became larger, up to 3  $\mu\text{m}$  in size. After 4 weeks of interaction (Fig. 3e), the formation of magnesite was characteristic with euhedral crystals up to 5  $\mu\text{m}$  in diameter. A thin layer of coarse alteration coating developed partly over the olivine surfaces, typically as scales sticking out from the surface and no thicker than 0.5  $\mu\text{m}$ ; this is an early stage of chrysotile/lizardite nucleation and serpentinization. Dissolution etch pits were also clearly observed on the olivine grain edges after four weeks of interaction.

The effect of changing initial  $\text{CO}_2$  concentration (Experiments H and E) on the olivine alteration mineralogy is shown in Fig. 3(e) and (f). At low  $\text{CO}_2$  ( $\sim 6$  mmol/kg; Exp. G, F, H; Fig. 3d, e), magnesite crystals were observed to form along the olivine edges and within conchoidal fractures whereas small chrysotile/lizardite needles formed randomly over the whole olivine surface. However, for experiments with initially elevated  $\text{CO}_2$  ( $\sim 21$  mmol/kg, Exp. E; Fig. 3f), the magnesite crystals grew up to 10  $\mu\text{m}$  in size with some of the olivine grains completely coated with conglomerates of euhedral magnesite crystals after 25 days. Honeycomb structures or mesh texture of chrysotile/lizardite coated some of the olivine surface (Fig. 3f) and formed conglomerates around the magnesite crystals.

## 5. DISCUSSION

### 5.1. Olivine alteration

The experimental results are compared with the calculated solution composition and mineralogy in Figs. 4 and 5. The experimental solution composition was reasonably well reproduced by the geochemical models (Fig. 4). A declining trend for  $\text{CO}_2$  concentration was observed in all experiments and models with time. Similarly pH values increased in both the experiments and models, reflecting the decreasing acid supply in the system. Some discrepancies were observed for Si (Fig. 4c), and are considered to be related to an initial non-stoichiometric dissolution of Si from the olivine and precipitation of silica coating (Pokrovsky and Schott, 2000; Daval et al., 2011; Saldi et al., 2013), supported by close to saturation values in the fluid samples. This could indicate the rapid formation of a  $\text{SiO}_2$ -rich coating (Saldi et al., 2015) and its subsequent breakdown after one day of reaction, which results in an increase of Si concentration. The experimental preferential release of Mg from olivine is probably masked by the incipient precipitation of magnesite from solution. For Mg, the modeled concentrations were lower than the experimental data until  $\sim 3$  days of interaction. Afterwards a close match was observed between experiments and models. It is likely that the difference between model and experimental data reflects an initial overestimation of the extent of secondary mineral precipitation or not accounted  $\text{SiO}_2$ -coating, as the changes in  $\text{CO}_2$  concentration showed good agreement between modeled and experimental system (Fig. 4).

The secondary mineralogy predicted by the geochemical models shows a clear trend with reaction time and solution pH (Fig. 5); at  $\text{pH} < 6.5$ , chrysotile and Mg-Fe carbonate solid solutions dominate the alteration mineralogy, but with increasing reaction time and pH brucite also becomes important. Brucite was not observed as a part of the alteration products in our experiments as the pH of the solutions was not high enough to initiate brucite formation (Pokrovsky and Schott, 2004; Li et al., 2014) at the end of the experiments. The amount of reacted initial  $\text{CO}_2$  (Fig. 5a, b) is reflected by the amount of dissolved olivine mass and formed secondary minerals. The high  $\text{CO}_2$  run dissolved  $\sim 6$  times more olivine than the low  $\text{CO}_2$  run (Fig. 5a, b), resulting in an order of magnitude difference in the amount of magnesite and talc that were precipitated. However, the relative proportion of the two minerals being formed was similar in both scenarios.

The results of the experiments and geochemical modeling demonstrate that the main factors controlling olivine-fluid interaction in  $\text{CO}_2$ -rich solutions are the extent of the reaction ( $\xi$ ) (or reaction time) and pH. Solution pH is in turn controlled by acid supply and the extent of reaction. For olivine alteration, where  $\text{CO}_2$  is the major carbonic acid, two alteration stages were distinguished based on the changes in pH (Figs. 4 and 5): (I) stage I was characterized by mildly acid to neutral pH values, buffered by dissolved  $\text{CO}_2$  and  $\text{H}^+$  consumption upon olivine dissolution, and by the formation of Mg-Fe carbonate solid solutions and chrysotile; stage II (only reached through the

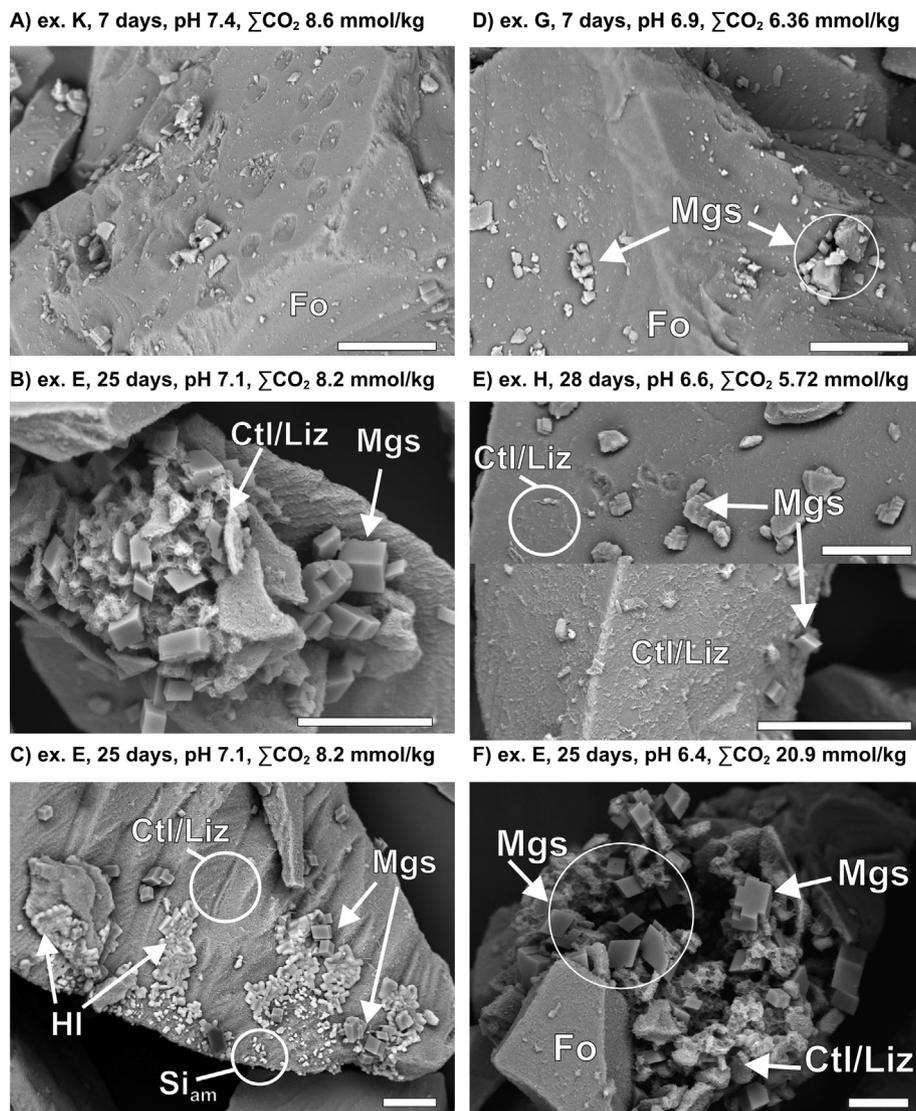


Fig. 3. SEM photomicrographs with typical surface of (A) reacted olivine surface showing the conical or funnel-shaped etch pits, (B) euhedral crystals of magnesite and conglomerates of chrysotile microtubes covering  $\text{Fo}_{93}$  grains, and (C) secondary magnesite and chrysotile together with spherical amorphous silica and halite flakes. Experimental conditions presented are the end of the runs (A, B, C). Magnesite formation as a function of reaction time for solutions with initially similar  $\text{CO}_2$  concentrations (D and E), and as a function of initial low and elevated  $\text{CO}_2$  concentrations (E and F). At low initial  $\text{CO}_2$  concentrations of  $\sim 6$  mmol/kg euhedral crystals of magnesite were observed to grow with reaction time from 1 to 5  $\mu\text{m}$  in about a 3 weeks (D and E). However, the quantity and size of magnesite crystals was predominantly found to depend on initial  $\text{CO}_2$  concentration (E and F); with elevated  $\text{CO}_2$  concentration the magnesite grew to  $\sim 10$   $\mu\text{m}$ . Starting experimental pH and  $\text{CO}_2$  conditions are presented (D, E, F). Scale bar is 15  $\mu\text{m}$  on all presented SEM images, mineral abbreviations are: Ctl-chrysotile, Fo-forsterite, HI-halite, Mgs-magnesite, Si am-amorphous silica.

geochemical modeling for the considered time-frames) was characterized by progressive olivine alteration, decrease of  $\text{CO}_2$  concentration due to carbonate mineral formation, and an increase in pH to  $>8$ . Under these alkaline conditions chrysotile, brucite and Mg and Fe containing carbonates were formed. Similar pH effects on the alteration product have been observed during fluid-rock reactions with basaltic glasses (Gysi and Stefánsson, 2012a,b).

The amount of secondary mineral formation was found to largely depend on the reactive surface area of the olivine

(Fig. 5c). The best fit corresponded to 30% ( $\zeta = 0.3$ ) and 80% ( $\zeta = 0.8$ ) (Eqn. (1)) coverage of the total olivine geometric surface under the low- and high  $\text{CO}_2$  concentrations, respectively. This is in agreement with other studies (e.g. Brantley and Mellott, 2000; Lüttge and Arvidson, 2008), and implies only fraction of mineral surface is commonly reactive (although the potential influence of stirring rate and water-rock ratios within the reactors cannot be discounted). In contrast, the nucleation surface area ( $A_n$ ) of secondary minerals was found to have a limited effect on

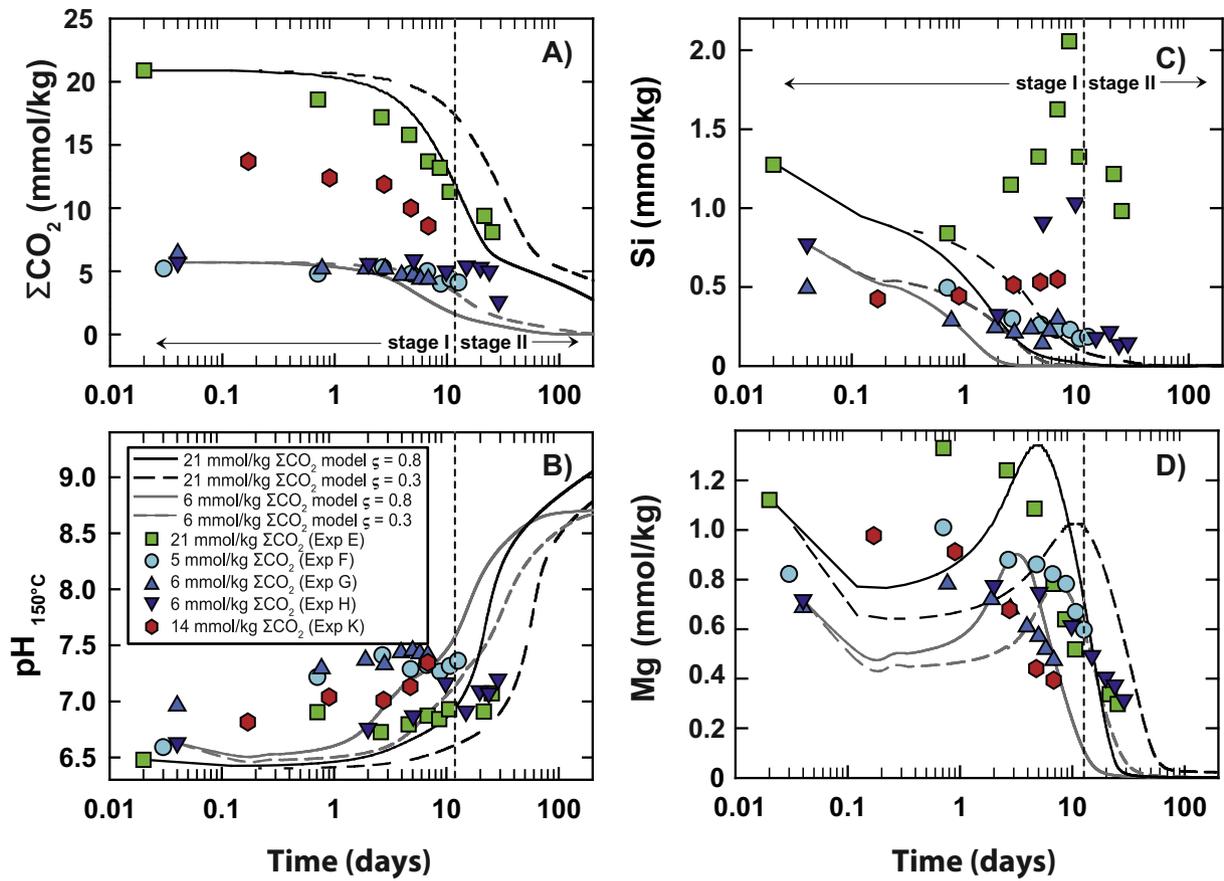


Fig. 4. Measured changes in pH, CO<sub>2</sub>, Mg and Si concentrations in the experimental solutions as a function of time and aqueous CO<sub>2</sub> concentration at 150 °C. The symbols denote the different CO<sub>2</sub> concentrations used in each experimental run, and the curved lines the results of the geochemical model. Two different models are shown, at low and elevated CO<sub>2</sub> concentrations of 6 and 21 mmol/kg, respectively, with low and high fraction of olivine reactive surface areas 0.3 and 0.8 ( $\xi$ ). The vertical dashed line separates the two stages of olivine alteration inferred by these experiments (see text for details).

the mass of secondary minerals formed. This observation is related to the fact that the secondary minerals reached close-to-equilibrium conditions with the fluid relatively quickly, thus their formation rates were primarily driven by the affinity term ( $1-SI^m$ ), rather than the surface area of the nuclei and crystals (Pokrovsky and Schott, 2004).

The rate limiting reaction controlling elemental transfer is generally thought to be the dissolution rate of the primary mineral (e.g. Park and Fan, 2004; Hänchen et al., 2006). However, as pointed out by Saldi et al. (2012), this may not always be the case, as the precipitation rate of magnesite is 3–5 orders of magnitude lower than the corresponding dissolution rate for olivine. Here, we observed that olivine alteration rate primarily depends on pH. For example; the dissolution rate of olivine at a pH of  $\sim 6.5$  was slightly greater than the formation rate of carbonates, demonstrating that the rate limiting factor of carbonation in the system was not the dissolution rate of olivine, but the precipitation rate of the carbonates. Similarly, with increasing reaction progression within the models the pH increased to  $>8$  and under these conditions the dissolution rate of olivine became slower than the formation rates of all secondary minerals, implying that the rate limiting factors

during water-rock interaction of olivine was its dissolution rate.

## 5.2. Magnesium isotope systematics during olivine carbonation and serpentinization

The only source of Mg in the experimental system was the olivine powder, which had a starting  $\delta^{26}\text{Mg}$  ratio of  $-0.22 \pm 0.07\text{‰}$  (Table 4). The initial alteration of the olivine in CO<sub>2</sub>-rich water (stage I) was characterized by Mg dissolution from the olivine, buffering of the pH at  $\sim 6.5$  and formation of Mg-Fe carbonates and chrysotile. Assuming equilibrium fractionation between the solution and the Mg-Fe carbonates ( $\alpha = 0.99975$ ) and chrysotile ( $\alpha = 0.9988$ ) at 150 °C, the modeled olivine alteration resulted in the solution becoming enriched in <sup>26</sup>Mg and the alteration product enriched in <sup>24</sup>Mg (Fig. 6a). This is indeed what was observed experimentally, as upon initial dissolution the  $\delta^{26}\text{Mg}$  ratio of the solution was similar to that of olivine (between  $-0.27$  and  $-0.14\text{‰}$ ), whereas the  $\delta^{26}\text{Mg}$  composition of the solution increased to between  $+0.26$  and  $+0.35\text{‰}$  following the formation of Mg-Fe carbonates and chrysotile (Fig. 6b).

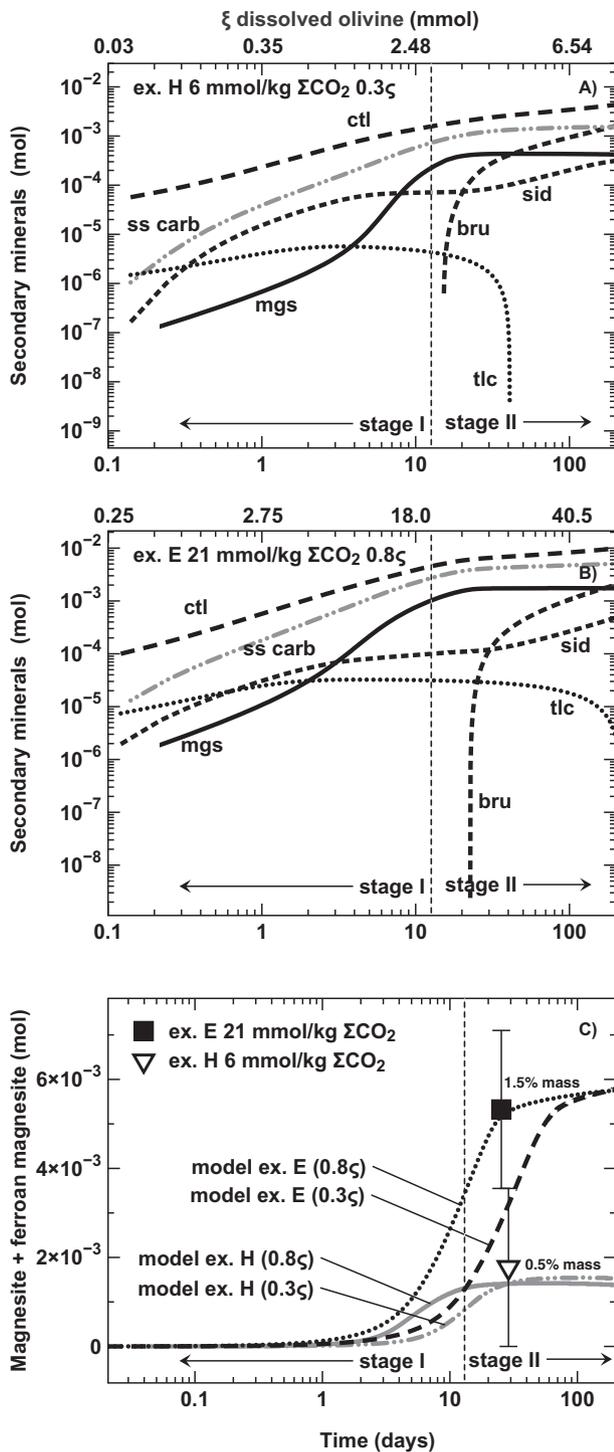


Fig. 5. Mass of secondary minerals precipitated according to the geochemical modeling for low (A) and high (B) initial  $\text{CO}_2$  concentration. Experimental magnesite mass precipitated was in agreement with results from the geochemical model (C). Quantification of magnesite is based on XRD analysis, SEM observations versus the geochemical model.  $\zeta$  is the fraction of total reactive surface area applied in the model. CtI: chrysotile; ss carb: Mg-Fe carbonate solid solutions; mgs: magnesite; sid: siderite; tlC: talc; bru: brucite.

In the subsequent alteration stage of olivine (stage II) the modeled  $\text{CO}_2$  concentration decreased due to carbonate mineralization and the solution pH increased to  $>8$ , with chrysotile and eventually brucite becoming the dominant alteration product. The equilibrium fractionation factors applied between the solution and brucite ( $\alpha = 1.0004$ ; Wimpenny et al., 2014; Li et al., 2014) and talc ( $\alpha = 1.0004$ ; Beinlich et al., 2014) resulted in the solution becoming enriched in  $^{24}\text{Mg}$  and the alteration product enriched in  $^{26}\text{Mg}$ , which is the reverse  $\delta^{26}\text{Mg}$  systematics compared to the initial phase of olivine alteration.

These results suggest that changes in the  $\delta^{26}\text{Mg}$  composition of the solution may be used to trace the extent of olivine alteration via carbonation and serpentinization reactions: Fig. 6 demonstrates that the  $\delta^{26}\text{Mg}$  composition can change rapidly (i.e. in a few days) under far from equilibrium to close to equilibrium conditions for both the carbonate minerals and the solution before stage II is reached. This is most likely caused by rapid element transfer during stage I, where the olivine dissolution and carbonation reactions predominantly occur under far-from equilibrium conditions. This indicates that the dominant reaction pathway can be identified with  $\delta^{26}\text{Mg}$ , thus the system could be used as a mechanism to verify ongoing carbonate formation within an ultramafic  $\text{CO}_2$  sequestration system, as the extensive precipitation of Mg-carbonate minerals (presented in studied system as stage I) with light  $\delta^{26}\text{Mg}$  composition will be reflected by the solution enriched in  $\delta^{26}\text{Mg}$ . Of course, the accurate determination of the fractionation factors associated with the secondary phases being formed is crucial for application of isotopic modeling approaches such as that applied here. There is still a significant lack of understanding about how Mg isotopes are fractionated between different phases, and what the fractionation factors are for specific minerals, thus an in-depth review and assessment of the reported fractionation factors is required before using such techniques to quantify the extent of carbonation in natural settings.

### 5.3. Comparison with natural analogues

The results of our experiments and isotopic modeling are compared with naturally altered basalts, groundwaters and geothermal waters in Fig. 7. The higher  $\delta^{26}\text{Mg}$  values of the solutions measured in this study (relative to the starting olivine composition) are similar to the elevated values of  $+0.23\text{‰}$  to  $+0.85\text{‰}$  observed in the groundwaters and geothermal waters of the basaltic terrain in Iceland (Pogge von Strandmann et al., 2008). This positive shift in the  $\delta^{26}\text{Mg}$  composition of the fluid is likely to be due to the formation of clay minerals (similar to serpentine minerals) and carbonate minerals that are enriched in  $^{24}\text{Mg}$  relative to the olivine and bulk Mg of the basalts. Similarly, the  $\delta^{26}\text{Mg}$  compositions of altered oceanic basalts in the western Pacific reveal large isotopic fractionation during oceanic crust alteration (Huang, 2013), with the most negative values being associated with the carbonation of the basalts, and less negative values associated with serpentinization. These observations are in good agreement with

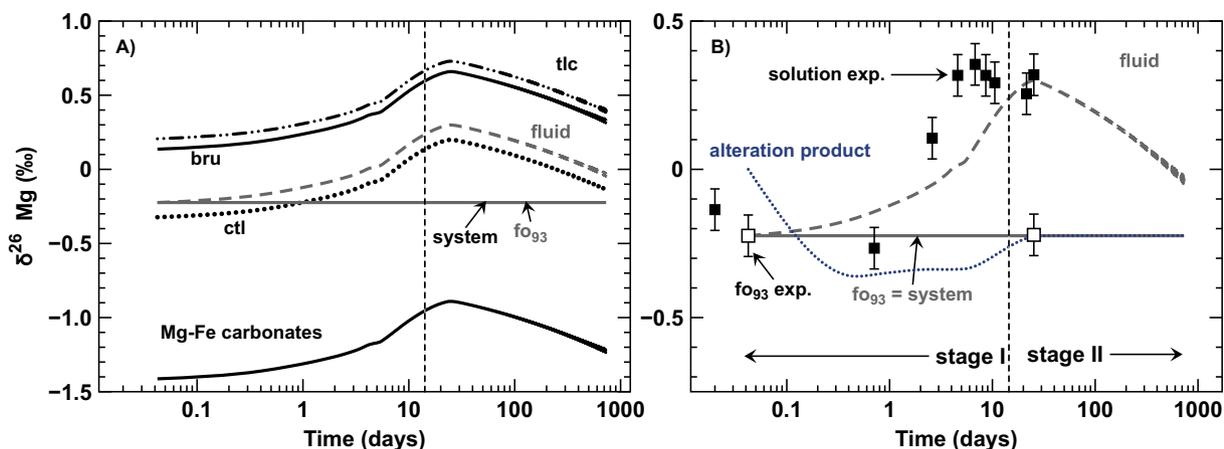


Fig. 6. (A) The result of the  $\delta^{26}\text{Mg}$  isotopic systematics of the secondary minerals obtained from the isotope modeling. (B) Comparison of the measured and calculated  $\delta^{26}\text{Mg}$  isotopic systematics of the water. Also shown are the  $\delta^{26}\text{Mg}$  for the bulk alteration product calculated using the isotope modeling results.

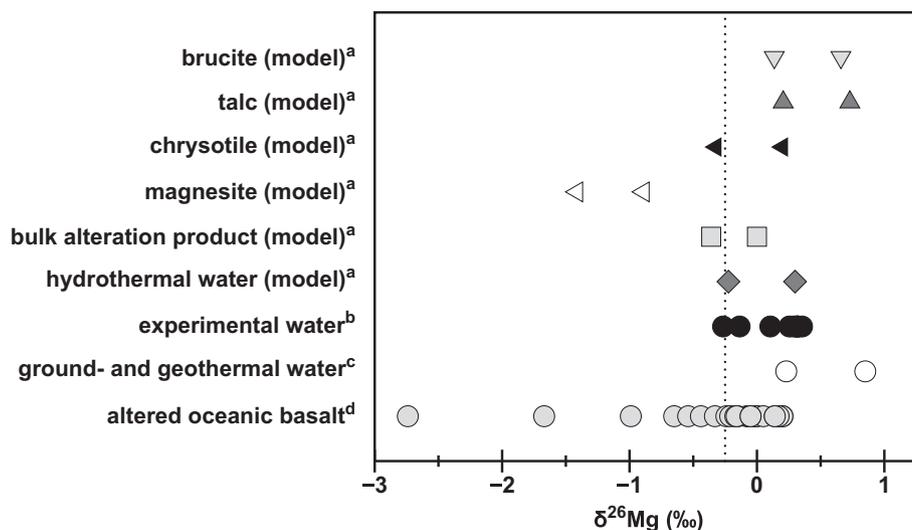


Fig. 7. Comparison of  $\delta^{26}\text{Mg}$  ratios of natural fresh and altered mafic and ultramafic rocks, natural ground- and hydrothermal water and the results obtained here experimentally and using isotope modeling (min-max values): <sup>a</sup>This study, <sup>b</sup>This study, <sup>c</sup>Pogge von Strandmann et al. (2008), <sup>d</sup>Huang (2013). The vertical line represents the average Mg isotopic composition of the mantle (i.e., bulk Earth; Teng, 2017).

our isotopic modeling, where the carbonates (and to a lesser extent chrysotile) are found to be enriched in the  $^{24}\text{Mg}$  isotope relative to olivine and the solution, whereas extensive serpentinization of oceanic crust and formation of brucite and talc may result in a reversed  $\delta^{26}\text{Mg}$  trend, with these minerals eventually becoming enriched in  $^{24}\text{Mg}$  and the resulting solutions enriched in  $^{26}\text{Mg}$ .

The hydrothermal carbonation of ultramafic rocks (and by analogy mafic rocks) is thought to be accompanied by significant inter-mineral fractionation resulting in the formation of  $^{24}\text{Mg}$  enriched magnesite and  $^{26}\text{Mg}$  enriched talc (Beinlich et al., 2014). The field results of Beinlich et al. (2014) suggest that Mg isotopes may not be fractionated during serpentinization reactions, as their olivine exhibits an invariant Mg isotope ratio. This study is in agreement that formation of Mg-bearing carbonates during ocean

water circulation through mid-ocean ridge flanks under hydrothermal conditions forms a sink for isotopically light Mg. Our models show that the late stage serpentinization with limited Mg supply from slowly dissolving olivine and slowly forming chrysotile-brucite caused hydrothermal water to be progressively enriched in  $^{24}\text{Mg}$ .

Together these analogues support our experiments and models and confirm the sensitivity of  $\delta^{26}\text{Mg}$  to the formation and dissolution of different minerals under different settings. Quantifying the extent of reaction progress in natural systems can be complicated, however, as they contain multiple sources and sinks that can be isotopically heterogeneous (Teng, 2017), and the isotopic fractionation effects are not always preserved during the course of the reaction, and may be even absent if the precipitation of secondary phases occurs at close to equilibrium conditions (cf. Tang

et al., 2008; Pearce et al., 2012; Mavromatis et al., 2017). Nevertheless, this study demonstrates that it can be possible to track these reactions in relatively simply Mg-rich systems by applying kinetic Mg isotope fractionation models for the rock-forming minerals that have been calibrated by laboratory experiments, theoretical calculation and the analysis of natural samples, and that under such settings the  $\delta^{26}\text{Mg}$  system could be used as a mechanism to test whether carbonate formation is ongoing within an ultramafic  $\text{CO}_2$  sequestration system.

## 6. CONCLUSIONS

Olivine carbonation and serpentinization in  $\text{CO}_2$ -rich fluids at 150 °C was studied experimentally and by geochemical modeling. The alteration of olivine was found to be dependent on reaction time, with two main stages being identified: Stage I was characterized by a low pH (buffered at  $\sim 6.5$ ), during which olivine dissolved to form Mg-Fe carbonate solid solutions and minor chrysotile. Mg-rich carbonates and chrysotile forming during this interval preferentially incorporated  $^{24}\text{Mg}$ , such that the alteration product had lower  $\delta^{26}\text{Mg}$  values and the solution higher  $\delta^{26}\text{Mg}$  relative to the olivine that provided the only source of Mg in the experiments. Stage II continued the extensive alteration of olivine, with the carbonation reactions ultimately driving a decrease of  $\text{CO}_2$  concentration and associated increase in pH (to  $>8$ ), under which chrysotile and brucite became the dominant alteration minerals. As a result, the alteration product became progressively enriched in  $^{26}\text{Mg}$  relative to the solution, such that the fluid may, given sufficient reaction time, display lower  $\delta^{26}\text{Mg}$  ratios than for the olivine source.

It follows that changes in the  $\delta^{26}\text{Mg}$  composition of the fluid phase and alteration products formed during olivine

alteration directly reflect the type and quantity of secondary Mg minerals formed, and thus in turn depend on pH and extent of reaction. Comparison of the experimental and isotopic modeling results with groundwaters and geothermal waters of basaltic terrains confirms that  $\delta^{26}\text{Mg}$  systematics of the natural waters are controlled by mafic rock dissolution and the incorporation of  $^{24}\text{Mg}$  into carbonates and Mg-Si minerals such as chrysotile and clays. The results also demonstrate that the extent of isotopic fractionation driven by geochemical processes such as water-rock interaction may exceed the differences observed between the various sources, highlighting the effects and importance of such reactions on the isotope characteristics of elements like magnesium. Although further studies are required to characterize the extent of Mg isotope fractionation occurring during the alteration of other Mg-rich rock-forming minerals in both simple and complex systems our results indicate that variations in fluid  $\delta^{26}\text{Mg}$  compositions could be used as a mechanism to help monitor  $\text{CO}_2$  sequestration in ultramafic systems.

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## APPENDIX A

See [Table A1](#).

Table A1  
Thermodynamic and kinetic database used for the kinetic reaction path simulations.

Phase	Symbol	Reaction	$\log K_{150^\circ\text{C}}$	$\log k_{i150^\circ\text{C}}$ (mol/m <sup>2</sup> /sec)	$r_{i\pm} = A_{\text{geo}} k$ (1-SI <sup>m</sup> )
<i>Aqueous Species and surface reactions</i>					
HCO <sub>3</sub> <sup>-</sup>		CO <sub>2</sub> + H <sub>2</sub> O = H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	-6.74 <sup>a</sup>		
CO <sub>3</sub> <sup>2-</sup>		HCO <sub>3</sub> <sup>-</sup> = H <sup>+</sup> + CO <sub>3</sub> <sup>2-</sup>	-10.30 <sup>a</sup>		
NaHCO <sub>3</sub> (aq)		Na <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup> = NaHCO <sub>3</sub> (aq)	0.42 <sup>a</sup>		
NaCO <sub>3</sub> <sup>-</sup>		Na <sup>+</sup> + CO <sub>3</sub> <sup>2-</sup> = NaCO <sub>3</sub> <sup>-</sup>	1.94 <sup>a</sup>		
MgHCO <sub>3</sub> <sup>+</sup>		Mg <sup>2+</sup> + HCO <sub>3</sub> <sup>-</sup> = MgHCO <sub>3</sub> <sup>+</sup>	1.76 <sup>b</sup>		
MgCO <sub>3</sub> (aq)		Mg <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup> = MgCO <sub>3</sub> (aq)	3.70 <sup>b</sup>		
MgOH <sup>+</sup>		Mg <sup>2+</sup> + H <sub>2</sub> O = MgOH <sup>+</sup> + H <sup>+</sup>	-8.06 <sup>c</sup>		
FeOH <sup>+</sup>		Fe <sup>2+</sup> + H <sub>2</sub> O = FeOH <sup>+</sup> + H <sup>+</sup>	-6.64 <sup>d</sup>		
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>		H <sub>4</sub> SiO <sub>4</sub> = H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup> + H <sup>+</sup>	-8.5 <sup>d</sup>		
<i>Mineral</i>					
Olivine	fo <sub>93</sub>	Mg <sub>1.86</sub> Fe <sub>0.14</sub> SiO <sub>4</sub> (s) + 4H <sup>+</sup> = 1.86Mg <sup>2+</sup> + 0.14Fe <sup>2+</sup> + H <sub>4</sub> SiO <sub>4</sub> (aq)	16.89 <sup>e</sup>	-4.12-0.256pH <sup>f</sup>	$A_{\text{geo}} k$ (1-SI)
Magnesite	mgs	MgCO <sub>3</sub> (s) + H <sup>+</sup> = Mg <sup>2+</sup> + HCO <sub>3</sub> <sup>-</sup>	-0.33 <sup>g</sup>	-10 <sup>h</sup>	$k$ (1-SI <sup>2</sup> )
Siderite	sid	FeCO <sub>3</sub> (s) + H <sup>+</sup> = Fe <sup>2+</sup> + HCO <sub>3</sub> <sup>-</sup>	-2.53 <sup>g</sup>	-10 <sup>h</sup>	$k$ (1-SI <sup>2</sup> )
Mg <sub>0.25</sub> Fe <sub>0.75</sub> CO <sub>3</sub>	carb-ss	Mg <sub>0.25</sub> Fe <sub>0.75</sub> CO <sub>3</sub> (s) + H <sup>+</sup> = 0.75Fe <sup>2+</sup> + 0.25Mg <sup>2+</sup> + HCO <sub>3</sub> <sup>-</sup>	-2.22 <sup>g</sup>	-10 <sup>h</sup>	$k$ (1-SI <sup>2</sup> )
Mg <sub>0.5</sub> Fe <sub>0.5</sub> CO <sub>3</sub>	carb-ss	Mg <sub>0.5</sub> Fe <sub>0.5</sub> CO <sub>3</sub> (s) + H <sup>+</sup> = 0.5Fe <sup>2+</sup> + 0.5Mg <sup>2+</sup> + HCO <sub>3</sub> <sup>-</sup>	-1.73 <sup>g</sup>	-10 <sup>h</sup>	$k$ (1-SI <sup>2</sup> )
Mg <sub>0.75</sub> Fe <sub>0.25</sub> CO <sub>3</sub>	carb-ss	Mg <sub>0.75</sub> Fe <sub>0.25</sub> CO <sub>3</sub> (s) + H <sup>+</sup> = 0.25Fe <sup>2+</sup> + 0.75Mg <sup>2+</sup> + HCO <sub>3</sub> <sup>-</sup>	-1.12 <sup>g</sup>	-10 <sup>h</sup>	$k$ (1-SI <sup>2</sup> )
Chrysotile	ctl		20.11 <sup>i</sup>	-8.20( $k_n$ ), -9.78( $k_b$ ) <sup>j</sup>	$(k_n + k_b a_{\text{H}^+}^{-0.23})$ (1-SI)
Talc	tlc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (s) + 4H <sub>2</sub> O + 6H <sup>+</sup> = 3Mg <sup>2+</sup> + 4H <sub>4</sub> SiO <sub>4</sub> (aq)	13.42 <sup>i</sup>	-9.83 <sup>j</sup>	$k$ (1-SI)
Brucite	bru	Mg(OH) <sub>2</sub> (s) = Mg <sup>2+</sup> + 2OH <sup>-</sup>	-12.35 <sup>k</sup>	-1.68( $k_a$ ), -6.07( $k_n$ ) <sup>j</sup>	$(k_a a_{\text{H}^+}^{0.5} + k_n)$ (1-SI)
Amorphous silica	am-Si	SiO <sub>2</sub> (s) + 2H <sub>2</sub> O = H <sub>4</sub> SiO <sub>4</sub> (aq)	-1.98 <sup>g</sup>	-9.43 <sup>l</sup>	$k$ (1-SI)

<sup>a</sup> Stefánsson et al. (2013).

<sup>b</sup> Stefánsson et al. (2014).

<sup>c</sup> Palmer and Wesolowski (1997).

<sup>d</sup> wateq4f.dat.

<sup>e</sup> Stefánsson (2001).

<sup>f</sup> Rimstidt et al. (2012).

<sup>g</sup> Gysi and Stefánsson (2011).

<sup>h</sup> Saldi et al. (2012).

<sup>i</sup> Gunnarsson and Arnórsson (2005).

<sup>j</sup> Palandri and Kharaka (2004).

<sup>k</sup> Holland and Powell (2011).

<sup>l</sup> Carroll et al. (1998).

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