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Simultaneous precipitation of magnesite and lizardite from hydrothermal alteration of olivine under high-carbonate alkalinity

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A B S T R A C T

The present study reports original experiments in order to investigate the simultaneous serpentinization and carbonation of olivine with relevance in Earth systems (e.g. functioning of hydrothermal fields) or in engineered systems (e.g. ex-situ and in-situ mineral sequestration of CO_2). For this case, specific experimental conditions were examined (200 °C, saturated vapor pressure $\approx$ 16 bar, solution/solid weight ratio = 15, olivine grain size < 30 μm and high-carbonate alkalinity $\approx$ 1 M $NaHCO_3$). Under these conditions, competitive precipitation of magnesite and serpentine (preferentially lizardite type) was clearly determined by using conventional analytic tools (XRD, FESEM, FTIR and TGA); excluding the fate of the iron initially contained in olivine, the alteration reaction for olivine under high-carbonate alkalinity can be expressed as follows:

$$2Mg_2SiO_4 + 2H_2O + HCO_3^- \rightarrow MgCO_3 + Mg_3Si_2O_5(OH)_4 + OH^-.$$

This reaction mechanism implied a dissolution process, releasing Mg and Si ions into solution until supersaturation of solution with respect to magnesite and/or serpentine. The released iron contained in the olivine has not implied any precipitation of iron oxides or (oxy)hydroxides; in fact, the released iron was partially oxidized (about 50%) via a simple reduction of water ($2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + H_2 + 2OH^-$). In this way, the released iron was incorporated in serpentine (Fe(II) and Fe(III)) and in magnesite (Fe(II)). The latter was clearly determined by FESEM/EDS chemical analysis on the single magnesite crystals. The nucleation and epitaxial growth processes at the olivine–fluid interfaces cannot be excluded in our investigated system.

The experimental kinetic data fitted by using a kinetic pseudo-second-order model have revealed a retarding process of serpentine formation with respect to magnesite (about three times slower); in fact, the magnesite seems to reach an apparent stabilization after about 20 days of reaction while the serpentine follows a progressive slower evolution. We assumed that the magnesite has reached a fast apparent equilibrium with solution because the available carbonate species are not renewed from fluid phase as typically constrained in aqueous carbonation experiments where a given CO_2 pressure is imposed in the system.

On the other hand, the reactivity of serpentinized olivine (chrysotile + brucite + small amount of residual olivine) and high-purity chrysotile at the same above investigated conditions; and the olivine serpentinization in initial acid pH $\approx$ 0.66 are also reported as complementary information in this study.

These novel experimental results concerning simultaneous serpentinization and aqueous carbonation of olivine expand the thermodynamic conditions where serpentine and magnesite can simultaneously precipitate; this could contribute to a better understanding of fluid–rock interactions in natural active hydrothermal fields on Earth.

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1. Introduction

The physicochemical reactions at the solid–fluid interfaces play a crucial role in the global cycle of major and trace elements in the Earth and other telluric planets. In this way, chemical weathering, metamorphic reactions, diagenetic reactions, hydrothermalism, volcanic activity, and crystal–melt reactions are important non-limited physicochemical processes that shape the Earth's surface and sub-surface. However, many physicochemical and textural aspects of these so-called rock–fluid interactions are still poorly understood. For example, when mantle peridotite is tectonically exposed with (sub-)surface fluids (e.g. seafloor water and meteoric water), the olivine and pyroxene anhydrous minerals contained in peridotite are far-from-equilibrium with respect to fluid composition. In this way, numerous physicochemical reactions at peridotite–fluid interfaces can take place such as hydration (–OH

incorporation or serpentinization) and carbonation processes if the required temperature and fluid compositions are enough to activate these reactions; both most important processes directly related to natural H_2 and abiotic methane production via redox reactions and the formation of other non-limited secondary minerals as it has been observed in various natural hydrothermal sites (e.g. Logatchev, Rainbow and The Lost City) (e.g. Charlou et al., 2002; Allen and Seyfried, 2004; Ludwig et al., 2006; Seyfried et al., 2007; Klein et al., 2009; McCollom and Bach, 2009; Rudge et al., 2010; Seyfried et al., 2011). Such reducing systems may represent analogs to early Earth environments and may provide insights into requirements for the emergence of life, probably initiated at the sea floor (e.g. MacLeod et al., 1994; Charlou et al., 2002; Früh-Green et al., 2003; Kelley et al., 2005). The field monitoring and ex-situ characterization have revealed complex fluid chemistry and generally low pH (from 2.8 to 4.3) and high temperature (from 275 to 365 °C) in the expelled fluids from various studied ultramafic-hosted hydrothermal systems at the Mid-Atlantic Ridge (Charlou et al., 2002). Conversely, the expelled fluids at the Lost City field and other sites for example in continental serpentinization systems (e.g. Samail Ophiolite in Oman) are highly alkaline (pH > 9) and lower temperatures have been monitored/determined (from 55 to 90 °C) (Kelley et al., 2001; Früh-Green et al., 2003; Ludwig et al., 2006; Kelemen et al., 2011). These surprising measurements and the recent discovery of spectacular carbonate towers at the Lost City hydrothermal field have stimulated interest in the role of serpentinization and carbonation processes on the production of hydrogen- and methane-rich fluids and on the biological communities that may be supported in these environments (Früh-Green et al., 2003; Kelley et al., 2005; Schrenk et al., 2013). Moreover, at the present time, the ex-situ and in-situ carbonation of mafic and ultramafic rocks (e.g. basalts and peridotite), extensively available in the oceanic crust and ophiolites, have been proposed as a promising solution to mitigate the global warming of Earth's atmosphere related to excessive anthropogenic and natural CO_2 emissions; because Mg-, Ca- or Fe-carbonates resulting from mineral carbonation of CO_2 can remain stable at the geological time scales as frequently observed in the Earth surface and/or sub-surface (e.g. Seifritz, 1990; Lackner et al., 1995; Bachu, 2000; Kaszuba et al., 2003; Xu et al., 2004; Kaszuba et al., 2005; Gerdemann et al., 2007; IPCC, 2007; Kelemen and Matter, 2008; Oelkers et al., 2008; Matter and Kelemen, 2009; Montes-Hernandez et al., 2009a, 2009b; Kelemen et al., 2011; Schwarzenbach et al., 2013). In this general context, numerous experimental studies concerning the serpentinization or carbonation of peridotite (or single olivine) have been recently performed using batch, semi-continuous or flow-through reactors in order to better understand the reaction mechanisms and kinetics, reaction and cracking propagation from the grain boundaries, nature and role of secondary phase formation, potential of hydrogen production, potential for mineral sequestration of CO_2 and role of P, T, pH, solid/fluid ratio and fluid chemistry (e.g. Wunder and Schreyer, 1997; James et al., 2003; Giammar et al., 2005; Bearat et al., 2006; Seyfried et al., 2007; Andreani et al., 2009; McCollom and Bach, 2009; Garcia et al., 2010; King et al., 2010; Daval et al., 2011; Hövelmann et al., 2011; Klein and Garrido, 2011; Marcaillou et al., 2011; Bonfils et al., 2012; Lafay et al., 2012; Malvoisin et al., 2012). However, the competitive and/or coexistence between serpentinization and carbonation at peridotite–fluid interfaces have been rarely investigated at the laboratory scale, remarking that serpentinization and carbonation of peridotite, leading to precipitation of serpentine (e.g. lizardite and chrysotile) and magnesite (or hydrated Mg carbonates), could occur simultaneously in natural hydrothermal systems if the interacting solution is supersaturated with respect to both minerals. For this simple reason, the main goal of this present study was focussed to determine the simultaneous precipitation of serpentine and magnesite from hydrothermal alteration of olivine under high-carbonate alkalinity. For this particular case, specific experimental conditions were used (200 °C, saturation vapor pressure ($\approx$ 16 bar), solution/solid weight ratio (= 15), olivine grain size (<30 μm) and high-carbonate alkalinity solution (1 M $NaHCO_3$)).

These experimental conditions were selected with help of previous-experimental studies, investigating independently the serpentinization or the carbonation of olivine (e.g. Giammar et al., 2005; Bearat et al., 2006; Seyfried et al., 2007; Garcia et al., 2010; King et al., 2010; Daval et al., 2011; Hövelmann et al., 2011; Marcaillou et al., 2011; Bonfils et al., 2012; Lafay et al., 2012; Malvoisin et al., 2012). High-purity synthetic chrysotile and serpentinized olivine (chrysotile + brucite mineral + small amount of residual olivine) obtained in our laboratory were also used as starting solids in complementary-similar experiments in order to determine their reactivity under high-alkalinity. As expected, the chrysotile was slightly altered and brucite quickly transformed to magnesite at the investigated conditions. Various analytical tools such as X-ray diffraction (XRD), Field Emission Gun Scanning Electron Microscopy (FESEM), Thermogravimetric analyses (TGA/SDTA) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the solid products. TGA analyses and the respective 1st derivative curves were particularly used to determine with high accuracy the temporal variation of magnesite and serpentine during olivine alteration.

2. Materials and methods

2.1. Preparation of solid reactants

2.1.1. Olivine grains

Millimetric grains of olivine San Carlos (Fo_{91}) were crushed using a Fritsh Pulverisette 7 micro-crusher. One class of grain/particle size (particle size < 30 μm) was isolated by sieving. The samples were washed three times using high-pure water in order to remove the ultrafine particles that possibly stuck at grain surfaces during crushing step. Optical and electron microscopy was performed to control the initial state/appearance of olivine surfaces. On the other hand, high specific surface area (2.3 m^2 g^{-1}) was deduced from N_2 adsorption isotherm using conventional Brunauer–Emmett–Teller (BET) method. This high specific surface area was probably due to a significant presence of very fine particles (<1 μm; not verified), not spherical morphology of grains and significant surface-defaults and/or roughness.

2.1.2. High-purity synthetic chrysotile

250 ml of 1 M NaOH solution, 1.302 g of silica gel (H_2SiO_3) and 5.082 g of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) were placed in a Parr *copper alloy* reactor (autoclave with internal volume of 0.5 L). This aqueous reactive system was immediately stirred using constant mechanical agitation (300 rpm) during the reaction. The aqueous system was then heated at 300 °C for 30 h by using a heating jacket adapted to the reactor. Based on several previous experiments, these experimental conditions were optimal to synthesize high-purity chrysotile with high specific surface area ($S_{BET} = 185$ m^2 g^{-1}), more specifically a mesoporous material (pore size 2 to 50 nm) (Lafay et al., 2013).

2.1.3. Serpentinized olivine (chrysotile + brucite + small amount of residual olivine)

Micrometric grains of olivine (<30 μm) were altered in concentrated NaOH solution (1 M) at 200 °C in static batch mini-reactors for 30 days. 30 days of olivine–fluid interactions were enough to obtain almost complete mineral replacement of olivine to chrysotile and brucite. This implied a spatial and temporal coupling of dissolution and precipitation reactions at the interface between olivine and chrysotile–brucite minerals. This coupled dissolution–precipitation led to the alteration of starting olivine grains (so-called primary or parent mineral) to a porous mineral assemblage of chrysotile and brucite with preservation of the initial olivine grain shape. For more specific details on the olivine replacement by chrysotile and brucite, including kinetics and reaction steps, refer to Lafay et al. (2012).