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The deleterious effect of secondary phases on olivine carbonation yield: Insight from time-resolved aqueous-fluid sampling and FIB-TEM characterization

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ABSTRACT

Geological storage of CO_2 in mafic and ultramafic rocks relies on the dissolution of their silicate components, followed by the precipitation of carbonates, the overall process being commonly referred to as carbonation. To gain a better understanding of the rate- and yield-controlling factors of mineral carbonation, three batch experiments were conducted in CO_2-saturated water, at (a) 90 °C, (b) 120 °C and (c) 170 °C, respectively (with citrate ligands added to the 90 °C experiment) in a Ti-reactor at $pCO_2 = 280$ bar, using San Carlos olivine (Fo_{88}) as a model mineral of (ultra)mafic environments. Those physicochemical conditions were purposely chosen so as to promote the dissolution rate of olivine. (a) At 90 °C, ~40 wt.% of olivine were dissolved within 3 weeks, a result which suggests that the passivation barrier evidenced in previous studies carried out in citrate-free media had been overcome. However, while saturation with respect to magnesite was overstepped in this experiment, the carbonation yield remained below ~1 wt.%, which we attributed to the slow kinetics of magnesite precipitation. (b) At 120 °C, the concentration of Mg and Si monitored by aqueous fluid sampling reached an apparent plateau for over 4 weeks, at conditions close to saturation with respect to amorphous silica, and with Fe concentration being below the detection limit. A resumption of the dissolution process was subsequently observed while the concentration of Fe suddenly increased in solution. The concentration plateau was attributed either to the formation of a protective Si–Fe(III) layer, or to the occurrence of Fe(III) phases clogging the porosity of a secondary silica layer. The resumption of olivine dissolution was ascribed to the increasingly reducing conditions that led to the breakdown of the protective phases. This late resumption led to a carbonation yield slightly above 2 wt.%. (c) At 170 °C, Fe was incorporated into a presumably permeable Fe-rich phyllosilicate layer, so that the dissolution process was likely less affected by such an interfacial layer. Nevertheless, carbonate minerals still formed in low quantity (~6 wt.%), while other amorphous phases represented the main sink for Mg cations. Overall, this study emphasizes that achieving carbonation reactions in reducing environments and circum-neutral aqueous solutions may represent a necessary requirement for making olivine carbonation a viable process in these temperature ranges. It also insists on the importance of transitory phases, which form both at the fluid-silicate interface and from the bulk solution. While they may not appear in overall carbonation equations or in thermodynamic databases, arguably they can drive the global kinetics of olivine dissolution and its transformation towards magnesite.

1. Introduction

As levels of atmospheric carbon dioxide (CO_2) keep rising, the scientific community is seeking potential ways to store CO_2 permanently. As such, the carbonation of metal-bearing silicates containing divalent cations is considered as one of the most secure and sustainable options for sequestering CO_2 over long time spans (Oelkers et al., 2008). Such a process relies on the dissolution of gaseous CO_2 into water and its speciation into carbonate species, which, by dissolving silicates, releases divalent metal cations (M^{2+}) in solution:

$$M_xSi_yO_{x+2y-z}(OH)_{2z} + (x-z)H_2O + 2xCO_2 \rightarrow xM^{2+} + 2xHCO_3^- + ySiO_2. \quad (1)$$

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Depending on the saturation conditions of the aqueous medium, divalent cations M^{2+} can react with bicarbonate ions to form solid carbonate minerals as described by the reaction:

$$xM^{2+} + 2xHCO_3^{\ -} \rightarrow xMCO_3 + xH_2O + xCO_2. \quad (2)$$

Taken together, those two steps represent the carbonation process, described by the overall reaction (Oelkers et al., 2008):

$$M_xSi_yO_{x+2y-z}(OH)_{2z} + xCO_2 \rightarrow xMCO_3 + ySiO_2 + zH_2O. \quad (3)$$

The efficiency of the carbonation process partly relies on the availability of cations released by the dissolution of the silicates. Rock formations rich in divalent cations and poor in silica are natural candidates for CO_2 geological storage. In ultramafic rocks like peridotites and to a lesser extent, in mafic rocks like basalts, olivine ($(Mg,Fe)_2SiO_4$) is one of the most prominent minerals, and presents the advantage of being a very favorable substrate for reaction (3) from a thermodynamic standpoint (Guyot et al., 2011). In the specific case of Mg-rich olivine carbonation, magnesite ($MgCO_3$), usually the most stable of Mg-carbonates, is the carbonate expected to form, since silicate dissolution will release mainly Mg to solution (and to a lesser extent, Fe). Though Fe-carbonates can potentially form as well, as separate phases, Fe is more likely to be incorporated within the Mg-carbonates if the conditions are reducing enough (e.g. Saldi et al., 2013). The carbonation of olivine is thus described by the reaction:

$$(Mg,Fe)_2SiO_4 + 2CO_2 \rightarrow 2(Mg,Fe)CO_3 + SiO_2. \quad (4)$$

Moreover, numerous studies dedicated to the measurement of the far-from-equilibrium dissolution kinetics of olivine showed that this mineral is among the fastest dissolving silicates (e.g. Blum and Lasaga, 1988; Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000; Golubev et al., 2005; Hanchen et al., 2006; Wolff-Boenisch et al., 2011), such that in spite of its lower abundance compared to e.g. plagioclase in basalts, olivine remains one of the main contributors to the release of cations (Gudbrandsson et al., 2011). Despite these observations, aqueous carbonation experiments of μm-sized olivine powders at temperature below 100 °C have shown negligible amount of carbonates formed after several weeks of experiment (e.g. Giammar et al., 2005; Daval et al., 2011; Wang and Giammar, 2013).

In order to make carbonation a viable process for sequestering CO_2, such a kinetic barrier needs to be understood in order to be, in turn, overcome. Schematically, olivine carbonation can be decomposed into successive steps: (1) species release by olivine dissolution; (2) transport of those dissolved species across a possible interfacial layer made of secondary phases (e.g.: amorphous silica); and (3) carbonate precipitation. Each of these steps, which may occur simultaneously, can potentially be rate-limiting. Regarding the competition between the processes (1) and (3) (Eqs. (1) and (2)), the comparison of magnesite precipitation rates with corresponding forsterite dissolution rates at conditions relevant to geologic CO_2 sequestration led some authors (e.g. Saldi et al., 2012) to propose that the slow kinetics of magnesite precipitation may be rate-limiting with respect to the overall process. In qualitative agreement with this idea, previous studies (e.g. Gerdemann et al., 2007) showed that the optimal pH and alkalinity conditions for olivine carbonation rate represent a compromise between promoting the magnesite precipitation step, without lowering too much the dissolution rate of olivine. This observation emphasizes that increasing pH and alkalinity as a consequence of olivine dissolution is not necessarily detrimental to the overall carbonate rate. However, as detailed below, a growing number of studies pointed out that the formation of (transient or stable) secondary phases during the course of Mg-bearing silicate carbonation potentially played an even more important role in influencing the carbonation yields and rates.

A first straightforward effect is the limitation of carbonation yields due to the formation of silicate by-products incorporating Mg (e.g. Davis et al., 2009; Dufaud et al., 2009; King et al., 2010; Gysi and Stefansson, 2012). For instance, in their experiments carried out at $T \geq 200$ °C, Dufaud et al. (2009) and King et al. (2010) showed that water–CO_2–olivine interactions resulted in the formation of serpentine together with magnesite. Dufaud et al. (2009) acknowledged that depending on the reaction conditions, serpentine and magnesite minerals were produced in various proportions, drastically affecting the maximum extent of olivine carbonation.

Although secondary Mg-bearing phases could negatively affect the carbonation yield, by-products of the carbonation reaction can also play a role in passivating the surface of the reactants, thereby decreasing the rate of the reaction. Such an effect has been widely documented for weathering reactions as a whole (e.g. Velbel, 1993; Nugent et al., 1998). Several studies emphasized that among the fundamental parameters which favor the protective nature of mineral surface coatings are (1) the molar volume ratio of product to reactant, a ratio larger than 1 leading to passivating properties (Velbel, 1993; Putnis, 2002; Putnis et al., 2005) and (2) the potential crystallographic relationships between coatings and underlying unaltered phases if both reactants and products are crystalline (e.g. epitaxial growth can dramatically affect the dissolution rate of the parent phase (Cubillas et al., 2005)).

Regarding carbonation processes, the effect of the two main reaction products (carbonates and amorphous silica, see Eq. (3)) on the carbonation rates has been investigated as well. The corresponding studies revealed that the microstructure of the secondary assemblages and their overall evolution as the reaction proceeds were a supplementary factor which was worth considering. Some key observations are summarized hereafter.

Dealing with carbonate minerals, their armoring ability depends both on the nature of the substrate and on the respective rates of carbonate nucleation and growth. For instance, Stockmann et al. (2011, 2013) did not measure any obvious decrease of basaltic glass and diopside dissolution rates at basic pH and $T = 70$ °C, in spite of the significant extent of $CaCO_3$ precipitation. They concluded that these materials were not favorable substrates for the heterogeneous precipitation of calcite, such that most of the calcite actually formed by homogeneous nucleation, which did not directly affect the surface of the dissolving solids. In their experiments of wollastonite carbonation, Daval et al. (2009a,b) reported that when the reaction was initiated in ultrapure water equilibrated with elevated pCO_2, a carbonation extent as high as 95% could be reached without observing any obvious negative feedback effect between carbonate precipitation and wollastonite dissolution. Conversely, when the reaction was initiated in a 0.4 M NaOH solution equilibrated with elevated pCO_2, the extent of carbonation leveled to a maximum value of ~80%. The differences between the two series of experiments were ascribed to the relation between fluid composition and calcite grain size: the more alkaline the solution, the smaller the carbonate crystals, and the more compact the coatings. Furthermore, Daval et al. (2009b) observed that nanocrystals of calcite could form within silica rims embedding the wollastonite crystals, thereby decreasing their porosity and ultimately rendering the silica layers passivating.

In the case of the transport properties of amorphous silica layers, opposite trends have been reported depending on the experimental conditions and the nature of the substrate. For instance, Daval et al. (2009a,b) showed that the formation of amorphous silica layers on the surface of wollastonite does not significantly affect its dissolution rate. Conversely, Park and Fan (2004) or Teir et al. (2007) proposed that silica layers formed on serpentine considerably slow down its dissolution kinetics. Likewise, a growing number of studies of olivine carbonation suggested that the formation of thin silica layers (<50 nm) could constitute a barrier to the transport of aqueous species (e.g. Bearat et al., 2006; Andreani et al., 2009; Daval et al., 2011; Wang and Giammar, 2013) and ultimately controls the rates of olivine carbonation. Importantly,