The effect of silica coatings on the weathering rates of wollastonite (CaSiO$_3$) and forsterite (Mg$_2$SiO$_4$): An apparent paradox?

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ABSTRACT: The carbonation of wollastonite and forsterite were investigated at 90°C and pCO$_2$ = 25 MPa. Whereas wollastonite carbonation proceeded rapidly, indicating that secondary coatings did not prevent the fluid from reaching the wollastonite surface, weathering of forsterite was inhibited by a passivating silica layer. These results suggest that silica coatings do not have "universal" transport properties, the texture of the layers being influenced by specific factors inherited from the parent mineral, which remain to be determined.

1 INTRODUCTION

A long-standing problem in water-rock kinetics has consisted in the attempt to correlate mineral dissolution and precipitation rates determined in laboratory experiments, conducted at far-from-equilibrium conditions, with rates measured in the field. Discrepancies of up to four orders of magnitude have been reported (e.g. White & Brantley 2003), with rates measured in the laboratory being generally far greater. In spite of this problem, the long term evolution of mineral assemblages and fluids during water-rock interactions are often modeled by integrating laboratory-based mineral dissolution rate laws into reactive transport codes, because of the lack of alternative methods. For instance, this protocol is extensively used to predict the fate of CO$_2$ over long time spans within the context of geological storage of CO$_2$. Keeping in mind the discrepancies that exist between field and laboratory measurements, the relevance of such numerical simulations can, in many cases, be questioned.

Among the possible factors which could be responsible for inaccurate weathering rates based on laboratory kinetic rate laws, it was proposed that secondary phases could have passivating properties (Nugent et al. 1998). In the present study, we examined this hypothesis by investigating the carbonation process of Ca- and Mg-bearing silicates:

$$M_xSi_yO_{x+2y} + x\ CO_2 \rightarrow x\ MCO_3 + y\ SiO_2(am) \quad (1)$$

where M is a divalent cation. Specifically, our study was directed at ascertaining whether a good correspondence exists between carbonation rates of single mineral powders measured in batch experiments, and rates predicted by numerical modeling of the process, using far-from-equilibrium dissolution and precipitation rate laws from the literature. Performing such experiments, where both the fluid and solid phases undergo complex changes as a function of time, was believed to represent a necessary intermediate step to (possibly) validate modeling approaches at larger scales. A detailed investigation of textural and mineralogical features of carbonation products down to the nm-scale helped us to decipher the reaction mechanisms of carbonation and the impact of secondary phases (see Eq. 1) on the overall reaction rate.

2 MATERIALS AND METHODS

2.1 *Starting materials and experimental setup*

A detailed description of the starting materials and the experimental setup can be found in

Daval et al. (2009a). To summarize, ultrasonically cleaned wollastonite and olivine crystals (with composition close to forsterite end-member) with 125–250 μm grain size and specific surface area of 660 cm²/g and 410 cm²/g (both determined by BET), respectively, were used to perform the carbonation experiments. The investigations were conducted at T = 90°C and pCO$_2$ = 25 MPa in Teflon capsules capped with porous alumina plugs, and stacked in a Ti-autoclave (18 capsules per run). Each capsule was filled with a small amount of single-mineral powder (~300 mg) and ultrapure water (~0.5 mL). We verified that this experimental configuration ensures that the liquid composition of each capsule was not affected by the others. Runs were stopped after different time durations (from 8 h to 45 days) in order to determine the extents of carbonation as a function of time.

2.2 *Quantitative determination of extents of weathering/carbonation and kinetic modeling*

For the experiments carried out with wollastonite, the normalized extents of carbonation (ξ_n, ranging between 0 and 1) were measured using three independent techniques: solid mass balance, Rietveld refinement of X-ray diffractograms (XRD) of carbonated powders, and selective acid attack of calcium carbonates followed by determination of Ca^{2+} released (for details, see Daval et al. 2009a). Basically, such techniques make possible the measurement of ξ_n values as low as ~0.05.

With respect to the forsterite carbonation experiments, none of these methods was sensitive enough to detect the formation of magnesium carbonates. Instead, the Rock-Eval technique was used, which consists of sample decarbonation at temperatures between 500 and 900°C, followed by the quantification of CO_2 released (see Garcia et al. (submitted) for details). Quantities of magnesium carbonate as small as ~0.15% wt. (corresponding to ξ_n values of ~0.005) are measurable using this protocol.

The liquid phase of each capsule was recovered at the end of each experiment, filtered, diluted 10 times, and acidified. The samples were analyzed by ICP-AES for Si, Ca, and Mg.

The extents of reaction were modeled with the geochemical code CHESS (van der Lee & De Windt 2002), using rate laws taken from the literature for each step of the carbonation process (silicate dissolution and carbonate precipitation).

2.3 *Analyses of solids*

The powders were either fixed on an adhesive carbon support or impregnated with epoxy resin, polished, and studied by scanning electron microscopy (SEM). Focused ion beam (FIB) milling was then used to cut ultrathin electron transparent cross-sections on selected samples for further examination by transmission electron microscopy (TEM).

3 RESULTS AND DISCUSSION

3.1 *Wollastonite carbonation*

Wollastonite carbonation reached completion within a couple of days (Fig. 1a). In all of the experiments, the main reaction products were identified to be calcite and amorphous silica. Whereas calcite crystals grew mainly in the free spaces between the reacted wollastonite grains, amorphous silica was evidenced to occur as thick (up to 100 μm), continuous coatings in direct contact with the unreacted cores of wollastonite (Fig. 1b).

To determine whether such coatings could act as passivating layers and limit the bulk fluid from attaining the pristine wollastonite/silica interface, the measured extents of carbonation as a function of time were compared to the ones obtained by kinetic modeling of the process. Schematically, the time needed for carbonation to be achieved (t_c) can be written as:

$$t_c = t_d + t_t + t_p \qquad (2)$$

where t_d, t_t and t_p stand for the time required for complete dissolution, transport, and precipitation, respectively. Since the kinetic modeling using CHESS does not include transport terms, this implies that (1) t_t = 0 during the course of the simulation and (2) any difference between data and modeling can be ascribed to transport limitations (in addition, this assumes that the dissolution and precipitation rate laws used are correct, see Daval et al. 2009a and Daval et al. 2010 for details). Comparing the measured ξ_n values to the modeled ones (Fig. 1a) indicates that the silica coating that forms on the wollastonite during the reaction does not affect its dissolution rate significantly. The non-passivating transport properties of the silica rim were confirmed by TEM tomography on FIB thin sections, which revealed that it is highly porous (Fig. 1c) and fractured (e.g. Fig. 5c in Daval et al 2009b). The fractures and pores were sparsely filled with nm-sized crystals of calcite and Ca-phyllosilicates, testifying that the fluid reached the pristine wollastonite surface via these internal structures.

Nanoscale chemical profiles were measured across the wollastonite-silica interfacial region in order to determine the mechanism of their formation (e.g. Hellmann et al. 2003). One possibility is via the leached layer mechanism. In this case, the incongruent dissolution of the wollastonite is due to the preferential release of Ca and coupled interdiffusion with protons from the bulk solution. A diffusion process would result in sigmoidal
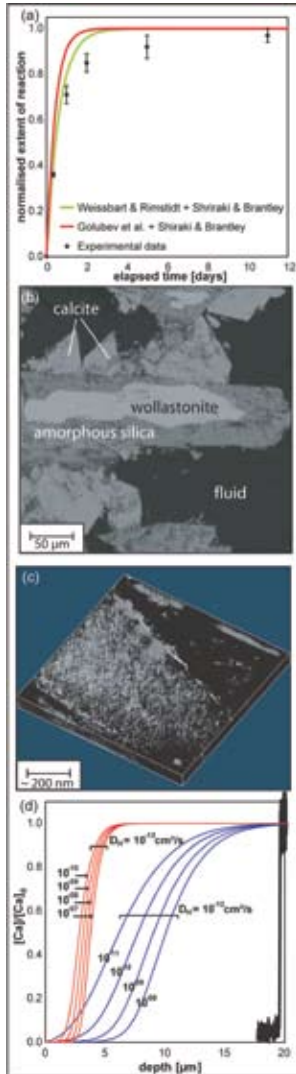
Figure 1. Main features of wollastonite carbonation. (a) Measured ξn values (diamonds) compared to the modeled ones (solid lines, see legend). (b) Back-scattered SEM image of carbonated powders in crosssection (reaction time: 2 days). (c) 3D-reconstruction of the amorphous silica texture based on TEM tomography. The colors range from black (no porosity) to white. (d) Comparison of measured Ca concentration profiles across the silica layer (black line) with modeled diffusion curves (colored lines). The numbers labeled on the curves stand for D_{Ca} values used for a given model.

diffusion profiles. To validate this, we used the following diffusion equation to model the interdiffusion of Ca and H:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C}{\partial x}\right) \qquad (3)$$

where t is time, C is the normalized concentration of Ca within the silica layer ($C = 1$ in wollastonite), x is the depletion depth and $\tilde{D}$ an interdiffusion coefficient, which depends on the diffusion coefficients of Ca (D_{Ca}) and H (D_H) (see Daval et al. 2009b for details). As shown in Figure 1d, the leached layer mechanism cannot reproduce both thick cation-depleted silica layers in conjunction with nm-wide interfacial chemical gradients. Similar conclusions were previously reached by Hellmann et al. (2003) for labradorite; they proposed as a consequence that the silica layer results from an interfacial dissolution-precipitation mechanism. Elevated porosity in the secondary phase, as evidenced in our study, is a typical characteristic of this mechanism (see Putnis 2002 and Daval et al. 2009b for details).

3.2 *Forsterite carbonation*

In the case of forsterite carbonation experiments, only a thin (~40 nm) non-porous amorphous silica layer was evidenced after 45 days of carbonation (Fig. 2a). The fluid composition remained roughly constant from the 1st to the 45th day of reaction, close to saturation with respect to $SiO_2(am)$. This result is at odds with the modeling of the process (Fig. 2b). Because the fluid rapidly reaches saturation with respect to $SiO_2(am)$, and then does not evolve anymore, we therefore propose that the forsterite grains were passivated by the silica phase, as previously suggested by Béarat et al. (2006).

To test this assumption, additional experiments were carried out using forsterite powders of different grain sizes (<50 μm and 500–800 μm) for 1 day and 21 days respectively. If the layer is passivating, then the total concentration of Mg released ($[Mg]_{tot}$) for each grain size only depends upon the thickness (dr) of the layer and the number of grains (N_0) initially introduced (the finer the grain size, the greater the number of grains). For a given initial amount of forsterite, one can write:

$$[Mg]_{tot} = \eta.[SiO_{2(aq)}]_{eq} + N_0.f(dr) \qquad (4)$$

where η is a stoichiometric number (2 for pure forsterite) and $[SiO_{2(aq)}]_{eq}$ the concentration of $SiO_2(aq)$ in equilibrium with $SiO_2(am)$. Both the number of grains and $f(dr)$ can be easily calculated following a simple geometric model (see Daval, 2009 for details). If we set dr to ~40 nm (according to TEM images), then $[Mg]_{tot}$ can be predicted for each grain size. The good agreement between data and model (Fig. 2c) indicates that passivation is a likely explanation for the observed trends.

4 CONCLUSIONS

Comparing the results for wollastonite and forsterite carbonation leads to an apparent paradox: the
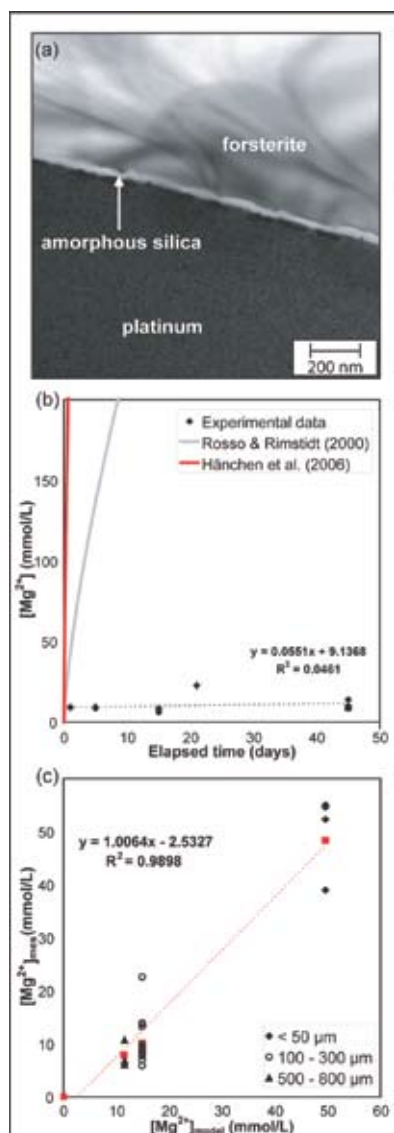
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Figure 2. Main features of forsterite carbonation. (a) TEM image of the fluid/solid interface (reaction time: 45 days). (b) Measured Mg concentration in the fluid as a function of time (diamonds) (note the statistic lack of evolution) compared with modeling results. (c) Measured Mg concentrations in the fluid for 3 grain sizes as a function of predicted concentrations using a passivation model (passivating layer thickness: ~40 nm).

passivating ability of silica layers is not universal but critically depends on the substrate from which they originate. Ongoing and future work aims to determine which parameter(s) mainly control(s) the texture and passivation potential of secondary layers: chemistry (Ca vs. Mg), crystallography (inosilicate vs. orthosilicate), and dissolution rate.

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