

# Carbonation of calcium-magnesium pyroxenes: A reaction-driven fracturing

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## INTRODUCTION

Geological Carbon Storage (GCS) via mineralization of CO<sub>2</sub> after its deep injection into mafic and ultramafic geologic formations is a promising strategy to solve the alarming rising levels of anthropogenic CO<sub>2</sub> emissions to the atmosphere (Lackner et al., 1995). Several studies have been focused on the fundamental understanding of the mechanisms involving dissolution of silicate minerals and the subsequent precipitation of carbonate phases. These studies have reported the formation of an amorphous and hydrated silica rich layer covering the mineral surface, also called as “leached layer” or “amorphous silica-rich surface layer” (Ruiz-Agudo et al., 2012). The formation of these layers has been related to a passivation effect of the mineral replacement reaction and therefore, plays a critical role in GCS strategies, controlling the dissolution rate of primary silicate materials and acting as a handicap for their effective CO<sub>2</sub> mineralization (Daval et al., 2009). Reaction-driven fracturing has been observed in carbonation processes and during weathering-related dissolution-precipitation replacement reactions involving volume changes (positive or negative), tensile stress generation and collapse (Røyne & Jamtveit, 2015). It is unknown, however, whether the latter reaction-driven fracturing occurs during primary silicate carbonation.

This study aims to determine experimentally the effects of pH, dissolved inorganic carbon (DIC) source, and carbon speciation in solution under hydrothermal conditions on the carbonation of two of the most abundant clinopyroxenes in the Earth’s crust: augite and diopside. In particular, we aim to shed light onto the effect of secondary silicate mineral formation during carbonation replacement, and its effect on reaction-driven fracturing. Finally, we strive to gather mechanistic and geochemical results of relevance for GCS strategies.

## MATERIALS AND METHODS

Augite and diopside crystal specimens of optical quality were cut with a diamond saw into single crystals 1 x 1 x 1 mm in size (~0.005 g). Two types of hydrothermal experiments were performed: (i) dissolution experiments with NaOH in the absence of added DIC and (ii) carbonation experiments in solutions prepared with NaHCO<sub>3</sub> (pH 7.5), or Na<sub>2</sub>CO<sub>3</sub> (pH 11.5). Single crystals were placed in PTFE vessels (polytetrafluoroethylene, V<sub>tot</sub> = 3 mL) with 1 mL of the different solutions described above and subsequently introduced into hydrothermal steel reactors, sealed and heated to 150 °C for 7, 14 and 28 days. At the given time intervals, reactors were cooled at room *T* and opened and crystals were separated and dried at room *T*.

Geochemical calculations and solution speciation were performed using PHREEQC computer code (version 3.3.12, USGS, Reston, VA, USA). The pH of the solutions was measured using a glass electrode (Metrohm) and the concentration of ions in reacted solutions was determined by ICP-OES (Perkin Elmer, Optima 8300). Scanning electron microscopy (SEM, FEI Quanta 400) was used for chemical microanalysis and high-resolution X-ray micro-computed tomography (Micro-CT, VERSA Xradia 510, ZEISS) was used to disclose and quantify the spatial distribution of reactant and product phases. Finally, all reacted crystals were thoroughly crushed using an agate mortar (grain size < 200 μm) and analyzed by X-ray diffraction (XRD) using an X’Pert PRO diffractometer (PANalytical) with the following instrumental parameters: Cu K $\alpha$ -radiation ( $\lambda$ = 1.5405 Å), 40 mA current, 45 kV tension, 3–70 °2 $\theta$  measurement range, 4 s per step, and 0.04 °2 $\theta$  step size. Diffraction patterns were analyzed using the computer software HighScore Plus 2.2.4 (PANalytical).

## RESULTS AND DISCUSSION

### Effect of pH and secondary phases precipitation during dissolution-carbonation

Dissolution, which is pH-dependent, is considered the rate limiting step of the carbonation reaction and therefore, the highest replacement to calcite should be observed in the pure water runs (i.e., lowest pH) while the lowest should be observed for Na<sub>2</sub>CO<sub>3</sub> experiments (i.e., highest pH). This model is in good agreement with the results obtained in augite runs. However, a higher replacement of diopside was achieved in Na<sub>2</sub>CO<sub>3</sub> runs than in water experiments. Geochemical calculations of the saturation index of calcite in our experiments are in good agreement with our experimental results, showing that in NaHCO<sub>3</sub> runs calcite precipitation reached the highest yield as compared to the other systems (24.6 wt. % in augite and 11.7 wt. % in diopside). Enhance dissolution-carbonation reaction was observed in NaHCO<sub>3</sub> systems due to the relative constant pH of the reaction. Regarding secondary phases formation, precipitation of iron oxides was observed, favorizing the progress of the reaction according to Le Chatelier's principle. Concerning silicate phases, amorphous silica, Magnesium-Silicate Hydrate (MSH) and Na-phillipsite precipitated in our experiments despite the undersaturation of all these phases in the bulk solution. All these phases were observed in etch pits and fractures. Their formation and their filling by secondary phases evidence a dissolution-precipitation mechanism taking place at the mineral-fluid interface (Ruiz-Agudo et al., 2012). In Na<sub>2</sub>CO<sub>3</sub> runs, no amorphous silica was observed for both pyroxenes replacement, due to the exponential increase of silica solubility at pH > 9 and indeed, lower mineral replacement was observed. Therefore, our experimental results demonstrate that the formation of secondary silicates (and oxides) played a key role in silicate carbonation due to the importance of side reactions in enhancing dissolution of primary silicates and the subsequent carbonation.

### Effect of reaction-driven fracturing

Reaction-induced fracturing is another crucial effect that strongly contributes to enhance the primary silicates carbonation. Augite crystals with Na-phillipsite precipitate showed pervasive fracturing whereas no fractures were observed in the rest of the crystals with the exception of diopside in high pH runs due to the presence of MSH. The precipitation of these phases started in the etch-pits of the host materials and continued by filling cracks generated by crystallization pressure. Due to the difference in chemical potential between ions in solution and in a solid phase, a pressure can be exerted by a solid crystallizing in a supersaturated solution, and such a crystallization pressure can be transmitted to confining surfaces such as the walls of pores or cracks. Our calculations for augite crystals showed values of critical stress in the order of 100 MPa (overcoming the tensile strength of the pyroxene, and thus enabling fracture generation) and a supersaturation  $\beta = 2.69$  for Na-phillipsite. Thus, the reaction-driven fracturing can be summarized as a fracture formation due to the crystallization pressure exerted by the precipitation of secondary phase in etch-pits that excess the critical stress of the hosting-material and causes the crack opening and the propagation of the fractures. Therefore, this reaction-driven fracturing is crucial for the advancement of the carbonation reaction, resulting in the highest carbonate yields observed in our experiments.

## CONCLUSIONS

This work highlights the important role of secondary phases precipitation in the advancement of the mineral carbonation reactions, the formation and propagation of fractures and the filling of dissolution pits and fractures by these phases, only achieved by interface-coupled dissolution-precipitation mechanism.

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