Carbonation of calcium-magnesium pyroxenes: Physical-chemical controls and effects of reaction-driven fracturing

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ABSTRACT

The weathering of primary silicates, and their carbonation in particular, is key for the geochemical cycling of elements, strongly affecting the C cycle and the long-term regulation of the Earth's climate. The knowledge on the controlling factors and mechanisms of aqueous carbonation of primary silicates is however still far from complete. This precludes a better understanding of their chemical weathering in nature and is a strong handicap to implement effective Carbon Capture and Storage (CCS) strategies. Here, dissolution-carbonation reactions of two abundant Ca-Mg pyroxenes, augite and diopside, have been investigated in experiments conducted at hydrothermal conditions, in the presence/absence of different carbonate sources (NaHCO_3 and Na_2CO_3). We show that the main reaction products are low-magnesium calcite and amorphous silica. A higher conversion of augite (~38 wt%) than diopside (~15 wt%) was achieved. The presence of abundant Fe and Al (and minor Na) in the former pyroxene strongly enhances the release of cations to the solution, and contributes to the formation of abundant secondary crystalline silicates as well as

carbonates (Na-phillipsite and magnesium silicate hydrate, MSH). In particular, Na-phillipsite nucleates in etch pits exerting a crystallization pressure ~100 MPa exceeding the tensile strength of augite and causing extensive fracturing. This takes place via an interface-coupled dissolution-precipitation mechanism, despite the bulk system being undersaturated with respect to this phase. Limited reaction-induced fracturing was also observed following MSH precipitation within diopside crystals. Reaction-induced fracturing increases exposed reactive surface area and creates channels for solution flow, thereby contributing to the progress of the reaction via a positive feedback loop. Ultimately, our results help to understand differences in the kinetics and mechanisms of chemical weathering of these two abundant rock forming inosilicates relevant for CCS strategies, showing that secondary phase formation (other than carbonates) are fostered by moderately alkaline pH and the presence of alkali metals, resulting in reaction-driven fracturing that enables the progress of silicate carbonation for an effective, safe, and permanent CO₂ mineral storage. We also show that under our experimental conditions the precipitation of amorphous silica and calcite cannot generate sufficient pressure as to create fracturing, an effect that limits carbonation of Mg-Ca-Fe pyroxenes.

1. INTRODUCTION

Weathering of primary silicate minerals caused by a range biogeochemical processes contributes to Earth's surface modeling, soil formation, the development of biota by supplying key nutrients (Nagajyoti et al., 2010) and the control of Earth's climate over geologic time-scales by the mineralization of CO₂ via carbonation (Walker et al. 1981; Pacala and Socolow, 2004). Carbonation of primary silicates is a key step in the carbon cycle and follows a "Urey-type" reaction (Urey, 1952; Daval et al., 2009a; Di Lorenzo et al., 2018; Monasterio-Guillot et al., 2019),

which in the case of mafic and ultramafic minerals can be expressed by the more general reaction (Daval et al., 2009a),

where M is an alkaline-earth metal such as Ca^{2+} , Mg^{2+} , or a divalent transition metal (e.g., Fe^{2+}).

These reactions highlight the key role of calcium- and magnesium-rich mafic and ultramafic rocks in Earth's climate control (Schott et al., 1981; Berner and Caldeira, 1997) .

Due to the alarming rising levels of anthropogenic CO_2 emissions to the atmosphere, principally caused by fossil fuel combustion, several initiatives have been developed for *ex situ* and *in situ* Carbon Capture and Storage (CCS). In this context, Geological Carbon Storage (GCS) via mineralization of CO_2 after its deep injection into mafic and ultramafic geologic formations (e.g., CarbFix pilot test, Iceland; Matter et al., 2016) is a promising strategy (Lackner et al., 1995; IPCC, 2014). This *in situ* CCS strategy can be considered the safest and most permanent way to store this greenhouse gas (Seifritz, 1990). In terms of *ex situ* mineral carbonation, the most promising strategies are aqueous-based mineral carbonation processes, such as the "pH swing" method (Park and Fan, 2004), or the direct carbonation, normally achieved under circumneutral pH conditions (Oelkers and Cole, 2008; Daval et al., 2009a,b; Di Lorenzo and Prieto, 2017; Monasterio-Guillot et al., 2019), aided by complexing agents or biomimetic processes involving the use of carbonic anhydrase, silicates, or metal organic frameworks (MOFs) to enhance the dissolution-carbonation processes during mineral replacement (Di Lorenzo et al., 2018).

Carbonation of silicates is an exothermic reaction that follows a combined dissolution-precipitation process, whereby divalent cations are released to the solution and, in the presence of a Dissolved Inorganic Carbon (DIC) source, form secondary carbonate phases (Daval et al., 2009a,b). Disclosing experimentally the key atomic- or molecular-scale processes and micro-to-macroscale

68 mechanisms of these coupled dissolution-carbonation reactions is crucial to model, implement and
69 enhance CCS processes and strategies, and to understand and model the fate of CO₂ injected during
70 GCS.

71 Several studies have focused on the fundamental understanding of the mechanisms
72 involving dissolution of silicate minerals and the subsequent precipitation of carbonate phases (e.g.,
73 Casey et al., 1988; Banfield et al., 1995; Lackner et al., 1995; Ruiz-Agudo et al., 2012; Ruiz-Agudo
74 et al., 2016; Di Lorenzo and Prieto, 2017; Monasterio-Guillot et al., 2019). Studies on the
75 dissolution of primary silicates have systematically reported the formation of an amorphous and
76 hydrated silica-rich layer covering the mineral's surface, the so-called "leached layer", surface
77 altered layer (SALs) or amorphous silica-rich surface layer (ASSLs), which can passivate mineral
78 dissolution (Casey et al., 1993; Daval et al., 2009a,b; Ruiz-Agudo et al., 2012; Hellmann et al.,
79 2013; Ruiz-Agudo et al., 2016; Wild et al., 2019). Furthermore, most studies on the carbonation of
80 primary silicates have reported an additional passivation effect caused by the formation of
81 carbonate mineral coatings on the primary mineral surface, decreasing the porosity and the
82 permeability of the starting material and limiting the progress of the reaction (O'Connor et al.,
83 2005;; Daval et al., 2009a,b; Kelemen et al., 2011). In general, passivation resulting in a reduction
84 of permeability and porosity of the host material will take place due to precipitation of a more
85 insoluble phase (Hellmann et al., 2012; Ruiz-Agudo et al., 2012; Wild et al., 2019). These effects
86 play a critical role in GCS processes, controlling the dissolution rate of primary silicate materials
87 and acting as a handicap for their effective CO₂ mineralization (McGrail et al., 2006; Stockmann et
88 al., 2008; Daval et al., 2009a,b; Ruiz-Agudo et al., 2012; Wild et al., 2019). However, the
89 replacement of a mineral phase can involve precipitation of a secondary phase in a confined volume
90 of the host material (dissolution pits, pores, and/or micro-fractures), and this can generate
91 crystallization pressure and an associated stress (Scherer, 1999; 2004) that can exceed the tensile

92 strength of the host material resulting in fracturing of the parent phase, in turn increasing
93 permeability and exposing fresh reactive surface (Emmanuel and Ague, 2011). Reaction-driven
94 fracturing has been observed during hydration of olivine (Kelemen and Hirth, 2012; Plümper et al.,
95 2013; Lafay et al., 2018), in carbonation processes (Matter and Kelemen, 2009;; Kelemen et al.,
96 2011) and during weathering-related dissolution-precipitation replacement reactions involving
97 volume changes (positive or negative), tensile stress generation and collapse (Jamtveit et al., 2000;
98 Plümper et al., 2012; Røyne and Jamtveit, 2015). Positive volume changes and an associated stress
99 can also occur upon precipitation of amorphous phases in a confined space, as exemplified by
100 fracturing during alkali-silica reaction in cement (Rajabipour et al., 2015 and refs. therein).
101 However, in this latter case, fracturing is associated with hydration of the resulting silica gel
102 (incorporating different alkali and alkaline-earth metals). It is unknown, however, whether the latter
103 reaction-driven fracturing occurs during primary silicate carbonation.

104 Despite the recent progress in the understanding of the mechanisms and kinetics of
105 dissolution-carbonation of silicate minerals, the current knowledge regarding the effects of neutral
106 to alkaline pH, carbonate speciation, secondary silicate formation (Daval et al., 2009a; King et al.,
107 2010; Sissmann et al., 2013; Monasterio-Guillot et al., 2019), with or without a passivation effect
108 (i.e., the formation of an impervious layer of product phase on the parent phase) (Ruiz-Agudo et al.,
109 2012; Ruiz-Agudo et al., 2016; Di Lorenzo et al., 2018; Wild et al., 2019), and its impact on
110 porosity and permeability (Jamtveit et al., 2000; Kelemen et al., 2011; Royne and Jamtveit, 2015),
111 is still far from complete. Moreover, most studies on silicate mineral carbonation have focused on
112 olivine (King et al., 2010; Daval et al., 2011), wollastonite (Di Lorenzo et al., 2018), or thermally
113 activated serpentine (O'Connor et al., 2005), while very little attention has been paid to other
114 abundant primary silicates such as Mg-Ca-Fe pyroxenes (Stockmann et al., 2008, 2013; Bodor et
115 al., 2013).

This study aims to determine experimentally the effects of pH, 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. In particular, we aim to shed light onto the effect of secondary silicate mineral formation during carbonation replacement, and their effect on reaction-driven fracturing (King et al., 2010; Kelemen et al., 2011; Lafay et al., 2018). Finally, we strive to gather mechanistic and geochemical results of relevance for CCS strategies, GCS in particular. To achieve these goals, we studied the dissolution-carbonation processes under near-neutral to moderately-alkaline pH, of diopside ($\text{CaMgSi}_2\text{O}_6$) and augite ($(\text{Ca,Mg,Fe}^{2+})_2\text{Si}_2\text{O}_6$), two calcium and magnesium primary silicates of the group of pyroxenes, one of the most abundant groups of rock-forming minerals in the Earth's crust (Deer et al., 1966; Schott et al., 1981; Knauss et al., 1993). Pyroxenes are inosilicate minerals with a general formula XYSi_2O_6 where X represents Na^+ , Ca^{2+} , Mn^{2+} , Fe^{2+} , Mg^{2+} , and Li^+ , and Y represents Mn^{2+} , $\text{Fe}^{2+/3+}$, Mg^{2+} , Al^{3+} , Cr^{3+} (Morimoto, 1988; Schott et al., 1981). Diopside was chosen because dissolution of this mineral has been thoroughly studied (Berner et al., 1980; Schott et al., 1981; Knauss et al., 1993; McGrail et al., 2006; Dixit and Carroll, 2007; Stockmann et al., 2008), and a few studies have focused on its carbonation (Stockmann et al., 2013), so that it can be used as a reference clinopyroxene. In contrast, the dissolution of augite has been sparsely studied (McAdam et al., 2008; Stockmann et al., 2013), and there are no studies on its carbonation other than the very preliminary one by O'Connor et al (2005).

The original features of this study are: (i) in contrast to most silicate weathering and carbonation studies, the selected pHs of this work include a wide range of natural groundwater pH (6.5 - 8.5) (Driscoll, 1986), which helps to directly extrapolate our results to natural environments; (ii) to the best of our knowledge, this is the first study performed using high purity single crystals of these pyroxenes instead of powders of these minerals, thus allowing a detailed spatially-resolved characterization of dissolution-carbonation reactions using high-resolution techniques such as X-ray

micro-computed tomography (Micro-CT); (iii) we combine dissolution-carbonation processes to reveal and quantify experimentally the effect of crystallization stress of newly formed secondary silicate phases on the progress of pyroxene carbonation.

2. MATERIALS AND METHODS

2.1 Starting materials

Augite and diopside crystal specimens, from science museum and undetermined localities, of optical quality (i.e., high purity and transparent) were cut with a diamond saw into single crystals 1×1×1 mm in size (~0.005 g). Crystals were cut along {001}, {100} and {010} planes as corroborated by means of electron backscattering diffraction (EBSD) analysis using a field emission scanning electron microscope (FESEM, Auriga Carl Zeiss SMT). The composition of diopside crystals used in this study is $\text{Ca}_{0.97}\text{Mg}_{0.84}\text{Fe}_{0.17}\text{Si}_2\text{O}_6$, whereas that of augite crystals is $\text{Na}_{0.05}\text{Ca}_{0.86}\text{Mg}_{0.76}\text{Fe}_{0.23}\text{Ti}_{0.07}\text{Al}_{0.3}\text{Si}_{1.7}\text{O}_6$, as calculated from ICP-OES analysis after acid digestion of the unreacted mineral (see details below). No minor phases were detected by X-ray diffraction (XRD) in diopside crystals. However, rutile (TiO_2) traces were detected in the augite crystals (see below).

2.2. Hydrothermal experiments

Two types of hydrothermal experiments were performed: (i) dissolution experiments in the absence of added dissolved inorganic carbon (DIC), and (ii) carbonation experiments involving the addition of DIC. Dissolution experiments were performed using 1 mL Milli-Q water (resistivity 18.2 $\text{M}\Omega\cdot\text{cm}$, Millipore) adjusted to pH 7.5 using NaOH (Sical). Carbonation experiments were performed in solutions prepared by mixing 1 mL Milli-Q water with 0.025 g of NaHCO_3 (pH 7.5),

162 or 0.031 g of Na_2CO_3 (pH of 11.5), to ensure an excess of carbonate and to achieve the desired pH
163 values (*i.e.*, pH = 7.5 and 11.5).

164 Single crystals (~0.022 mmol) were introduced in PTFE vessels (polytetrafluoroethylene,
165 $V_{\text{tot}} = 3$ mL) with 1 mL of the different solutions described above. Afterward, the PTFE vessels
166 were introduced into hydrothermal steel reactors, sealed and heated to 150°C for 7, 14 and 28 days.
167 The pressure was not independently controlled and corresponds to the vapor pressure at the
168 experimental T . At the given time intervals, reactors were cooled at room T and opened. Crystals
169 were separated and dried at room T . To ensure reproducibility, experiments were performed in
170 duplicate. Note that one individual crystal was used per experiment, three different hydrothermal
171 experiments were carried out (*i.e.* NaHCO_3 , Na_2CO_3 and water) and three different sampling times
172 were selected (*i.e.* 7, 14 and 28 days), a total of 36 individual experiments were performed (*i.e.*, 18
173 crystals of each pyroxene were used).

174 Geochemical calculations and solution speciation were performed using PHREEQC
175 computer code (version 3.3.12, USGS, Reston, VA, USA) and the llnl.dat database (Parkhurst and
176 Appelo, 1990) to model the evolution of the Saturation Index (SI_n) and free energy (ΔG) of the
177 different precipitates identified in our experimental conditions. Due to the absence of geochemical
178 information for augite in any database present in this PHREEQC version, information for this phase
179 was introduced manually following the geochemical data from Davidson and Lindsley (1985),
180 Loucks (1996), Palandri and Kharaka (2004) and Van Pham et al. (2012) ($\log K=21$; $-\Delta H = 122.775$
181 kJ/mol).

182 2.3. Analysis of the solutions and solids

183 The pH of the starting and reacted solutions was measured using a glass electrode (Metrohm)
184 calibrated with three standard solutions (pH = 4.01, 7.01 and 10.01 at 25 °C) with ± 0.01 of

185 uncertainty. The concentration of Ca, Mg and Si in reacted solutions was determined by ICP-OES
186 at Centro de Instrumentación Científica (CIC-UGR, Perkin Elmer, Optima 8300) and at Institut de
187 Sciences de la Terre (ISTerre, Varian 720ES).

188 In order to determine the mineralogical/structural changes undergone by the reacted
189 samples, they were analyzed using a JASCO IRT-7100 microscope coupled to a Micro-Raman
190 spectrometer (μ -Raman, JASCO NRS-5100) with a Nd-YAG laser ($\lambda = 785.11$ nm, 30 mW,
191 Elforlight G4-30), spectral range 1200–100 cm^{-1} . Reported spectra correspond to the average of 5
192 measurements.

193 The morphology, texture and composition of solids were characterized by scanning electron
194 microscopy (SEM, FEI Quanta 400) coupled to an X-ray energy dispersive spectrometer (EDS,
195 xFlash Bruker) for chemical microanalysis, working at an acceleration voltage of 20 kV.

196 Samples reacted for 28 days were analyzed by high-resolution X-ray Micro-Computed
197 Tomography (Micro-CT, VERSA Xradia 510, ZEISS) to disclose and quantify the spatial
198 distribution of reactant and product phases and cracks. Scans were performed at 40 kV and 75 μA .
199 Data were acquired with a 4x magnification objective and a charge coupled device (CCD) sensor
200 for a total scan time of 15 h including the collection of reference images. The voxel size achieved
201 under these conditions was 3 μm . Analyses of Micro-CT were performed on the same crystals first
202 analyzed by SEM-EDX to avoid any potential error on the selection of the grey-level/contrast
203 threshold to quantify the selected phases. The image analysis was performed using the ImageJ
204 software (Schneider et al., 2012) and Dragonfly software (Version 4.1, Object Research Systems).

205 Finally, all reacted crystals were thoroughly crushed using an agate mortar (grain size < 200
206 μm) and analyzed by X-Ray Diffraction (XRD) using an X'Pert PRO diffractometer (PANalytical)
207 with the following instrumental parameters: Cu $K\alpha$ -radiation ($\lambda = 1.5405$ Å), 40 mA current, 45 kV

208 tension, 3–70°2 θ measurement range, 4 s per step, and 0.04°2 θ step size. Prior to analysis, powder
 209 samples were placed on zero-background Si sample holders. Diffraction patterns were analyzed
 210 using the computer [software](#) HighScore Plus 2.2.4 (PANalytical) and minerals were identified
 211 matching the experimental diffraction peaks with those included in the Joint Committee for Powder
 212 Diffraction Standards (JCPDS) PDF-2 database. For the quantification of the crystalline products,
 213 we used the Rietveld method (Rietveld, 1969) and the crystal structures provided by the American
 214 Mineralogist Crystal Structure Database (Table S1) [using HighScore Plus 2.2.4 \(PANalytical\)](#). To
 215 corroborate the accuracy of the XRD Rietveld quantification, the normalized extent of carbonation
 216 (ξ_n) was calculated for Rietveld analyses and for mass balance analyses using the equation (Daval et
 217 al. 2009b):

$$218 \quad \xi_n = (x_{cal}/M_{cal})/(x_{py}/M_{py} + x_{cal}/M_{cal}) \quad (3)$$

219 where x_{cal} and x_{py} are the wt% of calcite and pyroxene (diopside or augite) determined by
 220 Rietveld analysis or mass balance calculation, and M_{cal} and M_{py} are the molecular masses ($\text{g}\cdot\text{mol}^{-1}$)
 221 of calcite and pyroxenes respectively, yielding dimensionless ξ_n .

222 To calculate the amount of Si-bearing amorphous phases obtained after 28 days of reaction,
 223 mass balance calculations were performed using the data obtained by Rietveld analysis of reacted
 224 solids and the results of ICP-OES chemical analysis of solutions, as follows:

$$225 \quad \Delta m = m_{pyr} - (m_{sol} + m_{phi}) \quad (4)$$

226 where m_{pyr} is the molar % of Si from the reacted (dissolved) pyroxene obtained from the Rietveld
 227 analyses and the values of the initial mass of pyroxene in the experiments, m_{sol} is the molar Si
 228 concentration in solution obtained by ICP-OES analyses and m_{phi} is the molar % of Si precipitated
 229 in the Na-phillipsite phase obtained by Rietveld analysis. A detailed description of the mass balance

calculations is presented in Supplementary Material. Note that Na-phillipsite is the only crystalline secondary silicate **that we could identify** in our runs. The difference in concentration obtained, Δm , is interpreted here as the Si contained in the Si-bearing amorphous phases (amorphous silica and magnesium silicate hydrate, see below).

Selected crystals were analyzed **to identify amorphous phases** by Fourier transform infrared spectroscopy using an attenuated total reflectance sample holder (ATR-FTIR, Jasco), spectral range 4000 – 400 cm^{-1} , and step size of 0.48 cm^{-1} . Reported spectra correspond to the average of 72 measurements.

3. RESULTS

3.1 Evolution of solution chemistry during dissolution-carbonation experiments

In all systems studied here, augite runs systematically presented a higher release of Ca, Mg and Si to the solution as compared to diopside runs (Figure 1).

3.1.1 Evolution of the solution chemistry in water runs

In water (initial pH 7.5) significant amounts of alkaline-earth metals were released from both pyroxenes and remained in solution after 28 days of reaction (Figure 1a-d), an effect that can be related to the relatively large extent of dissolution of the starting material and the very limited DIC source (*i.e.*, CO_2 present in the head space (**1.2 cm^3**) of the reactor). A slight decrease in the total concentration of Ca and Mg at 14 days, followed by a further increase was observed in water experiments, while the pH **increased** up to 14 days and subsequently decreased (pH 8.6 in augite and pH 9 in diopside runs). These results suggest that, after an initial period of pyroxene dissolution, Ca-Mg bearing carbonates formed **within** 14 days (corroborated by the analysis of reacted solids, see section 3.2). Precipitation of carbonates releases protons (O'Connor et al., 2005; Rodriguez-Navarro et al., 2015), causing a decrease in pH and, therefore, a renewed dissolution of

the primary silicate to feed cations to the solution. If only Mg-Ca carbonate were precipitated, Si in solution should display a constant increase due to the two dissolution steps. However, Figures 1e and 1f show that in the case of diopside runs, Si in solution showed a constant concentration during the whole experimental runs, whereas in augite systems, the concentration of Si presented an initial plateau between 7 and 14 days, matching the pH rise, and a later increase with a pH decrease. We suggest that in both runs, formation of amorphous silica ($\text{SiO}_{2\text{am}}$) took place, which is consistent with previous works on pyroxene dissolution (Schott et al., 1981; Dixit and Carroll, 2007; McAdam et al., 2008). Time-resolved variations in Si concentration during augite dissolution should be explained by the precipitation of an additional Si-bearing phase (Na-Phillipsite, Figure 1e) that fostered further release of Si from the parent phase.

3.1.2 Evolution of the solution chemistry in NaHCO_3 runs

Ca release to the solution from both pyroxenes in NaHCO_3 runs presented a first increase until 14 days, less pronounced in diopside runs, and a subsequent decrease caused by the precipitation of secondary Ca-bearing phases, as corroborated by XRD (see section 3.3). Mg release in augite runs showed a slight increase after 14 days of reaction. Logarithmic scale was used to unravel time differences (Figure S1). It can be observed a decrease up to 14 days and a further increase after 28 days of reaction. However, due to measurement error, we cannot infer a real increase or a more stable behavior. For this reason, we assume, in agreement with XRD results (Figure S9 and S11), a constant release of Mg from augite and the subsequent formation of a Ca-Mg secondary phase. In the case of diopside, the release of Mg showed a decreasing trend between 7 and 28 days in logarithmic scale (Figure S1), not observable using a linear scale figure (Figure 1). It can be assumed a constant sink of Mg, probably caused by the precipitation of Mg-calcite. The Si concentration in solution in NaHCO_3 systems was the lowest measured in this work as compared with the Na_2CO_3 and water runs, suggesting an important precipitation of Si-bearing secondary

277 phases. It must be noted that the starting pH was the same in water and NaHCO_3 solutions,
278 however, water systems underwent a higher pH increase over the first 14 days of reaction. We
279 hypothesize that the higher level of carbonate precipitation in NaHCO_3 runs and the associated
280 higher proton release led to such a limited pH rise in this run.

281 *3.1.3 Evolution of the solution chemistry in Na_2CO_3 runs*

282 In Na_2CO_3 runs, the concentration of Si in solution was up to two orders of magnitude
283 higher than in the other systems. This result is consistent with the pH-dependent solubility of silica,
284 which increases significantly at highly alkaline pHs (Fleming and Crerar, 1982; Monasterio-Guillot
285 et al., 2019). Interestingly, the Si concentration in augite runs was higher than in diopside runs. This
286 suggests that the dissolution rate of augite is higher than that of diopside, and that a secondary Si-
287 bearing phase formed in diopside runs.

288 *3.1.4 Evolution of the dissolution rates of pyroxenes*

289 Dissolution rates of pyroxenes were calculated based on Si concentration in solution at the three
290 sampling times (Figure S2). All our results show rates (LogR from -10.5 down to -13) that are in
291 partial agreement with those reported in the literature (LogR from -9 down to -11 $\text{mol.m}^{-2}\text{s}^{-1}$)
292 (Daval et al. 2010; Dixit and Carroll 2007). Yet they were systematically lower, especially in the
293 case of NaHCO_3 runs where our rates were two order of magnitude lower. This shows that in our
294 closed system we were closer to equilibrium than in other studied systems (flow-through
295 experiments). Our results are also consistent with the fact that we have precipitation of silicon-
296 containing secondary phases, which reduced the silicon content in solution, and as a consequence,
297 the values of LogR.

298

299 **3.2 Characterization of solids reacted in water**

300 3.2.1. Reacted augite

301 XRD patterns showed small changes after reaction of augite with water for 28 days (Figure 2a).
302 Rietveld analyses (Figure 2b) showed less than 15 wt% of augite replacement by: low Mg-calcite
303 (2.61 wt%), Na-phillipsite (~11 wt%) and iron oxides (hematite, 2.16 wt%). Na-phillipsite is a
304 zeolite composed by Na, Al and Si, with the possibility of Mg, Ca and K incorporation (theoretical
305 formula: $(\text{Na,K,Ca})_{1-2}(\text{Si,Al})_8\text{O}_{16}\cdot 6\text{H}_2\text{O}$). Hematite was also present from the early stages of
306 reaction, showing a continuous but minor increase in concentration over time due to Fe release from
307 the parent phases and the decrease in the solubility of iron oxides and hydroxides with increasing
308 pH (Schwertmann, 1991) causing fast precipitation. μ -Raman analyses confirmed the precipitation
309 of calcite (Figure 2c) showing the translational lattice mode (T) at 286 cm^{-1} , the ν_4 -symmetric CO_3
310 deformation at 717 cm^{-1} and the ν_1 -symmetric CO_3 stretching band at 1085 cm^{-1} (Gunasekaran et
311 al., 2006). Hematite was also identified by μ -Raman showing bands at 326 cm^{-1} , 449 cm^{-1} and 570
312 cm^{-1} corresponding to hematite E_g , E_u , and E_g vibrations, respectively (Bersani et al., 1999;
313 Chamritski and Burns, 2005). SEM-EDS analysis of augite crystals reacted for 28 days showed
314 fractures filled by a secondary Na-rich silicate, Na-phillipsite as demonstrated by XRD analysis
315 (Figure 1d-e and S1). EDS point analyses (Figure S4 and Table S2) confirmed the presence of this
316 zeolite phase with empirical formula $\text{Na}_{1.95}\text{Mg}_{0.05}\text{Al}_{3.21}\text{Si}_{4.79}\text{O}_{16}\cdot 6\text{H}_2\text{O}$. Despite the lack of added
317 DIC, a small amount of calcite was observed (Figure S5). The formation of calcite suggests that the
318 CO_2 present in the head space of the reactor (1.2 cm^3) dissolved in the solution forming HCO_3^- ,
319 which upon dissociation, supplied CO_3^{2-} ions that, in the presence of Ca^{2+} ions, caused the
320 precipitation of calcite and the release of H^+ . This is consistent with the pH and Ca^{2+} concentration
321 evolution in solution analyses (Figure 1a and d). SEM-EDS analysis of calcite showed that this
322 phase included Mg. To unravel the actual content of Mg in calcite, the lattice parameters of calcite
323 were calculated by Rietveld refinement and the Mg content was determined according to Goldsmith

et al. (1958) (Table S3). The calculated Mg amount in calcite was 8 mol%. Silica gel was also identified by SEM-EDS analysis (Figure S6) in dissolving areas, such as small fractures and etch pits. Micro-CT analysis showed the presence of two secondary phases (identified by their contrast due to differences in X-ray attenuation), already identified in the same crystals using SEM-EDS. In Figure 2f, the red phase is amorphous silica and the green one is Na-phillipsite. It can be observed that precipitates were present inside the reacted crystals filling fractures that in some cases cross-cut the whole pyroxene crystal. Image analysis of Micro-CT results showed 23 wt% augite replacement by 14.3 wt% Na-phillipsite and 8.7 wt% amorphous silica. These values do not agree with the mass balance for silicon calculated using Eq. (4): a deficit of Si in the solution was detected that should be present as a precipitate. We suggest that the amorphous SiO_2 content obtained from Micro-CT analysis actually included calcite and amorphous silica due to the resolution constraints of the Micro-CT equipment. Mass balance was recalculated using the values obtained by Micro-CT total amount of augite dissolved and the concentration of Si and Ca in solution, yielding 2.16 wt% SiO_2 and 2.61 wt% calcite. If we normalize the phase contents obtained by Rietveld analysis to the amorphous silica and calcite determined by mass balance calculations, the corrected values for the quantitative analysis are 83.97 wt% augite, 9.86 wt% Na-phillipsite and 0.85 wt% hematite (Table 1). Thus, we assume that due to the resolution constraints of our Micro-CT equipment, the amounts of Na-phillipsite and CaCO_3 + amorphous SiO_2 were slightly overestimated.

3.2.2. Reacted diopside

In the case of diopside subjected to dissolution in water at pH 7.5, XRD and Rietveld analyses (Figure 3a and S7) showed no major differences between unreacted and reacted samples, except for the presence of 1.23 wt% Mg-Calcite (12 mol% Mg, Table S3), also confirmed by SEM-EDS analyses (Figure 3b-c). As mentioned above, calcite precipitation could have been caused by the presence of CO_2 in the head space of the reactor. μ -Raman analyses also confirmed the precipitation

of this carbonate (Figure 3d). In addition, SEM-EDX and XRD analyses confirmed the presence of hematite (0.4 wt%). Rietveld analyses showed a very limited replacement of diopside by secondary phases (< 2 wt%) and, in contrast with augite runs, no secondary crystalline silicates were detected. However, SEM-EDS analyses showed the presence of Ca- and Mg-free Si-rich precipitates in dissolution pits and on the surface of diopside, which we interpret as silica gel (Figure 3e). Micro-CT analyses (Figure S8) showed silica gel (2.7 wt%) after 28 days of reaction, but only on the surface of the reacted material. As in the case of the augite run, mass balance calculations were performed to unravel the actual SiO₂ content. This analysis shows that the value obtained by Micro-CT analysis was overestimated, because our equipment could not differentiate between calcite and amorphous silica (identified by XRD and SEM-EDS, respectively) as they show no detectable X-ray attenuation contrast. Rietveld calculations were normalized to the 1.7 wt% amorphous SiO₂ calculated by mass balance yielding 96.73 wt% diopside, and 1.23 wt% calcite (Table 1). In contrast with augite runs, no pervasive fractures were identified by SEM or micro-CT analyses. Apparently, while the formation of secondary crystalline silicate phases induces fracturing, this is not the case for the precipitation of amorphous silica (see discussion section).

3.3 Characterization of solids reacted in sodium bicarbonate solutions

3.3.1. Reacted augite

XRD-Rietveld results (Figure 4a and S9) show that the reaction of augite in NaHCO₃ solution led to the formation of Na-phillipsite and calcite, as also occurred in the case of water. However, augite replacement was substantially higher (36.9 wt%) and secondary phases formation reached maximum values as compared with the whole set of experimental results: 12.7 wt% Na-phillipsite (value very similar to water runs) and 22.3 wt% calcite. Importantly, the mass balance between Si in solution (Figure 1c) and reacted augite from Rietveld analysis showed an excess of Si that would

be incorporated into an additional secondary Si-bearing phase, which was not detected by XRD or SEM-EDS analyses. Based on the results of water runs (see above), we suggest that the missing Si was incorporated into amorphous silica. Rietveld analyses were thus normalized to the 2.1 wt% of newly formed amorphous silica calculated from mass balance (Table 1). SEM-EDS analyses (Figure 4b,c) showed massive pervasive fracturing of the starting augite crystals and confirmed the presence of abundant Na-phillipsite and calcite precipitated within the fractures and on the surface of the starting material. Well-developed rhombohedral calcite crystals ~8 μm in size with surface-decorated iron-oxides were also identified. Calcite formation was confirmed by μ -Raman analyses (Figure 4d). Micro-CT analyses (Figure 4e) confirmed that the secondary phases precipitated within the fractures cross-cutting the crystal and in the pores of the host augite crystal. Interestingly, Na-phillipsite precipitated directly in contact with the fracture walls, filling the fractures inwards and fully covering the surface of the walls. In contrast, calcite crystals appeared on the surface of the pyroxene crystal and filling the cracks in contact with the Na-phillipsite (Figure S10), evidencing a first precipitation of the zeolite and the subsequent formation of calcite. However, it cannot be ruled out the possibility that, once the cracks appeared caused by the first precipitation of Na-phillipsite, calcite started to precipitate contemporaneously to this zeolite. It should be noted that in this run the amount of newly formed iron oxides reached the highest value of all experiments (2.01 wt%).

3.3.2. Reacted diopside

XRD-Rietveld analyses (Figures 5a and S11) of diopside showed a much higher level of replacement (12.6 wt%) by newly formed phases in NaHCO_3 solution than in water, but this value was significantly lower than that of augite reacted in bicarbonate solutions. Calcite was the most abundant secondary phase, showing a progressive increase up to 11.7 wt% over the whole span of the experiment, whereas iron oxides were, in all experiments, under 1 wt%. Mass balance calculations showed that a fraction of precipitated Si was missing. As in the previous cases, this is

interpreted as amorphous silica gel not detected by XRD. Quantitative Rietveld analysis results were normalized using the 1.27 wt% of amorphous SiO₂ calculated from mass balance (Table 1). Calcite precipitation was confirmed by μ -Raman (Figure 5b) showing the characteristic bands at 286 cm⁻¹, 717 cm⁻¹, and 1085 cm⁻¹, plus additional diopside bands, due to the relatively high beam penetration depth. These inosilicate bands include: the symmetrical stretching vibration of bridging oxygen in Si-O-Si (Si-O_{br}) at 663 cm⁻¹, the symmetrical stretching vibration of non-bridging oxygen in Si-O (Si-O_{nbr}) at 1012 cm⁻¹ and, in the lower frequency region, four bands at 206 cm⁻¹, 316 cm⁻¹, 350 cm⁻¹ and 385 cm⁻¹ corresponding to the Ca/Mg-O vibrations (Buzatu and Buzgar, 2010). Precipitation of calcite and iron oxides was also confirmed by SEM-EDS analyses (Figure 5c and d). Rhombohedral calcite crystals were observed on the surface and within dissolution pits of the diopside substrate. EDS analyses of calcite crystals showed a high Mg content (Figure 5c). From XRD analysis, the Mg content in calcite was determined to be 14.8 mol%. The highest Mg content in calcite was observed in these runs, whereas in pure water a higher Mg content was observed in diopside than in augite runs. Similar to the pure water systems, and in contrast with augite runs, diopside crystals did not show massive pervasive fracturing as in the case of augite runs (inset in Figure 5d). As a result, no secondary phases were detected in the interior of diopside crystals by Micro-CT.

3.4 Characterization of solids reacted in sodium carbonate solutions

3.4.1. Reacted augite

After 28 days, the formation of Mg-calcite (12 mol% Mg) was detected in augite samples along with hematite, whose content increased almost linearly with reaction time (Figures 6a and S12a). Augite replacement in the Na₂CO₃ system was the lowest observed here (7.95 wt%). Mg-calcite reached 6.9 wt%, in good agreement with Micro-CT analyses (7.7 wt%). Mg-calcite was principally

418 present as rhombohedral crystals ~16 µm in size on the surface of the starting material and inside
419 surface cracks and dissolution pores (some extending deep into the pyroxene crystal), as shown by
420 SEM-EDS analyses (Figure 6b,c) and Micro-CT (Figure 6d). However, pervasive fracturing was
421 not observed within reacted augite crystals (Figure 6d). Furthermore, no Si-bearing secondary
422 phases were identified.

423 3.4.2. Reacted diopside

424 XRD results (Figures S12b and S13) showed minimal replacement of diopside (2.25 wt%)
425 in Na₂CO₃ solution by low-magnesium calcite crystals (4 mol% Mg, the lowest value of all runs).
426 SEM-EDS analysis of solids collected after 7 days of reaction (Figure 7a) showed the presence of a
427 gel-like Mg- and Si-rich surface precipitate with no Ca, in addition to rhombohedral crystals of
428 calcium carbonate. Moreover, EDS analyses showed that the apparently amorphous Mg-silicate had
429 a Mg/Si ratio of 0.72, in good agreement with mass balance calculations yielding a Mg/Si ratio of
430 0.63. The Mg/Si ratio was calculated by mass balance as follows:

$$431 \quad \Delta_{Mg} = m'_{pyr} - (m'_{sol} + m'_{prec}) \quad (5)$$

432 where m'_{pyr} is the mol % of Mg from the dissolved pyroxene obtained from the Rietveld analyses,
433 m'_{sol} is the Mg concentration in solution obtained by ICP-OES analyses and m'_{prec} is the mol % of
434 Mg precipitated in the Mg-containing [crystalline phases obtained by Rietveld analysis using a](#)
435 [Pseudo-Voigt \(n=0.5\) for peak fitting and refinement](#). The difference in concentration obtained,
436 Δ_{Mg} , is interpreted here as the Mg contained in the Mg+Si-bearing amorphous phase.

437 Such values are in full agreement with the typical Mg/Si ratios observed for magnesium
438 silicate hydrate (MSH) gels (0.6-0.9) (Lothenbach et al., 2015; Bernard et al., 2017). After 28 days
439 of reaction (Figure 7b), the MSH gel suffered a morphological transformation [to a more condensed](#)
440 [\(less porous and more compact\) structure constrained within the limits of surface cracks](#), and filling

dissolution pits of diopside. Calcite crystals were associated with MSH on the surface and within etch pits of the pyroxene (Figure 7b). Micro-CT (Figure 7c) analyses showed the distribution of MSH along the dissolution areas and within the pores formed on the surface of diopside, but also in several small cracks extending from the surface to the interior of the crystal (without cross-cutting the whole crystal). Micro-CT based calculation of MSH + calcite content yielded 9.7 wt% of both phases. If we subtract from this value the Rietveld value obtained for calcite, the MSH content should be 7.45 wt%. However, mass balance did not match these values, showing an excess of Si in the system. Additional mass balance calculations were performed considering the Si and Mg content in solution, yielding a MSH content of 5 wt%. Rietveld analyses were normalized to this value (Table 1). Calcite could not be differentiated from MSH using micro-CT due to analytical constraints (*i.e.*, under our experimental conditions, the X-ray contrast of these two phases is very similar, so our micro-CT analysis could not differentiate them).

MSH precipitation was confirmed by FTIR analyses (Figure 7d) showing the broad ν -OH stretching around 3400 cm^{-1} and the δ -OH bending at $\sim 1615\text{ cm}^{-1}$ of water as well as a weak band at $\sim 1240\text{ cm}^{-1}$ attributed to the Q_3 stretching vibration of Si-O bonds, and a band at $\sim 1180\text{ cm}^{-1}$ corresponding to the ν_3 vibration of the Si-O bond in fresh MSH gels, which is red-shifted from the typical ν_3 Si-O band of calcium silicate hydrate (CSH) at 945 cm^{-1} (Ashraf and Olek, 2016; Lothenbach et al., 2015). The presence of a carbonate phase was also confirmed by the ν_3 band at $\sim 1458\text{ cm}^{-1}$ (Ashraf and Olek, 2016; Gunasekaran et al., 2006). Calcite bands at 874 and 713 cm^{-1} were not detected due to the overlapping of the broadband of ν_{as} Si-O-Si vibration of diopside (Omori, 1971; Mozgawa et al., 2004). To further corroborate the presence of MSH, μ -Raman analyses were performed (Figure 7e). The bands of diopside were detected, as well as the bands corresponding to O-H-O vibrations at 219 cm^{-1} , O-Si-O bending at 354 cm^{-1} and Si-O-Si

464 symmetrical bending at 450 and 661 cm^{-1} , corresponding to MSH (Lothenbach et al., 2015; Bernard
465 et al., 2017).

466 3.5 Quantitative comparison of the carbonation extent

467 To better assess the carbonation extent of the different starting materials, values determined by
468 Rietveld refinement (ξ_n^{RR}) were plotted as a function of mass balance values (ξ_n^{MB}) (Eq. 3) (Figure
469 S14). Extents of carbonation determined by both methods are listed in Table 1. The slope and
470 correlation coefficient of the linear regression of the corresponding data ($N=3$) for both analyses
471 were close to 1, showing that the ξ_n values obtained by Rietveld analysis are in excellent agreement
472 with those obtained by mass balance analysis. These results support, on the one hand, that Rietveld
473 analysis is an accurate method for quantitative crystalline phase analysis, even in the case of
474 mineral phases present in very small amounts, and on the other hand, it gives extra reliability to our
475 experimental work.

476 4 Discussion

477 4.1 Effect of pH and secondary phases precipitation during dissolution-carbonation

478 Dissolution kinetics of inosilicate minerals are positively correlated with $[\text{H}^+]$ (e.g., Schott et al.,
479 1981; McAdam et al., 2008; Schott et al., 2012). Therefore, the concentration of released divalent
480 metals susceptible to contribute to the carbonation reaction is expected to be higher at close-to-
481 neutral than at highly alkaline pHs. However, carbonate precipitation is dependent on $[\text{CO}_3^{2-}]$,
482 which increases with pH (for a given value of DIC). Thus, a proper balance between these two key
483 parameters (i.e. $[\text{CO}_3^{2-}]$ and pH), is of paramount importance to reach the highest possible
484 carbonation yield. In our case, this is achieved in sodium bicarbonate solution for both minerals
485 studied here. If dissolution is considered the rate limiting step of the carbonation reaction, the
486 highest replacement should be observed in the pure water run and the lowest replacement should

take place in Na_2CO_3 solutions. This holds true for augite experiments (Table 1). However, a higher level of diopside replacement was achieved in Na_2CO_3 than in water runs (Table 1), which points to the existence of another kinetic limiting step.

Regarding free energy calculations (Eq. S2 and S3 and Table 2), it was observed that all systems had a negative free energy, enabling the dissolution of the pyroxenes. It is important to note that, systematically, ΔG values of augite were lower (more negative) than those of diopside, resulting in higher expected dissolution rates and therefore, a higher augite replacement by secondary phases, as we observed experimentally in all runs.

Calculation of Saturation Index (SI_{cal}) from measured concentrations in ICP-OES analyses using PHREEQc (Figure 8) shows that the highest calcite supersaturation is reached for augite in NaHCO_3 runs. Due to the similar behavior of SI_{cal} for both pyroxenes, results for diopside SI modeling are not shown here. Low magnesium calcite (~8-10 mol%) presents a slightly lower solubility product than pure calcite (Morse and Bender, 1990). Thus, we can expect a slight increase of the calculated SI_{cal} due to the Mg content, favoring Mg-calcite precipitation. Furthermore, the precipitation of calcium carbonate causes a pH decrease (Figure 1) by proton release, which would foster further pyroxene dissolution. Thus, our model is in good agreement with our experimental results showing that in NaHCO_3 runs calcite precipitation reached the highest yield as compared to the other systems (24.6 wt% in augite and 11.7 wt% in diopside). To explain why the Mg content in precipitated calcite was maximum in diopside reacted in NaHCO_3 runs, and minimum in diopside reacted in Na_2CO_3 runs, we suggest that at neutral-to-moderately alkaline pH (bicarbonate and water runs), the higher $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}]$ ratio (closer to unity) as compared to higher pH runs (with higher $[\text{CO}_3^{2-}]$) in addition to the high SI_{cal} could enable faster calcite growth favoring Mg incorporation (Mavromatis et al., 2013). In addition, because Mg was incorporated in MSH, a phase which according to our SEM-EDX and micro-CT observations preceded the formation of Mg-

511 calcite in diopside runs with Na_2CO_3 solution, there was a lower amount of Mg available to be
512 incorporated into calcite.

513 In agreement with Gadikota et al. (2014), who showed that the addition of NaHCO_3 during
514 *ex situ* CCS fostered the carbonation of Ca-Mg silicates due to its buffer effect, we also observe
515 enhanced silicate dissolution-carbonation in NaHCO_3 runs due to the relatively constant pH of the
516 reaction ($7.5 < \text{pH} < 9$). This relatively constant moderately alkaline pH enhances the dissolution of
517 the pyroxenes as compared to a strongly alkaline pH. As a consequence, dissolution of these
518 silicates increases the amount of alkaline-earth metal ions fed to the solution susceptible to react
519 with CO_3^{2-} ions. This is one factor that helps to explain why we obtain the highest levels of calcium
520 carbonate precipitation in bicarbonate runs. But it is not the only one (see below).

521 Regarding iron oxide precipitation, PHREEQc calculations (Figure S15) show that under the
522 whole pH range of our experiments, hematite was supersaturated. Therefore, precipitation of Fe-
523 oxides was expected right after Fe release following dissolution of the starting materials, in
524 agreement with Schwertmann (1991). As in the case of Mg-calcite, precipitation of Fe-oxides
525 should also favor the progress of the dissolution/carbonation according to Le Chatelier's principle.

526 Regarding secondary silicate phases, amorphous silica, MSH and Na-phillipsite precipitated
527 in our experiments despite the fact that the bulk solution was undersaturated with respect to the
528 latter. Our analysis of the solution chemistry evolution and SEM-EDS observations revealed that
529 amorphous silica was precipitated after a moderate alkalization in NaHCO_3 and water runs.
530 Amorphous SiO_2 was found within etch pits and as isolated precipitates on the surface of the
531 pyroxene crystals. The formation of etch pits and their filling by amorphous silica reveals that a
532 coupled dissolution-precipitation reaction at the mineral-fluid interface (*i.e.*, interface-coupled
533 dissolution-precipitation, ICDP) was at work (Putnis, 2009; Ruiz-Agudo et al., 2012, 2016).

According to previous works (i.e., Daval et al., 2009a; Ruiz-Agudo et al., 2012; Wild et al., 2019), replacement processes taking place at the mineral-fluid interface result in strong compositional gradients and important pH differences between the bulk solution and the mineral-fluid interface. Such gradients enable the precipitation via an ICDP mechanism of secondary phases, thermodynamically not possible in the bulk solution (Putnis, 2009), thus explaining the observed formation of amorphous silica (as well as the other two secondary silicates, as discussed below) despite the fact that this phase was unsaturated in the bulk solution.

Under the highly alkaline pH of the Na_2CO_3 runs, we detected no amorphous silica precipitation; however, the highest Si concentration in solution was reached (Figure 1). This result is consistent with the nearly exponential increase in silica solubility at $\text{pH} > 9$ (Fleming and Crerar, 1982; Monasterio-Guillot et al., 2019), not favoring its precipitation. On the other hand, because pyroxene dissolution rates decrease with increasing pH (Schott et al., 2012), the Si release rate was substantially lower in highly alkaline systems than in moderately alkaline ones.

Augite dissolution-carbonation at neutral-to-moderately alkaline pH, led to the precipitation of Na-phillipsite. Previous works have reported the precipitation of secondary Na-phillipsite (commonly associated with amorphous Si-rich glass) during low- T hydrothermal weathering of basic and ultrabasic rocks rich in aluminum-augite in pelagic environments (Glaccum and Boström, 1976; Iyer et al., 2007). To model the evolution of the Saturation Index of Na-phillipsite (SI_{phi}) at our experimental conditions, PHREEQc calculations were performed, showing values of $\text{SI}_{\text{phi}} < 0$ (undersaturation) for all relevant pH values (i.e., $\text{pH} \geq 7.5$) in our studied systems (Figure 8). The latter indicates that it was not thermodynamically possible to precipitate this phase, contrary to our experimental observations. As in the case of the precipitation of $\text{SiO}_{2(\text{am})}$ above discussed, if a sufficiently high Na, Al and Si release rate is achieved, a high supersaturation will be reached at the mineral-fluid interface as to enable the heterogeneous precipitation of Na-phillipsite on the

dissolving augite via an ICDP mechanism. In this respect, it is important to underline that a high solute concentration can be achieved within the constrained volume of etch pits formed during pyroxene dissolution (Plümper et al., 2012), and their pore surface will offer a large amounts of sites for heterogeneous nucleation (Scherer, 1999; Putnis, 2009; Emmanuel and Ague, 2011; Schiro et al., 2012). Altogether, these combined effects would favor the observed precipitation of Na-phillipsite.

In our previous work (Monasterio-Guillot et al., 2019) we showed the formation of a secondary Ca+(Na/K)-bearing silicate (pectolite) during pseudowollastonite carbonation under equivalent conditions to those in this work. Other studies on pyroxenes and olivine carbonation demonstrated the formation of secondary crystalline Ca and Mg silicates (King et al., 2010; Sissmann et al., 2013), which fostered carbonation [by the effect of side-reactions](#), as also shown here, but underlined that divalent metal incorporation into the secondary silicates was a handicap for an effective CCS (Monasterio-Guillot et al., 2019). In our case, the observed incorporation of small amounts of Mg in Na-phillipsite will also pose a handicap, yet very limited, for effective carbonation of augite (Table S3).

The amount of Na^+ in Na_2CO_3 runs was double that in NaHCO_3 runs, and orders of magnitude higher than in water runs. However, no Na-aluminosilicates precipitated in the former runs. This is likely due to the low dissolution rates of pyroxenes under strongly alkaline pH, preventing the build-up of sufficient supersaturation at the mineral-fluid interface as to enable Na-phillipsite precipitation despite the higher Na content. The lack of secondary crystalline silicates in Na_2CO_3 solutions during augite carbonation led to the lowest level of replacement and calcite yield. This emphasizes that the formation of secondary silicate phases is crucial to promote carbonation of primary silicates (Monasterio-Guillot et al., 2019).

581 The lack of Na-phillipsite precipitation in diopside runs can be easily explained considering
582 the absence of Al in the elemental composition of this mineral. However, other crystalline
583 secondary Ca and/or Mg silicates could in theory be formed after diopside dissolution at neutral to
584 moderately alkaline pH, as observed for instance after carbonation of olivine (King et al., 2010;
585 Sissman et al., 2013) and wollastonite (Daval et al. 2009a,b). In our **closed** systems, however,
586 diopside shows a lower dissolution rate than augite, as demonstrated by our ICP-OES analyses and
587 the % replacement achieved after 28 days of reaction (Figure 1 and Table 1). Therefore, both the
588 slow kinetics of Si release to the solution, and the limited amount of dissolution pits/pores formed
589 on diopside as to favor heterogeneous nucleation of secondary crystalline silicates, seem to have
590 contributed to the reduced yield of secondary phases observed here at moderately alkaline pH.

591 The contrasting behavior of diopside as compared to augite in Na₂CO₃ solution is also
592 exemplified by the formation of MSH in the case of diopside runs. As indicated above, secondary
593 Mg-bearing silicate phases could be interpreted as a handicap for effective CO₂ capture. However,
594 Rietveld and mass balance analyses showed that carbonation yield of diopside during Na₂CO₃
595 experiments was double than that of water runs, in contrast to augite that reached similar carbonate
596 yield in both runs (Table 1). The formation of MSH after dissolution of a Mg-Ca-pyroxene is not
597 totally unexpected under our experimental conditions, because MSH is stable at moderately alkaline
598 pH (p_H ≈ 7.5) (Bernard et al., 2017). The formation of MSH has been previously reported during
599 olivine carbonation at 170 °C (Sissmann et al. 2013). However, the Mg/Si ratio reported by
600 Sissmann et al. (2013) was **much higher** (Mg/Si = 3.72) as compared to our experimental result
601 (Mg/Si ~ 0.7). We suggest that this difference is due to the molar concentration of Mg in the
602 starting material (double in forsterite than in our pyroxenes), and to the higher dissolution rate of
603 olivine as compared with diopside (Schott et al., 2012). Following Sissmann et al. (2013) and
604 Lothenbach et al. (2015), PHREEQC calculations were performed using talc as a proxy to MSH,

605 showing that such a Mg-rich silicate was supersaturated in the Na_2CO_3 solution and, therefore,
606 precipitation was expected. In this respect, we demonstrate that the precipitation of MSH during
607 diopside carbonation can foster its dissolution leading to enhanced Ca release. This effect helps to
608 explain why a higher amount of calcite was precipitated in this run as compared to the water run
609 (i.e., effect of side reactions). We suggest that the absence of MSH formation in augite during
610 Na_2CO_3 runs is due to the higher dissolution rate of this phase as compared with diopside, resulting
611 in higher compositional gradients at the mineral interface that promoted the formation of Mg-calcite
612 as a Mg sink, instead of a Mg-rich silicate phase. Note that SEM-EDX analysis demonstrates that
613 MSH formation precedes calcite formation on the surface of diopside, showing that the kinetics of
614 dissolution and carbonate precipitation in this system were sluggish.

615 To summarize, our results show that the formation of non-carbonate secondary [precipitates](#)
616 (i.e., Na-phillipsite, hematite, [Magnesium Silicate Hydrates](#) and amorphous silica), fostered the
617 [dissolution and subsequent carbonation](#) of the starting material. Altogether, our experimental results
618 demonstrate that the formation of secondary silicates (and oxides) played a key role [in silicate](#)
619 [carbonation](#) due to the importance of side reactions on enhanced dissolution of primary silicates and
620 on the subsequent effective carbonation (*e.g.*, [Frugier et al., 2008, and references therein](#)).

621 **4.2 Effect of reaction-driven fracturing**

622 There is also another crucial effect associated with the precipitation of secondary phases that
623 strongly contributed to enhance augite and diopside carbonation: reaction-induced fracturing. In all
624 runs where Na-phillipsite precipitated, augite crystals showed massive pervasive fracturing (Figure
625 2d-f and Figure 4b and e), whereas no such massive fracturing was observed in the rest of the
626 reacted crystals, with the exception of diopside run at high pH where some fracturing was observed
627 associated with MSH precipitation. As mentioned above, Na-phillipsite precipitation started in the

(wedge-like) etch pits or pre-existing surface cracks/pores of the host material, and continued by filling cracks generated by the crystallization of this phase. This reaction-driven fracturing is critical for the advancement of the carbonation process, resulting in the highest replacement and carbonate yields observed here. It is also expected to have an impact during GCS not just because Ca-Mg-Al pyroxenes are abundant in target rock-formation, but also because in such formations pore water is typically saline, showing high Na concentrations and neutral-to-moderately alkaline pHs (Matter et al., 2016), and volcanic glass and plagioclase dissolution may act as an additional Al source, which may favor secondary Na-aluminosilicate formation likely resulting in fracturing.

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. The crystallization pressure in pores large enough that curvature effects can be neglected is defined by (Correns, 1949; Scherer 1999; Steiger, 2005),

$$\Delta p = \frac{nRT}{V_m} \ln \frac{IAP}{k_{sp}} \quad (6)$$

where n is the number of ions forming the solid phase, R is the gas constant, T is the temperature, IAP is the ion activity product, k_{sp} is the solubility product (IAP/k_{sp} is the supersaturation, β) and V_m is the crystal molar volume. Eq. (6) shows that Δp depends on supersaturation, which acts as a driving force for crystallization pressure generation (Schiro et al., 2012). In general terms, the free energy change ΔG_r associated with the formation of a new phase within a subcritical crack, such as dissolution pits or pre-existing surface cracks in the pyroxenes, can lead to a significant Δp if a positive molar volume difference ΔV_s exists between the reactant and product phases, as predicted by thermodynamics,

$$\Delta p = - \frac{\Delta G_r}{\Delta V_s} \quad (7)$$

Pressures of up to 300-400 MPa have been predicted using Eq. (7) for common reactions such as olivine replacement by serpentine (Kelemen and Hirth, 2012) or alkali-silica reaction (ASR) in cement (Ichikawa and Miura, 2007).

Failure of materials due to crystallization pressure generation within an elastic material using an energy criterion will take place when the strain energy imposed by the growing crystals is higher than the strain energy obtained during an uniaxial tensile strength test (Espinosa-Marzal et al., 2011), i.e., when $\sigma_c > \sigma_T$, where σ_c is the critical stress and σ_T is the tensile strength. One way to determine σ_c involves the calculation of Δp using Eq. (6). In our experiments, however, the supersaturation at which Na-phillipsite crystallized is unknown, so we cannot calculate σ_c using this approach. However, we can estimate the stress required for the opening of a flaw or subcritical crack (e.g., a notch- or wedge-like dissolution pit or pre-existing crack) following crystallization pressure generation by a newly formed phase in such a confined space using fracture mechanics. The critical stress can be calculated knowing the critical stress intensity (or fracture toughness) of a particular solid, and for a particular flaw geometry. Here, we can consider the case of a semi-circular flaw normal to the face exposed to the solution of a solid of semi-infinite length undergoing internal pressurization (Jacobsen et al., 2015), as the geometry that can best represent surface etch pits and preexisting surface cracks in pyroxene crystals (Figure 9a). In this case and for mode-I fracturing, the stress intensity is (Tada et al., 1993),

$$K_I = \frac{2}{\sqrt{\pi}} (1.211 - 0.186\sqrt{\sin(\theta)}) \sigma \sqrt{c} \quad (8)$$

where σ is the internal stress within the flaw (or tensile stress pulling apart the surfaces of the flaw), c is the radius of the semicircular flaw, and θ is the angle of the flaw with respect to the solid surface. For a crack normal to the surface, the peak stress is at $\theta=\pi/2$, and the critical stress to reach the critical stress intensity K_{Ic} is (Jacobsen et al., 2015),

$$\sigma_c \cong \frac{K_{Ic}}{1.156\sqrt{c}} \quad (9).$$

Because no actual K_{Ic} value for augite single crystals has been reported, we have calculated K_{Ic} according to the Griffith's criterion for a brittle material under plane strain using the equation (Griffith, 1920),

$$K_{Ic} = \sqrt{\frac{2E\gamma}{1-\nu^2}} \quad (10)$$

where E is the Young modulus, ν is the Poisson ratio, and γ is the surface energy (2γ is the energy required to create new surfaces at the crack tip). In the case of augite, the reported values of E and ν are 143.76 GPa (Aleksandrov et al., 1964) and 0.25 (Ji et al., 2009), respectively. Due to the scarcity of (reliable) reported values for γ of augite, we have used two different ones which help us to establish a lower and upper bound of K_{Ic} for this pyroxene. The values are: 0.4 J m⁻² reported for augite by Miller (2010), and the theoretical value of 1.19 J m⁻² for augite calculated using the equation (Gilman, 1960),

$$\gamma = \frac{Ea^2}{d_0\pi^2} \quad (11)$$

where a is the atomic radius (or interatomic distance) of the atoms laying in the cleavage plane (here this value is taken as the average bond distance between oxygen and metal cations in M1 (*i.e.*, Al, Fe, Ti) and M2 (*i.e.*, Ca, Mg) positions, equal to 2.28 Å; Cameron and Papike, 1981), and d_0 is the d -spacing of $\{hkl\}$ cleavage planes (*i.e.*, weakest bond) in a particular crystal, which is d_{110} = 6.42 Å for the main $\{110\}$ cleavage planes of augite. The fact that the theoretical value of γ for augite calculated using Eq. (11) is nearly identical to the surface energy value of 1.2 J m⁻² reported for aegirine (Li et al., 2019) give us confidence about the reliability of our calculation method. Note that augite and aegirine are isostructural and form a solid solution, so it is not unexpected for their surface energy values to be very similar. Using the γ values 0.4 and 1.19 J m⁻², Eq. (10) yields the

696 following K_{Ic} values: 0.35 MPa m^{1/2} and 0.61 MPa m^{1/2}, respectively. For comparison, we have also
697 considered the K_{Ic} value of 1.28 MPa m^{1/2} reported for a diopside ceramic (Herman and Krzos,
698 2009). With the exception of the lowest value, the rest fall within the range of K_{Ic} values reported
699 for common silicate single crystals including olivine, quartz, feldspars, garnets and Al₂SiO₅
700 polymorphs (Atkinson, 1984; Whitney et al., 2007).

701 Figure 9b shows the variation of the critical stress (σ_c) vs. the radius of the semicircular flaw
702 (c) calculated using Eq. (9), for the three K_{Ic} values indicated above. Using the measured value of c
703 = 32±3 µm for the case of augite subjected to crack opening following precipitation of Na-
704 phillipsite in wedge-like each pits (measurements performed on SEM images, see Figure 9c-e), and
705 the three K_{Ic} values above indicated (ordered from lowest to highest value), Eq. (9) yields values of
706 σ_c equal to 53±6, 93±10, and 196±20 MPa, respectively. The first value is rather low, likely because
707 the low surface energy reported for augite by Miller (2010) using contact angle measurements is
708 affected by surface reaction during measurement (i.e. SiO_{2am} formation). The σ_c value obtained for
709 the case of the augite ceramic is likely higher than that expected for a single crystal, as
710 monomineralic aggregates tend to have higher K_{Ic} values than single crystals (Van Noort et al.,
711 2017). The σ_c value obtained using the calculated surface energy for augite seems to be the most
712 realistic. Despite the uncertainties in the above reported values of critical stress σ_c , values in the
713 order of 100 MPa are apparently necessary for fracture opening in augite single crystals, meaning
714 that crystallization of Na-phillipsite has to exert Δp values higher than ~100 MPa within dissolution
715 pits or preexisting cracks on the surface of augite crystals.

716 Our analysis yields σ_c values of the same order of magnitude, but smaller than those
717 calculated for reaction-driven fracturing associated with olivine serpentinization (~300 MPa)
718 (Kelemen and Hirth, 2012; Plummer et al., 2013). In any case our calculated σ_c values are
719 necessarily larger than the tensile strength of (unconstrained) augite crystals, otherwise no reaction-

720 driven fracturing would have been observed. Note that while the theoretical maximum tensile
721 strength for a crystal is $\sim E/10$ (i.e., ~ 15 GPa for augite), the actual value is typically much lower
722 because of the presence of flaws (Idrissi et al., 2016), explaining why fracturing of augite is
723 observed under the calculated σ_c values. To the best of our knowledge, the tensile strength of augite
724 single crystals has not been reported. However, a spalling fracture stress of 58 MPa (equivalent to
725 tensile strength failure under very high strain rates) has been reported for an augite-rich (65%)
726 peridotite (He et al., 1996). This stress can be considered as a lower bound for the stresses actually
727 resulting in fracturing of our augite single crystals upon Na-phillipsite crystallization.

728 Using Eq. (6), and the most reliable critical stress of 93 MPa obtained here using fracture
729 mechanics, a supersaturation $\beta = 2.69$ for Na-phillipsite ($\text{NaAlSi}_3\text{O}_8 \cdot 3\text{H}_2\text{O}$, $n = 4$, and $V_m = 149.69$
730 $\text{cm}^3\text{mol}^{-1}$; data from Blanc et al., 2015) crystallization within augite is obtained (at 423 K). Such a
731 relatively high, yet reasonable β value, corresponding to a SI_{phi} of 0.42, underlines that the
732 supersaturation that can be reached at the mineral-solution interface during an ICDP process can be
733 significantly high, even when the bulk system is undersaturated to a particular phase, as shown here
734 by our PHREEQc modeling. If we consider a lower bound for the crystallization pressure equal to
735 the dynamic tensile strength of augite-rich peridotite (58 MPa), then a β value of 1.85 is calculated
736 from Eq. (6), which also demonstrates that for fracture generation a significant but reasonable
737 supersaturation has to be generated at the mineral-solution interface in dissolution pits. Still, there is
738 a potential problem regarding the calculated crystallization pressure: for a crystal to transmit such a
739 pressure to a confining surface, a fluid (few nm thick) has to exist between the crystal and the
740 confining surface, so that a disjoining pressure must exist that is at least equal to such a
741 crystallization pressure (Scherer, 2004). It is not clear whether a fluid would not be squeezed out
742 leading to direct contact between the crystals and the confining wall under a crystallization pressure
743 of several tens or even hundred MPa, so that no crystallization pressure can be transmitted. In this

744 respect, Zheng et al. (2018) report that confining pressures higher than 30 MPa prevented reaction-
745 induced fracturing during the hydration of MgO (which can in theory generate crystallization
746 pressure values of over 1 GPa). This was interpreted assuming that the liquid was squeezed out of
747 the reaction interface, and no disjoining pressure could be developed. Yet, this could be also due to
748 relaxation of crystallization pressure through viscous creep due to the fact that brucite is a
749 mechanically weak mineral. Disjoining pressures higher than 75 MPa have been predicted by
750 Renard and Ortoleva (1997) to explain pressure solution at crustal depth of over 5 km. It can thus be
751 argued that in our experiments effective disjoining pressures of the same order of magnitude of
752 predicted crystallization pressures can be attained. Alternatively, it could be argued that a
753 significantly lower crystallization pressure (few tens of MPa) could easily develop in our system,
754 and generate stress on the surrounding confining fluid within an etch pit as to trigger a phenomenon
755 of stress corrosion (Ciccotti, 2009), enabling the opening of a crack at the tip of wedge-like
756 dissolution pits or pre-existing cracks at crystallization pressures significantly lower than those
757 calculated here.

758 Once crack opening has taken place, further propagation of the cracks would take place by
759 additional crystallization of Na-phillipsite within such a constrained space, provided that such a
760 phase crystallizes at a sufficiently high supersaturation. The fact that our SEM and micro-CT
761 images show augite crystals cross-cut by fractures completely filled by Na-phillipsite, leading to a
762 very wide fractures (widths of more than several tens of μm) is direct evidence that crystallization
763 pressure was exerted, enabling fracture propagation. This should be facilitated by the fact that once
764 fractures have been opened, the effective bulk modulus will be a fraction of the modulus of the
765 intact crystal.

766 A similar approach could be used to calculate the effective pressure and supersaturation at
767 the onset of MSH crystallization within diopside crystals, leading to its fracturing. In this case,

768 however, the level of reaction-driven fracturing was more limited (i.e., no large, cross-cutting
769 fractures were observed), but in any case, reaction-driven stresses larger than the tensile strength of
770 diopside had to be generated to produce the observed fractures filled by MSH. Because MSH is an
771 amorphous gel-like material, and its solubility should be relatively high, a sufficient high
772 supersaturation as to create enough crystallization pressures to fracture diopside is unlikely.
773 However, it could be argued that fracturing takes place not by crystallization pressure generation,
774 but most likely via an expansion mechanism similar to that observed for ASR resulting in cement
775 fracturing (Rajabipour et al., 2015). Amorphous silica gel hydration can reportedly result in
776 pressures of over 20-30 MPa (Reinhardt and Mielich, 2012) and, in theory, pressures of up to 400
777 MPa could be generated during alkali-silica reaction (ASR, Ichikawa and Miura, 2007). If a stress
778 corrosion effect takes place concurrently, fracture opening and propagation would likely take place
779 even at the relatively low gel hydration pressures above indicated.

780 Large amounts of calcite were identified within fractures generated in the NaHCO_3 system
781 during augite carbonation. It could therefore be argued that calcite crystallization also contributed to
782 fracture generation, as reported for newly formed carbonates during primary silicate mineral
783 carbonation (Kelemen et al., 2011; Kelemen and Hirth, 2012). However, due to the no contact
784 between calcite and the fracture walls cross-cutting augite crystals observed in the Micro-CT
785 analyses (Figure 4e), as well as SEM-EDS (Figure 4b) results showing that Na-phillipsite is directly
786 in contact with augite walls, whereas calcite precipitated on the surface of the pyroxene and in
787 contact with the newly formed zeolite, we conclude that calcite did not generate the cracks but
788 likely contributed to their widening.

789 The fact that no pervasive fractures were observed in any other experiments despite the
790 precipitation of calcite and amorphous silica, demonstrates that the supersaturation at the onset of
791 crystallization of these phases within preexisting cracks and newly-formed dissolution (wedge-like)

etch pits was not high enough to generate an effective pressure higher than the tensile strength of the pyroxene crystals. Similarly, possible expansion due to amorphous silica gel by a process similar to ASR, was not sufficient to create any fracturing.

In addition to the above-mentioned mechanisms, other reaction-driven fracturing mechanism have been proposed. Jamtveit et al. (2000) explored the idea that fracture generation was caused by tensile stress generation due to solid volume decrease during mineral dissolution. However, this kind of process is ruled out here based on the absence of fracture generation during augite and diopside reactions in runs where no Na-phillipsite or MSH precipitated, but still dissolution occurred and a certain degree of replacement was obtained. Zhu et al. (2016) suggested that volume expansion of carbonated areas in porous granular aggregates of olivine, could induce tensile stresses and associated fracturing in non-reacted areas resulting in a crack pattern very similar to drying-cracks. However, such an effect is not observed in any of our experiments. Note that Zhu et al. (2016) experiments showed intergranular cracks whereas our experiments resulted in intragranular cracks.

Typically, precipitation of newly formed phases during replacement reactions such as silicate carbonation can passivate the reaction by decreasing the reactive surface area in turn reducing porosity and permeability (e.g. Emmanuel and Ague, 2011; Di Lorenzo and Prieto, 2017). Dissolution processes without crack development can create porosity and increase the reactive surface area (Lafay et al., 2018), especially if wormholing (channelized dissolution) takes place (Ott and Oedai, 2015). However, our results show that in the case of the studied pyroxenes, dissolution without pervasive cracking does not enable a significant advance of the replacement reaction. Conversely, our results demonstrate that reaction-driven fracturing due to crystallization pressure generation (Scherer, 1999; Schiro et al., 2012) likely associated with stress corrosion, or amorphous MSH gel expansion, is critical for the advance of silicate dissolution and carbonate precipitation,

because it increases the permeability of the substrate and the available reactive surface area (Kelemen et al., 2011; Kelemen and Hirth, 2012).

4.3. Origin of the differences in carbonation behavior of diopside and augite

Despite their very similar chemical composition and structure, augite and diopside display a very different dissolution and carbonation behavior. In particular, a systematically higher extent of augite dissolution and carbonation was observed (Table 1). Previous studies showed that augite has a higher dissolution rate than diopside over a whole range of pHs (McAdam et al., 2008; Schott et al., 2012). Furthermore, previous works on dissolution of iron-bearing pyroxenes (Siever and Woodford, 1979; Hoch et al., 1996) showed that they present a higher dissolution rate than non-iron-bearing pyroxenes due to the formation of highly insoluble Fe-oxides and hydroxides that shift the equilibrium to the product side. In particular, Hoch et al. (1996) showed that the higher dissolution rate of augite as compared with diopside was related to the oxidation of iron present in higher amounts in the former clinopyroxene. Our augite crystals include 2.3 mol% Fe, while diopside includes 1.7 mol% Fe. The higher Fe content in augite likely contributed to its faster dissolution according to the effect indicated above. Furthermore, we suggest that the presence of Na and Al in augite contributed both to a faster release of divalent metals and silicate species to the solution and to the formation of secondary Na-aluminosilicates, thereby increasing the overall dissolution rate of this pyroxene (Berger et al., 1994). Altogether, our results suggest that the presence of Al and the faster and ultimately higher release of Si, Fe, alkali, and alkaline-earth metals to the solution in the case of augite fostered, on the one hand, the shift of the dissolution-carbonation reaction to the products side and, on the other hand, the precipitation of secondary phases in etch pits and surface pores/cracks at a sufficiently high supersaturation as to generate

839 crystallization pressure sufficient to result in massive fracturing and a significant increase in
840 reactive surface area. These two effects created a strong positive dissolution-precipitation feedback-
841 loop in the case of augite, which was not so strong in the case of diopside, thereby explaining the
842 observed higher conversion and carbonate yield.

843 **5. Conclusions**

844 The implications of the results obtained during this work are manifold. A critical aspect highlighted
845 by our results is the important role of secondary phase precipitation on the advancement of the
846 reactions, not contemplated in the conversion of pyroxenes into carbonates. The formation of
847 secondary iron oxides and crystalline and amorphous secondary silicates provides a free energy
848 contribution to the system, allowing the progress of the carbonation reaction. The high amounts of
849 secondary phases observed in augite experiments with DIC in solution enhanced the progress of the
850 reaction as compared with pure water, while in diopside systems, the small amount of secondary
851 phases did not enhance this progress. These results show that the presence of DIC in the system is
852 crucial for the progress of the reaction, acting as a generator of secondary phases that contribute to
853 shift the reaction towards the product side, but the effectiveness of this process is strongly
854 dependent of the specific crystal chemistry of the pyroxenes.

855 Also, we show the formation of secondary phases filling dissolution pits and fractures whose
856 precipitation was, in theory, thermodynamically not possible in our systems. This demonstrates that
857 these latter transformations could only be achieved by an interface-coupled dissolution-precipitation
858 mechanism, [where supersaturation with respect to specific phases could be reached at the interface](#)
859 [between the mineral and the solution \(Putnis 2009, Putnis 2014, Ruiz-Agudo et al. 2012, 2016\).](#)

860 Another important outcome of this work was the effect of pH in the systems' evolution. The
861 advancement of the reaction was strongly pH-dependent, showing higher dissolution rates in

862 moderately-alkaline than in strongly alkaline pH systems. This effect has a direct impact on the
863 formation of secondary phases, fostering their precipitation in large amounts in the former case and
864 hampering the progress of the reaction in the latter.

865 Our experimental results also demonstrate that the in-pore crystallization of secondary
866 crystalline phases (Na-phillipsite) and, to a lesser extent amorphous ones (MSH), is responsible of
867 the fracture generation and propagation during dissolution-carbonation processes. We show that the
868 reaction-driven fracturing derives from crystallization pressure, and in the case of MSH, most likely
869 due to gel expansion. In both cases stress corrosion should also contribute to the observed crack
870 development. Reaction-driven fracturing is shown to be crucial for the progress of the
871 dissolution/carbonation reaction, because it exposes fresh reactive mineral surface and enables fluid
872 transport within pyroxene crystals. The calculated critical stress for pyroxene (augite) fracture is
873 ~100 MPa. This value implies that fracturing will likely occur during clinopyroxene carbonation in
874 real GCS scenarios, down to a depth of ~4 km, when the lithostatic pressure equals such pressure.
875 Note that if the lithostatic pressure (plus pore fluid pressure) were higher than the stress associated
876 to secondary silicate formation, then no fracturing would take place (Malvoisin et al., 2017). Our
877 results therefore show that reaction-driven fracturing of pyroxenes would be a major contributor to
878 CO₂ mineral capture during standard low-to-medium depth GCS.

879 Finally, we experimentally demonstrate that the amount of Al, Fe (and Na) ions in the
880 pyroxenes has a strong effect during dissolution-carbonation processes, explaining why augite,
881 which includes a higher Fe, Na, and Al content than diopside, shows the highest dissolution rate and
882 the highest conversion and carbonate yield.

883 Altogether, these results provide relevant information to be considered for the enhancement
884 of the GCS using silicate carbonation strategies. In particular, this study sheds light on the

importance of the silicate mineral composition of rock formations during *in situ* CCS, showing the importance of secondary (alumino)silicate formation on reaction-driven fracture development, providing flow channels and fresh reactive surface areas to improve the carbonation reaction.

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Figure 1. Chemistry of solutions during augite and diopside dissolution and carbonation. Error bars show standard deviation of both replicas. Total concentration of aqueous calcium (a), magnesium (c) and silicon (e) in augite experiments; Total concentration of aqueous calcium (b), magnesium (d) and silicon (f) in diopside experiments; pH of augite (h) and diopside (i) experiments. Solid lines are used as a guide to the eye.

Figure 2. Products of the reaction of augite in water (pH 7.5): (a) XRD patterns of reacted augite, unreacted augite and reference phases (Mg-calcite, Na-phillipsite and Iron Oxide) . (b) Time evolution of crystalline phases content determined by XRD Rietveld analyses (Error bars show standard deviation of both replicas). (c) μ -Raman spectra of precipitated calcite (cal, blue) and hematite (hem, red) crystals. (d) Low-magnification SEM image of augite crystal after 28 days reaction. (e) SEM image overlaid with EDS compositional map showing a detail of the augite (aug) crystal fractured after 28 days reaction, with Na-phillipsite (phi) filling the fractures. (f) Micro-CT image showing in red the 3D distribution of amorphous silica (SiO_2) and in green the Na-phillipsite (phi) in augite crystal after 28 days reaction. The red dashed line in the left image represents the virtual cut performed to observe the interior of the newly-formed filled fracture, shown in the right image

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1165 **Figure 3.** Products of the reaction of diopside in water (pH 7.5): (a) Time evolution of the
1166 crystalline phases content determined by XRD Rietveld analysis (error bars show standard
1167 deviation). (b) SEM-EDS compositional map showing calcite (Cal) crystals in the dissolution pits of
1168 diopside (Di) after 14 days reaction. (c) SEM image and EDS compositional variation of Ca, Si and
1169 C along the red line in (b). (d) μ -Raman spectra of calcite crystal formed on our experiment, along
1170 with that of calcite reference (RRUFF database). (e) SEM-EDS compositional map showing
1171 diopside (Di) after 28 days of reaction including a Si-bearing phase (SiO_2) inside a dissolution pit
1172 and on the surface of the pyroxene. The inset shows the SEM image of the reacted diopside crystal.

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Figure 4. Products of the reaction of augite in NaHCO_3 solution: (a) Time evolution of the crystalline phases content determined by XRD Rietveld analysis (error bars show StDev). (b) SEM image of augite (aug) crystal after 28 days of reaction, overlaid with EDS compositional map showing phillipsite (phi) and a few crystals of calcite (cal) inside the fractures and on the augite surface. The inset shows the SEM image of the reacted crystals displaying pervasive cracking. (c) SEM-EDS compositional map showing calcite (cal) crystals on the surface of augite (aug) and iron oxides (Fe-Ox) in dissolution areas. (d) μ -Raman spectra of newly formed calcite (the spectra of reference calcite -RRUFF database- is also shown). (e) Micro-CT image showing in red the 3D distribution of phillipsite (phi) and in purple that of calcite (cal) in an augite crystal after 28 days of reaction. The red dotted line on the left image represents the virtual cut displayed on the right image.

1205 **Figure 5.** Products of the reaction of diopside in NaHCO_3 solution: (a) Time evolution of the
1206 crystalline phases determined by XRD Rietveld analyses (error bars show StDev). (b) μ -Raman
1207 spectra of calcite crystal formed after 28 days reaction (labeled Cal/Di), along with reference
1208 spectra (RRUFF database) of calcite and diopside for comparison. (c) SEM-EDS compositional map
1209 showing magnesium calcite crystals (cal) and diopside (di) after 28 days of reaction. EDS spectra of
1210 Mg-calcite in inset. (d) SEM-EDS compositional map showing calcite (cal) crystals inside the
1211 fractures of the diopside (di) and iron-oxide particles on the surface (Fe-Ox). The inset shows the
1212 reacted pyroxene crystal.

Figure 6. Products of the reaction of augite in Na_2CO_3 solution: (a) Time evolution of the crystalline phases content determined by XRD Rietveld analyses (error bars show StDev). (b) SEM-EDS compositional map of 28 days reacted augite (aug) showing calcite (cal) crystals inside (pre-existing) surface fractures and iron oxides (Fe-Ox) lining the fracture walls. (c) SEM image of the entire crystal after reaction. (d) Micro-CT image showing the 3D distribution of calcite (purple) in augite crystal after 28 days of reaction. The red dashed line in the left image represents the virtual cut performed to observe the inside of the crystal, shown in the right image. Note: the white bright inclusions are rutile (detected by XRD).

Figure 7. Products of the reaction of diopside in Na_2CO_3 solution: (a) SEM-EDS compositional map showing a proto magnesium silicate hydrate (MSH) and calcite particles (cal) on the surface of diopside (di). The right SEM image shows the entire crystal after reaction. (b) SEM-EDS compositional map showing MSH in the dissolution pits and fractures of diopside (di) with calcite crystals (cal). (c) Micro-CT image showing the 3D distribution of MSH (red) and calcite (purple) in diopside crystal after 28 days of reaction. The red dashed line in the left image represents the virtual cut performed to observe the inside of the crystal, shown on the right image. (d) FTIR spectra of the diopside before and after 28 days reaction in Na_2CO_3 solution. (e) μ -Raman spectra of the diopside reacted 28 days in Na_2CO_3 solution showing the bands corresponding to MSH (Lothenbatch et al., 2015) and the spectrum of diopside from RRUFF database.

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1251 **Figure 8.** PHREEQC simulations of saturation index (SI) evolution vs. pH for calcite and sodium
1252 zeolite during augite mineral replacement reaction at equilibrium. The red dashed line represents
1253 equilibrium (i.e., SI = 0).

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Figure 9. Fracture mechanics of carbonated augite crystals. (a) Scheme of the case of a semi-circular flaw normal to the face exposed to the solution of a solid of semi-infinite length undergoing internal pressurization (σ = stress; θ =angle between the flaw plane and the xz plane; r = radius of the flaw). (b) Critical stress (σ) for fracture opening vs. c (flaw radius) for different values of augite fracture toughness (green curve= $0.35 \text{ MPa m}^{1/2}$, blue curve= $0.61 \text{ MPa m}^{1/2}$, and red curve= $1.28 \text{ MPa m}^{1/2}$). The blue-shaded vertical bar marks the average depth ($\pm\text{SD}$) of etch pits (i.e., flaw radius c in (a)) in augite filled with Na-phillipsite. (c) SEM image of augite subjected to 7 days reaction in NaHCO_3 solution showing etch pits (red circles) where cracks are formed at their tips. (d) Detail of an etch pit filled with Na-Phillipsite, showing a crack originating at the pit tip. (e) Detail of cracks emerging from the tip of an etch pit filled with Na-Phillipsite.

Tables

Table 1. Results of the quantitative Rietveld analysis (wt%) after normalization to amorphous phase content determined using mass balance analysis. Data for pyroxene samples after 28 days of reaction. The last two columns report the extent of carbonation (i.e., mass fraction of pyroxene converted into calcium carbonate) calculated using Rietveld refinement (ξ_n^{RR}) and mass balance (ξ_n^{MB}).

Reactant	Augite	Diopside	Phillipsite-Na	Hematite	Calcite	SiO ₂	MSH	ξ_n^{RR}	ξ_n^{MB}
Water	83.97		9.86	0.85	2.61	2.16		0.0016	0.0018
NaHCO ₃	61.93		12.39	2.01	21.71	2.09		0.1669	0.1842
Na ₂ CO ₃	96.34		0	1.05	2.65			0.0131	0.0147
Water		96.73		0.37	1.23	1.62		0.0004	0.0004
NaHCO ₃		86.32		0.81	11.5	1.27		0.0328	0.0379
Na ₂ CO ₃		93.09			2.13		5.01	0.0011	0.0012

Table 2. Free energy (kJ.mol⁻¹) values for all experiments calculated using PREEQC and experimental values obtained by ICP-OES of the ionic concentration in solution and measured pH after each experiment.

		Time (days)		
Mineral	Reactant	7	14	28
Diopside	Water	-39.37	-45.93	-6.16
	NaHCO ₃	-61.49	-64.08	-59.06
	Na ₂ CO ₃	-20.17	-28.11	-157.65
Augite	Water	-43.99	-51.28	-16.28
	NaHCO ₃	-74.04	-84.90	-80.61
	Na ₂ CO ₃	-38.64	-46.50	-179.52

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