



## Do carbonate precipitates affect dissolution kinetics? 2: Diopside

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### ABSTRACT

Diopside dissolution rates were measured in mixed-flow reactors at neutral and basic pH at 25 °C and 70 °C. Experiments were performed in aqueous solutions 1) supersaturated with respect to calcite for up to 63 days, and 2) strongly undersaturated with respect to calcite and other secondary phases for up to 164 days. Inlet solutions were comprised of NaHCO<sub>3</sub>, CaCl<sub>2</sub>, NH<sub>4</sub>Cl, NaOH, and/or HCl with ionic strengths ranging from 0.01 to 0.09 mol/kg. In the experiments performed at 25 °C, calcite nucleated and grew extensively on both the diopside surfaces, and as <1000 μm discrete crystals in experiments performed in CO<sub>2</sub>-bearing inlet solutions but no precipitates were formed on or adjacent to the diopside in experiments performed in CO<sub>2</sub>-free inlet solutions. Measured diopside dissolution rates in calcite precipitating experiments at 25 °C based on Si are both 1) time independent, and 2) equal to that of corresponding control experiments performed in NaHCO<sub>3</sub>-free inlet solutions. These observations indicate that diopside dissolution rates are unaffected by the simultaneous precipitation of calcite. Calcite likely forms a porous coating on diopside, which allows ions from the dissolving diopside to be transported readily to the bulk fluid. It seems therefore likely that carbonate precipitation will not slow pyroxene dissolution during carbon storage efforts.

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### 1. Introduction

A large number of recent studies have been aimed at providing the scientific basis for the in-situ carbonatization of CO<sub>2</sub> in an effort to attenuate the consequences of anthropogenic carbon emissions (e.g. Oelkers and Schott, 2005; McGrail et al., 2006; Wolff-Boenisch et al., 2006; Marini, 2007; Matter et al., 2007; Goldberg et al., 2008; Kelemen and Matter, 2008; Oelkers and Cole, 2008; Oelkers et al., 2008; Schaefer and McGrail, 2009; Schaefer et al., 2009, 2010, 2011; Wakahama et al., 2009; Flaathen et al., 2010; Gislason et al., 2010; Alfredsson et al., 2011; Aradóttir et al., 2011; Gysi and Stefansson, 2011; Matter et al., 2011; Rudge et al., 2011; Wolff-Boenisch et al., 2011; Aradóttir et al., 2012a, b; Gysi and Stefansson, 2012a,b,c). In-situ CO<sub>2</sub> carbonatization is promoted by the dissolution of silicate rocks that release divalent metal cations such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Fe<sup>2+</sup> to the fluid phase. These ions can react with dissolved CO<sub>2</sub> and precipitate as carbonate minerals. The rate-limiting step for CO<sub>2</sub> carbonatization is commonly thought to be the release of divalent cations (c.f., Oelkers et al., 2008). As such, any process that can potentially slow the dissolution rates of divalent metal bearing silicate minerals, such as secondary carbonate precipitation, could be detrimental to carbon storage efforts.

The dissolution rates of minerals and glasses are commonly believed to be proportional to their interfacial surface area (e.g. Pačes, 1983; Helgeson et al., 1984; Lasaga, 1984; Siegel and Pfannkuch, 1984; Schott and Oelkers, 1995; Oelkers, 2001; Schott et al., 2009). It seems likely therefore, that the precipitation of secondary phases, such as calcite during subsurface carbon storage efforts, could potentially decrease the dissolution rates of those phases on which they precipitate. Such precipitates could, therefore, be detrimental to mineral carbonatization efforts. This study is aimed at determining the extent to which diopside dissolution rates are affected by calcite precipitation on its surfaces. Towards this goal, diopside has been dissolved for up to 5 months in aqueous fluids that are either supersaturated or undersaturated with respect to calcite. The goal of this paper is to report the results of this experimental study and to use these results to assess the degree to which carbonate precipitation on silicate minerals might affect the efficiency of subsurface carbon storage efforts.

Diopside was chosen for this study of the potential effect of mineral coatings on mineral carbonation efforts for three major reasons. First, pyroxenes are an important source of the divalent cations required for mineral carbonation. Second, the presence of Ca in diopside could promote calcite precipitation during the experiments. Third, extensive studies of diopside dissolution are available in the literature for comparison (e.g. Schott et al., 1981; Eggleston et al., 1989; Knauss et al., 1993; Chen and Brantley, 1998; Golubev et al., 2005; Golubev and Pokrovsky, 2006; Dixit and Carroll, 2007; Daval et al., 2010). Knauss et al. (1993)

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reported diopside dissolution rates as a function of pH at 25, 50, and 70 °C. Measured diopside dissolution rates decrease with increasing pH to at least pH ~ 7. At higher pH, rates are either pH independent or decrease weakly with increasing pH (Knauss et al., 1993; Golubev et al., 2005). Chen and Brantley (1998) reported diopside dissolution rates as a function of pH at 25 and 90 °C; these rates also decrease with increasing pH at pH < 7 but they are approximately one order of magnitude lower than corresponding rates reported in other studies. Chen and Brantley (1998) suggested that this difference was most likely due to their rates being normalized to the BET surface area of the post-experiment powders, whereas the majority of other studies normalized rates to the BET surface area of the initial solids. Knauss et al. (1993) reported that diopside dissolution rates are independent of aqueous CO<sub>2</sub> concentration. Daval et al. (2010) found that diopside dissolution rates varied significantly as a function of solution saturation state ( $\Delta G_r$ ) at acidic conditions and 90 °C.

A number of past studies have focused on the effect of mineral coatings on the dissolution rates of divalent metal bearing silicates, in part due to the significance of this process to the carbonatization of ultramafic and mafic rocks. These studies include efforts on basaltic glasses (Gysi and Stefansson, 2011; Stockmann et al., 2011; Gysi and Stefansson, 2012a,b,c), crystalline basalts (McGrail et al., 2006; Schaefer et al., 2009, 2010, 2011), wollastonite (Daval et al., 2009a,b), olivine (Giammar et al., 2005; Béarat et al., 2006; Andreani et al., 2009; Daval et al., 2011), serpentine (Park and Fan, 2004), and anorthite (Hodson, 2003). These past studies provide ambiguous results; in some cases dissolution rates are unaffected by coatings, but in others significant effects are observed. The presence of carbonate precipitates on basaltic glass (Stockmann et al., 2011), olivine (Giammar et al., 2005), and wollastonite at acidic pH conditions (Daval et al., 2009a) was reported to have no effect on the dissolution rates of the primary minerals as these coatings formed discontinuous and porous layers. Similarly, Hodson (2003) observed that the presence of discontinuous iron-rich coatings had little effect on anorthite dissolution rates. In contrast, Daval et al. (2011) reported that olivine dissolution rates decreased by two orders of magnitude by the presence of an amorphous silicate layer. Daval et al. (2009a,b) reported that wollastonite dissolution rates were significantly decreased at neutral and basic conditions due to the presence of a surface coating consisting of amorphous silica and calcite. Park and Fan (2004) suggested that the presence of silica-rich layers inhibited serpentine dissolution rates. Both Béarat et al. (2006) and Andreani et al. (2009) reported that silica-rich layers on dissolving olivine surfaces slowed carbonate formation, and inhibited olivine dissolution. Based on the results of the experiments mentioned above and those of Cubillas et al. (2005), it seems likely that crystallographic properties might play an important role in this process, especially during the early stages of dissolution–precipitation. Cubillas et al. (2005) showed that CaCO<sub>3</sub> dissolution rates were strongly affected by otavite (CdCO<sub>3</sub>) precipitation on its surface because there was a close structural match between the dissolving and precipitating phases. Putnis (2009) noted that the replacement of one mineral by another is closely related to the degree of epitaxy between the product phase and the parent surface, their molar volumes, and the relative solubilities of the phases involved. Similarly, Velbel (1993) emphasized that the molar volume ratio of product to reactant has to be > 1 to provide the volume needed to completely passivate the reactant surface. This study aims to provide further insight into this coupled process through a series of diopside dissolution experiments performed in the presence and absence of co-precipitating calcite.

## 2. Materials and methods

The standard state adopted in this study is that of unit activity of pure minerals and H<sub>2</sub>O at any temperature and pressure. For aqueous species other than H<sub>2</sub>O, the standard state is unit activity of the species in a hypothetical 1 mol/kg solution referenced to infinite dilution at any temperature and pressure. All thermodynamic calculations reported in

this study were performed using the PHREEQC 2.17 computer code (Parkhurst and Appelo, 1999) together with its llnl.dat database.

The diopside crystals used in this study were obtained from the Transbaikal region of Russia and are identical to those studied by Golubev et al. (2005) and Golubev and Pokrovsky (2006). Golubev et al. (2005) determined the chemical composition of the diopside to be: Ca<sub>0.99</sub>Mg<sub>0.98</sub>Fe<sub>0.02</sub>Cr<sub>0.01</sub>Si<sub>2</sub>O<sub>6</sub> with minor amounts of Al<sub>2</sub>O<sub>3</sub> (0.15 wt.%), MnO (0.03 wt.%), Na<sub>2</sub>O (0.4 wt.%), and TiO<sub>2</sub> (0.03 wt.%).

Prior to the experiments, the diopside crystals were reacted in concentrated HCl for several hours to remove impurities from the crystal surfaces. Following this acid cleaning, the diopside crystals were rinsed with MilliQ™ water and dried at 60 °C before being crushed with an agate mortar and pestle. After crushing, the material was sieved and the 45–125 μm size fraction was obtained. Fine particles were removed from this powder by ultrasonically cleaning in acetone. Several ultrasonic cleaning cycles were performed and the ultra-fine suspension was discarded at the end of each cycle. The cleaning cycles were repeated until the discarded fluid phase appeared clear. The resulting diopside powder was dried overnight at 60 °C. A representative Scanning Electron Microscope (SEM) image of this diopside powder is displayed in Fig. 1a, and this image shows the resulting diopside powder to be free of fine particles. All SEM images in this study were performed using a LEO Supra 25, JEOL 6360 LV or a HITACHI S3400N Scanning Electron Microscope after particles were coated with a fine gold layer. Further analysis of the solids in this study was performed using an Oxford Instruments INCA Energy Dispersive X-ray Spectrometer (EDS), and an INEL CPS 120 X-ray diffractometer (XRD).

The specific surface area of the cleaned dried diopside powder is 1013 ± 40 cm<sup>2</sup>/g as determined by 3-point krypton adsorption using the BET method. Golubev et al. (2005) reported a BET specific surface area of 1250 ± 20 cm<sup>2</sup>/g for their cleaned 50–100 μm size fraction of this diopside; Golubev and Pokrovsky (2006) reported a BET specific surface area of 1045 ± 50 cm<sup>2</sup>/g for their cleaned 100–200 μm size fraction of this diopside. The average density of diopside, as reported by Klein (2002), is 3.27 g/cm<sup>3</sup>. Taking account of this density and equations reported by Wolff-Boenisch et al. (2004a), the geometric surface area of the diopside used in this study,  $A_{geo}$ , is calculated to be 234 cm<sup>2</sup>/g. Dividing the BET surface area by this geometric surface area yields a roughness factor of 4.3.

The mixed-flow reactor system used in this study is illustrated in Fig. 2. This reactor system is similar to that used in past dissolution rate measurement studies (e.g., Wolff-Boenisch et al., 2004a,b; Cubillas et al., 2005; Pokrovsky et al., 2005; Chairat et al., 2007; Gautelier et al., 2007). The physical and chemical conditions of the experiments performed in this study were identical to those of basaltic glass experiments described in Stockmann et al. (2011). All reactors, connectors, and tubing were cleaned in a 0.1 M HCl bath for ~24 h and rinsed with MilliQ™ water prior to each experiment. All outlet fluid sample bottles went through the same cleaning procedure prior to sampling to prevent contamination. Diopside dissolution experiments were initiated by placing between 5 and 10 g of cleaned diopside powder and a quantity of the selected inlet solution into the 300 mL polyethylene mixed-flow reactors. These reactors were sealed and placed into a temperature controlled water bath. Temperature was kept constant during the experiment at either 25 or 70 °C. Teflon® coated floating stir-bars from Nalgene™ were placed on the bottom of the reactors and rotated at ~300 rpm using a multi-position magnetic stirrer located underneath the water bath.

Inlet fluids were comprised of Millipore™ water and Merck/Sigma-Aldrich analytical grade NaHCO<sub>3</sub>, CaCl<sub>2</sub>, NH<sub>4</sub>Cl, NaOH, and/or HCl with ionic strengths ranging from 0.01 to 0.09 mol/kg; the composition of all inlet fluids is listed in Table 1. Compositions of the inlet fluids were based on calculations made using PHREEQC to yield 1) the desired pH and ionic strength, 2) to achieve calcite saturation in the reactive fluids, and 3) to be similar to those that might be present during mineral carbonation efforts. The inlet fluids were stored in 8 or 12 L compressible

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