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Research paper

## Changes in mineral assemblages during serpentine carbonation

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### ABSTRACT

The carbonation of serpentine (lizardite [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>]) was investigated at a fixed temperature of 290 °C under a 30-bar CO<sub>2</sub> atmosphere in aqueous solutions of different alkalinities to understand the pH-dependence of the process. To activate the carbonation, the serpentine was heat-treated at 650 °C beforehand for 2 h. At pH 6, the main reaction products were magnesite (MgCO<sub>3</sub>) and well-crystallized saponite [Na<sub>x</sub>Mg<sub>3</sub>(Si<sub>4</sub>Al<sub>4-x</sub>)O<sub>10</sub>(OH)<sub>2</sub>]. The carbonation rate of the Mg ions was limited at acidic pH, and thermogravimetry (TG) analysis of the solid product showed that only 13% carbonation rate of serpentine to magnesite was achieved. The partial dissolution of Si—O—Si and the resultant Mg-rich solution provided a favorable environment for the formation of saponite. In weakly alkaline and neutral solutions, the rate of carbonation was dramatically enhanced well-faceted rhombohedral magnesite crystals of approximately 1 μm in size with a round shape appeared together with a small amount of “curled-flaky type” saponite. The conversion of silicate to carbonate was found to be approximately 45%. As the pH of the solution increased further, the dissociation of carbonic acid accelerated and the free Mg<sup>2+</sup> cations then reacted with the bicarbonate ions to form magnesium carbonate. Thus, active conversion to magnesite resulted in poor formation of saponite because of the low concentration of Mg ions in the solution. At pH 2, well-crystallized saponite appeared, but magnesite was not observed. Under strongly alkaline conditions, saponite may form by a mechanism wherein the undissolved Mg layer of serpentine is available to act as a substrate for saponite precipitation. The transformation of serpentine to saponite and magnesite was influenced mostly by temperature, alkalinity, and mineral composition.

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### 1. Introduction

Mineral carbonation is one of the most promising methods for the sequestration of CO<sub>2</sub> that are currently being studied. Mineral carbonation mimics the natural rock-weathering process and is commonly associated with a complex series of other chemical and mineralogical transformations (Belevi et al., 1992; Zevenbergen and Comans, 1994; Meima and Comans, 1997, 1999; Bodéan et al., 2000; Sabbas et al., 2003). The formation of carbonate minerals, the principal products of the process, offers the advantage of CO<sub>2</sub> disposal in a geologically stable and environmentally benign form (Daval et al., 2009) because CO<sub>2</sub> is crystal-chemically incorporated into the minerals and immobilized. The Ca and Mg containing minerals have a vast sequestration capacity because of the widespread and abundant occurrence of suitable feedstock (Lackner, 2002). The processes currently under study are based on the aqueous reaction of materials containing divalent cations, such as wollastonite (CaSiO<sub>3</sub>) and olivine [(Mg,Fe)<sub>2</sub>SiO<sub>4</sub>], and multi-oxide silicates, such as serpentine [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>] or glauconite

[(K,Na)(Mg,Fe,Al)<sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>] clays (Fernandez-Bastero et al., 2005).

Dissolution kinetics is an important factor in aqueous mineral carbonation, and the enhancement of silicate mineral carbonation by increasing the dissolution rate of the mineral has been extensively studied under different temperatures, CO<sub>2</sub> pressures, and solution compositions (Haug et al., 2010; Prigiobbe et al., 2009; Hänchen et al., 2006). However, mineral carbonation requires a very delicate balance between the conditions favoring dissolution and those favoring precipitation. As such, the process requires a precise control on pH. A study of forsterite dissolution and magnesite (MgCO<sub>3</sub>) precipitation under a high partial pressure of CO<sub>2</sub> (Pco<sub>2</sub> = 1 and 100 bar) at 30 °C and 95 °C in batch reactors showed that nucleation of magnesite, which required a large critical saturation index, was the limiting factor for the global reaction (Giammer et al., 2005). Experiments on olivine and serpentine exposed to high CO<sub>2</sub> pressure (115 bar) and high temperature (155 °C) achieved a 55% stoichiometric conversion to carbonate in 30 min (O'Connor et al., 2005).

In spite of recent research in this area, there is still considerable work necessary to address the unanswered questions and discrepancies that remain regarding the reaction kinetics and carbonation mechanisms (Park et al., 2003). Initially, a number of the direct solution carbonation

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experiments for serpentine were conducted under high pressure to develop an in situ carbonation reaction (Giammer et al., 2005; Dufaud et al., 2009). Additionally, early carbonation work showed that a mixture of weak acids and chemical additives enhanced the dissolution of serpentine; further efforts were thus focused on enhancing mineral dissolution and developing a pH swing process in indirect methods. Therefore, the study of ex situ sequestration under high temperature and low pressure by a direct aqueous method and additional studies on the implied link between pH and mineral carbonation were also needed. In particular, the study of phase assemblage has never been reported for direct aqueous carbonation at various pH levels and temperatures.

In this work, experiments were conducted to investigate the pH-dependence of the direct aqueous carbonation of serpentine at a fixed temperature (290 °C) and low pressure (30 bar) after it was activated physically using heat pre-treatment under supercritical CO<sub>2</sub> pressures.

## 2. Materials and methods

Serpentine was obtained from the Bibong mine in Chungyang, Korea. The carbonation process requires size reduction of the mined ore. The sample was initially crushed in a jet mill to grains that were passed could pass through a 325 mesh sieve. The grain size was measured by a particle-size analyzer (Mastersizer 2000, Malvern Co.). The chemical composition of the starting material was determined by ICP-AES (JY 38 Plus, JobinYvon, France).

For each experiment, the desired amount of mineral reactant was mixed with a carrier solution, which was usually distilled water, bicarbonate, and a solution to make a slurry (10% solid concentration, 20 g of mineral reactant and 200 mL of solution). The pH of the solution was adjusted to between 6 and 12 by adding HCl (OCI Co., Korea), NH<sub>4</sub>Cl (DC Chem., Korea), and NaOH (DC Chem., Korea) solutions. When only distilled water was used as the carbonation carrier solution, the reaction rates were very low. The addition of 0.5 M NaHCO<sub>3</sub> (Junsei Co., Japan) as a catalyst resulted in a higher conversion rate. After completion of the carbonation, the pH was 7 and 8.

All of the carbonation reactions were conducted in a 1 L cold-seal type stainless steel vessel. The vessel was sealed and purged with 30 bar CO<sub>2</sub> after the heat-treated mineral and solution were loaded in the vessel. The mineral/solution/CO<sub>2</sub> mixture was continuously agitated at 100 rpm to prevent settling of the solids. The autoclave was operated at 290 °C for 5 h.

The starting materials and reaction products were analyzed with an X-ray diffractometer (XRD; X'pertMPD, Phillips Co.) with graphite-monochromatized CuK $\alpha$  radiation. Fourier transform infrared spectra (FT-IR; NICOLET 380, Thermo Electron Corporation) were recorded in the frequency range 400–4000 cm<sup>-1</sup> at a 4 cm<sup>-1</sup> resolution. The data were obtained in the transmission mode using pressed KBr pellets, which were prepared by homogeneous mixing of a 1 mg sample with 150 mg of KBr. Thermogravimetric analyses (TGA, DTG 60H, Shimadzu Co.) were performed on the product at a heating rate of 10 °C min<sup>-1</sup> to determine the extent of carbonation.

The morphology of the synthesized products was examined using a field-emission scanning electron microscope (FE-SEM, S-4700, Hitachi) at a working voltage of 15 keV. The sample powder was applied to a Cu-micro grid and coated with osmium tetroxide (OsO<sub>4</sub>) for analysis. The Brunauer-Emmet-Teller (BET) method (Quadrasorb SI, Quantachrome, USA) was then applied to calculate the specific surface areas of the products, whereby nitrogen gas molecules are absorbed onto a solid surface. BET surface area determination is carried by measuring the volume of nitrogen which is adsorbed onto sample when P/Po = 0.05; 0.1; 0.15; 0.2; 0.25; 0.3 (at 6 points). Here, P represents pressure when nitrogen is injected and Po is atmosphere pressure.

The carbonation rate in the product is calculated using following equation:

$$\text{Carbonation rate} = \frac{\text{Actual amount of carbonation}}{\text{Theoretic amount of carbonation}} \times 100$$

## 3. Results and discussion

The series of XRD patterns and FT-IR analysis results in Figs. 1 and 2 reveal the raw material and the reaction sequence during the conversion of the meta-lizardite samples to magnesite. The XRD results indicated that the primary phase present in the serpentine feed sample was lizardite [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>] and included quartz (SiO<sub>2</sub>) and small amounts of impurities (Fig. 1a). The chemical composition of the starting material was approximately 27.3 wt% MgO, as shown in Table 1. A lower MgO content corresponds to a higher SiO<sub>2</sub> impurity content.

The FT-IR spectra of the raw material were acquired and the results are shown in Fig. 2a. The characteristic vibrations of lizardite were observed in three spectral regions: the O—H stretching vibration region (3691, 3646 and 3429 cm<sup>-1</sup>), the Si—O—Si stretching vibrations

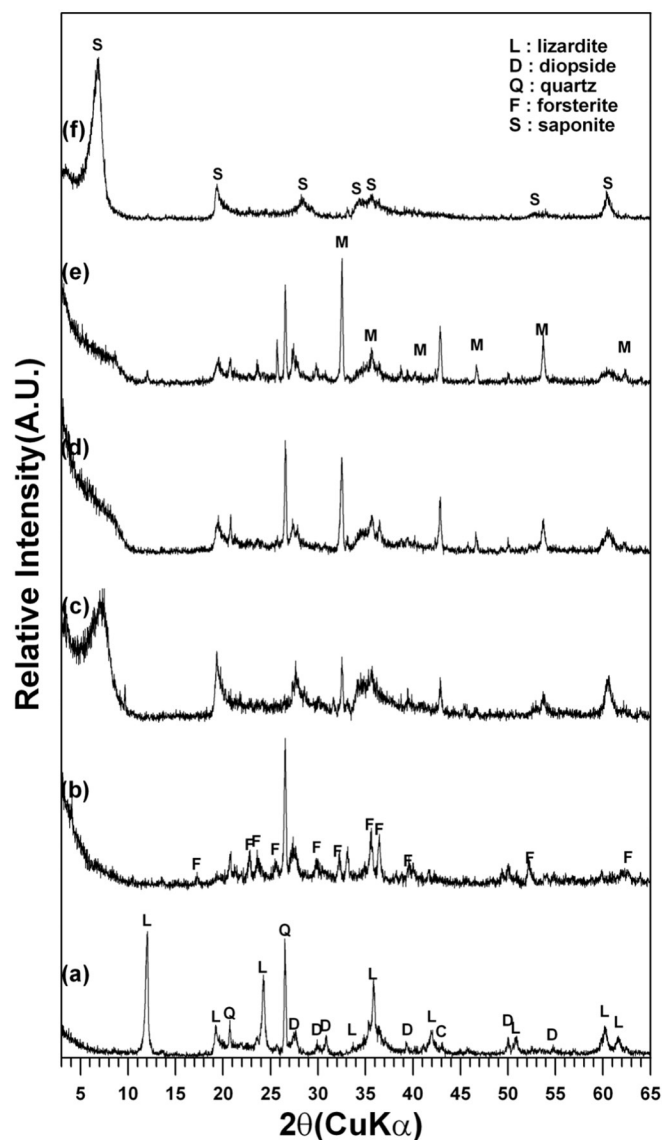


Fig. 1. XRD patterns of the starting material and products synthesized at various pH values: (a) raw lizardite, (b) heat-treated lizardite, (c) synthesized at pH 6, (d) synthesized in distilled water, (e) synthesized at pH 8, (f) synthesized at pH 12.

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