



Carbon dioxide storage in olivine basalts: Effect of ball milling process



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ABSTRACT

The goal of this study is to propose a cost-effective method for the optimization of the *ex situ* carbonation of basaltic rocks. The ball milling process was applied to a sample of olivine basalt from the Troodos ophiolite complex (Cyprus) for the first time, in order to fabricate novel nanomaterials for CO₂ storage. The purpose was to accelerate the kinetics of rock–fluid reactions during the carbonation procedure. Various methodologies were used for the characterization of the starting rock material and the ball-milled samples. Preliminary results reveal that only a few hours of wet ball milling with ethanol as process control agent can induce significant changes to olivine basalt towards improvement of its performance for CO₂ storage. Specifically, CO₂ uptake measurements *via* the use of the temperature-programmed desorption (TPD) technique indicate that 4 h of ball milling with 50 wt.% ethanol can lead to an enhancement of the carbonation of olivine basalt by 295%. The experimental results strongly suggest that (i) olivine basalts have important CO₂-storage capacity and are very promising lithotypes for *ex situ* carbonation, and (ii) the ball milling process provides hopes for its use at an industrial scale as a preparation technique for the safe and permanent *ex situ* storage of CO₂.

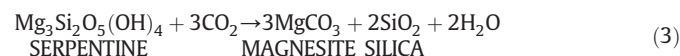
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1. Introduction

Carbon dioxide is a significant component of the Earth's atmosphere, which has also a determinative role in the greenhouse effect. Anthropogenic impact (use of fossil fuels) on the global carbon cycle over the past century has led to a dramatic increase of CO₂ emissions in the atmosphere, which are considered to be a substantial reason for the observed global warming. A popular proposed solution to this problem is the so-called Carbon Capture and Storage – CCS [1–3]. The main types of CCS are: (i) *geological storage*, (ii) *ocean storage*, and (iii) *mineral carbonation*.

The purpose of mineral carbonation, which is the subject of the present work, is to create stable carbonate minerals such as magnesite (MgCO₃), calcite (CaCO₃) and dolomite (CaMg(CO₃)₂), by reacting CO₂ with natural metal oxides [4–6]. These metal oxides are principally the oxides of divalent cations Mg²⁺, Ca²⁺ and Fe²⁺ that are found in the crystal structure of many mineral phases. Silicate minerals with the highest potential for CO₂ mineralization are olivine, pyroxene, serpentine and plagioclase, while the fastest mineral carbonation rates

known are for the mineral forsterite (Mg₂SiO₄) [4], which is the magnesium rich end-member of the olivine solid solution series. Substantial quantities of all the above mineral phases occur in the ultramafic and mafic rocks of ophiolite complexes. The main carbonation reactions of ophiolitic rocks are summarized below:



Various studies have been carried out to investigate the feasibility of *in situ* mineral carbonation [7,8]. The dissolution rate of forsterite in relation to its CO₂-storage capacity has also been widely studied by many scientists [9–11]. Additionally, a few studies have tried to optimize *ex situ* mineral carbonation methods by increasing temperature or grinding the raw materials and dissolving them in acidic solutions [12,13]. However, there are some important questions related to the *ex situ*

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mineral carbonation methods, which include: (i) the huge sources of raw materials required for carbonation and, therefore, the large scale of the CO₂ storage operations; (ii) the energy costs that may make such operations impractical; and (iii) the necessity to accelerate the kinetics of rock–fluid reactions during the carbonation procedure [4,14].

In this work we propose an effective method for the optimization of the *ex situ* carbonation of basaltic rocks taking into consideration the following: (i) the method of mineral carbonation provides a safe and essentially permanent CO₂ storage and does not require long-term monitoring [1,8,15]; (ii) the formation of carbonate minerals is energetically favorable, since the thermodynamic driving force promotes these reactions [1]; and (iii) enormous volumes of basaltic rocks are present on the Earth's surface [5]. The basic concept of this study is to accelerate the carbonation rate (or CO₂ uptake) of basaltic rocks via the *ball milling process*. It has been demonstrated that long milling can improve the performance of CO₂ capture, even when the gas is present at standard atmospheric conditions [16,17]. Milling techniques have been recently applied to magnesium-based silicates in order to mechanically activate such materials and hence improve their performance [13,18,19]. However, there are still important gaps in our knowledge of mineral reactions in the presence of CO₂, particularly for mineral assemblages of ophiolitic lithologies.

In the current investigation, the experiments were carried out using a sample of olivine basalt from the Troodos ophiolite, which is considered the most well preserved ophiolite suite worldwide. This lithotype was selected due to its high content of forsterite-rich olivine. A few studies have investigated the mineralization of basaltic rocks [e.g. 20, 21]. Recently, pilot projects began to test the feasibility of *in situ* mineral carbonation in basalts as a way to permanently and safely store CO₂ [22–26]; however, a study for the optimization of the *ex situ* carbonation of basaltic rocks via the ball milling technique is attempted for the first time in this work.

2. Materials and methods

2.1. Sample selection, characterization and preparation

The well known Troodos ophiolite complex, which is considered to be the most intact worldwide, was formed in a supra-subduction zone environment around 92–90 Ma ago [27,28]. The mantle section of the Troodos ophiolite has been divided in two units [29]. The first unit (eastern) consists of spinel lherzolite with dunite bodies and zones of clinopyroxene-bearing harzburgite, while the second unit (western) is principally composed of clinopyroxene-poor harzburgite and dunite. The overlying cumulate ultramafic and mafic lithotypes are cut by gabbroic intrusives, while the upper, massive gabbros are locally overlain by plagiogranite bodies. The overlying sheeted dyke complex, which covers a significant area of the Troodos ophiolite suite, is overlain by well developed pillow lavas with various degrees of hydrothermal alteration. The latter are traditionally divided into the “Lower” and “Upper” Pillow Lava units (LPL and UPL, respectively). The LPL and UPL primary melts originated from distinct mantle sources [30,31]. The LPL is mainly andesitic, while the younger UPL consists of basaltic andesites and basalts with picritic lava flows and dykes [32]. The presence of forsteritic olivine in the UPL has been referred by various scientists [31].

In the present study, a representative sample of olivine basalt from the UPL unit of the Troodos ophiolite was collected (coordinates: 3876000N 528870E, WGS 84 Zone 36N) and experimentally analyzed. The mineralogical and textural characteristics of the studied olivine basalt were determined by petrographic analysis of a representative thin section using a polarizing microscope. Powdered samples were also prepared with a laboratory agate pulverizer. The pulverized rock material was then sieved in order to acquire the 104–150 µm fraction, which was used as starting material for the ball milling process. In addition, a reference sample of forsterite (Alfa Aesar, Forsterite, naturally occurring mineral) was experimentally analyzed in terms of CO₂ capture for

comparison purposes. The fraction acquired for the forsterite is similar to that of the starting rock material.

2.2. Ball milling

The ball milling process was carried out in a Fritsch Pulverisette 6 planetary mono mill. The olivine basalt was subjected to wet milling in an 80 mL tungsten carbide bowl using deionized H₂O or ethanol as process control agent (PCA). The ball-to-powder mass ratio was 20:1 w/w, the fluid-to-powder mass ratio 1:10 or 1:2 and the rotation speed 300 rpm. The process was carried out using 30 tungsten carbide balls with a diameter of 10 mm. The reason for using tungsten carbide bowl and balls is to avoid possible contamination of the material, taking into account the high hardness of basaltic rocks. The ball milling process was automatically interrupted every 5 min with 5-min stay and with a view to avoid heating of the test sample. Although the periodical interruption of milling makes the whole process time-consuming, it is of great significance in order to avoid possible phase transformations that will reduce the CO₂-storage capacity of the rock material. Powders taken were left to dry out overnight. The milling conditions are summarized in Table 1.

2.3. Powder X-ray diffraction (XRD)

Powder X-ray diffraction analyses were also performed, using a Bruker D8 Advance system, in order to identify the mineral phases of the olivine basalt and investigate possible mineralogical transformations occurred during the ball milling process. The analyses were carried out with a continual rotation of the samples and a step of 1°/min, within the angle range 2θ of 3–80°. The ICDD PDF 2 database was used for the qualitative identification of the constituent minerals.

2.4. Surface texture

The BET method (adsorption of N₂ at 77 K) was carried out in a Micromeritics Gemini III Surface Area and Pore size Analyzer in order to determine the specific surface area (m² g⁻¹), the specific pore volume (cm³ g⁻¹), and the average pore diameter (nm) of the starting material, the milled powders, and the reference forsterite. Each measurement was taken after the samples were outgassed in dry nitrogen flow at 250 °C for 3 h.

2.5. Electron microscopy

A JEOL, JSM-6610 LV scanning electron microscope (SEM), equipped with a BRUKER type QUANTAX 200 energy dispersive spectrometer (EDS), was used to characterize the unmilled and milled samples of olivine basalt. The effect of the ball milling process on the studied rock type was observed using secondary electron images (SEI).

Samples for conventional (TEM) as well as high resolution transmission electron microscopy (HR-TEM) observations were prepared by gently grinding the sample in high-purity ethanol using an agate pestle and mortar. A drop of the solution was subsequently deposited onto a lacey C-film supported on a Cu grid and allowed to evaporate under

Table 1
Ball milling conditions of the studied olivine basalt.

No	Sample code	Milling time	Type of milling
1	BM1	1 h	Wet (10 wt.% ethanol)
2	BM2	1 h	Wet (10 wt.% H ₂ O)
3	BM5	1 h	Wet (50 wt.% ethanol)
4	BM6	2 h	Wet (50 wt.% ethanol)
5	BM7	4 h	Wet (50 wt.% ethanol)
6	BM11	2 h	Wet (10 wt.% ethanol)
7	BM12	4 h	Wet (10 wt.% ethanol)
8	BM15	8 h	Wet (50 wt.% ethanol)

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