



Kinetic evaluation of mineral carbonation of natural silicate samples

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HIGHLIGHTS

- Different silicate minerals showed highly different carbonation behaviours.
- Olivine dissolution was the rate controlling step during natural silicate carbonation.
- Carbonation capacity of natural silicates should be corrected for application.
- Kinetics of natural silicates carbonation should be based on corrected capacity.
- Carbonating mixtures of various silicates is more realistic for potential scale-up.

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ABSTRACT

Carbon sequestration by mineral carbonation of basic silicate minerals is an important technique for climate change mitigation, because of the formation of stable mineral carbonate products and the abundant resources of amenable minerals in nature. In practice, direct aqueous mineral carbonation may need to treat natural multiple-mineral mixtures including partially serpentinized ultramafic silicates, as potentially combined with mineral processing operations and enhanced metal recovery. This work investigated the kinetics of direct mineral carbonation of multiple-minerals natural silicate samples under conditions of 34.5 bar CO₂ partial pressure, 175 °C and concentration of 1.5 m NaHCO₃, with corresponding carbonation efficiency more than 85% in 3 h. It was found that the carbonation of a natural mixture of minerals was kinetically controlled by chemical reaction of the olivine dissolution under moderate CO₂ partial pressure and aqueous ionic strength, regardless of olivine content and associated mineral compositions. It was important for kinetics analysis to calculate the effective mineral carbonation capacity based on the magnesium and iron contents in olivine. If the carbonation capacity was calculated based on the total content of magnesium, calcium and iron as is conventional, the mineral carbonation efficiency was proportional to the olivine content in natural silicate samples. The carbonation process of the natural mixtures could be completely attributed to the reaction of olivine while the other silicate minerals including serpentine and diopside, as well as iron sulfides and magnetite, did not significantly participate.

1. Introduction

Carbon sequestration through mineral carbonation is an important technology for climate change mitigation [1–4]. It can permanently convert CO₂ gas to stable mineral carbonates [5]. There are abundant resources of basic silicate minerals all over the world, which are suitable for mineral carbonation [6–10]. However, though the mineral carbonation between silicate minerals and CO₂ is thermodynamically favourable, it is limited by the kinetics [4,11]. To accelerate the carbonation process, it usually needs strict conditions including the fine particle size ($\leq 75 \mu\text{m}$) [12–14], high CO₂ partial pressure ($\geq 130 \text{ bar}$)

[13–15] and high temperature ($\geq 180 \text{ °C}$) [13,15,16]. In turn, each strict condition makes the mineral carbonation economically less favourable [17,18]. The industrial application is still waiting for improvements of this promising technology. Therefore, it is important to carry out the kinetics analysis for the mineral carbonation process to begin to optimize and reduce cost for carbon sequestration.

At present, the kinetic analysis of the direct aqueous mineral carbonation process of silicate minerals has been widely studied but mainly focused on the carbonation of high-purity minerals [12,19–23]. Kwon et al. [19] studied the kinetics of mineral carbonation of 99% purity forsterite Mg₂SiO₄ by using a fluidized-bed reactor with

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simulated flue gas pressure and more than 150 °C temperature. It was found that the activation energy for the mineral carbonation of Mg_2SiO_4 was more than 43 kJ/mol. It was controlled by chemical reaction between CO_2 and Mg_2SiO_4 . Gadikota et al. [21] investigated the kinetics of mineral carbonation of high-purity olivine and serpentine. It was found that the dissolution of minerals was under surface reaction control in initial 5 min, followed by under control of diffusion through Si-rich layer. The dissolution of fine particles $< 5 \mu\text{m}$ significantly contributed to the carbonation kinetics. Wood et al. [23] discovered that Fe(II) may had detrimental effects on carbonation of high-grade olivine because of Fe(II) competitive oxidation [22,23]. Our previous kinetics studies [20,12] on the carbonation of a high-grade olivine from the olivine deposit at Åheim, Norway confirmed that the mineral carbonation of olivine was controlled by chemical reaction of dissolution of olivine under the conditions of CO_2 partial pressure (PCO_2) more than 28 bar with addition of more than 0.5 m sodium salts regardless of temperature and particle size. Numerous other studies have confirmed that dissolution of olivine is the kinetic control step for mineral carbonation of olivine [20,12,24–26]. Surface area, temperature, CO_2 partial pressure (PCO_2), pH value and ionic strength are the most important factors influencing dissolution of olivine [20,24–30]. The other kinetic research studies were mainly focussed on the carbonation of industrial wastes, such as coal fly ash [31], metallurgical slags [32,33] and municipal solid wastes [34].

However, the potential application of the mineral carbonation technology usually needs to treat natural silicate samples containing a range of minerals where the industries need to extract valuable minerals (e.g. nickel sulfides) [35] or metals (e.g. nickel and chromium) [36] to compensate the costs of direct carbonation process [17,36] ranging from \$50 to \$300 per ton sequestered CO_2 [3,14,37]. Mineral carbonation of natural silicate mixtures is more realistic to scale up than carbonation of high-purity minerals. In addition, the direct mineral carbonation technology may also be directly utilized for enhanced metal recovery (EMR) [38,39] to motivate application of carbonation in natural silicates. The utilization of mineral carbonation for EMR highly depends on the kinetics and mechanisms of carbonation. The fast mineral carbonation under olivine dissolution control with PCO_2 greater than 21 bar and concentration of $\text{NaHCO}_3 > 0.32 \text{ m}$ is favourable for the potential EMR process. The Turnagain nickel-sulfide (partially serpentinized ultramafic) deposit in northern British Columbia, Canada is a potential target for application of mineral carbonation. This mine operation intends to recover nickel and cobalt sulfide-containing concentrate via conventional flotation with power supply from combustion of liquid natural gas (LNG), as shown in Fig. 1. The 87,000 t/d production scale is in reference to a total deposit containing 761 Mt of ore. As a result, the estimated natural silicate tailings for this mine are around 756 Mt with 86,434 t/d production rate. The target mineral for flotation recovery is pentlandite ($\text{Fe,Ni}_9\text{S}_8$) accounting for $< 1\%$ of the ore mass, while up to 41% of the total nickel is in silicate minerals (non

sulfide) which is non-recoverable via flotation. Therefore, the natural silicate tailings and waste CO_2 gas can be utilized for direct mineral carbonation with potential sequestration scale of around 390 Mt CO_2 (44,600 t CO_2/d). In addition, the carbonation process may be directly utilized for potential EMR which will be discussed in detail in another paper. There are abundant similar silicate deposits in the western and eastern coastal areas of Canada [6]. Even a high-grade olivine contains 0.27% nickel [12,40]. Therefore, this proposed process may be reasonable to scale up.

Thus far, there is no study on the kinetics of direct aqueous carbonation of natural multiple-minerals silicates. The natural silicates usually contain various silicate minerals, such as olivine, serpentine, diopside. The different minerals may show considerably different carbonation behaviours under identical conditions. O'Connor et al. [14,41,42] stated that olivine has much higher mineral carbonation rates compared to other minerals and mineral carbonation of serpentine needs heat pre-treatment [43]. Therefore, the presence of serpentine, diopside and other minerals may affect the kinetic control step of mineral carbonation of multi-minerals natural silicate samples. Correspondingly, the practical mineral carbonation ability of multi-minerals natural samples under specific conditions may need to be re-evaluated. It is important for potential application of mineral carbonation technology.

This research is to investigate the kinetics of direct aqueous mineral carbonation of natural silicate samples which contain various olivine content and mineral compositions. The kinetics analysis continues to use the shrinking core model (SCM) [44–48] which is the most classical for the reactions between aqueous reactants and mineral particles, based on our previous kinetic research of a high-grade olivine. The PCO_2 for mineral carbonation is limited as 31 bar and 34.5 bar in order to make sure that carbonation of olivine is under control of olivine dissolution [12]. The moderate PCO_2 and elevated temperature for this research are set to facilitate fundamental study of the kinetics of carbonation.

2. Materials and methodology

2.1. Materials

The natural silicate ore samples were provided by Giga Metals Corporation from the Turnagain partially serpentinized ultramafic deposit in northern British Columbia, Canada. The chemical composition of the five natural silicate samples is shown in Table 1. The corresponding mineral composition of the silicate samples is shown in Fig. 2 and Table 2. The samples have considerably different mineral and chemical compositions, and belong to different lithologies varying from serpentinized wehrlite, wehrlite to serpentinized dunite. The olivine content varies from 30.2% (for sample SN1) gradually increasing to 79.5% (for sample SN5). Sample SN1 – SN3 are serpentinized wehrlite:

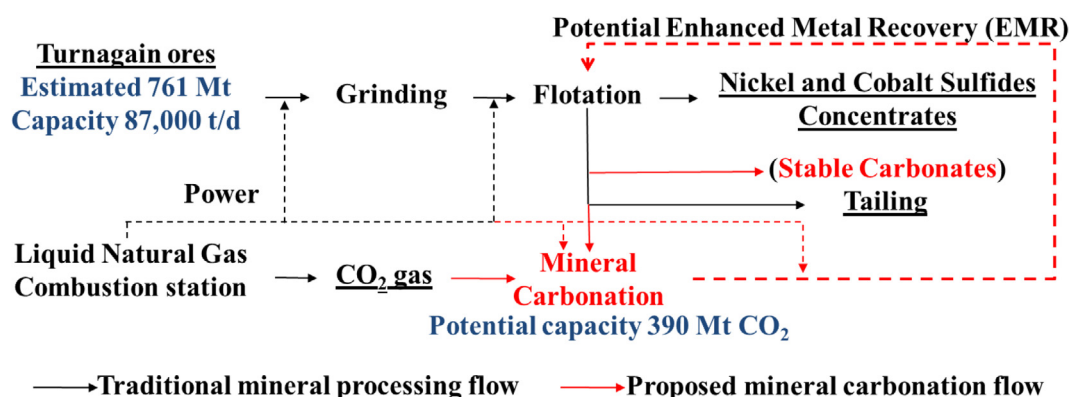


Fig. 1. Proposed engineering flow diagram of Turnagain mine, Giga Metals Corporation.

Table 1
Chemical composition of natural silicate samples.

Samples	SN1	SN2	SN3	SN4	SN5
S, %	1.40	7.19	1.13	2.30	2.16
Ni, %	0.33	0.70	0.23	0.40	0.26
Mg, %	19.07	18.24	18.32	21.21	22.47
Fe, %	7.79	15.62	7.88	9.77	10.06
Co, %	0.02	0.05	0.01	0.02	0.02
Cu, %	0.05	0.20	0.03	0.09	0.03
Al, %	0.44	0.22	0.58	0.19	0.06
Ca, %	1.21	0.51	3.90	1.05	0.57
K, %	0.09	0.03	0.12	0.02	< 0.01
Na, %	< 0.01	< 0.01	0.03	0.01	< 0.01
C, %	0.05	0.03	0.05	0.04	0.06

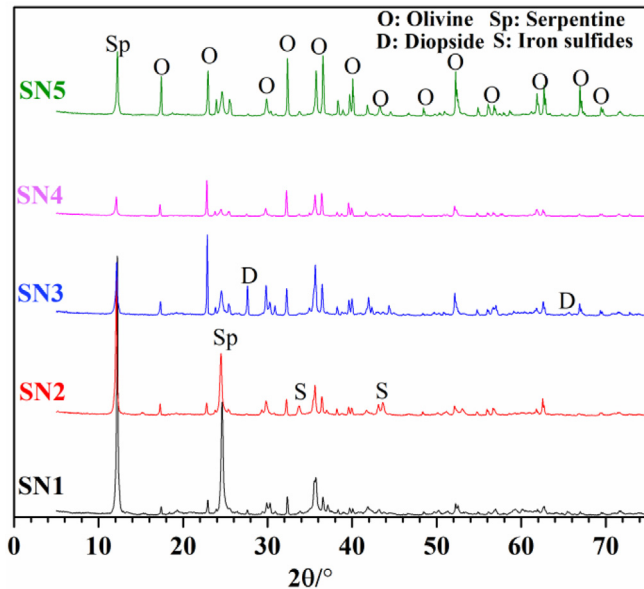


Fig. 2. X-ray diffraction images of the natural silicate samples.

Table 2
Mineral composition of natural silicate samples through the quantitative X-ray diffraction (QXRD) analysis.

Minerals	Natural silicate sample				
	SN1	SN2	SN3	SN4	SN5
Olivine: (Mg, Fe) ₂ SiO ₄	30.2	40.1	50.5	73.3	79.5
Brucite: Mg(OH) ₂	–	–	–	0.3	–
Quartz: SiO ₂	–	–	0.4	–	–
Magnetite: Fe ₃ O ₄	10.0	4.4	6.4	4.6	3.9
Troilite: FeS	1.3	8.1	0.5	2.0	4.6
Pyrrhotite: Fe _{1-x} S	1.7	11.4	1.3	2.8	–
Calcite: CaCO ₃	1.1	2.5	0.3	0.7	0.3
Diopside: CaMgSi ₂ O ₆	12.5	4.9	29.4	9.1	4.9
Serpentine: Mg ₃ Si ₂ O ₅ (OH) ₄	43.3	28.6	11.1	7.2	6.8
Total	100	100	100	100	100

Sample SN1 has the highest serpentine content, accounting for 43.3%, with 12.5% diopside and 10.0% magnetite; Sample SN2 has the highest iron content, 15.6%, which are in forms of 11.4% pyrrhotite, 8.1% troilite and 4.4% magnetite. Correspondingly, SN2 has the highest sulfur content with 7.19% and the lowest magnesium content with 18.24%. It also owns the second highest serpentine content (28.6%) and the second lowest olivine content (40.1%); Sample SN3 has the highest diopside content (29.4%) and the intermediate olivine content 50.5%, followed by 11.1% serpentine. Sample SN4 – SN5 are wehrlite and serpentinized dunite, which have the highest olivine content 73.3% and

79.5%, respectively. Correspondingly, the highest magnesium content is in sample SN4 and SN5 with 21.2% and 22.5%, respectively. In contrast, the contents of brucite and quartz are not significant, only accounting for < 0.4%. The original carbon content is < 0.06%. The iron content for all samples except for SN2 is between 7.8% and 10.1%. The calcium content is < 1.2% for all samples except for SN3 (in which 3.9% is calcium) and is mainly in the form of diopside.

This mine's flotation target mineral pentlandite (Fe,Ni)₉S₈ accounts for < 1% of the ore mass and thus the waste streams after flotation contain essentially the same mineral composition. The P₈₀ of particles after grinding is around 85 μm. Since the target mineral is naturally hydrophobic, there is no need to add sulfide reagents (e.g. NaHS) during flotation to alter the surface properties of particles. The waste streams after mineral processing still present the similar mineral compositions and surface properties to the raw natural silicate ore samples. Therefore, the mineral carbonation behaviour of the natural samples is unchanged. These raw natural silicate samples are directly used for the kinetic study of mineral carbonation in this research.

2.2. Methods

The natural silicate ore samples were crushed to < 5 mm from more than 40 mm size. To compare the mineral carbonation behaviours, the samples were dry pulverized to the particle size P₈₀ = 30 ± 3 μm. The pulverized samples were used for mineral carbonation under conditions of PCO₂ = 31.0 bar, 175 °C, 1.5 m NaHCO₃, P₈₀ = 30 ± 3 μm of particle size, pulp density = 10%, 1200 rpm for 5 h. The addition of 1.5 m NaHCO₃ was to accelerate the mineral carbonation process [13,12] and PCO₂ greater than 28 bar and concentration of NaHCO₃ > 0.32 m were to make sure that mineral carbonation of olivine was under control of olivine dissolution [20,12]. In other words, olivine dissolution is the rate-limiting step for mineral carbonation of olivine under these conditions.

To investigate the kinetics of the carbonation of the natural silicate samples, the crushed samples at < 5 mm size were ground by a rod mill and screened by a 500 mesh sieve to obtain < 25 μm particle size fractions (P₈₀ around 21 μm). The kinetic study was under the carbonation conditions of PCO₂ = 34.5 bar, 175 °C, 1.5 m NaHCO₃, < 25 μm narrow-sized particle fractions, pulp density = 10%, and 1200 rpm. The pulverized and ground samples were analyzed by Malvern Mastersizer 2000 Instrument for the particle size distributions, as shown in Fig. 3a and 3b respectively. The particle size distribution used for this study was much finer than that expected from the Turnagain mine's production process. This was done to speed up the carbonation kinetic study because particle size distribution did not alter the kinetic control step [12].

The mineral carbonation tests were carried out in a 600 mL stainless steel autoclave (Model 5103) with a No. 4842 control system (provided by Parr instrument Company) as a batch experimental setup [12]. A 12 mL sampling kit was used to sample during mineral carbonation process. The sampled slurry through the sampling kit was centrifuged and the solids were dried at 60 °C for 24 h. LECO CS3200 instrument was used to analyze the total carbon content throughout the research. The mineral carbonation efficiency is calculated using the following equation [20,12]:

$$\alpha = \frac{\theta_2 - \theta_1}{m \times \left(\frac{12.011}{44.0098} - \theta_2 \right)} \quad (1)$$

where, m is the mineral carbonation capacity of the raw materials with unit of t CO₂/t material, which is only calculated based on the bivalent metal content of the sample; θ₁ and θ₂ are the total carbon content in %, of the solid before and after carbonation, respectively; and α is the mineral carbonation efficiency in %.

The chemical composition of the natural silicate samples was analyzed via Inductively Coupled Plasma – Optical Emission

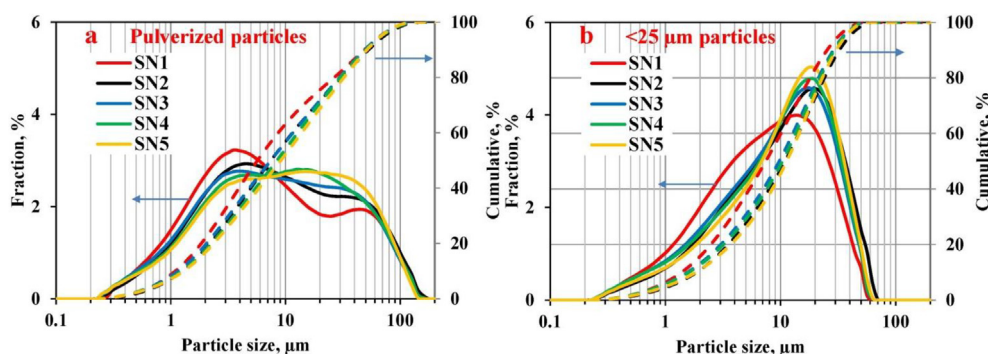


Fig. 3. Particle size distributions of natural silicate minerals: a) Pulverized particles and b) < 25 μm particles ground by a rod mill.

Spectrophotometry (ICP-OES, Spectro Ciros Vision) analysis after lithium borate fusion. The mineral composition was obtained through the Quantitative X-ray Diffraction (QXRD, Bruker D8 Focus) with Rietveld Analysis. Scanning Electron Microscopy with Energy Diffraction X-ray (SEM-EDX) analysis through a FEI Quanta 650 Instrument was used to investigate the behaviour of different minerals during mineral carbonation. The transverse surface of particles after carbonation was the analysis target.

In order to study the kinetics of mineral carbonation of the natural silicate samples, the classical SCM was used for the kinetic analysis, which has been confirmed to be suitable for the carbonation of a high-grade olivine in our previous research [20,12]. The autoclave impeller rotation speed in this research was fast at 1200 rpm to address the mass transport of reactive ions. In this research, only the chemical reaction control model and the product layer diffusion control model based on the SCM were considered. The corresponding equation expressions are the following Eqs. (2)–(3):

$$t = k_2 \times [1 - (1 - \alpha)^{1/3}] \quad (2)$$

$$t = k_3 \times [1 - 2\alpha/3 - (1 - \alpha)^{2/3}] \quad (3)$$

where, t is reaction time, hours; k_2 and k_3 are the rate constants for chemical reaction control (Eq. (2)) model and product layer diffusion control model (Eq. (3)), respectively, and are determined in this study for each sample.

3. Results and discussions

3.1. Comparison of mineral carbonation behaviours

The comparison of the mineral carbonation efficiencies of the pulverized five natural silicate samples is shown in Fig. 4(a). It is seen that there were considerably different carbonation efficiencies among the samples where the majority of the differences in mineral compositions was the olivine content. The sample SN1 which has the lowest olivine content 30.2% had the lowest carbonation efficiency at 20.4%. In contrast, the sample SN5 which has the highest olivine content 79.5% had the correspondingly highest carbonation efficiency at 69.3%. From samples SN2 to SN4, the mineral carbonation efficiency gradually increased with the similar trend to the increase of the olivine content. Fig. 4(b) reveals that the mineral carbonation efficiency was proportionally linear to the olivine content of the natural silicate ore samples with $R^2 = 0.98$. This is because the carbonation process was optimized for olivine [12] rather than serpentine. Heat pre-treatment may be still needed to achieve higher carbonation efficiency for natural silicates that contain both olivine and serpentine. With comparing XRD images of natural silicates before and after mineral carbonation, as shown in Fig. 5 and Fig. 2, it also can be seen that peaks of olivine have been considerably decreased and correspondingly magnesite has been significantly generated. In contrast, there is no obvious change in serpentine, diopside and iron sulfides. The results of XRD analysis (Fig. 5)

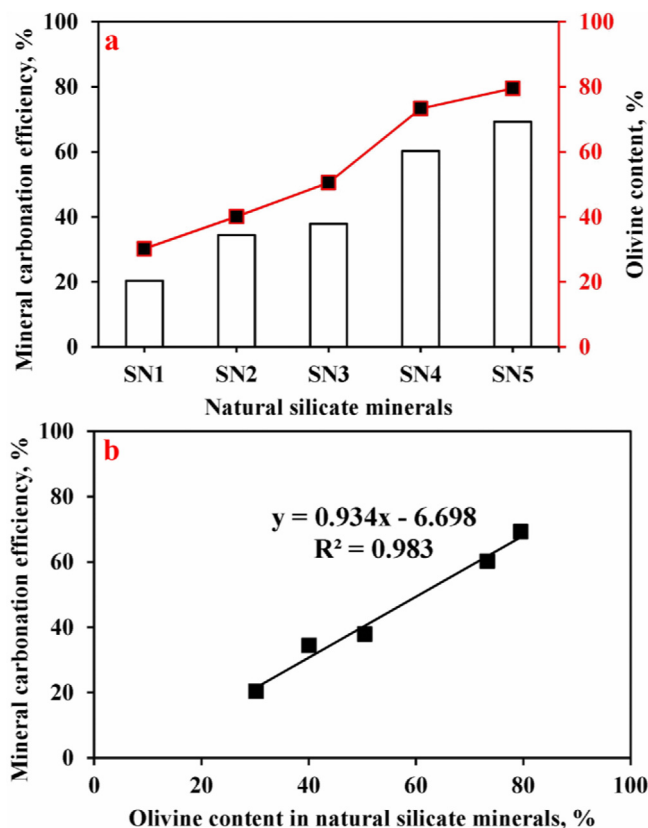


Fig. 4. Comparison of mineral carbonation behaviours of natural silicate minerals under conditions of $\text{PCO}_2 = 31.0$ bar, 175°C , 1.5 m NaHCO_3 , $P_{80} = 30 \pm 3$ μm of pulverized particle size, pulp density = 10%, 1200 rpm for 5 h: a) Comparison of mineral carbonation behaviours and b) Relationship between mineral carbonation efficiency and olivine content.

are identical to the findings from experimental results (Fig. 4); the carbonation process of the natural mixtures was directly proportional to the reaction of olivine while the other minerals did not carbonate.

The conventional method to evaluate the mineral carbonation capacity of a sample is based on the contents of total magnesium, iron and calcium [20], which is shown in Table 3. However, as shown in Fig. 6(a–f) together with preceding results from Figs. 4–5, the minerals of olivine (Fig. 6a), serpentine (Fig. 6b), magnetite (Fig. 6c–e), iron sulfides (Fig. 6e) and diopside (Fig. 6f) without heat-pretreatment behaved differently during mineral carbonation. Not all of the magnesium, iron and calcium are expected to be involved in the carbon mineralization process. The presence of iron may even inhibit the carbonation process due to the competitive oxidation of Fe(II) [23]. In detail, it has been discovered in this research that serpentine

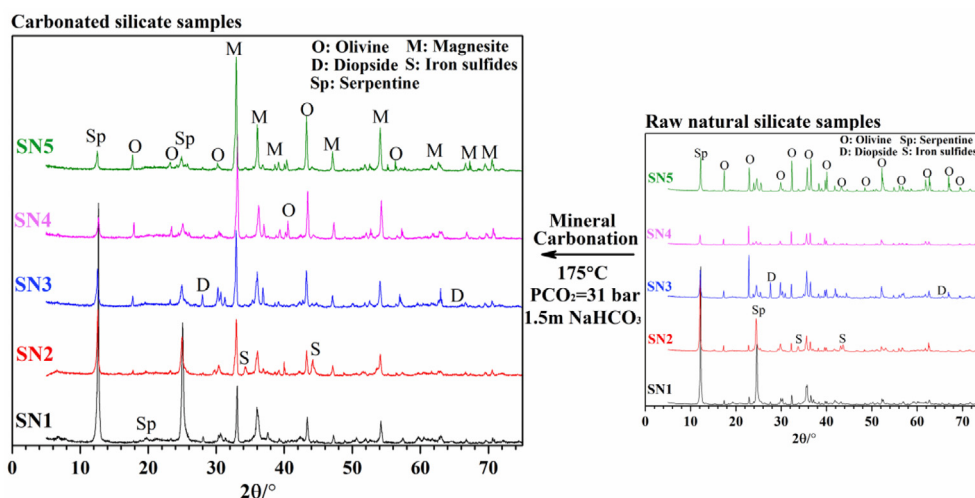


Fig. 5. X-ray diffraction images of carbonated natural silicate samples.

Table 3

Mineral carbonation capacity of natural silicate samples.

	SN1	SN2	SN3	SN4	SN5
Total mineral carbonation capacity, t CO ₂ /t sample ^a	0.42	0.46	0.44	0.47	0.49
Effective mineral carbonation capacity, t CO ₂ /t sample ^b	0.12	0.17	0.22	0.34	0.39

^a Total mineral carbonation capacity based on total magnesium, iron and calcium contents in samples.

^b Effective mineral carbonation capacity based on the difference between total contents of magnesium, iron and calcium in samples and the contents of iron, magnesium and calcium in magnetite, iron sulfides, serpentine and diopside.

(Mg₃Si₂O₅(OH)₄, Fig. 6b), magnetite (Fe₃O₄, Fig. 6c-6e), iron sulfide (Fig. 6e) including troilite (FeS) and pyrrhotite (Fe₇S₈), and diopside (CaMgSi₂O₆, Fig. 6f) were not significantly reacted during mineral carbonation. The reaction of olivine was the dominant process of mineral carbonation and thus the mineral carbonation capacity should be only based on the magnesium and iron contents in olivine. However, it is difficult to determine the contents of magnesium and iron in olivine since the molar ratio of Mg/Fe varied considerably in natural samples. Herein, the following research used the difference between total contents of magnesium, iron and calcium in samples and the contents of iron, magnesium and calcium in magnetite, iron sulfides, serpentine and diopside, to calculate the effective mineral carbonation capacity. The comparison between the two types of mineral carbonation capacity, total capacity and effective capacity, is shown in Table 3.

3.2. Effects of olivine content on kinetics

The mineral carbonation of olivine was the dominant process. In order to discover the effects of olivine content on the kinetics of mineral carbonation, a high-purity silica with < 25 μm particle size was used to dilute the high-grade olivine content for mineral carbonation under the conditions of PCO₂ = 34.5 bar, 175 °C, 1.5 m NaHCO₃, < 25 μm narrow-sized particle fractions, pulp density = 10% and 1200 rpm. The olivine content in the mixed sample of high-grade olivine and high-purity silica was from 30% to 70%. It can be seen from Fig. 7 that the carbonation process was still controlled by the dissolution of olivine regardless of the olivine content. Fig. 7a and b are corresponding to Eqs. (2) and (3), respectively. The R² for the chemical reaction model was always more than 0.95 whereas R² for the product layer diffusion model was < 0.87 for all mixed samples. This is to say that the change of

olivine content did not affect the kinetic rate-controlling step (i.e. under control of olivine dissolution), when the majority of a mineral carbonation process was the carbonation of olivine. Although the carbonation process was still kinetically controlled by dissolution of olivine, it is also noticed that the detailed mineral carbonation rate slightly decreased with the decrease of the olivine content of the mixed sample. The detailed reason for the decreased efficiency is not clear yet but might be due to the complex behaviour of silica at high temperature and pressure (dissolved and/or reprecipitated) [49,50].

3.3. Kinetics of mineral carbonation of natural silicate minerals

The preceding results and discussion have confirmed that the carbonation of olivine was the dominant reaction during the mineral carbonation process of the natural silicate samples. Meanwhile, the change in olivine content did not alter the kinetic rate-limiting step for mineral carbonation of the high-grade olivine and high-purity silica mixtures. In principle, the mineral carbonation process of the natural samples under the above conditions should also be kinetically controlled by chemical reaction of the dissolution of olivine. In order to investigate the carbonation kinetics of the natural silicate samples, the tests were carried out under the conditions of < 25 μm narrow-sized particle fractions, PCO₂ = 34.5 bar, 175 °C, 1.5 m NaHCO₃, pulp density = 10%, and 1200 rpm [12]. The mineral carbonation efficiency was calculated based on the total contents of magnesium, iron and calcium as shown in Fig. 8. The results illustrate a similar trend to Fig. 4(a) whereby the decrease of olivine content had the detrimental effect on the mineral carbonation rates. The sample SN5 which had the highest olivine content showed the highest mineral carbonation efficiency at each specified time. In contrast, with the decrease of olivine content from sample SN4 to SN1, the mineral carbonation efficiency gradually decreased.

According to the mineral carbonation efficiencies based on the total magnesium, iron and calcium contents, the kinetics plots were calculated and shown in Fig. 9. It is surprising that the R² for the relationship of $1 - (1 - \alpha)^{1/3}$ vs t of the chemical reaction control model was poor to < 0.91 for all the natural samples, which is shown in Fig. 9(a). In contrast to the results of the chemical reaction control model, the relationship of $1 - 2\alpha/3 - (1 - \alpha)^{2/3}$ vs t of the product layer diffusion control model showed a good match with the R² more than 0.98 for all samples, as shown in Fig. 9(b). If only based on the plots of the control expressions of the SCM model, the mineral carbonation of the natural silicate samples seemed to be controlled by diffusion through a product layer. However, it is a conflict between the preceding results and the kinetic plots based on the total contents of magnesium, iron and

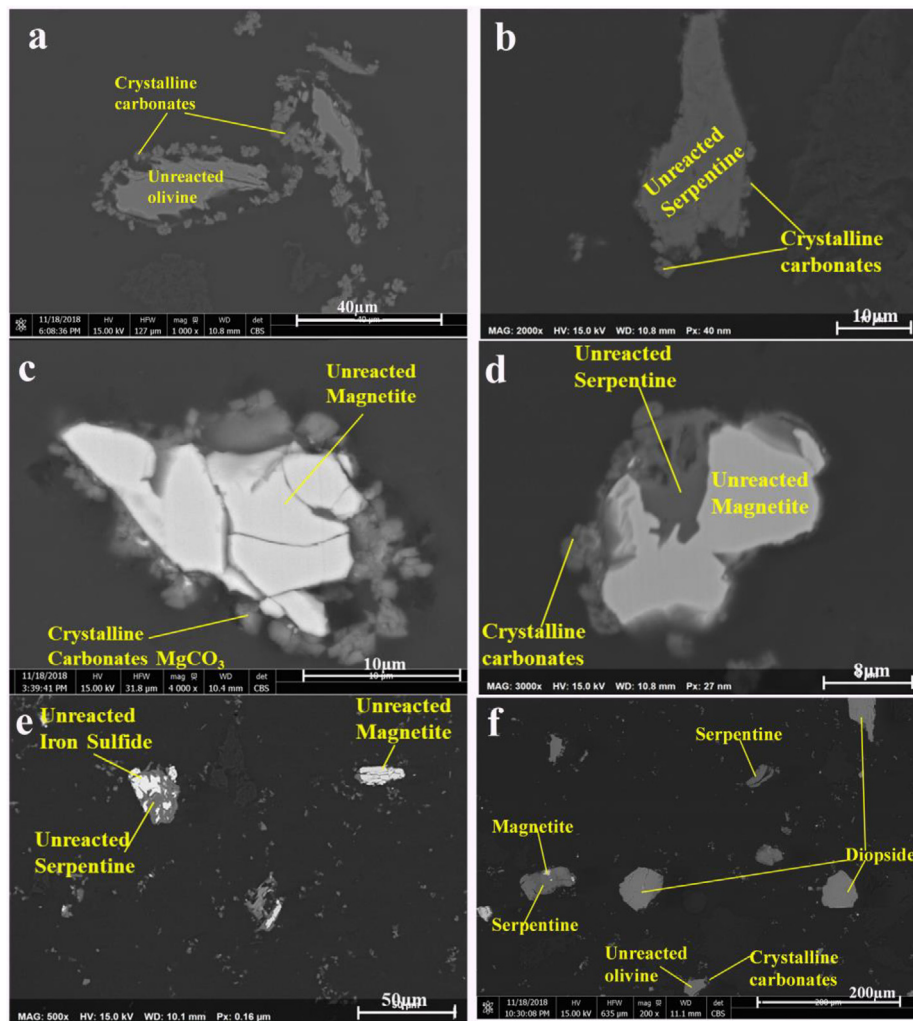


Fig. 6. SEM-EDX images of carbonated products of natural mineral samples under carbonation conditions of $< 25 \mu\text{m}$, $\text{PCO}_2 = 31.0 \text{ bar}$, 175°C , and with 1.5 m NaHCO_3 for 5 h with mineral carbonation efficiency of 80%: a) olivine; b) serpentine; c) magnetite; d) magnetite-serpentine; e) serpentine-iron sulfide and f) diopside-serpentine-magnetite-olivine.

calcium for the carbonation of the natural samples.

To address this issue, it is necessary to combine the kinetics analysis through the SCM expressions and the carbonation behaviours shown by the SEM-EDX analysis. The SEM-EDX analysis has shown that the olivine was the majority of the minerals involved in the mineral carbonation reaction while the other minerals did not significantly participate in the reaction. The other minerals were the serpentine, diopside, iron sulfides and magnetite, which contained the important

magnesium, calcium and iron contents. However, with the mineral carbonation reaction proceeding, the olivine content gradually decreased. In contrast, the contents of serpentine, diopside, iron sulfides and magnetite in the unreacted samples relatively increased. In other words, the contents of magnesium and iron in olivine gradually decreased but the contents of magnesium, calcium and iron in the other unreacted silicate minerals compared to the total magnesium, iron and calcium contents significantly increased. It would be less accurate for

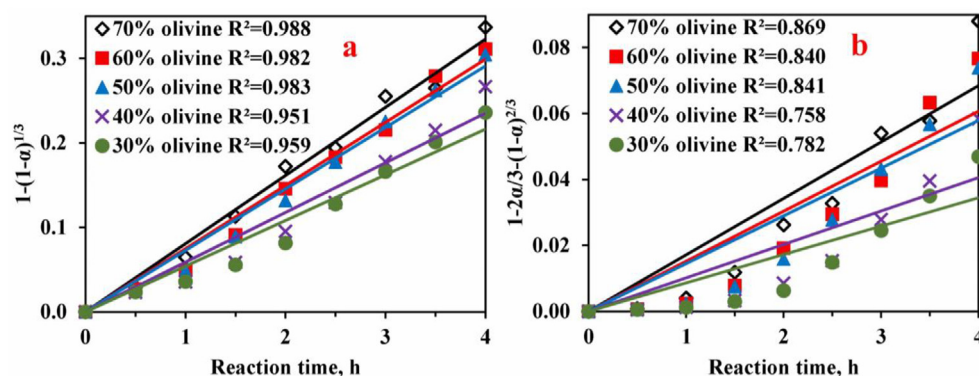


Fig. 7. Effects of olivine content on kinetics: a) chemical reaction control model and b) diffusion through product layer control model.

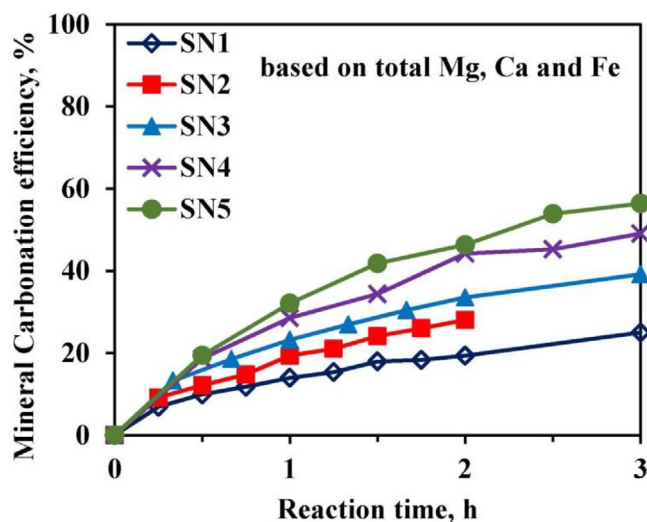


Fig. 8. Mineral carbonation efficiency of natural silicate samples under conditions of $\text{PCO}_2 = 34.5$ bar, 175°C , 1.5 m NaHCO_3 , $< 25\ \mu\text{m}$ narrow-sized particle fractions, pulp density = 10%, 1200 rpm, and carbonation capacity based on the total magnesium, calcium and iron.

the mineral carbonation efficiency to be calculated based on the total bivalent metals for the kinetic analysis. It is reasonable to re-calculate the carbonation efficiency only based on the magnesium and iron contents in olivine for all natural samples, as shown in Fig. 10. The mineral carbonation efficiency for all the natural samples became quite similar to the average 79% within the range 74%–88% at 2 h.

According to the efficiencies based on the only magnesium and iron contents in olivine, the kinetics plots were re-calculated in Fig. 11. It is clear that the R^2 for the relationship between $1 - (1 - \alpha)^{1/3}$ and t of the chemical reaction control model increased from < 0.91 in Fig. 9(a) to approximately 0.98 in Fig. 11(a). Correspondingly, the R^2 for the relationship between $1 - 2\alpha/3 - (1 - \alpha)^{2/3}$ and t of the product layer diffusion control model decreased from originally more than 0.98 in Fig. 9(b) to around 0.92 in Fig. 11(b). As a result, the kinetics control expressions also show that the mineral carbonation of the natural silicate samples was controlled by chemical reaction of the dissolution of olivine. In addition, it is also noted that the carbonation of the natural silicate samples presented the higher rate constant than that of high-grade olivine ($k_2 < 0.08$) [20], although there is no absolute relationship between olivine content and rate constant. This indicates that it may be easier for the natural silicate samples than the high-grade olivine to sequester CO_2 via direct mineral carbonation.

Therefore, it is possible to carry out the kinetics analysis even for the natural silicate samples which contained various basic minerals.

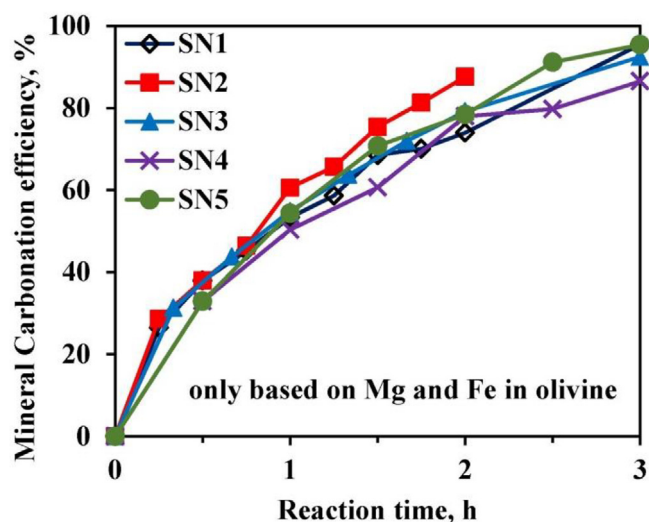


Fig. 10. Effective mineral carbonation efficiency of natural silicate samples under conditions of $\text{PCO}_2 = 34.5$ bar, 175°C , 1.5 m NaHCO_3 , $< 25\ \mu\text{m}$ narrow-sized particle fractions, pulp density = 10%, 1200 rpm, and effective carbonation capacity only based on the magnesium and iron contents in olivine.

The SCM is still suitable for the kinetics analysis of the silicates carbonation. However, it is important for the kinetics analysis to only consider the magnesium and iron contents in olivine for the calculation of effective mineral carbonation capacity.

4. Conclusions

In this paper, the kinetics analysis of the mineral carbonation of naturally impure silicate samples which contained various basic minerals in addition to olivine has been carried out under conditions of 34.5 bar CO_2 partial pressure, 175°C and concentration of 1.5 m NaHCO_3 , with corresponding carbonation efficiency of more than 85% in 3 h. The following conclusions can be determined:

- (1) Olivine carbonation significantly contributed to the mineral carbonation process of impure, multi-mineral silicate samples. The serpentine, diopside, iron sulfides and magnetite did not participate in the carbonation process. The mineral carbonation efficiency was proportional to the olivine content of the impure samples when the mineral carbonation capacity was based on the total magnesium, iron and calcium contents as a conventional way.
- (2) The mineral carbonation of the natural silicate samples was still kinetically controlled by chemical reaction of the dissolution of olivine regardless of the olivine content and mineral compositions.

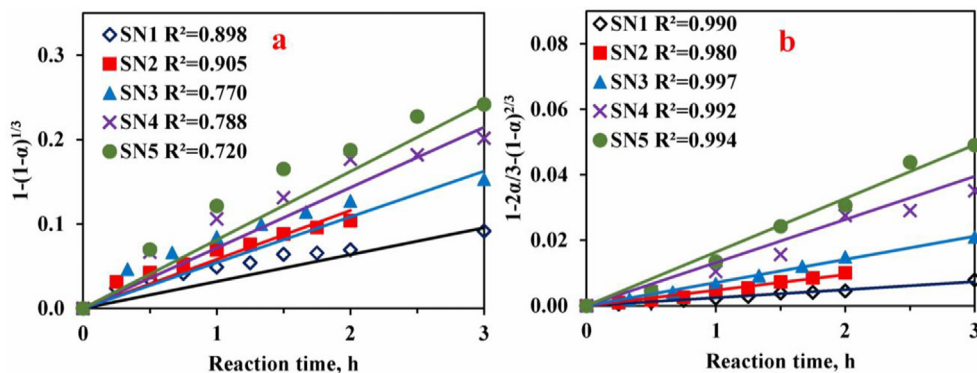


Fig. 9. Kinetics plots of mineral carbonation of natural silicate samples based on the total magnesium, calcium and iron contents: a) chemical reaction control model and b) diffusion through product layer control model.

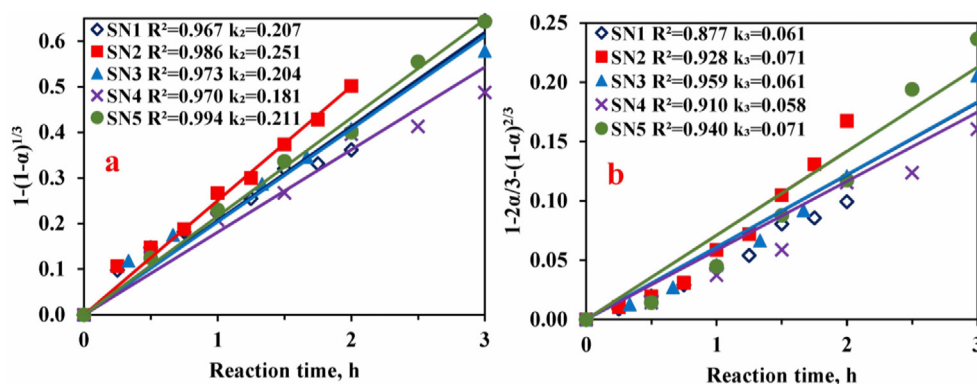


Fig. 11. Kinetics plots of mineral carbonation of natural silicate samples only based on the magnesium and iron contents in olivine: a) chemical reaction control model and b) diffusion through product layer control model.

It is important for the kinetic analysis of carbonation of natural samples to calculate the effective mineral carbonation capacity based only on the magnesium and iron contents in olivine.

This study is applicable to wider feedstock availability owing to the research on natural mixtures of minerals other than a high-grade olivine. Based on this study, future work about combination of direct mineral carbonation and EMR may need to consider more the mineralogy containing target metals and may need to heat pre-treat the multi-mineral silicates to increase CO_2 sequestration rate and potential metal recovery.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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