

**Accelerated carbonation of brucite in mine tailings for
carbon sequestration**

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6 **Accelerated carbonation of brucite in mine tailings for carbon sequestration**
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Abstract

Atmospheric CO₂ is sequestered within ultramafic mine tailings via carbonation of Mg-bearing minerals. The rate of carbon sequestration at some mine sites appears to be limited by the rate of CO₂ supply. If carbonation of bulk tailings were accelerated, large mines may have the capacity to sequester millions of tonnes of CO₂ annually, offsetting mine emissions. The effect of supplying elevated partial pressures of CO₂ ($p\text{CO}_2$) at 1 atm total pressure, on the carbonation rate of brucite [Mg(OH)₂], a tailings mineral, was investigated experimentally with conditions emulating those at Mount Keith Nickel Mine (MKM), Western Australia. Brucite was carbonated to form nesquehonite [MgCO₃·3H₂O] at a rate that increased linearly with $p\text{CO}_2$. Geochemical modeling indicated that HCO₃⁻ promoted dissolution accelerated brucite carbonation. Isotopic and aqueous chemistry data indicated that equilibrium between CO₂ in the gas and aqueous phases was not attained during carbonation, yet nesquehonite precipitation occurred at equilibrium. This implies CO₂ uptake into solution remains rate-limiting for brucite carbonation at elevated $p\text{CO}_2$, providing potential for further acceleration. Accelerated brucite carbonation at MKM offers the potential to offset annual mine emissions by ~22-57%. Recognition of mechanisms for brucite carbonation will guide ongoing work to accelerate Mg-silicate carbonation in tailings.

Introduction

The accumulation of anthropogenic greenhouse gases (GHGs), predominantly CO₂, in the atmosphere has been identified as a cause of climate change.¹ Carbon sequestration is one of many strategies necessary to stabilize CO₂ concentrations while transitioning to alternative energy sources.²⁻⁵ Carbon mineralization involves dissolution of non-carbonate minerals (e.g., silicates, hydroxides, and oxides) and subsequent precipitation of carbonate minerals, which sequesters CO₂.⁵⁻⁸ This is a promising option for carbon sequestration as carbonate minerals are environmentally benign and stable, providing little possibility of accidental release and reducing the need for post-storage monitoring.^{7,9} Research in carbon mineralization has largely focused on industrial processes that use elevated temperatures and pressures to accelerate carbonation reaction rates (e.g., 185°C, 150 atm),⁹⁻¹⁵ however, the financial and energy costs of such methods limits their viability. To avoid such costs, research has been directed towards developing carbon mineralization strategies at low temperature and pressure conditions.¹⁶⁻²² Carbonation of industrial wastes such as steel and blast furnace slag, and alkaline and saline waste water is advantageous as it exploits available waste materials.²³⁻³⁵

Passive carbon mineralization in mine tailings under normal mining conditions has been well documented.^{18,21,24,30,36} This process has been recognized at historic and active Canadian chrysotile and diamond mines,^{18,21,24} and at the active Mount Keith Nickel Mine (MKM) in Western Australia.³⁷ Carbonation of tailings is facilitated by high surface areas,¹⁸ yet at MKM, reaction rates are limited by the uptake of CO₂ into solution.^{30,38} If passive carbonation of bulk tailings were accelerated at large mines, it could more than offset the GHG emissions of mining operations. Supplying elevated

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3 (above atmospheric) partial pressures of CO₂ (*p*CO₂) into tailings may accelerate
4 carbonation both by enhancing mineral dissolution due to increased acidity³⁹⁻⁴¹ and
5 promoting carbonate mineral precipitation due to elevated dissolved inorganic carbon
6 (DIC) concentration.
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13 Carbonation of brucite [Mg(OH)₂], a common but minor component of ultramafic
14 mine tailings, offers significant sequestration potential. It has been documented at
15 between 1-15 wt.% in chrysotile tailings, nickel tailings and deposits, and in chromite ore
16 processing residue.^{22,37,42} In Québec, Canada, there is an estimated 2 Gt of chrysotile
17 mining residue,⁴³ some of which contains 1.8 wt.% brucite.²² If these brucite contents are
18 representative of the entire chrysotile stockpile, up to 27 Mt of CO₂ could be sequestered
19 via brucite carbonation alone. At active mine sites, accelerated carbonation of brucite in
20 tailings provides the potential to significantly offset the annual GHG emissions of mining
21 operations. At MKM, ~11 Mt of tailings are produced annually, containing 0.11-0.28 Mt
22 brucite.^{37,44} Carbonation of the brucite produced annually would offset mine emissions
23 (370 kt/year CO₂ equivalent)⁴⁴ by 22-57%. Yet, passive carbonation rates at MKM and
24 the Black Lake chrysotile mine in Québec are estimated at only ~56³⁷ and ~0.6 kt/year,³⁶
25 respectively. Incorporation of accelerated carbonation methods in the design of
26 prospective mines offers the potential to significantly offset emissions throughout the
27 lifetime of mining operations. At the Dumont Nickel deposit in Québec, for instance,
28 assuming homogeneous brucite distribution in processed nickel ore of 10-15 wt.%²² and a
29 similar scale of operations as MKM, accelerated brucite carbonation could exceed that
30 predicted for MKM. Therefore, despite its minor abundance, brucite carbonation could
31 provide a meaningful CO₂ sink on the scale of mine emissions.
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3 The goal of this study was to investigate the mechanisms of brucite carbonation in
4 mine tailings and to identify the rate-limiting steps in order to design methods for
5 accelerating carbon sequestration in tailings. The effect of elevated $p\text{CO}_2$ at 1 atm total
6 pressure on the carbonation rate of brucite was investigated experimentally in batch
7 reactors. Investigation of brucite carbonation may also guide ongoing work to accelerate
8 carbonation of Mg-silicate minerals in tailings, which constitute the majority of
9 ultramafic tailings and offer greater total sequestration capacity.
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22 **Methods**

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24 Brucite slurries (3.0 L) were prepared in side arm flasks (SI Figure S1). The
25 solution composition mimicked that of pore water at MKM (1.0 M NaCl, and 0.1 M
26 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).⁴⁵ High purity pulverized brucite ore (150 g; grain size = 2-40 μm
27 diameter; surface area = 6.6 m^2/g) from Brucite Mine, Nevada was added to each solution
28 just prior to supplying CO_2 gas. Rietveld refinement of X-ray diffraction (XRD) data
29 indicated the brucite ore was between 90-95 wt.% brucite with minor dolomite and trace
30 lizardite. Mixtures of CO_2 and N_2 gas were bubbled into continuously stirred slurries
31 using glass sparge tubes. Gases were blended using a two-tube gas blender. CO_2
32 concentration of the supplied gas stream was varied between experiments for values of
33 10%, 50%, and 100% CO_2 at a total flow rate of 540 mL/min, which was divided evenly
34 between duplicate experiments that were run simultaneously. Duplicate experiments are
35 henceforth referred to as 'X% CO_2 1 and 2.' Three experiments were run using laboratory
36 air ($p\text{CO}_2 \approx 0.04\%$) supplied at ~270 mL/min using a peristaltic pump to act as
37 experimental controls and establish the carbonation rate at low $p\text{CO}_2$. Slight differences
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3 in the reactivity of duplicate reactors occurred due to imperfect mixing that resulted in
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5 occasional settling of brucite particles, which were re-suspended manually when
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7 observed.
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10 Flasks were vented through the side arm to maintain atmospheric pressure. The
11 exhaust of high $p\text{CO}_2$ experiments was directed into a Los Gatos Research (LGR)[®] off-
12 axis integrated cavity output laser spectrometer for continuous measurement of CO_2
13 concentration.⁴⁶ All gas composition data represent the combined exhaust from duplicate,
14 simultaneous, high $p\text{CO}_2$ reactors.
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22 Slurry temperature and pH were measured routinely and water samples for DIC
23 and Mg concentrations ([Mg]), and $\delta^{13}\text{C}_{\text{DIC}}$ ⁴⁷ were collected regularly. Solid samples
24 were taken at the same time for mineralogical analysis using XRD, $\delta^{13}\text{C}$ and carbon
25 abundance (%C) analysis, and imaging using scanning electron microscopy (SEM).
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27 System mass before and after sampling and the mass of each sample were measured. At
28 the end of each experiment, slurries were filtered to collect and weigh all solids.
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36 The experimental durations were 198, 56, and 72 h for the 10%, 50%, and 100%
37 CO_2 experiments, respectively. Two short-term experiments using atmospheric CO_2 were
38 run for 56 and 72 h to serve as experimental controls (i.e., systems with negligible
39 carbonation). A third atmospheric CO_2 experiment was conducted for 2856 h to establish
40 background carbonation rates. The high $p\text{CO}_2$ experiments were terminated upon
41 achievement of steady-state conditions. For further details regarding experimental setup
42 and analytical techniques, refer to the Supporting information (SI).
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55 **Results and Discussion**

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6 **Chemical environment.** There are three main requirements to allow carbonation
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8 to occur *in situ* in tailings facilities: (1) CO₂ is available in solution as DIC, (2) cations
9 are available, and (3) the chemical environment promotes both tailings mineral
10 dissolution (cation leaching), and carbonate mineral precipitation (Figure 1).
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15 In all reactors, initial pH values following brucite addition were between 9.3 and
16 9.4 and initial DIC concentration ranged from 15 to 26 mg/L. Initial DIC content is
17 attributed to dissolution of laboratory air into the saline solutions prior to sparging of gas.
18 In the 10% and 50% CO₂ reactors, an abrupt initial drop in pH was followed by a period
19 of relatively constant pH before declining to a final stable pH of ~7.6 and ~7.1 in the 10%
20 and 50% experiments, respectively (Figure 2A). In the 100% CO₂ reactors pH declined
21 rapidly to a minimum stable value of ~6.9 after 10 h. Initial drops in pH were coincident
22 with rapid increases in both DIC and [Mg] in all high *p*CO₂ reactors owing to CO_{2(g)} and
23 brucite dissolution, respectively (Figures 2A, 3A-B). The pH value and duration of the
24 first pH stabilization and final pH were dependent on the *p*CO₂ in the reactor atmospheres
25 (Figure 2A). During the first 6-8 h in the 10% CO₂ experiments, DIC and [Mg] increased,
26 before declining to reach near constant values during the period of 12-46 h (Figures 3A-
27 B). The relatively stable DIC during this period is indicative of a quasi-steady-state
28 wherein brucite carbonation was balanced by CO₂ uptake into solution. The final stable
29 pH value was lower at higher *p*CO₂, resulting in a greater proportion of Mg and DIC
30 remaining in solution (Figures 2A, 3A-B, Table 1). Final DIC and [Mg] stabilized
31 approximately at equilibrium with the hydrated carbonate mineral, nesquehonite
32 [MgCO₃·3H₂O], as calculated with PHREEQC⁴⁸ using the Pitzer database (Figure 3A-B).
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4 In the long-term atmospheric CO₂ experiment, pH reached a minimum of 9.0. An
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6 initial increase in DIC in this experiment to 80 mg/L after 192 h was followed by a
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8 decline to 33 mg/L after 2856 h (Figure 2B). This implies DIC was removed faster than it
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10 was replaced by uptake of CO_{2(g)} into solution, with the converse true at early time. A
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12 0.02 M increase in [Mg] in this experiment was consistent with evapoconcentration, with
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14 no significant change in [Mg] in the controls (SI Figure S2). This implies brucite
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16 dissolution was slow in the controls, and was balanced by the rate of Mg-carbonate
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18 precipitation in the long-term experiment.
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23 In all high *p*CO₂ experiments, the decline in pH from alkaline to circumneutral
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25 conditions was driven by the uptake of CO₂. Although low pH accelerates brucite
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27 dissolution,⁴¹ carbonate precipitation is generally favored at higher pH values.^{27,49-51} As
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29 such, some mineral carbonation processes have been designed such that cation extraction
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31 and carbonate precipitation are achieved in separate steps.^{9,49,50,52} *In situ* carbon
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33 mineralization in mine tailings requires these processes to occur concurrently. The
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35 chemical environment must promote tailings mineral dissolution yet permit carbonate
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37 precipitation. The high *p*CO₂ experiments indicated that both brucite dissolution and
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39 carbonate precipitation are promoted with elevated *p*CO₂ at atmospheric pressure and
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41 temperature, suggesting that accelerated *in situ* carbonation of brucite may be achieved in
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43 ultramafic tailings, provided the brucite content is sufficient.
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49 CO₂ concentration in the exhaust gas from duplicate reactors in the 10% CO₂ and
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51 50% CO₂ experiments was reduced by up to 45% and 44%, respectively at the onset of
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53 each experiment, implying carbonation began immediately (SI Figure S3). No change in
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55 gas composition was measurable in the 100% CO₂ experiment as the entire volume of gas
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3 consisted of CO₂. In all high *p*CO₂ experiments, 43-51% of CO₂ supplied during the
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5 carbonation reaction was sequestered (Table 1).
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8 Owing to the exothermic nature of the reaction, an increase in slurry temperature
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10 in high *p*CO₂ reactors over that of experimental controls was noted throughout
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12 carbonation, although the experiments were not insulated (SI Figure S4). Diurnal
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14 temperature variations in the laboratory resulted in periodic fluctuations in slurry
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16 temperature in all experiments (SI Figure S4). Control temperature was exceeded by a
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18 maximum of 5.4 ± 0.5°C. The enthalpy of reaction for brucite carbonation is -75.1
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20 kJ/mol,⁵³ corresponding to a total of ~129 kJ of energy released in the 100% CO₂
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22 experiments based on the average mass of nesquehonite formed, providing the potential
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24 to heat the 3.0 L of water by 10.3°C. This suggests heat was lost to the surroundings.
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26 Temperature may provide a useful indicator for reaction progress and be utilized to
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28 monitor and map carbonation in tailings facilities that contain sufficient brucite.³⁶
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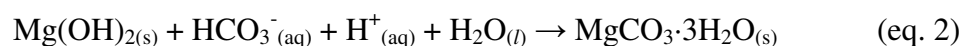
36 **Brucite dissolution and carbonation rates.** The rates of brucite dissolution and
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38 carbonation were accelerated linearly with *p*CO₂, resulting in a ~2400-fold increase in
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40 carbonation rate with an increase from atmospheric *p*CO₂ (~0.04%) to 100% CO₂ (Figure
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42 4). Both dissolution and carbonation rates were calculated as averages over the entire
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44 reaction, making comparison with published dissolution rates difficult, as the
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46 instantaneous rate of reaction may change with time. Brucite dissolution was calculated
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48 as follows (eq. 1):
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$$51 \text{ Rate} = m_{\text{ibr}} / (\text{SA}_{\text{ibr}} \times t_c) \quad (\text{eq. 1})$$

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Where m_{ibrc} is the initial moles of brucite, SA_{ibrc} is the total initial brucite surface area (m^2), and t_c is the time for complete carbonation (s) as estimated with XRD, %C, and pH data (Figure 2A, SI Figures S5-S6). Reaction end times of 75 h for 10% CO_2 1 and 2, 14 and 12 h for 50% CO_2 1 and 2, respectively, and 7 h were estimated for both 100% CO_2 experiments. Average dissolution rates in duplicate reactors were 9.7×10^{-9} , 5.6×10^{-8} and 1.0×10^{-7} $\text{mol}/\text{m}^2/\text{s}$ with 10%, 50%, and 100% CO_2 , respectively. The brucite dissolution rates with atmospheric CO_2 were too slow to be estimated.

XRD results indicated brucite was replaced by nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$] (eq. 2) in all high $p\text{CO}_2$ reactors (SI Figure S6):



Nesquehonite was first detected within 8 h in 10% CO_2 1 and within 6 h in 10% CO_2 2 using carbon abundance analysis. It was detected within 2 h in the 50% and 100% CO_2 experiments. Minor amounts of phases that were not identifiable by XRD were formed in all high $p\text{CO}_2$ reactors and the atmospheric CO_2 experiment (SI Figure S6-S7). In the atmospheric CO_2 experiment, carbon abundance in the solids increased by 2.6%, identifying this phase as a carbonate. The unidentified phase was replaced by dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$] as the reaction progressed in 10% 1 and 2. XRD and %C data indicated carbonation was completed within 102 h in the 10% CO_2 reactors, by the 22 h and 12 h sampling points in 50% CO_2 1 and 2, respectively, and between 6 and 10 h in both 100% CO_2 reactors (SI Figure S6). Reaction end points between these times were inferred by the final decline in pH indicative of brucite removal.

As observed by SEM, precipitates from the 10% and 50% CO_2 experiments included elongate crystals consistent with the morphology of nesquehonite,²⁷ along with

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3 flaky, poorly crystalline material and pseudo-rosettes (SI Figure S8). This morphology is
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5 typical of dypingite,^{19,54} and is likely representative of both dypingite and the unidentified
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7 carbonate phase in the high $p\text{CO}_2$ experiments. Precipitates from the 100% CO_2
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9 experiments were dominated by nesquehonite crystals (SI Figure S8).
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13 Other experimental studies have used elevated CO_2 concentrations to precipitate
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15 nesquehonite by replacement of brucite or carbonation of MgCl_2 in solution,^{27,31,55,56}
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17 which is consistent with this study. With a Mg:C ratio of 1:1, nesquehonite optimizes the
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19 amount of carbon stored per cation, an advantage for sequestration purposes. Dypingite
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21 and the unidentified carbonate phase may be reaction intermediates⁵⁷ or products of
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23 nesquehonite dehydration⁵⁸ between sampling and analysis, as depicted in SEM images,
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25 wherein flaky material armors nesquehonite crystals (SI Figure S8).
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30 Initial %C values of solids ranged from 0.76-1.10% owing to the presence of
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32 primary dolomite [$\text{CaMg}(\text{CO}_3)_2$]. Carbon abundance in solid samples increased with time
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34 in each high $p\text{CO}_2$ experiment, followed by stabilization between 7.85 and 8.29% within
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36 100, ~12, and 10 h in the 10%, 50%, and 100% CO_2 experiments, respectively (SI Figure
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38 S5). This is consistent with formation of nesquehonite, which ideally contains 8.68%
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40 carbon. Carbon abundance increased to 3.6% after 2856 h in the atmospheric CO_2
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42 experiment. The mass of CO_2 sequestered in the high $p\text{CO}_2$ experiments was calculated
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44 using %C data assuming that dolomite mass remained constant and that CO_2 was stored
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46 primarily within nesquehonite. A total of 317 g of nesquehonite (~101 g CO_2) and 253 g
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48 (~81 g CO_2) were formed in 10% CO_2 1 and 2, respectively. In 50% CO_2 1 and 2, 275 g
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50 of nesquehonite (~88 g CO_2) and 244 g of nesquehonite (~78 g CO_2) were formed,
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53 respectively. A total mass of 223 g of nesquehonite (~71 g CO_2) and 254 g of
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nesquehonite (~81 g CO₂) was precipitated in 100% CO₂ 1 and 2, respectively.

Discrepancies between duplicate reactors are attributed to imperfect mixing causing minor amounts of brucite to remain uncarbonated. The mass of carbon mineralized in the atmospheric CO₂ experiment was calculated using %C data assuming that brucite mass remained relatively unchanged, which is justified by the relative peak heights in the XRD data. A total of ~14 g CO₂ was captured over 2856 h.

Carbonation rates in the high *p*CO₂ experiments were calculated as follows (eq. 3):

$$\text{CO}_2 \text{ sequestration rate (g CO}_2\text{/g brucite/h)} = [(m_{\text{fnsq}} / M_{\text{nsq}}) \times M_{\text{CO}_2}] / (m_{\text{ibr}} \times t_{\text{h}}) \quad (\text{eq. 3})$$

Where m_{fnsq} is the final mass of nesquehonite (g), m_{ibr} is the initial brucite mass (g), t_{h} is the time of reaction completion (h), and M_{nsq} and M_{CO_2} are the molar masses of nesquehonite and CO₂ (g/mol), respectively. In the atmospheric CO₂ experiment, the carbonation rate was calculated based on the rate of increase of %C in the solids. The rates of CO₂ sequestration using laboratory air, and average rates between duplicate 10%, 50%, and 100% CO₂ experiments were $\sim 3.30 \times 10^{-5}$, 7.78×10^{-3} , 4.26×10^{-2} , and 8.00×10^{-2} g CO₂/g brucite/h, respectively. Dissolution and carbonation rates and CO₂ mass balances are summarized in Table 1.

Reaction mechanism. Brucite dissolution is a surface controlled reaction^{39,41,59} that is accelerated with increased acidity and concentration of certain organic and inorganic ligands, such as HCO₃⁻.^{39,41,60} Proton and ligand promoted dissolution occur in

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3 parallel; their effect is additive.⁶⁰ Ligands that promote brucite dissolution are those that
4 form protonated ions at neutral to weakly alkaline pH (e.g., HCO_3^-), whereas those that
5 are deprotonated inhibit dissolution (e.g., CO_3^{2-}).^{39,60} Therefore, aqueous carbonate
6 species may enhance or inhibit brucite dissolution depending on the solution pH.
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8 Previous studies have documented a dependence of brucite and MgO dissolution rate on
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10 HCO_3^- concentration.^{31,60} As HCO_3^- is the dominant aqueous carbonate species in the
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12 experimental pH range,⁶¹ dissolution and hydration of CO_2 may accelerate brucite
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14 dissolution via the direct effect of increasing HCO_3^- concentration and the indirect effect
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16 of increasing acidity. These effects cannot be separated in the high $p\text{CO}_2$ experiments, as
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18 neither pH nor DIC were fixed. Increased DIC concentration should also promote brucite
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20 carbonation by facilitating carbonate precipitation at lower Mg concentration, as
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22 suggested by Chen et al.⁶² to account for enhanced carbonation of olivine in NaHCO_3
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24 solutions.
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34 To discern the effect of elevated $p\text{CO}_2$ on brucite carbonation rate, experimental
35 conditions were modeled using PHREEQC.⁴⁸ Experimentally determined, steady-state,
36 far from equilibrium rate laws dependent on pH^{41} and ligand (HCO_3^-) concentration⁶⁰
37 were used, and are provided in the SI. Nesquehonite precipitation and CO_2 uptake were
38 simulated as equilibrium processes. Modeling revealed that experimental dissolution and
39 carbonation rates exceeded those predicted with proton promoted dissolution and high
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41 DIC promoted carbonate precipitation alone. With 100% CO_2 , the experimental
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43 carbonation rate is 6-fold faster than predicted due to acidity promoted dissolution
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45 (Figure 4). Comparison of experimental dissolution rates with the pH-dependent rate law
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47 of Pokrovsky and Schott⁴¹ highlights the discrepancy between the experimental rates and
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3 those predicted due to proton promoted dissolution (SI Figure S9). In this study,
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5 dissolution rate is calculated based on the time to dissolve brucite of a specified mass,
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7 rather than an instantaneous rate based on the flux of Mg^{2+} ; this could in part explain the
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9 divergence from the Pokrovsky and Schott rate law,⁴¹ as the instantaneous rate was likely
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11 not constant. Experimental carbonation rates fell between those predicted by pH and
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13 HCO_3^- promoted dissolution (Figure 4), implying that HCO_3^- promoted brucite
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15 dissolution is likely an important mechanism enhancing brucite carbonation, yet the CO_2
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17 supply was insufficient to achieve the maximum predicted rates.
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25 **Rate limitation.** The fractionation of carbon stable isotopes can be used to infer
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27 the relative rates of processes that involve CO_2 and thus help identify rate limitations.³⁰
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29 All isotopic data are reported in δ -notation relative to Vienna Pee Dee Belemnite (VPDB)
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31 in units of per mil (‰). The $\delta^{13}\text{C}_{\text{CO}_{2(\text{g})}}$ values of the gas supply for the 10%, 50%, and
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33 100% CO_2 experiments were -35‰, -37‰, and -32‰, respectively. Differences in initial
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35 $\delta^{13}\text{C}_{\text{CO}_{2(\text{g})}}$ values are due to the use of different CO_2 tanks for each experiment.
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38 Equilibrium fractionation between $\text{CO}_{2(\text{g})}$ and HCO_3^- is +7.9‰ at 25°C,⁶³ therefore, the
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40 equilibrium $\delta^{13}\text{C}_{\text{DIC}}$ values for the high $p\text{CO}_2$ experiments should be between ~-24‰, to -
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42 29‰. Divergence from the equilibrium $\delta^{13}\text{C}_{\text{DIC}}$ value increased in the first 36 h in 10%
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44 CO_2 1 and 2, before rising to reach equilibrium composition after ~175 h (Figure 5A).
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47 Wilson et al. observed a similar negative trend in $\delta^{13}\text{C}_{\text{DIC}}$ values during carbonation of a
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49 MgCl_2 solution using atmospheric CO_2 , which was attributed to a kinetic isotope
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51 fractionation effect due to slow uptake of $\text{CO}_{2(\text{g})}$ into solution.³⁰ In the 50% and 100%
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53 CO_2 experiments, equilibrium $^{13}\text{C}_{\text{DIC}}$ composition was obtained after 56 and 43 h,
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3 respectively (Figure 5A). Yet, mineralogical data indicated carbonation was complete
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5 within 75, 12, and 7 h in the 10%, 50% and 100% CO₂ experiments, respectively. This
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7 implies that isotopic equilibrium between CO₂ in the gas and aqueous phase was not
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9 achieved during the carbonation reaction, but is only approached when the DIC sink,
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11 carbonate mineral precipitation, is ceased.
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15 Due to the presence of dolomite in the initial material, early time $\delta^{13}\text{C}$ values of
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17 solids are not representative of precipitated carbonate ($\sim -4.4\text{‰}$). A cut off of a minimum
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19 of 4% carbon in the solids (at least 80% of carbon in nesquehonite) was chosen to be
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21 representative of nesquehonite stable isotopic composition. Nevertheless, the presence of
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23 minor dolomite results in the solids being enriched relative to the precipitated
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25 nesquehonite. The $\delta^{13}\text{C}$ values of the solids (primarily nesquehonite) remained between -
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27 28.3‰ to -30.8‰ , and -29.6‰ to -32.6‰ in 10% CO₂ 1 and 2, respectively. A greater
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29 range in $\delta^{13}\text{C}$ values was recorded in the 50% CO₂ experiment, with values between -
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31 29.6‰ to -37.4‰ , and -31.2‰ to -36.1‰ in 50% CO₂ 1 and 2, respectively. In 100%
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33 CO₂ 1 and 2, $\delta^{13}\text{C}$ values were between -25.0‰ to -30.1‰ , and -25.6‰ to -31.0‰ ,
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35 respectively. Fresh carbonate could not be sampled therefore $\delta^{13}\text{C}$ values are cumulative
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37 for carbonate formed throughout each experiment. Insufficient carbonate precipitation
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39 occurred in the atmospheric CO₂ experiment to determine the ^{13}C composition of the
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41 carbonate.
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48 The equilibrium $\delta^{13}\text{C}$ fractionation factor between nesquehonite and HCO₃⁻ has
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50 not been determined. However, the observed fractionation is consistent with the
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52 equilibrium carbon isotopic fractionation factor estimated by Wilson et al. for dypingite
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54 and HCO₃⁻ ($3.8 \pm 1.3\text{‰}$ at 25°C).³⁰ The $\delta^{13}\text{C}$ values of solids generally deviate between
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3 0-5‰ from values predicted assuming isotopic equilibrium is maintained with the
4 average $\delta^{13}\text{C}_{\text{DIC}}$ value during carbonation (Figure 5B). The majority of $\delta^{13}\text{C}$ values of
5 solids fall within the range of equilibrium composition estimated with the observed range
6 of $\delta^{13}\text{C}_{\text{DIC}}$ values during carbonation (shaded area in Figure 5B). This suggests that
7 nesquehonite precipitated approximately at isotopic equilibrium with DIC throughout
8 carbonation. Moreover, nesquehonite saturation indices calculated using PHREEQC⁴⁸
9 indicate nesquehonite precipitated near chemical equilibrium (SI Figure S10). This
10 implies carbonate mineral precipitation is not rate limiting for carbonation, rather the
11 slow approach to isotopic equilibrium between $\text{CO}_{2(\text{g})}$ and DIC indicates uptake of CO_2 is
12 the limiting step for brucite carbonation.
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27 During carbonation, DIC concentrations in experiments were consistently below
28 $\text{CO}_{2(\text{g})}\leftrightarrow\text{DIC}$ equilibrium levels as predicted by PHREEQC⁴⁸ modeling (Figure 3A). This
29 further indicates equilibrium between CO_2 in the gas and aqueous phase was not obtained
30 during carbonation. Experimental carbonation rates were generally lower than predicted
31 by modeling due to HCO_3^- promoted dissolution, with divergence increasing at lower
32 $p\text{CO}_2$ (Figure 4). This is consistent with a kinetic limitation to uptake of CO_2 into
33 solution, as equilibrium DIC concentrations were not achieved in the experiments, and
34 divergence from $\text{CO}_{2(\text{g})}\leftrightarrow\text{DIC}$ equilibrium was greatest at lower $p\text{CO}_2$. This is in
35 agreement with the stable isotopic data, indicating that uptake of CO_2 into solution is rate
36 limiting for brucite carbonation even at elevated $p\text{CO}_2$. The implication is that if
37 $\text{CO}_{2(\text{g})}\leftrightarrow\text{DIC}$ equilibrium could be attained, the brucite carbonation rate would be further
38 accelerated. CO_2 uptake into solution is divided into two steps: (1) $\text{CO}_{2(\text{g})}$ dissolution and
39 (2) $\text{CO}_{2(\text{aq})}$ hydration. $\text{CO}_{2(\text{g})}$ dissolution involves the phase transfer from gaseous to
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3 aqueous CO₂, whereas CO_{2(aq)} hydration is the subsequent formation of H₂CO₃ or HCO₃⁻
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5 depending on solution pH, which dissociate to form CO₃²⁻.⁶⁴ It is well understood that
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7 dissociation is rapid, whereas the hydration of CO_{2(aq)} is relatively slow.⁶⁴⁻⁶⁶ An option
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9 for further enhancing CO₂ uptake into solution is to accelerate CO₂ hydration, which may
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11 be achieved through use of biological catalysts such as the carbonic anhydrase enzyme.⁶⁷⁻
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Implications for carbon sequestration in mine tailings. Experimental data show a linear increase in brucite carbonation rate with *p*CO₂, resulting in a ~2400-fold acceleration with an increase from atmospheric *p*CO₂ (~0.04% CO₂) to 100% CO₂. Conversely, modeling using PHREEQC⁴⁸ reveals a non-linear relationship between carbonation rate and *p*CO₂ with both proton and HCO₃⁻ promoted dissolution (Figure 4). This implies that use of 100% CO₂ may not be necessary to achieve maximum carbonation rates if CO₂ uptake into solution were enhanced (Figure 4). Direct use of flue gas (e.g., ~17% CO₂)⁷⁰ from mine site power plants could be sufficient to achieve similar carbonation rates as use of purified CO₂. This is highly advantageous as it eliminates the cost of purifying CO₂.

Despite a kinetic limitation for uptake of CO₂ into solution, brucite carbonation rates achieved in experiments exceed that required to carbonate all the brucite produced annually at MKM. MKM produces ~0.11-0.28 Mt of brucite in tailings annually, and emits 370 kt/year of CO₂ equivalent GHGs.^{37,44} Carbonation of brucite produced annually would offset mine emissions by ~22-57% (Figure 6), which is up to 4-fold faster than estimated passive carbonation rates.³⁷ A tax on carbon emissions implemented in July

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3 2012 in Australia implies tailings carbonation may offer a significant financial benefit for
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5 Australian mines such as MKM (e.g., up to \$4.8 million saved annually).⁷¹ Complete
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7 carbonation of brucite accumulated in tailings stockpiles at MKM would sequester a total
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9 of 1-3 Mt of CO₂. This is a comparable sequestration rate to what is currently achieved at
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11 the largest geologic carbon sequestration demonstration projects (~1-2.8 Mt
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13 CO₂/year).^{72,73}
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17 Brucite is present in ultramafic tailings from other deposit types, such as
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19 chrysotile. In Québec, Canada, there are approximately 2 Gt of chrysotile mining
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21 residues.⁴³ At the Black Lake mine in Quebec, chrysotile milling residues contain ~1.8
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23 wt.% brucite.²² If these brucite contents are representative for the entire stockpile, up to
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25 27 Mt of CO₂ could be sequestered via brucite carbonation alone.
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29 Brucite carbonation represents only a small proportion of the total sequestration
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31 potential of ultramafic tailings, which consist primarily of Mg-silicate minerals. At MKM,
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33 accelerated carbonation of Mg-silicate minerals has the potential to sequester much more
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35 CO₂ than is emitted annually (Figure 6). Accelerated dissolution of silicate tailings
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37 minerals such as serpentine [Mg₃Si₂O₅(OH)₄] and forsterite [Mg₂SiO₄] is predicted with
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39 increased *p*CO₂ owing to proton promoted dissolution.^{40,74} The effect of inorganic carbon
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41 ligands on silicate mineral dissolution is less certain (c.f., forsterite,⁷⁵ wollastonite,⁷⁵ and
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43 anorthite⁷⁶), and the effect on serpentine dissolution is not well understood under
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45 conditions prevalent in mine tailings. The presence of ligands such as citrate have been
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47 found to enhance serpentine dissolution by several orders of magnitude over that
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49 predicted by pH promoted dissolution, and can be significant in pH ranges appropriate for
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51 carbonate precipitation.⁵¹ If serpentine dissolution were similarly affected as brucite by
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3 surface reactions involving the HCO_3^- ligand, total carbonation rates in tailings may be
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5 underestimated based on pH effects alone.
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34 **Supporting Information Available**

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36 A detailed description of the experimental setup, analytical techniques, and
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38 additional results can be found in the Supporting Information. This information is
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40 available free of charge via the Internet at <http://pubs.acs.org>.
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Figure Captions

Figure 1. Schematic of carbon mineralization *in situ* in a tailings storage facility.

Figure 2. Plots of pH (A) in high $p\text{CO}_2$ experiments versus time. Dashed lines are results from PHREEQC⁴⁸ models assuming kinetically controlled brucite dissolution and equilibrium $\text{CO}_{2(\text{g})}$ dissolution. Dissolved inorganic carbon (DIC) (diamonds) and pH (+) in the long-term atmospheric CO_2 experiment, and DIC (triangles) and pH (circles) in controls versus time (B). The dashed line in (B) indicates the DIC concentration at equilibrium with atmospheric CO_2 . Open symbols and solid symbols in (A) represent duplicates 1 and 2, respectively. Arrows above the graph in (A) represent the duration of the carbonation reaction in the 100%, 50% and 10% CO_2 experiments, respectively.

Figure 3. Plots of dissolved inorganic carbon concentration (DIC) (A), and Mg concentration (B) in high $p\text{CO}_2$ experiments versus time. Dashed lines are results from PHREEQC⁴⁸ models assuming kinetically controlled brucite dissolution and equilibrium $\text{CO}_{2(\text{g})}$ dissolution. Open symbols and solid symbols represent duplicates 1 and 2, respectively. Arrows above the graphs represent the duration of the carbonation reaction in the 100%, 50% and 10% CO_2 experiments, respectively.

Figure 4. Experimentally determined and modeled (PHREEQC)⁴⁸ brucite carbonation rate versus $p\text{CO}_2$ in experiments using ligand (Pokrovsky et al.)⁶⁰ and pH (Pokrovsky and

1
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3 Schott)⁴¹ dependent brucite dissolution rate laws. Open symbols and solid symbols
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5 represent duplicates 1 and 2, respectively.
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10 **Figure 5.** Deviation from calculated equilibrium $\delta^{13}\text{C}_{\text{DIC}}$ values relative to VPDB in high
11 $p\text{CO}_2$ experiments versus time using the fractionation factor of Mook et al. (A).⁶³
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13 Deviation from calculated equilibrium $\delta^{13}\text{C}$ values of solids with the average $\delta^{13}\text{C}_{\text{DIC}}$
14 during carbonation using the fractionation factor of Wilson et al.³⁰ in high $p\text{CO}_2$
15 experiments versus time of sampling (B). Shaded area represents the range of equilibrium
16 $\delta^{13}\text{C}$ values of solids with the observed range in $\delta^{13}\text{C}_{\text{DIC}}$ values during carbonation. Open
17 and solid symbols represent duplicates 1 and 2, respectively. Arrows above the graphs
18 represent the duration of the carbonation reaction in the 100%, 50% and 10% CO_2
19 experiments, respectively.
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34 **Figure 6.** Comparison of range of passive annual carbonation rates at Diavik Diamond
35 Mine, Northwest Territories, Canada,²¹ Clinton Creek Chrysotile mine, Yukon Territory,
36 Canada,¹⁸ and the Mount Keith Nickel Mine (MKM), Western Australia³⁷ with annual
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38 GHG emissions at various mine sites, total sequestration capacity, and potential annual
39 carbonation rates at MKM via accelerated brucite carbonation.
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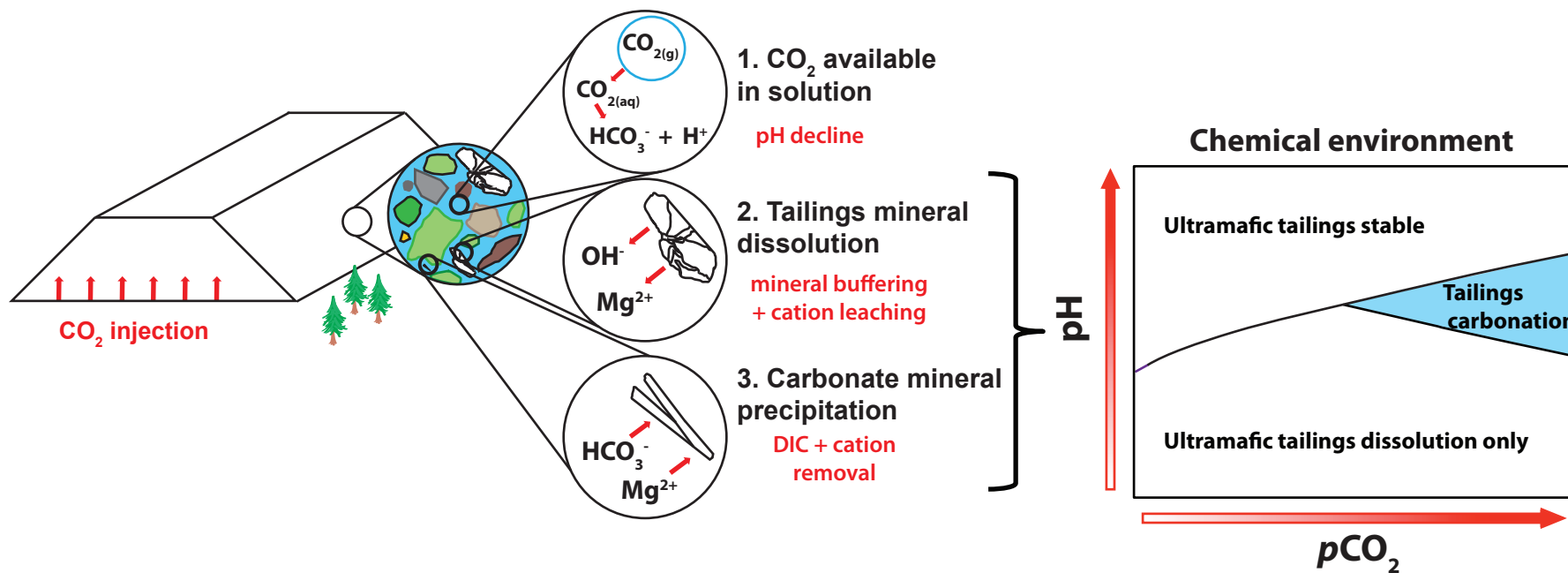
Table 1. CO₂ mass balance and brucite dissolution and carbonation rates[‡]

<i>p</i> CO ₂	Dissolution rate*	Carbonation rate*	CO _{2(g)} supplied	CO ₂ in aqueous phase	CO ₂ in solid	Total CO ₂ sequestered	**Efficiency
(% of 1 atm)	(mol brucite/h)	(mol CO ₂ /h)	(g)	(g)	(g)	(g)	(%)
0.04	No data	1.1×10^{-4}	1768	8×10^{-2}	14	14	0.8%
10	0.03	0.03	223	6	91	97	43%
50	0.22	0.15	180	9	83	92	51%
100	0.36	0.27	211	16	76	92	44%

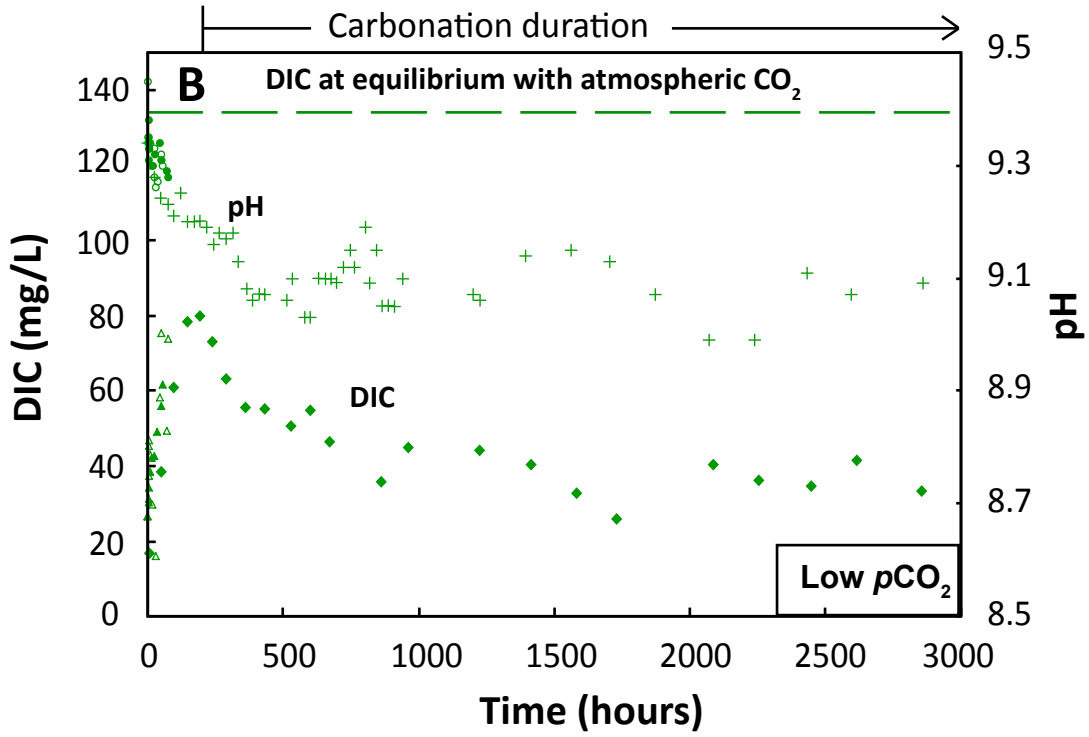
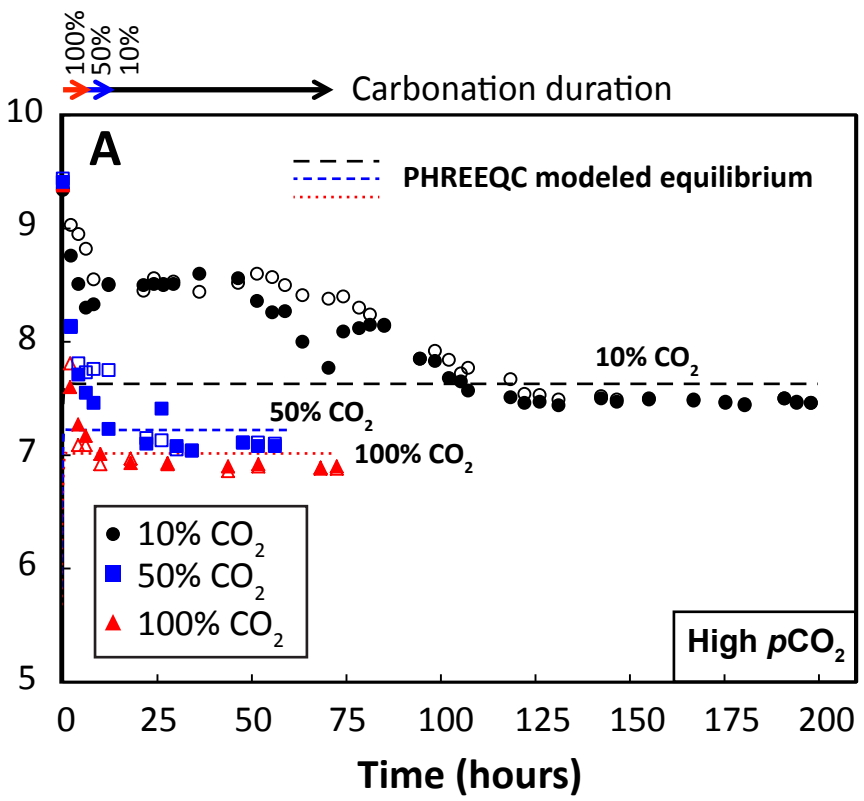
[‡]All values are averages for duplicate reactors.

*Dissolution and carbonation rates have been converted to mol/h for ease of comparison.

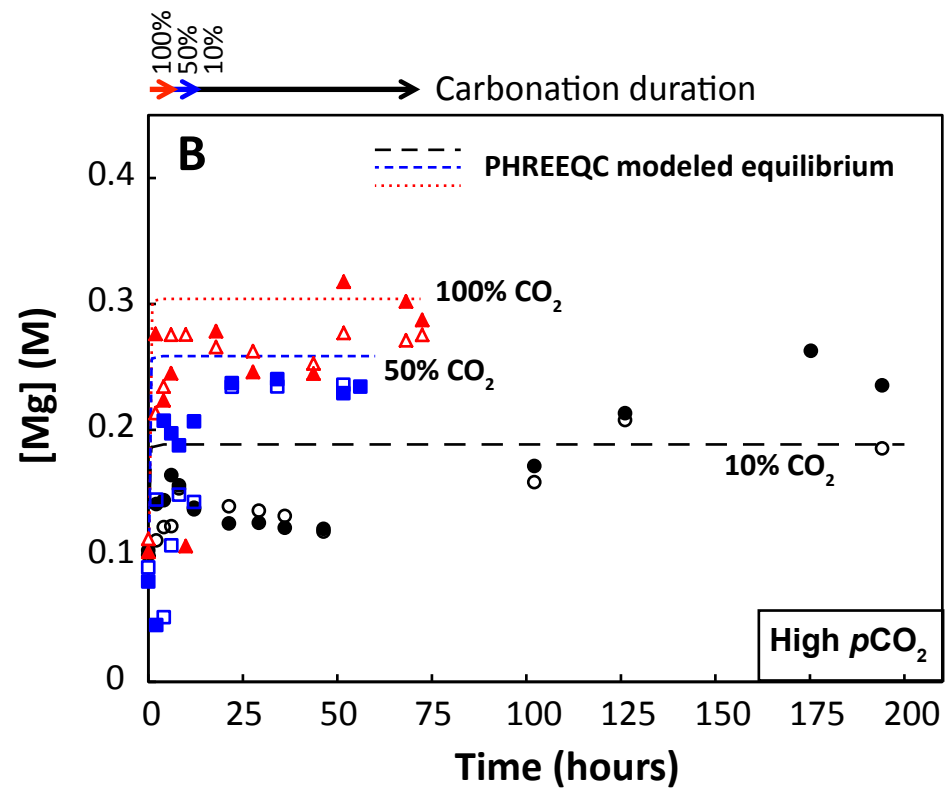
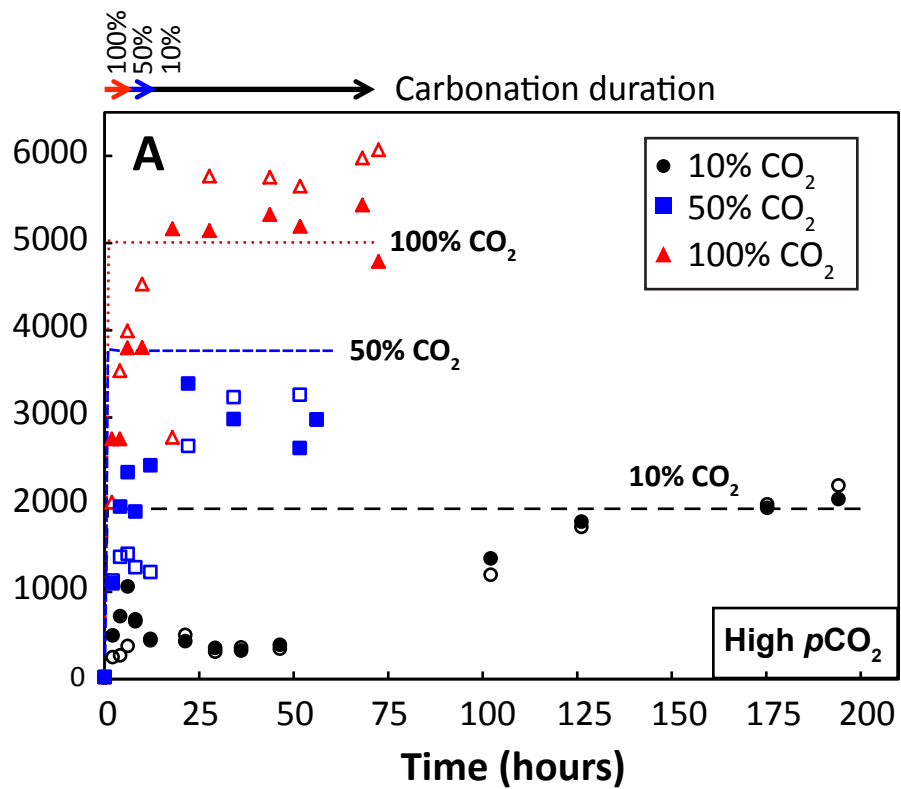
**Efficiency calculated as Mass CO₂ sequestered in solid ÷ Mass CO_{2(g)} supplied during carbonation.

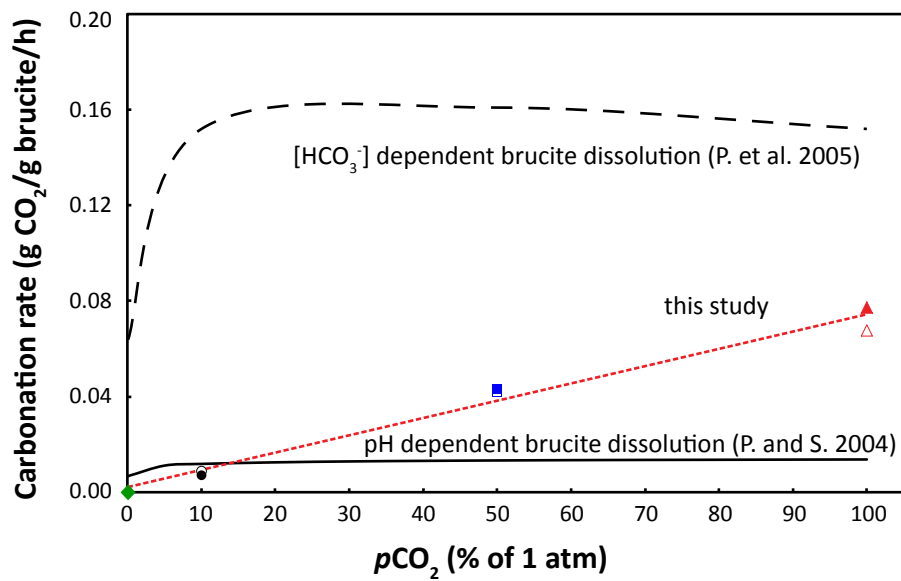


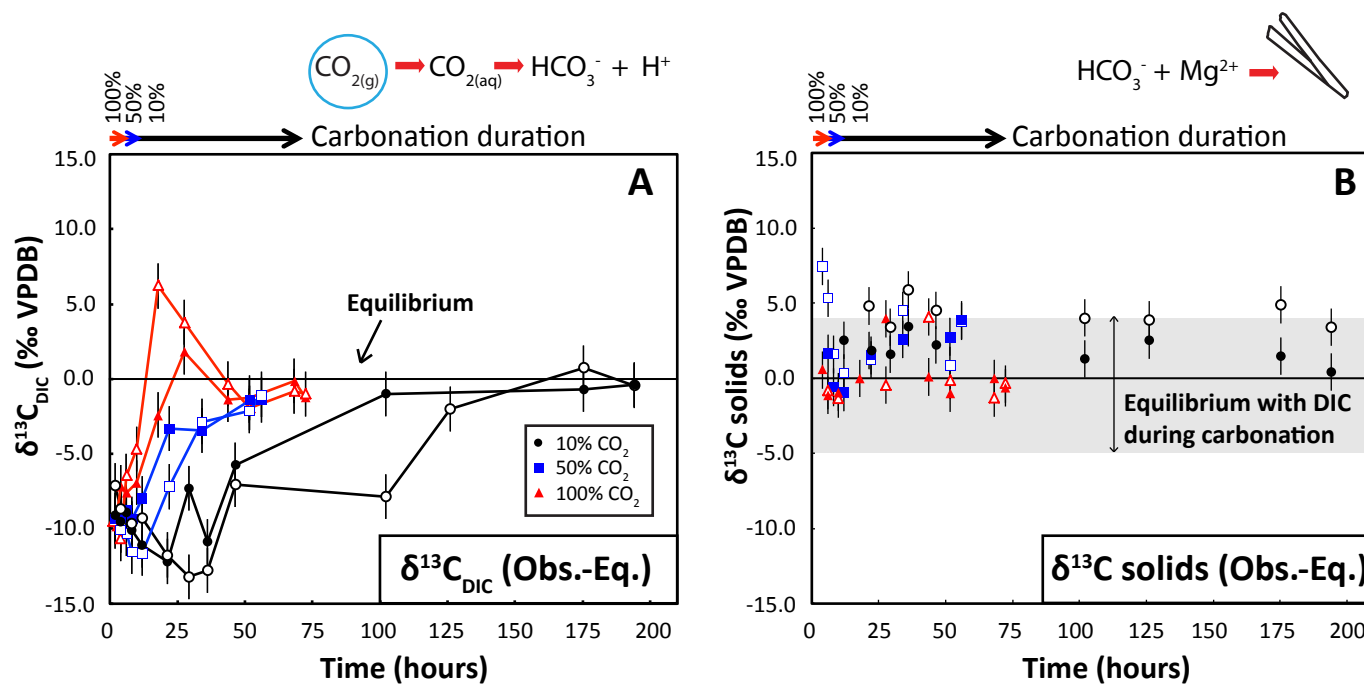
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