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International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc



Rates of atmospheric CO₂ capture using magnesium oxide powder

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ARTICLE INFO

Keywords: Direct air capture CO₂ mineralization Negative emissions technologies Carbon dioxide removal Atmospheric CO₂ capture

ABSTRACT

Magnesium oxide (MgO) looping is a proposed technology for gigatonne-scale carbon dioxide (CO₂) removal from the atmosphere. Here, we determined CO₂ removal rates by measuring CO₂ fluxes and total inorganic carbon (TIC) using a deposit of MgO powder (10 cm thickness; 76 kg MgO/m²). The majority of the MgO powder (~87 wt%) was transformed to brucite [Mg(OH)₂] after the first two wetting and drying cycles. CO₂ fluxes varied depending on water content and porosity: -3.9 (saturated/wet), -12.5 (optimal), and -2.2 (dry) kg CO₂/m²/yr. At these rates, only 3–18% of the MgO would react in 1 yr and require areas of 80,000–455,000 km² to sequester 1 Gt CO₂/yr. Gas-filled porosity of $\sim39-58\%$ and water contents of 7–17 wt% were optimal for CO₂ ingress and carbonation. Dypingite [Mg₅(CO₃)₄(OH)₂· \sim 5H₂O] was the sink of atmospheric CO₂ and TIC increased from 0.2% to 7.5% CO₂. The δ^{13} C values of the solids (avg. -14.9%; VPDB) were well below those expected for dypingite precipitated in equilibrium with laboratory CO₂, demonstrating that CO₂ supply was rate-limiting, despite daily tilling of the deposit. A linear extrapolation of the CO₂ fluxes shows that 90% carbonation of MgO will require 5–27 yr. CO₂ removal rates slowed down with time over 1 yr, in agreement with the expectation that the progressive depletion of reactants (MgO/brucite) is likely to substantially slow CO₂ removal rates and greatly extend the time needed to achieve complete carbonation.

1. Introduction

Reducing carbon dioxide (CO₂) emissions alone will be insufficient to limit anthropogenic global warming to no greater than 1.5-2 °C (Dong et al., 2018). Rather, the development and deployment of carbon dioxide removal (CDR) approaches and technologies including afforestation (Bastin et al., 2019), bioenergy with carbon capture and storage (BECCS; Humpenöder et al., 2014), direct air capture (DAC; Fasihi et al., 2019; Terlouw et al., 2021), and enhanced rock weathering (ERW; Beerling et al., 2020; Goll et al., 2021; Manning and Renforth, 2013; Myers and Nakagaki, 2020) are unavoidable if the worst impacts of climate change are to be avoided (Dong et al., 2018; IPCC, 2022; Smith et al., 2016). Magnesium oxide (MgO) looping is a proposed technology for atmospheric CO₂ capture by which magnesite (MgCO₃) is calcined to MgO with the release of high purity CO_2 being stored (Eq. (1)) and the regenerated MgO being repeatedly used to capture additional CO2 (Eq. (2)) (Kelemen et al., 2020; McQueen et al., 2020a). The CO₂ that is released during calcination can be either utilized or stored, e.g., underground injection.

$$MgCO_3 \rightarrow MgO \text{ (for capture)} + CO_2 \text{ (for storage)}$$
 (1)

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https://doi.org/10.1016/j.ijggc.2022.103701

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Received 5 December 2021; Received in revised form 27 April 2022; Accepted 26 May 2022 Available online 5 June 2022 1750-5836/© 2022 Elsevier Ltd. All rights reserved.

 $MgO + CO_2 \rightarrow MgCO_3$ (for calcination)

(2)

McQueen et al. (2020a) propose using a 10 cm thick deposit of MgO powder, spread over large areas (e.g., 1000 s km²) and tilled daily, to capture atmospheric CO₂ by forming Mg-carbonates such as magnesite (MgCO₃). A key advantage of using magnesium carbonates instead of calcium carbonates is the much lower calcination temperature, 350-600 (Hollingbery and Hull, 2012; Lin et al., 2018) versus ~650-1000°C (Ćwik et al., 2018; Grasa and Abanades, 2006; Rodriguez-Navarro et al., 2009), which results in lower energy requirements. However, worldwide magnesite reserves are significantly less than limestone (CaCO₃) reserves (U.S. Geological Survey, 2020). Disregarding any process inefficiencies or material losses, capturing 1 Gt CO2/yr from the atmosphere would require ~ 1.9 Gt MgCO₃, equivalent to $\sim 25\%$ of the estimated world magnesite reserves (U.S. Geological Survey, 2020). Furthermore, McQueen et al. (2020a) estimate that 5-10% of the deposited material would be lost to the environment per year, based on the dissolution of MgO and MgCO₃ as well as considering soil erosion. Based on the authors' assumptions, their proposed process can conservatively achieve 90% carbonation of MgO powder with a particle size of 20 µm to form magnesite (MgCO₃) in 1 yr. The authors suggest that this atmospheric CO₂ capture approach could potentially capture 2–3 Gt CO₂/yr, be cost-competitive, and require a similar land footprint to DAC technologies that use synthetic sorbents or solvents to capture CO₂ (Kelemen et al., 2020; McQueen et al., 2020b; Terlouw et al., 2021) or porous portlandite [Ca(OH)₂] structures (Abanades et al., 2020). These CO₂ removal rates and land requirements are based on the assumptions made by McQueen et al. (2020a) that include MgO (periclase) having the same reactivity as Mg(OH)₂ (brucite) and its dissolution is rate-limiting, and that magnesite will be the carbonation product. However, the lack of experimental data makes it difficult to assess if such assumptions are realistic and thus, the feasibility of such technology is yet to be tested.

The CO₂ removal rates proposed by McQueen et al. (2020a) were based on aqueous brucite carbonation to form Mg-carbonate at a rate of 3×10^{-8} mol/m²/s when mineral dissolution kinetics are rate-limiting (McQueen et al., 2020a; Pokrovsky and Schott, 2004). The brucite dissolution experiments by Pokrovsky and Schott (2004) for which the atmospheric CO₂ capture rates are based, do not account for water availability and CO₂ supply that are often rate-limiting for brucite carbonation (Power et al., 2020, 2013; Rigopoulos et al., 2018). Water is needed for mineral dissolution, hydration of CO₂, and carbonate precipitation (Power et al., 2013). For example, microfluidics experiments used to visualize brucite carbonation at the pore scale showed that water availability, including its abundance and distribution within pores, can be heterogeneous and will affect brucite carbonation (Harrison et al., 2017). In general, brucite carbonation at low temperatures is usually limited by the CO₂ supply rate as opposed to mineral dissolution when using atmospheric or even CO2-rich gasses (Harrison et al., 2013; Power et al., 2020, 2016; Wilson et al., 2014, 2010). For example, CO2 removal rates into brucite-bearing ultramafic tailings at the Mount Keith Nickel Mine in Western Australia were 2.4 kg CO₂/m²/yr. Carbonates had ¹³C-depleted compositions, indicating that they formed under CO₂-limited conditions (Wilson et al., 2014). Although these tailings only contained ~ 2.5 wt% brucite, it is unclear if using 100% MgO with a similar reactivity of brucite will achieve the CO2 capture rate of 160 kg $CO_2/m^2/yr$ as proposed in McQueen et al. (2020a). Furthermore, the rates proposed by McQueen et al. (2020a) are unlikely to be similar to field rates where an MgO deposit will experience less-than-optimal conditions for atmospheric CO₂ removal, including variable water content (Nowamooz et al., 2018).

The main goal of this study was to experimentally test the CO_2 capture technology proposed by McQueen et al. (2020a); (i.e., MgO looping) at a laboratory scale. Atmospheric CO_2 removal rates were determined using MgO powder during wetting and drying cycles to simulate weathering, elucidating reaction pathways and limiting factors. CO_2 flux experiments directly measured atmospheric CO_2 capture rates, which were confirmed by measuring the total inorganic carbon of the solids. Accurate CO_2 removal rates are necessary to design processes and technologies for implementation as these rates impact mass balances, process times, and cost estimates. The CO_2 removal rates determined in this study are significantly slower than predicted, resulting in much greater land requirements for gigatonne-scale CO_2 removal.

2. Material and methods

The magnesium oxide (MgO; CAS: 1309-48-4) powder used in experiments was made by ACROS OrganicsTM and was 98% pure, having a median particle size of 8.1 μ m, specific surface area of 5.56 m²/g, and density of 3.58 g/cm³ (Fig. S1). The manufacturer supplied the material in plastic containers with 2.5 kg MgO that were flushed with nitrogen gas.

The experimental setup used a polyvinyl chloride (PVC) column with a solid base (20 cm inner diameter, 14 cm height). MgO powder (2.4 kg) was added to create a 10 cm layer (76 kg m⁻²), a thickness proposed by McQueen et al. (2020a); (Table 1). The deposit had an exposed area of 320 cm^2 and occupied 3140 cm^3 . The MgO powder was not compacted.

Table 1

Summary of CO2 sequestration capacities and rates.

	This study	McQueen et al. (2020a)
Depth (cm)	10 (0.5, 2.5 and 5.0)	10
MgO amount (kg/m ²)	76	195 ^a
Median particle size (µm)	8.1	20
Porosity during period IV (%)	0–58	
CO ₂ sequestration	67	213 ^a
capacity (kg CO ₂ /m ² /yr)	(5:4 Mg:C)	(1:1 Mg:C)
Carbonation product	Dypingite	Magnesite
Measured CO ₂ fluxes ^b	-9.9	-160
(kg CO ₂ /m ² /yr)	Avg. over 5 months	When accounting for
	-12.5	inefficiencies including only 90%
	Optimal carbonation	MgO carbonation
	-2.2	
	Dry	
	-3.9	
	Saturated/wet	
Calculated CO ₂ fluxes	-10.3^{d}	
based on TIC	by 5 months of	
$(\text{kg CO}_2/\text{m}^2/\text{yr})$	reaction	
	-9.0°	
	reaction	
	reaction	
Rate limitation	CO ₂ supply	Brucite dissolution
MgO consumed in 1 year	3–18% ^f	Assumed to be 90%
Time required for 90% conversion	5–27 yr ^f	Assumed to be 1 yr
Area needed for capturing 1 Gt CO ₂ / yr (km ²)	80,000-455,000 ^f	6100

^a Calculated based on spreading 21,500 t of MgO over 11 ha as a 0.1 m thick sediment, and using a MgO density of 3.58 t/m^3 (McQueen et al., 2020a).

^b Negative fluxes represent CO₂ removal from the atmosphere.

 $^c\,$ Optimal conditions refer to a water content ranges from ${\sim}7$ to 17 wt% and a porosity of $\geq {\sim}39{-}58.$

^d Calculated CO₂ fluxes are based on a linear extrapolation of the latest nine TIC measurements over 5 months.

 $^{\rm e}\,$ Calculated CO $_2$ fluxes are based on a linear extrapolation of the latest eight TIC measurements over 1 year.

 $^{\rm f}$ MgO consumption in 1 yr, time required for 90% MgO carbonation, and land requirements for capturing 1 Gt CO_2/yr are based on the linear extrapolation of the 5-month CO_2 fluxes.

 CO_2 fluxes were measured in the laboratory using an LI-8100 automated soil CO_2 flux system coupled with an LI-8150 multiplexer and 8100–104 long-term chambers (LI-COR, Lincoln, Nebraska, USA; Fig. 1). This equipment was used to determine *in situ* CO_2 fluxes as a measure of the rate of CO_2 emission or drawdown of the material being tested (Stubbs et al., 2022). The CO_2 flux system and a computer were plugged into an uninterrupted power supply (900 W capacity), which was connected to backup power. This equipment automatically measured CO_2 fluxes of the MgO deposit every 4 h for 5 min (300 s) with a 5-min post purge. The rate of change in CO_2 concentration inside the chamber is used to calculate the CO_2 fluxes (μ mol/m²/s). CO_2 flux data were processed using SoilFluxPro 4.0.1, an application designed for viewing and



Fig. 1. Experimental setup for CO₂ measurements using an LI-8100 automated soil CO₂ flux system coupled with an LI-8150 multiplexer and two 8100-104 long-term chambers. Modified after Stubbs et al. (2022).

processing data from the LI-8100 system. Fluxes were calculated based on the change in CO_2 concentration from typically 10–50 s of the 300 s measurement fitted to a linear trend. Calculation of CO_2 fluxes requires an offset to be inputted, i.e., the distance from the sediment surface to the top of the column. An average offset of 4 cm was used to allow mixing of the MgO powder without the loss of material. This offset was applied to all measurements despite this distance changing during the experiment due to variable compaction of the deposit. Importantly, the volume of air inside the chamber remained relatively constant as porosity was the main factor affecting the offset distance.

The MgO deposit was subjected to wetting and drying cycles to simulate weathering (i.e., rainfall and evaporation). This allowed for CO2 flux measurements over variable water contents, helping to determine an optimal range for carbonation. Dry fluxes were measured for 2 days prior to the first water addition (I - initial dry period). Preliminary tests determined that a 1:3 water to powder ratio achieved a desirable initial water content (i.e., wet sediment but not saturated). Aliquots of water (800 mL) were added once per week for the first 2 weeks (II - MgO to brucite transition period), and biweekly for four more additions (III wetting and drying period). After seven water additions, the MgO deposit was allowed to dry for \sim 3 months (IV - extended drying period). The deposit was mixed daily (i.e., tilling) to improve aeration during periods I-IV. Lastly, the MgO deposit received a water addition every 4 weeks and was only tilled during the first 5 days after wetting (V - longterm period: 5-12 months) to avoid compaction and cementation. CO_2 fluxes were in good agreement with CO₂ removal rates calculated using total inorganic carbon (TIC) data; thus, they were not measured during period V. A YesAir air quality monitor from Critical Environment Technologies was used to track laboratory temperature, relative humidity, and CO₂ concentration, recording a measurement per minute.

Triplicate surface samples (2–5 g each) were routinely collected with a greater sampling frequency near the beginning of the experiment (e.g., once per day). During the long-term period (V), surface samples were collect prior to and the day after wetting. In addition, hardened aggregates (~0.3–2 cm) were sampled twice during the experiment to compare their CO₂ content to the bulk deposit. Samples were kept in a desiccator containing DrieriteTM under a dry nitrogen gas atmosphere to prevent samples from reacting with H₂O and CO₂. The moisture content (wt%) of samples was determined by measuring the mass lost after being stored in the desiccator for a minimum of 5 days. Gas samples were collected throughout the laboratory using syringes with the purpose of measuring the ¹³C isotopic composition of laboratory CO₂. The sample was pressurized into 125 mL serum vials.

The mineralogical composition and TIC content of solids was determined using X-ray diffraction (XRD) and coulometry, respectively. Select samples were also imaged using scanning electron microscopy (SEM). Surface areas and particle size distributions of initial solids and those after 15 days were determined using the N₂ absorption method and a particle size analyzer, respectively. Stable carbon and oxygen isotopes of the carbonate products and laboratory CO_2 were determined by mass spectrometry. The stable carbon and oxygen isotope values are

reported in the conventional δ notation in per mil (‰) relative to Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW), respectively. Details of the analytical methods are provided in the Supplementary Material.

Additional CO₂ flux experiments were conducted using deposits with thicknesses of 0.5, 2.5, and 5.0 cm. The MgO masses required to achieve these thicknesses were 120 g (3.8 kg/m²), 600 g (19.1 kg/m²) and 1200 g (38.2 kg/m²), respectively. The initial porosity of each deposit was similar to the 10 cm experiment (~78%). Dry measurements were taken for 1 day before adding water. Each experiment received single water addition and was run for 5 days. The amount of water added maintained the 1:3 water to powder ratio used in the 10 cm experiment (e.g., 200 mL for 2.5 cm MgO). These shallower deposits were not tilled and only CO₂ flux measurements were used to monitor these experiments.

3. Results

3.1. CO_2 flux measurements

During the experiment, the thickness of the MgO deposit varied from 7 to 12 cm (Fig. 2). Although the initial porosity of the deposit was calculated at 78% (Table 1), the estimated porosity during wetting and drying cycles varied considerably depending on water content, tilling, and the MgO transition to brucite and its subsequent carbonation. For example, during the extended drying period (IV), gas-filled porosity (φ_g) ranged from ~0 to 58% (Eqs. (S1)-(S5); Fig. 2). The initial MgO powder was loosely added to the column and not compacted (period I). The deposit dried relatively rapidly after the first and second water additions, which can be explained by the consumption of water due to brucite formation (period II). Subsequent water additions (period III) caused the deposit to become compacted (down to ~7 cm) and saturated with water (Fig. 2). Drying and daily tilling caused the MgO powder to clump together, which increased the thickness of the deposit up to 12 cm, providing greater porosity and permeability than even the initial state. As the experiment progressed, some aggregates developed that were too hard to be broken by hand, likely owing to cementation caused by brucite and carbonate precipitation. When the deposit was nearly or completely dry (period IV), the sediments became more powder-like, similar to the initial MgO, but with the addition of numerous hard aggregates. At this stage, dusting occurred while tilling the deposit and its height ranged between 8 and 9 cm. During periods I through V, the laboratory conditions ranged from 21.9 to 23.9 °C, 16.7–51.6% relative humidity, and 394-447 ppm CO₂ concentration (1₅; Fig. S2).

 CO_2 fluxes averaged $-5.9 \text{ kg } CO_2/\text{m}^2/\text{yr}$ during the initial dry period (I; Fig. 3; Table 1). Note that negative fluxes represent CO_2 removal from the atmosphere, i.e., negative CO_2 emissions. The first water addition caused the CO_2 fluxes to become significantly more negative, reaching $-46.7 \text{ kg } CO_2/\text{m}^2/\text{yr}$ after one day from the initial wetting. These fluxes became less negative as the deposit dried. The second water addition caused fluxes to become less negative for one day ($\sim -8.7 \text{ kg } CO_2/\text{m}^2/\text{yr}$), followed by a rapid increase in CO_2 removal that stabilized at



Fig. 2. Photographs and diagrams showing water and textural changes that affect gas permeability (red arrows) and carbonation reactions (purple arrows) that in turn influence atmospheric CO_2 capture during wetting and drying cycles. (a) Under wet or saturated conditions, CO_2 removal is hindered by the low permeability as the deposit is compacted and pores are filled with water. (b) The presence of clumps, created by tilling, provides structure, and increases porosity. CO_2 removal is greatest due to high permeability and sufficient water for carbonation reactions. (c) At very dry conditions, the deposit gives off dust and there is insufficient water for carbonation reactions. Gas-filled porosity (φ_g) estimations are shown for each state of the wetting and drying cycles.



Fig. 3. Measured CO_2 fluxes (kg/m²/yr; gray circles) based on CO_2 flux measurements for the first 5 months (periods I–IV). The experiment is divided into five periods: initial dry (I), MgO to brucite transition (II), wetting and drying cycles (III), extended drying (IV), and long-term (without CO_2 flux measurements). CO_2 fluxes were converted to MgO carbonation in 1 yr (e.g., complete carbonation = 100%) as shown on the secondary y-axis. Water additions are represented by blue dashed lines and numbered drops. The water content (wt%) of samples is plotted as stars as shown on the tertiary y-axis. Optimal water content ranged is represented within the dashed area. Ranges when the deposit was too wet and dry and at the optimal water content are noted during period IV. Tilling was particularly beneficial when the deposit had water contents above the optimal range as it created soft clumps, thereby increasing porosity.

approximately -19.3 kg CO₂/m²/yr. These first two water additions coincided with substantial hydration of MgO to form brucite (II - MgO to brucite transition period; Fig. 3). The wetting and drying period (III) consisted of four more water additions, one every 2 weeks, during which a pattern emerged whereby fluxes immediately increased upon wetting (approximately at -3.9 kg CO₂/m²/yr) followed by an exponential increase in CO₂ removal (Fig. 3). The MgO deposit had a higher water content with each water addition during the wetting and drying period (III), as there was a buildup of water. Consequently, the deposit took longer to reach the optimal water content, whereby fluxes stabilized at -12.5 kg CO₂/m²/yr. During the extended drying period (IV), fluxes followed a similar pattern observed during the wetting and drying

period (III) during the first 3 weeks, after which fluxes slowly became less negative as the deposit fully dried. Fluxes stabilized after approximately 2.5 months from the seventh water addition. At this point, fluxes of $-2.2 \text{ kg CO}_2/\text{m}^2/\text{yr}$ were less negative than those measured during the initial dry period (I; Table 1).

3.2. MgO thicknesses

Short-term experiments (5 days) were performed using shallower MgO deposits (5, 2.5 and 0.5 cm) for determining the thickness that could be reacted in 1 yr (Fig. 4). The average flux decreased with decreasing MgO thickness (Fig. 4a). The most negative fluxes were –



Fig. 4. (a) CO_2 fluxes for MgO deposits with thicknesses of 10, 5.0, 2.5 and 0.5 cm. The blue dashed line and drop indicates when water was added. (b) Average CO_2 fluxes for 5 days normalized to the mass distribution of the 10 cm deposit (76 kg MgO/m²) and extrapolated MgO conversion in 1 yr (%). The 0.5 and 2.5 cm deposits may achieve complete and nearly complete carbonation within 1 yr, respectively. These extrapolated conversion rates assume that the initial reactivity is maintained for an entire year.

47.7, -28.0, -23.1 and -15.9 kg CO_2/m²/yr for the 10, 5, 5 and 2.5 cm deposit during 5 days of reaction, respectively.

 CO_2 fluxes were normalized by the mass distribution of the 10 cm deposit (76 kg MgO/m²; Fig. 4b). A linear extrapolation of the CO_2 fluxes was used estimate the conversion of MgO over 1 yr. Shallower deposits (≤ 2.5 cm) are expected to achieve nearly complete carbonation in 1 yr, despite having lower CO_2 fluxes.

3.3. Characterization of solids

Brucite had mostly replaced MgO (79% conversion) after 14 days, and it reached a maximum abundance at ~24 days (86% conversion). No other phases were identified during this period. The surface area of the sediments also increased from 5.56 (initial MgO) to $9.38 \text{ m}^2/\text{g}$ after 2 weeks, owing to the platy crystal morphology of brucite (Fig. S4). After 24 days, the abundance of brucite steadily declined throughout the experiment, reaching 83% and ~74% at 5 and 12 months, respectively (Fig. S3).

XRD detected no carbonate phases during the first 2 months despite increases in TIC. The initial carbonate may have either been at too low an abundance or amorphous (Figs. S5, S6). However, a broad diffraction peak at ~15° 20 (Cu K- α) was detected after ~2 months and indicated the presence of dypingite [Mg₅(CO₃)₄(OH)₂·~5H₂O] (Fig. S6; Kristova et al., 2014; Rausis et al., 2020). Furthermore, a flaky rosette-like morphology was observed, which is consistent with dypingite (Fig. S4; Power et al., 2007; Rausis et al., 2020). The intensity of dypingite peaks steadily increased with reaction time. No other carbonate phases were observed during 1 year.

The $\delta^{13}C$ values of the precipitated carbonates in the MgO sediments ranged -16.4% to -12.5% VPDB with an average of $-14.9\pm1.0\%$ VPDB (1 σ) during the first 5 months (Fig. S7). The $\delta^{13}C$ values were less negative (-12.5% VPDB) after the first water addition. The less negative $\delta^{13}C$ values were observed only during the first two weeks of reaction, coinciding with the moment that CO₂ fluxes were the most negative. The ^{13}C composition of the solids at \sim 5 months of reactions was -15.0% VPDB, similar to the initial composition of the MgO powder (-15.8% VPDB; TIC = $0.22\%CO_2$).

3.4. Total inorganic carbon

The initial TIC content of the MgO powder was 0.22%CO₂ and increased somewhat logarithmically to \sim 3.8 \pm 0.24%CO₂ by 5 months

 $(1\sigma; Fig. 5)$. Daily tilling and the heterogeneity of the deposit led to there being some variability in TIC.

Note that TIC measurements are expressed as a percentage of sample mass. Although the initial mass of the deposit was 2.4 kg, the transformation of MgO to brucite resulted in a substantial mass increase. Therefore, the mass of the deposit (m_d) must be calculated to make use of the TIC data for determining CO₂ removal rates (Eqs. (S6)–(S12)). A linear extrapolation of the calculated CO₂ fluxes based on TIC data ($-10.3 \text{ kg CO}_2/\text{m}^2/\text{yr}$) during the first 5 months shows that $\sim 16\%$ of the MgO would be consumed in 1 yr, requiring ~ 6.5 years to achieve complete carbonation (Table 1; Fig. 6).

3.5. Yearlong CO₂ removal rates

Period V extended the experiment to 1 yr with only samples being analyzed for mineralogy and TIC to determine CO_2 removal rates (Fig. 7). Brucite abundance steadily decreased from ~83 to ~74 wt% from 5 to 12 months, respectively (Fig. S3). TIC increased from the start of the experiment until the end of the extended drying period (IV; 0–5 months) at a rate of ~0.8%CO₂/month. This rate slowed to ~0.5%CO₂/ month during the long-term period (V; 5–12 months), reaching CO₂ content of ~7.8%CO₂ after 12 months (Fig. S5). The calculated CO₂ removal rate based on TIC data over the 1 yr is -9.0 kg CO₂/m²/yr, slightly lower than that obtain during 5-month period (-10.3 kg CO₂/ m²/yr; I–IV).

4. Discussion

4.1. Effects of water and porosity on CO₂ capture rates

 CO_2 fluxes were variable and largely depended on water content (Figs. 2, 3). Measurements ranged from -3.9 (saturated/wet), -12.5 (optimal), and -2.2 (dry) kg $CO_2/m^2/yr$, with an average of -9.9 kg $CO_2/m^2/yr$ (Table 1). At these rates, only 3–18% of the MgO would be consumed in 1 yr. Complete carbonation would require 5–30 yr assuming a linear extrapolation of these rates.

Changes in the porosity and permeability were expected to influence the ability of the deposit to remove CO_2 as they limit gas exchange with the atmosphere. Furthermore, CO_2 diffusion is greater at high porosity and permeability (Wilson et al., 2014), which is explained by the significantly slower CO_2 diffusion in water than air (Cadogan et al., 2014; Massman, 1998). Consequently, and in addition to carbonation



Fig. 5. Total inorganic content (TIC;%CO₂) and deposit mass over the first 5 months (periods I–IV). The calculated deposit masses (m_d) are plotted as open squares. The total mass of dry samples is expressed as $m_{s.}$ The measured and calculated deposit masses that exclude the total dry sample mass $(m_d - m_s)$ are shown as solid black and gray squares, respectively. The average TIC values of the triplicates (open triangles) are plotted as solid red triangles. The TIC values of the hardened aggregates are shown as solid black diamonds.

reactions that consume CO_2 , water content, porosity and permeability were the main parameters influencing the ingress of CO_2 (i.e., CO_2 supply) into the MgO deposit (Figs. 2 and 3). Those parameters are interconnected and depend mainly on water content and tilling during the wetting and drying cycles (Fig. 2).

Water is known to play a crucial role in driving the ingress of CO₂ (Fig. 2). For instance, previous studies found that the rate of brucite carbonation partially depends on the porous water content as there must be sufficient water for mineral dissolution and pH buffering; however, excess water reduces porosity and permeability, thereby limiting CO₂ supply (Assima et al., 2013; Harrison et al., 2016, 2015; Nowamooz et al., 2018; Stubbs et al., 2022). Similarly, experiments using materials containing portlandite [Ca(OH)2] demonstrated that the carbonation of this mineral was affected by pore distribution and moisture content (Mehdipour et al., 2019). Furthermore, carbonation was hindered when excessive pore saturation limited CO₂ diffusion. In contrast, porewater scarcity limited the dissolution of Ca(OH)2. With particular relevance to our study, CO₂ flux experiments by Stubbs et al. (2022) showed that optimizing pore water saturation can result in greater carbonation of sediments containing 10 wt% brucite, owing to the pore availability and saturation.

CO₂ fluxes of the MgO deposit were most negative when it had a water content of ~7–17 wt% and an estimated gas-filled porosity (φ_g) of ~39–58% (Table 1; Figs. 2, 3; Eqs. (S1)–(S5)). Hereafter, these water contents and porosities are referred to as the optimal carbonation conditions. Water additions compacted the deposit and saturated gas-filled pore spaces, hindering the ingress of CO₂ ($\varphi_g \cong 0\%$; water content $\geq ~26$ wt%, deposit thickness $\cong 7$ cm; Fig. 2). When the deposit was dry (e. g., end of extended drying period IV), there was significant pore space for CO₂ ingress but insufficient water for mineral dissolution and pH buffering, which limited CO₂ capture ($\varphi_g \cong 44\%$, water content $\cong 4.5$ wt%, deposit thickness $\cong 9$ cm).

Daily tilling aerated the deposit to enhance the CO₂ supply (Fig. S8). This mixing caused daily fluctuations in the CO₂ fluxes, which were more pronounced when the water content of the deposit was above or below the optimal range (7–17 wt%). Tilling created clumps at high or even saturated water contents that increased the deposit thickness from \sim 7 to 12 cm. The resulting increase in porosity and permeability enhanced CO₂ ingress. At water contents below optimal, tilling brought wetter sediments from deeper in the deposit to the surface, increasing water availability and thus CO₂ drawdown. Finally, tilling of very dry sediments (<4 wt%) had no meaningful effect on fluxes. For practical

purposes, tilling is only necessary if the deposit becomes compacted, as may occur due to heavy rainfall (Fig. 2). For this reason, the MgO deposit was only tilled daily for the first 5 days after wetting during period V (Fig. 7). Furthermore, tilling also promotes evaporation (Stubbs et al., 2022), which is only beneficial if the water content is above the optimal range.

The ingress of CO₂ into the deposit was independently corroborated by measuring the TIC content of the solids. While CO₂ fluxes are instantaneous measurements of atmospheric CO₂ capture, TIC increases are cumulative and represent the average CO₂ capture rate. Consequently, the average measured CO₂ flux ($-9.9 \text{ kg CO}_2/\text{m}^2/\text{yr}$ Table 1; Fig. 6) was in good agreement with the calculated CO₂ removal rate based on TIC during the first 5 months ($-10.3 \text{ kg CO}_2/\text{m}^2/\text{yr}$), demonstrating that the captured CO₂ is mineralized as carbonates. Furthermore, it demonstrates that TIC data could be used for monitoring the CO₂ removal rates of the MgO deposit, justifying the no necessity to record CO₂ fluxes during period V. The CO₂ removal rate of the MgO deposit after 1 yr of exposure is $-9.0 \text{ kg CO}_2/\text{m}^2/\text{yr}$ (Fig. 7).

Shallower deposits with less MgO, and thus lower CO_2 sequestration capacities, will achieve greater MgO conversions in 1 yr despite having slower CO_2 removal rates. For example, the 0.5 cm deposit is predicted to achieve complete carbonation within 1 yr, while the 2.5 cm deposit may also achieve nearly complete carbonation. However, this conclusion requires that the fast initial rates be maintained for the entire year. As observed for the 10 cm deposit (Fig. 3), the initial fast rates only lasted approximately 2 weeks.

4.2. Carbonation pathways

MgO readily reacts with water to form brucite, as confirmed using powder X-ray diffraction (XRD; Eq. (3)).

$$MgO + H_2O \rightarrow Mg(OH)_2$$
 (3)

The hydration of MgO to form brucite requires an equal number of moles of water. This additional water demand led to relatively rapid drying of the deposit after the first two water additions. Because of this transformation, brucite is the main mineral that reacts with CO_2 to form Mg-carbonate (Eq. (4)).

$$5Mg(OH)_2 + 4CO_2 + H_2O \rightarrow Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$$

$$(4)$$

Magnesite ($MgCO_3$) is very unlikely to form at Earth's surface conditions in the period of years due to its very slow formation rates



Fig. 6. CO_2 calculated fluxes (kg/m²/yr) based on total inorganic carbon (TIC) of the solids. The open triangles are TIC contents of triplicate samples and solid triangles are their average. Also shown are the measured CO_2 fluxes (gray circles) from Fig. 3. CO_2 removal rates were converted to MgO carbonation in 1 yr (e.g., complete carbonation = 100%; secondary y-axis). Stable carbon isotopes of dypingite are shown on the tertiary y-axis along with a range of predicted $\delta^{13}C$ values of dypingite in equilibrium with laboratory CO_2 . Measured ¹³C isotopic composition of laboratory CO_2 was -9.30 ± 0.29 % VPDB (1 σ). Dashed lines and numbered drops indicate when water additions occurred.



Fig. 7. CO_2 fluxes (kg/m²/yr) based on total inorganic carbon (TIC) of the solids over 1 yr, periods (I-V). Green lines indicate when the deposit was tilled daily. The open triangles are TIC contents of triplicate samples and solid triangles are their average. Also shown are the measured CO_2 fluxes (gray circles) obtained during periods I–IV from Fig. 3. CO_2 removal rates were converted to MgO carbonation in 1 yr (e.g., complete carbonation = 100%; secondary y-axis). Dashed lines and numbered drops indicate when water additions occurred. Water content (wt%) of samples is plotted as stars as shown on the tertiary y-axis.

(Hänchen et al., 2008; Königsberger et al., 1999; Power et al., 2019). Consequently, hydrated carbonate phases such as dypingite, nesquehonite [MgCO₃·3H₂O] and hydrated amorphous Mg-carbonate were expected to form from the carbonation of MgO and brucite (Power et al., 2020; Wilson et al., 2014; Zarandi et al., 2017; Zhang et al., 2021). Nesquehonite tends to form under evaporative conditions or at greater pCO_2 than atmospheric (Harrison et al., 2019), whereas dypingite is favored under atmospheric pCO_2 or in association with microbes (McCutcheon et al., 2016; Power et al., 2007). Hydromagnesite formation is typically kinetically controlled at low temperatures (<40 °C; Gautier et al., 2014; Konigsberger et al., 1999). However, its transformation from dypingite has been documented at Earth's surface conditions (Harrison et al., 2019; Hopkinson et al., 2012).

Dypingite was formed in the MgO deposit, possibly coexisting with amorphous carbonate phases (Figs. S4–S6). No other carbonate phases were observed after 1 yr (Fig. S6), despite the instability of dypingite relative to hydromagnesite at atmospheric conditions. A disadvantage of forming dypingite instead of magnesite is that less carbon is sequestered per mole of MgO (5Mg:4C molar ratio). Consequently, 1 t of MgO can theoretically sequester 0.87 t CO₂, assuming complete carbonation to form dypingite. Furthermore, the formation of hydrated Mg-carbonates also consumes water. Another consideration is the greater volume and weight of hydrated Mg-carbonates compared to magnesite (+44 wt%; Gadikota et al., 2014), which will likely result in higher transportation and processing costs. An advantage of these hydrated phases is their lower calcination temperature (\sim 350–500°C) compared to magnesite (\sim 400–600°C Lin et al., 2018), which is likely to reduce energy requirements.

4.3. CO₂ removal rate limitations

Field and laboratory experiments have shown that brucite carbonation at low temperatures is limited by the CO_2 supply rate when using atmospheric CO_2 or CO_2 -rich gases (Harrison et al., 2013; Power et al.,

2020, 2016; Wilson et al., 2014, 2010). This limitation has been identified using stable carbon isotopes. When carbonate precipitation outpaces the uptake of CO₂, the δ^{13} C values of carbonates are below equilibrium with the gas phase. The provisional equilibrium fractionation factor between dypingite and aqueous bicarbonate ($\Delta^{13}C_{dyp-HCO_3^-}$) is 3.8% (VPDB; ± 1.4 ; 1 σ ; Wilson et al., 2010). Therefore, dypingite that forms in equilibrium with laboratory CO_2 will have a $\delta^{13}C$ value in the range of 1.0–3.8‰ (VPDB). However, the dypingite formed in the MgO experiment had $\delta^{13}C$ values ranging from -16.4% to -12.5% VPDB (Figs. 6 and S7). Highly depleted ¹³C isotopic compositions of carbonates may result from a kinetic fractionation effect when these minerals form in very alkaline waters (O'Neil and Barnes, 1971; Wilson et al., 2010), such as those within the MgO/brucite sediments (pH =10.2-10.5). Similarly, stable carbon isotopic data of hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O] in mine tailings from the Mount Keith Nickel Mine demonstrated that brucite carbonation was limited by the ingress of CO₂ into porewaters (Wilson et al., 2014).

The isotopic evidence demonstrates that carbonate precipitation outpaced the ingress of CO₂ into the MgO deposit (i.e., CO₂ supply), even at optimal carbonation conditions. As previously discussed, the rate of CO₂ ingress was mainly controlled by water content, porosity, and permeability (Figs. 2, 3). Therefore, the rate of carbonation is limited by CO₂ supply, rather than by the dissolution of brucite. Accelerating carbonation would require an increase in CO₂ supply to the deposit. For instance, Power et al. (2020) found that the CO₂ capture rate of brucite-bearing mine tailings (0.6 wt%) from the Baptiste deposit in British Columbia, Canada could be increased by ~5 times from 3.5 to 19 kg CO₂/m²/yr if the *p*CO₂ in pore spaces could be maintained at atmospheric levels.

The formation of aggregates and passivation due to carbonate formation can also limit CO₂ supply (Harrison et al., 2015; Power et al., 2021). Carbonate and brucite formation caused aggregates to become cemented. For example, hardened aggregates (\sim 1–2 cm) had CO₂ contents that were 10–58% less than the bulk deposit. Smaller reactive surface area and reduced permeability of these aggregates explain these lower TIC contents (Fig. 5). However, an advantage of having clumps or aggregates, formed mainly from tilling, is that they give the deposit structure with larger pore spaces, which aides CO₂ ingress (Fig. 2). At the grain scale, surface passivation of MgO or brucite crystals by Mg-carbonates is unlikely given their small sizes (e.g., initial MgO = 8.1 µm diameter; Harrison et al., 2015). This study confirms that brucite carbonation at low temperatures is limited by CO₂ supply rather than by mineral dissolution rate, as is the case with Mg-silicates [e.g., forsterite (Mg₂SiO₄); Miller et al., 2019].

4.4. CO₂ removal rates at large scales

McQueen et al. (2020a) describe a process of calcining magnesite (MgCO₃) to produce MgO that is estimated to have the capacity to sequester 1 Gt CO₂/yr over an area of 6100 km² (Table 1). The authors assume that 90% of MgO (20 μ m diameter particles) is converted to MgCO₃ within 1 yr, provided that brucite dissolution is rate-limiting. However, our study demonstrates that CO₂ ingress is rate-limiting rather than brucite dissolution. McQueen et al. (2020a) have overestimated the carbonation rates and thus underestimated the cost and land requirements for gigatonne-scale CO₂ removal.

The MgO deposit (76 kg MgO/m²) used in our experiment provides a maximum CO_2 sequestration capacity of 67 kg $CO_2/m^2/yr$ as the Mgcarbonate product dypingite has a 5Mg:4C molar ratio (Table 1). This CO_2 sequestration capacity is approximately a third of the capacity suggested by McQueen et al. (2020a; 213 kg $CO_2/m^2/yr$), who considered a denser deposit (195 kg MgO/m²). Although a more densely packed or thicker MgO deposit would increase the CO_2 sequestration capacity on a per-area basis, this would decrease porosity and permeability and negatively impact CO_2 ingress. For comparison, the initial porosity of the MgO powder used in this study was 78% compared to 45% proposed by McQueen et al. (2020a). In experiments, thicker deposits produced greater CO_2 removal rates; however, these deposits would take longer to achieve complete carbonation due to the additional MgO that must react. Based on experiments, the deposit thickness that may fully react in 1 yr is within the range of 0.5–2.5 cm (Fig. 4). Consequently, deposits that are thicker or more densely packed than the one used in the yearlong experiment are expected to require longer reaction times.

Based on the measured CO₂ fluxes (-2.2 to $-12.5 \text{ kg CO}_2/\text{m}^2/\text{yr})$, 90% carbonation of the initial MgO will require 5–27 yr. In comparison, McQueen et al. (2020a) assumed that 90% carbonation could conservatively be achieved in 1 yr based on a CO_2 removal rate of -160 kg $CO_2/m^2/yr$ (Table 1). Thus, capturing 1 Gt CO_2/yr will require an area of ~80,000–455,000 km², significantly larger than 6100 km² estimated in McQueen et al. (2020a). Our larger estimated areas reflect the use of a less densely packed MgO deposit and the significantly slower CO₂ removal rates. For perspective, the total area of Sweden is \sim 450,000 km², and similarly, the agricultural land area in Texas, United States, is \sim 515,000 km². To place our findings in the same context as those of McQueen et al. (2020a), the CO₂ drawdown of a MgO deposit across the Nevada Test Site and surrounding areas (15,000 km²) would be 0.03-0.19 Gt CO₂/yr, instead of the predicted 2.5 Gt CO₂/yr. The estimated land requirements for capturing 1 Gt CO₂/yr from air using DAC with synthetic sorbents or solvents is 7000 km² if powered by natural gas, significantly smaller than the estimated if spreading MgO over land (Kelemen et al., 2020).

Reported carbonation rates for brucite-bearing ultramafic mine tailings are ~0.1–5 and 2.4 kg $CO_2/m^2/yr$ for Woodsreef asbestos mine (minor brucite content) and Mount Keith Nickel Mine (2.5 wt% brucite), respectively (Oskierski et al., 2013; Wilson et al., 2014). The CO_2 removal rates determined in this study are up to ~5 times faster (-2.2 to -12.5 kg $CO_2/m^2/yr$) than those for Mount Keith if conditions are kept within the optimal range (unrealistic for outdoor deployment), despite having ~33 times more brucite content (~83 wt% by 5 months). CO_2 removal rates at Mount Keith have to be accelerated ~67 times to meet the rate assumed by McQueen et al. (2020a) (160 kg $CO_2/m^2/yr$).

CO₂ capture rates were generally less negative in experiments that used smaller initial MgO thicknesses (e.g., 0.5 cm versus 10 cm; Fig. 4). This observation is consistent with the expectation that CO₂ removal rates will progressively slow as reactants (MgO/brucite) are consumed by carbonation (Harrison et al., 2015; Power et al., 2020). Consequently, the linear extrapolation of the CO₂ removal rates when only a limited amount of MgO had reacted (e.g., ~7 and ~14% at 5 and 12 months of reaction), represents a favorable scenario. Furthermore, these rates were measured in a controlled environment (constant temperature and regular watering; Fig. S2). CO₂ removal rates were steadily decreasing over time. The average CO₂ removal rates calculated from TIC data were -13.3, -10.8, -10.3, and -9.0 kg CO₂/m²/yr for periods I–II, –III, –IV, and –V, respectively. This trend was expected as reactants (MgO/brucite) become depleted over time (Fig. 7).

The laboratory experiment in this study experienced minimal temperature variations (21.9–23.9 °C; 1σ ; Fig. S2); however, CO₂ removal rates will vary with temperature, being greater at higher temperatures (Nowamooz et al., 2018; Pogge von Strandmann et al., 2022; Romero-Mujalli et al., 2018). For example, Nowamooz et al. (2018) reported that the CO₂ mineralization rate of 110 Mt of chrysotile [Mg₃Si₂O₅(OH)₄] tailings at the Black Lake Mine in Thetford Mines, Quebec, Canada was 6 times slower than that of laboratory experiments. This discrepancy is largely explained by the exposure of tailings to less-than-optimal conditions for CO₂ removal. CO₂ removal rates of a MgO deposit will differ from the measured rates in this study due to temperature, humidity, rainfall variations and exposure to sunlight and wind. These climatic conditions will affect CO₂ removal rates, particularly those affecting the water content, porosity, and permeability of the deposit (Fig. 2; Nowamooz et al., 2018). Specifically, longer reaction times will be required for complete carbonation if water contents remain outside the optimal range for extended periods. CO_2 removal rates can be assessed using field trials and monitoring under specific climatic conditions.

Field deployment of a MgO deposit may potentially impact the environment beyond the requirements for vast land (e.g., 1000s km²). For example, the dissolution of MgO and brucite in waters creates highly alkaline and caustic waters. For reference, a slurry composed mainly of brucite formed from the MgO powder had a pH of 10.2. Leaching these waters into the underlying soil will negatively affect soil biota. Another serious issue is the potential for dust emissions when the deposit remains dry for prolonged periods, particularly when tilling (Borlina and Rennó, 2017; Cahill et al., 1996). Leaching and dust emissions also represent material losses that reduce the efficiency of the MgO looping process. Daily tilling of the MgO deposit will likely contribute to mixing with topsoil, reducing the amount and purity of recoverable material. Furthermore, the land can serve no other purpose when having a blanket of MgO powder at the surface. For comparison, spreading mafic or ultramafic rock powder on cropland for CO₂ removal via enhanced weathering improves soil fertility as it provides essential nutrients, stabilizes organic matter, aids water retention and buffers soil acidity (Beerling et al., 2020; Goll et al., 2021; Strefler et al., 2018). There are no co-benefits to the oxide looping technology.

The utilization of MgO over lime (CaO) for CO₂ removal is justified by the lower calcination temperatures of Mg-carbonates compared to Ca-carbonates (Grasa and Abanades, 2006; Hollingbery and Hull, 2012; Lin et al., 2018), resulting in lower energy requirements and costs. One important advantage of using CaO is the abundant near-surface limestone deposits that can be mined for calcite (CaCO₃). However, the use of CaO will still face many of the same challenges discussed in this study, despite the expected faster CO2 removal rates compared to MgO (Erans et al., 2020; Falzone et al., 2021; Varzina et al., 2020). As observed in this study, the reactants [Mg(OH)2, MgO] dissolved faster than the precipitation of dypingite due to insufficient CO₂ supply. Thus, CO₂ supply will undoubtedly be rate-limiting in a CaO looping system. However, a slurry of Ca(OH)2 is more caustic than a Mg(OH)2 slurry (pH of 12.7 and 10.2, respectively); thus, a deposit of CaO will have greater buffering capacity which will positively affect the drawdown of CO₂. This process has not been experimentally tested, and it is unclear if a CaO deposit will achieve greater CO₂ removal rates than a MgO deposit. For instance, Erans et al. (2020) assessed the carbonation of CaO under ambient air in the context of DAC and observed that thin layers (\sim 5 mm) of CaO reached ~75% carbonation in weeks to months. Thicker layers will reduce the carbonation extent and increase the time required. Spreading CaO over more land in thinner layers or stacking infrastructure can alleviate this limitation; however, the CO₂ supply is still likely to be rate-limiting. CaO carbonation rates will likely be highly variable depending on water availability which is subject to climatic conditions (e.g., rainfall, temperature, and humidity) as observed for the carbonation of MgO in this study. As previously discussed, there are environmental concerns about the large-scale exposure of highly alkaline powders that can produce caustic waters and become airborne as dust.

In addition to environmental concerns and rate-limitations, a major obstacle for the deployment of the oxide looping technology is the colocation of suitable mineral deposits, a dispersal site for CO_2 capture, a geologic reservoir for CO_2 storage, abundant renewable energy sources, and a favorable climate. The co-location of all five of these requirements will limit the implementation of this technology.

5. Conclusions

MgO looping is an innovative approach for mitigating climate change, for which our study will aid its development as a direct air capture technology. CO_2 capture rates, ranging from -2.2 to -12.5 kg $CO_2/m^2/yr$, were greatly influenced by water content, porosity, and permeability. Notably, the carbonation of MgO/brucite was limited by

CO₂ supply rather than by the dissolution of these reactants. Furthermore, the carbonation product was the hydrated Mg-carbonate mineral dypingite, which will affect material handling and transport and calcination energy requirements. Our estimates of the land requirements are ~1300-7500% greater than previously predicted. Similarly, 90% MgO carbonation would take 500-2700% longer than previously assumed. Importantly, the measured CO₂ capture rates were obtained in a controlled laboratory environment and assuming a linear extrapolation of the CO₂ removal rates when only a limited amount of MgO had reacted (up to \sim 14%), and thus they represent a favourable scenario. CO2 removal rates progressively slowed from 5 to 12 months. A longterm (≥1 yr) field application is likely to suffer from slower atmospheric CO₂ capture rates, requiring larger areas and more extended periods for complete carbonation than those presented in this study. Moreover, several concerns about the recovery of the material after carbonation and the potential impacts on the environment remain unaddressed. The rate of CO2 capture using MgO will need to be accelerated to make this technology a competitive alternative to existing DAC technologies.

Supplementary material

Detailed descriptions of the analytical methods and additional results.

CRediT authorship contribution statement

Kwon Rausis: Conceptualization, Investigation, Writing – original draft, Visualization. Amanda R. Stubbs: Methodology, Investigation. Ian M. Power: Conceptualization, Resources, Writing – review & editing, Project administration, Visualization. Carlos Paulo: Validation, Methodology, Formal analysis.

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.

Acknowledgments

We acknowledge the support of the Natural Sciences and Engineering Research Council (NSERC) of Canada through a Discovery grant and Tier 2 Canada Research Chair to I.M.P.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ijggc.2022.103701.

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