Thermal Ca$^{2+}$/Mg$^{2+}$ Exchange Reactions to Transform Abundant Silicates Into Alkaline Materials for Carbon Dioxide Removal

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Summary paragraph
The removal of CO$_2$ from the atmosphere (CDR) on the multi-hundred gigaton (Gton) scale is essential for nearly all strategies to achieve net-zero greenhouse gas emissions and limit global warming to 2 $^\circ$C by 2100[1–5]. CDR must capture CO$_2$ from air and safely sequester it. Mg-rich silicate minerals have the capacity to remove $\sim 10^5$ Gton CO$_2$ and sequester it in the form of stable and innocuous carbonate minerals or dissolved bicarbonate ions[3, 6, 7], but their reaction rates under ambient conditions are far too slow for practical and scalable CDR. Here we show that CaO reacts quantitatively with diverse Mg silicates (olivine, serpentine, augite) under thermochemical conditions to form Ca$_2$SiO$_4$ and MgO. Upon exposure to ambient air under wet conditions, Ca$_2$SiO$_4$ is quantitatively converted to CaCO$_3$ and SiO$_2$, and MgO is partially converted into a Mg carbonate within weeks, while the input Mg silicate shows no reactivity over 6 months. The mixture of Ca$_2$SiO$_4$ and MgO can also be completely carbonated to CaCO$_3$ and Mg(HCO$_3$)$_2$ under 1 atm CO$_2$ at ambient temperature within hours. By combining it with CaCO$_3$ calcination to generate CaO, this chemistry enables a new process for CDR wherein the output Ca$_2$SiO$_4$/MgO material is used to remove CO$_2$ from air or soil to form stable (bi)carbonates and the CO$_2$ process emissions are sequestered. Analysis of the energy requirements indicates that this process could provide CDR at less than 1 MWh per ton CO$_2$ removed, approximately half the energy required just to capture CO$_2$ with leading direct air capture technologies. We also demonstrate analogous transformations using CaSO$_4$ as the CaO source. The
chemistry described here could unlock the use of Mg-rich silicates as a vast resource for safe, permanent, and verifiable CDR.

1 Introduction

Greater than 95% of the IPCC scenarios in which global temperatures rise <2 °C above pre-industrial levels assume hundreds of gigatons (Gton) of carbon dioxide removal (CDR) by 2100[1, 3], yet CDR is currently limited to a few small-scale demonstration projects (<0.01 megaton (Mton))[8]. The key challenges for making CDR a viable component of carbon management are minimizing the energy demand and the cost, achieving permanent sequestration, and providing facile verification. Much recent emphasis has been placed on improving and scaling technologies for direct air capture (DAC)[9–13]. While substantial progress has been achieved to this end, DAC technologies that have been demonstrated on pilot scale are currently limited by relatively large energy demands corresponding to 1.8-2.7 MWh per ton CO₂ captured and high costs[9, 14, 15].

An alternative to DAC is to use a source of alkalinity to remove CO₂ via bicarbonate (HCO₃⁻) or carbonate (CO₃²⁻) formation [6]. The Earth’s crust has a vast excess of alkalinity relative to atmospheric CO₂ in the form of silicate minerals containing Mg²⁺, Ca²⁺, and/or monovalent cations. These minerals naturally remove CO₂ under wet conditions by a process known as weathering, which is depicted by a simplified schematic using a generic representation of a weatherable silicate, MSiO₃, in Eqns. 1-3. Under wet conditions where CO₂ is in equilibrium with its hydrated form, carbonic acid (H₂CO₃), protonation of the silicate releases cations and sequesters CO₂ as HCO₃⁻. Depending on the conditions, bicarbonates can form precipitated carbonate minerals[16, 17]. While silicate weathering is thermodynamically favorable at surficial conditions, it is very slow. Across the entire planet, silicate weathering is estimated to remove ~0.13 Gton y⁻¹ of CO₂ and transport it as HCO₃⁻ via rivers to the ocean, where it has a residence time of 100,000 years [18].

\[
H_2O + CO_2 \rightarrow H_2CO_3 \quad (1)
\]

\[
MSiO_3 + 2H_2CO_3 \rightarrow M^{2+} + SiO_2 + 2HCO_3^- \quad (2)
\]

\[
M^{2+} + 2HCO_3^- \rightarrow MCO_3 + CO_2 + H_2O \quad (3)
\]

Utilizing silicates for CDR on the multi-Gton y⁻¹ scale needed to counteract anthropogenic GHG emissions requires finding ways to dramatically accelerate the weathering process or transform naturally abundant silicates into more reactive alkaline materials. To this end, the Mg-rich silicates olivine (with Mg endmember forsterite: Mg₂SiO₄) and serpentine (with Mg endmember Mg₃Si₂O₅(OH)₄) offer the two highest alkalinity contents per mass of the minerals that are sufficiently abundant for Gton-scale CDR. While olivine and serpentine are relatively minor constituents of the crust, the estimated accessible geological reserves are >100,000 Gton, providing ample capacity to permanently sequester far more CO₂ than humans have ever emitted[7].
Moreover, there are >400 Mt of ultramafic/mafic mine tailings generated annually worldwide[19]. Other attractive silicate resources are Mg- and/or Ca-containing pyroxenes such as diopside (CaMgSi$_2$O$_6$), which are major constituents of basaltic rocks.

Various CDR proposals involve trying to enhance the natural weathering process by grinding silicate minerals to small particle sizes and spreading them in soils or aquatic environments[20–22]. While these approaches are appealing in their simplicity, enhanced weathering experiments performed with silicates that are available on CDR-relevant scales have shown very limited efficacy. For example, soil column experiments with moderately-sized (~100-200 µm) olivine under idealized conditions with constant irrigation indicated an initial dissolution rate of 0.2 kg m$^{-2}$ y$^{-1}$ for an application of 12.5 kg m$^{-2}$[23]. A field trial in soil plots showed only 8% olivine dissolution after 2 years, nearly all of which was attributed to weathering of an ultrafine (<2 µm) component[24] that would be extremely energy-intensive to produce on large scale (>1000 kWh/ton)[22, 25, 26]. As demonstrated below, moderately sized olivine kept under wet conditions in the laboratory shows no appreciable carbonation in air after 6 months. Olivine particles suspended in bicarbonate solution and stirred under 1-10 atm CO$_2$ showed negligible carbonation (<1%) at ambient temperature; olivine can only be carbonated in high yield in measurable reaction times by subjecting them to very forcing conditions (e.g., 155 bar CO$_2$ at 185°C)[27]. Since olivine is the most reactive Mg-rich silicate, these results demonstrate the intrinsic limitations of using naturally abundant silicates directly for CDR. While there are some natural silicates such as wollastonite (CaSiO$_3$) that have been shown to weather relatively rapidly in field studies[28], these minerals are too scarce for Gton-scale CDR; global reserves of wollastonite are estimated at only ∼100 megatons[29].

Compared to Mg-rich silicates, Mg(OH)$_2$ is a much more reactive alkaline material. Wetted, large particles of MgO, which form Mg(OH)$_2$ spontaneously, react with CO$_2$ in ambient air at rates corresponding to 18% carbonation in 1 year[30]; with 1 atm CO$_2$, Mg(OH)$_2$ can be completely carbonated at ambient temperature within hours[31]. The critical challenge to utilizing Mg-rich silicates for CDR on a meaningful scale is therefore to release the alkalinity (i.e., MgO) that is effectively trapped in the silicate lattice using as little energy and resources as possible. One approach is to use acid to leach Mg$^{2+}$ from silicates and then use base to generate Mg(OH)$_2$. This chemistry generates a salt byproduct that can be recycled into the requisite acid and base solutions using electrochemical salt splitting technology[32, 33]. Implementing acid/base processing for CDR requires substantially improving the energy efficiency of salt splitting and bringing such technology to massive scale[34].

Here we show a simple and general thermochemical reaction that could greatly facilitate the use of Mg silicates for CDR. We describe conditions in which a CaO source (CaCO$_3$ or CaSO$_4$) reacts quantitatively with diverse Mg silicates to form Ca-enriched silicates and MgO. When the ratio of Ca:Si is 2:1, Mg silicates are converted into Ca$_2$SiO$_4$ and MgO, a net reaction we term Ca$^{2+}$/Mg$^{2+}$ ion exchange. Unlike Mg$_2$SiO$_4$, Ca$_2$SiO$_4$ is a very reactive silicate that can be fully carbonated under ambient air with appropriate hydration conditions within weeks[35, 36]. Thus, the
The Ca\textsuperscript{2+}/Mg\textsuperscript{2+} exchange reaction transforms kinetically inert Mg silicates into a comparatively highly reactive alkaline Mg material (MgO) while retaining a reactive Ca material, thereby resulting in the net production of kinetically competent alkalinity from Mg silicates.

The chemistry and its use for CDR are illustrated schematically in Figure 1 using forsterite (Mg\textsubscript{2}SiO\textsubscript{4}), the Mg endmember of olivine, as an example. First, CaO is generated by calcination of CaCO\textsubscript{3}. This endothermic reaction constitutes the principal energy demand of the process and releases CO\textsubscript{2}, which could be sequestered by subsurface injection. The ion exchange reaction then combines CaO with 1/2 molar equivalent of Mg\textsubscript{2}SiO\textsubscript{4} to form 1/2 Ca\textsubscript{2}SiO\textsubscript{4} and MgO. This reaction takes place at a slightly higher temperature than calcination but is exothermic, thus adding a modest additional energy demand (see below). We refer to the ion-exchanged product as a "CDR material", which could be deployed in various contexts to remove CO\textsubscript{2} from air or CO\textsubscript{2}-enriched environments (e.g., soil) to form solid carbonates (CaCO\textsubscript{3} and MgCO\textsubscript{3}) or soluble bicarbonates (Ca(HCO\textsubscript{3})\textsubscript{2} and Mg(HCO\textsubscript{3})\textsubscript{2}). We also describe the chemistry for an analogous process using CaSO\textsubscript{4} as CaO source, which results in additional net carbonation but generates H\textsubscript{2}SO\textsubscript{4} as a byproduct.

**Fig. 1** Schematic depiction of targeted cycle for CDR using Ca\textsuperscript{2+}/Mg\textsuperscript{2+} exchange to release MgO from Mg-rich silicates. Scheme is shown using Mg\textsubscript{2}SiO\textsubscript{4} (forsterite, the Mg end member of olivine) as an example.

## 2 Results

### 2.1 Thermal Ion Exchange Reactions to Generate CDR Materials

The thermodynamic products of ion exchange reactions between CaO and Mg silicates are predicted by the CaO-MgO-SiO\textsubscript{2} ternary phase diagram available from the Fact-sage database [37], which is shown in Figure 2a for T=1200 °C. The phase diagram shows that when the Ca:Si ratio is ≥ 2 : 1, the silicate species present at equilibrium is Ca\textsubscript{2}SiO\textsubscript{4} (bold line corresponds to Ca:Si = 2:1). The red lines show the evolution of the equilibrium composition with addition of CaO to Mg\textsubscript{2}SiO\textsubscript{4} and CaMgSi\textsubscript{2}O\textsubscript{6} (diopside).

With the addition of less than 2 molar equivalents of CaO to Mg\textsubscript{2}SiO\textsubscript{4}, the equilibrium shifts to a mixed Ca/Mg silicate and MgO, such as CaMgSi\textsubscript{4} (monticellite)-MgO with 1 equivalent of CaO added. Upon addition of 2 equivalents of CaO, there is complete ion exchange at equilibrium to form Ca\textsubscript{2}SiO\textsubscript{4} + 2 MgO. Similarly, for CaMgSi\textsubscript{2}O\textsubscript{6},
Fig. 2  a. Ternary ‘CaO-MgO-SiO$_2$’ phase diagram at T=1200 °C from Factsage database. The red arrows show the composition changes with the addition of different amounts of CaO to Mg$_2$SiO$_4$ (forsterite) and CaMgSi$_2$O$_6$ (diopside). b. Equilibrium compositions resulting from adding different molar equivalents of CaO to forsterite and diopside.
addition of 1 equivalent of CaO decomposes the silicate chain structure to form the sorosilicate Ca$_2$MgSi$_2$O$_7$ (akermanite), while addition of another 2 equivalents (corresponding to a total Ca:Si of 2:1) results in 2 Ca$_2$SiO$_4$ + MgO (See Figure 2b). Thus, the phase diagram indicates that it is thermodynamically possible to transform Mg silicates into the CDR-competent alkaline solids with stoichiometric addition of CaO.

Given these calculated equilibrium compositions, we first targeted the transformation of olivine (Mg$_{2-x}$Fe$_x$SiO$_4$; $x \approx 0.1$, Table S1) into Ca$_2$SiO$_4$-MgO by reacting it with CaCO$_3$. Reaction conditions were evaluated on a 1 mmol scale by mixing powders of olivine and CaCO$_3$ with a mortar and pestle and heating the mixture in a muffle furnace. Products were analyzed semi-quantitatively using powder X-ray diffraction (pXRD). CaCO$_3$ decomposes to release CO$_2$ and form CaO in situ at $\approx 700$ °C. Starting with a 2:1 CaCO$_3$:Mg$_{2-x}$Fe$_x$SiO$_4$ molar ratio, a reaction at 1200 °C for 4 h resulted in formation of the desired ion exchange products Ca$_2$SiO$_4$ and MgO in addition to Ca$_2$Fe$_2$O$_5$, which arises from the minor Fe$^{2+}$ cation in olivine reacting with CaO and O$_2$ (Table 1, Entry 1). However, substantial peaks for the olivine and CaO reactants

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<th>t / h</th>
<th>Flux / wt%</th>
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Table 1. Thermal Ca$^{2+}$/Mg$^{2+}$ exchange reactions. Equations show targeted reactions for olivine, serpentine, and augite. Simplified formulas are shown to emphasize the principal cation components. See SI for elemental analysis. Table entries show outcome of reaction as assessed by the phases observed in pXRD patterns of the products.
Fig. 3  a-b. pXRD patterns of exchange reactions performed at 1200 °C with indicated CaCO₃:mineral ratios and flux wt%. Patterns correspond to reactions from Table 1 Entries 1, 2, 9, 11 (a) and Entries 7, 10, 12 (b). c-d. Electron microscopy. SEM image and EDX analysis of CaCO₃ + olivine + Na₂SO₄ mixture before (c) and after (d) reaction at 1200 °C.

were also present in the pXRD pattern, with phase quantification indicating that the reaction was less than 50% complete (Figure 3a). Repeating the reaction with a 3:1 CaCO₃:Mg₂₋ₓFeₓSiO₄ molar ratio resulted in complete consumption of the olivine peak after 1 h (Figure S1). However, the use of a superstoichiometric amount of CaCO₃
(more than 2 equivalents) is undesirable because the endothermic decomposition of CaCO₃ is the principal energy demand for the process (see below).

We hypothesized that the CaO-Mg₂₋ₓFeₓSiO₄ reaction is hindered by the slow diffusion of ions in the solid state. We therefore tried adding a small amount of Na₂SO₄ (5 wt%) as a flux to facilitate ion mobility. Na₂SO₄ melts at 890°C and remains stable up to 1200°C. With the addition of 5 wt% Na₂SO₄ to a reaction with 2:1 CaCO₃:Mg₂₋ₓFeₓSiO₄ at 1200°C, the starting material peaks disappeared and Ca₂SiO₄, MgO, and Ca₂Fe₂O₅ were the only observed phases by pXRD after just 1 h of reaction time (Table 1, Entry 2 and Figure 3a). The use of 2 wt% Na₂SO₄ gave similar results as 5 wt% for the reactions at 1200°C (Table S2 and Figure S2). To assess the dependence on the gas environment, the same reaction was evaluated at 1100°C under flowing N₂, CO₂, or air in a tube furnace. Comparison of the reaction at 2 h and 4 h showed no difference in conversion between these three gas atmospheres, indicating no sensitivity of the ion exchange reaction to these relevant gases (Table S3).

We note that the calcination of CaCO₃ can still go to completion at <1000°C under 1 atm CO₂.[38]

To obtain a quantitative reaction yield, the products of a reaction with 2:1 CaCO₃:Mg₂₋ₓFeₓSiO₄ and 5 wt% Na₂SO₄ flux at 1200°C were carbonated under mild conditions and the amount of carbonates formed was assessed by thermal gravimetric analysis (TGA) (see below). These experiments indicated that the yield of the ion exchange reaction to form Ca₂SiO₄ and 2 MgO was essentially 100%. Scanning electron microscopy (SEM) before and after a reaction showed that the Ca₂SiO₄ and MgO products formed significantly larger particles than the input reactants (Figure 3c and 3d), while analysis by energy dispersive X-ray spectroscopy (EDX) indicated that the particles were a mixture of the two phases (Figure 3d). EDX also showed that the Na:S ratio in the product was close to 2:1, suggesting minimal decomposition of the Na₂SO₄ flux during the reaction. By washing the product with water, Na₂SO₄ can be separated (Figure S3). BET analysis shows that the sintered product has a low surface area <1 m² g⁻¹ (See Table S4).

At a lower reaction temperature of 1100°C, the reaction produced Ca₃Mg(SiO₄)₂ and MgO after 1 h, with unreacted CaO remaining (Entry 3 and Figure S4). Extending the reaction time to 4 h resulted in conversion to Ca₂SiO₄ (Figure S4). Reaction at 1000°C for 4 h converted 72% of the starting material to Ca₂SiO₄ and MgO (Entry 4, Figure S5). Reaction at 800°C and 900°C for 4 hours only converted 9% and 33% of the starting material (Table S5). When the reaction was performed at 1200°C with substoichiometric CaO source, mixed Mg/Ca silicate phases were formed: using 1.5 or 1 equivalents of CaCO₃ resulted in the formation of Ca₃Mg(SiO₄)₂ + MgO and CaMgSiO₄ + MgO, respectively (Entries 5 and 6; Figure S6).

To test the feasibility of scaling, the reaction between CaCO₃ and olivine was performed under optimized conditions (Table 1, Entry 2) on a 40x larger scale (with a 2 h reaction time) to generate 5 g of CDR material. pXRD analysis showed Ca₂SiO₄, MgO and Ca₂Fe₂O₅ phases (Figure S7).

Apart from CaCO₃, which is by far the most abundant Ca²⁺ resource on Earth, CaSO₄ is another potential Gton-scale source of CaO for thermal transformations of silicates. CaSO₄ is known to decompose in air to form CaO at temperatures exceeding...
1400 °C[39]. Heating CaSO$_4$ by itself at 1200 °C in air did not yield any CaO. However, reaction of 2:1 CaSO$_4$:Mg$_{2-x}$Fe$_x$SiO$_4$ with 5 wt% Na$_2$SO$_4$ at 1200 °C for 1 h resulted in complete consumption of CaSO$_4$ and formation of Ca$_2$SiO$_4$ and MgO by pXRD (Entry 7 and Figure 3b). Interestingly, when the same reaction was performed at 1100 °C, the product mixture after 1 h consisted of CaMgSiO$_4$ and MgO as well as unreacted CaSO$_4$ and olivine, but no CaO was observed (Entry 8 and Figure S8). This result indicates a mechanistic difference between transforming the silicate with CaSO$_4$ vs CaCO$_3$. Whereas CaCO$_3$ decomposes to CaO prior to reacting with Mg$_{2-x}$Fe$_x$SiO$_4$, the decomposition of CaSO$_4$ appears to be promoted by its reaction with the silicate. Consistent with this observation, TGA experiments showed that the addition of SiO$_2$ or Mg$_{2-x}$Fe$_x$SiO$_4$ to CaSO$_4$ substantially lowers its decomposition temperature (Figure S9).

Other alkali metal salt additives such as K$_2$SO$_4$, NaBO$_2$ and NaOH also proved effective in promoting the formation of Ca$_2$SiO$_4$ at 1200 °C using either CaCO$_3$ or CaSO$_4$ as CaO sources (Table S2). The use of NaCl in CaSO$_4$-SiO$_2$ was less effective, most likely because chloride tends to vaporize upon melting (Figure S10). Optimization of the reaction conditions may enable significantly shorter reaction times and lower temperatures with little or no flux.

We also tested the reactions of CaCO$_3$ and CaSO$_4$ with other ultramafic and mafic minerals of diverse structure and composition including serpentine (a sheet silicate), augite (a chain silicate), and andradite (a Ca/Fe orthosilicate). Reactions were performed under a standard set of conditions at 1200 °C with 5 wt% Na$_2$SO$_4$ as a flux. For serpentine (Mg$_3$(Si$_2$O$_5$)(OH)$_4$ with minor Al, Fe, and Ca impurities, Table S1), reaction with 4 molar equivalents of either CaCO$_3$ or CaSO$_4$ resulted in disappearance of the starting material peaks and formation of Ca$_2$SiO$_4$ and MgO by pXRD (Entries 9 and 10 and Figure 3a and 3b). Serpentine is known to undergo a dehydration reaction at 900 °C to form Mg$_2$SiO$_4$ and SiO$_2$ [40]. Thus, the reaction with CaCO$_3$/CaSO$_4$ likely proceeds through a Mg$_2$SiO$_4$ intermediate. Reactions of serpentine with lower amounts of Ca reactant resulted in mixed Ca/Mg silicate phases (Table S6, Figure S11). For augite (CaMgSi$_2$O$_6$ with minor Al and Fe impurities, Table S1), reaction with 3 molar equivalents of either CaCO$_3$ or CaSO$_4$ resulted in full conversion to Ca$_2$SiO$_4$ and MgO by pXRD (Entries 11 and 12 and Figure 3a and 3b). With only 2 or 1 molar equivalents of CaCO$_3$/CaSO$_4$, CaMgSi$_2$O$_6$ was transformed into the orthosilicate Ca$_3$Mg(SiO$_4$)$_2$ and the sorosilicate Ca$_2$MgSi$_2$O$_7$, respectively, which is consistent with equilibrium compositions in the calculated phase diagram (Figure 2a). Finally, for andradite (Ca$_3$Fe$_2$(SiO$_4$)$_3$ with minor Al and Mg impurities, Table S1), reaction with 3 equivalents of CaCO$_3$ or CaSO$_4$ resulted in Ca$_2$SiO$_4$ and Ca$_2$Fe$_2$O$_5$ as the observed phases (Figure S12).

In all the thermochemical reactions described above, the silicates are transformed into Ca$_2$SiO$_4$ and alkaline oxides (MgO, Ca$_2$Fe$_2$O$_5$) with no other observable phases provided that the total Ca:Si stoichiometry is 2:1. Thus, these results demonstrate the wide applicability of using CaCO$_3$ and CaSO$_4$ to transform Mg and Ca silicates into alkaline solids that are sufficiently reactive to form carbonates directly from air (see below). For comparison, acid/base processing of Ca/Mg silicates is constrained to ultramafic minerals, as the dissolution of mafic minerals in acid is extremely slow[41].
2.2 Carbonation of CDR Materials

Carbonation reactions were evaluated in air at ambient temperature to assess the rate of CO\textsubscript{2} uptake under conditions targeted for CDR. A sample of CDR material (Ca\textsubscript{2}SiO\textsubscript{4}-MgO-Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5}) was prepared by the reaction of CaCO\textsubscript{3} with olivine under optimized conditions (Table 1, Entry 2) and left exposed to air in a watch glass. Since an aqueous layer is needed to enable carbonate formation, the CDR material kept wet by adding 1 g DI water per g of material whenever the material became dry (once a day). The progress of carbonation was monitored by removing aliquots and analyzing by various methods.

The phase evolution of the CDR material during carbonation in air was monitored by pXRD. As seen in Figure 4a, the pXRD pattern after 2 weeks of exposure to air showed substantial peaks for calcite (CaCO\textsubscript{3}) in addition to remaining Ca\textsubscript{2}SiO\textsubscript{4} and MgO. After 4 weeks, the Ca\textsubscript{2}SiO\textsubscript{4} peaks were barely detectable and the CaCO\textsubscript{3} peaks were more prominent, while a large MgO peak remained. After 7 weeks, pXRD showed mostly CaCO\textsubscript{3}; Ca\textsubscript{2}SiO\textsubscript{4} was absent and only a small MgO peak remained. The minor product Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} peak was not detected, which is consistent with previous reports of its carbonation in air [42]. The lack of peaks attributable to Mg carbonates suggests that any such species produced are amorphous or microcrystalline.

When the material carbonates in air, CO\textsubscript{2} first hydrates into carbonic acid, then protonates silicate/oxide and releases Ca\textsuperscript{2+}/Mg\textsuperscript{2+}. In the end, Ca\textsuperscript{2+}/Mg\textsuperscript{2+} reacts with CO\textsubscript{3}\textsuperscript{2-} to form carbonate [43]. SEM-EDX element mapping of the material after 4 weeks in air showed that CaCO\textsubscript{3} and SiO\textsubscript{2} formed separate phases (Figure 4b). SEM-EDX element mapping of the material after 45 days and 60 days shows that the relatively fast dissolution of Ca\textsubscript{2}SiO\textsubscript{4} promotes further break-down of the sintered particle into small MgO grains, which is associated with a large increase in surface area seen by BET analysis (Table S4). This process exposes more surface for dissolution (Figure S13 and S14).

Thermal gravimetric analysis-mass spectrometry (TGA-MS) was used to quantify the amount of Ca and Mg carbonates formed at different time points (Figure 4c). Weight loss below 200°C corresponds to the dehydration and dehydroxylation of hydromagnesite (Mg\textsubscript{5}(CO\textsubscript{3})\textsubscript{4}(OH)\textsubscript{2})[44]. Weight loss from 300°C to 450°C corresponds to the loss of CO\textsubscript{2} from MgCO\textsubscript{3} and weight loss from 450°C to 750°C corresponds to the loss of CO\textsubscript{2} from CaCO\textsubscript{3} [45]. The mass remaining at 750°C corresponds to 2 MgO + 2 CaO + SiO\textsubscript{2}. The extent of carbonation of Ca\textsubscript{2}SiO\textsubscript{4} and MgO for the sample was quantified by comparing the CO\textsubscript{2} mass losses corresponding to the CaCO\textsubscript{3} and MgCO\textsubscript{3} decompositions to the mass remaining at 750°C (Table S4). Based on this analysis, 72% of the Ca\textsubscript{2}SiO\textsubscript{4} in the initial CDR material was carbonated in 25 days and essentially 100% was achieved in 50 days (i.e., full conversion to 2 CaCO\textsubscript{3} + SiO\textsubscript{2}). The extent of carbonation of the MgO in the CDR material was 25% after 50 days (Figure 4c and Figure S15).

The carbonation of CDR material in air stands in sharp contrast to the inertness of the parent silicate under the same conditions. IR provides a quick method to test if any appreciable carbonation has taken place (Figure 4d). Olivine powder kept wet and exposed to air for 6 months showed no CO\textsubscript{3}\textsuperscript{2-} peak in the IR spectrum, in contrast to the large peak corresponding to a CO\textsubscript{3}\textsuperscript{2-} stretch at ~1415 cm\textsuperscript{-1} for the CDR material.
under the same conditions. A dry CDR material showed a very minimal CO$_2$ peak, underscoring the need for an aqueous layer to allow the carbonation to proceed.

The faster air carbonation of Ca$_2$SiO$_4$ compared to MgO in the CDR material reflects the difference in alkalinity between these two solids. The carbonation of Mg$^{2+}$ or Ca$^{2+}$ alkaline solids requires a wetting layer to enable ion dissolution. The intrinsic rate of carbonation (i.e., the rate per wetted surface area) depends on the pH of the wetting layer. The pH of the solution for a slurry of Ca$_2$SiO$_4$ is $\sim$11.3, whereas the pH of a slurry of MgO is $\sim$10.3 (See supporting information).

Ca$_2$SiO$_4$ carbonates in air substantially faster than mixed Ca/Mg silicates formed by reactions of Mg silicates with $<2$ equivalents CaO sources. While Ca$_2$SiO$_4$ reached 72\% carbonation in air in 25 days, only 33\%, 21\% and 3\% of the Ca in Ca$_3$Mg(SiO$_4$)$_2$, CaMgSiO$_4$ and Ca$_2$Mg$_2$Si$_2$O$_7$, respectively, was carbonated in air in over three weeks (See Figure S16). In addition, TGA analysis indicated that no Mg was released from these silicates in air in 20 days. However, all three of these Ca/Mg silicates have been shown to dissolve completely within hours in mildly acidic to neutral solutions (pH 4-7)\cite{46, 47}, which indicates that they may be susceptible to rapid weathering in soils.

We also tested carbonation under 1 atm CO$_2$ to provide an assessment of the range of carbonation rates that are possible depending on the CO$_2$ source available. Samples of 50-100 mg CDR material were suspended in 10 mL DI H$_2$O, stirred at ambient temperature under 1 atm CO$_2$ for 2 h, and then dried (see supporting information). TGA analysis of the solid residue indicated that all of the Ca originally present in the CDR material was converted to CaCO$_3$ and all the Mg was converted to hydromagnesite Mg$_5$($\text{CO}_3$)$_4$(OH)$_2$\cite{48} (Figure S17). To gain further insight into the carbonation chemistry, a sample was carbonated as above but the solid was separated from the supernatant by centrifugation and the supernatant was dried to a separate solid residue. TGA analysis of the residue from the supernatant showed that the characteristic weight loss features for hydromagnesite but very little weight loss from 600$^\circ$C to 900$^\circ$C, indicating a very small amount of CaCO$_3$ (Figure S18). Thus, the solution in a slurry of CDR material carbonated under 1 atm CO$_2$ consists primarily of Mg(HCO$_3$)$_2$ with minimal amount of Ca(HCO$_3$)$_2$. As the Ca$_2$SiO$_4$ is carbonated under these conditions, it forms CaCO$_3$ directly (Figure S19).

### 2.3 Process concept and high-level analysis of the energy demand for CDR

A high-level process concept for using the ion exchange reactions above to perform CDR with Mg silicates is shown in Figure 5 using forsterite as an example. The input minerals are first ground to moderate particle sizes to facilitate mixing and then pre-heated using the hot gases coming from the reactor. The preheated mixture is subsequently calcined at $\sim$900$^\circ$C to decompose CaCO$_3$ and then heated to 1200$^\circ$C to perform the ion exchange reaction that forms the CDR material. We envision that this step could readily be performed using available calciner or kiln technology wherein the heat is provided by oxyfuel combustion of CH$_4$ (either natural gas or biogas)\cite{9}, generating a stream of wet CO$_2$ that could be dried and pressurized for subsurface sequestration. Alternatively, emerging electric kiln technologies may enable the use of...
Fig. 4 Carbonation of the CDR material generated from the reaction of olivine with 2 CaCO\textsubscript{3} and 5 wt% flux at 1200\textdegree{}C upon exposure to air under wet conditions. a. pXRD patterns of the CDR material after 2 to 7 weeks in air. b. SEM-EDX of the CDR material after 4 weeks in air. c. TGA-MS of the CDR material after 7 weeks in air. The mass loss from the MgCO\textsubscript{3} and CaCO\textsubscript{3} features are used to quantify the extent of carbonation. d. IR spectra demonstrating no carbonation of olivine exposed to air under wet conditions. CDR material exposed to air under wet conditions shows prominent CO\textsubscript{2} peak while CDR material under dry conditions does not carbonate.

renewable electricity as the energy source. Upon exiting the kiln, the CDR material is cooled, with potential for further heat recovery.

The CDR material could be deployed in containers or open systems to remove CO\textsubscript{2} from air, soil, or other gas streams provided it is at least periodically in contact with water. Full carbonation to calcite and magnesite results in uptake of 1 CO\textsubscript{2} per Ca\textsuperscript{2+}/Mg\textsuperscript{2+}. If used for enhanced weathering in a soil application, carbonation results in a maximum uptake of 2 CO\textsubscript{2} per Ca\textsuperscript{2+}/Mg\textsuperscript{2+} in the form of HCO\textsubscript{3} ions\cite{49}, which ultimately can be transported to the river-ocean system. To estimate the energy demand per net ton of CO\textsubscript{2} removed, we consider the energy required for mineral sourcing and grinding, and the heat required for the calcination and ion exchange reactions, energy in compressing CO\textsubscript{2} for sequestration and energy in air...
Fig. 5  a. Process concept showing major unit operations for generation of CDR material and its use to remove CO2 from air. b. The calcination and ion exchange reactions with associated enthalpies and total thermal energy demand are shown for forsterite. Energy demand assumes 25% heat loss and 40% recovery of the sensible heat. See SI for details.

separation unit to get pure O2 for oxyfuel combustion. As a baseline, we assume forsterite as the mineral input and that the energy is provided by oxyfuel combustion or renewable electricity (See SI for energy analysis on scenario using renewable electricity). Extracting and grinding rock to <100 µm requires ∼20 kWh/ton [50], compressing CO2 for geological storage requires 75 kWh/tonCO2 [51], and air separation unit requires 236 kWh/tonO2 [9]. The calcination of CaCO3 is strongly endothermic (+166 kJ/mol at 900°C) [37] and constitutes the largest component of the energy demand. The ion exchange reaction, however, is moderately exothermic (~27 kJ/mol for Mg2SiO4). The remaining heat requirements are the sensible heat to reach the calcination and ion exchange temperatures of 900°C and 1200°C, respectively (See supporting information).

Starting with Mg2SiO4 and 2 molar equivalents of CaCO3, the overall energy demand at 100% thermal efficiency with no sensible heat recovery is 851 kWh per ton of CDR material composed of CaSiO3 and 2 MgO. This material can capture 4 molar equivalents of CO2 in the form of 2 CaCO3 and 2 MgCO3 or 8 equivalents in the form of 2 Ca(HCO3)2 and 2 Mg(HCO3)2. Assuming that the CO2 emissions from the calcination/ion exchange reaction are sequestered and there are negligible emissions from energy for sourcing, grinding and sequestering, the theoretical energy demand is 1.2 MWh/tonCO2 removed as CaCO3/MgCO3 and 0.6 MWh/tonCO2 as Ca(HCO3)2/Mg(HCO3)2. With a more realistic assumption of 75% thermal efficiency but with recovery of 40% of the sensible heat, the estimated energy demands are 1.3 MWh/tonCO2 as CaCO3/MgCO3 and 0.65 MWh/tonCO2 in the form of Ca(HCO3)2/Mg(HCO3)2 [52].

The above analysis assumes the input is the ideal mineral (forsterite), which has the maximum possible Mg:Si ratio of 2. Using a mineral with a lower Mg:Si ratio
will lower the CO₂ removed while keeping the energy demand the same. The energy demand per CO₂ removed would therefore increase slightly for realistic olivine inputs with Fe²⁺ impurities and more substantially for other silicates with lower ratios such as serpentine (Mg:Si = 1.5) or diopside ((Ca+Mg):Si = 1). In the case of serpentine, there is an extra energy demand associated with its endothermic dehydration at ~600 °C (128.7 kJ/mol) [53]. For a pure serpentine input, it may therefore be better to perform serpentine dehydration and CaCO₃ calcination separately and use the CO₂ emitted from calcination to carbonate the thermally activated serpentine while using CaO for CDR from air [54, 55]. Nonetheless, the ability to perform the ion exchange reactions with a wide range of silicate minerals has practical value since many inputs would have a heterogeneous mineral composition.

Substantial reduction of the energy demand and material inputs may be possible by using a lower Ca:Si ratio, assuming the mixed Ca/Mg silicates products (CaMg-SiO₄, Ca₂MgSi₂O₇, Ca₃MgSi₂O₈) are reactive under enhanced weathering conditions (see above). For example, when using forsterite and 1 equivalent of CaCO₃ to make CaMgSiO₄ and MgO, the energy demand (at 75% thermal efficiency and 40% sensible recovery) corresponds to 0.51 MWh/tCO₂ in the form of Ca(HCO₃)₂/Mg(HCO₃)₂ and 1.02 MWh/tCO₂ in the form of CaCO₃/MgCO₃. Further investigation of the carbonation chemistry of CDR materials generated from thermochemical reactions with Ca:Si < 2:1 is a promising avenue for minimizing energy demand.

By comparison, DAC cycles based on CaO/CaCO₃ looping require 1.4 MWh of heat (sensible + latent) per ton CO₂ captured at 100% thermal efficiency just for the calcination [9]. By amplifying the alkalinity of CaO via ion exchange, the process described in Figure 5 offers a way to lower the energy demand per CO₂ removed, reduce the amount of CO₂ that needs to be sequestered per CO₂ removed from the atmosphere, and enable the use of Mg silicates as a CO₂ sink.

3 Conclusions

This works presents a general method to transform Mg-rich silicates into reactive materials for CDR, providing a way to mobilize one of the only permanent carbon sinks large enough to meaningfully impact atmospheric CO₂ levels. Given the expectations for CDR contributions in achieving GHG targets this century, scalability on a short timeline is paramount. The use of thermochemical reactions is potentially advantageous in this respect since it could leverage reactors and solids processing technologies that are already used to generate Gtons of material annually for the concrete industry.

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5 Competing interests

M.W.K. and Y.C. have filed a provisional patent application based on this work.

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