

Thermal Ca²⁺/Mg²⁺ Exchange Reactions to Synthesize CO₂ Removal Materials

Corresponding Author: Professor Matthew Kanan

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Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)

The article describes a series of high temperature reactions for the direct air capture of CO₂. The rationale underlying this work is the relatively high reactivity of Ca-silicate as opposed to Mg-silicate for CO₂ capture and conversion to carbonate in air. The following comments need to be considered before moving forward:

- (i) The sensitivity of the silicate exchanges to temperature and the influence of gaseous environments on these exchanges is not clear.
- (ii) The associated activation energies of these thermal exchange reactions are not clear.
- (iii) The influence of moisture and relative humidity is not clear. This is an important consideration for direct air capture of CO₂.
- (iv) The authors discuss the structural changes but do not discuss the changes in the morphological features such as pore size, particle size, and the associated passivation impacts.
- (v) The life cycle impacts are not clear. Achieving high temperatures using fossil energy would severely limit the carbon removal efficiencies of this process.

Referee #2

(Remarks to the Author)

The manuscript presents findings on an ion-exchange-based process to transform Mg₂SiO₄ and CaO into Ca₂SiO₄ and MgO, increasing the reactivity of the solids to CO₂ and corresponding carbonation rates. It is interesting work with a sound experimental plan. However, the scope of work does not seem to be well-suited to Nature. The work focuses on process development rather than gaining new scientific understanding of phase transformation and mechanisms of carbonation. For example, the finding that "Together, these results indicate that with a higher Mg content and a more complicated silicate network, the dissolution kinetics of Ca are slower" is superficial, and understanding operative mechanisms is beyond the scope of the work. The TGA interpretation of the data seems incorrect. The decomposition at 400 °C does not correspond to calcination of MgCO₃, but rather to dehydroxylation. Decomposition at <200 °C corresponds to dehydration of molecular water. These data need to be re-analyzed and re-interpreted.

Referee #3

(Remarks to the Author)

Summary of the key results

The paper proposes an ambitious process based on a thermochemical Ca²⁺/Mg²⁺ exchange reaction that, once and if validated, could provide a significant contribution to the general objective of limiting atmospheric CO₂ concentration. The main strength of the process, in my opinion, is that it is based on the use of cheap materials (even though it involves significant amounts of energy and temperatures as high as 1200°C) and aims at a stable geological sequestration of CO₂ in the form of MgCO₃, rather than to its –probably more cumbersome– underground confinement. The process is described with adequate clarity, and it is (in a rather general way) examined also from the point of view of energy requirements.

Originality and significance: if not novel, please include reference

The general theme under investigation (CO₂ removal from atmosphere) is definitely significant, and the fact that –differently from typical DAC processes– in this case a stable geological solution is proposed and discussed appears of significant interest.

Data & methodology: validity of approach, quality of data, quality of presentation

The experimental approach is valid, and clearly described, also in terms of a possible validation in future works. The data are adequate quality for the scope of the paper.

Appropriate use of statistics and treatment of uncertainties

N/A.

Conclusions: robustness, validity, reliability

Even though at present the proposed process is just in its conceptual definition, the proposed analysis appears definitely interesting, and the “Conclusions” reflect this.

Suggested improvements: experiments, data for possible revision

The proposed process will need an adequate validation, in terms of deeper verification of the proposed reactions and their kinetics, of verification of its engineering feasibility, and of techno-economic feasibility. However, the most appropriate site for such analysis will be further, independent papers.

I would advise trying to put the “ocean” (p. 13) solution in perspective: while, after all, finding a place on earth on which depositing huge amounts of rocks without having an excessive environmental impact might be feasible, I would be much more skeptical on the proposal of alkalinizing seawater on a large scale. Similarly, I am not sure that the suggestion of producing huge amounts of sulfuric acid, on the scale which would theoretically follow from the amounts of rocks and CO₂ under consideration, is really sensible.

References: appropriate credit to previous work?

References are generally appropriate.

Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions

The described items (Summary, Introduction, Conclusions) are adequate.

Minor observations

- as long as the “Summary” does not belong to the paper proper, “CDR” in the second line of the Introduction should be defined;
- the terms “mafic”/“ultramafic” should be defined, since they are not familiar with many potential readers;
- toward the bottom of p. 2 there is a “1” that should probably be “<1”;
- in the last line of the Introduction (p. 3) probably there is something missing between “CaSO₄” and “CaO”;
- at the bottom of p. 12 “teh” should probably be “the”;
- “Conclusion” should probably become “Conclusions”.

Version 1:

Reviewer comments:

Referee #1

(Remarks to the Author)

The authors provide considerable scientific evidence in response to the prior comments. However, several outstanding considerations still remain as noted below.

(1) Naturally occurring olivine is rich in iron and can contain iron. The studies are conducted without considering the influence of iron and nickel on the exchange reactions. Without this information, it is challenging to assess the efficacy of this approach as a CDR technology.

(2) The manuscript does not provide insights into the influence of varying particle size on the kinetics of ion exchange and the associated economics. This factor is important to consider since particle size influences grinding and the subsequent impacts on energetics.

(3) Experimental results with “real” olivine samples are needed and a detailed discussion of all the factors that influence the proposed exchange mechanisms to help inform subsequent TEA and LCA is essential. Without these analyses, the reported results are still preliminary and can be disputed. Also, error bars are not provided for Figure S5 associated with ion exchange. More robust experimental analyses is essential.

Version 2:

Reviewer comments:

Referee #1

(Remarks to the Author)

The authors show that calcination of Ca-carbonate and Mg-silicate results in MgO and Ca-silicate which are more reactive

with CO₂. While the authors do demonstrate that these products are indeed produced, the energy needs associated with this approach are significant. Several approaches already exist to valorize Mg-silicate (or olivine) to co-produce carbonates, silica, and energy relevant metals which are more energy efficient than the proposed route. The authors make the argument that more CO₂ can be stored than what is initially released during the calcination of Ca-carbonate. However, a full process LCA would be needed to justify this approach. While the authors present scientific evidence supporting the feasibility of this approach, the overall whole system life cycle emissions would challenge the implementation of this approach.

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Responses to Comments from Referees

Referee expertise:

Referee #1: CO₂ capture, mineralization, solid-state chemistry

Referee #2: CO₂ mineralization, geochemist

Referee #3: LCA/TEA of CO₂ capture

Referees' comments:

Referee #1 (Remarks to the Author):

The article describes a series of high-temperature reactions for the direct air capture of CO₂. The rationale underlying this work is the relatively high reactivity of Ca-silicate as opposed to Mg-silicate for CO₂ capture and conversion to carbonate in air. The following comments need to be considered before moving forward:

(i) The sensitivity of the silicate exchanges to temperature and the influence of gaseous environments on these exchanges is not clear.

Response:

We thank the reviewer for raising these points. We have performed additional experiments to investigate the temperature and gas-dependence of the ion exchange reaction. **We have added two tables to the Supplementary Materials (Tables S3 and Table S5) and additional text to the manuscript describing these experiments.** To summarize the results, the ion exchange reaction has an onset temperature of ~800 °C and proceeds to 100% completion within an hour at 1200 °C. The reaction shows no dependence on the gas environment when the reaction is performed under air, N₂, or CO₂.

Table S3. Ion exchange reaction at 1100°C under different atmospheres

Olivine	<u>CaO Source</u> 2 CaCO ₃	<u>Simplified formula</u> + Mg ₂ SiO ₄	<u>5wt% Na₂SO₄</u> →	<u>CDR Materials</u> Ca ₂ SiO ₄ + 2 MgO
	Temperature/ °C	Time/ h	Conversion of CaO/ %	
	800	4	9	
	900	4	33	
	1000	4	61	
	1100	2	64	
	1100	4	100	
	1200	1	100	

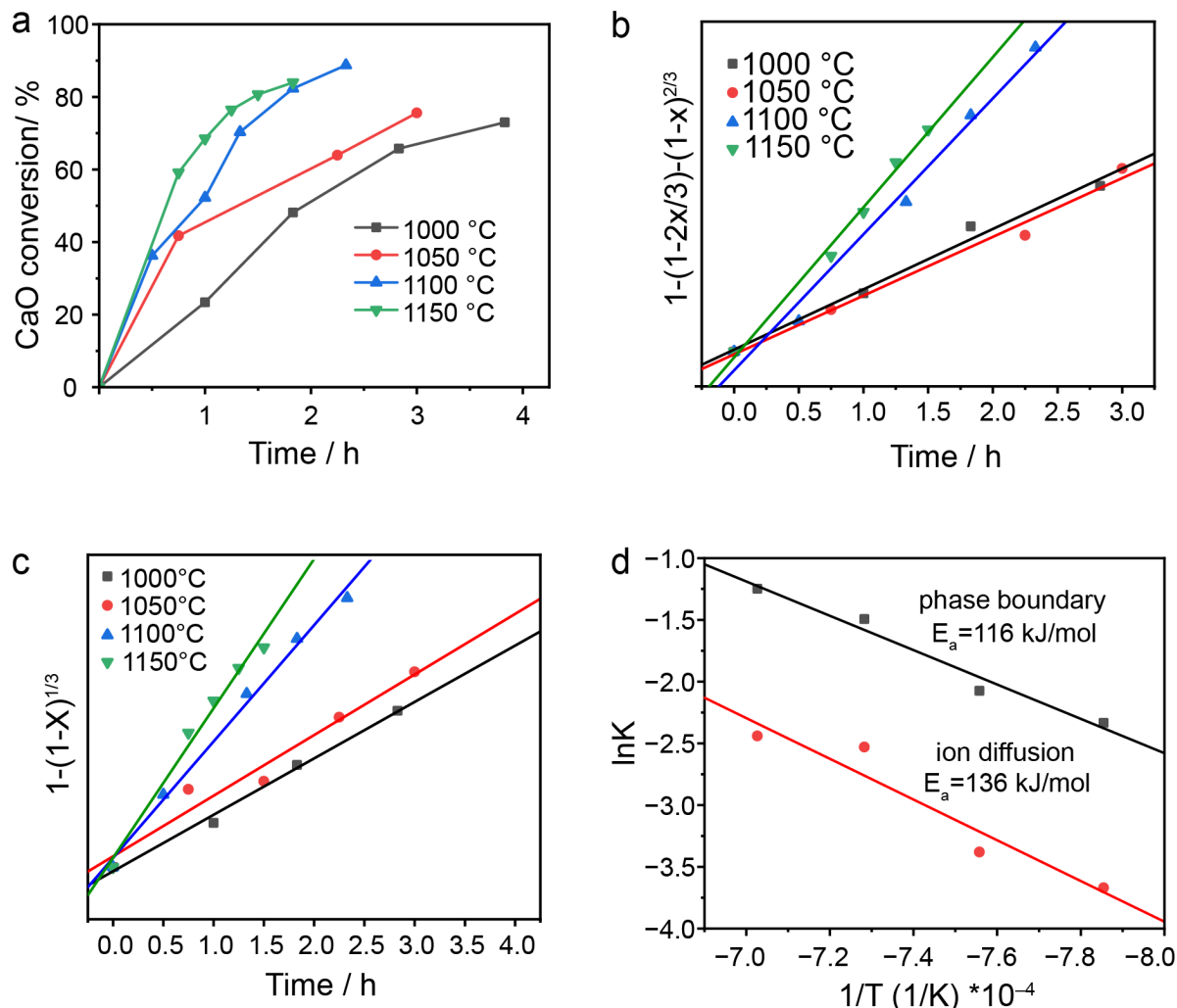
Table S4. Ion exchange results in air at different temperatures

Olivine	<u>CaO Source</u>	<u>Simplified formula</u>	<u>Different Gas flow</u>	<u>CDR Materials</u>
	2 CaCO ₃	+ Mg ₂ SiO ₄	5wt% Na ₂ SO ₄ 1100 °C, 1-4 h	Ca ₂ SiO ₄ + 2 MgO
	Atmosphere	Time/h	Conversion/%	Phase observed in pXRD
	Air	2	82	CaO, Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅
	Air	4	100	Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅
	N ₂	2	79	CaO, Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅
	N ₂	4	100	Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅
	CO ₂	2	83	CaCO ₃ , CaO, Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅
	CO ₂	4	100	Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅

(ii) The associated activation energies of these thermal exchange reactions are not clear.

Response:

We have investigated the ion-exchange kinetics within the temperature range of 1000 to 1150 °C and analyzed the results according to different models to probe ion exchange dynamics (see Figure below). We fit the conversion vs time at different temperatures to the phase-boundary-controlled reaction equation and Gentling equation². The activation energy obtained from fitting to the phase-boundary controlled model is +116 kJ/mol, while fitting the data to the Gentling equation gives an activation energy of 136 kJ/mol. These values are reasonably close to the Ca diffusion activation energy (+141 kJ/mol) in CaO melt² but much less than Mg self-diffusion (343 kJ/mol)³. **The conversion vs time data has been added as Figure S5.**



Ion exchange dynamics. **a.** CaO conversion vs time at different reaction temperatures in air. **b.** Data fitting using ion-diffusion model. **c.** Data fitting using phase-boundary controlled model. **d.** Arrhenius plot for ion-diffusion model and phase-boundary controlled model in the temperature range of 1000-1200 °C.

(iii) The influence of moisture and relative humidity is not clear. This is an important consideration for direct air capture of CO₂.

Response:

To clarify, our carbonation experiments in ambient air are performed under wet conditions, whereby a mass of water equal to the CDR materials was added to the CDR material daily to maintain a bulk wetting layer. (The materials became visibly dry over the course of each day). Under these conditions, carbonation proceeds by the transport of CO₂ into the water layer, reaction with H₂O/OH⁻ to form H₂CO₃/HCO₃⁻, and the reaction of these species with the alkaline solid⁵. An experiment performed in the absence of adding any water, with just the ambient humidity in the laboratory air, showed no evidence of carbonation by IR (**Fig. 4d** in main text) over the course of several weeks. This result is expected given the low surface area of the CDR materials as prepared and the very low reactivity of alkaline Ca/Mg solids with CO₂ from air in the absence of added water.

We have not optimized (i.e., minimized) the amount of water or source of water (such as seawater) used to achieve acceptable rates and extent of carbonation of the CDR materials, although we anticipate that significantly less water could be used. A previous study of the carbonation of $\text{Mg}(\text{OH})_2$ determined that 18 wt% water was the optimal amount for maximizing carbonation kinetics.⁴ Studies of Ca_2SiO_4 carbonation have observed ~50% extent of carbonation with a single initial charge of 15 wt% water and 98% relative humidity to maintain the hydration state.⁶⁻⁸ With too little water, the extent of carbonation becomes limited by passivation of the silicate surface by CaCO_3 deposition. We note wetting alkaline solids to promote air carbonation is a common practice and is also employed in industry, e.g., by Heirloom and Origen in their direct air capture cycles.

(iv) The authors discuss the structural changes but do not discuss the changes in the morphological features such as pore size, particle size, and the associated passivation impacts.

Response:

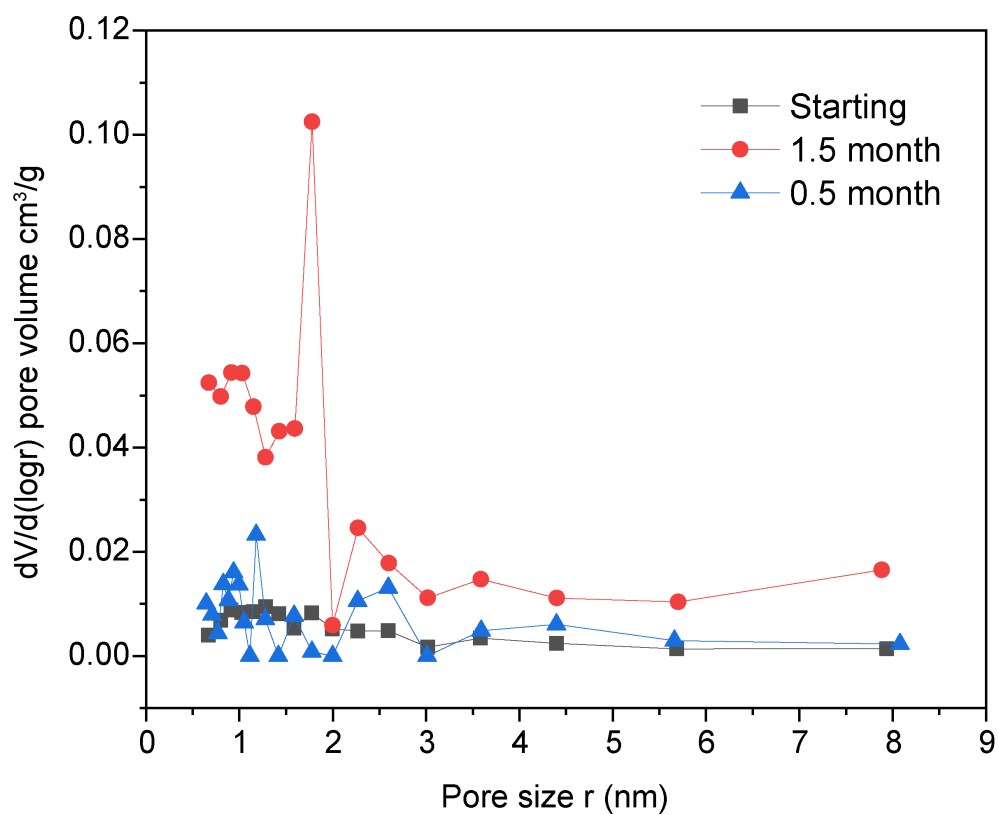
We have performed additional SEM/EDS and BET gas sorption experiments to obtain more information about the morphological changes as the CDR material is carbonated under wet conditions in air. These experiments complement the pXRD and TGA-MS results to provide more insight into the mechanism of carbonation. **The additional SEM/EDS images at different time points of carbonation have been added as Fig. S13 and the BET specific surface areas for the CDR material at different carbonation time points have been added as Table S4.**

As seen by SEM/EDS, the CDR material as synthesized consists of large (~200 μm) particles that are composed of small, sintered domains of Ca_2SiO_4 and MgO (**Fig. 3d** and **Fig. S13**). Upon carbonation under wet conditions in air, there is a dramatic change in morphology. After one month, large (~50 μm) Ca-rich particles are observed (**Fig. 4b** in main text), which based on pXRD and TGA-MS can be assigned as CaCO_3 . Smaller particles (~10 μm) containing Si or Mg are observed by SEM/EDS, which we assign as amorphous SiO_2 deposits that are the byproduct of Ca_2SiO_4 carbonation and the partially carbonated $\text{MgO}/\text{Mg}(\text{OH})_2$ component of the CDR material. After six weeks, the CaCO_3 particles are up to 200 μm in size, while the Si and Mg phases remain relatively small (**Fig. S13b**). At the end of the two-month period (**Fig. S13c**), in addition to the large CaCO_3 particles, there are also ~100- μm size Mg-rich particles that we assign as hydromagnesite based on the TGA-MS data (please see Response to Reviewer 2 below).

From the BET measurements, the CDR material as synthesized has a low specific surface area that could not be reliably measured by BET (<1 m^2/g). After exposure to air under wet conditions for 0.5 months, the specific surface area was still low but had increased to 1.6 m^2/g . However, after 1.5 months, the a dramatic increase to 57 m^2/g was observed. A similar values was observed after 2 months. Analysis of the pore size distribution by the BJH method suggested an increase in pore volume but did not show peaks that could be assigned to specific pore sizes in the nm regime, indicating that the materials are not mesoporous (see figure below).

The morphological changes, combined with the phase information from pXRD and extent of carbonation from TGA-MS, provide insight into the mechanism of carbonation under wet conditions. **We have added an illustration as Fig. S14 to convey the key findings.** The results are consistent with a mechanism in which the Ca_2SiO_4 domains of the original sintered CDR material particles are first dissolved by protonation with H_2CO_3 and the CaCO_3 nucleates as separate particles. As the dissolution proceeds, the originally sintered particles effectively disintegrate, leaving small $\text{MgO}/\text{Mg}(\text{OH})_2$ particles and amorphous SiO_2 deposits behind and resulting in a large increase in surface area. Meanwhile, the CaCO_3 particles grow to >100 μm . The carbonation of Ca_2SiO_4 goes to completion without passivating because the original Ca_2SiO_4 domains are small (~10 μm) and CaCO_3 precipitates distal from the silicate surface. As Ca_2SiO_4

dissolves, the relatively large surface area of $\text{MgO}/\text{Mg}(\text{OH})_2$ exposed aids the dissolution and subsequent carbonation of this material.



Pore size analysis. Pore size distribution of material made from the ion-exchange reaction, and materials that have been exposed in air for 0.5 and 1.5 months.

Table S4. BET analysis of CDR material after carbonation under air in wet conditions.

Material	Surface area/ $\text{m}^2 \text{ g}$
Starting CDR material	--
Carbonation in air, 0.5 month	1.63
Carbonation in air, 1.5 month	57.29
Carbonation in air, 2 month	59.76

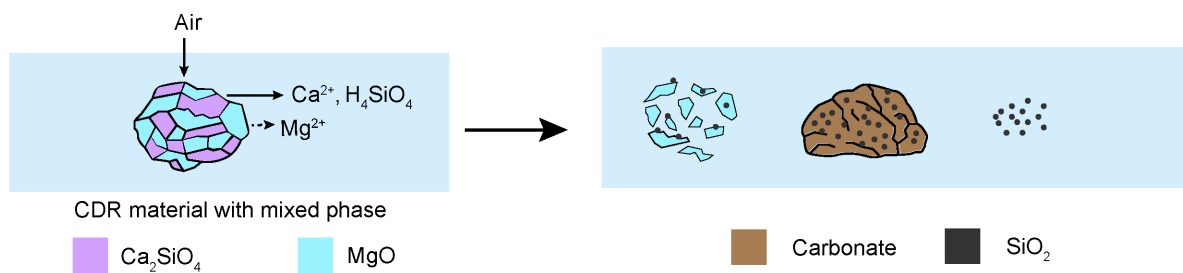
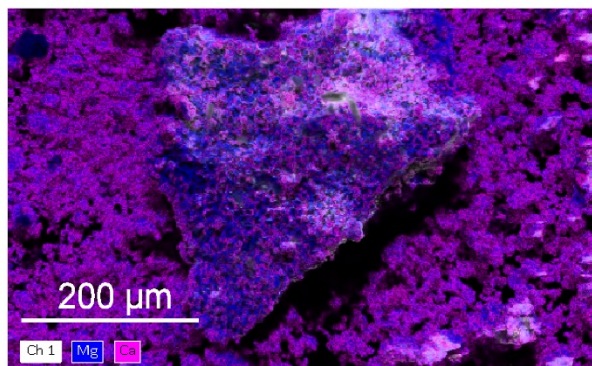
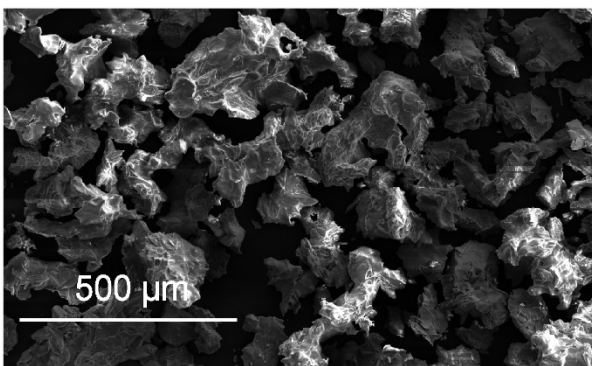
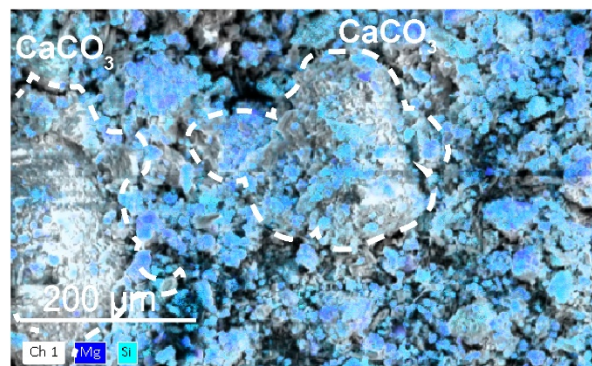
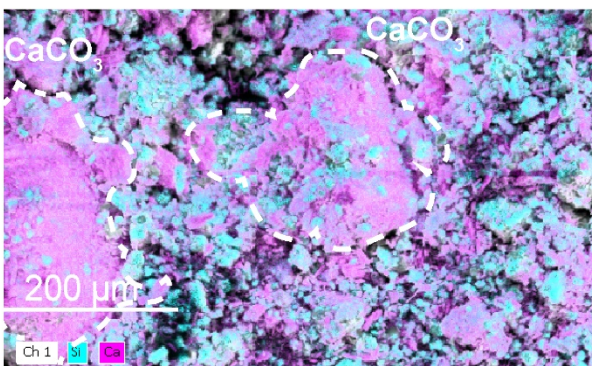


Fig. S14. Scheme of natural carbonation in air. During the natural carbonation in water, quick release of Ca^{2+} and H_4SiO_4 disintegrates the sintered particle. MgO dissolves at a slower rate. $\text{Ca}^{2+}/\text{Mg}^{2+} + \text{CO}_3^{2-}$ nucleates as a separate phase, having a comparable size as the starting material. H_4SiO_4 nucleates randomly on starting material, carbonate, or as separate phases.

a



b



c

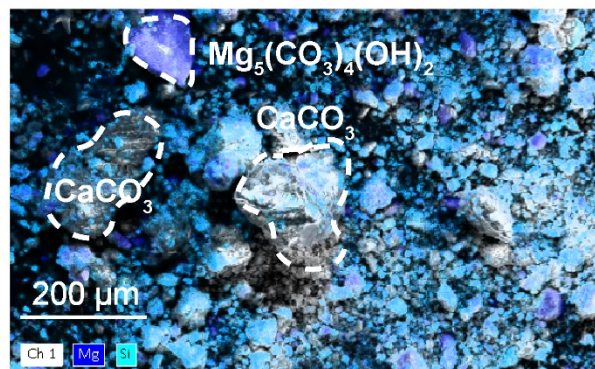
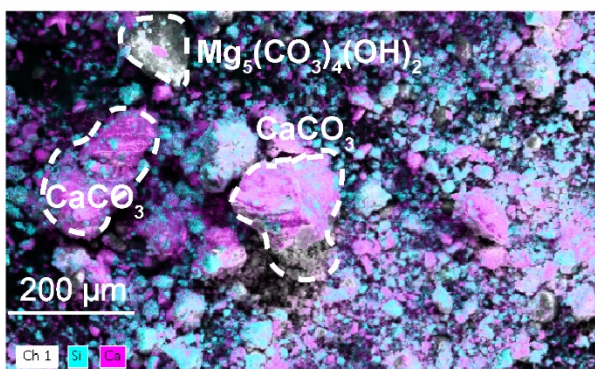


Fig. S13: SEM-EDX analysis of CDR material before and after carbonation in air under wet conditions. **a)** CDR material as synthesized; **b)** after carbonation for 45 days; **c)** after carbonation for 60 days.

(v) The life cycle impacts are not clear. Achieving high temperatures using fossil energy would severely limit the carbon removal efficiencies of this process.

Response:

At this stage of analysis, the key life cycle metric is the amount of energy expended per CO₂ removed, which we calculate in terms of MWh/tCO₂. The CO₂ removed is equal the total amount of CO₂ sequestered by the CDR material as $M\text{CO}_3/M(\text{HCO}_3)_2$ minus any CO₂ emissions associated with the process, which come from the CO₂ released from CaCO₃ upon calcination and CO₂ emissions associated with the energy inputs.

In the original manuscript we presented a process in which a portion of the CDR material generated was used to re-capture the CO₂ emitted in the process. We have now revised the process concept to incorporate sequestration of the CO₂ emissions by subsurface injection, which is straightforward to achieve because the process emits a concentrated CO₂ stream (see below). With this modification, all the CDR material that is generated by the process can be used to remove CO₂ from the atmosphere, which greatly reduces the energy demand per CO₂.

Our energy analysis includes the energy for grinding the mineral inputs, the sensible heat and latent heat for the calcination and ion exchange reaction, and, with this new scheme, the energy for sequestering CO₂ emitted by the process and energy for air separation unit to get pure O₂ for oxyfuel combustion. We assume that the calcination and ion exchange reactions will be performed in a kiln, for which there is ample precedent on massive scale. The vast majority of the energy input is for the latent and sensible heat. We assume a 75% thermal efficiency (i.e. conversion of the energy input into the requisite sensible and latent heat) and a 40% recovery of the sensible heat, which is achieved primarily by using the hot gases generated by the calcination to pre-heat the solid inputs.

For the provision of the thermal energy, there are two options. One design is to supply the thermal energy using oxyfuel combustion of CH₄ and O₂ directly in the kiln. Kilns that are directly heated by CH₄ combustion are currently used on a massive (Gton y^{-1}) scale in the cement industry. To facilitate CO₂ sequestration, it is beneficial to operate using oxyfuel combustion, wherein concentrated O₂ is supplied instead of air, resulting in an emissions stream that has a very high concentration of CO₂ (from calcination and combustion). Providing the heat using oxyfuel combustion adds modest energy demands for the air separations unit to generate concentrated O₂ and the compression of the additional CO₂ from the combustion reaction. We note that only 0.9 molar equivalent of CH₄ is needed for every 2 CaCO₃ + Mg₂SiO₄, resulting in an extra 0.9 molar equivalent of CO₂ in addition to the 2 equivalents from the 2 CaCO₃. **The estimated total energy demand per net CO₂ removed for the case where oxyfuel combustion is used (at 75% thermal efficiency with 40% recovery of the sensible heat) is 1.3 MWh/tCO₂ if the final carbonation products are MgCO₃ and CaCO₃, and 0.65 MWh/tCO₂ if the final carbonation products are Mg(HCO₃)₂ and Ca(HCO₃)₂.**

We note that oxyfuel combustion + sequestration is already used by Carbon Engineering and Origen for their CaO looping DAC processes. The key difference is that, with our novel chemistry, for a small additional energy input (the sensible heat in going from the calcination temperature to the temperature at which CaO reacts with the Mg silicate), there is a doubling of the alkalinity, which greatly reduces the energy demand per CO₂ removed.

Alternatively, one could use an electrified kiln to provide the energy using renewable electricity. There are multiple emerging technologies for providing high-temperature heat using electricity. For example, Leilac has also announced the development of fully electric kilns and Heirloom has announced that they are partnering with Leilac to use their electric kiln for the CaCO₃ calcination step of their CaO-looping direct air capture process. Alternatively, Coolbrook has developed an

electric turbine that can heat gases up to 1700 °C and is partnering with two major cement manufacturers to use these heaters as the thermal energy source for CaCO_3 calcination as well as cement clinker formation. With the idealized assumption that the electricity source has negligible GHG emissions, the **estimated total energy demand per net CO_2 removed for the case where an electric kiln is used (at 75% thermal efficiency with 40% recovery of the sensible heat) is 1.2 MWh/t CO_2 if the final carbonation products are MgCO_3 and CaCO_3 , and 0.60 MWh/t CO_2 if the final carbonation products are $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$.**

We have replaced Figure 5 with a new version that depicts the updated scheme and energy analysis. The energy analysis highlights the potential advantage that our chemistry offers for CDR. Leading DAC technologies require 1.8 to 2.7 MWh per ton of CO_2 captured, vs 0.6 to 1.3 MWh per ton of CO_2 removed for our scheme. Moreover, a process based on our chemistry reduces the amount of CO_2 that is sequestered subsurface per CO_2 that is removed from the atmosphere (1:1 ratio with DAC + sequestration vs 0.725:1 to 0.36:1 with our scheme).

Referee #2 (Remarks to the Author):

The manuscript presents findings on an ion-exchange-based process to transform Mg_2SiO_4 and CaO into Ca_2SiO_4 and MgO , increasing the reactivity of the solids to CO_2 and corresponding carbonation rates. It is interesting work with a sound experimental plan. However, the scope of work does not seem to be well-suited to Nature. The work focuses on process development rather than gaining a new scientific understanding of phase transformation and mechanisms of carbonation. For example, the finding that “Together, these results indicate that with a higher Mg content and a more complicated silicate network, the dissolution kinetics of Ca are slower” is superficial, and understanding operative mechanisms is beyond the scope of the work.

Response:

The major scientific finding of our work is a novel chemical reaction that overcomes the principal barrier to using Mg silicates for CDR, namely their extremely slow reaction with CO_2 at ambient conditions. It is critical to find ways to transform Mg silicates into more reactive materials because they are the most concentrated natural source of alkalinity available and arguably the only resource with the capacity to remove and permanently sequester CO_2 on the scale needed to impact climate change. We emphasize that the reactions of CaO or CaSO_4 with Mg silicates to form Ca_2SiO_4 and MgO were previously unknown. We show that these reactions are not only possible but that they can be performed in quantitative yield across a diverse set of silicate structures using simple solid-state reaction conditions akin to the way many solid-state reactions are performed today on the multi-Gton per year scale. Our findings break the general belief that pH swing is necessary to release alkalinity from silicates, which only works with olivine and serpentine because other silicates dissolve too slowly in acids and passivate quickly.

We think that these findings are very important because they enable new processes for performing CO_2 removal (CDR) that have substantial advantages over existing approaches. Please see the response to comment (v) from Reviewer 1 for an updated analysis of the energy demand for a process enabled by our chemistry and comparison to leading DAC technologies. We have taken some space in the manuscript to outline a specific process concept for using the chemistry to perform CDR so that the reader can see a clear example of the application understand our high-level energy analysis. The process concept is not meant to be the emphasis of the paper, but we think that providing a concrete example will aid in understanding the mass and energy balance and may stimulate ideas for how to further improve the process.

Regarding the mechanism of carbonation of CDR materials, for the CDR material consisting of Ca_2SiO_4 and MgO , we have provided additional characterization and mechanistic discussion as discussed above in response to comments (iii) and (iv) from Referee 1. Regarding the mixed Ca/Mg silicates resulting from partial exchange, an in-depth study of the reactivity of these materials is beyond the scope of this paper. We do think it is important to point out, however, that the minerals we prepare from partial exchange – (merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$), from reaction of Mg_2SiO_4 with 1.5 equivalent of CaO), monticellite (CaMgSiO_4 , from reaction of Mg_2SiO_4 with 1 equivalent of CaO), and akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$, from reaction of $\text{CaMgSi}_2\text{O}_6$ with 1 equivalent of CaO) – are all known to dissolve rapidly (within hours for particle sizes of 10s of μm) at pH 4-7 (see Engstrom et al *Minerals Engineering* **2013**, 41, 46 and Strandkvist et al *Canadian Metallurgical Quarterly* **2015**, 54, 446). This reactivity suggests that these materials may weather rapidly if deployed in soils. We are embarking on a study to investigate this question and probe the mechanism of weathering/carbonation because it requires less energy and resources to prepare these materials and therefore they provide a path to further lowering the energy demand per CO_2 removed.

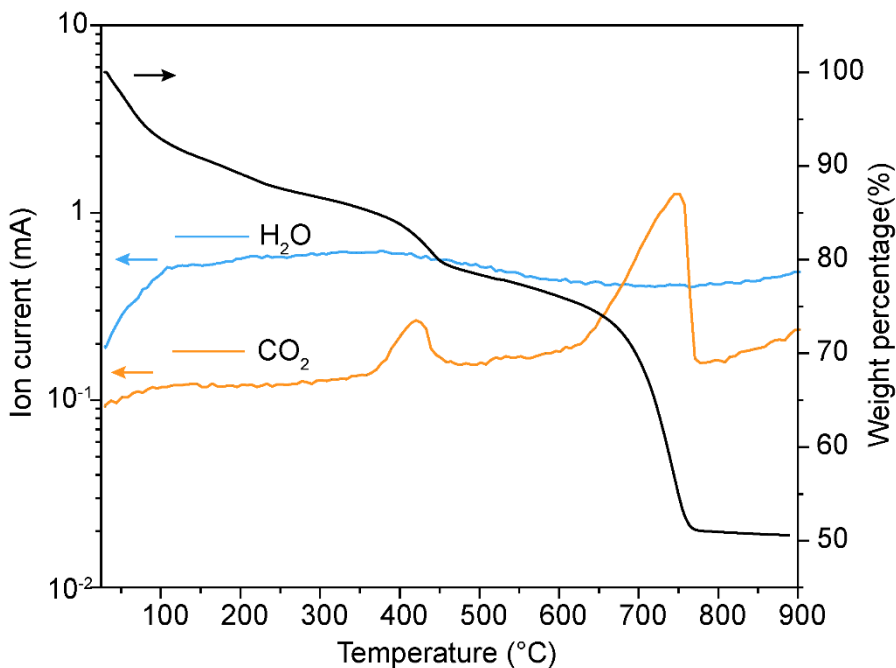
We have replaced the sentence “These results indicate that with a higher Mg content and a more complicated silicate network, the dissolution kinetics of Ca are slower” with “However, all three of these Ca/Mg silicates have been shown to dissolve completely within hours in mildly acidic to neutral solutions (pH 4-7) (citations), which indicates that they may be susceptible to rapid weathering in soils.”

The TGA interpretation of the data seems incorrect. The decomposition at 400°C does not correspond to calcination of MgCO_3 , but rather to dehydroxylation. Decomposition at $<200^\circ\text{C}$ corresponds to dehydration of molecular water. These data need to be re-analyzed and re-interpreted.

Response:

To clarify the origin of the TGA feature at 400°C , we have performed additional TGA experiments with in-line mass spectrometry (TGA-MS) to identify the gaseous species evolved. These experiments have confirmed our assignment of the 400°C feature as a CO_2 loss from MgCO_3 (calcination). Three samples have been analyzed by TGA-MS: i) an independently synthesized sample of hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2$); ii) CDR material after 7 weeks of carbonation in air under wet conditions; iii) CDR material after carbonation under 1 atm CO_2 in a slurry and subsequent drying. The TGA-MS trace for hydromagnesite shows a mass loss at $\sim 200^\circ\text{C}$ with a small peak in the H_2O MS signal and a mass loss at 400°C with a peak in the CO_2 MS signal (**Fig. S18** below). Thus, we assign the 200°C peak as the dehydroxylation and the 400°C peak as calcination of MgCO_3 . The TGA-MS trace for the CDR material after 7 weeks of carbonation in air shows a mass loss feature at 400°C that coincides with peak in the CO_2 MS signal, which confirms our assignment of the 400°C degree mass loss as a MgCO_3 calcination in this sample (**Fig. 4c** below). We note that while there is a mass loss feature at 200°C in this sample, there is not a discernible peak in the H_2O MS signal, which is a consequence of the high H_2O background and the weak H_2O signal from the relatively small amount of hydromagnesite in this sample. The TGA-MS trace for the CDR material after carbonation in 1 atm CO_2 shows a mass loss at 200°C with a small peak in the H_2O MS signal and mass loss at $400\text{--}500^\circ\text{C}$ with an associated set of 2 peaks in the CO_2 MS signal. For this sample, all of the Mg is converted into soluble $\text{Mg}(\text{HCO}_3)_2$ during carbonation under 1 atm CO_2 , which forms hydromagnesite and other Mg carbonates upon drying, hence the more complex calcination feature at $400\text{--}500^\circ\text{C}$. Nonetheless, the primary purpose of the TGA-MS data is to quantify the extent of carbonation of Mg and Ca in the CDR materials under different carbonation conditions. Confirmation that the mass losses at $\sim 400^\circ\text{C}$ and $\sim 700^\circ\text{C}$ correspond to CO_2 loss from MgCO_3 and CaCO_3 , respectively, demonstrates that

this quantification method is valid. **We have replaced the TGA in Figure 4c with this new TGA-MS data to clearly show that the 400 °C feature corresponds to calcination of MgCO_3 and have added the TGA-MS traces for CDR material after carbonation with 1 atm CO_2 and for hydromagnesite as a comparison sample as figs. S17 and S18. We thank the reviewer for prompting us to make these additional measurements to confirm the TGA assignments.**



New Fig. 4c: TGA-MS trace for CDR material after 7 weeks of carbonation in air under wet conditions. The CO_2 released at 400 °C corresponds to MgCO_3 calcination and the CO_2 released at 750 °C corresponds to CaCO_3 calcination.

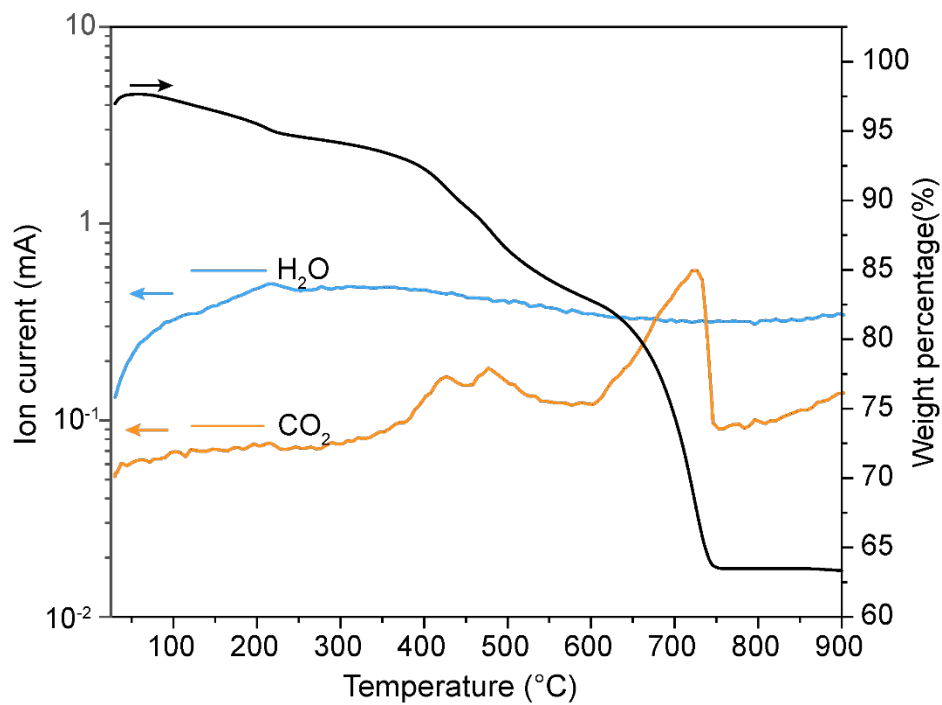


Fig. S17. TGA of the carbonation product of CDR material suspended in H_2O under 1 atm CO_2

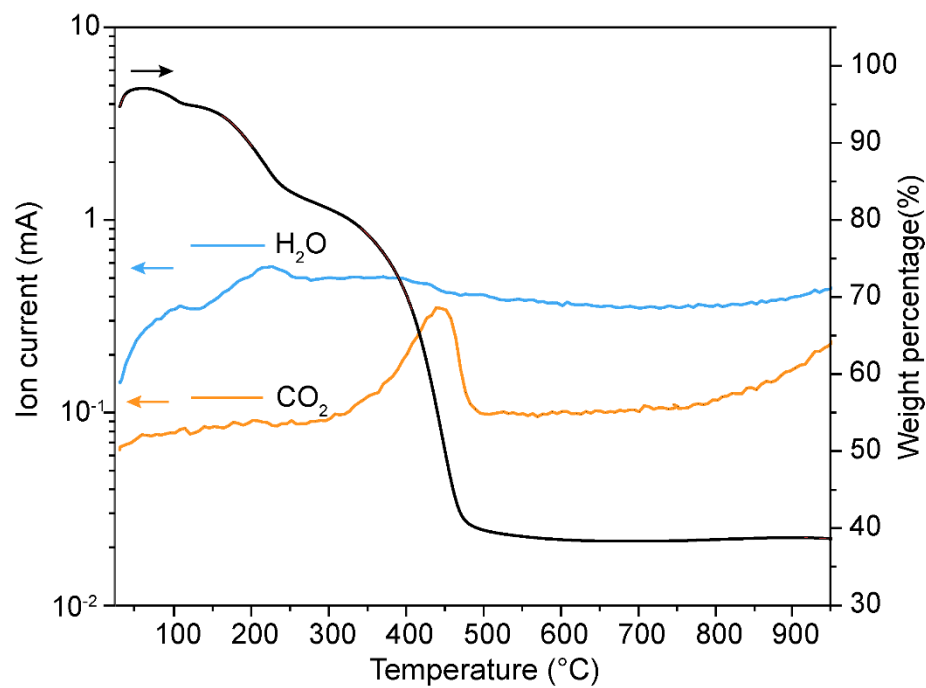


Fig. S18. TGA of synthesized sample of hydromagnesite ($Mg_5(CO_3)_4(OH)_2$).

Referee #3 (Remarks to the Author):

Summary of the key results

The paper proposes an ambitious process based on a thermochemical $\text{Ca}^{2+}/\text{Mg}^{2+}$ exchange reaction that, once and if validated, could provide a significant contribution to the general objective of limiting atmospheric CO_2 concentration. The main strength of the process, in my opinion, is that it is based on the use of cheap materials (even though it involves significant amounts of energy and temperatures as high as 1200°C) and aims at a stable geological sequestration of CO_2 in the form of MgCO_3 , rather than to its –probably more cumbersome– underground confinement. The process is described with adequate clarity, and it is (in a rather general way) examined also from the point of view of energy requirements.

Response: Thank you. Please note that, in response to comments from the editor and Reviewer 1 and 2, we have revised the process depicted in the main text to include subsurface injection of the process emissions for generating CDR materials instead of using a portion of those materials to re-capture the process emissions (please see revised Figure 5). This change substantially reduces the energy demand per net CO_2 removed and illustrates the potential value of our approach on a level basis with DAC approaches. While we agree that underground confinement is potentially cumbersome on the very large scale targeted for CDR, we think it would be an acceptable option for initial deployment. Please see response to Reviewer 1 comment (v) for a detailed description of the process energy analysis.

Originality and significance: if not novel, please include a reference. The general theme under investigation (CO_2 removal from atmosphere) is definitely significant, and the fact that –differently from typical DAC processes– in this case a stable geological solution is proposed and discussed appears of significant interest.

Data & methodology: validity of approach, quality of data, quality of presentation. The experimental approach is valid, and clearly described, also in terms of a possible validation in future works. The data are adequate quality for the scope of the paper.

Appropriate use of statistics and treatment of uncertainties N/A.

Conclusions: robustness, validity, reliability

Even though at present the proposed process is just in its conceptual definition, the proposed analysis appears definitely interesting, and the “Conclusions” reflect this.

Suggested improvements: experiments, data for possible revision

The proposed process will need an adequate validation, in terms of deeper verification of the proposed reactions and their kinetics, of verification of its engineering feasibility, and of techno-economic feasibility. However, the most appropriate site for such analysis will be further, independent papers.

Response: Thank you. We agree that the verification of engineering and technoeconomic feasibility are appropriate for a further, independent study. In response to Reviewer 1, we have performed some additional experiments to provide additional insight into the ion exchange reactions and carbonation of CDR materials. Please see responses to Reviewer 1 comments (i) through (iv).

I would advise trying to put the “ocean” (p. 13) solution in perspective: while, after all, finding a place on earth on which depositing huge amounts of rocks without having an excessive environmental impact might be feasible, I would be much more skeptical on the proposal of alkalizing seawater on a large scale. Similarly, I am not sure that the suggestion of producing huge amounts of sulfuric acid, on the scale which would theoretically follow from the amounts of rocks and CO₂ under consideration, is really sensible.

Response: We agree that much research needs to be done to assess the efficacy (with respect to CDR) and ecological impacts of large-scale ocean alkalization. **We have removed statements proposing use of CDR materials for direct alkalization of the ocean.** We have replaced ocean alkalization with the application of CDR materials as soil amendments, where enhanced weathering in the soil can lead to removal of CO₂ in the form of soluble bicarbonates. While bicarbonates formed in the soil often make their way to the ocean via runoff, groundwater, or rivers, this approach of adding alkalinity to the ocean is far less perturbative than adding it to seawater directly in concentrated form. Enhanced weathering of (ultra)mafic rocks and industrial slags is gaining traction as a CDR approach and we think it is valuable to present an analysis of our CDR materials used in that application to highlight their potential advantages.

Regarding the use of CaSO₄ and production of H₂SO₄ as a co-product, we think that there is still potential in this process because H₂SO₄ is one of the highest volume chemicals in the world and is consumed stoichiometrically in phosphate (i.e. fertilizer) production. However, the process would be considerably more complex and **we have therefore removed discussion of a CaSO₄ process from the manuscript.**

References: appropriate credit to previous work?

References are generally appropriate.

Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions The described items (Summary, Introduction, Conclusions) are adequate.

Minor observations

- as long as the "Summary" does not belong to the paper proper, “CDR” in the second line of the Introduction should be defined;
- the terms “mafic”/“ultramafic” should be defined, since they are not familiar with many potential readers;
- toward the bottom of p. 2 there is a “₁” that should probably be “<1”;
- in the last line of the Introduction (p. 3) probably there is something missing between “CaSO₄” and “CaO”;
- at the bottom of p. 12 “teh” should probably be “the”;
- “Conclusion” should probably become “Conclusions”.

Response:

Thank you very much for your thorough and very careful reading of the manuscript. We have made the suggested changes.

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9. Pardakhti, Maryam, Tahereh Jafari, Zachary Tobin, Biswanath Dutta, Ehsan Moharreri, Nikoo S. Shemshaki, Steven Suib, and Ranjan Srivastava. "Trends in solid adsorbent materials development for CO₂ capture." *ACS applied materials & interfaces* 11, no. 38 (2019): 34533-34559.

Referee #1 (Remarks to the Author):

Referee comments

The authors provide considerable scientific evidence in response to the prior comments. However, several outstanding considerations still remain as noted below.

(1) Naturally occurring olivine is rich in iron and can contain iron. The studies are conducted without considering the influence of iron and nickel on the exchange reactions. Without this information, it is challenging to assess the efficacy of this approach as a CDR technology.

Response

We thank the reviewer for raising these points. We apologize for potentially creating confusion by using a “simplified formula” in Table 1. To clarify, all silicates used in this paper are real mineral samples (i.e. sourced from nature). We provided X-ray fluorescence (XRF) analysis in Table S1, which shows ~6 wt% Fe in the olivine and a few wt% in the other Mg-rich silicates. Other constituents include Al, Na, and various metal ion impurities. The silicates were received from vendors as rocks and were crushed in our lab. The Fe in olivine is the origin of the Fe in the $\text{Ca}_2\text{Fe}_2\text{O}_5$ byproduct of the exchange reaction observed in Figure 2 (see below for more discussion of the Fe byproduct). We also showed that the reaction works with andradite, a Ca/Fe silicate ($\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$) (Fig. S11).

To clarify the composition of the silicates in Table 1 while still retaining the focus on the $\text{Ca}^{2+}/\text{Mg}^{2+}$ exchange transformations, we have indicated for each entry the name of the silicate (olivine, serpentine, augite), the formula for the Mg-rich end member, and the other metal constituents that are detected at >0.5 wt% by XRF. The Revised Table 1 is presented below. ***We have also added the pXRD patterns for each of the silicates used as reactants in the manuscript as Figure S1.*** The ability to form the Ca_2SiO_4 and MgO from multiple Mg-rich silicates containing Fe and various other metal ions demonstrates the generality of this chemistry. The Mg end members are optimal for CDR purposes because they contain the maximum amount of useful alkalinity to be released by the exchange reaction, but the impact of other metals in Mg-rich silicates on the overall energy balance is modest, as discussed in response to comment (3) below.

<u>Silicate Reactant</u>		<u>End Member</u>	<u>Other Constituents</u>	<u>CaO Source</u>	<u>CDR Materials</u>		
Olivine		Mg ₂ SiO ₄	Fe, Na	2(CaCO ₃ /CaSO ₄)	—————>	Ca ₂ SiO ₄ + 2 MgO	
Serpentine		Mg ₃ Si ₂ O ₅ (OH) ₄	Fe, Al, Ca	4(CaCO ₃ /CaSO ₄)	—————>	2 Ca ₂ SiO ₄ + 3 MgO	
Augite		CaMgSi ₂ O ₆	Fe, Al, Na	3(CaCO ₃ /CaSO ₄)	—————>	2 Ca ₂ SiO ₄ + MgO	
Entry	Silicate	End Member Formula	CaO Source	T / °C	t / h	Flux / wt%	Phases observed in pXRD
1	Olivine	Mg ₂ SiO ₄	2 CaCO ₃	1200	4	None	Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅ , CaO, olivine
2	Olivine	Mg ₂ SiO ₄	2 CaCO ₃	1200	1	5	Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅
3	Olivine	Mg ₂ SiO ₄	2 CaCO ₃	1100	1	5	Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅ , CaO, olivine
4	Olivine	Mg ₂ SiO ₄	2 CaCO ₃	1000	4	5	Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅ , CaO, olivine
5	Olivine	Mg ₂ SiO ₄	1.5 CaCO ₃	1200	1	5	Ca ₃ Mg(SiO ₄) ₂ , MgO
6	Olivine	Mg ₂ SiO ₄	1 CaCO ₃	1200	1	5	CaMgSiO ₄ , MgO
7	Olivine	Mg ₂ SiO ₄	2 CaSO ₄	1200	1	5	Ca ₂ SiO ₄ , MgO, Ca ₂ Fe ₂ O ₅
8	Olivine	Mg ₂ SiO ₄	2 CaSO ₄	1100	1	5	CaMgSiO ₄ , MgO, CaSO ₄ , olivine
9	Serpentine	Mg ₃ Si ₂ O ₅ (OH) ₄	4 CaCO ₃	1200	1	5	Ca ₂ SiO ₄ , MgO
10	Serpentine	Mg ₃ Si ₂ O ₅ (OH) ₄	4 CaSO ₄	1200	1	5	Ca ₂ SiO ₄ , MgO
11	Augite	CaMgSi ₂ O ₆	3 CaCO ₃	1200	1	5	Ca ₂ SiO ₄ , MgO
12	Augite	CaMgSi ₂ O ₆	3 CaSO ₄	1200	1	5	Ca ₂ SiO ₄ , MgO

Revised Table 1

To investigate the formation of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ byproduct in greater detail, we performed a reaction using a little bit lower loading of CaCO_3 – 1.8 molar equivalents with respect to olivine instead of 2 equivalents. pXRD analysis of the products showed $\text{Ca}_{14}\text{Mg}_2(\text{SiO}_4)_8$, Ca_2SiO_4 , MgO , and Fe_3O_4 instead of $\text{Ca}_2\text{Fe}_2\text{O}_5$. ($\text{Ca}_{14}\text{Mg}_2(\text{SiO}_4)_8$ results from incomplete $\text{Ca}^{2+}/\text{Mg}^{2+}$ exchange on account of the lower amount of CaO). The observation of Fe_3O_4 in this reaction suggests that it is an intermediate to the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ when the reaction is performed with 2 equivalents. The formation of Fe_3O_4 can be explained by reaction of CaO with olivine to release FeO (i.e. $\text{Ca}^{2+}/\text{Fe}^{2+}$ exchange) and its subsequent oxidation by O_2 from air. (While Fe_2O_3 is the thermodynamic oxidation product, the oxidation of Fe_3O_4 to Fe_2O_3 may be hindered by O_2 mass transport limitations under the reaction conditions). When there is sufficient CaO in the system, Fe_3O_4 reacts with CaO to form $\text{Ca}_2\text{Fe}_2\text{O}_5$ and release FeO , which is subsequently oxidized. We have confirmed by Gibbs free energy calculations that the following reactions are exergonic: $2\text{CaO} + 2/3 \text{Fe}_3\text{O}_4 + 1/6 \text{O}_2 \rightarrow \text{Ca}_2\text{Fe}_2\text{O}_5$; and $2\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow \text{Ca}_2\text{Fe}_2\text{O}_5$.

These additional results show that it is possible to perform $\text{Ca}^{2+}/\text{Mg}^{2+}$ exchange reactions without consuming any CaO by reaction with an Fe oxide generated from the Fe content of a Mg-rich silicate. To maximize the efficiency of CaO use while still producing Ca_2SiO_4 as the major silicate product, it is optimal to use slightly less than 2 equivalents of CaCO_3 and CaSO_4 in the exchange reaction.

We have added a description of the experiment with 1.8:1 CaCO_3 :olivine ratio producing Fe_3O_4 byproduct to the main text and Table 1. The pXRD pattern and thermodynamic calculations have been added as Fig. S6. To improve the clarity, we have included all the experiments with less than 2 equivalents of CaCO_3 in one paragraph.

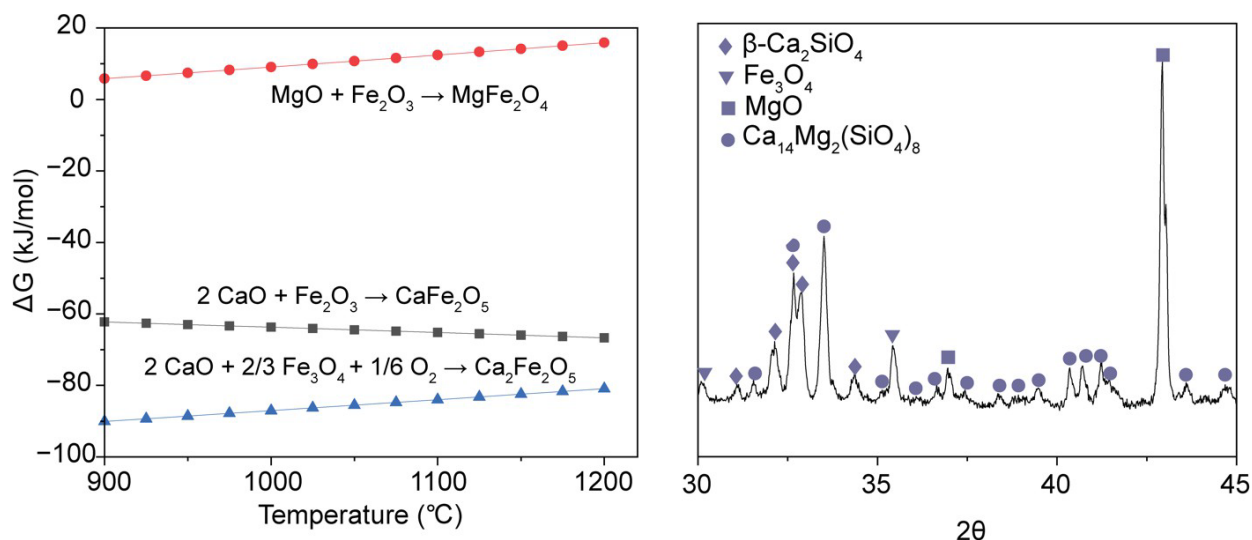


Figure S6

The presence of Fe in olivine means that there is less MgO available for removing CO₂ (per Si atom) after ion exchange because the Fe(III) byproducts do not form stable carbonates. To illustrate the impurity effect on the system's energy consumption and mass balance, we updated the LCA to account for different Fe impurity content. Since these other metals are relatively minor constituents, they have a minor effect on the LCA. Please see response to Question 3.

Regarding Ni, the Ni content in our olivine is ~2700 ppm according to XRF (2000-3000 ppm is typical for olivine samples we have encountered; Ni was not detected in the other silicate samples). Therefore, using pXRD to identify the Ni byproducts is not practical. We used phase diagram to look at the evolution of Ni species in the ion-exchange reactions. The phase diagram shows that CaO will exchange with Ni in Ni₂SiO₄¹. CaO and NiO will stay as separate oxides but will form a solid solution². Given the low Ni content in olivine samples (<1%), it has a negligible effect on the LCA.

Referee comments

(2) The manuscript does not provide insights into the influence of varying particle size on the kinetics of ion exchange and the associated economics. This factor is important to consider since particle size influences grinding and the subsequent impacts on energetics.

Response

We have used a moderate silicate particle size of 76-106 µm for our experiments. This particle size was chosen because it can be achieved using any of several widely available milling technologies with a low energy input. Based on the plot shown in the figure below, the energy required to achieve 76-106 µm is 10-20 kwh/ton mineral³ (ref. 43 in the main text). For our LCA, we assumed 20 kWh/ton. With this value, the energy for milling is a very minor contributor to the overall energy demand of our process. We note that achieving ultrafine (<10 µm) will require significantly more energy (>100 kwh/t) and is also undesirable because ultrafine particles are a health hazard.

[FIGURE REDACTED]

While the particle size regime we used does not impose a major energy cost, larger particles may be preferred in the scaled-up manufacturing process. To test the feasibility of using larger particles, we have performed a reaction using 300-400 μm olivine (at 1200 °C with 5 wt% Na_2SO_4). Analysis by pXRD shows that this reaction conversion is ~50% in 2 h and 91% after 6 h. **We have added this experiment with larger olivine to the main text and the pXRD of the product as Figure S5.** We note that the reaction time required for a static mixture in a furnace as we are using for these experiments does not predict the residence time that would be needed in a continuous process performed on scale in a direct-fired rotary kiln. Based on the precedent with cement clinker production, we anticipate that we will be able to optimize the particle size of the feedstocks and operating parameters of a rotary kiln to achieve continuous production of CDR material at comparable throughput and thermal efficiency.

Referee comments

(3) Experimental results with "real" olivine samples are needed and a detailed discussion of all the factors that influence the proposed exchange mechanisms to help inform subsequent TEA and LCA is essential. Without these analyses, the reported results are still preliminary and can be disputed. Also, error bars are not provided for Figure S5 associated with ion exchange. More robust experimental analyses is essential.

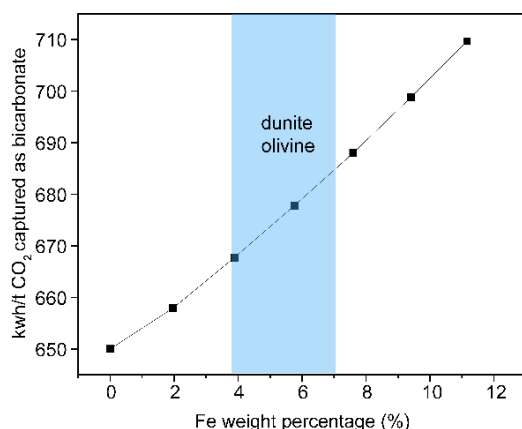
Response

As discussed above in the response to comment (1), all the silicates used in this paper are real, natural samples and the presence of the other metal constituents including several wt% Fe does not interfere with the $\text{Ca}^{2+}/\text{Mg}^{2+}$ exchange.

In the LCA, we used forsterite (Mg_2SiO_4 , the Mg end member of olivine) as the model input silicate because it makes it easy to follow the carbon balance. We acknowledged that this case is ideal and that silicates with lower Mg content would require more energy per carbon removed in the paragraph beginning with "The above analysis assumes the input is the ideal mineral (forsterite), which has the maximum possible Mg:Si ratio of 2.". We agree that it is valuable to provide a more quantitative analysis for minerals with other metal ion constituents.

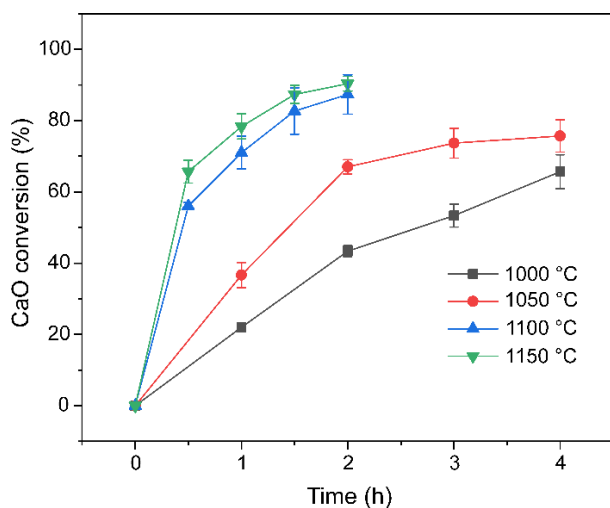
As discussed in the response to comment (1), the presence of Fe in olivine reduces the CDR capacity because the Fe oxide byproducts do not form stable Fe carbonates. We have therefore updated our energy analysis to account for different levels of metal ion constituents that cannot sequester carbon. The effect is small because it simply decreases the amount of MgO per CaO input. For example, each mole of $\text{Mg}_{1.9}\text{Fe}_{0.1}\text{SiO}_4$ can only give 1.9 mol of MgO with 2 mol of CaO input, instead of 2 mol of MgO in the case of forsterite. (Since we have shown that it is possible to perform $\text{Ca}^{2+}/\text{Mg}^{2+}$ ion exchange without consuming any CaO by $\text{Ca}_2\text{Fe}_2\text{O}_5$ formation (see response to comment (1)), there is no need to "waste" CaO by unproductive reaction with Fe_3O_4 .)

Olivine that commonly exists in the crust (dunite olivine in peridotite) has an iron level 4 - 8 wt%. With these levels, the energy increases by only 3 - 6% per ton CO_2 captured. A plot of the energy demand vs wt% Fe in olivine is shown below.



Energy consumption (including grinding, latent heat, sensible heat and compression) energy to capture 1 ton CO₂ as dissolved bicarbonate ions.

Regarding Figure S5, we have now performed 3 replicates of this experiment and have added error bars to the plot. Please see below. The Figure is now Fig. S4 because of figure reordering in the revision.



Updated Figure S4. Error bars for the first two data points at 1000 °C overlap with the data symbols.

References

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Referees' comments:

Referee #1 (Remarks to the Author):

- (1) The authors show that calcination of Ca-carbonate and Mg-silicate results in MgO and Ca-silicate which are more reactive with CO₂. While the authors do demonstrate that these products are indeed produced, the energy needs associated with this approach are significant. Several approaches already exist to valorize Mg-silicate (or olivine) to co-produce carbonates, silica, and energy relevant metals which are more energy efficient than the proposed route.

Response: To our knowledge there is no other approach to valorizing Mg silicates that rivals the energy efficiency of the method demonstrated in this paper. As summarized in the Introduction and demonstrated by direct comparison with olivine in the paper, approaches to CO₂ removal that consist of simply grinding and dispersing Mg silicates or silicate-containing rocks suffer from extremely slow dissolution/carbonation rates and very low conversions. Electrochemical pH swing approaches have been described for valorizing Mg silicates, but the energy cost just for producing acid and base using conventional technologies or using what has been demonstrated in previously published literature greatly exceeds the total energy demand of our process.

- (2) The authors make the argument that more CO₂ can be stored than what is initially released during the calcination of Ca-carbonate. However, a full process LCA would be needed to justify this approach. While the authors present scientific evidence supporting the feasibility of this approach, the overall whole system life cycle emissions would challenge the implementation of this approach.

Response: The ability to remove more CO₂ than what is released during the calcination is a critical enabling feature of our chemistry. By reacting CaO with Mg silicates, the Mg alkalinity that is kinetically trapped in the Mg silicate is released as MgO without compromising the Ca alkalinity. As detailed in Figure 5 and described in the main text and SI, we have provided an analysis of the energy demands of a process using our chemistry including grinding, heating, the thermal energy for calcination/ion exchange, thermal losses, air separation for oxyfuel combustion, and energy for CO₂ compression for subsurface storage. Accounting for all these contributions and accounting for the composition of real olivine inputs, the energy per ton CO₂ removed is 1.3 MWh/tCO₂ if the carbonation products are carbonates and 0.65 MWh/tCO₂ if the products are bicarbonates. These numbers are for operating the process using 2:1 Ca:Si ratio. As discussed in the paper, reducing the ratio to 1:1 would further reduce the energy demand (1.02 MWh/tCO₂ and 0.51 MWh/tCO₂). While the partially exchanged materials do not weather as quickly as the fully exchanged materials, they may still be viable for CDR in soil or other open systems. A more detailed LCA would include factory siting, LCA of factory construction materials, and feedstock and product transport considerations. Such a study is beyond the scope of this work but will be included in a future study.