Magnesium hydroxide is a sustainable material for CO_2 sequestration, according to an acid digestion and electrolysis method using olivine-rich silicate rocks in a fully recoverable system.

Transformation of abundant magnesium silicate minerals for enhanced CO_2 sequestration

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Abstract:

Global climate change related to anthropogenic CO_2 emissions is one of the most significant challenges for the future of human life on Earth. There are many potential options for reducing or even eliminating atmospheric CO_2 emissions including underground sequestration, carbon mineralization and ocean storage. One of the most promising materials for carbon mineralization is $Mg(OH)_2$ which is highly reactive and capable of forming stable carbonates. Here we show a novel low-carbon method of producing $Mg(OH)_2$, from globally abundant olivine-rich silicate rocks. A combination of acid digestion and electrolysis of olivine were used to produce $Mg(OH)_2$ in a fully recoverable system. The use of $Mg(OH)_2$ from olivine provides a viable pathway for significant industrial scale reductions in global anthropogenic greenhouse gas emissions.

Introduction:

The effects of unchecked CO_2 emissions on global climate change are being increasingly seen and felt across the world. Examples of issues include increased land and sea temperatures, glacier and sea ice loss, and sea level rise (1). Urgent action is needed to limit future emissions and sequester existing atmospheric CO_2 in order to circumvent issues related to global warming (2). In 2018, ~37 billion tonnes of CO_2 was released into the atmosphere (*3*). Point source emissions such as power generation and industrial production account for approximately 60% of the total CO_2, but this is expected to decrease to 50% by 2050 (4).

Methods for long-term storage of CO_2 can be classified as either underground sequestration or carbon mineralization, of which underground sequestration in sedimentary formation is considered the most mature technology (5). Carbon mineralization can be further divided into 3 approaches: 1) *ex-situ*, where material is transport to the site and reacted with CO_2 typically at elevated temperatures and pressures, 2) *surficial*, using dilute or concentrated CO_2 and 3) *in-situ*, where the CO_2 is transported to site with suitable geological formations, typically containing serpentine or olivine-bearing basalts (5). Ocean storage has also been proposed as a potential means of CO_2 sequestration, but comes with a number of environmental consequences (4).

A number of materials have been proposed for carbon mineralization including serpentine, olivine, wollastonite, magnesium oxide and magnesium hydroxide (6-10). Of the various materials which may be suited for transport to the emissions source, $Mg(OH)_2$ is one of the most reactive for carbonization (5). Aqueous carbonation of $Mg(OH)_2$ can result in the formation of a hydrated Mg-carbonate such as nesquehonite ($MgCO_3 \cdot 3H_20$), dypingite ($Mg_5(CO_3)_4(OH)_2.5H_2O$), and hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) under atmospheric or near atmospheric conditions (11). The formation of magnesite ($MgCO_3$) is also possible but this typically requires higher temperatures (>100 ^oC) and pressures above 100 bar. Seeding $Mg(OH)_2$ slurries with magnesite at elevated pressures and temperatures has been shown to produce a stable anhydrous magnesite (12). One of the benefits of $Mg(OH)_2$ with regard to overall conversion rates and transportation is that it does not contain significant quantities of unreactive material, such as silica or iron which are typically found in olivine or serpentine.

MgO and $Mg(OH)_2$ are usually sourced from either the calcination of magnesite or precipitated from Mg-rich brines and sea water (13). Recovery of $Mg(OH)_2$ from seawater has the potential to provide virtually limitless supplies of the material; however, its commercial production typically requires the use of lime, which itself has significant embodied CO_2, resulting in little overall environmental benefit. The high temperature pyrohydrolysis process of using $MgCl_2 \cdot 6H_2O$ to form MgO and HCl (14) could potentially provide a low carbon $Mg(OH)_2$ alternative; however, concentrations of Mg-chloride in seawater are relatively low which limits the efficiency of the process unless highly concentrated brines are used.

Magnesium-rich silicate minerals, such as olivine ($(Mg,Fe)_2SiO_4$), in ultramafic and mafic rocks have the potential to produce reactive $Mg(OH)_2$ with zero CO_2 emissions. Until now, $Mg(OH)_2$ recovery from olivine has not been used primarily because of the slow rate of hydration (i.e., serpentinization)(15, 16) or ultramafic mineral extraction efforts have been focused on silica recovery (17) rather than $Mg(OH)_2$ production. Furthermore, a satisfactory energy efficient industrial process has not been developed yet (18).

Here, we extract $Mg(OH)_2$ directly from olivine using a combination of acid digestion and electrolysis. The acid used in the digestion process is completely recoverable and provides a source of usable energy. Recovered $Mg(OH)_2$ was found to have a similar level of reactivity compared to commercially available $Mg(OH)_2$. A slurry of recovered $Mg(OH)_2$ and water was shown to effectively sequester CO_2 forming a hydrated Mg-carbonate. In addition to $Mg(OH)_2$, amorphous silica, which has the potential for use as a partial cement replacement, was also recovered from the olivine.

Methods: Synthesis of $Mg(OH)_2$

The synthesis of $Mg(OH)_2$ uses olivine from ultramafic rocks and/or olivine-rich basalts as the raw material and source of magnesium (**Fig. 1**). Olivine is sparingly soluble under standard state conditions with a total Mg concentration of less than 6 mg L^{-1} resulting in excessive energy demands for the recovery process. As the pH of the reaction solution decreases, the solubility of Mg increases considerably. In our investigation, 100 g of finely ground forsteritic ($(Mg_{0.9}Fe_{0.1})_2SiO_4$) olivine (19), with a mean particle size of 28 µm, was combined with 500 ml of 2 M HCl, resulting in the formation of a solution containing $MgCl_2$ and $FeCl_2$ and SiO_2. The silica is produced through a process of hydrolysis and subsequent polymerization and condensation of silicic acid ($Si(OH)_4$). Strong acids such as HCl are known to accelerate the hydrolysis process, whereas, a high pH favours the polymerization and condensation process that is supported by the addition of $Mg(OH)_2$ in this study. Here the pH of the solution increased rapidly from less than 0 to ~3 after 4 hours of mixing at 20 ^{o}C.

The concentration of Mg^{2+} in solution was determined by complexometric titration used to measure total hardness of water. 1 ml of sample solution was added in a conical flask containing 10 ml of 0.05 M ethylenediaminetetraacetic acid (EDTA) solution and 10 ml of ammonia buffer solution. Eriochrome black T was used as an indicator. The solution was titrated using a 0.025 M magnesium chloride solution until its colour changed from blue to pink. The concentration of complexed EDTA solution was used to determine the magnesium ion concentration. Since the concentration of calcium ions in the sample solution was negligible, it was assumed that all the ions complexed with EDTA were magnesium. The Mg concentration was found to be ~24 g L^{-1}, which is more than 19 times the concentration of Mg in seawater and over three orders of magnitude greater than the concentration resulting from serpentinization reactions involving pure water. The potential Mg extraction efficiency, therefore, is considerably higher using an acid digestion solution than it is from seawater.

Once the initial digestion phase was completed the solution was allowed to settle for 1 hour after which it was decanted to separate the solution containing the Mg, Fe and Si ions from any unreacted olivine (**Fig. 1**). Silica was precipitated from solution by increasing the pH to >3.5 through the addition of 1 g of $Mg(OH)_2$. The pH of the remaining solution was further increased to almost 7 to precipitate the dissolved iron using 0.32 g of NaOH. The silica and iron were separated from the solution using a centrifuge in this proof of principal testing, whereas, an industrial filtration system would be used in practice. It should be noted that the formation of gel-like products during the precipitation of silica and iron can cause challenges to any filtration system. Regular flushing and cleaning of the membranes would be necessary and likely require a number of cross flow filters, such as those used for silica removal from geothermal waters, to be run in parallel to maintain operations. An alternative approach and potentially more efficient method for the removal and recovery of the silica and iron is by precipitate flotation.

The $MgCl_2$ solution was electrolysed in an H-cell with a carbon anode and platinum cathode. A DC power supply was used to generate a current of approximately 100 mA resulting in the formation of Cl_2 gas at the anode and H_2 gas at the cathode. $Mg(OH)_2$ was formed at the cathode where the pH of the solution increased rapidly to ~9.5. The recovered $Mg(OH)_2$ was placed in a drying oven at 105 ^{o}C for 1 day after which it was analysed by scanning electron microscope (SEM), thermo gravimetric analysis (TGA) and X-ray powder diffraction (XRD). For the commercial production of $Mg(OH)_2$, H_2 and Cl_2 would be combined to produce HCl for re-use and as an energy resource, as is typically done in the chemical process and manufacturing industry.

Results and Discussion

From this process, a total of 35 g of $Mg(OH)_2$ was produced from 100 g of olivine, with 1 g of $Mg(OH)_2$ added in the silica precipitation stage. Approximately 5 g of iron oxide was precipitated with the addition of 0.32 g of NaOH, which represented less than 1 % of the total $Mg(OH)_2$ recovered. 35 g of amorphous silica was also recovered from the precipitation stage. The SEM image and TGA graph provided in **Fig. 2 a,b** show the material recovered after electrolysis was primarily $Mg(OH)_2$. XRD results provided in **Fig 2c.** show the recovered silica was predominantly amorphous SiO_2 with some residual unreacted olivine and confirm the material recovered after electrolysis was predominately $Mg(OH)_2$. The composition of the raw olivine sand, recovered $Mg(OH)_2$, and recovered silica from olivine, determined by X-ray fluorescence (XRF), are provided in **Table 1** and are consistent with the other material characterization analysis.

In addition to the primary recovered $Mg(OH)_2$, secondary materials of iron hydroxide and silica may also be of use. The iron hydroxide for instance could be used as a high purity raw material for iron production or as an absorbent while the amorphous silica can be used as a partial replacement for Portland cement, in the production of concrete, which is a significant industrial contributor to global CO_2 emissions (20). Our approach provides an almost completely closed system for the production of $Mg(OH)_2$ with the only additions being olivine, as the source of Mg, and minor amounts of NaOH.

CO_2 and energy implications of Mg-hydroxide extraction

Overall, conversion of olivine into $Mg(OH)_2$ produces no direct CO_2 emissions and the HCl used for digestion was completely recoverable. The large scale and industrial use of strong acids such as HCl have serious consequences if released into the environment. However, this is only an issue if there is a loss of containment from the process. The large scale handling of HCl without loss of containment is well established in the chemical process industries due to its use in commodity materials such as the manufacture of PVC and pickling of steel. What is most important is that neither HCl nor chlorine leave the process described in our work, as they are recycled within the process.

The total energy required, including quarrying and grinding, to produce $Mg(OH)_2$ from olivine was calculated to be 6.28 GJ tonne^{-1} (see **Fig. 1** and **Supplementary Methods** for energy determinations and calculations). Further refinement of the process may allow greater use of recovered $Mg(OH)_2$ for pH control, a decrease in the total energy required, and a reduction in NaOH. The $Mg(OH)_2$ could be further processed into MgO but for CO_2 sequestration; however, $Mg(OH)_2$ is known to be a faster reactant than MgO (*10*).

For every tonne of CO_2 sequestered as a Mg-carbonate, including nesquehonite and hydromagnesite, 1.3 tonnes of $Mg(OH)_2$ is required, resulting in an energy consumption 8.17 GJ $tonne^{-1}$ of CO_2 (**Fig. 1**, see **Supplementary Methods** for calculations). Using the method outlined in this paper would result in a net negative CO_2 emission, even if coal was used to provide the necessary energy, though at ~25% sequestration efficiency. The overall carbon sequestration benefits would improve substantially if a low carbon energy sources, or even a mixed electrical supply, was used. For example, in California where roughly 50% of the electricity is from non-fossil fuels , ~500 kg of CO_2 would be emitted for every 1,000 kg of CO_2 captured and turned into Mg-carbonate.

To confirm the ability of the recovered $Mg(OH)_2$ to sequester CO_2, a $Mg(OH)_2$ water slurry was pressurized to 4 bar with concentrated CO_2. Over a 48 hour period more than 50% of the $Mg(OH)_2$ was converted to a hydrated Mg-carbonate, demonstrating the potential conversion of CO_2 into a solid. The reactivity of the recovered $Mg(OH)_2$ was also confirmed by the rapid increase in pH to ~10.5 when it was added to de-ionized water. As previously noted, there are a number of other methods for sequestering CO_2 with $Mg(OH)_2$ using either aqueous (12,21) or direct solid-gas reaction methods (10). Our proposed process has the potential to provide a substantial source of energy efficient, low-carbon $Mg(OH)_2$ for use in various carbon sequestration techniques currently being developed by other investigators.

Olivine resources and feasibility

Ultramafic rocks, enriched in olivine, constitute ~1% of Earth's terrestrial landscape, a high proportion of oceanic crust, and >50 % of the upper mantle (22). Olivine-rich deposits (**Fig. 3**) are primarily present within populated areas of the Circum-Pacific and Mediterranean regions (23, 24). Olivine is present in many rocks such as basalt and other ultramafics. We would like to note that although olivine was assessed and used in this study, its metamorphic equivalent, serpentine ($Mg_3Si_2O_5(OH)_4$) with its high reactivity in HCl and worldwide deposits, could expand the scope and implications of this study. Our preliminary investigations have shown Mg can also be extracted from basalt; however, we will primarily focus our discussion on two enriched and accessible olivine deposits: the Semail ophiolite (Oman) and the Red Hills Ultramafic Complex (New Zealand) which conservatively contain 1.4×10^5 and 871 billion tonnes of olivine, respectively (see **Supplementary Methods** for sources and estimate calculations).

Using $Mg(OH)_2$ to remove and sequester anthropogenic CO_2 estimated for 2020 (40 billion tonnes) in a Mg-carbonate would require ~105 billion tonnes of olivine. Reducing global atmospheric CO_2 levels by an additional 10 billion tonnes would necessitate a further 26 billion tonnes of olivine. The sum of olivine required to do all of this would be 131 billion tonnes; 0.1 % of the Oman ophiolite or 16 % of Red Hills, New Zealand (**Fig. 3**). To sequester all anthropogenic CO_2, these two deposits would last on the order of nearly a decade (Red Hills) to one thousand years (Semail), assuming the deposits contained at least 60% olivine. The degree of serpentinization of each deposit and abundance of other minerals such as ortho- and clinopyroxene would affect the overall extraction efficiency. Smaller deposits, compared to the Semail ophiolite or Red Hills, around the world could significantly aid the global reduction of anthropogenic CO_2.

Implications

The concept of using ultramafic rocks and its metamorphic equivalents as sources of Mg for CO_2 sequestration has been considered for at least two decades. However, one limitation with regards to previous and current approaches is related to the distance between the CO_2 gas source and the ultramafic site. Currently, concentrated CO_2 is being transported/piped to ultramafic sites to be directly injected into the subsurface. Although ultramafic sites are around the world, many are not sufficiently close to areas of high CO_2-producing industries. Our approach allows bulk $Mg(OH)_2$ to be transported more efficiently to locations/industries where it can be used on site for point source emissions control. For example, transporting enough $Mg(OH)_2$ to sequester 1 tonne of CO_2, from its production location to a point source such as a cement plant 1,000 km away by rail, would result in 37 kg of CO_2 emissions (25).

Additionally, slight modifications to this approach through the further refinement of $Mg(OH)_2$ to MgO has the potential to produce construction materials such as Mg-masonry blocks (26) rather than simply burying the CO_2. There is considerable interest in the potential use of MgO as an alternative to traditional Portland cement (13); however, there are a number of issues which must be addressed, including: the low pH of the pore solution, which makes its use in steel reinforced structures challenging, and high water demand which makes handling more difficult. One of the major environmental issues associated Mg-based cements is the vast majority of MgO is produced from $MgCO_3$ which results in the release of CO_2 at a similar proportion to that of Portland cement. The alternative of recovering MgO from sea water, as previously noted, also has considerable embodied CO_2 due to the use of CaO, sourced from carbonates, in the recovery process. If MgO is to be used as a construction material then a low carbon mineral extraction approach will be needed. The scale and scope to mitigate climate change using Mg-bearing minerals from ultramafic and mafic rocks is massive, but our experiments and others support that this is feasible.

Scaling up and improving efficiencies with regards to the processes described and proven here will require a significant development and industrialization effort. We anticipate that the engineering challenges to produce $Mg(OH)_2$ for use in CO_2 sequestration, as shown in **Fig. 1,** are comparable to other well known industrial processes. One of the great challenges, however, is how to use the billions of tonnes of carbonate produced to offset anthropogenic CO_2 emissions and this requires further circumspection. A more realistic and efficient approach to addressing global warming is to reduce CO_2 emissions. Until then, we have demonstrated a process that is feasible and globally communal where many countries and industries can participate. Overall, the recovery of magnesium hydroxide from olivine-rich (and potentially serpentine-rich) rocks provides the basis for a direct route to reduce global anthropogenic CO_2 and its associated climate change impacts.

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Figures and Tables

Figure 1: Simplified mineral extraction and carbon sequestration.

Energy requirements are shown where $E_1 = 0.32$, $E_2 = 6.6$ and $E_3 = -0.64$ GJ $tonne^{-1}$ of $Mg(OH)_2$ produced. Energy consumption details are provided in **Supplementary Methods**. Note: Direct solid-gas carbon mineralization is also possible and the most likely approach for point source CO_2 sequestration.

*Note: The carbonation product is likely to be hydrated Mg-carbonate such as nesquehonite, dypingite, or hydromagnesite, but $MgCO_3$ formation is also possible depending on reaction conditions (27).

Figure 2: Characterization of recovered material.

a) SEM image of recovered $Mg(OH)_2$ from electrolysis of olivine digestion solution, **b)** TGA of recovered $Mg(OH)_2$ from olivine, **c)** XRD of recovered $Mg(OH)_2$ and of recovered silica (B: brucite, L: lizardite, F: forsterite).

Figure 3: Distribution of ultramafic rocks and olivine lifetime estimates.

The general distribution of ultramafic rocks (including peridotites and serpentinites) is shown worldwide. Ultramafic rock distributions are based on location data from Oze et al. (24) and compared to Real and Vishal (23). Please note that more ultramafic rock deposits are present than shown and that the squares do not represent particular sites. The billions of tonnes of olivine per year needed to sequester all anthropogenic CO_2, and reduce global atmospheric CO_2 as well as the lifetime supply of olivine from the Red Hills (New Zealand) and Semail Ophiolite (Oman) is shown and based on calculations provided in the **Supplementary Methods**.

Table 1. Elemental compositions of raw olivine sand and recovered $Mg(OH)_2$ and silica from olivine, determined by XRF analysis.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI	Total
	---------------------				-Wt. %-			----------------------	
Raw olivine	39.6	0.38	10.7	0.73	45.0	0.14	0	3.2	100.0
$Mg(OH)_2$-olivine	0.1	0.11	6.4	0.30	60.4	0.03	<0.01	32.3	99.9
Silica-olivine	63.2	0.23	4.7	0.57	13.9	0.03	0.06	16.4	99.0

Data Availability

Data files containing XRD and TGA results of the recovered materials from this investigation are available from the figshare data set repository: DOI 10.6084/m9.figshare.13543091.

Author Contributions

AS: Conceptualization, Methodology, Resources, Formal Analysis, Funding Acquisition, Writing-original draft, **VS**: Conceptualization; Methodology, Formal Analysis, Investigation, Writing-review, **CO**: Conceptualization; Writing-review & editing, **BS**: Investigation, Methodology, **CC:** Writing-review & editing, **NY**: Investigation, Methodology, **MW**: Conceptualization, Writing-review & editing, **AM**: Conceptualization, Writing-review & editing

Competing Interests

All authors declare no competing interesting

References:

1. Stocker, T.F., et al. Technical Summary. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.(2013).

2. IPCC, 2018: Summary for Policymakers. In: Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty [Masson-Delmotte, V., P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, T. Maycock, M. Tignor, and T. Waterfield (eds.)]. In Press.

3. Tollefson, J. Global industrial carbon emissions to reach all-time high in 2018. *Nature*, 3 (2018).

4. Chapter2 Sources of CO_2, Carbon Dioxide Capture and Storage, IPCC, 2005 – Bert Metz, Ogunlade Davidson, Heleen de Coninck, Manuela Loos and Leo Meyer (Eds.) Cambridge University Press, UK. pp 431. Cambridge University Press, Cambridge, UK.

5. Kelemen, P. Benson, S.M. Pilorge, H. Psarras, P. Wilcox, J. An Overview of the Status and Challenges of CO_2 Storage in Minerals and Geological Formations, *Frontiers in Climate*, 1-9 (2019).

6. Prigiobbe, V. Hänchen, M. Werner, M. Baciocchi, R. Mazzotti, M. Mineral carbonation process for CO_2 sequestration. *Energy Procedia*. **1**, 4885–4890 (2009).

7. Olsson, J. et al. Olivine reactivity with CO_2 and H_2O on a microscale: Implications for carbon sequestration. *Geochimica et Cosmochimica Acta*. **77**, 86–97 (2012).

8. Munz, I. A. et al. A continuous process for manufacture of magnesite and silica from olivine, CO_2 and H_2O. *Energy Procedia*. **1**, 4891–4898 (2009).

9. Goff, F. et al. Evaluation of ultramafic deposits in the Eastern United States and Puerto Rico as sources of magnesium for carbon dioxide sequestration (LA-13694-MS, Los Alamos National Lab., NM (US), 2000), , doi:10.2172/754045.

10. Fagerlund, J. Zevenhoven, R. An experimental study of Mg $(OH)_2$ carbonation. *International Journal of Greenhouse Gas Control*. 5, 1406–1412 (2011).

11. Zarandi, A. Larachi, F. Beaudoin, G. Plante, B. Sciortino, M. Nesquehonite as a carbon sink in ambient mineral carbonation of ultramafic mining wastes, *Chemical Engineering Journal*, 314, 160-168 (2017).

12. Swanson, E. Fricker, K. Sun, M. Park, A. Directed precipitation of hydrated and anhydrous magnesium carbonates for carbon storage, *Physical Chemistry Chemical Physics*, 16, 23440-23450 (2014)

13. Walling, S. A. Provis, J. L. Magnesia-Based Cements: A Journey of 150 Years, and Cements for the Future? *Chemical Reviews*. **116**, 4170–4204 (2016).

14. Shand, M.A. The Chemistry and Technology of Magnesia; John Wiley & Sons: Hoboken, NJ, (2006).

15. Neubeck, A. et al. Olivine alteration and H2 production in carbonate-rich, low temperature aqueous environments. *Planetary and Space Science*. **96**, 51–61 (2014).

16. McCollom, T. M. Bach, W. Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. *Geochimica et Cosmochimica Acta*. **73**, 856–875 (2009).

17. Justnes, H. Ostnor, T. Pozzolanic, amorphous silica produced from the mineral Olivine. Proceedings of the 7th CANMET/ACI. *American Concrete Institute Special Publication*. **199**, 769–782 (2001).

18. Gartner, E. Sui, T. Alternative cement clinkers. *Cement and Concrete Research*. 114, 27–39 (2018).

19. Pawson, J. F. Abiotic Methane Formation at the Dun Mountain Ophiolite, New Zealand. Msc Thesis, University of Canterbury (2015) (available at https://ir.canterbury.ac.nz/handle/10092/10280).

20. Scrivener, K. L. John, V. M. Gartner, E. M. Eco-efficient cements: Potential economically viable solutions for a low-CO_2 cement-based materials industry. *Cement and Concrete Research*. **114**, 2–26 (2018).

21. Zhao, L. Sang, L. Chen, J. Ji, J. Teng, H. H. Aqueous carbonation of natural brucite: relevance to CO_2 sequestration. *Environmental Science & Technology*. **44**, 406–411 (2010).

22. Winter, J. D. Principles of igneous and metamorphic petrology (Pearson education, 2013).

23. García del Real, P. Vishal, V. Geologic Carbon Sequestration: Understanding Reservoir Behavior, V. Vishal, T. N. Singh, Eds. (Springer International Publishing, Cham, 2016; https://doi.org/10.1007/978-3-319-27019-7_11), pp. 213–229.

24. Oze, C. Bird, D. K. Fendorf, S. Genesis of hexavalent chromium from natural sources in soil and groundwater. *Proceedings of the National Academy of Sciences*. **104**, 6544–6549 (2007).

25. Kirschstein, T. Meisel, F. GHG-emission models for assessing the eco-friendliness of road and rail freight transports, *Transportation Research Part B*, 13-33 (2015)

26. Vlasopoulos, N. Cheeseman, C. R. Binder composition (2013), (available at https://patents.google.com/patent/US8496751/en).

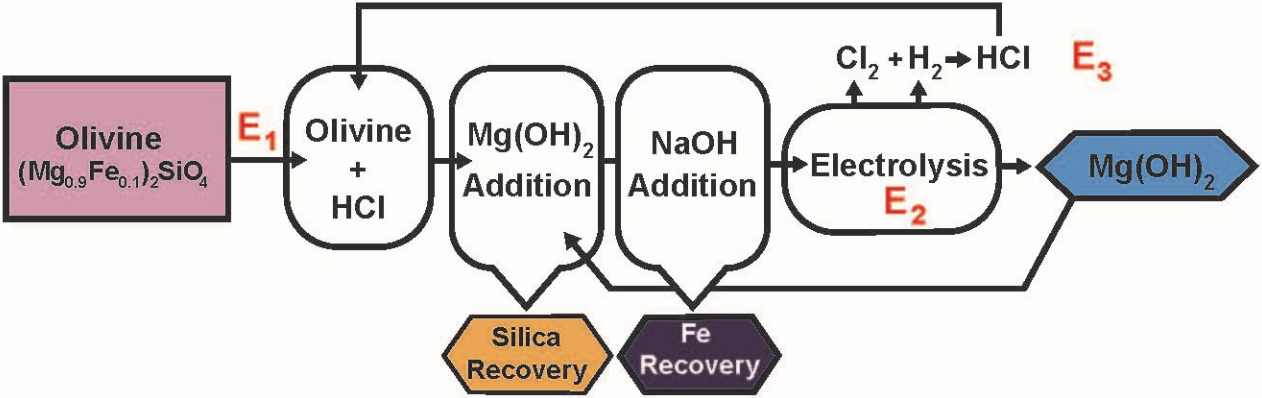
27. Rausisa, K. Ćwika, A. Casanova, I. Phase evolution during accelerated CO_2 mineralization of brucite under concentrated CO_2 and simulated flue gas conditions, *Journal of CO_2 Utilization*, 37, 122-133 (2020).

28. Barcelo, L. Kline, J. Walenta, G. Gartner, E. Cement and carbon emissions. *Mater Struct*. **47**, 1055–1065 (2014).

29. CO_2 storage as carbonate minerals, IEA greenhouse gas R&D programme, Report Number PH3/17. **185** (2000).

30. Kelemen, P. B. Matter, J. In situ carbonation of peridotite for CO_2 storage. *Proceedings of the National Academy of Sciences*. **105**, 17295–17300 (2008).

Processing



Olivine $(Mg_{0.9}Fe_{0.1})_2SiO_4$

E_1

Olivine + HCl

$Mg(OH)_2$ Addition

NaOH Addition

$Cl_2 + H_2 \rightarrow HCl$

E_3

Electrolysis E_2

$Mg(OH)_2$

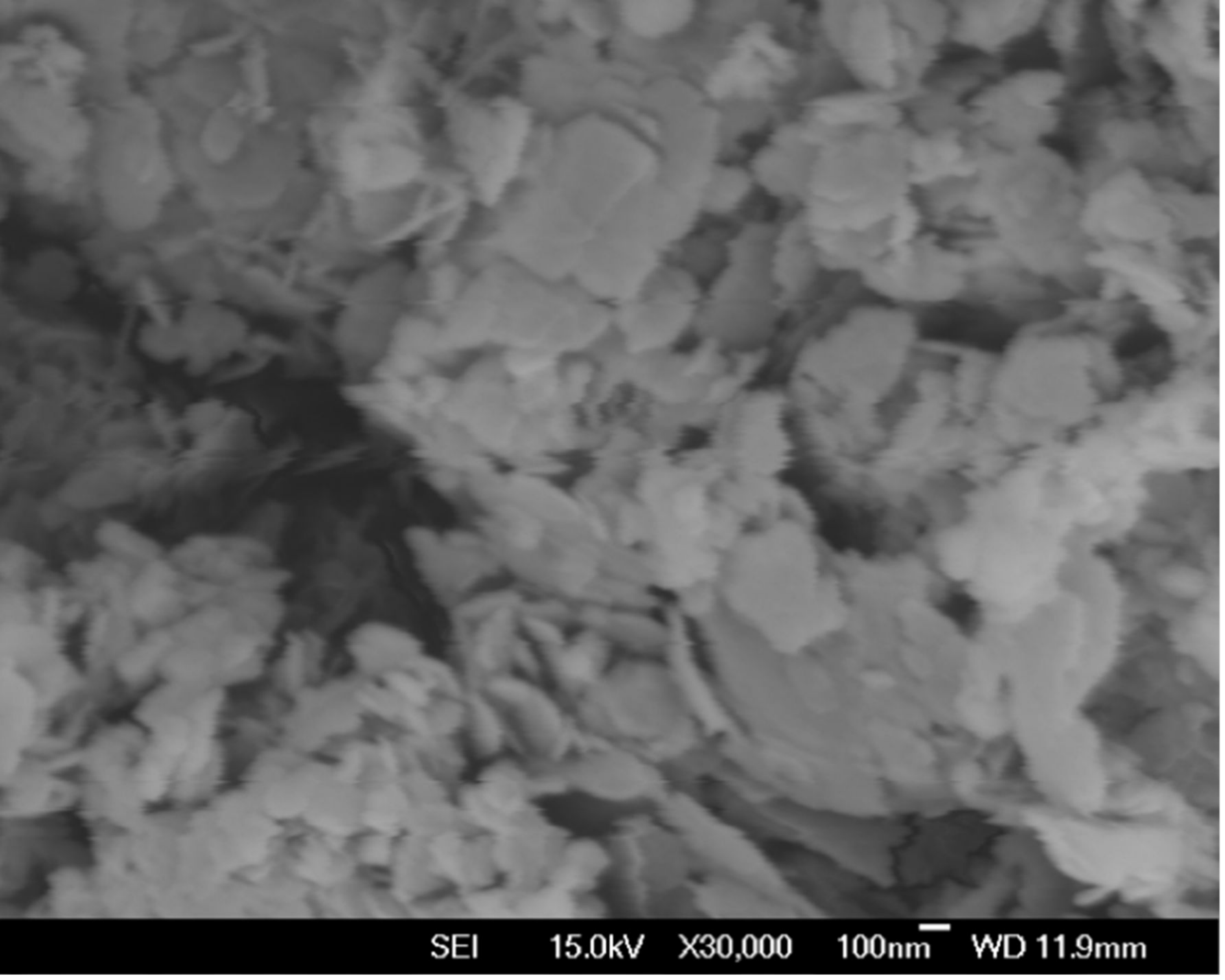
Silica Recovery

Fe Recovery

CO_2 Sequestration

$$Mg(OH)_2 + H_2O + CO_2 \longrightarrow \text{Carbonate}^* \ (MgCO_3)$$

For sequestering 1 tonne of CO_2, 1.3 tonnes of $Mg(OH)_2$ is required.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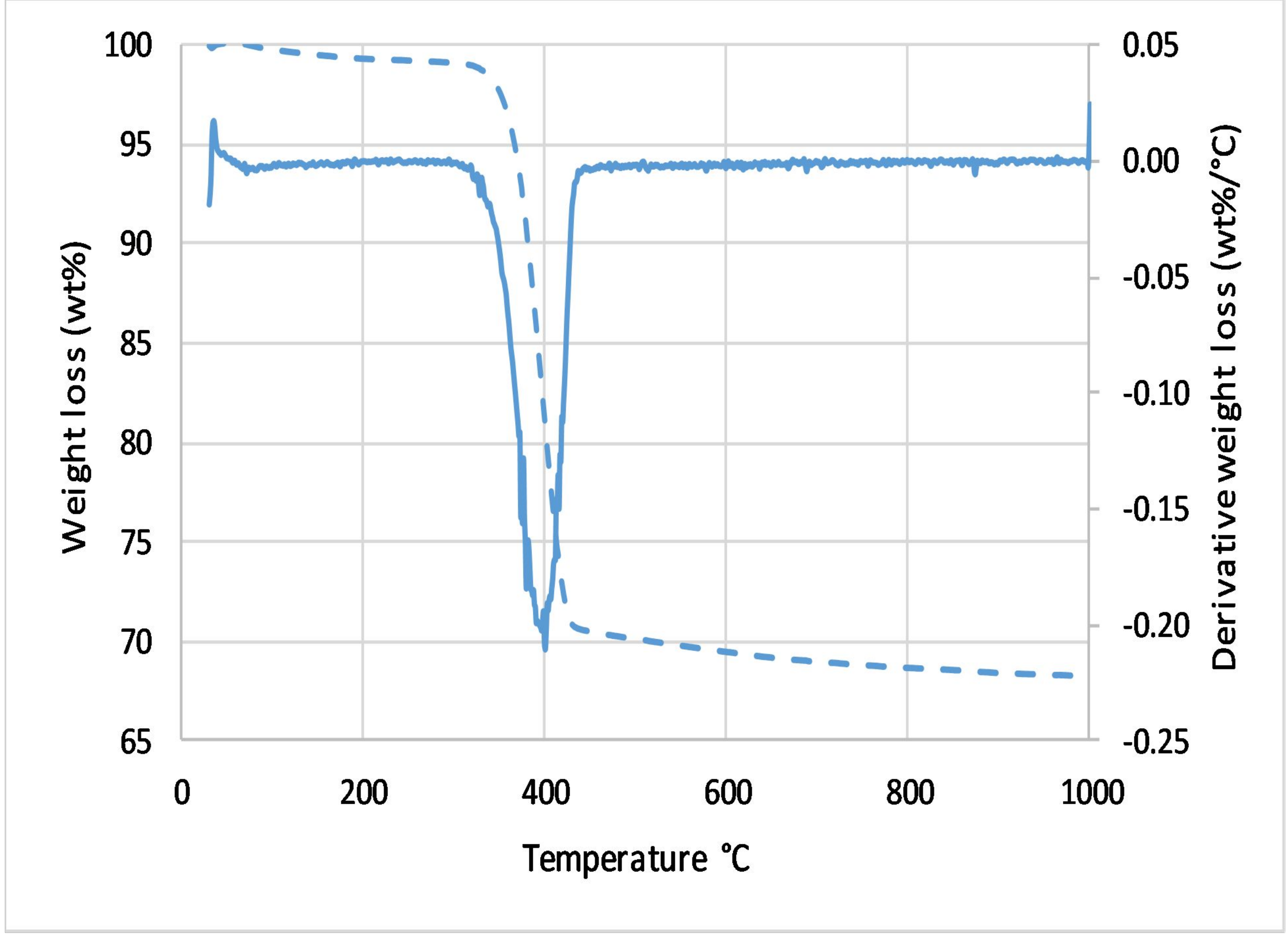
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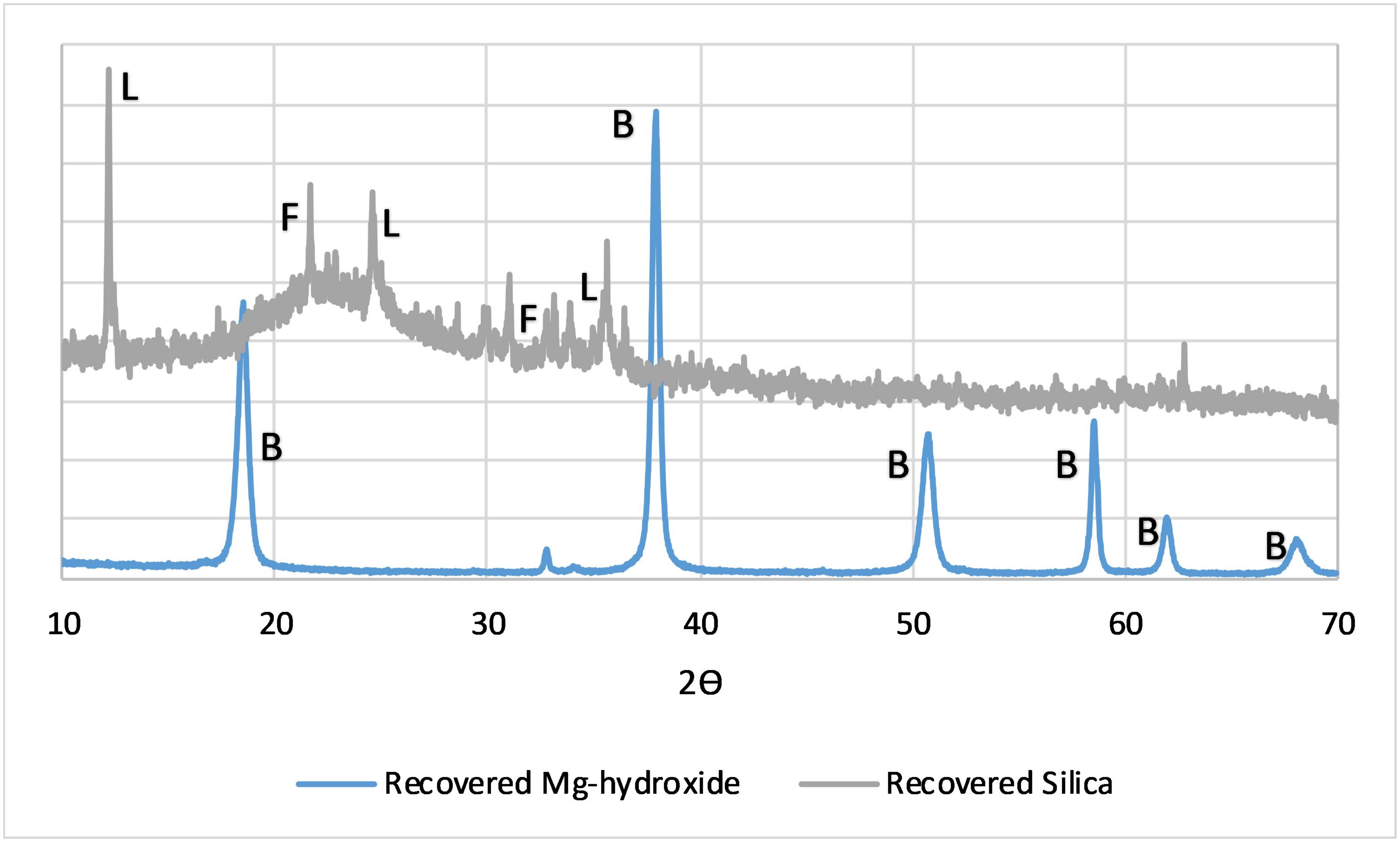
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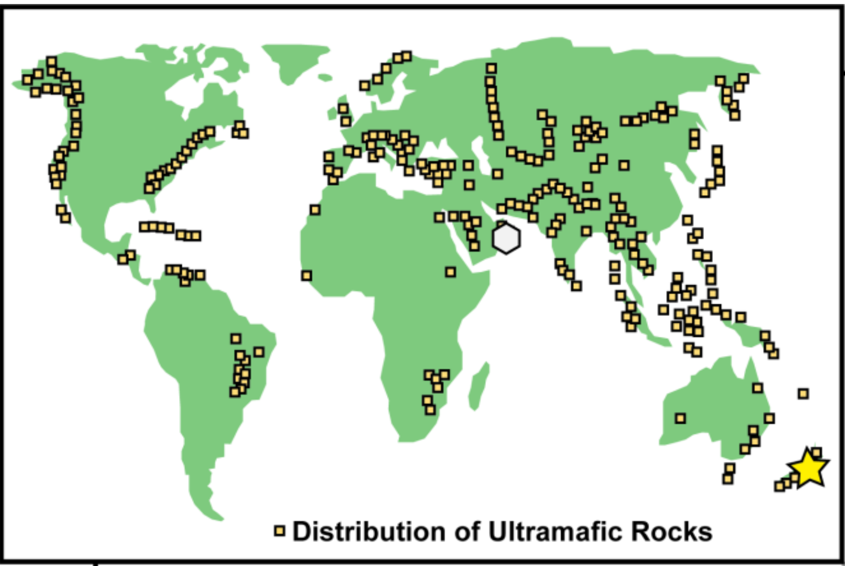
Recovered Silica

c)



Red Hills, New Zealand ☆

871 Billion Tonnes Olivine (Estimated)
(Assuming 60% Olivine)

Deposit Lifetime
6.6 years

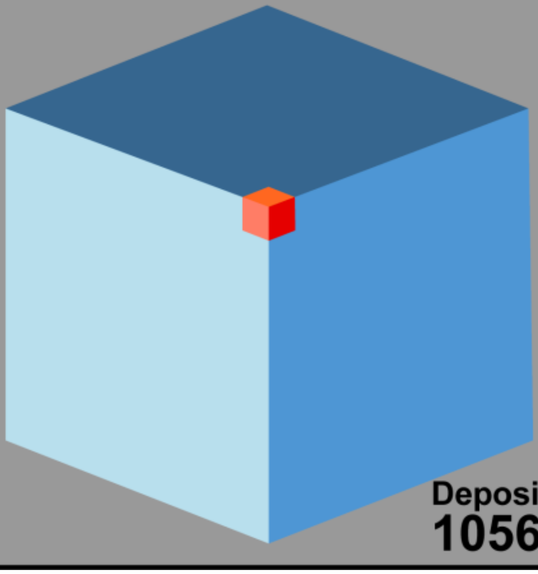
Billions of tonnes of olivine per year required to:

105	**Sequester All Anthropogenic CO_2**
+	
26	**Global Reduction of 10 Billion Tonnes CO_2**

131 Billion Tonnes

Semail Ophiolite, Oman ⬡

1.4×10^5 Billion Tonnes Olivine (Estimated)
(Assuming 60% Olivine)



Deposit Lifetime
1056 years

Table 1. Elemental compositions of raw olivine sand and recovered $Mg(OH)_2$ and silica from olivine, determined by XRF analysis.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI	Total
	--				Wt. %			------------------------------	
Raw olivine	39.6	0.38	10.7	0.73	45.0	0.14	0	3.2	100.0
$Mg(OH)_2$-olivine	0.1	0.11	6.4	0.30	60.4	0.03	<0.01	32.3	99.9
Silica-olivine	63.2	0.23	4.7	0.57	13.9	0.03	0.06	16.4	99.0