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Direct mineralization of atmospheric CO\(_2\) using natural rocks in Japan

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Abstract

Gas-solid mineralization of atmospheric CO\(_2\) using naturally abundant surface rocks under ambient conditions and without thermochemical treatment was analyzed for application in Japan. Based on an empirically-verified theoretical framework, a tiered greenhouse containing finely ground rocks was designed with low-speed induced airflow to realize CO\(_2\) mineralization reactions over 1 year. Negative CO\(_2\) emissions were calculated accounting for CO\(_2\) emissions from energy generation, materials production, and removal of vegetation and soil. Under practicable operating conditions, negative emissions using crystalline surface rocks in Japan can reach \(\sim 7.6 \text{ Gt-CO}_2/\text{y}\) achieved across 726 sites. The average energy requirement was calculated to be 1.5 GJ \(\text{t}^{-1}\text{CO}_2\) with an average land requirement of 1.1 km\(^2\) per Mt-CO\(_2\) annual removal capacity. Carbon debt is paid off after 60 d of operation.

1. Introduction

The need to deploy negative emission technologies (NETs) at the gigatonne per year scale to meet the Paris Climate Agreement is becoming unavoidable, with discussions moving to equity in deployment (Pozo et al 2020). Many NETs propose stabilizing CO\(_2\) using the calcium and magnesium content of the lithosphere (rocks). Such rock-based methods can be subdivided into those where reactions occur in the environment (‘dispersive’) and those that make use of reactors (‘centralized’). Dispersive methods leverage the large scale of the environment, and in some cases biological processes, to more easily reach megatonnes to gigatonnes of negative CO\(_2\) emissions (Minx et al 2018, Kelemen et al 2019). When occurring above ground, the Mg/Ca content is generally intermixed with the ecosystem, complicating verification of CO\(_2\) removal. Dispersive methods create additional concerns related to alteration of the biosphere and carbon cycles (Keller et al 2018). Carbon dioxide mineralization in geological reservoirs avoids the above issues but requires the capture of CO\(_2\), adding cost and complication. By using reactors, centralized methods avoid the issues associated with dispersive methods. However, the reactors often become the process bottleneck, leading centralized methods to typically utilize some combination of grinding, chemical additives, high temperatures, and elevated CO\(_2\) concentrations to accelerate reactions (Power et al 2013). Full life cycle assessments reveal centralized methods often become net CO\(_2\) emitters (Ncongwane et al 2018).

We propose a middle-ground solution: directly mineralize atmospheric CO\(_2\) via gas-solid reaction with finely ground rocks in a tiered greenhouse (direct air mineralization). Operating in a greenhouse prevents dispersion of Mg/Ca and simplifies quantification of net CO\(_2\) removal. The tiered structure increases the rock-air surface area for a given footprint, avoiding issues with insufficient air supply that have typically limited mineralization of atmospheric CO\(_2\) (Nowamooz et al 2018). High relative humidity, necessary for continuous CO\(_2\) mineralization (Mckelvy et al 2001, Smith et al 2014, Longo et al 2015), is passively maintained by trays of water-saturated salt in the greenhouse. As direct air mineralization occurs without additives—and at ambient temperature, pressure, and CO\(_2\) concentration—the energy and materials-related CO\(_2\) emissions that often hobble centralized methods are minimized. The carbonated powder can then be used in infrastructure and construction as a filler. Approaches utilizing similar principles are found in the literature but lack a detailed engineering design of equipment (e.g. Power et al 2020). Likewise, global-scale
potential of rock-based NETs is often reported (Strefter et al. 2018), but the lack of country-level detail provides little guidance to the governments and companies who could implement them.

We provide a general equipment design for direct air mineralization and examine its feasibility and applicability in Japan. We calculate the negative CO\textsubscript{2} emissions based on rock-dependent empirical CO\textsubscript{2} mineralization rates and include CO\textsubscript{2} emissions from materials production, energy generation, vegetation loss, and soil removal.

2. Methods

2.1. Gas-solid CO\textsubscript{2} mineralization

Gas-solid mineralization of CO\textsubscript{2} using minerals as a climate change mitigation strategy was first researched in detail in the mid 1990s (Lackner et al. 1995). The work failed to produce CO\textsubscript{2} mineralization in industrially relevant time scales due to the lack of humidity and a failure to appreciate the passivating nature of the product layer. Ion diffusion through the product layer, not gas phase diffusion or the mineralization reaction, is typically the rate-limiting step in engineered processes. Product layer passivation is conventionally modeled using the shrinking core model (SCM) per equation (1) (Yagi and Kunii 1955). The time \( t \) for a reaction to reach a depth \( d \) is a function of the density of Ca and Mg in the solid \( \rho_{\text{solid}} \) (moles/m\textsuperscript{3}-rock), the gas phase concentration of CO\textsubscript{2} \( C_{\text{gas}} \) (moles/m\textsuperscript{3}-gas), and the ion diffusivity through the product layer \( D \) (m\textsuperscript{2}/s).

\[
t = \frac{\rho_{\text{solid}} r^2}{6 D C_{\text{gas}}} \left\{ 1 - 3 \left( \frac{r-d}{r} \right)^2 + 2 \left( \frac{r-d}{r} \right)^3 \right\}
\] (1)

Equation (1) indicates the relative effectiveness of different methods to accelerate CO\textsubscript{2} mineralization. Increasing the CO\textsubscript{2} concentration from atmospheric to pure CO\textsubscript{2} at standard temperature and pressure accelerates mineralization by \( \sim 10^{34} \). Grinding from 10 mm to 10 \( \mu\text{m} \) accelerates mineralization by \( 10^6 \). In comparison, \( D \) varies by a factor of \( \sim 10^7 \) for relevant crystalline minerals (Myers et al. 2019). Additionally, the \( D \) for most amorphous compounds is \( \sim 10^{-3} \) times slower than compositionally equivalent crystalline minerals. Thus, rock selection is the critical step in achieving rapid gas-solid CO\textsubscript{2} mineralization. Further acceleration of CO\textsubscript{2} mineralization can be achieved simply and cheaply by grinding.

An additional consideration for direct air mineralization is the mixed nature of most rock formations. The bulk diffusivity \( D_{\text{bulk}} \) of rock can be calculated from the constituent mineral diffusivities \( D_i \) and volume concentrations \( \varphi_i \) by effective medium theory (EMT) as shown in equation (2).

\[
\sum_i \left[ \varphi_i \frac{D_i - D_{\text{bulk}}}{D_i + 2D_{\text{bulk}}} \right] = 0
\] (2)

However, EMT does not account for instances when reactive minerals are completely occluded by neighboring unreactive minerals (‘mineral locking’). Since mineral locking emerges from geometric relationships, it can be remedied by extensive grinding. Note that when particles are ground close to the internal crystal grain size, \( D_{\text{bulk}} \) reverts to \( D \). However, as particle diameters approach \( \sim 1 \mu\text{m} \), grinding tends to plastically disrupt the crystal structure producing amorphous minerals (Tromans and Meech 2001, Atashin et al. 2015). As amorphous compounds exhibit much lower diffusivity, such extensive grinding reduces the CO\textsubscript{2} mineralization rate.

2.1.1. Verification of SCR + EMT method

Gas-solid CO\textsubscript{2} mineralization is mechanistically equivalent for natural minerals and ‘artificial’ minerals arising from industrial processes. One such artificial mineral is the solid waste from steelmaking called ‘slag’. Slag is typically a mixture of calcium silicates and aluminates, with significant quantities of iron, manganese, and magnesium (Piatak et al. 2015). The mineralogy and crystallinity of slag varies based on composition and solidification conditions (Gautier et al. 2013). Due to slag’s substantial variability, it offers a stringent test of the predictive skill of SCM + EMT. The eight slags shown in table 1 were tested for CO\textsubscript{2} mineralization using the methods in Myers et al. 2019. Figures (a)–(h) demonstrate the accuracy of the SCR + EMT model across the different mineral ensembles, crystallinites, particle sizes, and CO\textsubscript{2} concentrations. As the model is based on empirically determined, mineral-specific \( D \), it can be applied to any mineral ensemble for which relevant data is available.

2.1.2. Direct air mineralization of natural rocks

Using SCM + EMT, the CO\textsubscript{2} mineralization rate of several crystalline compounds was modeled to highlight both general trends and the importance of rock selection. Note that these represent a small selection of compounds present in actual rock formations. In figure 2, minerals were assumed to be ground in a vertical roller mill such that small particles (diameter < 3 \( \mu\text{m} \)) are elutriated to limit amorphization (CMIC 2016). The particle size number distribution can be approximated by a lognormal distribution characterized by a mean and standard deviation of the ln of particle diameters of 0.35 \( \mu\text{m} \) and 0.66 \( \mu\text{m} \), respectively (Kolmogorov 1940). Operating conditions were set to 30 °C, a relative humidity of 90%, and 415 ppm CO\textsubscript{2} air. Figure 2 provides the predicted CO\textsubscript{2} mineralization extent over one year. The logic behind targeting the oxide/hydroxide content of mine tailings as suggested by Zarandi et al. 2017 is obvious from their rapid CO\textsubscript{2} mineralization rate. However, the scarcity of oxides/hydroxides means they are unable to provide the hundreds of gigatonnes of negative emissions required over the
21st century. Likewise, the rapid CO$_2$ mineralization displayed by calcium silicates supports the targeting of waste cement, ironmaking and steelmaking slag, and similar industrial wastes. However, the low natural abundance of calcium silicates limits their use for NETs. Also apparent from figure 2 is that the CO$_2$ mineralization rate of magnesium silicates and calcium aluminosilicates are significantly slower than that of oxides and calcium silicates. Figure 2 highlights that the specific mineral ensemble of a rock formation can dramatically alter not only its total CO$_2$ mineralization potential but also its CO$_2$ mineralization rate.

2.2. Equipment design and CO$_2$ emissions

The envisioned direct air mineralization system is shown in figure 3. It consists of a mining site and a 23 m-high, 1 km-long greenhouse whose width varies to accommodate the mine size. After clearing vegetation and removing soil, surface rocks are mined, transported, and finely ground. Field studies of mine tailings (Lechat et al 2016) and slag piles (Pullin et al 2019) show limited CO$_2$ mineralization over the course of years to decades. This relative lack of CO$_2$ mineralization is largely due to the pressure drop through the bulk solids impeding ingress of fresh air. To ensure adequate supply of CO$_2$, the direct air mineralization system uses a tiered geometry within the greenhouse to reduce the pressure drop. Additionally, fans provide a slightly negative pressure in the greenhouse to continuously draw in fresh air. A purpose-built solar photovoltaic system sits atop the greenhouse and is tied to a lithium ion battery storage system (PV + LiB) which provides the power for all activities in the direct air mineralization system. The amount of PV + LiB is based on operational energy consumption calculated in this section. Lifetime CO$_2$ intensity for purpose-built solar PV of 9.8 g-CO$_2$/kWh (Pehl et al 2017) and LiB of 61 Kg-CO$_2$/kWh of battery capacity with a 3,000 cycle lifetime (Emilsson and Dahllof 2019) were assumed. The negative CO$_2$ emissions for the direct air mineralization system is calculated per the logic in figure 4.

2.2.1. Energy for the extraction, handling, and grinding of rocks

The energy required for the extraction and handling of rock was set to 13.1 kWh t$^{-1}$-rock, based on average industry values for metals and minerals mining (CIPEC 2005, US DOE: Industrial Technologies Program 2007). As the current analysis covers many sites, industry averages were judged to be sufficiently accurate (i.e. site-specific analysis deemed unnecessary). Though extraction and handling equipment is traditionally fossil fuel powered, large scale battery-powered mining equipment is now commercially available. As such, this analysis assumes a fully electrified system. Rock handling after direct air mineralization is dependent on the final use case (e.g. filler in construction, refilling of mined site), and so was simply set equal to the initial handling energy.

The energy to finely grind rocks was calculated based on the quantity of newly generated surface

![Figure 1](image-url)
Figure 2. CO$_2$ mineralization extent over one year for various minerals ground to <3 µm at atmospheric CO$_2$ concentrations, 30 °C, and relative humidity of 90%.

### Table 1. Elemental composition, mineralogical composition, and crystallinity of slags used to test SCM + EMT method.

| Slag # | Slag 1 | Slag 2 | Slag 3 | Slag 4 | Slag 5 | Slag 6 | Slag 7 | Slag 8 |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| SiO$_2$ | 42.1%  | 13.4%  | 38.8%  | 26.6%  | 32.8%  | 18.1%  | 34.1%  | 35.4%  |
| CaO    | 22.5%  | 44.4%  | 24.7%  | 29.6%  | 24.4%  | 53.8%  | 38.8%  | 37.8%  |
| MgO    | 1.4%   | 2.6%   | 1.6%   | 1.7%   | 1.6%   | 4.4%   | 7.1%   | 6.6%   |
| FeO$^a$| 15.0%  | 29.0%  | 15.7%  | 26.4%  | 23.4%  | 15.2%  | 0.1%   | 0.3%   |
| MnO$^b$| 8.0%   | 3.6%   | 7.6%   | 7.3%   | 8.8%   | 2.6%   | 0.1%   | 0.2%   |
| Al$_2$O$_3$ | 5.9% | 2.6%   | 7.2%   | 4.0%   | 4.5%   | 2.1%   | 17.4%  | 16.4%  |
| Others$^c$ | 5.3%   | 4.5%   | 4.6%   | 4.4%   | 4.5%   | 3.7%   | 2.3%   | 3.3%   |
| Mineral composition | Ca$_2$SiO$_4$ | 5.7% | 23.4%  | 10.8%  | 19.4%  | 5.5%   | 24.5%  | —      | 33.2%  |
|       | Ca$_3$Al$_2$O$_6$ | —    | —      | —      | —      | —      | —      | —      | —      |
|       | CaSiO$_3$ | 24.9% | 3.9%   | 17.9%  | 20.0%  | 17.3%  | —      | —      | —      |
|       | MgSiO$_3$ | —    | —      | —      | —      | —      | 4.3%   | —      | —      |
|       | FeSiO$_3$ | 13.0% | —      | 0.7%   | 3.4%   | 9.7%   | —      | —      | —      |
|       | Fe$_2$SiO$_4$ | 3.3% | —      | 0.4%   | 1.9%   | 2.0%   | —      | —      | —      |
|       | Fe$_3$O$_4$ | 11.7% | 20.8%  | —      | 7.5%   | 7.8%   | 1.3%   | —      | 0.7%   |
|       | FeO      | —     | —      | —      | —      | 4.3%   | —      | —      | 37.0%  |
|       | SiO$_2$ | 12.3%  | —      | 12.8%  | 7.3%   | 9.5%   | —      | —      | —      |
|       | Ca$_{0.82}$Fe$_{0.18}$SiO$_2$ | 20.5% | —      | —      | —      | —      | —      | —      | —      |
|       | Fe$_2$O$_3$ | 0.4% | —      | 9.7%   | 6.2%   | 7.1%   | —      | —      | —      |
|       | Ca$_2$Fe$_2$O$_3$ | —    | 25.8%  | —      | 6.0%   | 5.3%   | 9.1%   | —      | —      |
|       | (CaFe)$_3$SiO$_3$ | —    | —      | 15.0%  | 10.3%  | —      | —      | —      | —      |
|       | CaO      | —     | 17.5%  | —      | 2.4%   | 12.5%  | —      | —      | 4.9%   |
|       | Ca(Fe/Mg)Si$_2$O$_6$ | —    | —      | 24.7%  | 5.4%   | 9.5%   | —      | —      | —      |
|       | Ca$_3$Si$_2$O$_7$ | —    | —      | —      | —      | 6.2%   | —      | —      | —      |
|       | CaFe$_2$Si$_2$O$_6$ | —    | —      | —      | —      | 9.7%   | —      | —      | —      |
|       | Ca$_3$Fe$_2$Si$_2$O$_12$ | —    | —      | —      | —      | 2.7%   | —      | —      | —      |
|       | Others$^d$ | 8.1%  | 8.5%   | 7.9%   | 9.9%   | 7.6%   | 30.4%  | —      | 18.2%  |
|       | Amorphous | 34.1% | 27.6%  | 23.3%  | 17.4%  | 16.0%  | 25.2%  | 100%   | 25.6%  |

$^a$all Fe converted to FeO  
$^b$all Mn converted to MnO  
$^c$including phosphates and sulfates  
$^d$including phosphates and sulfates

area, the mineral-dependent surface energy, and the grinding efficiency. The particle size distribution from section 2.1.2 and mineral-specific surface roughness were used to calculate the newly generated surface area ($\sim 3.6 \times 10^6$ m$^{-2}$). The mineral-dependent surface energy has previously been calculated from the mineral structure (Myers and Nakagaki 2018). Despite higher grinding efficiencies expected from the compression-based grinding used here, we conservatively set grinding efficiency to 1% (Tromans 2008).

2.2.2. Energy for fan operation

Fans were selected based on the necessary flowrate and resultant pressure drop in the greenhouse. The greenhouse consists of tiers of finely ground rock...
spread 3 mm deep with air gaps of 19 mm. While convective and diffusive mass transport of CO₂ applies to the air gap, CO₂ transport through the pore spaces between finely-ground rocks is limited to molecular diffusion. Effective molecular diffusion through the finely-ground rock layer, accounting for the details of the macroporous geometry, was calculated to ensure that CO₂ mineralization rate was not limited by CO₂ diffusion (Gaiselmann et al. 2014).

The mineralization of CO₂ reduces its gas phase concentration, thereby slowing the mineralization rate. Increasing the flowrate stabilizes the gas phase CO₂ concentration and the overall reaction time trends towards the SCM + EMT prediction. However, higher velocities also increase the pressure drop, energetic penalties, and risk of entraining ground rock. The air flowrate was based on optimizing against these competing influences. The tiered geometry and low flow velocity produce a laminar flow. Pressure drop through the greenhouse was calculated based on the Darcy–Weisbach equation with pressure drop from expansion and contraction zones calculated based on ventilation industry standards (ASHRAE 2001).

A radial type fan was selected using the Cordier diagram based on the dimensionless specific speed \(N_s = 0.9\) and dimensionless specific diameter \(D_s = 1.8\) (Wright 1999). Even with the tiered design, the greenhouse induces a large pressure drop, meaning a radial-type fan is preferable over the axial-type fans seen in many direct air capture systems. A backward inclined centrifugal fan with a \(\sim 0.56\) m diameter impeller, powered by a 14.9 kW motor was selected from commercially available models. The number of fans required depends of the site-specific greenhouse size.

### 2.2.3. Materials production

The CO₂ emissions related to the manufacture of materials used to construct the greenhouse, fans, grinding equipment, and mining equipment was based on recent material-specific data (Bousted 2005, Olivier et al. 2017, Zheng and Suh 2019). Material requirements for the greenhouse foundation and structure were based on standard practices (Salazar and Rios 2010). The greenhouse sits atop a concrete pad and is constructed from square steel piping with a 1 cm thick polycarbonate skin to withstand the frequent typhoons in Japan. Internal tiers are made of woven, high density polyethylene (HDPE) sheets pulled taut. The polycarbonate skin and HDPE sheets were assumed to be replaced every 25 years and 10 years, respectively. Though mineralization of CO₂ with the clinker content of the concrete pad is expected, it was not included in the analysis to provide a conservative estimate.

The mass of centrifugal fans and motors was provided by vendors. Fans and motors were assumed to be replaced every 10 years. The material requirements for grinding equipment was based on vertical roller mills used in the cement industry with the internals replaced every 10 years. Materials requirements for rock mining and transportation equipment was modeled on commercially available electric
excavators and haulers with an assumed service life of 5 years. The size and number of excavation, transport, and grinding equipment was based on the assumption of continuous operation.

2.2.4. Biological emissions and losses
The carbon content of vegetation and soil removed to access rocks was estimated from Japan-specific analyses of organic carbon content and converted completely to CO$_2$ (Morisada et al. 2004, Sasaki and Kim 2009, Takahashi et al. 2010). The depth of soil was based on site-specific information (Pelletier et al. 2016). In addition to the one-time loss of carbon due to excavation, there is an annual loss in CO$_2$ removal capacity from the destroyed vegetation. For the land occupied by the greenhouse, there is the one-time emission from vegetation removal and the annual loss of productive capacity. The effect of re-wilding after the closure of the mine site and greenhouse were not included due to the high uncertainty in the recovery of natural environments (Poorter et al. 2016).

2.3. Quantity and geological distribution of CO$_2$-mineralizing rocks in Japan
The CO$_2$ mineralization potential of surface rocks in Japan was determined by reviewing geological maps that segregate Japan into 157,915 discrete regions of 127 surface rock types (Geological Survey of Japan/AIST 2020). Rock types lacking large quantities of Mg or Ca were removed. The original maps and literature were then used to manually set the ensemble of mineral compounds and the formation depth of the remaining locations. Areas containing pyrite were removed to avoid potential sulfuric acid dissolution of innate carbonates (Ross et al. 2018). Densely populated areas were excluded to avoid public backlash (MLIT 2015). National parks and other areas protected under Japanese law from the erection of structures were removed from consideration (MOE Ministry of the Environment 2009). Areas less than 1 km$^2$ in footprint were also removed from consideration due the increased potential for mining large quantities of gangue. Topography was not used to exclude sites from analysis.

3. Results

3.1. CO$_2$ mineralization potential in Japan
All sites with potentially suitable rocks are mapped in figure 5 (i.e. prior to exclusion of populated and protected areas) with quantitative data in table 2. As rocks are at the surface, the CO$_2$ mineralization potential is defined as a function of the depth of mining per year over the entire site: Gt-CO$_2$/(m $\times$ y). At a mining rate of 1 m $\gamma^{-1}$, the CO$_2$ mineralization potential of rock type and site footprint are provided in figure 6 (note that the greenhouses designed in this study can accommodate a mining depth of 2 m/y). Very large sites are primarily volcanic and pyroclastic in origin. These rocks are more likely to have considerable amorphous content, and thus, slower gas-solid CO$_2$ mineralization rates. Figure 6(b) removes rocks of volcanic and pyroclastic origin.

Consistent with global analyses, the total potential CO$_2$ mineralization of surface rocks in Japan (17,069 Gt-CO$_2$) vastly exceeds NETs requirements regardless of long-term climate change mitigation goals. Surprisingly, excluding densely populated and legally protected areas only reduces the CO$_2$ mineralization potential by ∼9% (15,609 Gt-CO$_2$). Unsurprisingly for Japan, volcanic and pyroclastic rocks dominate the total CO$_2$ mineralization potential (∼90%). As such, the practical CO$_2$ mineralization potential of surface rocks in Japan hinges on the amorphous content of these rocks. Even so, focusing only on crystalline rocks in non-protected, sparsely populated areas still yields a CO$_2$ mineralization potential for Japanese surface rocks of 1525 Gt-CO$_2$.

3.2. Negative emissions in Japan via direct air mineralization
Direct air mineralization applied to crystalline surface rocks in sparsely populated, un-protected areas in Japan yields an average and median net CO$_2$ removal efficiency of 59.8% and 65.0%, respectively. Figure 7 shows that the low efficiency is due almost entirely to incomplete mineralization of rock after 1 year. Since the CO$_2$ mineralization rate is controlled by the mineral-specific diffusivity, significant improvements are unlikely. After rocks are removed from the greenhouse, CO$_2$ mineralization may continue; however, the lack of a controlled gas-solid geometry and humidity will drastically reduce mineralization rates.

Carbon dioxide emissions from operations and materials manufacture reduces the net CO$_2$ removal by ∼1.6%, the bulk of which is attributable to the energy for extraction, movement, and fine grinding of rock. The average and median energy consumption are 1.51 and 1.45 GJ t$^{-1}$-CO$_2$, respectively. This is substantially less than the ∼4.7–10 GJ t$^{-1}$-CO$_2$ of direct air capture and storage methods (Creutzig et al. 2019). Based on current PV power output applied in Japan (GSA 2020), PV panels mounted to the greenhouse roof would supply an average of ∼1.7 times more energy than needed for operations. Higher efficiency PV + LiB with lower CO$_2$ footprints are likely in the coming years, only increasing the system performance. More efficient fine grinding systems are theoretically possible, but unlikely given the mature nature of the mining industry.

Emissions from removal of vegetation and soil reduce the net CO$_2$ removal efficiency by only ∼0.34% thanks to the small footprint of the direct air mineralization system. The average and median land requirements are 1.13 km$^2$ and 1.08 km$^2$ per Mt-CO$_2$ removed per year, roughly equivalent to direct air capture and storage methods. This area is equally split between the mining site and greenhouse. The
average payback period of the combined carbon debt from all sources is 60 days.

In increasing order of size, with a mining depth of 2 m y$^{-1}$, yields the net CO$_2$ emissions in Japan as shown in figure 8 (averaged over 50 years of operation). Maximum negative emissions are $\sim$ 7.6 Gt-CO$_2$/y. For allocation of negative emissions quotas to Japan, we use the multi-criteria approach of Pozo et al. 2020 to set a lower bound of 11.5 Gt-CO$_2$ by 2100. We set the upper bound to 98.9 Gt-CO$_2$ by 2100, equal to all emissions from 1850 to 2100 assuming emissions reductions inline with Japan’s mid-century strategy and assuming linear reductions thereafter to a net zero CO$_2$ society (Government of Japan 2019). This upper bound represents an aspiration to return to the pre-industrial revolution climate. Meeting these negative emissions targets by 2100 requires 0.144–1.236 Gt-CO$_2$/y of negative emissions if started in 2021. This would require $\sim$80–619 km$^2$ spread across 74–393 sites.

3.3. Utilization of carbonated rock powder

The mass of carbonated rock powder produced by direct air mineralization as a function of negative emissions is shown in figure 9(a). This rock powder is similar in size to clays often used in mechanically stabilized earth construction, backfill, and general infrastructure projects. Recent regulations (ASTM A1115/A1115M-19 2019) support such earth-based construction methods in accordance with the United Nations Sustainable Development Goal 12. Japan has a long history of large-scale land reclamation projects using rocks. For example, the building of artificial islands in Osaka Bay from rocks obtained by nearby mountains utilized $\sim$263 million m$^3$ of fill material to create 15.59 km$^2$ of land from 1953–1981 (Tanaka et al 1983). Figure 9(b) shows the potential for land reclamation using carbonated rock powder. Other potential usage pathways include breakwaters, seawalls, foundations for buildings and roadways, and filler in concrete.

4. Discussion

Using direct air mineralization, Japan could unilaterally remove gigatones of CO$_2$ annually. This suggests that expert reviews merit upward revision for the potential scale of rock-based NETs (Smith et al. 2015, Fuss et al. 2018). Such reviews have rightly highlighted the unknown biogeochemical feedbacks and difficulties of verifying rock-based methods deployed at the gigatonne scale. Direct air mineralization overcomes these valid concerns by separating CO$_2$ mineralization from the soil and hydrological systems. Further, we have demonstrated the ability to accurately predict gas-solid CO$_2$ mineralization for heterogeneous mineral ensembles at different particle sizes and CO$_2$ concentrations using SCM + EMT. It is worth highlighting that direct air mineralization is a coupling of TRL 9 technologies. Greenhouses with footprints >1 km$^2$ exist in the produce industry (e.g. Thanet Earth in the UK) and effectively much larger scales are seen by co-located greenhouses (e.g. in the Almeria region of Spain). Extraction, handling, and grinding of rocks at scales $\sim$10 times larger than assumed in this paper are commonplace (Crowson 2003). Induced draft centrifugal fans are amongst the most ubiquitous technologies in industry. Battery-powered mining equipment is already being sold by major manufacturers. Purpose-built PV + LiB systems of the size necessary for direct air mineralization are not only available, their costs continue to drop (Lazard 2019). As no technological breakthroughs are needed, and direct air mineralization operates equivalently at the kg-CO$_2$ and Gt-CO$_2$ scales, it can be rapidly scaled-out and scaled-up.

While net negative emissions of $\sim$7.6 Gt-CO$_2$/y do not rise to that required to likely stay below 2 $^\circ$C, much less 1.5 $^\circ$C in 2100, Japan accounts for only $\sim$0.24% of the world’s sovereign land. Concurrent adoption of direct air mineralization by countries with suitable surface rocks would likely provide sufficient negative emissions to meet Paris ambitions.

### Table 2. CO$_2$ mineralization potential of surface rocks in Japan.

| Classification | Total area (km$^2$) $^a$ | Number of sites $^a$ | Potential w/ depth (Gt-CO$_2$/m) $^a$ | Total potential (Gt-CO$_2$) $^{a,b}$ |
|----------------|-------------------------|----------------------|-----------------------------------|-----------------------------------|
| AMV            | 836                     | 124                  | 1.272                             | 64                                |
| Diorite        | 47                      | 5                    | 0.052                             | 26                                |
| Gabbro         | 761                     | 127                  | 1.082                             | 271                               |
| Mafic Gneiss   | 118                     | 29                   | 0.196                             | 98                                |
| Mafic Plutonic | 1304                    | 253                  | 1.831                             | 458                               |
| Mafic Schist   | 635                     | 102                  | 0.945                             | 189                               |
| Mafic Volcanic | 610                     | 103                  | 0.787                             | 197                               |
| n-AMV          | 35 626                  | 2547                 | 54.703                            | 13 676                            |
| n-APF          | 1760                    | 127                  | 2.636                             | 132                               |
| Ultramafic     | 1402                    | 210                  | 2.410                             | 482                               |
| Total          | 43 100 (47 191)$^c$     | 3627 (3827)$^c$      | 65.914 (72.175)$^c$              | 15 591 (17 069)$^c$               |

$^a$excluding densely populated areas, protected zones, and sites with area <1 km$^2$

$^b$based on minimum reported thickness

$^c$including densely populated areas and protected zones. AMV: alkaline mafic volcanic; n-AMV: non-alkaline mafic volcanic; n-APF: non-alkaline pyroclastic flow
Japan can meet its negative emissions quota put forward by Pozo et al. 2020 of 11.5 Gt-CO$_2$ using an area 79.6 km$^2$, or about 1.35 Manhattan’s. Assuming Japan meets its current emissions reduction pledge, it could compensate for all of its historical emissions to 2100 ($\sim$98.9 Gt-CO$_2$) by applying direct air mineralization to an area of $\sim$619 km$^2$. For perspective, this is less than 1% of Japan’s land area and roughly the size of St. Lucia, Liechtenstein and Andorra combined, or Singapore.

With an abundance of potential sites for direct air mineralization, a key question becomes ‘which sites are most promising?’ This question can be interpreted in terms of technical feasibility, social acceptance, and co-benefits. To determine technical feasibility, the most critical aspect is the specific mineral ensemble of a site. While detailed geological maps were used in the current study, the inherent variability in rock formations means that detailed field studies of the mineral composition...
and formation depth of prospective sites should be performed. Assuming viable rocks are available, technical aspects such as topology, accessibility via extant roads, and availability of a local workforce become important when selecting a site. Many of these technical issues bleed over into social acceptance and co-benefits. The direct air mineralization system requires decades of full-time employment of the mining operations, greenhouse, and transport of carbonated rocks to the usage site. For rural areas with depressed economies, or traditional mining economies undergoing transition (e.g. coal), the direct air mineralization system may offer long-term employment in the ‘green economy’. The acute losses to local vegetation means that areas that have already been altered for other purposes (e.g. monoculture forestry, farming) are preferable to mature, biodiverse sites. In terms of co-benefits, sites located near
large infrastructure projects (e.g. land reclamation, sea walls) are favored as they provide a re-use pathway for the carbonated rock while also reducing the aggregate mining required for the infrastructure project.

In contrast to other NETs methods, the direct air mineralization produces a stable, concentrated form of CO\textsubscript{2}, which can be held in the hand. While this makes CO\textsubscript{2} accounting simple and assuages many public perception issues, it also raises the question of ‘what to do with the material?’. Our initial analysis suggests that the quantity of material is within the realm of experience of Japanese land reclamation projects. Pelletization and aggregation of carbonated powder into larger solids would further expand its usage pathways. Actual adoption will of course require study of the behavior of the carbonated rock in such applications and proper regulatory scrutiny. However, such increased circularity is a desirable and required trait of the global society in the 21st century.

5. Conclusion

Gas-solid CO\textsubscript{2} mineralization of mixed-composition rocks was found to be accurately modeled by the SCM supplemented with EMT. It was determined that rock type and crystallinity are the strongest controls over the CO\textsubscript{2} mineralization rate. Moreover, acceleration of CO\textsubscript{2} mineralization is best achieved by grinding, though grinding to sub micrometer levels reduces CO\textsubscript{2} mineralization through amorphization of the crystal structure. Based on an analysis of geological maps, the maximum potential of surface rocks in Japan to mineralize CO\textsubscript{2} was found to be 17 069 Gt-CO\textsubscript{2}. Exclusion of natural parks protected by Japanese law and densely populated areas reduced the potential to 15 591 Gt-CO\textsubscript{2}. Removal of volcanic and pyroclastic rocks—due to high amorphous content—results in a CO\textsubscript{2} mineralization potential of 1525 Gt-CO\textsubscript{2} spread across 726 sites.

A direct air mineralization system was designed to realize gas-solid CO\textsubscript{2} mineralization at ambient temperatures and CO\textsubscript{2} concentrations without the use of chemical additives. Mined surface rocks are finely ground and thinly spread on tiers within a high humidity greenhouse. Fresh air is continually supplied by induced flow centrifugal fans. Rocks are left in the greenhouse for 1 year for CO\textsubscript{2} mineralization to proceed. Site-specific net CO\textsubscript{2} emissions were calculated, accounting for CO\textsubscript{2} mineralization extent, CO\textsubscript{2} emissions from energy production, CO\textsubscript{2} emissions from materials manufacture, and carbon lost from soils and vegetation removal. Based on reasonable engineering assumptions, the negative CO\textsubscript{2} emissions potential for direct air mineralization in Japan is ∼7.6 Gt-CO\textsubscript{2}/y. The average energy consumption is 1.5 GJ t\textsuperscript{-1}-CO\textsubscript{2}. The average land requirement is 1.1 km\textsuperscript{2} per Mt-CO\textsubscript{2} annual removal capacity. On average, carbon debt is paid off with 60 d of operation.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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