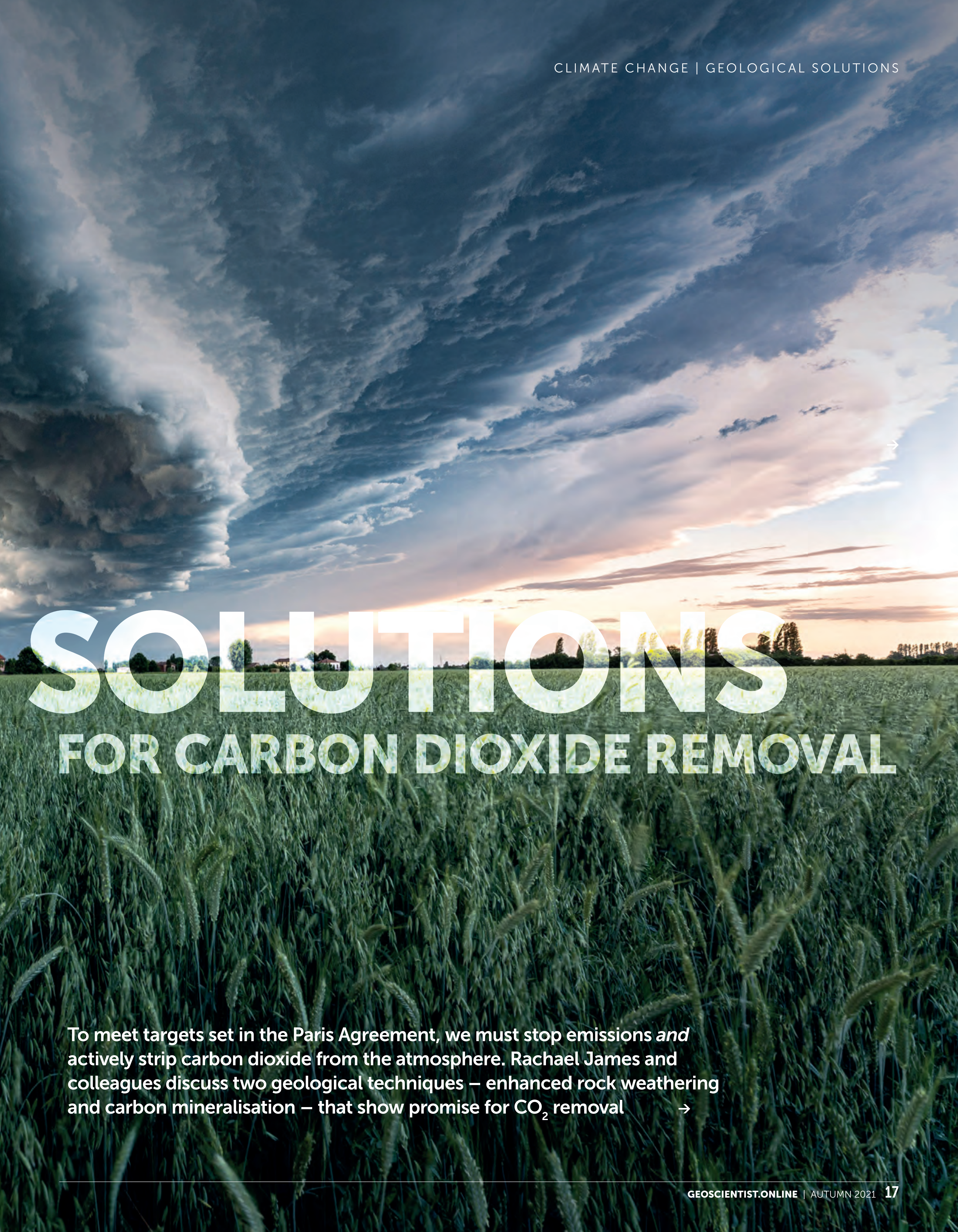
GEOLOGICAL

Agricultural soil can be amended to increase rock weathering rates, which helps to remove CO_2



SOLUTIONS FOR CARBON DIOXIDE REMOVAL

To meet targets set in the Paris Agreement, we must stop emissions *and* actively strip carbon dioxide from the atmosphere. Rachael James and colleagues discuss two geological techniques – enhanced rock weathering and carbon mineralisation – that show promise for CO_2 removal →

WHILE SIGNIFICANT reductions in greenhouse gas emissions are essential for managing the climate crisis, it is now recognised that the Paris Agreement goal of limiting the increase in global temperature to less than 2°C above pre-industrial levels cannot be achieved without active removal of carbon dioxide (CO_2) from the atmosphere. This is because between about 4% and 8% of global CO_2 emissions are "hard to avoid", either because some industries are difficult to decarbonise (such as agriculture), or because of the need to uphold principles of social justice. To reach net zero, these hard-to-avoid emissions must be offset (*Fig. 1*).

Modelling studies indicate that of the order of 5-20 $GtCO_2e$ (CO_2 equivalent, i.e., the mass of all greenhouse gases converted to the equivalent mass of CO_2 that would have the same global warming effect) will need to be removed from the atmosphere each year by the end of the century. This represents a significant challenge – 1 Gt of CO_2 is equivalent to the total annual emissions from all cars and vans in the USA (~250 million vehicles), or the amount taken up each year by ~50 billion trees.

Carbon dioxide can be removed from the atmosphere in various ways. Approaches include 'natural' methods, such as planting trees, improving crop and soil management, and restoring coastal habitats, such as mangroves and seagrass beds. Technological methods include direct air capture, whereby CO_2 is stripped from the atmosphere by sorbents, and subsequently released for safe storage or utilisation. Somewhere in between are methods that involve the technological enhancement of natural processes. These include enhanced rock weathering and carbon mineralisation – and this is where geology can play a key role in addressing the climate emergency.

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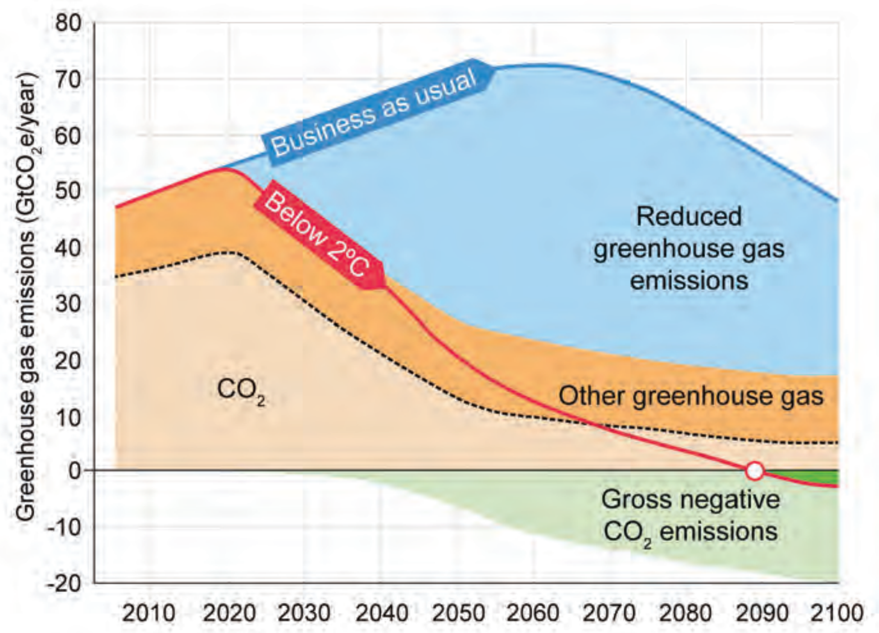


Figure 1: Predicted emissions and removals of greenhouse gases. To meet the 2°C goals of the Paris Agreement, significant reductions in emissions (blue) are required, as well as active removal (green) to offset emissions that are "hard to avoid" (orange). Figure adapted from The Royal Society (2018) Greenhouse Gas Removal (CC BY 4.0) and based on data from the United Nations Environment Programme (2018) The Emissions Gap Report 2018.

Geological processes and CO_2

Weathering is a natural geological process whereby atmospheric CO_2 dissolved in rainwater attacks rocks and soils, partly dissolving them (*Eq. 1* and *Eq. 2*). The CO_2 is converted into hydrogen carbonate ions (alkalinity) that are eventually captured in the ocean where they are securely stored for more than 100,000 years. Some of the hydrogen carbonate ions may, under some circumstances, precipitate as carbonate minerals (carbon mineralisation) that are stable on timescales of more than 10,000 years (*Eq. 3*).

"Weathering rates are controlled by environmental factors – principally water availability and temperature, as well as the properties of the rocks or soils themselves"

E1

$$\underbrace{CaSiO_3}_{\text{silicate rock}} + \underbrace{2CO_2 + 3H_2O}_{\text{rainwater}} \rightarrow \underbrace{Ca^{2+} + 2HCO_3^-}_{\text{soil water}} + \underbrace{H_4SiO_4}_{\text{plants/soils}}$$

Equation 1: Weathering (dissolution) of silicate rock

E2

$$\underbrace{CaCO_3}_{\text{carbonate rock}} + \underbrace{CO_2 + H_2O}_{\text{rainwater}} \rightarrow \underbrace{Ca^{2+} + 2HCO_3^-}_{\text{soil water}}$$

Equation 2: Weathering (dissolution) of carbonate rock

E3

$$\underbrace{Ca^{2+} + 2HCO_3^-}_{\text{From Eq 1 or 2}} \rightarrow \underbrace{CaCO_3}_{\text{soil}} + \underbrace{CO_2 + H_2O}_{\text{soil water}}$$

Equation 3: Carbonate precipitation (carbon mineralisation)

Note, however, that during precipitation of carbonates, half of the CO_2 captured by silicate minerals and all of the CO_2 captured by carbonate minerals is re-released back into the atmosphere (*Eq. 3*). Thus, carbon mineralisation of silicates is half as effective as mineral dissolution (weathering) for CO_2 removal, and dissolution and reprecipitation of carbonate minerals has no net impact on levels of atmospheric CO_2.

On a global scale, weathering removes about 1 Gt of CO_2 every year and plays a key role in the long-term regulation of Earth's climate. However, natural weathering and carbon mineralisation take time. To remove significant volumes of CO_2 from the atmosphere by the end of the century, geologists are investigating ways to speed up these processes.

Enhanced rock weathering

Weathering rates are controlled by environmental factors – principally water availability and temperature, as well as the properties of the rocks or soils themselves, such as mineralogy, grain size, porosity and permeability. Enhanced rock weathering is a CO_2-removal strategy that amends agricultural soils with crushed calcium- and magnesium-rich silicate rocks and harnesses the photosynthetic energy of the crops to increase weathering rates.

Modelling studies: Initial model simulations of enhanced rock weathering (Taylor et al., 2016) indicated that application of 1–5 kg m^2 per year of pulverised silicate rock (basalt and harzburgite) to all of the agricultural land located within 30° of the equator (~20 x 10^6 km^2) could lower levels of atmospheric CO_2 by between 30 and 300 ppm (depending on rock type and application rate) by the end of the century (*Fig. 2*). The model simulations also showed that enhanced rock weathering could increase delivery of alkalinity to the oceans to an extent sufficient to mitigate the effects of ocean acidification caused by uptake of anthropogenic CO_2.

A more recent study (Beerling et al., 2020) made a quantitative techno-economic assessment of the CO_2-removal capacity and costs for implementing enhanced rock weathering, constrained by the available agricultural land area and energy production. The model results showed that roll-out of enhanced rock weathering to between 10% and 50% of available agricultural land area in the world's major economies, even taking into account emissions associated with crushing and transporting the pulverised rock, could contribute to the removal of between 0.5–2 Gt of CO_2 per year. This would equate to between 2.5% and →

Figure 2: Modelled simulations of the effects of application of pulverised basalt or harzburgite to agricultural land on (a) levels of atmospheric CO_2 and (b) ocean surface pH. Projected atmospheric CO_2 concentrations are "business as usual" (RCP8.5); blue line shows RCP8.5 projection of atmospheric CO_2 without enhanced rock weathering. Adapted from Taylor et al. (2016) Nat. Clim. Chang. 6, 402–406, doi: 10.1038/nclimate2882

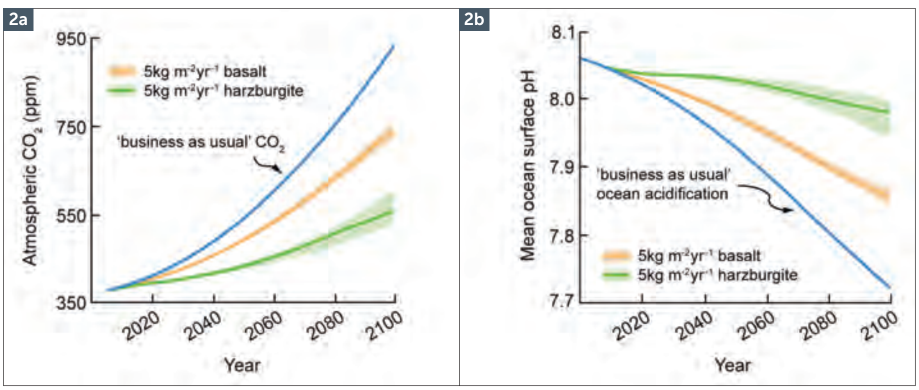


Image credit: Ilsa Kantola, University of Illinois

Figure 3: Application of pulverised silicate rock to a field site in Illinois, USA.

40% of the amount required by 2100 to meet the Paris Agreement target, similar to quantities estimated for other CO_2-removal strategies, including bio-energy with carbon capture and storage, and direct air capture (Fuss et al., 2018).

Field studies: Before wide deployment, we need to confirm the efficacy of enhanced rock weathering as a CO_2-removal strategy using large-scale field trials on a wide range of agricultural soils and crop types, under different climatic regimes. The net amount of CO_2 removal will be reduced if pulverised rock is transported over long distances, so tests must also be undertaken using a variety of rock types, including those that may have lower-than-ideal CO_2-removal potential (*Fig. 5*). Moreover, we must develop methodologies for full greenhouse-gas budgeting, monitoring of crop and soil health, and robust, repeatable and relevant measurements for verifying CO_2 removal and security.

In support of this, the Leverhulme Centre for Climate Change Mitigation (www.lc3m.org) is conducting multi-year field trials of enhanced rock weathering in the UK, Malaysia, Australia and the US (*Fig. 3*). Crop types include maize (corn), miscanthus (a bioenergy crop), sugarbeet, sugarcane, oil palm, barley and peas, and soil type varies from slightly acidic (pH ~6) to basic (pH ~8). Pulverised rock was obtained from as close to the field sites as possible, and primarily consists of waste material from road aggregate mining – these wastes are too fine to be used for road building, so they are stockpiled at the mine sites.

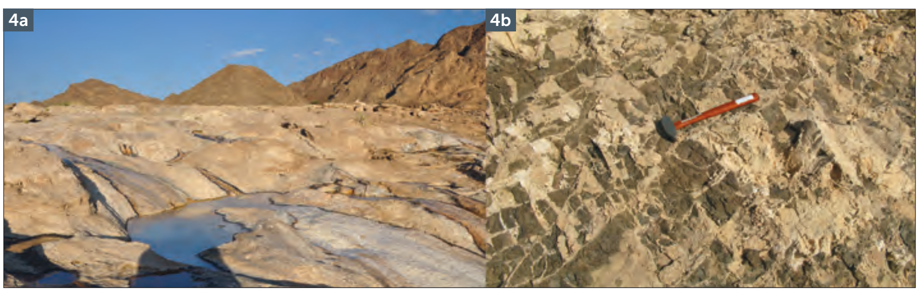
The waste materials are silicate-rich and range in composition from relatively unweathered basalt to metabasalt. The trials are only in their early stages, but preliminary results indicate that dissolution products from weathering of the applied rock can be detected in soil waters within a few weeks of application, with higher soilwater alkalinity in plots amended with pulverised rock relative to control plots (that have not been amended with pulverised rock). The soil, soil waters and crops are also being monitored for heavy metal concentrations (such as arsenic, lead and chromium) to ensure the safety of enhanced rock weathering; no significant differences have been observed between any of the rock-amended and control plots to date.

Carbon mineralisation

Calcium, magnesium and hydrogen carbonate ions produced by weathering of silicate minerals (*Eq. 1*) can subsequently precipitate as carbonate minerals (*Eq. 3*). This process occurs naturally during weathering of ultramafic to mafic rocks, such as mantle peridotites and basalts. Peridotites undergo hydration (serpentinisation) and carbonation reactions at geologically relatively rapid rates at low temperature, as evidenced in the Oman ophiolite (*Fig. 4*). Mafic and ultramafic rocks have the potential to store tens of gigatonnes of CO_2 at the global scale (both onshore and offshore), but, in reality, the overall degree of carbonation also depends on the availability of CO_2 and the chemical conditions, such as pH, salinity, temperature, and pressure, as well as on the permeability of the storage formation.

Engineered carbon mineralisation is essential for effective CO_2 removal. It can be accomplished by (1) ex-situ mineralisation, whereby calcium- and/or magnesium-rich silicate minerals

Figure 4: Carbon mineralisation of peridotites via CO_2-water-rock reactions in the Oman ophiolite from (a) travertine terraces on the surface and (b) carbonate filled veins in fractures in the subsurface. (Image credit: Juerg Matter, University of Southampton)



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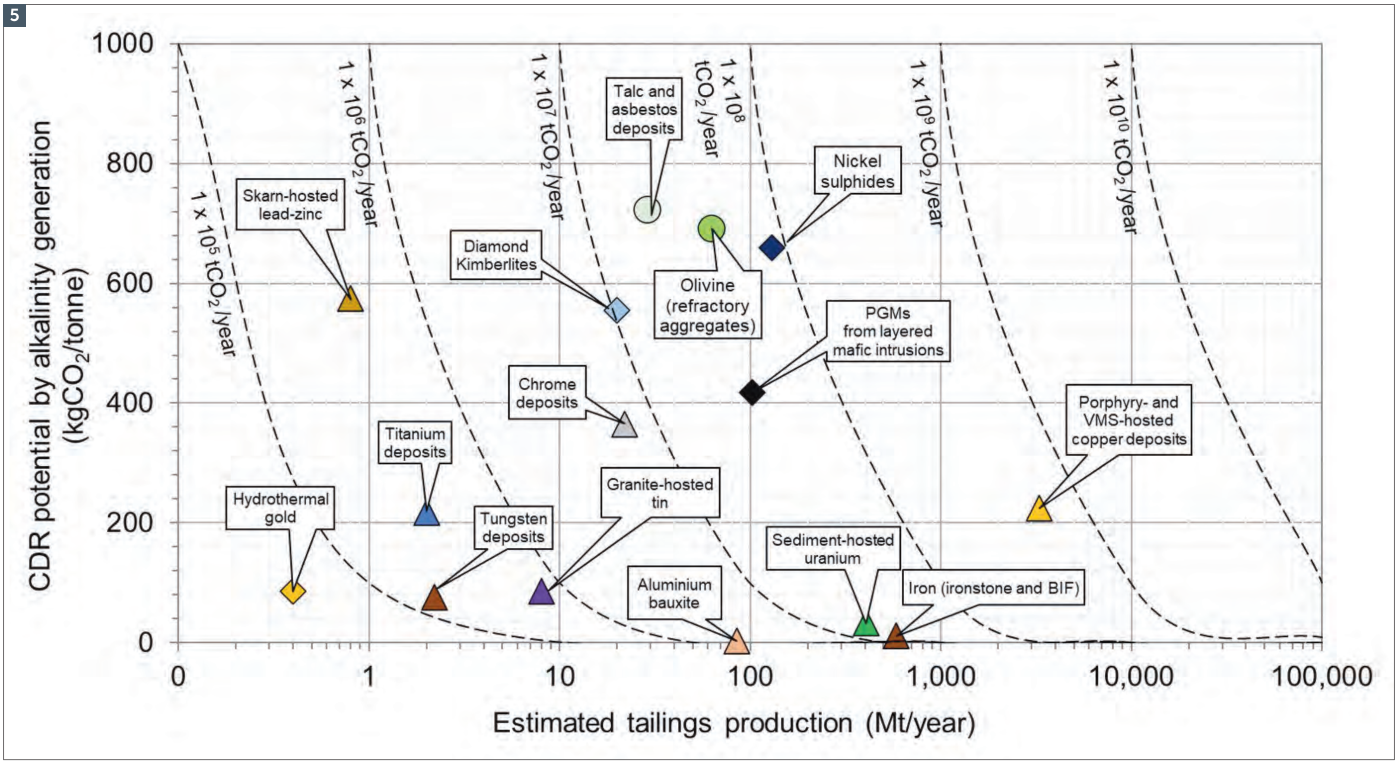

Figure 5: Estimated annual production of mine tailings vs calculated CO_2-removal potential via weathering and generation of alkalinity per tonne of rock for different types of ore deposit. Contours show total quantity of CO_2 removal in tonnes CO_2 per year. Adapted from Bullock et al. (2021) Front. Clim. 3:694175; doi: 10.3389/fclim.2021.694175 (CC BY 4.0).

are reacted with CO_2-rich fluid or gas in a reactor; (2) in-situ mineralisation, whereby CO_2 gas or CO_2-bearing fluids are injected into suitable subsurface reservoirs for geologic storage; and (3) surficial mineralisation with CO_2 from the air using mafic to ultramafic mine tailings or alkaline industrial waste material.

In-situ mineralisation has been tested at the field-scale, with pilot experiments in Iceland (CarbFix project) and the USA (Wallula Basalt Project). In Iceland, the geothermal company Reykjavik Energy and a consortium of research scientists, have injected ~230 tonnes of CO_2 dissolved in water into a highly permeable, fractured basalt reservoir at depths of 400 m to 800 m. By using novel chemical and isotopic tracers, the CarbFix experiment demonstrated rapid CO_2 mineralisation of more than 95% of the injected CO_2 within less than two years (Matter et al, 2016).

Since 2014, Reykjavik Energy has injected more than 20,000 tonnes of CO_2 into a basalt reservoir at about 2,000 m depth. Tracer results reveal nearly complete CO_2 mineralisation (Clark et al., 2020), but estimates of CO_2 uptake to date indicate that the CarbFix storage process may be limited by CO_2 supply. To increase the overall supply of CO_2 and to speed up mineralisation, carbon mineralisation can be combined with other CO_2-removal technologies, such as direct air capture, as demonstrated by the world's first combined direct air capture mineralisation plant in Iceland (https://climeworks.com/orca).

Mine tailings as feedstock

The mining industry extracts tens of gigatonnes of rock material each year, generating large amounts of freshly exposed, reactive surface area that could be used both as feedstock for enhanced rock weathering and mineral carbonation.

Most common base metals (e.g., copper, lead, zinc, nickel) are profitably mined at concentrations as low as ~1% by mass, precious metals (gold, silver, platinum group metals) at parts per million levels, and diamonds at hundreds of parts per billion. So, most processed mine material is effectively "waste" that is stockpiled in dumps and tailings ponds. These mine tailings have been ground to clay-silt to sand-sized particles. Depending on the target metal, for every tonne of rock mined, around 60 to >99 % becomes mine tailings.

Our recent assessment of the CO_2-removal potential of tailings from the mining of silicate mineral-hosted ore deposits is between 1.1 and 4.5 Gt of CO_2 per year via weathering and alkalinity generation, or approximately half that value (0.5–2.3 Gt of CO_2 per year) via →

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mineral carbonation (Bullock et al., 2021). Ore deposits with the highest CO_2-removal capacity are those that are mined in high quantities and have an abundance of calcium- and magnesium-bearing silicate minerals. These include ores that are derived from mafic and ultramafic magmas, as well as some copper-bearing ores (*Fig. 5*). The former includes the platinum group metals and chromium-bearing ores. By contrast, mine tailings that contain high quantities of silica or sulphide minerals have low CO_2-removal potential.

Figure 5 shows only the CO_2-removal potential of different ore deposits and takes no account of reaction kinetics. Depending on particle size, only a few minerals are expected to weather on timescales of less than a decade (notably olivine, wollastonite and brucite) and these minerals are usually minor constituents of mine wastes. This means that new approaches will be required to unlock the full potential of mine waste as a feedstock for CO_2 removal. These approaches could include the acceleration of reaction kinetics through enhanced rock weathering with agriculture, or reaction with CO_2-rich fluids and gases, as well as techniques that exploit microbial metabolisms that enhance mineral dissolution and/or carbonation.

As global mining operations are currently estimated to emit ~3.6 Gt CO_2e per year (Azadi et al., 2020), and demand for raw materials continues to grow, implementation of effective CO_2-removal schemes at mine sites (combined with emissions-reduction technologies) is attractive because it would greatly improve the carbon footprint of the mining industry.

Outlook

There are potential barriers to the large-scale roll-out of the above methods. Such barriers include a lack of scientific knowledge, such as unknowns relating to the longer-term effects of rock application on soil quality, but also broader aspects including the public perception of the risks and benefits of these CO_2 removal techniques, as well as governance and ethical issues.

That said, farmers are used to applying fertilisers, such as lime, to their fields, so the enhanced weathering technique is compatible with agricultural practices. It may also bring important co-benefits for agriculture, such as improvements to crop yield, pest resistance, and increased plant nutritional quality that are key to catalysing farmer adoption. Furthermore, utilising mine waste as a feedstock has the benefit of creating a circular economy.

CO_2 removal via enhanced rock weathering and mineral carbonation clearly have the potential to make a significant contribution towards achieving the Paris Agreement targets and their cost is comparable to other CO_2-removal strategies (see Beerling et al., 2020 for a full evaluation). Both techniques essentially involve speeding up natural processes, and may be less controversial than engineered climate solutions, such as cloud seeding and solar radiation management. G

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FURTHER READING
A full list of further reading is available at geoscientist.online.

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