

# Fizzy ore processing sequesters CO<sub>2</sub> while supplying critical metals

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**PNAS** 

#### Mining for the Clean Energy Transition

Human society can only emit another ~300 Gt of  $CO_2$  if we want to limit global warming to 1.5 °C with a high level of certainty (1). This amounts to ~10 Gt of  $CO_2$  per year over the next 28 y leading up to 2050; thereafter, the global economy will need to sustain carbon neutrality after briefly becoming carbon-negative (1). For perspective, global  $CO_2$ emissions were 31.5 Gt in 2020 during the first year of the COVID-19 pandemic, a decrease from 2019 when 33.4 Gt  $CO_2$  were emitted, but they bounced back to 33.0 Gt  $CO_2$ per year in 2021 (2). Decarbonization, retrofitting industrial  $CO_2$  emitters for carbon capture utilization and storage (CCUS), and removal of  $CO_2$  from air are needed to stabilize the climate.

Decarbonization and the clean energy transition require rapid deployment of renewable energy technologies ranging from solar panels to wind turbines to advanced battery storage accompanied by a switch to electric transportation. Increased mining of critical metals is necessary to build this infrastructure for the clean economy (3). Nickel and cobalt in particular are needed for electric vehicles and battery storage; nickel is also a key raw material for hydrogen production and hydrogen fuel cells (4). Between 6 and 19 times more nickel and 6 and 21 times more cobalt are expected to be mined by 2040 relative to 2020 production (4). The magnesium-rich ultramafic rocks that are mined for nickel and cobalt are also among the best feedstocks for carbon mineralization (also called mineral carbonation), a CCUS technology that traps and stores CO<sub>2</sub> in highly stable carbonate minerals (5, 6). Carbonate minerals are the primary components of seashells and common rocks such as limestone and dolostone, which store most of the carbon on Earth for timescales of thousands to millions of years. In PNAS, Wang and Dreisinger (7) describe a metallurgical process that converts CO<sub>2</sub> into stable carbonate minerals while simultaneously enhancing recovery of nickel and cobalt.

### CO<sub>2</sub> Mineralization is an Ore-Processing Technique

The connection between recovery of critical metals during carbonation of ultramafic rocks was made early in the development of this CCUS technology. The potential for recovery of first-row transition metals such as nickel and cobalt was mentioned in the first description of a pH swing process for ex situ carbon mineralization of ultramafic rocks and minerals (8). Ex situ carbon mineralization at elevated temperatures and pressures yields fast and efficient conversion of  $CO_2$  into carbonate minerals; however, its implementation has been limited by 1) high energy and materials transport costs and 2) the challenge of potentially having to

utilize its products (precipitated silica and magnesium carbonate minerals) at gigatonne scale to finance CCUS (9).

A recent shift in thinking reimagines ex situ carbon mineralization as an ore-processing technique (10, 11) rather than a separate CCUS process that is either tacked onto the end stage of mining or developed as an entirely new industry that relies on mining for raw materials. Tying recovery of critical metals such as nickel and cobalt to carbon mineralization makes the economics of CCUS much more favorable, particularly when it has potential to double recovery of these metals from ore. It is common for approximately half of the nickel in the low-grade deposits we are mining and exploring for today to be hosted by magnesium silicates such as olivine and serpentine minerals (10, 11). In sulfide deposits, nickel is typically extracted using a froth flotation process that is optimized to recover relatively large grains of nickel-bearing sulfide minerals. This process misses out on the many tiny grains of nickel sulfides locked inside larger silicate grains and it cannot extract nickel bound within the crystal structures of olivine and serpentine minerals. It is not uncommon for a large, low-grade nickel mine to remit in the vicinity of 30% of the nickel in its ore to waste as mine tailings (12). As a result, for every world-class nickel mine there is a second worldclass nickel deposit in its tailings storage facility.

A handful of studies have used pH swing methods to process ore and mine tailings to enhance recovery of nickel, cobalt, and associated metals from silicate minerals while sequestering  $CO_2$  in carbonate minerals (11, 13, 14). These "indirect" or "two-step" processes for enhanced metal recovery dissolve silicate minerals at low pH and sequentially precipitate critical metals and carbonate minerals in a separate step. In PNAS, Wang and Dreisinger (7) demonstrate carbonation of olivine with concurrent separation of nickel and cobalt in a single step with nearly 90% efficiency. This is a "direct" or "one-step" ex situ carbonation process developed for enhanced metal recovery.

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The authors declare no competing interest.

Published September 14, 2022.

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See companion article, "Carbon mineralization with concurrent critical metal recovery from olivine," 10.1073/pnas.2203937119.

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### Sticky Molecules and Fizzy Water Enhance Metal Recovery

Wang et al. (15) previously used differences in the solubilities of magnesium and nickel carbonates versus sulfides to convert nickel-bearing olivine into a mixture of magnesite (MgCO<sub>3</sub>) and nickel sulfide minerals. Separation of the magnesium and nickel released during dissolution of olivine is possible using a pressurized mixture of 95%  $CO_2$  and 5%  $H_2S$  at neutral pH because nickel sulfide is much less soluble than magnesium sulfide and nickel carbonate under these conditions (15). Nickel is forced to precipitate as sulfide minerals while magnesium and the small amount of iron dissolved from olivine bind and sequester CO<sub>2</sub> in iron-bearing magnesite. In their previous study, carbonation of olivine to magnesite was greater than 80% efficient at 115 to 150 °C, but a maximum of only 32% of the nickel was converted to sulfides (15). Now, Wang and Dreisinger (7) have added nickel- and cobaltgrabbing organic molecules to their process to achieve 90% conversion of olivine to magnesite with nearly 90% conversion of nickel and cobalt to sulfides. Wang and Dreisinger (7) added ethylenediaminetetraacetic acid (EDTA), as well as citrate and glycine. These chelating ligands have a high affinity for binding metals and can be used to mine them out of olivine at the atomic level. EDTA is best for mining nickel and it preferentially forms metal-grabbing complexes in the order nickel > cobalt > iron > magnesium. When a sufficient amount of EDTA is added to olivine in contact with solution, and the fizzy mix of  $CO_2$  and  $H_2S$ , it grabs the nickel and cobalt, transporting them in solution so they can react to form sulfides. The addition of EDTA also accelerates the carbon mineralization process by shifting the reaction style from diffusion-controlled to surface-reactioncontrolled. What this means is that Wang and Dreisinger (7) saw that rather than magnesite forming thick, impenetrable coatings on olivine (like chocolate-covered raisins) it instead formed patchy and porous coatings that allowed EDTA to continue mining nickel and cobalt from olivine grains while enhancing production of magnesite from the shrinking core of olivine. As such, the addition of EDTA not only improved metal recovery efficiency but also improved carbon sequestration efficiency. Another benefit of using EDTA is that it is already employed in mineral processing and can be recycled so long as temperatures below 175 °C are used for carbonation and enhanced metal recovery.

A previous study by Khan et al. (16) explored the use of ex situ carbon mineralization to convert serpentine minerals into magnesite during ore processing. The authors' motivation was to prevent formation of slimy coatings (the technical term is, in fact, "sliming") of serpentine on nickel sulfide grains because this adversely affects nickel recovery and decreases concentrate grade during froth flotation. A preliminary technoeconomic analysis done by Khan et al. (16) suggests that building ex situ carbonation reactors of the sort used by Wang and Dreisinger (7) into ore processing circuits can reduce the cost of froth flotation as well as pumping and dewatering of process slurries. Wang and Dreisinger's (7) work in PNAS is compatible with the froth flotation methods that are currently used for recovery of nickel- and cobalt-bearing sulfide minerals, which means it could be integrated into ore processing plants at new mines and potentially used to retrofit plants at existing mines.

## Mining's Gigatonne-Scale Potential for CO<sub>2</sub> Removal

Carbon mineralization at mines is attractive because mining is one of the few industries that extracts and moves CO<sub>2</sub>-reactive material on the gigatonne-per-year scale. Approximately 420 Mt of ultramafic ore is currently mined each year with a maximum carbonation potential of ~175 Mt CO<sub>2</sub> per year (5). The amount of ultramafic rocks processed for nickel, cobalt, and other critical metals is expected to at least double by 2100 (6), which would provide a carbonation potential of  $\sim$ 350 Mt CO<sub>2</sub> per year, although the International Energy Agency (4) predicts at least a sixfold increase (i.e., 1.05 Gt CO<sub>2</sub> per year). With more research and development, it may be possible to extend carbon mineralization to less favorable rock types. For instance, if more calcium- and silica-rich mafic and intermediate ores can be carbonated, the global annual CO<sub>2</sub> removal potential of the mining sector increases to 1 to 5 Gt  $CO_2$  per year (17). Ultimately, utilization of  $CO_2$ for enhanced metal recovery could help achieve carbonneutral, or carbon-negative, mining during the race to build the clean economy.

**ACKNOWLEDGMENTS.** This work was supported by a Discovery Grant and Discovery Accelerator Supplement from the Natural Sciences and Engineering Research Council of Canada and a Canada Research Chair to S.A.W.

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