

Subarctic Weathering of Mineral Wastes Provides a Sink for Atmospheric CO₂

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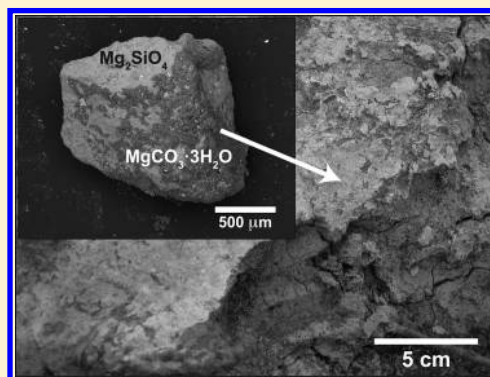
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S Supporting Information

ABSTRACT: The mineral waste from some mines has the capacity to trap and store CO₂ within secondary carbonate minerals via the process of silicate weathering. Nesquehonite [MgCO₃ · 3H₂O] forms by weathering of Mg-silicate minerals in kimberlitic mine tailings at the Diavik Diamond Mine, Northwest Territories, Canada. Less abundant Na- and Ca-carbonate minerals precipitate from sewage treatment effluent deposited in the tailings storage facility. Radiocarbon and stable carbon and oxygen isotopes are used to assess the ability of mine tailings to trap and store modern CO₂ within these minerals in the arid, subarctic climate at Diavik. Stable isotopic data cannot always uniquely identify the source of carbon stored within minerals in this setting; however, radiocarbon isotopic data provide a reliable quantitative estimate for sequestration of modern carbon. At least 89% of the carbon trapped within secondary carbonate minerals at Diavik is derived from a modern source, either by direct uptake of atmospheric CO₂ or indirect uptake through the biosphere. Silicate weathering at Diavik is trapping 102–114 g C/m²/y within nesquehonite, which corresponds to a 2 orders of magnitude increase over the background rate of CO₂ uptake predicted from arctic and subarctic river catchment data.



INTRODUCTION

Since carbon mineralization was first proposed as a method for storing CO₂,¹ much of the work on this subject has focused on the development of rapid, large-scale methods for trapping and storing CO₂ at industrial point sources.^{2–5} However, high temperatures and pressures are needed to induce carbon mineralization reactions on the short time scales (i.e., hours) required for development and deployment of industrial carbonation reactors.⁵ As a result, this approach to carbon mineralization remains both costly and energy intensive.^{5,6}

Recently, there has been increased research on low-temperature, low-pressure procedures for carbon mineralization that emulate or exploit natural processes that occur at the surface of the Earth. An expanding body of work suggests that in situ weathering of mineral waste may be used to sequester a significant amount of CO₂ within carbonate minerals that form at low temperatures. Proposed technologies include enhanced weathering of mineral wastes produced by mining, smelting, energy generation, or construction,^{7–17} accelerated formation of pedogenic carbonates in soils,^{18–20} and capture of anthropogenic

CO₂ emissions by direct carbonate precipitation or carbonation of brucite [Mg(OH)₂] precipitated from saline wastewater.^{21,22}

Nesquehonite [MgCO₃ · 3H₂O] and Na- and Ca-carbonate minerals form by weathering of silicate minerals within kimberlitic mine tailings at the Diavik Diamond Mine, Northwest Territories, Canada.⁹ Secondary hydrated Mg-carbonate minerals such as nesquehonite are effective and durable traps for carbon, and their occurrence in a mine tailings storage facility can represent offsetting of a mine's greenhouse gas emissions.^{8,10} The rate of silicate weathering (and thus carbonate mineral precipitation) in ultramafic mine tailings is greatly accelerated because milling and mineral processing lead to orders-of-magnitude increases in reactive surface area.¹⁰ Many of the world's operating diamond mines, including the Diavik Diamond Mine, are located in subarctic or arctic climates in Canada and Russia.²³ Because the rate of silicate weathering also depends upon

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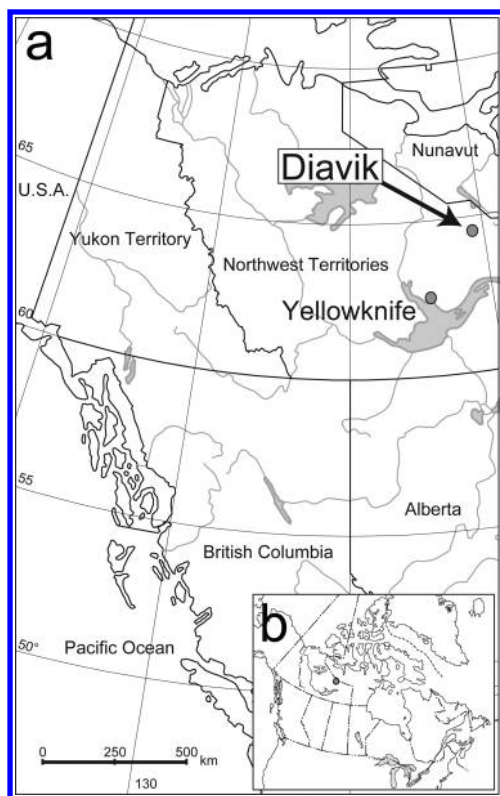


Figure 1. Location of the Diavik Diamond Mine, Northwest Territories, Canada.

temperature and the availability of water, one might expect weathering rates to be slower in subarctic or arctic climates. However, the impact of a subarctic or arctic climate upon the ability of an operational mine tailings storage facility to trap and store atmospheric CO_2 has not previously been assessed.

With regard to CO_2 sequestration, it is of significant concern that the presence of secondary carbonate minerals at sites like Diavik may not represent net trapping of atmospheric CO_2 . Potential carbon sources for mineral precipitation in an active mine tailings storage facility include the atmosphere (either directly or indirectly through the biosphere), industrial process chemicals, and milled bedrock carbonate minerals. Stable carbon and oxygen isotopic compositions of carbonate minerals have traditionally been used to trace the origin of carbon fixed within secondary carbonate minerals. In addition, radiocarbon isotopic data have been used to confirm that the tailings from several historical mine sites are trapping and storing CO_2 from the modern atmosphere.¹⁰ However, the ability of stable and radiogenic isotope tracer methods to identify trapping of modern, atmospheric carbon within minerals has not been tested in as geochemically complex a setting as an active mine tailings storage facility.

Here, we present new radiocarbon and stable carbon and oxygen isotopic data for primary and secondary carbonate minerals from processed kimberlite mine tailings at the Diavik Diamond Mine. The reliability of stable and radiogenic isotope data as tracers is evaluated in this setting. Isotopic results are used to assess uptake and storage of modern, atmospheric CO_2 within mine tailings at Diavik and to gauge the ability of mining operations in subarctic regions to sequester CO_2 by enhanced silicate weathering.

Table 1. Carbonate and Sulfate Mineral Phases Detected at Diavik

mineral name	cation(s)	formula	occurrence at Diavik ^a
nesquehonite	Mg	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	EP
dolomite	Ca, Mg	$\text{CaMg}(\text{CO}_3)_2$	B
calcite	Ca	CaCO_3	EP, B
vaterite	Ca	CaCO_3	EP
gaylussite	Na, Ca	$\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$	EP
natrite	Na	Na_2CO_3	EP
natron	Na	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	EP
thermonatrite	Na	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	EP
trona	Na	$\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$	EP
northupite	Na, Mg	$\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}$	EP
pentahydrate	Mg	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$	EP
hexahydrate	Mg	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	EP
epsomite	Mg	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	EP
anhydrite	Ca	CaSO_4	EP
bassanite	Ca	$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	EP
gypsum	Ca	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	EP
ettringite	Ca, Al	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$	EP
langbeinite	K, Mg	$\text{K}_2\text{Mg}_2(\text{SO}_4)_3$	EP
syngenite	K, Ca	$\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	EP
jarosite	Fe, K	$\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$	EP
butlerite ^b	Fe	$\text{Fe}^{3+}(\text{SO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$	EP

^a EP — effluorescent precipitate; B — bedrock carbonate mineral.

^b Butlerite may have been detected in XRD patterns, by its most intense peak, at $>3\sigma$ above background intensity.

CARBONATE MINERALS AT THE DIAVIK DIAMOND MINE

The Diavik Diamond Mine is located on East Island in Lac de Gras, approximately 300 km northeast of Yellowknife, Northwest Territories, Canada and 220 km south of the Arctic Circle (Figure 1). The kimberlites being mined for diamonds at Lac de Gras, including those at Diavik, intrude Late Archean granitoids and supracrustal rocks of the Yellowknife Supergroup in the Slave Structural Province.²⁴ Kimberlites are ultramafic, intrusive, hybrid rocks that are composed of mantle-derived xenocrysts and magmatic megacrysts (primarily forsterite) in a fine-grained matrix of serpentine minerals, calcite, dolomite, and other phases.²⁵ The Diavik kimberlites also contain mudstone xenoliths (composed predominantly of quartz, feldspar, muscovite, and pyrite) that were assimilated during emplacement.²⁶

At the time of sampling in 2006, approximately 2 Mt/year of kimberlite ore were being mined from the A154 open pit. After undergoing processing to remove diamonds, the residual kimberlite (approximately 2 Mt/year, as only a small mass of diamonds was removed) was transported to one of two locations for permanent storage. Most of this material was piped, suspended in water, into a natural basin (called the Fine Processed Kimberlite Containment Facility or “fine PKC”) where it was stored subaqueously in a pond of process water. A much smaller amount of coarse-grained waste material was stored subaerially in a pile (called the Coarse Processed Kimberlite Containment Facility or “coarse PKC”). Detailed descriptions of sampling techniques and sampling locations are reported elsewhere.⁹

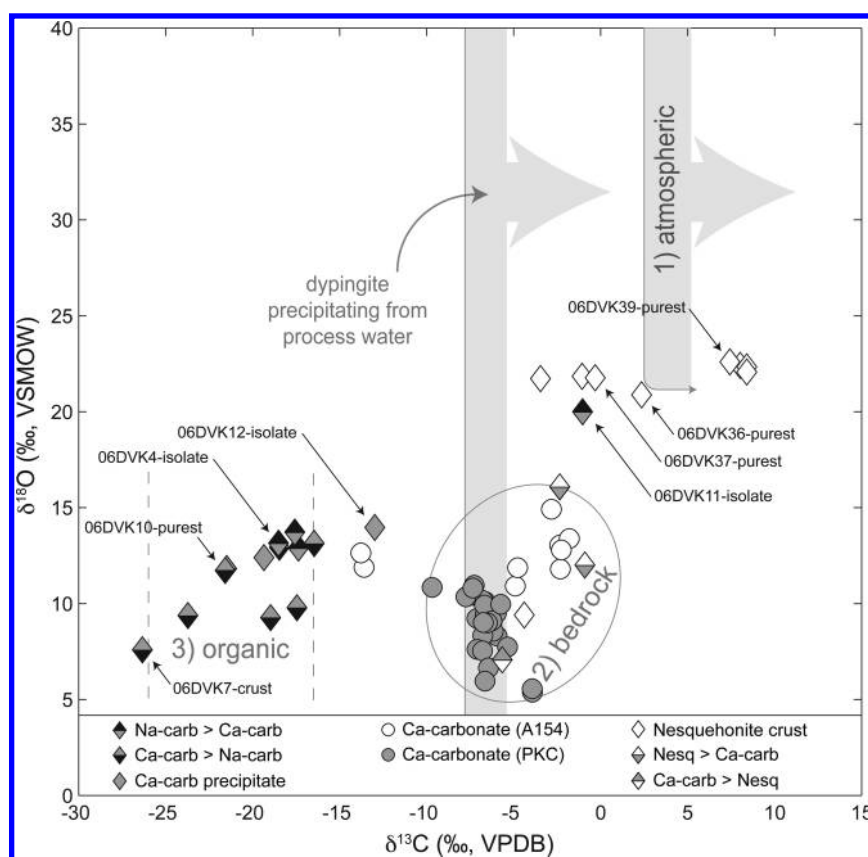


Figure 2. Stable oxygen and carbon isotope data by mode of occurrence and mineralogy for Diavik. Numbers indicate fields for carbonate minerals in equilibrium with specific reservoirs for carbon and oxygen. Radiocarbon data are available for all individually labeled specimens. In most cases, 2 σ measurement errors are smaller than the symbols employed.

Processed kimberlite from the fine PKC is a mixture of kimberlitic material and assimilated xenoliths (i.e., mudstone) characterized by serpentine minerals (predominantly lizardite) and high-Mg forsterite with minor amounts of calcite, Cr-diopside, Mg-rich garnet, plagioclase, phlogopite, quartz, and clay minerals (e.g., vermiculite, smectites, and possibly interstratified clays).^{9,26} Traces of chromite, dolomite, muscovite, perovskite, and an amphibole group mineral have been observed.⁹ The calcite and dolomite found throughout the fine PKC are primary (bedrock) carbonate minerals of kimberlitic origin.

Effluorescent crusts of secondary carbonate and sulfate minerals are commonly observed in the fine PKC at Diavik. A list of effluorescent minerals observed at Diavik is provided in Table 1. These effluorescents occur within the fine PKC in three distinct modes: (1) white, powdery films of nesquehonite or sulfate minerals (commonly gypsum) that form on surfaces, (2) preserved effluorescents of nesquehonite located at depth within the tailings, and (3) thick (>1 mm) crusts of portlandite, Na- and Ca-carbonate minerals (primarily calcite, gaylussite, natrite, thermatrite, trona, and vaterite), with occasional nesquehonite, gypsum, and ettringite, that occur in parts of the fine PKC where processed sewage effluent has been deposited.⁹ More detailed information about these effluorescences is provided in the Supporting Information.

Nesquehonite is the most common secondary carbonate mineral at Diavik. It has been observed forming directly on the surfaces of grains of forsterite (Figure S1), suggesting precipitation from dissolved forsterite and/or serpentine mined from

kimberlite. Nesquehonite typically forms continuous films (i.e., the first type of effluorescent crust) at the surface of the tailings at Diavik (Figure S1), but it has also been detected in trace (or greater) amounts in the other types of crusts. Despite the surface expression of nesquehonite and Na- and Ca-carbonate-rich effluorescences, preserved effluorescent crusts of nesquehonite found at depth within the fine PKC likely represent the bulk of carbon mineralization in the tailings at Diavik.⁹

ANALYTICAL METHODS

Qualitative Powder X-ray Diffraction Methods. Mineral phases in all specimens analyzed for isotopic compositions were identified from powder X-ray diffraction (XRD) patterns. Finely ground aliquots of sample were mounted as slurry onto a zero-diffraction quartz plate with anhydrous ethanol and allowed to dry at room temperature. XRD data were collected on a Siemens (Bruker) D5000 θ – 2θ diffractometer equipped with a VÅN-TEC-1 detector. The long, fine-focus Co X-ray tube was operated at 35 kV and 40 mA. Data for mineral identification were collected with a step size of 0.04° 2θ and counting time of 0.8 s/step over a range of 3–80° 2θ . Constituent mineral phases were identified from XRD patterns with reference to the ICDD PDF-4+ 2008 database using the program DIFFRAC^{plus} EVA 10.²⁷ Carbonate phases identified by XRD are reported in Table S1 for all specimens that were analyzed for stable and radiogenic isotope compositions.

Stable Isotopic Methods. Specimens were analyzed using a gas bench attached to a Thermo Finnigan DeltaPlus XL IRMS at the Pacific Centre for Isotopic and Geochemical Research (PCIGR), The University of British Columbia. Aliquots, weighing approximately 200 μg , were loaded into septum vials, flushed with helium, and dissolved in 99% phosphoric acid at 72 °C for a minimum of 1 hour. Isotopic compositions of the evolved headspace gas were measured in a helium flow. Some samples, particularly nesquehonite-rich samples, were split into multiple aliquots to assess heterogeneity in their stable carbon and oxygen isotopic composition. The $\delta^{13}\text{C}$ compositions are given relative to Vienna Pee Dee Belemnite (VPDB) and the $\delta^{18}\text{O}$ compositions are given relative to Vienna Standard Mean Ocean Water (VSMOW). The external precision (1σ deviation) for isotopic analyses was $<0.1\text{‰}$ for $\delta^{13}\text{C}$ and $<0.2\text{‰}$ for $\delta^{18}\text{O}$, as estimated from repeated analysis of NBS-18 and NBS-19. At least three in-house calcite standards, which have been previously calibrated relative to NBS-18 and NBS-19, were analyzed for every eight specimens. Further analytical details are provided in the Supporting Information.

Radiocarbon Methods. Highly pure specimens of secondary carbonate minerals were isolated from nine samples of mine tailings by picking mineral grains under a binocular microscope with fine tweezers. Powdered specimens were acidified with 85% phosphoric acid to extract CO_2 using a vacuum line in the Department of Earth and Ocean Sciences, The University of British Columbia. The CO_2 was contained within ampules and was converted to graphite by hydrogen reduction in the presence of iron powder at 550 °C at the Research School of Earth Sciences, The Australian National University. Graphite targets were placed in a small mold and compressed into pellets. The pellets were run on the Single Stage Accelerator Mass Spectrometer (SSAMS) at The Australian National University. Background contamination, from preparation of graphite targets, was determined from analyses of ^{14}C -free coal and wood and was subtracted from sample data. The Cambridge half-life (5730 ± 40 years) was used to calculate the fraction of modern carbon (F^{14}C).^{28,29} Reservoir corrections were made to F^{14}C values using $\delta^{13}\text{C}$ data collected with the SSAMS.

ANALYTICAL RESULTS FOR THE DIAVIK DIAMOND MINE

Stable Carbon and Oxygen Isotopic Results. The $\delta^{13}\text{C}_{\text{VPDB}}$ data for specimens of carbonate minerals from Diavik (Figure 2 and Table S1) vary from -26.3‰ to 8.4‰ , with $\delta^{18}\text{O}_{\text{VSMOW}}$ values ranging from 5.4‰ to 22.6‰ . Samples rich in effluorescent Na- and Ca-carbonate minerals (e.g., calcite, gaylussite, natron, northupite, thermonatrite, trona, vaterite), and containing occasional nesquehonite, are characterized by $-26.3\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -13.0\text{‰}$ and $7.6\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 14.0\text{‰}$. Bedrock carbonate minerals (i.e., calcite \pm dolomite) from the A154 mine pit have $-13.8\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -1.8\text{‰}$ and $10.9\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 14.9\text{‰}$, and calcite \pm dolomite from bulk tailings are defined by $-9.7\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -3.9\text{‰}$ and $5.4\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 11.0\text{‰}$. Samples of calcite \pm dolomite from bulk tailings are on average more depleted in ^{13}C and ^{18}O than samples of the same minerals collected from the A154 mine pit. Aliquots of effluorescent nesquehonite give values of $-4.4\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq 8.4\text{‰}$ and $9.4\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 22.6\text{‰}$. Aliquots of nesquehonite obviously contaminated with calcite give relatively

depleted values of $-5.7\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -0.9\text{‰}$ and $7.1\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 16.1\text{‰}$.

The $\delta^{13}\text{C}_{\text{VPDB}}$ values of dissolved inorganic carbon (DIC) were measured for two specimens of filtered water. The lower of these values, $\delta^{13}\text{C}_{\text{VPDB}} = -17.9\text{‰}$, comes from water in the North Inlet of East Island (06DVK24). DIC in stored process water, collected from near the center of the tailings pond in the fine PKC (06DVK9), has a $\delta^{13}\text{C}_{\text{VPDB}}$ of -10.4‰ .

Radiocarbon Results. Radiocarbon analysis of nesquehonite and samples of Na- and Ca-carbonate minerals from Diavik provides values of F^{14}C , the fraction modern carbon. These values are given in Table S1 and are plotted with $\delta^{13}\text{C}_{\text{VPDB}}$ data in Figure 3. Values of F^{14}C range between 0.954 and 1.057.

Four highly pure specimens of nesquehonite crusts sampled from the fine PKC give F^{14}C values slightly less than unity: 0.954 ± 0.006 (06DVK36-purest), 0.972 ± 0.009 (06DVK37-purest), 0.972 ± 0.006 (06DVK39-purest), and 0.982 ± 0.005 (06DVK28). No other mineral phases were detected to a limit of approximately 0.5 wt % in the XRD patterns collected on these specimens of nesquehonite.

Five specimens of secondary minerals collected from Na- and Ca-carbonate crusts have F^{14}C values near or greater than unity. Calcite-rich specimens give values of 0.946 ± 0.007 (06DVK7-crust), 1.057 ± 0.005 (06DVK10-purest), and 1.038 ± 0.003 (06DVK12-isolate). Specimens rich in Na-carbonate minerals have F^{14}C values of 1.009 ± 0.006 (06DVK4-isolate) and 1.028 ± 0.003 (06DVK11-isolate).

ISOTOPIC FINGERPRINTING AT DIAVIK

Fingerprinting with Stable Isotopic Data. *Primary Bedrock Carbonate Minerals.* Primary calcite in kimberlite has been reported as having values approximately $\delta^{13}\text{C}_{\text{VPDB}} = -10\text{‰}$ to -1‰ , and $\delta^{18}\text{O}_{\text{VSMOW}} = 7\text{‰}$ to 27‰ .²⁵ Secondary calcite, associated with bituminous matter in kimberlite has been documented as being more depleted in ^{13}C , with $\delta^{13}\text{C}_{\text{VPDB}}$ values in the range of approximately -32‰ to -10‰ .³⁰ Some samples of calcite from the A154 mine pit at Diavik have $\delta^{13}\text{C}_{\text{VPDB}}$ values lower than expected for primary calcite (Figure 2). These samples were found in association with lenses of mud and fragments of preserved wood (personal communication, S. Moss, UBC), suggesting possible incorporation of organic carbon during precipitation.

More negative values for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in calcite \pm dolomite sampled from the fine PKC may reflect different sources within the A154 mine pit for fresh samples versus mine tailings or partial dissolution and reprecipitation of primary bedrock calcite \pm dolomite with an input of organic carbon, which would manifest as carbonate minerals with an intermediate isotopic signature. However, the relatively small footprint of sewage effluent deposits at the surface of the fine PKC suggests that the input of organic carbon via effluent is probably too localized and volumetrically insufficient to influence the isotopic composition of calcite \pm dolomite throughout the fine PKC. Furthermore, it is unlikely that calcite would be prone to significant dissolution and reprecipitation under the neutral to basic pH conditions in the fine PKC at Diavik.³¹

Secondary Na- and Ca-Carbonate Minerals. The ^{13}C -depletion measured for the Na- and Ca-carbonate minerals in the fine PKC may suggest precipitation from (1) an organic source of carbon or (2) a high-pH solution.

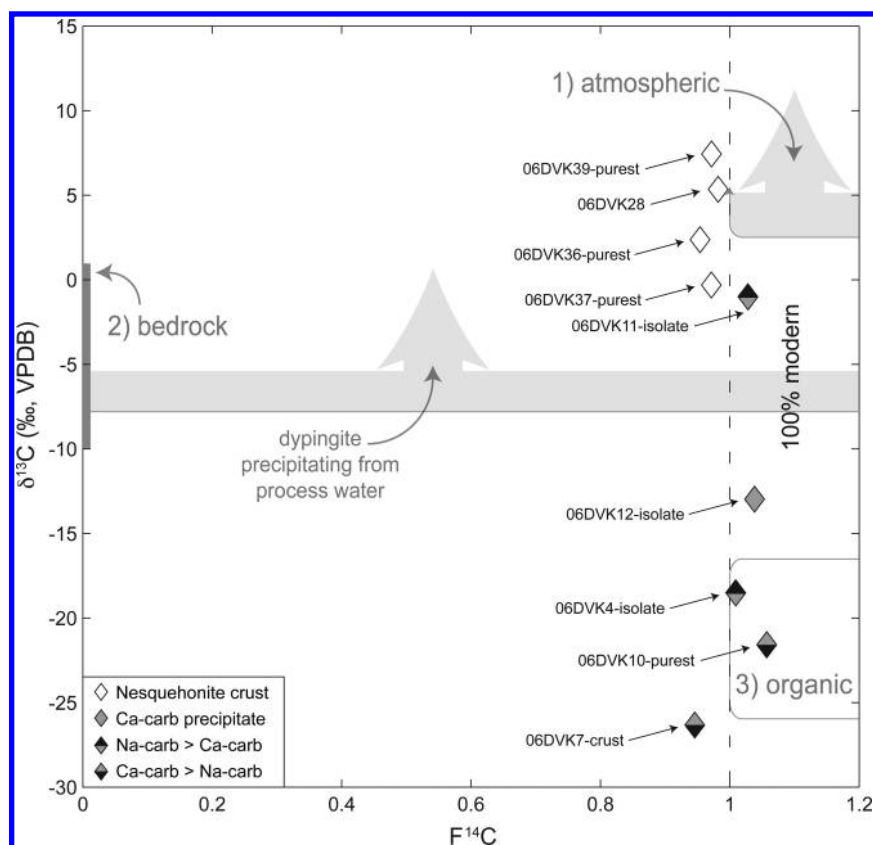


Figure 3. Variation of $\delta^{13}\text{C}$ with $F^{14}\text{C}$ for samples from Diavik. Numbers indicate fields for carbonate minerals in equilibrium with specific reservoirs for carbon and oxygen. In most cases, measurement errors are smaller than the symbols employed.

At Diavik, treated sewage effluent from the mine camp has been disposed of at the surface of the tailings in the fine PKC (personal communication, C. English, Diavik Diamond Mines Inc.). Sewage treatment effluent had been deposited near the road that follows the perimeter of the fine PKC where crusts of Na- and Ca-carbonate minerals were observed. Sewage typically has $\delta^{13}\text{C}_{\text{VPDB}}$ values for dissolved organic carbon (DOC) and particulate organic matter (POM) between approximately -26‰ and -21‰ ,^{32–38} but these values can reach -16‰ .³⁹ In the absence of isotopic data for sewage and sewage treatment effluent from Diavik, we have defined the field for organic carbon in Figures 2 and 3 to reflect literature values for sewage from cities in North, Central, and South America.^{32–39}

Because aerobic oxidation of organic matter produces CO_2 with a carbon isotopic ratio close to that of the parent material,⁴⁰ carbonate minerals precipitated from an organic source could have a similarly depleted isotopic signature. For instance, calcite precipitated in a closed system under equilibrium conditions from sewage-derived aqueous HCO_3^- , at temperatures from 0 to 25 °C , could have a $\delta^{13}\text{C}$ value that is only 1.0‰ to 1.1‰ more positive relative to the aqueous species from which it formed.^{41,42} The more negative values of $\delta^{13}\text{C}_{\text{VPDB}}$ obtained for most of the Na- and Ca-carbonate specimens are consistent with precipitation of carbonate minerals from sewage in a closed system. However, formation of pedogenic carbonate minerals from organic carbon is also known to take place in open systems.⁴³ Because gaseous CO_2 generated by oxidation of organic matter diffuses out of soil and soil-like systems, this carbonation process is accompanied by an isotopic fractionation. Due to the

difference in the diffusion rate of gaseous $^{13}\text{CO}_2$ versus $^{12}\text{CO}_2$ to the atmosphere during soil respiration, soil CO_2 is typically more enriched in ^{13}C than soil organic matter.⁴³ Consequently, carbonate minerals precipitated in soil-like environments should be significantly enriched in ^{13}C compared to the organic C from which they formed.

The ^{13}C -depletion observed in these Na- and Ca-carbonate minerals could also be explained by diffusion fractionation of atmospheric CO_2 into a very high-pH (>11), high-ionic strength solution.^{44–49} Experiments have shown that similarly ^{13}C - and ^{18}O -depleted carbonate minerals form at very high pH (<11) by kinetic depletion of ^{13}C during hydroxylation of aqueous CO_2 with OH^- and depletion of ^{18}O via the same reaction ($\epsilon^{18}\text{O}_{\text{OH}^--\text{H}_2\text{O(l)}} \approx -40\text{‰}$).⁴⁷ Moderately alkaline solutions (pH < 11) can produce carbonate minerals equally depleted in ^{13}C , but with $\delta^{18}\text{O}$ values that reflect oxygen isotopic equilibrium.⁴⁸ This is thought to be caused by a change in reaction mechanism by which carbonate minerals form at pH < 11 , at which point hydroxylation reactions may lose influence over the stable oxygen isotopic signature of carbonate minerals.⁴⁸

The tailings pond itself would not necessarily need to have a very high pH in this scenario, because microenvironments within the tailings may have higher or lower pH than the pond and the scale of Na- and Ca-carbonate deposits is limited. Indeed, the presence of high-pH, low-temperature mineral phases such as portlandite, ettringite, and Na-carbonate minerals in these deposits suggests that this could be a viable explanation for the observed depletion in ^{13}C . The stable oxygen and carbon isotopic signatures produced by (1) precipitation of carbonate minerals

from saline, very-high-pH brines under isotopic disequilibrium or (2) mineralization of oxidized sewage organic matter in a closed system are indistinguishable. In both scenarios, modern carbon could be trapped and stored within carbonate minerals in mine tailings. The difference lies in the pathway by which CO_2 was trapped: either directly from the atmosphere or indirectly through the biosphere. No matter their source of carbon, it is clear that the data for Na- and Ca-carbonate minerals do not plot within the field in Figure 2 for mineralization of DIC in isotopic equilibrium with atmospheric CO_2 . The close spatial association between sites of sewage deposition and precipitation of Na- and Ca-carbonate minerals strongly suggests that these ^{13}C -depleted carbonate minerals precipitated from these effluents, but the pathway by which they formed (from either atmospheric CO_2 or modern organic carbon) remains ambiguous.

Secondary Nesquehonite, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. The equilibrium carbon isotopic fractionation factor for nesquehonite- CO_2 is not known; however, the fractionation factor for dypingite, another hydrated Mg-carbonate mineral, has been measured to be $10^3 \ln \alpha_{\text{dypingite-HCO}_3^-} = (3.8 \pm 1.2)\text{‰}$ between 20 and 25 °C.¹¹ Therefore, we have used the fractionation factor of dypingite [i.e., $10^3 \ln \alpha_{\text{dypingite-HCO}_3^-} = (3.8 \pm 1.2)\text{‰}$ between 20 and 25 °C] to define a field for precipitation of nesquehonite in equilibrium with atmospheric CO_2 ($\delta^{13}\text{C}_{\text{VPDB}} \approx -8\text{‰}$) in Figures 2 and 3. The temperature dependence of the fractionation factor of dypingite is not known; however, values for equilibrium precipitation of dypingite (and nesquehonite) can be expected to plot toward higher $\delta^{13}\text{C}$ with decreasing temperature, as is known to occur for other carbonate minerals.⁵⁰ Because the air and water temperatures at Diavik are usually significantly lower than 25 °C, values of $\delta^{13}\text{C}$ for nesquehonite precipitated in equilibrium with atmospheric CO_2 should be several per mil more positive than is expressed by the range of $\delta^{13}\text{C}$ shown in Figures 2 and 3. The lower limit to $\delta^{18}\text{O}$ in the field for equilibrium precipitation from atmospheric CO_2 is defined by the equilibrium oxygen isotopic fractionation factor for hydromagnesite (another hydrated Mg-carbonate mineral) reported by O'Neil and Barnes⁴⁴ at 25 °C, $10^3 \ln \alpha_{\text{hydromagnesite-H}_2\text{O}} = 31.2\text{‰}$, and assuming a $\delta^{18}\text{O}_{\text{VSMOW}}$ value of -10‰ for water in the tailings pond, which is typical of near-surface groundwater in Canada.⁵¹

The wide range of stable carbon and oxygen isotopic values observed for nesquehonite may imply precipitation from several distinct and mixed sources of carbon. Based on significant enrichment in ^{13}C and ^{18}O , data for highly pure aliquots of nesquehonite picked from samples 06DVK36 and 06DVK39 are broadly consistent with an atmospheric source of CO_2 (Figure 2). Sample 06DVK28, which is not plotted in Figure 2 because $\delta^{18}\text{O}$ data are not available, also has a $\delta^{13}\text{C}$ value that is consistent with precipitation in equilibrium with atmospheric CO_2 . Because the temperature dependence of the equilibrium carbon isotopic fractionation factor for dypingite (and nesquehonite) is not known, it is not possible to determine the extent to which CO_2 degassing during crystallization of nesquehonite may have enriched some samples in ^{13}C .

Data for highly pure aliquots of nesquehonite, picked from sample 06DVK37, show similar enrichment in ^{18}O (consistent with equilibrium precipitation), but give $\delta^{13}\text{C}_{\text{VPDB}}$ values that are inconsistent with precipitation in equilibrium with atmospheric CO_2 . These data fall within a region of $\delta^{18}\text{O}_{\text{VSMOW}}-\delta^{13}\text{C}_{\text{VPDB}}$ space that lies between the equilibrium reservoir fields identified as sources of carbon at Diavik (i.e., atmospheric CO_2 ,

mined carbonate minerals, and sewage organic matter). Based on the $\delta^{13}\text{C}$ values for the DIC in the fine PKC pond, nesquehonite precipitating in equilibrium with ^{13}C -depleted tailings water will have $\delta^{13}\text{C}_{\text{VPDB}}$ values between approximately -7.6‰ and -5.4‰ at 20–25 °C (using the carbon isotopic fractionation factor for dypingite¹¹). Data for the aliquots of highly pure nesquehonite from sample 06DVK37 fall between the fields defined for equilibrium precipitation from atmospheric CO_2 and DIC from the fine PKC pond.

Because typical temperatures at Diavik are considerably less than 25 °C, inclusion of temperature dependence for dypingite–DIC fractionation would increase the breadth of this field toward more positive $\delta^{13}\text{C}$ values. Additionally, the water chemistry (including pH and dissolved solids content) of the PKC pond is known to vary seasonally, which could also impact the $\delta^{13}\text{C}$ of DIC within the pond. This suggests that some highly pure samples of nesquehonite could have precipitated from pond water DIC at low temperatures. Mixing with an organic carbon source, or kinetic diffusion fractionation of atmospheric CO_2 into the relatively saline and alkaline ($7 \leq \text{pH} \leq 10$) tailings pond water,¹¹ could also be invoked to explain the ^{13}C -depletion observed in these specimens of nesquehonite. Either scenario would explain the depletion in ^{13}C relative to the anticipated value of $\delta^{13}\text{C} \approx 0\text{‰}$ for DIC in equilibrium with atmospheric CO_2 .

Data for another four nesquehonite-rich aliquots (which were split from three of the four nesquehonite-rich samples analyzed: 06DVK36, 06DVK37, and 06DVK39) plot within the field defined by bedrock carbonate minerals. This is consistent with contamination by bedrock carbonate minerals, which was confirmed by detection of calcite in XRD patterns.

Fingerprinting with Radiocarbon. Values of $F^{14}\text{C}$ for nine specimens of secondary carbonate minerals range from 0.946 to 1.057 (Figure 3). Four of the specimens have $F^{14}\text{C} > 1.0$, which indicates unambiguously that these minerals contain distinctly modern carbon. The remaining five specimens give $0.9 \leq F^{14}\text{C} \leq 1.0$, which suggests minor input from a source of ^{14}C -free carbon. These results imply that 89–100% of the carbon bound within the effluents was derived from atmospheric carbon; either directly from the atmosphere or indirectly through the biosphere (i.e., CO_2 derived from sewage organic carbon).

Data for two specimens of Na- and Ca-carbonate minerals (06DVK4-isolate and 06DVK10-purest) fall within the field defined for precipitation from sewage organic carbon, which could also reflect precipitation from an atmospheric source of carbon at high pH (Figure 3). One of these two specimens, 06DVK10-purest (which contains calcite and gaylussite), has an $F^{14}\text{C}$ value of 1.057, which is consistent with the composition of the atmosphere in 2006, the year of sampling.⁵² Data for specimen 06DVK7-crust are also broadly consistent with precipitation from modern carbon with minor incorporation of ^{14}C -free carbon.

Carbon isotopic data for three specimens of nesquehonite (06DVK28, 06DVK36-purest, and 06DVK39-purest) are broadly consistent with precipitation from DIC in equilibrium with atmospheric CO_2 with a minor input of ^{14}C -free carbon. Data for two other specimens (one of nesquehonite, 06DVK37-purest, and one of Na- and Ca-carbonate minerals, 06DVK11-isolate) may imply (1) low-temperature precipitation in equilibrium with modern, ^{13}C -depleted DIC in the tailings pond or (2) precipitation at equilibrium from a mixed organic and atmospheric source of carbon. Data for one specimen of secondary calcite

(06DVK12-isolate) also fall between equilibrium reservoir fields, suggesting either (1) precipitation from a mixed source of carbon or (2) precipitation under isotopic disequilibrium from a moderately high pH solution. Significantly, the $F^{14}C$ value for this specimen is greater than 1, confirming a modern source for carbon within the calcite.

In spite of near-unity values of $F^{14}C$ for all specimens analyzed, the possibility exists that a nontrivial amount of the carbon fixed within nesquehonite and the less common secondary Na- and Ca-carbonate minerals has been recycled from dissolution of bedrock calcite within the tailings at Diavik. One mole of atmospheric CO_2 is drawn into solution for each mole of bedrock carbonate mineral that is dissolved during dissolution of carbonate minerals in an open system.^{53,54} As carbonate minerals precipitate from this solution, one mole of CO_2 will be released back to the atmosphere. Repeated dissolution and reprecipitation of carbonate minerals can therefore lead to mixing of carbon from bedrock and atmospheric sources. The resulting carbonate minerals will develop a mixed source for CO_2 , and after approximately six cycles of dissolution and reprecipitation they will become so enriched in ^{13}C and ^{14}C that they will be indistinguishable from minerals precipitated solely from an atmospheric source of carbon and cations derived from silicate weathering.⁵⁵ In this scenario, bedrock carbonate minerals would remain the original source for cations and CO_2 within these secondary minerals and therefore no net trapping of CO_2 would have occurred.¹⁰

Nesquehonite typically forms by evaporation of high-pH, saline waters^{8–10,14,56–60} and it is stable in saline, neutral to high-pH waters of the sort found within the fine PKC. It is highly unlikely that, first, calcite or dolomite would have dissolved in high-pH water and, second, nesquehonite would have dissolved and reprecipitated a sufficient number of times to obscure a bedrock $F^{14}C$ signature under these conditions. Furthermore, radiocarbon data are very sensitive to mixing^{10,61–63} via either batch reaction or cyclic dissolution/precipitation of minerals. $F^{14}C$ data for secondary carbonate minerals at Diavik clearly show no indication of a mixing trend between ^{14}C -free bedrock calcite and atmospheric CO_2 (Figure 3). Therefore, our results are only consistent with nesquehonite forming from a noncarbonate source of cations, and incorporating a modern, noncarbonate source of carbon (i.e., atmospheric CO_2).

■ IMPLICATIONS FOR ASSESSING CO_2 FIXATION IN MINERALS

Silicate weathering in the fine PKC at the Diavik Diamond Mine is trapping and storing carbon within the carbonate mineral, nesquehonite. A lesser amount of carbon is stored by Na- and Ca-carbonate minerals. The process of silicate weathering in tailings storage facilities can produce secondary carbonate minerals with diverse isotopic signatures as evidenced by the range of $\delta^{13}C$ and $\delta^{18}O$ values measured at Diavik. Poor constraint on equilibrium stable isotopic fractionation factors for Mg-carbonate minerals, and many other hydrated carbonate minerals, compounds the challenge of interpreting stable isotopic data from these minerals. Additionally, kinetic isotope fractionation effects may play a significant role during precipitation of carbonate minerals from alkaline process water in some tailings storage facilities, particularly at active mines.¹¹ All of these factors have the potential to complicate interpretation of stable isotopic data in the ultramafic mine tailings environment. At Diavik, the

use of radiocarbon data and field observations can help with the interpretation of stable isotopic data. Radiocarbon data indicate that in excess of 89% of the carbon trapped and stored within secondary nesquehonite and Na- and Ca-carbonate minerals is ultimately sourced from the modern atmosphere, either directly or indirectly through the biosphere.

In the mine tailings environment, stable isotopic signatures tend to reflect the processes (either equilibrium or kinetic) by which carbon and oxygen are cycled rather than their original sources.¹¹ This behavior can complicate efforts to assess and quantify carbon capture and storage within the framework of enhanced silicate weathering. A good example of this at Diavik is the inability of stable isotopic data alone to distinguish the source of carbon in ^{13}C -depleted Na- and Ca-carbonate minerals. Thus, as has been previously shown,¹⁰ radiocarbon data were required to determine unambiguously whether these secondary minerals are trapping and storing modern atmospheric CO_2 . Using radiocarbon isotopic fingerprinting a previously unrecognized trap for modern carbon in mine tailings was discovered (i.e., the Na- and Ca-carbonate minerals that precipitated in association with sewage treatment plant effluent). The details of the mechanism by which these Na- and Ca-carbonate minerals were produced remain unknown; however, these deposits clearly act as a sink for modern carbon. Thus, the tailings management strategy at Diavik could potentially be modified to promote increased trapping of carbon by selective disposal of this effluent along the banks of the tailings pond or by mixing it with Mg-rich tailings leachate.

Although nesquehonite is metastable under conditions that prevail at the Earth's surface, it is known to decompose in sequence to more stable mineral phases: first to dypingite and then to hydromagnesite, which represents a stable, long-term host to carbon.^{8,14} Large deposits of hydromagnesite are found in association with ophiolitic terrane near Atlin, British Columbia, Canada.¹⁴ These hydromagnesite playa deposits directly overlie Holocene glacial till, demonstrating their persistence and the stability of hydromagnesite over thousands of years.¹⁴ Should the nesquehonite in the fine PKC ultimately decompose it will form hydromagnesite, a more stable mineral trap for carbon.

Diavik is situated approximately 200 km from the Arctic Circle and is above the tree line within the zone of continuous permafrost. Mean annual temperature at the nearby EKATI diamond mine, Northwest Territories, Canada is $-11.8\text{ }^{\circ}C$, mean annual precipitation is 250–300 mm/year, and mean annual open-water evaporation is 200–350 mm/year.⁶⁴ Rates of silicate mineral weathering are known to depend strongly upon temperature and the availability of water.⁶⁵ A 2009 estimate, based on quantitative mineralogical data, suggested that on the order of 1.8×10^3 t of CO_2 may have been trapped and stored within nesquehonite during the first 6 years of mining at Diavik.⁹ Taking $F^{14}C$ values from this study into account, this amounts to an average annual sequestration of 270–300 t of modern atmospheric CO_2 within 840–940 t of secondary nesquehonite. Approximately 560–630 t of lizardite or 427–480 t of forsterite (or more likely some combination of these two minerals) must weather each year to produce the amount of nesquehonite observed.

The amount of CO_2 uptake that results from naturally occurring silicate weathering has been estimated as 1.2–2.8 g $C/m^2/y$ for several major river catchments in arctic and subarctic Canada and Russia.^{66,67} Application of the estimated annual rate of nesquehonite formation to the subaerially stored fraction of tailings in the fine PKC suggests that silicate weathering at Diavik is trapping 102–114 g $C/m^2/y$ within nesquehonite.

This corresponds to a 2 orders of magnitude increase over the expected weathering rate predicted from river catchment data. This estimate is only for the surface area of the fine PKC that is not covered by the tailings pond. It is likely that subaqueous storage of tailings has limited precipitation of effluorescent nesquehonite at Diavik.⁹ Acid mine drainage is generally not a concern in the ultramafic tailings produced by mining of kimberlite-hosted diamond deposits like Diavik, which contain very low abundances of sulfide minerals,²⁶ which means that subaqueous storage of tailings is not required to suppress acid generation. Thus, the capacity of kimberlitic mine tailings to trap and store modern carbon in an arctic or subarctic climate could be enhanced by employing subaerial storage of tailings⁹ and strategic disposal of sewage treatment plant effluent within these tailings. For instance, the tailings at the Clinton Creek chrysotile mine in Yukon, Canada also experience a subarctic climate but these tailings have not been stored subaqueously. The chrysotile-rich tailings at Clinton Creek have sequestered an average of 1700 g C/m²/y within hydrated Mg-carbonate minerals since 1978,⁶⁸ which corresponds to a 16-fold increase over the rate of sequestration observed at Diavik.

The Diavik Diamond Mine emits approximately 150 000 t of CO₂ equivalent greenhouse gases each year.⁶⁹ Precipitation of nesquehonite at Diavik represents only a small offsetting (approximately 0.2%) of the mine's annual greenhouse gas emissions. However, it is significant that CO₂ is being sequestered at an accelerated rate (relative to the natural weathering rate) in a very cold and arid environment and at a mine whose tailings management practices could be severely limiting carbon mineralization.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed descriptions of effluorescent mineralogy, analytical techniques, and geochemical results. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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