Carbon Dioxide Fixation within Mine Wastes of Ultramafic-Hosted Ore Deposits: Examples from the Clinton Creek and Cassiar Chrysotile Deposits, Canada

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Abstract
Carbon dioxide (CO₂) is sequestered through the weathering and subsequent mineralization of the chrysotile mine tailings at Clinton Creek, Yukon Territory, and Cassiar, British Columbia, Canada. Accelerated weathering is attributed to a dramatic increase in surface area, which occurs during the milling of ore. We provide a detailed account of the natural process of carbon trapping and storage as it occurs at Clinton Creek and Cassiar, including mineralogy, modes of occurrence, methods of formation for carbonate alteration, light stable isotope geochemistry, and radiocarbon analysis. Powder X-ray diffraction data were used to identify weathering products as the hydrated magnesium carbonate minerals nesquehonite [MgCO₃·3H₂O], dypingite [Mg₅(CO₃)₄(OH)₂·5H₂O], hydromagnesite [Mg₅(CO₃)₄(OH)₄·4H₂O], and less commonly lansfordite [MgCO₃·5H₂O]. Textural relationships suggest that carbonate precipitates formed in situ after milling and deposition of tailings. Samples of efflorescent nesquehonite are characterized by δ¹³C values between 6.52 and 14.36 per mil, δ¹⁸O values between 20.93 and 26.62 per mil, and F¹⁴C values (fraction of modern carbon) between 1.072 and 1.114, values which are consistent with temperature-dependent fractionation of modern atmospheric CO₂ during mineralization. Samples of dypingite ± hydromagnesite collected from within 0.2 m of the tailings surface give δ¹³C values between −1.51 and +10.02 per mil, δ¹⁸O values between +17.53 and +28.40 per mil, and F¹⁴C values between 1.026 and 1.146, which suggests precipitation from modern atmospheric CO₂ in a soil-like environment. Field observations and isotopic data suggest that hydrated magnesium carbonate minerals formed in two environments. Nesquehonite formed in an evaporative environment on the surface of tailings piles, and dypingite and hydromagnesite formed in the subsurface environment with characteristics similar to soil carbonate. In both cases, these minerals

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have been trapping and storing the greenhouse gas, CO₂, directly from the atmosphere. Combined use of δ¹³C, δ¹⁸O, and F¹⁴C data has been applied effectively as a tool for verifying and monitoring sequestration of atmospheric CO₂ within mine tailings. A number of other deposit types produce tailings suitable for CO₂ sequestration, including Cu-Ni-PGE deposits, diamondiferous kimberlite pipes, and podiform chromite deposits. Our results suggest that conversion of about 10 wt percent of tailings to carbonate minerals could offset the greenhouse gas emissions from many ultramafic-hosted mining operations.

Introduction

Current warming of the Earth’s climate has been linked to the emission of anthropogenic greenhouse gases (i.e., CO₂, CH₄, N₂O) into the atmosphere. In 2004, carbon dioxide (CO₂) constituted 77 percent of total anthropogenic greenhouse house emissions (IPCC, 2007). The global atmospheric concentration of CO₂ increased exponentially from a pre-industrial (i.e., pre-1750) level of 280 ± 20 to 379 ppm in 2005. Approximately two-thirds of this increase is attributed to the combustion of fossil fuels and one-third to changes in land use since 1750 (IPCC, 2007). Strategies for decarbonizing energy sources, increasing efficiency of energy production, and trapping and storing CO₂ are required to help stabilize concentrations of atmospheric CO₂ (e.g., Hoffert et al., 2002; Lackner, 2003; Pacala and Socolow, 2004; Breecker, 2007). To achieve this, geologically stable, energy efficient, and cost-effective strategies for sequestering CO₂ must be developed and implemented.

More than 90 percent of carbon on Earth is bound within minerals with a mean residence time on the order of 10⁶ years or more (Sundquist, 1985, 1993). As a result, fixing carbon within the crystal structures of minerals has been recognized as a safe and durable method for sequestering anthropogenic carbon (Seifritz, 1990; Lackner et al., 1995; Lackner, 2003). Dissolution of silicate minerals and precipitation of carbonate minerals in mine tailings is one potential implementation of this process. Mineral-fluid reaction is greatly accelerated during mineral-fluid reaction in mine tailings at the Kidd Creek copper-zinc mine near Timmins, Ontario (Al et al., 2000), and the Lower Williams Lake uranium mine near Elliot Lake, Ontario (Packtunc and Davé, 2002), for example. The source of bound carbon at these localities is not known but likely includes a substantial component of recycled bedrock carbon (Al et al., 2000). More recently, carbonate mineralization has been noted in tailings from the chrysotile mines at Thetford, Québec (Huot et al., 2003), Clinton Creek, Yukon Territory (Wilson et al., 2004), and Cassiar, British Columbia (Wilson et al., 2005). Carbonate minerals are rare in the ore of these mines.

This work is part of a broader study of natural analogues to CO₂ sequestration (Hansen et al., 2005; Power et al., 2007) and passive methods for sequestering CO₂ within mine tailings (Wilson et al., 2006). Here we describe in detail the precipitation of secondary carbonate minerals in chrysotile mine tailings at Clinton Creek and Cassiar. The hydrated magnesium carbonate minerals nesquehonite [Mg₃CO₃·3H₂O], dypingite [MgsCa(CO₃)₄(OH)₂·5H₂O], hydromagneite [Mg₅(CO₃)₄(OH)₂·4H₂O], and lansfordite [MgCO₃·3H₂O] precipitate in the tailings as a natural consequence of silicate weathering. The fine grain size of these chrysotile mine tailings appears to have resulted in rapid and widespread development of carbonate mineral precipitates. We attribute the accelerated rate of silicate weathering observed in chrysotile mine tailings to be a direct result of the mining process. The accelerated weathering of silicate minerals and precipitation of carbonate minerals in ultramafic mine tailings environments could therefore represent a viable means of trapping and storing atmospheric CO₂. Accounting of CO₂ sequestration in mine tailings could help to offset costs associated with remediation projects and emissions penalties through trade of CO₂ credits.

Weathering of magnesium silicate minerals to secondary carbonates is best assessed at inactive mines where tailings are not reworked, saturated with water, or regularly treated with industrial chemicals. As a result, field relationships among primary and secondary minerals can be used to identify the environments in which the mineral hosts for atmospheric CO₂ develop. Because more than a decade has passed since Clinton Creek and Cassiar were closed, the stability of secondary carbonate mineral hosts for CO₂ can be assessed and an average annual rate of CO₂ sequestration can be determined using quantitative mineralogical analysis. We also employ stable and radiogenic isotope analysis of carbon and oxygen to fingerprint the source of mineralized CO₂.

Field Localities and Sampling Strategy

The Clinton Creek chrysotile deposit is a partially carbonate-altered serpentinitized peridotite (Htoon, 1979). The Clinton Creek mine, situated near Dawson City, Yukon Territory, Canada (Fig. 1A), operated from 1967 to 1978 (Htoon, 1979). Eleven million tons (Mt) of chrysotile ore were extracted from the four open pit mines at Clinton Creek, producing 1 Mt of long-fiber chrysotile and 10 Mt of tailings (Government of Yukon, 2007). The tailings pile, situated on a topographic high overlooking Wolverine Creek, slumped into the creek in two stages: the southern lobe of the pile dammed the creek in 1974 followed by the northern lobe which destabilized in 1985 (Government of Yukon, 2007). In an effort to mitigate instability in the tailings pile, the lower sections of the northern and southern lobes were reworked into a series of terraces (Fig. 1B). The extensive carbonate mineral efflorescences found on these terrace structures are likely to have formed no earlier than the 1990s when the terraces were initially constructed. Forty-seven samples of tailings and 15 samples of waste rock were taken from Clinton Creek. Sampling focused on the Wolverine Pit and the southern lobe of the tailings pile. Tailings samples were collected from within the top 2 m of the pile by trowel, auger, or trenching. Twenty-four of the 47 samples at Clinton Creek were selected because of high concentrations of secondary carbonate minerals. Most of these samples were collected from within 0.2 m of the surface of the tailings pile. Carbonate-rich tailings were sampled...
preferentially to aid in the identification of carbonate phases by powder X-ray diffraction and to facilitate grain-picking for stable and radiogenic isotope analyses. Locations for samples discussed in this work are given in Table 1 and Figure 2.

The chrysotile deposit at Cassiar, northern British Columbia, Canada (Fig. 1A) forms part of a serpentinized harzburgite tectonite (Wicks and O’Hanley, 1988). During the 39-year operational lifetime of the Cassiar mine from 1953 to 1992, at least 17 Mt of mine tailings were produced. These tailings were stored in an elongate pile (Fig. 1C). Mining operations were renewed for a brief period in 2000 (Government of British Columbia, 2007). Fifty-four samples of tailings and one sample of waste rock were taken at Cassiar. Tailings samples were collected at depths varying from 0 to 1.7 m below the surface of the tailings pile by trowel, auger, or trenching. The sample of waste rock and 14 samples from the surface of the tailings pile were selected because of high concentrations of secondary carbonate minerals. Locations for samples used in this study are provided in Table 1.

Samples from Clinton Creek and Cassiar were collected during the dry summer season. Several samples of waste rock from the lake in Porcupine Pit at Clinton Creek and of tailings from the base of the pile at Cassiar were saturated with water at the time of sampling. All samples were left to dry under a drying hood for 48 h and were then homogenized mechanically with a spatula. One bulk sample of tailings, weighing in excess of 20 kg, was taken from approximately half a meter below the surface at each site (samples 04CC1401 from Clinton Creek and 03CA1601 from Cassiar). A 5-kg aliquot of each bulk sample was dried, homogenized, and divided into smaller aliquots for analysis. These samples were chosen to provide a baseline estimate for mineral carbonation at each site.

Analytical Methods

Qualitative powder X-ray diffraction

Mineral phases were identified with powder X-ray diffraction (XRD). Finely ground aliquots of sample were smear-mounted onto petrographic slides with anhydrous ethanol and allowed to dry at room temperature. XRD data for mineral identification were collected with a scanning step of 0.04° 2θ and counting time of 2 s/step on a Siemens D5000 0-2θ diffractometer over a range of 3° to 70° 2θ with each scan taking 55 min. Minerals were identified with reference to the ICDD PDF-4 database using the program DIFFRACplus EVA (Bruker AXS, 2004, Karlsruhe, Germany). The normal-focus Cu X-ray tube was operated at 40 kV and 40 mA. In order to
TABLE 1. Mineralogical and Isotopic Data for Carbonate Samples from Mine Wastes at Clinton Creek (CC) and Cassiar (CA)

<table>
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<tr>
<th>Sample no.</th>
<th>Mode</th>
<th>Major carbonate phases</th>
<th>Minor carbonate or hydrotalcite phases</th>
<th>$\delta^{13}C$ (‰, VPDB)</th>
<th>$\sigma^{13}C$ (‰, VPDB)</th>
<th>$\delta^{18}O$ (‰, VSMOW)</th>
<th>$\sigma^{18}O$ (‰, VSMOW)</th>
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<th>NAD 27 Northing</th>
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<th>( 2\sigma^{13}C ) (‰, VPDB)</th>
<th>( \delta^{18}O ) (‰, VSMOW)</th>
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<td>Crust, atop cement</td>
<td>Dyp</td>
<td>5.88</td>
<td>0.09</td>
<td>20.42</td>
<td>0.20</td>
<td>0514038</td>
<td>7147832</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>05CC6-bottom</td>
<td>Cement</td>
<td>Dyp</td>
<td>4.41</td>
<td>0.07</td>
<td>21.83</td>
<td>0.12</td>
<td>0514038</td>
<td>7147832</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>05CC6-CA</td>
<td>Cement, cobble within</td>
<td>Dyp</td>
<td>6.85</td>
<td>0.20</td>
<td>26.27</td>
<td>0.18</td>
<td>0514038</td>
<td>7147832</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>05CC8-1</td>
<td>Cement, bedrock contam.</td>
<td>Mgs</td>
<td>–7.74</td>
<td>0.19</td>
<td>12.85</td>
<td>0.15</td>
<td>0513570</td>
<td>7147900</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>05CC8-2</td>
<td>Cement, bedrock contam.</td>
<td>Mgs</td>
<td>–7.72</td>
<td>0.10</td>
<td>13.02</td>
<td>0.15</td>
<td>0513570</td>
<td>7147900</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>04CA0101</td>
<td>Coating on Fibers</td>
<td>Arg</td>
<td>–6.66</td>
<td>0.52</td>
<td>12.81</td>
<td>0.66</td>
<td>0452332</td>
<td>6571710</td>
<td>Surface</td>
</tr>
<tr>
<td>04CA0202-CA</td>
<td>Cobble</td>
<td>Cal, Dol</td>
<td>–2.50</td>
<td>0.21</td>
<td>12.83</td>
<td>0.21</td>
<td>0452685</td>
<td>6571590</td>
<td>Surface</td>
</tr>
<tr>
<td>04CA0202-CC</td>
<td>Cobble</td>
<td>Cal, Arg</td>
<td>–0.42</td>
<td>0.13</td>
<td>13.99</td>
<td>0.13</td>
<td>0452685</td>
<td>6571590</td>
<td>Surface</td>
</tr>
<tr>
<td>04CA0202-CD</td>
<td>Cobble</td>
<td>Cal, Arg</td>
<td>0.57</td>
<td>0.48</td>
<td>15.17</td>
<td>0.33</td>
<td>0452685</td>
<td>6571590</td>
<td>Surface</td>
</tr>
<tr>
<td>04CA0202-CB</td>
<td>Cobble</td>
<td>Cal, Arg</td>
<td>1.09</td>
<td>0.25</td>
<td>15.45</td>
<td>0.18</td>
<td>0452685</td>
<td>6571590</td>
<td>Surface</td>
</tr>
<tr>
<td>04CA0301-CA</td>
<td>Cobble</td>
<td>Cal</td>
<td>–5.50</td>
<td>0.18</td>
<td>12.22</td>
<td>0.18</td>
<td>0452956</td>
<td>6571578</td>
<td>Surface</td>
</tr>
<tr>
<td>04CA0601</td>
<td>Crust</td>
<td>Nsq</td>
<td>5.55</td>
<td>0.14</td>
<td>26.62</td>
<td>0.19</td>
<td>0452548</td>
<td>6571969</td>
<td>Surface</td>
</tr>
<tr>
<td>04CA1001</td>
<td>Stream</td>
<td>Cal</td>
<td>–3.46</td>
<td>0.17</td>
<td>12.75</td>
<td>0.18</td>
<td>0452518</td>
<td>6577648</td>
<td>Surface</td>
</tr>
<tr>
<td>03CA1601</td>
<td>Bedrock, within bulk tailings</td>
<td>Cal, Arg</td>
<td>–1.83</td>
<td>0.23</td>
<td>18.77</td>
<td>0.30</td>
<td>0452197</td>
<td>6572049</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>03CA1601</td>
<td>Bedrock, within bulk tailings</td>
<td>Cal, Dol</td>
<td>–9.41</td>
<td>0.29</td>
<td>14.38</td>
<td>0.26</td>
<td>0452197</td>
<td>6572049</td>
<td>&gt;1.0</td>
</tr>
</tbody>
</table>

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1 Arg = aragonite, Cal = calcite, Dol = dolomite, Dyp = diopside, Hmg = hydromagnesite, Lns = lansfordite, Mgs = magnesite, Mhc = monohydrocalcite, Nsq = nesquehonite, Pyr = pyroxmellite
2 Clinton Creek is in NAD 27 zone 07 and Cassiar is in NAD 27 zone 09
3 Depth of sampling for “Surface” samples varies from 0 to 0.2 m
4 Denotes that grains were picked under a binocular microscope to maintain high sample purity
5 Sample immersed in 5% acetic acid solution for 40 min to dissolve hydrated magnesium carbonate minerals
6 Sample immersed in 5% acetic acid solution for 5 h to dissolve hydrated magnesium carbonate minerals
7 Average values for UBC in-house standards for analyses done in this study; accepted values of \( \delta^{13}C \) (‰) and \( \delta^{18}O \) (‰) are Internal Std 1, 1.842, 13.644; Internal Std 2, 4.353, 19.380; Internal Std 3, –0.692, 3.826

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Internal Std 1: 1.79, 0.12; 13.79, 0.32
Internal Std 2: 4.42, 0.07; 19.35, 0.21
Internal Std 3: –0.65, 0.10; 3.85, 0.28
NBS 18: 5.06, 0.11; 7.37, 0.17
NBS 19: 1.88, 0.06; 28.37, 0.32

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CO2 FIXATION IN MINE TAILINGS AT CLINTON CREEK & CASSIAR CHRYSOTILE DEPOSITS, CANADA

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The table provides data on the carbon and oxygen isotopes from various samples collected from different locations in the Clinton Creek and Cassiar Chrystophile Deposits, Canada. The isotopic values are given in parts per thousand (‰) relative to VPDB (Vienna Pee Dee Belemnite) and VSMOW (Vienna Standard Mean Ocean Water). The samples are categorized by their mineralogical composition and depth of sampling.
detect hydrated magnesium carbonate minerals at low abundance, a scanning step of 0.04° 2θ and a counting time of 40 s/step over a range of 12° to 17° 2θ were used, giving a scan time of 1 h and 24 min.

**Scanning electron microscopy**

Mineral habits and the textural relationships among minerals were characterized using a Philips XL-30 scanning electron microscope (SEM), equipped with a Princeton Gamma-Tech energy dispersive X-ray spectrometer (EDS) system. Selected samples were impregnated with epoxy and thin-sectioned for petrographic analysis. Small segments of carbonate crusts and cobble coatings were also mounted on aluminum stubs to image mineral habit with the SEM. Secondary electron imaging was used to observe the surface morphology of carbonate crusts. Backscattered electron imaging was used to observe textural relationships in thin section. EDS was used for the identification of minerals and to distinguish between magnesium carbonate minerals and other magnesium-bearing phases.

**Light stable isotopes**

Stable carbon and oxygen isotope compositions were determined for 59 specimens derived from 33 samples of mine tailings from Clinton Creek and Cassiar (Table 1). For 12 of the 59 specimens, grains of carbonate minerals were picked with fine tweezers under a binocular microscope to maintain high purity. Two specimens of bulk tailings (from sample 04CC1401) were leached with 5 percent acetic acid at 23ºC, for either 40 min or 5 h, to dissolve hydrated magnesium carbonate minerals.

Specimens were analyzed using a gas bench attached to a Thermo Finnigan DeltaPlus XL LS-IRMS at the Pacific Centre for Isotopic and Geochemical Research (PCIGR), University of British Columbia. Aliquots weighing approximately 200 µg were loaded into septum vials, flushed with helium, and dissolved in 99 percent phosphoric acid at 72°C for a minimum of 1 hr. Isotope compositions of the evolved headspace gas were measured in a helium flow. The δ13C compositions are given relative to VPDB and the δ18O compositions are relative to VSMOW. The external precision (1σ) for isotopic analyses was <0.1 per mil δ13C and <0.2 per mil δ18O, as estimated from repeated analysis of in-house calcite standards, NBS-18 and NBS-19. One aliquot of each in-house standard was analyzed for every eight specimens. The δ18O compositions of carbonate minerals were corrected for reaction with phosphoric acid using the fractionation factors from Das Sharma et al. (2002), taking into account the proportions of calcium and magnesium-carbonate minerals in mixed specimens. The fractionation factor for magnesite was used as a proxy for the hydrated magnesium carbonate minerals. Instrument fractionation was corrected using factors calculated from the in-house standards. Replicate analyses were done on seven specimens to confirm the reproducibility of the data.

Specimens of hydrated magnesium carbonate minerals were analyzed in bulk, without removing crystallographic water by heating, following standard practise for stable isotope studies of hydrated carbonates (e.g., O’Neil and Barnes, 1971; Taylor, 1975; Grady et al., 1989; Zedef et al., 2000). During analysis, exchange fractionation of oxygen may have occurred between H2O and CO2 evolved from acidified specimens of hydrated magnesium carbonate minerals. The phosphoric acid used to dissolve the hydrated magnesium carbonates is expected to have absorbed a component of the evolved crystallographic water, however, the extent to which this occurs has not been documented. As a result, the δ18O values reported in this study may reflect the oxygen isotope composition of both carbonate and structurally bound water within these minerals.
Results

Tailings mineral content

Tailings from Clinton Creek contain kaolinite-serpentine group minerals, primarily chrysotile, with minor magnetite, calcite, dolomite, magnesite, quartz, clinoclore, and pyroaurite [MgFe\textsubscript{1+2}CO\textsubscript{3}(OH)\textsubscript{6}]. The hydrated magnesium carbonate minerals nesquehonite [MgCO\textsubscript{3}:3H\textsubscript{2}O], dypingite [Mg\textsubscript{5}(CO\textsubscript{3})\textsubscript{4}(OH)\textsubscript{2}:5H\textsubscript{2}O], hydromagnesite [Mg\textsubscript{5}(CO\textsubscript{3})\textsubscript{4}(OH)\textsubscript{2}:4H\textsubscript{2}O], and more rarely lansfordite [MgCO\textsubscript{3}:5H\textsubscript{2}O] occur at the surface of the tailings and as a matrix between grains within the tailings pile. Quantitative mineralogical data for tailings from Clinton Creek and Cassiar are given by Wilson et al. (2006). Samples taken at water level from the flooded Porcupine Pit at Clinton Creek contain the hydrated sulfate minerals epsomite [MgSO\textsubscript{4}7H\textsubscript{2}O] and hexahydrite [MgSO\textsubscript{4}6H\textsubscript{2}O]. Hexahydrite was also observed in two samples of carbonate crust on vertical surfaces of the tailings pile. The most likely sources of sulfur in these minerals are pyrite and minor magnetite, clinochlore, and local quartz, calcite, and dolomite. Less than 1 percent of the surface area of the tailings pile contains efflorescences of nesquehonite, dypingite, and aragonite.

Hydrated magnesium carbonate minerals

Hydrated magnesium carbonate minerals can be organized into three groups based on their chemical formulas (after Canterford et al., 1984). The first group consists of minerals with formulas based on magnesite (MgCO\textsubscript{3}) with variable waters of hydration. Three such minerals are known to occur in nature: barringtonite [MgCO\textsubscript{3}:2H\textsubscript{2}O] (Nashar, 1965), nesquehonite [MgCO\textsubscript{3}:3H\textsubscript{2}O] (Stephan and Mac-Gillivray, 1972), and lansfordite [MgCO\textsubscript{3}:5H\textsubscript{2}O] (Hill et al., 1982). The second group of hydrated magnesium carbonate minerals is distinguished from the first by the addition of hydroxyl groups or a brucite-like formula component, Mg(OH)\textsubscript{2}. Artinite [Mg\textsubscript{2}(CO\textsubscript{3})(OH)\textsubscript{2}:3H\textsubscript{2}O] is the only known member of this group (Akao and Iwai, 1977a; Canterford et al., 1984). Three minerals with the chemical formula Mg\textsubscript{5}(CO\textsubscript{3})\textsubscript{4}(OH)\textsubscript{2}:xH\textsubscript{2}O comprise the third group: hydromagnesite with x = 4 (Akao and Iwai, 1977b), dypingite with x = 5 (Raade, 1970), and giorgiosite with x = 5 or 6 (Friedel, 1975; Canterford et al., 1984). Hydromagnesite is the only one of the latter three minerals for which the crystal structure has been determined (Akao and Iwai, 1977b). The minerals in the third group are distinct because they have a molar ratio of MgO to CO\textsubscript{2} of 5/4, whereas artinite has a ratio of 2/1.

The formation of the magnesium carbonate minerals barringtonite, nesquehonite, lansfordite, and magnesite optimizes trapping of CO\textsubscript{2} on a per-cation basis. This can be demonstrated with the H\textsubscript{2}O-MgO-CO\textsubscript{2} ternary plot for hydrated magnesium carbonate minerals (Fig. 3). Those minerals observed at Clinton Creek and Cassiar (nesquehonite, lansfordite, and magnesite) have a molar ratio of MgO to CO\textsubscript{2} of 1 per formula unit, whereas for dypingite and hydromagnesite the ratio is 5/4. It should be preferable to trap CO\textsubscript{2} in nesquehonite, lansfordite, and magnesite. However, the thermodynamic stability of magnesium carbonates is known to increase from lansfordite (the least stable) through nesquehonite, dypingite, and hydromagnesite, to magnesite (Langmuir, 1985; Canterford et al., 1984). As a result, sequestration of CO\textsubscript{2} in magnesite optimizes both the amount of bound carbon and the thermodynamic stability of trapping at pCO\textsubscript{2} ≤ 1 atm and at temperatures between 0°C and 60°C (Königsberger et al., 1999).

Table 2. Fraction Modern Values for Ca and Mg Carbonate Samples

<table>
<thead>
<tr>
<th>Sample no.\textsuperscript{1}</th>
<th>Measured \textsuperscript{14}C Age \textsuperscript{2} (in pMC or yBP)</th>
<th>Conventional \textsuperscript{14}C age \textsuperscript{2} (in yBP)</th>
<th>(\delta^{13}C) \textsuperscript{3} (‰)</th>
<th>F\textsuperscript{14}C</th>
<th>(\alpha^{14}C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>03CC01B</td>
<td>119.1 ± 0.6 pMC</td>
<td>8.0</td>
<td>1.114</td>
<td>0.006</td>
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<tr>
<td>04CC0104</td>
<td>&gt;40 000 yBP</td>
<td>-8.3</td>
<td>&lt;0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>04CC0105</td>
<td>107.6 ± 0.5 pMC</td>
<td>-1.7</td>
<td>1.026</td>
<td>0.005</td>
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</tr>
<tr>
<td>04CC0101A</td>
<td>121.7 ± 0.6 pMC</td>
<td>4.3</td>
<td>1.146</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>04CA0101</td>
<td>2.380 ± 40 yBP</td>
<td>2.790 ± 40 yBP</td>
<td>-0.3</td>
<td>0.707</td>
<td>0.004</td>
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<tr>
<td>04CA0202-CA</td>
<td>1.170 ± 40 yBP</td>
<td>1.560 ± 40 yBP</td>
<td>-1.4</td>
<td>0.823</td>
<td>0.004</td>
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<td>04CA0601</td>
<td>114.3 ± 0.5 pMC</td>
<td>6.2</td>
<td>1.072</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>04CA1001</td>
<td>9.550 ± 40 yBP</td>
<td>9.840 ± 40 yBP</td>
<td>-7.2</td>
<td>0.294</td>
<td>0.002</td>
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</tbody>
</table>

\textsuperscript{1}CA in the sample name denotes Cassiar and CC denotes Clinton Creek

\textsuperscript{2}pMC denotes percent modern carbon relative to the AD 1950 reference standard

\textsuperscript{3}\(\delta^{13}C\) values from AMS were used to correct F\textsuperscript{14}C (fraction of modern carbon) data for machine fractionation
Carbonate mineral precipitates

Hydrated magnesium carbonate and calcium carbonate minerals occur in four distinct modes in the mine tailings at Clinton Creek and Cassiar: (1) as crusts on vertical and horizontal surfaces (Fig. 4A-C), (2) as disseminated precipitates that cement tailings grains in the interior of the tailings pile (Fig. 4D), (3) as thin coatings (<1 mm in thickness) on cobbles of serpentine (Fig. 4E), and (4) as precipitates lining the beds of ephemeral runoff streams (Fig. 4F). Hydrated magnesium carbonate crusts, cements, and cobbles are abundant in the tailings at Clinton Creek. Hydrated magnesium carbonate cements and calcium carbonate cobble coatings are observed at Cassiar.

Crusts on tailings surfaces: Crusts typically contain nesquehonite, dypingite, hydromagnesite, and more rarely lansfordite. Textural relationships among hydrated magnesium carbonate phases within crusts are readily observed in thin section using backscattered electron imaging on the SEM. Nesquehonite is differentiated from dypingite and hydromagnesite by habit and slight variation in the intensity of backscattered electrons, which is a function of the mean atomic number of a mineral (Fig. 3). As a result of their similar chemical composition, mean atomic number, and habit, dypingite and hydromagnesite are indistinguishable in backscattered electron images. Mineralogical observations made using the SEM were confirmed with XRD data.

At both localities, a distinct zonation between nesquehonite and dypingite ± hydromagnesite is seen throughout the crust samples with nesquehonite forming subaerially over grains of serpentine cemented with dypingite ± hydromagnesite (Fig. 5A). The nesquehonite zone in crusts contains few clasts. The dypingite ± hydromagnesite zone is composed of fine-grained clasts of serpentine cemented together by Mg carbonate precipitates that have nucleated on the surfaces of these grains. The latter zone represents the interface between nesquehonite-rich efflorescences at the surface of the tailings and the damp, cemented tailings below. Replacement textures, which would suggest that dypingite and hydromagnesite are forming via decomposition of nesquehonite, are not observed at interfaces between the two zones.

The composition of crusts is found to vary from predominantly nesquehonite with minor dypingite ± hydromagnesite to dypingite ± nesquehonite ± hydromagnesite. Crusts rich in dypingite are observed less commonly and may result from the loss of the outer nesquehonite-rich layer. Development of magnesium carbonate crusts on vertical surfaces may be structurally controlled by the relative permeability of horizons within the tailings (Fig. 6A). Carbonate crusts likely develop on horizontal surfaces by wicking of pore water along fibers of chrysotile. Nesquehonite-rich crusts are observed on the walls of the Porcupine Pit at Clinton Creek, but their extent appears limited to the surfaces of heavily fractured veins of cross-fiber chrysotile.

![Fig. 3. H2O-MgO-CO2 ternary plot (in mole fraction units) showing compositions of the hydrated magnesium carbonate minerals with lines of constant MgO/CO2 and contoured for mean atomic number, Z. Abbreviations: Art = arsinite, Bar = barringtonite, Brc = brucite, Dyp = dypingite, Grg = giorgiosite, Hmg = hydromagnesite, Lns = lansfordite, Mgs = magnesite, Nsq = nesquehonite.](https://example.com/filename.png)
Carbonate cements: Trenching to a depth of 2.0 m in the older, southwestern section of the tailings at Clinton Creek reveals horizons within the pile that are heavily cemented by hydromagnesite (Figs. 4D, 6B). This suggests a hydrological control on the development of these structures and that hydromagnesite may precipitate preferentially in some regions of the tailings pile. Samples of tailings, taken from heavily cemented horizons, can contain on the order of 10 wt percent hydromagnesite (Wilson et al., 2006). Less heavily cemented samples (e.g., the bulk sample 04CC1401) can contain on the order of 1 to 2 wt percent hydromagnesite (Wilson et al., 2006). Near the surface of the tailings pile, where samples are easier to extract, fine-grained, radiating crystals of dypingite and hydromagnesite are observed nucleating on the surfaces of serpentine grains, cementing them together (Fig. 5B). The cementation of milled particles and the delicate structure of the radiating cements indicate that precipitation of dypingite and hydromagnesite occurred after milling. Fine-grained crystals of dypingite and hydromagnesite commonly are seen filling gaps in serpentine grains in the damp regions below surface efflorescences. Similar textures are also observed in nesquehonite-rich crusts (Fig. 5C). These textures appear to be the result of silicate dissolution, as the grains cannot be reassembled without assuming a loss of material. It is also common to see

Fig. 4. Modes of occurrence of carbonate mineral precipitates at Clinton Creek and Cassiar. (A) and (B). Crusts on vertical surfaces (Clinton Creek). (C). Crust on horizontal surface (Clinton Creek). (D). Carbonate cement (Clinton Creek). (E). Thin coatings on cobbles (Cassiar). (F). Precipitates in the beds of runoff streams (Cassiar).
nesquehonite filling the cracks in heavily fractured grains of serpentine (Fig. 5D). These textures may represent infilling of fine fractures generated by freeze-thaw cycles or during milling. Fractures may have been forced open as nesquehonite crystallized. Although carbonate cements were observed at Clinton Creek, none were seen in the tailings at Cassiar.

Coatings on cobbles: Loose cobbles coated with dypingite are common in the tailings and in the waste rock near the base of the Porcupine Pit at Clinton Creek, whereas coatings of dypingite + hydromagnesite occur less commonly. Coatings may form by local dissolution of serpentine followed by direct reprecipitation of carbonate minerals or by nucleation from outflowing tailings water during the spring melt or rainfall events. Cobble coatings, when observed on a single grain surface, are typically on the underside, suggesting long contact with moisture from the tailings pile. Cobbles with more extensive coatings commonly bear several discrete patches of carbonate mineralization whereas others are coated almost entirely. On unstable slopes, cobbles are coated on multiple sides. In our interpretation, multiple or extensive coatings may form as cobbles are dislodged from their original sites of deposition and roll downhill (Fig. 6C). The previously uncoated surfaces receive increased exposure to moisture and develop coatings.

At Cassiar, cobbles are coated with aragonite ± calcite. Also, thin coatings of calcite + aragonite occur in the beds of ephemeral streams in the waste rock pile. A significant amount of the waste rock at Cassiar comes from the Precambrian to Mississippian limestone of the Sylvester allochthon (Wicks and O’Hanley, 1988). During rainfall events and the spring melt, calcite from this limestone unit is likely dissolved in runoff from the waste rock pile. Subsequently, calcite and aragonite would precipitate upon evaporation.

Stable carbon and oxygen isotopes

Stable carbon and oxygen isotope data were used to identify the sources for carbon dioxide in magnesium and calcium carbonate minerals. The δ¹³C data for specimens of carbonate minerals from Clinton Creek and Cassiar (Table 1, Fig. 7) vary from −9.41 to +14.36 per mil (VPDB), with δ¹⁸O values ranging from +12.22 to +28.40 per mil.
A relationship between mineralogy, mode of occurrence, and $\delta^{13}C$ is observed in the isotope data. Specimens of bedrock carbonate minerals from both sites yield $\delta^{13}C$ values in the range of –9.41 to –1.83 per mil and $\delta^{18}O$ values between +14.38 and +18.77 per mil. These specimens are mostly bedrock calcite and dolomite from Cassiar and magnesite from Clinton Creek. It is notable that cobble coatings of aragonite ± calcite and the stream-bed precipitate also have low values of $\delta^{13}C$ and $\delta^{18}O$, between –6.66 and +1.09 per mil and +12.22 and +15.71 per mil, respectively. There is no silicate mineral source for calcium at Cassiar, suggesting that recently precipitated aragonite and calcite formed from dissolved bedrock carbonate. Specimens of tailings containing hydromagnesite-rich cements (which are commonly contaminated by bedrock carbonate minerals) or minor amounts of hydrated magnesium carbonate minerals also tend to plot within the field defined by bedrock carbonate minerals. Such specimens contain a significant amount of bedrock magnesite ± pyroaurite, which could lead to lower values of $\delta^{13}C$.

Generally, dypingite- and hydromagnesite-rich cobble coatings, crusts, and near-surface cements are isotopically heavier than bedrock carbonate minerals, being characterized by $\delta^{13}C$ values between –1.51 and +10.02 per mil and $\delta^{18}O$ values between +17.53 and +28.40 per mil. Nesquehonite-rich crusts are further enriched in $^{13}C$, with $\delta^{13}C$ values in the range of 6.52 to 14.36 per mil and $\delta^{18}O$ values between 20.93 and 26.62 per mil.

The $\delta^{13}C$ and $\delta^{18}O$ data for specimens of mineral carbonates taken from three samples cemented with hydromagnesite ± dypingite (04CC1401, 05CC6, and 05CC8) vary from bedrock values for the bulk sample (04CC1401, which is lightly cemented and contaminated by bedrock magnesite) and the deepest sample of cement (05CC8, which is heavily cemented and contaminated by bedrock magnesite) to significantly higher values for the near-surface cement (05CC6). The latter sample, representing a depth interval from 0 to 20 cm, can be separated into zones; below the surface, a well-developed cement containing cobbles coated with isotopically lighter dypingite ± hydromagnesite and an efflorescent crust of isotopically heavier nesquehonite at the surface (Table 1, Fig. 7). Similarly, each of four samples from the surface of the tailings pile at Clinton Creek (04CC0701, 04CC0702, 04CC0703, and 04CC1001) could be divided into two aliquots: a surficial crust of nesquehonite and a cement of dypingite ± hydromagnesite from immediately below the crust. For these samples, the $\delta^{13}C$ of the efflorescent nesquehonite is between
1.83 and 9.07 per mil greater than that for the underlying cement (Table 1, Fig. 7). Two specimens of tailings from sample 04CC1401 were leached with 5 percent acetic acid in order to dissolve hydrated magnesium carbonate minerals while leaving bedrock magnesite intact. The δ13C data for leached specimens show that they are more depleted in 13C after treatment (Table 1), confirming the presence of bedrock contamination in specimens of bulk mineral carbonate from cemented tailings and that the hydrated magnesium carbonates in cements are isotopically distinct and heavier than the bedrock magnesite.

Radiocarbon

Radioactive 14C can be used as an indicator of modern precipitation of carbonate minerals. As a result of the artificial enrichment of atmospheric 14C caused by nuclear testing in the mid-twentieth century (the so-called “Bomb Effect”), minerals precipitated from modern atmospheric CO2 will contain a greater proportion of 14C than the 1950 AD reference standard. Radiocarbon dating relies upon the relative proportion of radiogenic 14C to stable 12C in a sample to be less than or equal to the reference ratio in order to obtain ages. Values of this ratio in excess of the reference can only be expressed as a fraction of the reference ratio (Stuiver and Polach, 1977).

Radiocarbon analysis of hydrated magnesium carbonate minerals from Clinton Creek and Cassiar provided values of F14C, the fraction of modern carbon (after Donahue et al., 1990; Reimer et al., 2004), ranging from 1.026 to 1.146 for cobble coatings and crusts (Table 2). These results suggest a postbomb (i.e., F14C > 1) date of formation and confirm that precipitation of hydrated magnesium carbonate minerals occurred after mining.

The negligible amount of 14C remaining in the magnesite sample from Clinton Creek (04CC0104) implies that it is bedrock carbonate having formed by silica-carbonate alteration of the serpentinite (Htoon, 1979). The aragonite ± calcite samples from Cassiar (04CA0101, 04CA0202-CA, and 04CA1001) gave conventional radiocarbon ages of 2 790 ± 40 years before present (yBP), 1 560 ± 40 yBP, and 9 840 ± 40 yBP, respectively. These conventional ages correspond to F14C values of 0.707, 0.823, and 0.294, respectively. The three samples of aragonite ± calcite were removed from the surfaces of
individual cobbles (04CA0101 and 04CA0202-CA) and a thin bed of waste rock (04CA1001) that were produced no earlier than 1953 when the Cassiar mine began operations. Despite the radiocarbon ages associated with the samples of calcium-carbonate minerals, field relationships require that their formation was recent.

Discussion

Mechanisms of carbonate formation

The modes in which hydrated magnesium carbonate minerals occur can be grouped into two classes: surface efflorescences (crusts on vertical and horizontal surfaces) and precipitates from damp environments (subsurface cements and cobble coatings). In general, nesquehonite efflorescences are found only in dry, surface conditions. It is generally accepted that efflorescences from damp environments (subsurface cements and cobble coatings) are at saturation with respect to carbonate minerals through evaporation; and at depth, within the tailings piles, where changes in local chemistry may bring about supersaturation and precipitation of carbonate minerals. Inputs of surface waters from nearby streams, rivers, and lakes will also have an impact on ground-water chemistry in mine tailings and may play a deciding role in whether carbonate minerals develop.

Surface area increases with the decrease in average grain size (e.g., White et al., 1996) that accompanies milling. The surface area of high-grade, milled chrysotile ore from the Cassiar mine varies from 13 to 50 m²/g (Thom and Dipple, 2005) and is much larger than that of unmilled serpentine. This increase in surface area may facilitate leaching of magnesium, contributing to accelerated precipitation of carbonate minerals. The concentrations of silica (SiO₂) in waters draining from the tailings piles at Clinton Creek and Cassiar are at saturation with chalcedony (Thom and Dipple, unpub. data). The silica released from serpentine minerals during dissolution may be precipitated as chalcedony (which may result in some amount of the quartz detected by XRD) or leached from the tailings piles. The frustules of diatoms, which are very common in the pit lake at Clinton Creek, represent another possible sink for silica at that site.

Sources and cycles for carbon

There are three potential sources for carbon in historical mine tailings, one or more of which may have been tapped during recent precipitation of carbonate minerals at Clinton Creek and Cassiar: (1) atmospheric carbon, (2) bedrock carbon from mined carbonate minerals, and (3) organic carbon from organic sediments, decay of local organic material, or microbial pathways.

Carbon and oxygen stable isotope data can be used to identify the source of carbon tapped in the precipitation of carbonate minerals. Values for δ¹³C in the range of about −10 to +1 per mil with δ¹⁸O between 10 and 20 per mil commonly reflect the isotopic compositions of metamorphic (bedrock) magnesite (e.g., Králík et al., 1989; Hansen, 2005). Samples for which the major carbonate phases include calcite, aragonite, dolomite, magnesite, and pyroxene give typical bedrock to organic signatures. Crusts, cobble coatings, and cements contaminated by bedrock carbonate plot within or near the region populated by samples of bedrock carbonate minerals.

The δ¹³C composition of hydrated magnesium carbonate minerals in equilibrium with atmospheric CO₂ is indicated in Figure 7. Mineral-gas fractionation factors and their dependence upon temperature were derived from Deines (2004),
using magnesite-\(\text{CO}_2\) fractionation factors as a proxy for fractionation between hydrated magnesium carbonates and \(\text{CO}_2\). Theoretical values of \(\delta^{13}\text{C}\) for hydrated magnesium carbonates were calculated assuming that atmospheric \(\text{CO}_2\) has a \(\delta^{13}\text{C}\) value of \(-8\) to \(-7\) per mil. Consideration of direct fractionation between magnesite and \(\text{CO}_2\) assumes that dissolved inorganic carbon in aqueous solution was in exchange equilibrium with the atmosphere (e.g., Dugan and Borthwick, 1986) and with hydrated magnesium carbonate minerals during precipitation (e.g., Chacko et al., 2001). The \(\delta^{13}\text{C}\) values of magnesite in equilibrium with atmospheric \(\text{CO}_2\) range between \(-6.5\) and \(-12.5\) per mil at \(0^\circ\) to \(40^\circ\) C, spanning the typical range of temperatures for liquid water at Clinton Creek and Cassiar. This range of values is broadly consistent with that employed by Léveillé et al. (2007) in a recent stable isotope study of calcium and magnesium carbonate minerals. Relatively high, positive values of \(\delta^{13}\text{C}\) and \(\delta^{18}\text{O}\) are typical of carbonate minerals that have formed at low temperature from atmospheric \(\text{CO}_2\) (e.g., Kralik et al., 1989; Zedef et al., 2000). Nesquehonite-rich crusts are interpreted as having developed in an evaporative environment with an atmospheric source of \(\text{CO}_2\), based on extreme enrichment in \(\text{C}_{\text{IC}}\) and \(\text{O}_{\text{IC}}\). Most data for nesquehonite-rich samples fall within the range of values explained by temperature-dependent fractionation of \(\text{CO}_2\) between \(0^\circ\) and \(40^\circ\) C.

Surface precipitates with comparatively low \(\delta^{13}\text{C}\) values, in the range of about 0 to 5 per mil, and with \(\delta^{18}\text{O}\) values between 18 and 24 per mil are documented by Knauth et al. (2003). They described depletion of \(\delta^{13}\text{C}\) in calcitic caliche on basaltic lava flows in the San Francisco volcanic field, Arizona U.S.A. Their study identified an isotopic distinction between pedogenic calcitic caliche that has developed in heavily weathered basaltic soils and subaerial calcitic caliche on recent (<900 yBP) basaltic flows. Pedogenic caliche has \(\delta^{13}\text{C}\) values of about \(-9\) to \(-4\) per mil and \(\delta^{18}\text{O}\) values of 13 to 32 per mil, whereas subaerial caliche is characterized by \(\delta^{13}\text{C}\) values of about 4 to 15 per mil and \(\delta^{18}\text{O}\) values of 24 to 32 per mil. Pedogenic caliches become isotopically heavier when a soil horizon experiences greater exposure to atmospheric \(\text{CO}_2\) and during times of significant water loss due to evaporation (Schlesinger et al., 1998). In such cases, covariation between \(\delta^{18}\text{O}\) and \(\delta^{13}\text{C}\) reflects a transition from subsurface environments that are dominated by microbial \(\text{CO}_2\) to surface conditions in which soil waters are increasingly exposed to atmospheric \(\text{CO}_2\) and subject to evaporative enrichment in \(\text{O}_{\text{IC}}\). Isotopically intermediate caliche develops within the soil horizon in contact with respired carbon and with less exposure to the atmosphere than subaerial caliche (Knauth et al., 2003). The same trend of covariation in \(\delta^{18}\text{O}\) and \(\delta^{13}\text{C}\) can be seen in our isotope data between subsurface dypingite and hydromagnesite and subaerially precipitated nesquehonite.

Samples of dypingite ± hydromagnesite that are uncontaminated by bedrock carbonate (Table 1) plot in a distinct region of \(\delta^{18}\text{O}\)-\(\delta^{13}\text{C}\) space that could reflect either a mixing line between atmospheric \(\text{CO}_2\) and bedrock sources of carbon or an atmospheric source with an “intermediate-caliche” or soil-like influence. In the former case, dissolution of bedrock carbonate minerals may play a role in the precipitation of dypingite and hydromagnesite. During dissolution of carbonate minerals in an open system, one mole of atmospheric \(\text{CO}_2\) is drawn into solution for each mole of bedrock mineral carbonate that is dissolved (Holland et al., 1964; Drever, 1982). Upon precipitation of carbonate minerals from this solution, one mole of \(\text{CO}_2\) is released back to the atmosphere. Repeated dissolution and reprecipitation of carbonate minerals could therefore lead to very efficient mixing of carbon from the bedrock and atmospheric reservoirs. Although such mineral precipitates may develop a mixed source for \(\text{CO}_2\), the original source for cations and \(\text{CO}_2\) is the bedrock. As a consequence of this recycling process, no net trapping of \(\text{CO}_2\) can occur without a silicate source for cations. Conversely, the formation of “intermediate caliche” would represent trapping of atmospheric \(\text{CO}_2\) either directly or indirectly through the biosphere.

The ambiguity in the \(\delta^{13}\text{C}\) data for dypingite and hydromagnesite can be resolved using radiogenic \(^{14}\text{C}\). Sample data fall within two isotopically distinct fields on a plot of \(\delta^{13}\text{C}\) vs. \(\delta^{14}\text{C}\) (Fig. 8). The first field contains two crusts of nesquehonite, one crust of dypingite, and one cobble coating of dypingite + hydromagnesite with minor contamination by bedrock carbonate, which collectively are characterized by \(\text{F}_{\text{IC}} > 1\) and \(\delta^{13}\text{C} \geq -1.53\) per mil. The second field is populated by bedrock with \(\text{F}_{\text{IC}} = 0\) and \(\delta^{13}\text{C}\) values of about \(-10\) to +1 per mil. Recently precipitated aragonite and calcite, with \(\text{F}_{\text{IC}} < 1\) and \(\delta^{13}\text{C} < 0\) per mil, span the range between these two populations.

Modern precipitates of aragonite and calcite contain more \(^{14}\text{C}\) than expected for bedrock carbonate. However, they are less enriched in \(^{14}\text{C}\) than the modern atmosphere, containing between 17.7 and 70.6 percent less radiocarbon than anticipated for postbomb carbonate minerals with an atmospheric source for \(\text{CO}_2\). Reprecipitated bedrock carbon will become more enriched in \(^{14}\text{C}\) and \(^{13}\text{C}\) as it draws \(\text{CO}_2\) from the atmosphere. This behavior is reflected in a mixing trend that is present between the bedrock field and the precipitates of calcium carbonate (Fig. 8). In contrast, hydrated magnesium carbonate minerals all have modern, atmospheric \(^{14}\text{C}\) signatures despite a wide spread in \(\delta^{13}\text{C}\) values. The modern \(^{14}\text{C}\) signature in the hydrated magnesium carbonate minerals is inconsistent with carbonate derived from repeated cycles of mineral dissolution and precipitation.

Natural samples of hydrated magnesium carbonate minerals from a playa deposit near Atlin, British Columbia, Canada (Fig. 1A) and precipitates from controlled microcosm experiments (Power et al., 2007) give rise to a strikingly similar trend in stable carbon and oxygen (Fig. 9). Results and methods are discussed in detail by Power et al. (2007). Nesquehonite- and dypingite-rich samples from the surface of the playa have \(\delta^{13}\text{C}\) and \(\delta^{18}\text{O}\) values of about 8 to 9 per mil and 24 to 26 per mil, respectively. Nesquehonite-rich precipitates from evaporative abiotic microcosm experiments, using water from the playa filtered to remove cyanobacteria, are similarly enriched. This enrichment can be explained by temperature-dependent fractionation of atmospheric \(\text{CO}_2\). Microcosm experiments using unfiltered water and benthic microbial mats from an adjacent wetland and samples of natural microbial mats produced dypingite ± hydromagnesite with \(\delta^{13}\text{C}\) values in the range of about 4 to 7 per mil and \(\delta^{18}\text{O}\) values of 16 to 19 per mil. These results are inconsistent with temperature-dependent fractionation of atmospheric \(\text{CO}_2\), having significantly lower values of \(\delta^{13}\text{C}\) than anticipated for carbonate
precipitation at observed temperatures between about 2°C and 25°C. This result suggests that microbial carbon (potentially sourced from the modern atmosphere) may have been integrated into the crystal structures of dypingite and hydromagnesite, giving rise to lower values for δ¹³C. In this system, stable oxygen and carbon isotope data clearly distinguish hydrated magnesium carbonate minerals that have been precipitated in abiotic (i.e., nesquehonite) and soil-like, microbial environments (i.e., dypingite and hydromagnesite).

Modern precipitation of hydromagnesite has also been documented in the hydromagnesite playas at Salda Göli, western Turkey (Braithwaite and Zedef, 1996). Explanations for this occurrence include microbial influence or perhaps salinity and the Mg/Ca ionic ratio of lake water (Renaut and Long, 1989). These environmental controls may also be active in mine tailings environments. In these natural systems, it is probable that depletion of δ¹³C in hydrated magnesium carbonate minerals represents a combination of atmospheric (caliche) and microbially mediated precipitation of carbonates. Thus, the differences in mineralogy and isotopic signatures observed in precipitates of hydrated magnesium carbonates at Clinton Creek and Cassiar likely reflect at least two separate pathways for formation: in an evaporative, abiotic environment on the surface of the tailings, and in a subsurface environment that is more akin to precipitation of soil carbonates.

**Trapping carbon dioxide**

Hydrated magnesium carbonate minerals are highly stoichiometric, making it possible to estimate the amount of CO₂ bound within them using Rietveld refinement results for XRD data (Rietveld, 1969). We previously used bulk samples from Clinton Creek and Cassiar to estimate the amount of CO₂ stored in secondary magnesium carbonate minerals in the tailings piles (Wilson et al., 2006). We did not detect hydrated magnesium carbonate minerals above a detection limit of 1 wt percent in the bulk sample from Cassiar (03CA1601). Assuming that the lightly cemented bulk sample, 04CC1401, represents a lower limit to the abundance of hydrated magnesium, a minimum of 82,000 t of CO₂ is bound in the tailings pile at Clinton Creek. Sample 04CC1401, which contains 2.2 wt percent hydromagnesite, was taken from the lower terraces of the southern lobe of the tailings pile at Clinton Creek (Wilson et al., 2006). This implies that the cementation observed in this sample began to form no earlier than the 1990s when the terraces were constructed as
a measure to improve slope stability. Well-developed hydro-magnesite cements occur farther up the southern lobe (e.g., sample 05CC8), where cementation may have begun in the mid-1970s. Sample 05CC8 contains 8.7 wt percent hydro-magnesite (Wilson et al., 2006), which suggests that serpentinite in this sample may have been carbonated at an average rate of 0.3 wt percent/year. Wilson et al. (2006) gave a best estimate of 164,000 t of atmospheric CO2 bound in hydrated magnesium carbonate minerals at Clinton Creek. Over the course of 26 years, from the date the mine was closed to the time of sampling, this amounts to an average rate of sequestration of approximately 6,300 t of atmospheric CO2/year.

Carbon dioxide sequestration at Clinton Creek and Cassiar is the result of a passive process of mineral weathering. Our findings suggest that procedures for tailings management could be modified to increase uptake of CO2. Potentially, this could be done by optimizing the surface area of tailings grains or seeding tailings storage facilities with micro-organisms such as cyanobacteria. Large-scale implementation of accelerated CO2 trapping and storage by mining operations could help to reduce their net greenhouse gas emissions by trapping CO2 directly from the atmosphere. Reactions that transform silicate minerals to carbonate minerals are exothermic (e.g., Lackner, 2003) and are accompanied by significant increases in solid volume (Hansen et al., 2005), the effects of which on mine tailings are not known. As such, it is important to consider that the input of energy caused by carbonation reactions could induce undesirable chemical reactions and the volume increase could lead to structural instability in aboveground tailings piles. However, it is notable that DeJong et al. (2006) have demonstrated that biomineralization of calcite in the voids between mineral grains can increase shear strength of geologic samples, thereby enhancing load-bearing capacity and slope stability. In this regard, CO2 sequestration in mine tailings may provide an added benefit at some mines.

Carbon dioxide sequestration is determined by rock type and gangue mineralogy. Using dunite for mineral carbonation could consume approximately 0.6 times the mass of the rock in CO2 (Lackner et al., 1995). Serpentinite and basalt can trap and store 0.4 and 0.1 times their mass in CO2, respectively (Lackner et al., 1995). Under acidic conditions, dissolution reactions for the Mg silicate minerals in these rock types proceed most rapidly for olivine group minerals, then serpentine minerals, and more slowly for pyroxene group minerals (Palandri and Kharaka, 2004). Therefore, sequestration of atmospheric CO2 is not necessarily restricted to tailings from chrysotile deposits but may be applied, albeit with varying reaction rates and efficiency, to mine residues from other ultramafic- and mafic-hosted deposit types. Recent geochemical modeling by Rollo and Jamieson (2006) suggests that atmospheric CO2 may be sequestered into magnesium
carbonate minerals at the kimberlite-hosted EKATI Diamond mine, Northwest Territories, Canada. Deposit types that produce suitable tailings include, but are not limited to, Cu-Ni-PGE deposits hosted by dunite, serpentinite, and gabbro-norite; serpentinite-hosted chrysotile; diamondiferous kimberlite pipes, and podiform chromite deposits in layered mafic intrusions. The only mineralogical prerequisites to efficient CO₂ sequestration in mine tailings are high abundance of Mg silicate minerals and low abundance of acid-generating sulfide minerals.

The annual sequestration capacity of a large mine can exceed its annual emissions of greenhouse gases. For example, the Mount Keith Nickel mine, which is hosted in the serpentinized komatiite of the Agnew-Wiluna greenstone belt, Western Australia (Grguric, 2003), produces approximately 11 Mt of serpentine-rich tailings and emits approximately 350,000 t of greenhouse gases each year, given as CO₂-equivalent emissions (BHP Billiton, 2005, http://hsecreport.bhp billiton.com/wmc/2004/performance/mko/data/index.htm). These tailings have the capacity to bind approximately 4 Mt of CO₂ each year, which exceeds the annual emissions of the mine by more than a factor of ten.

Mineral carbonation in mine tailings represents a readily available and viable implementation of the carbon sequestration process. Wilson et al. (2006) provided a procedure for measuring trapping of CO₂ in serpentine-rich mine tailings and the results presented here represent a protocol that can be used to fingerprint atmospheric CO₂. Together, these methods can be used to confirm and quantify CO₂ sequestration in ultramafic and mafic mine tailings.

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