

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 (CO_2) 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)₂·4H₂O], 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 δ^{13} C values between 6.52 and 14.36 per mil, δ^{18} O 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 δ^{13} C values between -1.51 and +10.02 per mil, δ^{18} O values between +17.53 and +28.40 per mil, and $F^{14}C$ 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, CO_2 , directly from the atmosphere. Combined use of $\delta^{13}C$, $\delta^{18}O$, and $F^{14}C$ data has been applied effectively as a tool for verifying and monitoring sequestration of atmospheric CO_2 within mine tailings. A number of other deposit types produce tailings suitable for CO_2 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 gas 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; Broecker, 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 in mine tailings because the milling process leads to dramatic increases in reactive surface area (e.g., White et al., 1996; Molson et al., 2005). Carbonate minerals are known to precipitate 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 (Paktunc 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 CO_2 sequestration (Hansen et al., 2005; Power et al., 2007) and passive methods for sequestering CO_2 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 [MgCO₃·3H₂O], dypingite [Mg₅(CO₃)₄(OH)₂·5H₂O], hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O], and lansfordite [MgCO₃·5H₂O] precipitate in the tailings as a natural consequence of silicate weath-

ering. 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 serpentinized 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

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FIG. 1. Location of Clinton Creek, YT, and Cassiar, BC (A). The northern and southern lobes of the tailings pile at Clinton Creek are marked in (B) (trees for scale). The tailings at Cassiar are shown in C (road for scale).

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 39year 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 smearmounted 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 θ -2 θ diffractometer over a range of 3° to 70° 2 θ with each scan taking 55 min. Minerals were identified with reference to the ICDD PDF-4 database using the program DIFFRAC^{plus} EVA (Bruker AXS, 2004, Karlsruhe, Germany). The normal-focus Cu X-ray tube was operated at 40 kV and 40 mA. In order to

Sample no.	Mode	Major carbonate phases ¹	Minor carbonate or hydrotalcite phases ¹	δ ¹³ C (%c, VPDB)	$2\sigma_{\delta^{13}\mathrm{C}}$ (%oo, VPDB)	δ ¹⁸ O((%o, VSMOW)	$2\sigma_{\delta}^{18}$ O (%co, VSMOW)	NAD 27 Easting ²	NAD 27 Northing ²	Sample depth ³ (m)
03CC01B 03CC0401B	Crust Cobble	Nsq Dyp	Dyp, Cal, Mgs, Pyr Mgs, Pyr	14.36 8.39	0.09	25.70 18.18	0.06 0.13	0514038 0513856	7147794 7147841	Surface 0.2
03CC0601B 04CC0104	Cobble Bedrock	Dyp, Hmg Møs	Mgs, Pyr Pvr	4.00 -7.48	0.20 0.07	19.52 14.99	0.12 0.10	0513667 0513461	7147842 7146632	0.8 Surface
04CC0105	Cobble, bedrock contaminated	Dyp, Hmg, Pvr		-1.53	0.21	19.13	0.13	0513461	7146632	Surface
04CC0106	Crust	Nsq	Dyp	7.61	0.14	20.93	0.14	0513461	7146632	Surface
04CC010/-CA 04CC0108-CA	Cobble Cobble	Arg Arg	Pvr	0.39 1.04	0.11	15.04	0.16	0513461 0513461	7146632	Surface
04CC0109	Cobble	Dyp	Pyr	2.29	0.19	20.61	0.29	0513461	7146632	Surface
04CC0201A-1	Crust	Nsq	Dyp, Lns, Pyr	10.55	0.24	25.01 20.10	0.20	0514038	7147794	Surface
04CC0201A-2 ⁴ 04CC0201A-CA ⁴	Crust Crust, cobble 	Nsq	Dyp, Lns, Fyr Dyp, Lns, Pyr	11.11 12.48	0.10	23.19 24.68	0.07	0514038	7147794 7147794	Surface
04CC0202A	Crust	Dyp		10.02	0.23	28.40	0.14	0514038	7147794	Surface
04CC0202B-1	Crust	Dyp		4.77	0.14	26.06	0.17	0514038	7147794	Surface
04CC0202B-2	Crust	Dyp		5.66	0.75	25.73 17.05	0.49	0514038	7147794	Surface
04CC0401-CA	beurock Cobble, bedrock	Dyp	Doi Mgs, Pyr	-1.09	0.08	17.53	0.12	0514037	7147790	Surface
04CC0601A	contaminated Crust	Dyp	Mgs, Pyr	4.85	0.15	20.80	0.12	0513981	7147861	Surface
04CC0601B-CA	Cobble	Hmg, Dyp?	Pyr	2.41	0.19	22.79	0.22	0513981	7147861	Surface
04CC0601B-CB	Cobble	Dyp		6.61	0.11	20.81	0.11	0513981	7147861	Surface
04CC0701	Crust Crust	Nsq	Dyp, Hmg, Pyr Dyn, Hmg, Pyr	10.63 10.95	0.08	21.95 01.86	0.06 0.16	0513954 0513954	7147895	Surface
04CC0701-N	Crust, atop cement	Nsq	Dyp, Hmg, Ly1 Dyp, Hmg, Pyr	8.64	0.23	23.35	0.21	0513954	7147895	Surface
04CC0701-DH	Cement	Dyp, Hmg	Nsq, Pyr	5.85	0.18	22.55	0.12	0513954	7147895	Surface
04CC0702	Crust	Nsq	Dyp, Hmg	8.03 2 20	0.17	23.32	0.15	0513954	7147895	Surface
04CC0702-N 04CC0702-DH	Urust, atop cement Cement	Nsq Dvp. Hmg	Uур, нтg Nsa	0.52 4.69	0.10	23.20 22.18	0.16 0.16	0513954	7147895	Surface
04CC0703	Crust	Nsq	Dyp, Hmg	13.32	0.30	23.71	0.21	0513954	7147895	Surface
04CC0703	Crust	Nsq	Dyp, Hmg	13.60	0.15	23.58	0.09	0513954	7147895	Surface
04CC0703-N 04CC0703-DH	Crust, atop cement Cement	Nsq Hmơ	Dyp, Hmg Dyn Nso	13.60 4.53	01.0	22.37 18 23	010	0513954 0513954	7147895 7147895	Surface
04CC0901	Crust	Dyp, Pyr	har dia	6.68	0.18	28.24	0.17	0513915	7148145	Surface
04CC1001	Crust	Nsq	Dyp, Hmg, Mgs	11.43	0.28	24.62	0.21	0513969	7148156	Surface
04CC1001-N	Crust, atop cement	Nsq Dum Hing	Dyp, Hmg, Mgs Nea, Mae	12.57 7.64	0.09 0.95	24.89 99 43	0.13	0513969 0513060	7148156 7148156	Surface
04CC1101	Crinst	Ner Ner	Dvn Hma	12.68	0150	23.80	0.1.9	0513980	7148156	Surface
04CC1201	Crust	Dvp, Hmg	Mgs	3.79	0.26	22.37	0.25	0514011	7147999	Surface
04CC1301	Bedrock	Mgs	Dol	-4.40	0.11	15.78	0.05	0514052	7147936	Surface
04CC1301	Bedrock	Mgs	Dol	4.27	0.07	15.56	0.06	0514052	7147936	Surface
04CC1401-1	Cement, bed- rock contam.	Hmg, Mgs	Pyr	67.G-	01.0	10.12	0.13	6014100	/14//38	c.0>
04CC1401-2 ⁴	Cement, bed-	Hmg, Mgs	Pyr	-5.33	0.08	15.28	0.26	0514109	7147738	<0.5
04CC1401-	Cement, bed-	Hmg, Mgs	\mathbf{Pyr}	-0.98	0.13	15.13	0.11	0514109	7147738	<0.5
bulkcarb [*] 04CC1401-	rock contam. Cement, cobble 	Hmg, Dyp?	Mgs, Pyr	-4.57	0.06	16.87	0.11	0514109	7147738	<0.5
cobblecarb [*]	within, contam?									

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TABLE 1. Mineralogical and Isotopic Data for Carbonate Samples from Mine Wastes at Clinton Creek (CC) and Cassiar (CA)

(Cont.)	
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TABLE	

Sample no.	Mode	Major carbonate phases ¹	Minor carbonate or hydrotalcite phases ¹	$\delta^{13}C$ (%co, VPDB)	$2\sigma_{\delta}^{13}$ C $(\%o, \text{VPDB})$	δ ¹⁸ O (%oo, VSMOW)	$2\sigma_{\delta^{18}O}$ (%co, VSMOW)	NAD 27 Easting ²	NAD 27 Northing ²	Sample depth ³ (m)
04CC1401-CA ⁴	Cement, cobble	Hmg, Dyp?	Mgs, Pyr	2.17	0.07	15.34	0.10	0514109	7147738	<0.5
04CC1401-CA ⁴	within Cement, cobble within	Hmg, Dyp?	Mgs, Pyr	2.16	0.18	15.42	0.24	0514109	7147738	<0.5
04CC1401-CB4	within Cement, cobble within	Hmg, Dyp?	Mgs, Pyr	2.12	0.08	14.90	0.12	0514109	7147738	<0.5
04CC1401-40	Cement, bed-	Mgs	Pyr	-5.60	0.26	14.43	0.23	0514109	7147738	<0.5
04CC1401-5 h ⁶	rock component Cement, bed- wol ^s commonent	Mgs	Pyr	-6.00	0.19	14.44	0.30	0514109	7147738	<0.5
05CC6-surface ⁴	Crust, atop	Nsq, Dyp	Pyr	9.98	0.17	23.40	0.12	0514038	7147832	<0.2
05CC6-bottom ⁴ 05CC6-CA ⁴	Cement Cement, cobble t.t.:	Dyp Dyp	Pyr Pyr	5.88 4.41	0.09 0.07	20.42 21.83	$0.20 \\ 0.12$	0514038 0514038	7147832 7147832	<0.2 <0.2
05CC6-CB ⁴	Within Cement, cobble	Dyp	Pyr	6.85	0.20	26.27	0.18	0514038	7147832	<0.2
05CC8-1	Cement, bed-	Hmg, Mgs	Pyr	-7.74	0.19	12.85	0.15	0513570	7147900	<2.0
05CC8-24	rock contain. Cement, bed- work contam	Hmg, Mgs	Pyr	-7.72	0.10	13.02	0.15	0513570	7147900	<2.0
	rock contam.	V		555	0 10	10.01	0 66	0120000	0121233	U. U.
04CA0101 04CA0202-CA	Cobble Cobble	Arg Cal. Dol		-0.00 -2.50	0.21	12.83 12.83	0.00 0.21	0452685	6621120 6271599	Surface
04CA0202-CB	Cobble	Cal, Arg		-0.42	0.13	13.99	0.13	0452685	6571599	Surface
04CA0202-CC	Cobble	Cal, Dol		0.57	0.48	15.17	0.33	0452685	6571599	Surface
04CA0202-CC	Cobble	Cal, Dol		1.09 0.44	0.25	15.45 15.62	0.18	0452685 0459685	6571599 6571500	Surface
04CA0202-CD	Cobble	Cal. Arg		1.08	0.08	12.71	10.0	0452685	00/1299 6571599	Surface
04CA0301-CA	Cobble	Cal	Mhc	-5.50	0.19	12.22	0.18	0452936	6571578	Surface
04CA0601	Crust	Nsq	Dyp	8.55	0.14	26.62	0.19	0452548	6571969	Surface
04CA1001 03CA1601	Stream Bedrock. within	Cal Cal. Dol	Arg	3.46 1.83	0.17 0.23	12.75 18.77	0.18 0.30	0452518 0452197	6577648 6572049	Surface <1.0
03CA1601	bulk tailings Bedrock, within	Cal, Dol		-9.41	0.29	14.38	0.26	0452197	6572049	<1.0
Internal Std 1 ⁷	DULK CALILLES			1.79	0.12	13.79	0.32			
Internal Std 27				4.42	0.07	19.35	0.21			
Internal Std 3'				-0.05 7	01.0	0.00	0.28			
NBS 197 NBS 197				00.c- 1.88	0.06	28.37	0.17 0.32			
¹ Arg = aragoni ² Clinton Creek ³ Depth of sam ⁴ Denotes that { ⁵ Sample immen ⁶ Sample immen ⁷ Average values	te, Cal = calcite, Dol = is in NAD 27 zone 07 pling for "Surface" saml grains were picked und reed in 5% acetic acid s reed in 5% acetic acid s is for UBC in-house star	dolomite, $Dyp = \frac{d}{dr}$ and Cassiar is in N ples varies from 0 t er a binocular micr er a binocular micr olution for 40 min olution for 5 h to d ndards for analyses	vpingite, Hmg = hyd AD 27 zone 09 o 0.2 m o cscope to maintain h to dissolve hydrated ma issolve hydrated ma done in this study; a	romagnesite, Lns = igh sample purity magnesium carbonate ccepted values of ð	= lansfordite, Mg tate minerals minerals 1:3C (%c) and d ¹⁸	s = magnesite, M O (%c) are Interr	hc = monohydroca al Std 1, 1.842, 13	lcite, Nsq = ness. .644; Internal St	quehonite, Pyr = d 2, 4.353, 19.38(pyroaurite), Internal Std
$3, -0.692, \overline{3.826}$				4						

 $CO_2 \ \textit{FIXATION IN MINE TAILINGS AT CLINTON CREEK \circlearrowright CASSIAR \ \textit{CHRYSOTILE DEPOSITS, CANADA}$



FIG. 2. Sampling locations within the tailings pile at Clinton Creek, YT. Sampling locations are identified by the year and a location number (e.g., 4–7 indicates location 04CC07 from which samples 04CC0701, 04CC0702, and 04CC0703 were collected). Approximate UTM coordinates are given for two corners of the map (NAD 27, zone 07).

detect hydrated magnesium carbonate minerals at low abundance, a scanning step of $0.04^{\circ} 2\theta$ and a counting time of 40 s/step over a range of 12° to $17^{\circ} 2\theta$ 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 23°C, 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 $200 \, \mu g$ 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 δ^{13} C compositions are given relative to VPDB and the δ^{18} O compositions are relative to VSMOW. The external precision (1σ) for isotopic analyses was <0.1 per mil δ^{13} C and <0.2 per mil δ^{18} O, 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 δ^{18} O 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 δ^{18} O values reported in this study may reflect the oxygen isotope composition of both carbonate and structurally bound water within these minerals.

Radiocarbon fingerprinting

Radiocarbon contents were measured for four samples of hydrated magnesium carbonate minerals from Clinton Creek and Cassiar, three samples of calcium carbonate minerals from Cassiar, and one sample of bedrock magnesite from Clinton Creek (Table 2). Radiocarbon data were obtained with Accelerator Mass Spectrometric (AMS) dating by Beta Analytic Radiocarbon Dating Laboratory in Miami, Florida U.S.A.

Results

Tailings mineral content

Tailings from Clinton Creek contain kaolinite-serpentine group minerals, primarily chrysotile, with minor magnetite, calcite, dolomite, magnesite, quartz, clinochlore, and pyroaurite $[Mg_6Fe^{3+2}(CO_3)(OH)_{16}\cdot 4H_2O]$. The hydrated magnesium carbonate minerals nesquehonite [MgCO₃·3H₂O], dypingite $[Mg_5(CO_3)_4(OH)_2 \cdot 5H_2\hat{O}]$, hydromagnesite $[Mg_5(\dot{CO}_3)_4]$ (OH)₂·4H₂O], and more rarely lansfordite [MgCO₃·5H₂O] 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 [MgSO₄·7H₂O] and hexahydrite [MgSO₄·6H₂O]. 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 present in the carbonaceous argillite that underlies the Clinton Creek valley (Htoon, 1979) and disseminated sulfides in the serpentinite. Given that the hydration states of sulfate minerals are sensitive to changes in temperature and relative humidity (e.g., Chou and Seal, 2003; Peterson and Grant, 2005; Chipera and Vaniman, 2007; Chou and Seal, 2007), the relative abundance of hexahydrite to epsomite measured in the laboratory may not reflect abundance in the field.

Tailings at Cassiar are composed primarily of kaolinite-serpentine group minerals (predominantly chrysotile) with 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 (MgCO₃) with variable waters of hydration. Three such minerals are known to occur in nature: barringtonite [MgCO3·2H2O] (Nashar, 1965), nesquehonite [MgCO₃·3H₂O] (Stephan and Mac-Gillavry, 1972), and lansfordite $[MgCO_3 \cdot 5\hat{H}_2O]$ (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 $(OH)_2$. Artinite $[Mg_2(CO_3)(OH)_2 \cdot 3H_2O]$ is the only known member of this group (Akao and Iwai, 1977a; Canterford et al., 1984). Three minerals with the chemical formula $Mg_5(CO_3)_4(OH)_2 \cdot xH_2O$ 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_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_2 on a per-cation basis. This can be demonstrated with the H₂O-MgO-CO₂ 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 CO₂ of 1 per formula unit, whereas for dypingite and hydromagnesite the ratio is 5/4. It should be preferable to trap CO_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, 1965; Canterford et al., 1984). As a result, sequestration of CO₂ in magnesite optimizes both the amount of bound carbon and the thermodynamic stability of trapping at $p_{CO_2} \leq 1$ atm and at temperatures between 0° and 60°C (Königsberger et al., 1999).

Sample no. ¹	Measured ¹⁴ C Age (in pMC ² or yBP)	Conventional ¹⁴ C age (in yBP)	$\delta^{13}\mathrm{C}^3$ (‰)	$F^{14}C$	$\sigma_{ m F}{}^{14}{ m c}$
	I J				
03CC01B	$119.1 \pm 0.6 \text{ pMC}$		8.0	1.114	0.006
04CC0104	>40 000 yBP		-8.3	< 0.003	
04CC0105	$107.6 \pm 0.5 \text{ pMC}$		-1.7	1.026	0.005
04CC0601A	$121.7 \pm 0.6 \mathrm{pMC}$		4.3	1.146	0.006
04CA0101	$2,380 \pm 40 \text{ yBP}$	$2,790 \pm 40 \text{ yBP}$	-0.3	0.707	0.004
04CA0202-CA	$1,170 \pm 40 \text{ yBP}$	$1,560 \pm 40 \text{ yBP}$	-1.4	0.823	0.004
04CA0601	$114.3 \pm 0.5 \text{ pMC}$		6.2	1.072	0.005
04CA1001	$9,550 \pm 40 \text{ yBP}$	$9,840 \pm 40 \text{ yBP}$	-7.2	0.294	0.002

¹CA in the sample name denotes Cassiar and CC denotes Clinton Creek

² pMC denotes percent modern carbon relative to the AD 1950 reference standard

³ δ^{13} C values from AMS were used to correct F¹⁴C (fraction of modern carbon) data for machine fractionation



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, \overline{Z} . Abbreviations: Art = artinite, Bar = barringtonite, Brc = brucite, Dyp = dypingite, Grg = giorgiosite, Hmg = hydromagnesite, Lns = lansfordite, Mgs = magnesite, Nsq = nesquehonite.

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 cobble coatings are abundant in the tailings at Clinton Creek. Hydrated magnesium carbonate crusts and calcium-carbonate cobble coatings and stream linings 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 \pm hydromagnesite is seen throughout the crust samples with nesquehonite forming subaerially over grains of serpentine cemented with dypingite \pm hydromagnesite (Fig. 5A). The nesquehonite zone in crusts contains few clasts. The dypingite \pm 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 \pm hydromagnesite to dypingite \pm nesquehonite \pm 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. 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).

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 nesquehoniterich 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. 5. Backscattered electron (BSE) images of horizontal crust sample 04CC0702 (A), (C), and (D) and vertical crust sample 04CC0201B (B). (A). Nesquehonite at the surface of sample 04CC0702 with dypingite + hydromagnesite nucleating on serpentine. (B). Rosettes of dypingite nucleating on grains of serpentine at depth in sample 04CC0201B. (C). Nesquehonite infilling dissolution fissures in a grain of serpentine near the surface of crust sample 04CC0702. (D). Nesquehonite filling cracks in a fractured grain of serpentine. D = dypingite, H = hydromagnesite, M = magnetite, N = nesquehonite, S = serpentine.

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 \pm 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 δ^{13} C 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 δ^{18} O values ranging from +12.22 to +28.40 per mil



FIG. 6. Summary diagram of mechanisms of formation for three modes of occurrence of secondary carbonate minerals: (A) nesquehonite-rich efflorescences on vertical and horizontal surfaces, (B) grains of serpentine cemented by dypingite \pm hydromagnesite below the surface of the tailings pile, and (C) coatings of dypingite \pm hydromagnesite on grains of serpentine. Details of mineral occurrences are illustrated in the corresponding boxes. Small grains of serpentine are not shown in the main figure for simplicity but are included in boxes A, B, and C.

(VSMOW). A relationship between mineralogy, mode of occurrence, and δ^{13} C is observed in the isotope data. Specimens of bedrock carbonate minerals from both sites vield δ^{13} C values in the range of -9.41 to -1.83 per mil and δ^{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 \pm calcite and the stream-bed precipitate also have low values of δ^{13} C and δ^{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 \pm pyroaurite, which could lead to lower values of δ^{13} C.

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

The δ^{13} C and δ^{18} O data for specimens of mineral carbonates taken from three samples cemented with hydromagnesite \pm 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 \pm hydromagnesite from immediately below the crust. For these samples, the δ^{13} C of the efflorescent neguebonite is between



FIG. 7. Stable oxygen and carbon isotope data for different modes of occurrence and mineralogy of secondary carbonates. Numbers indicate reservoirs and letters indicate processes by which carbon is cycled. Temperature effect on fractionation of carbon is calculated after the method of Deines (2004) for magnesite. The temperature scale corresponds to the typical range of nonfreezing temperatures at Clinton Creek and Cassiar. Analyses from a single sample are joined by a solid or dashed line. Data labeled "Ca-carbonate coatings" include cobble coatings, a streambed precipitate, and a coating on chrysotile fibers. In most cases, 2σ measurement errors are smaller than the symbols employed.

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 δ^{13} C 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 $F^{14}C$, 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., $F^{14}C > 1$) 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 \pm calcite samples from Cassiar (04CA0101, 04CA0202-CA, and 04CA1001) gave conventional radiocarbon ages of 2 790 \pm 40 years before present (yBP), 1 560 \pm 40 yBP, and 9 840 \pm 40 yBP, respectively. These conventional ages correspond to F¹⁴C values of 0.707, 0.823, and 0.294, respectively. The three samples of aragonite \pm 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 calciumcarbonate 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 and well documented that precipitation of nesquehonite can be induced by evaporation (e.g., Suzuki and Ito, 1974; Jull et al., 1988; Grady et al., 1989; McLean et al., 1997; Kloprogge et al., 2003; Power et al., 2007). Our observations of mineral occurrence and texture in addition to highly enriched values of δ^{18} O for nesquehonite (discussed below) are consistent with evaporative precipitation. Dypingite and hydromagnesite are observed in damp environments on the sheltered faces of loose cobbles, as loosely aggregated cement between silt to cobble-sized grains of serpentine at shallow depth, usually below a surficial cap of nesquehonite, and deeper within the tailings as a hardened cement. Acero et al. (2007) used column experiments to show that efflorescent crusts of sulfate minerals can form rapidly by evaporation at the surface of unsaturated mine tailings during the initial stage of drying. They note that the presence of an efflorescent crust caused a reduction in porosity and permeability, and as a consequence the rate of evaporation within the column slowed to half the rate for a column with no surficial crust. Based on our field observations, similar conditions of evaporation may apply in chrysotile mine tailings. It is likely that nesquehonite formed by evaporation rapidly produces a crust, which slows evaporation from the tailings below. Furthermore, excavation within the tailings pile at Clinton Creek shows that precipitation of dypingite and hydromagnesite extends to a depth of at least 2.0 m. Consequently, evaporation is not necessarily the driving factor behind precipitation of dypingite and hydromagnesite.

The much lower abundance of hydrated magnesium carbonate minerals at Cassiar than at Clinton Creek may be the result of less favorable hydrologic conditions within the tailings pile. At Clinton Creek, water may be channelled through regions of higher permeability within the hummocky terrane of the tailings pile, collecting at topographic lows. Carbonation may be limited at Cassiar because the tailings are contained within a steeply sloping, compact pile. The interior of the tailings pile is frozen year round to within several meters of the surface (E. Hatzl, pers. commun.), which potentially hastens the runoff of rainwater through the tailings and limits the amount of magnesium silicate material available for dissolution to the upper meters of the pile. Confirmation of this hypothesis awaits detailed hydrological studies of the two tailings piles.

Weathering of bedrock silicates by dissolution leads to precipitation of carbonate minerals under conditions of atmospheric pressure and temperature. This is one of the most

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significant mechanisms for geochemical exchange of CO2 between the atmosphere and the surficial environment (Schwartzman and Volk, 1989; Berner, 1990). Weathering of ultramafic mine tailings, like those at Clinton Creek and Cassiar, is likely to occur by the following series of reactions (after Berner, 1990): (1) atmospheric carbon dioxide is dissolved in meteoric or surface water as bicarbonate; (2) bicarbonate acid is consumed by silicate mineral dissolution, which releases cations into solution; and (3) carbonate minerals precipitate from bicarbonate and available cations from dissolved bedrock. Carbonate mineralization occurs in two environments: at the surface of the tailings piles, where tailings water arrives by preferential flow or capillary action, and becomes supersaturated 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 serpentinite. 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 δ^{13} C in the range of about –10 to +1 per mil with δ^{16} O between 10 and 20 per mil commonly reflect the isotopic compositions of metamorphic (bedrock) magnesite (e.g., Kralik et al., 1989; Hansen, 2005). Samples for which the major carbonate phases include calcite, aragonite, dolomite, magnesite, and pyroaurite 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 δ^{13} C 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-CO₂ fractionation factors as a proxy for fractionation between hydrated magnesium carbonates and CO₂. Theoretical values of δ^{13} C for hydrated magnesium carbonates were calculated assuming that atmospheric CO₂ has a δ^{13} C value of -8 to -7 per mil. Consideration of direct fractionation between magnesite and CO₂ 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 δ^{13} C values of magnesite in equilibrium with atmospheric CO₂ range between ~6.5 and ~12.5 per mil at 0° to 40°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 δ^{13} C and δ^{18} O are typical of carbonate minerals that have formed at low temperature from atmospheric CO₂ (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 CO₂, based on extreme enrichment in ¹³C and ¹⁸O. Most data for nesquehonite-rich samples fall within the range of values explained by temperature-dependent fractionation of CO₂ between 0° and 40°C.

Surface precipitates with comparatively low δ^{13} C values, in the range of about 0 to 5 per mil, and with δ^{18} O values between 18 and 24 per mil are documented by Knauth et al. (2003). They described depletion of δ^{13} 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 δ^{13} C values of about –9 to –4 per mil and δ^{18} O values of 13 to 32 per mil, whereas subaerial caliche is characterized by δ^{13} C values of about 4 to 15 per mil and δ^{18} O values of 24 to 32 per mil. Pedogenic caliches become isotopically heavier when a soil horizon experiences greater exposure to atmospheric CO2 and during times of significant water loss due to evaporation (Schlesinger et al., 1998). In such cases, covariation between δ^{18} O and δ^{13} C reflects a transition from subsurface environments that are dominated by microbial CO₂ to surface conditions in which soil waters are increasingly exposed to atmospheric CO_2 and subject to evaporative enrichment in ¹⁸O. 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 δ^{18} O and δ^{13} C can be seen in our isotope data between subsurface dypingite and hydromagnesite and subaerially precipitated nesquehonite.

Samples of dypingite \pm hydromagnesite that are uncontaminated by bedrock carbonate (Table 1) plot in a distinct region of δ^{18} O- δ^{13} C space that could reflect either a mixing line between atmospheric CO₂ 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 CO₂ 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 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 CO_2 , the original source for cations and CO_2 is the bedrock. As a consequence of this recycling process, no net trapping of CO_2 can occur without a silicate source for cations. Conversely, the formation of "intermediate caliche" would represent trapping of atmospheric CO_2 either directly or indirectly through the biosphere.

The ambiguity in the δ^{13} C data for dypingite and hydromagnesite can be resolved using radiogenic ¹⁴C. Sample data fall within two isotopically distinct fields on a plot of δ^{13} C versus F¹⁴C (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 F¹⁴C >1 and δ^{13} C \geq -1.53 per mil. The second field is populated by bedrock with F¹⁴C = 0 and δ^{13} C values of about -10 to +1 per mil. Recently precipitated aragonite and calcite, with F¹⁴C <1 and δ^{13} C <0 per mil, span the range between these two populations.

Modern precipitates of aragonite and calcite contain more ¹⁴C than expected for bedrock carbonate. However, they are less enriched in ¹⁴C 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 CO₂. Reprecipitated bedrock carbon will become more enriched in ¹⁴C and ¹³C as it draws CO₂ 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 ¹⁴C signature in the hydrated magnesium carbonate minerals all spread in δ^{13} C values. The modern ¹⁴C 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 δ^{13} C and δ^{18} 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 temperaturedependent fractionation of atmospheric CO₂. Microcosm experiments using unfiltered water and benthic microbial mats from an adjacent wetland and samples of natural microbial mats produced dypingite \pm hydromagnesite with δ^{13} C values in the range of about 4 to 7 per mil and δ^{18} O values of 16 to 19 per mil. These results are inconsistent with temperaturedependent fractionation of atmospheric CO₂, having significantly lower values of δ^{13} C than anticipated for carbonate



FIG. 8. Plot of δ^{13} C vs. F¹⁴C (fraction of modern carbon) for seven samples from Cassiar and Clinton Creek. Numbers indicate reservoirs and letters indicate processes by which carbon is cycled. The hydrated magnesium carbonate minerals do not fall on the mixing line between the bedrock and atmospheric carbonate reservoirs, indicating that the precipitation of these minerals is not driven by the dissolution of bedrock carbonate minerals. Values for δ^{13} C were determined in the Pacific Centre for Isotopic and Geochemical Research at the University of British Columbia. Values for F¹⁴C are corrected for machine fractionation using AMS results for δ^{13} C. Data labelled "Ca-carbonate coatings" are for one cobble coating, a streambed precipitate, and a coating on chrysotile fibers. In most cases, measurement errors are smaller than the symbols employed.

precipitation at observed temperatures between about 2° 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 δ^{13} C. 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 Gölü, 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 ¹³C 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 carbonate minerals, 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



FIG. 9. Stable oxygen and carbon isotope data (from Power et al., 2007) for natural samples of carbonate minerals from Atlin, British Columbia, and carbonate precipitates from field-based microcosms and laboratory-based experiments. Numbers indicate reservoirs and letters indicate processes by which carbon is cycled. Temperature effect on fractionation of carbon is calculated after the method of Deines (2004) for magnesite. The temperature scale corresponds to the typical range of nonfreezing temperatures at Atlin.

a measure to improve slope stability. Well-developed hydromagnesite 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 hydromagnesite (Wilson et al., 2006), which suggests that serpentine 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, CO_2 sequestration in mine tailings may provide an added benefit at some mines.

The sequestration capacity of mine tailings 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 CO_2 (Lackner et al., 1995). Serpentinite and basalt can trap and store 0.4 and 0.1 times their mass in CO_2 , 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 CO_2 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 CO_2 -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 CO_2 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 CO_2 in serpentine-rich mine tailings and the results presented here represent a protocol that can be used to fingerprint atmospheric CO_2 . Together, these methods can be used to confirm and quantify CO_2 sequestration in ultramafic and mafic mine tailings.

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