Verifying and quantifying carbon fixation in minerals from serpentine-rich mine tailings using the Rietveld method with X-ray powder diffraction data

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ABSTRACT

Most carbon on Earth is bound within minerals, and increasing the uptake of atmospheric carbon dioxide into minerals may reduce the greenhouse gas content of the atmosphere. We document carbon disposal through the mineralization of mine tailings at Clinton Creek, Yukon Territory, and Cassiar, British Columbia. We confirm crystallographic binding of carbon in these tailings and quantify carbon dioxide uptake using quantitative phase analysis with the Rietveld method for X-ray powder diffraction data. Planar disorder in the structures of the kaolinite-serpentine group minerals makes Rietveld refinements of X-ray powder diffraction data for serpentinites problematic. Using structureless pattern fitting and with the addition of a known quantity of a well-crystallized material, the problem of structural disorder is overcome by considering the serpentine minerals as amorphous phases. We test the accuracy and precision of this refinement method using synthetic serpentine-rich mine tailings of known composition. Estimates of the abundance of hydrated magnesium carbonates in these tailings have a precision of approximately 5% relative for mineral species present in amounts greater than 10 wt%. Precise estimates of carbonate mineral content and crystallographically bound atmospheric CO_2 are made for samples of serpentine-rich tailings from Clinton Creek and Cassiar. Results for mine tailings are also compared to mineralogically similar samples from a carbonate playa at Atlin, British Columbia. The potential for decomposition of metastable hydrated magnesium carbonate phases to geologically stable magnesite may represent long-term stability of the products of mineral sequestration in mine tailings.

Keywords: Carbon disposal, mineral sequestration, quantitative phase analysis, Rietveld method, Pawley method, X-ray powder diffraction, serpentinite, mine tailings, carbonation, order-disorder

INTRODUCTION

The release of anthropogenic greenhouse gases (e.g., CO_2, CH_4, N_2O, and SO_2) into the atmosphere has been linked to environmental degradation and global climate change (Houghton et al. 2001). Production of atmospheric pollutants, CO_2 in particular, is associated with the combustion of fossil fuels—which accounts for as much as 90% of greenhouse gas emissions in the past 20 years (Houghton et al. 2001). It is expected that development and implementation of new carbonless sources of energy will require another 50 to 100 years (e.g., Lackner 2003; Pacala and Socolow 2004), during which time fossil fuels will see continued widespread use (Lackner 2003). Current models require that atmospheric CO_2 levels be stabilized on this timescale to curtail irreversible climate change (Pacala and Socolow 2004). Carbon dioxide sequestration or disposal is an essential component in the international effort to stabilize CO_2 emissions. Of the proposed sequestration schemes, mineral sequestration represents the most geologically stable and environmentally benign method for carbon disposal (Lackner et al. 1995). Mineral sequestration mimics natural silicate weathering processes that bind CO_2 in

carbonate minerals. An estimated 87% of the Earth's carbon, or 9×10^{16} tons, is bound in carbonate minerals (Sundquist 1993). Kump et al. (2000) have predicted that, given a time scale of 10^6 years, carbonate minerals will be the ultimate sink for most anthropogenic CO_2. Mineral sequestration seeks to accelerate this natural process.

Carbonate minerals in mine tailings are of general interest for their role in suppressing acid generation (e.g., Jambor and Blowes 1991; Blowes et al. 1998). Carbonate precipitates were observed in tailings from the Kidd Creek copper-zinc mine near Timmins, Ontario, Canada, in 2000 (Al et al. 2000). Similar carbonation phenomena have been observed in tailings from the Lower Williams Lake uranium mine near Elliot Lake, Ontario (Paktunc and Davé 2002) and in tailings from the chrysotile mines at Thetford, Québec (Huot et al. 2003), Clinton Creek, Yukon Territory (Wilson et al. 2003) and Cassiar, British Columbia (Wilson et al. 2005). The carbon bound in many tailings environments may not have an atmospheric origin, but our unpublished isotopic data indicate that the millions of tons of serpentinite tailings from the abandoned chrysotile mining operations at Clinton Creek, Yukon Territory, and Cassiar, British Columbia, Canada (Fig. 1) are actively fixing atmospheric CO_2 in mineral carbonates. The magnesium-carbonate minerals dypingite, hydromagnesite,
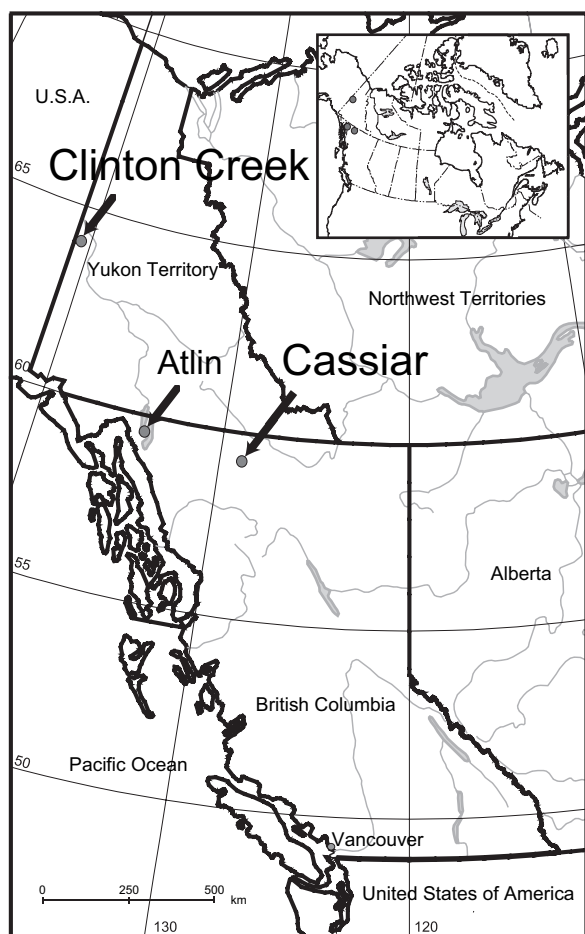
FIGURE 1. Locations of Clinton Creek, Yukon Territory, Cassiar, British Columbia, and Atlin, British Columbia.

nesquehonite, and more rarely, lansfordite, are forming in situ at the surface of the tailings piles at these historical mine sites.

The hydrated magnesium carbonate minerals found at Cassiar and Clinton Creek are of interest as they have potential for long-term storage of greenhouse gases (Lackner et al. 1995; Lackner 2003). CO_2 futures or credit trading could also provide a revenue stream if enhanced sequestration were to be implemented in historical or active mining operations. In January 2006, futures of CO_2 sequestration traded for US$ 1.75 per ton ($/tCO_2$) at the Chicago Climate Exchange (2006), while long-term forecasts approach US$ 100/tCO_2 (Ciorba et al. 2001). In the European Union, emissions allowances currently trade for approximately €23/tCO_2 through Carbon Pool Europe (Climate Corporation 2006). In this paper, we discuss the mineralogy of magnesium carbonates at Clinton Creek and Cassiar and develop a quantitative method for carbonate determination in serpentine-rich mine tailings. The isotopic data and implications for fingerprinting the source of carbon will be published separately.

Carbonate crusts are observed in mine tailings within months of tailings deposition, indicating that mineral sequestration in chrysotile tailings can be a rapid process (Huot et al. 2003). The

rapidity and extent of carbonate formation in mine tailings is almost certainly linked to the vast increases in silicate mineral surface area that are a direct result of mineral processing. Acceleration of the carbonation process in historical and active mining operations could be used to render large mining operations, with high-magnesium and low-sulfur tailings, CO_2-neutral and may help to reduce the greenhouse gas content of the atmosphere on a global scale.

Quantification of the amount of atmospheric carbon sequestered in geologic samples from Clinton Creek and Cassiar gives an estimate for the sequestration capacity of ultramafic mine tailings in general and provides a framework for the development of standard policies relating to the trading of CO_2 emissions for enhanced mineral sequestration at mine sites. Standard bulk geochemical measures of CO_2 abundance cannot be used to quantify mineral trapping as they cannot distinguish between carbonate phases, nor can they discriminate between the sources of carbon—bedrock, atmospheric, or industrial. Stable and radiogenic fingerprinting of carbon can be used to identify which carbonate minerals in a geological sample are the sinks for atmospheric, industrial, or bedrock carbon. Quantitative phase analysis using the Rietveld method provides a measure of the weight-percent contribution of each carbonate mineral in a sample. From this measure, the amount of CO_2 stored in well-crystallized, atmosphere-derived carbonate minerals can be determined. Quantitative phase analysis is therefore essential to verification and quantification of carbon disposal via mineral sequestration.

To develop and test a practical method of quantitative phase analysis for serpentinites, a series of synthetic serpentinite mine tailings of typical and known composition were prepared by weighing and mixing pure mineral constituents. At issue here is that kaolinite-serpentine group minerals generally exhibit planar disorder and thus cannot be fitted by diffraction patterns calculated from the ideal structures, which is the basis of the Rietveld method (Rietveld 1967, 1969). A previous study made use of a combined reference intensity ratio and Rietveld method to measure serpentine abundance (Gualtieri and Artioli 1995). If, however, the experimental pattern of the disordered phase can be fitted independently by some means and if a known weight of a spike of an extraneous phase is added to the sample, the amount of serpentine in the sample could be measured as if it were an amorphous phase. Spikes have been used successfully as internal standards for largely amorphous materials (e.g., Gualtieri 2000; De La Torre et al. 2001; Orlhac et al. 2001), but have not been applied to disordered crystalline phases. We seek to develop a standardless method that is applicable to many geological samples containing a disordered mineral phase. For this study, we used annealed CaF_2 as a spike and fitted the diffraction pattern of the disordered kaolinite-serpentine group mineral with the Pawley method (Pawley 1981). This procedure was subsequently applied to samples of tailings from the mines at Cassiar and Clinton Creek. We propose that the Rietveld method with X-ray powder diffraction data can be used to accurately quantify the amount of carbonation occurring in serpentinite mine tailings.

SAMPLE LOCALITIES

The Clinton Creek chrysotile deposit is a partially carbonate-altered serpentinized peridotite (Htoon 1979). The Clinton Creek Mine, situated near Dawson City, Yukon Territory, operated from 1967 to 1978 (Htoon 1979). A total of 16 Mt of chrysotile ore were extracted from the four open pit mines at Clinton Creek during this 11 year period. In addition to the ore, 60 Mt of waste rock and 10 Mt of tailings were produced as a by-product of the mining process (EMAN-North 2003). Tailings materials are characterized by short-fiber chrysotile and serpentinite cobbles containing massive serpentine and minor amounts of magnetite, calcite, dolomite, magnesite, quartz, clinochlore, and pyroaurite. Carbonate mineral formation occurs in four distinct modes at Clinton Creek: disseminated hydromagnesite precipitates that cement grains in bulk samples of tailings, crusts on vertical surfaces (composed of nesquehonite, dypingite, hydromagnesite, and occasional lansfordite), carbonate spires on horizontal tailings surfaces (composed of nesquehonite, dypingite, and hydromagnesite and caused by wicking-up of pore fluids), and as thin crusts of dypingite with occasional hydromagnesite (<1 mm in thickness) on serpentinite cobbles (Fig. 2). Carbonate crusts are abundant and easily recognized by their off-white color, coloform habit, and reactivity with dilute hydrochloric acid (10% HCl).

The chrysotile deposit at Cassiar, British Columbia, forms part of a serpentinized harzburgite tectonite (Wicks and O'Hanley 1988). Cassiar is located approximately 130 km north of Dease Lake, British Columbia. During the 39-year operational lifetime of the mine, from 1953 to 1992, 17 Mt of mine tailings were produced. These tailings were stored outdoors in an elongate pile. Beginning in 1993, the mine underwent a six-year process of renovation and revitalization. By January 2000 commercial production of chrysotile had been renewed. Mining proceeded until December 25, 2000 when the mill was severely damaged by fire (MINFILE 2005). Tailings are composed primarily of short-fiber chrysotile with cobbles of massive serpentine with minor magnetite, clinochlore, and occasional quartz and carbonates. The carbonate minerals nesquehonite and dypingite form crusts on vertical tailings surfaces at Cassiar.

EXPERIMENTAL METHOD

Sample preparation and data collection

Twenty-four mixtures of pure mineral samples were prepared to simulate serpentinite mine tailings. Minerals commonly found in the tailings at Clinton Creek and Cassiar were used: kaolinite-serpentine group (antigorite and chrysotile), magnetite, quartz, calcite, dolomite, magnesite, and hydromagnesite. Synthetic
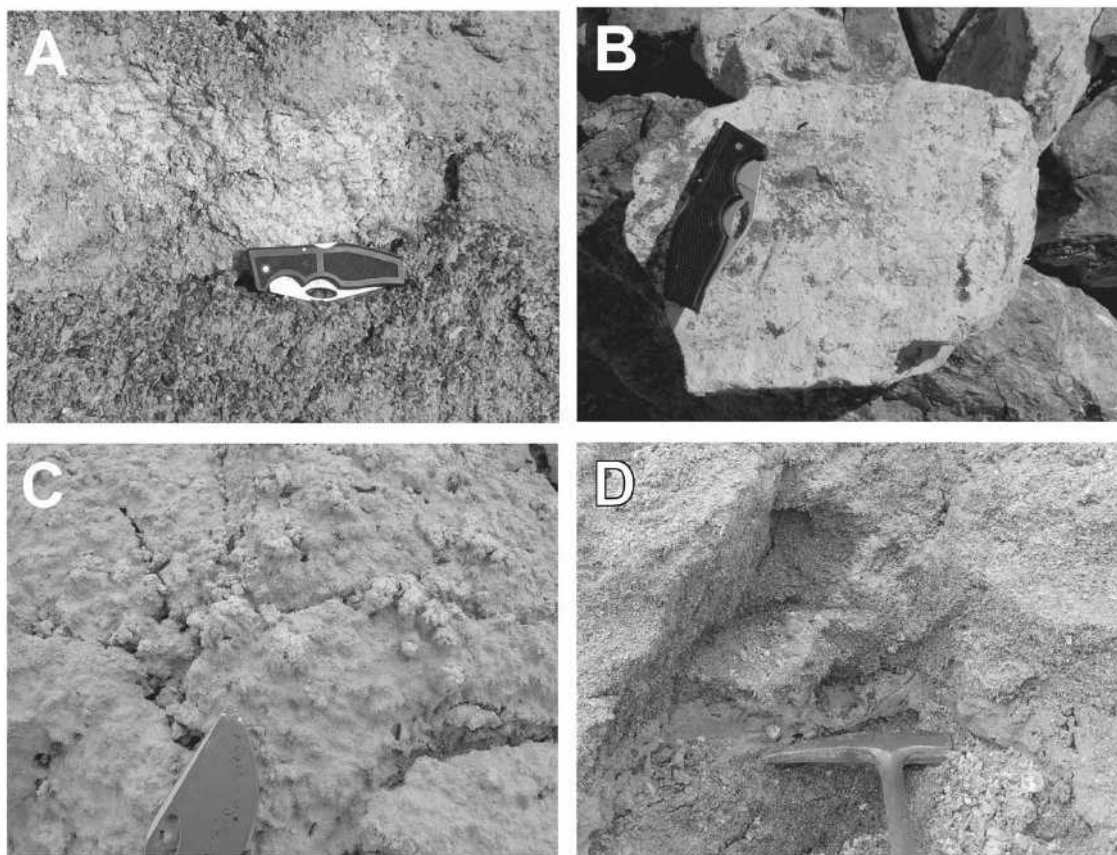

FIGURE 2. Modes in which hydrated magnesium carbonate minerals have been identified at Clinton Creek, Yukon Territory and Cassiar, British Columbia: (**A**) nesquehonite/dypingite crust from Cassiar, (**B**) dypingite on cobble from Clinton Creek, (**C**) nesquehonite/dypingite/hydromagnesite spires from Clinton Creek, and (**D**) disseminated cement of hydromagnesite from Clinton Creek.

serpentinite samples were prepared according to the method outlined in Appendix A. Natural and synthetic mixtures were ground under anhydrous ethanol with synthetic corundum grinding elements in a McCrone mill to reduce the mean particle size of the samples to micrometer or sub-micrometer level and to ensure homogenization. Samples were dried at room temperature and disaggregated with an agate mortar and pestle.

In addition, two specimens of tailings from Cassiar and eight specimens from Clinton Creek were prepared to assess the method on real mine tailings. Two samples from a hydromagnesia playa in Atlin, British Columbia, were also included to demonstrate Rietveld refinements on carbonate-rich samples that lack serpentine. Samples were left in a drying hood for 48 hours and were then homogenized mechanically with a spatula. A 5-kg aliquot was taken from a bulk sample (weighing in excess of 20 kg) from each locality. These large aliquots were dried and homogenized prior to division into smaller, more workable aliquots for X-ray powder diffraction. An aliquot of each sample was powdered using a tungsten carbide ringmill. A 10 wt% spike of annealed CaF_2 was added to 3.00 g of each sample of tailings and the mixture was ground under ethanol for 10 minutes in the McCrone mill. Knowledge of the mean grain size of the narrow size distribution afforded by use of the mill allows for the use of the Brindley (1945) correction for microabsorption in Rietveld refinements.

Samples were mounted in a back-loading aluminum cavity holder of the design described by Raudsepp and Pani (2003). Preferred orientation of inequant crystallites was minimized by covering the top of the cavity with a sheet of ground glass and loading powdered samples against the roughened surface. To further inhibit preferred orientation of crystallites, particularly those of chrysotile, the surface of each sample was serrated with a razor blade along two axes: one parallel to the axis of the diffractometer goniometer and the second in the perpendicular direction. X-ray powder-diffraction data were collected on a Siemens D5000 θ-2θ diffractometer with a step size of 0.04°2θ and counting time of 1s/step over a range of 3–90°2θ. The normal-focus Cu X-ray tube was operated at 40 kV and 40 mA.

Rietveld refinement and quantitative phase analysis

Rietveld refinements were done with refinement software Topas Version 3 (Bruker AXS 2004) using the fundamental parameters approach (Cheary and Coelho 1992). Sources of crystal structure data for the constituent phases are listed in Table 1. To avoid the unpredictable effect of planar disorder on the diffraction patterns of the serpentine minerals, the Pawley method (Pawley 1981) was used to extract peak intensities independently of atomic scattering from the powder diffraction patterns of pure chrysotile and antigorite. The extracted intensities with the appropriate space groups and cell dimensions of antigorite and chrysotile were subsequently used to fit the serpentine component in the powder diffraction patterns of the mixtures as a peak phase using the Pawley method. As the relative intensities of peaks during Pawley refinement are not constrained by atomic scattering, the relative intensities of the peaks for the serpentine were initially held constant to avoid the interference of serpentine peaks with peaks from the other phases. After the correct fitting of these peaks, the relative intensities of the serpentine peaks were refined. To provide an estimate of the combined abundance of serpentine, both antigorite and chrysotile structures were used as a basis to fit serpentine in samples containing both phases.

Backgrounds for samples containing chrysotile, or both chrysotile and antigorite, were modeled using third-order Chebychev polynomials with an additional $1/x$ term to aid in the fitting of the background curve at low angles of diffraction. Second-order Chebychev polynomials were adequate to model the background for samples in which antigorite was the only serpentine phase. The zero error, Lorentzian crystallite size and strain, and cell parameters were refined for all phases. Preferred orientation of phases other than serpentine was corrected for using the method of March and Dollase (March 1932; Dollase 1986). Contamination from the corundum grinding elements of the McCrone mill accounted for less than 1% of most samples and was not treated as an additional phase in refinements.

All Rietveld refinements were done assuming a 10 wt% spike. To model the effects that weighing error for the spike may have had on results, refined abundances were recalculated using an exaggerated weighing error of ±10% relative. Refinement results were recalculated and renormalized for each sample using the method of Gualtieri (2000), assuming spike abundances of 9 and 11%. As observed by Gualtieri (2000), the amorphous phase is underestimated with the assumption of an increased abundance of the spike phase. The 10% overestimate of the spike leads to an underestimate of the disordered phase, while a 10% underestimate leads to a general overestimate. The converse holds for all other phases in the mixture, as the refined weights are compelled to increase by the normalization criterion (Fig. 3).

TABLE 1. Sources of crystal-structure data for Rietveld refinement

Mineral	Source
Antigorite	Uehara (1998)
Calcite	Maslen et al. (1995)
Chrysotile	Falini et al. (2004)
Dolomite	Ross and Reeder (1992)
Fluorite	Batchelder and Simmons (1964)
Hydromagnesite	Akao and Iwai (1977)
Magnesite	Markgraf and Reeder (1985)
Magnetite	Tsukimura et al. (1997)
Nesquehonite	Giester et al. (2000)
Palygorskite	Chisholm (1992)
Pyroaurite	Olowe (1995)
Quartz	Glinnemann et al. (1992)

To correct for microabsorption, a Brindley radius of 2.5 µm was used for all phases (Brindley 1945). Scanning electron microscopy showed that the radii of carbonate particles were seldom greater than 2.5 µm, while particles of magnetite and quartz frequently exceeded this value. The radii of approximately one-half of magnetite and quartz particles are within the range 3.0 to 5.0 µm. As expected, the harder minerals are more resistant to particle-size reduction via milling. Serpentine particles, chrysotile in particular, were significantly larger than those for other phases with most particle radii falling within the range of 5.0–7.5 µm. The serpentines were the only phases in the mixtures to be ground for less than 17 minutes, as grinding times in excess of 10 minutes were found to cause deterioration of the crystal structure. Laser-diffraction based particle-size analysis gave average particle diameters of 3.40 µm (r = 1.70 µm) and 4.00 µm (r = 2.00 µm) for the antigorite stock mixture ("A1") and the 50 wt% antigorite sample ("AMIX50"), respectively. Based on observations in the scanning electron microscope, the results of the laser-diffraction based analyses, and the fact that an accurate estimate of particle size for each phase is not practical, a Brindley radius of 2.5 µm was taken to be representative of a typical mixture.

RESULTS AND DISCUSSION

Synthetic mine tailings

Results of quantitative phase analysis for the synthetic serpentine mine tailings are displayed in Table 2 and Figures 3 and 4. Measured abundance vs. the nominal abundance for most phases deviates slightly from the ideal 1:1 trend (Fig. 4). The deviation results at least in part from the large increase in relative error for the refinements of minor phases. Raudsepp et al. (1999) and Dipple et al. (2002) report that for the conditions of data collection used in our laboratory, the relative error increases rapidly for measurements of concentrations below 6 wt%. However, although the relative error is high for phases of less than approximately 6 wt%, the absolute errors are small (Fig. 5). The relationship between absolute and relative errors is typical for measurements of hydromagnesite (Fig. 6). The relative error in the amount of hydromagnesite increases with decreasing abundance, but the corresponding absolute error is well within the range for estimates of mineral binding of CO_2. A 5% relative error can be expected on estimates of hydromagnesite content for abundances greater than 10 wt%. Relative error is expected to increase as hydromagnesite abundance approaches the 1 wt% detection limit for our X-ray data. A relative error of 10 to 15% is expected for hydromagnesite abundances less than 10 wt%. Thus, precise and accurate estimates of the crystalline component for hydrated magnesium carbonate abundance can be made for samples containing disordered mineral phases such as kaolinite-serpentine group minerals. Note that the type of serpentine used in the weighed mixtures has no significant effect on the results of the Rietveld refinement (Figs. 4a and
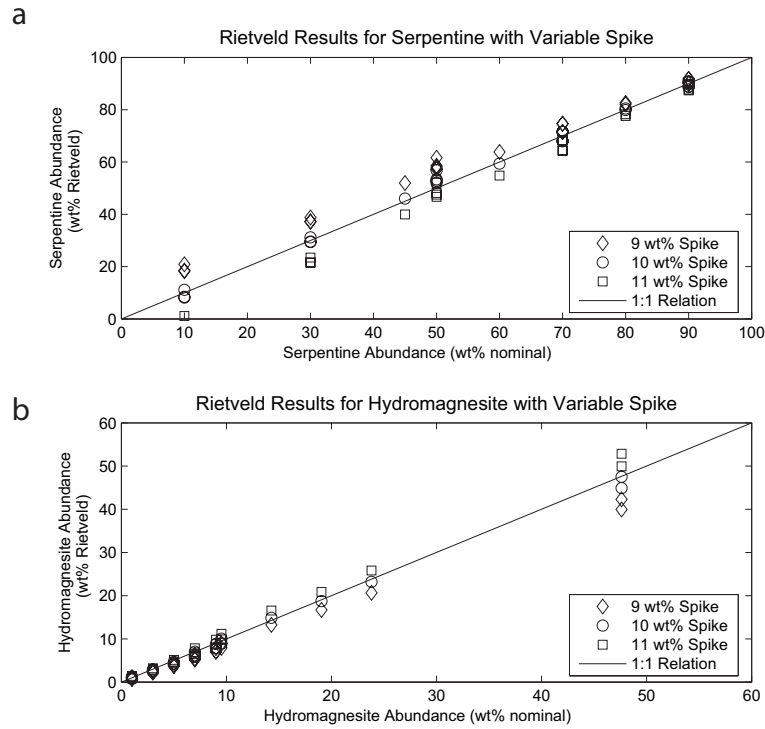
FIGURE 3. Abundance of mineral phase from Rietveld refinement vs. nominal abundance for three different concentrations of the fluorite spike (9, 10, and 11% CaF_2): (**a**) serpentine; (**b**) hydromagnesite.
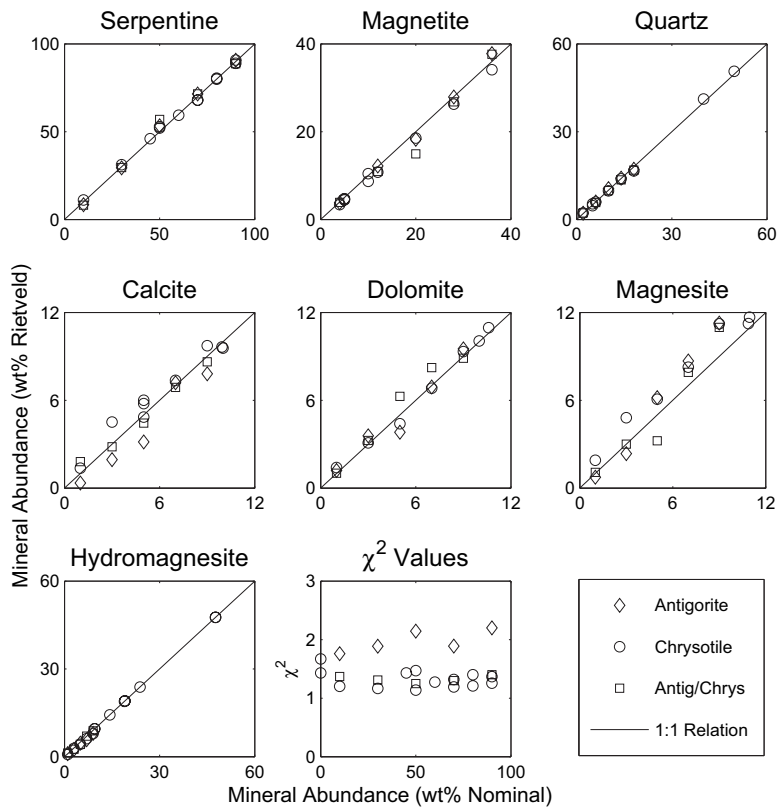

FIGURE 4. Modal abundances from Rietveld refinement vs. nominal abundances in synthetic serpentinites.

TABLE 2. Results of quantitative phase analysis of synthetic serpentinite mine tailings

Phase (wt%)	AMIX10	AMIX30	AMIX50	AMIX70	AMIX90	CMIX10	CMIX30	CMIX50	CMIX70	CMIX90	ACMIX10	ACMIX30
Chrysotile	8.5	29.4	53.4	71.5	90.7	11.1	31.2	52.1	67.9	88.9	8.2	29.6
difference	1.5	0.6	3.4	1.5	0.7	1.1	1.2	2.1	2.1	1.1	1.8	0.4
Magnetite	37.8	27.9	18.3	12.2	3.8	34.1	26.3	18.5	10.8	3.4	37.6	26.8
difference	1.8	0.1	1.7	0.2	0.2	1.9	1.7	1.5	1.2	0.6	1.6	1.2
Quartz	17.2	14.1	10.6	6.0	2.2	16.6	13.9	9.8	6.0	2.3	16.9	13.5
difference	0.8	0.1	0.6	0.0	0.2	1.4	0.1	0.2	0.0	0.3	1.1	0.5
Calcite	7.8	7.2	3.2	1.9	0.3	9.7	7.4	4.9	4.5	1.4	8.6	6.9
difference	1.2	0.2	1.8	1.1	0.7	0.7	0.4	0.1	1.5	0.4	0.4	0.1
Dolomite	9.5	6.9	3.8	3.6	1.2	9.3	6.8	4.4	3.1	1.4	8.9	8.2
difference	0.5	0.1	1.2	0.6	0.2	0.3	0.2	0.6	0.1	0.4	0.1	1.2
Magnesite	11.3	8.7	6.2	2.4	0.7	11.2	8.3	6.1	4.8	1.9	11.0	7.9
difference	1.8	1.4	0.9	0.8	0.3	1.8	0.9	0.8	1.7	0.9	1.5	0.6
Hydromagnesite	8.0	5.8	4.6	2.5	1.1	7.9	6.2	4.3	2.9	0.8	8.8	7.0
difference	0.6	0.8	0.1	0.4	0.1	0.7	0.5	0.5	0.0	0.2	0.3	0.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
χ^2*	1.8	1.9	2.1	1.9	2.2	1.2	1.2	1.1	1.2	1.3	1.4	1.3
R_{wp}†	8.1	8.2	8.3	7.1	6.8	9.5	8.4	7.7	7.3	7.0	8.2	7.0

* χ^2 is the reduced chi-squared statistic for the least-squares fit.
† R_{wp} is the weighted pattern index, a function of the least-squares residual.

5a). We do not know why the abundance of hydromagnesite is consistently underestimated at low abundances. It was initially thought that the original hydromagnesite used in the mixtures was not entirely crystalline; however, Rietveld refinements of pure hydromagnesite do not show evidence of significant deterioration of crystallinity with increased grinding time during preparation of the mixtures. These underestimates may be an artifact of the Pawley fitting procedure or the result of undetected amorphous content in the CaF_2 spike. As such, there is no need for concern that estimates of carbonate abundance are being compromised by deterioration of crystallinity due to grinding.

Accurate determination of carbonate mineral abundances in synthetic geological samples allows for the implementation of the Rietveld method as a standard for assessing carbonate precipitation in mine tailings. The advantage imparted by the use of the Rietveld method over chemical methods is that it can be used to confirm crystallographic trapping of CO_2. Based on the results for refinements of synthetic samples, an absolute error of 3% or less can be expected on estimates of modal abundances for carbonate phases present in natural samples of mine tailings in abundances greater than 10 wt%. A maximum relative error of 15% can be expected on estimates for carbonate phases present in abundances less than 10 wt%. Refinement results for modal abundance can be used to measure the amount of carbon dioxide that is crystallographically bound in hydrated magnesium carbonate minerals. Application of this method to representative samples of serpentine-rich bulk tailings provides an estimate of the amount of mineral carbonation occurring per kilogram of tailings material. As such, the amount of carbon dioxide bound in a tailings pile can be estimated. This procedure can also be applied to the measurement of acid neutralization potential of carbonate minerals in acid-generating mine tailings containing disordered mineral phases.

Application of this method to other geologic systems should be approached with due caution. The Rietveld method for X-ray powder diffraction can only be used indirectly as a tool for elemental analysis. As such, estimation of bound CO_2 is only feasible for phases with minor solid solution. Successful characterization of the tailings from Cassiar and Clinton Creek is due in part to the negligible solid solution to which the hydrated magnesium carbonate minerals are subject. This method does not account for additional amorphous phases and cannot be used to quantify more than one disordered phase per sample. Because our goal is to quantify the abundance of a crystalline phase (hydromagnesite), the presence of multiple amorphous phases is not of concern. The use of the Pawley method for complicated mineral phases may cause low-abundance mineral phases to be underestimated in refinements. Misestimates of disordered phases are likely to occur at low abundance (i.e., <5 wt%) due to limitations in the fundamental parameters approach and preferred orientation corrections, and the way in which complex Pawley phases usurp peaks from other phases. The effect of grinding time on the crystallinity of ordered phases should be considered prior to application of this method to any geological or synthetic samples.

Natural mine tailings

Two samples of mine tailings from Cassiar, British Columbia (04CA0601 and 03CA1601), and six samples from Clinton Creek, Yukon Territory (04CC0702, 04CC0703, 04CC1001, 04CC1201, 04CC1401, and 05CC8), were analyzed using the method developed for synthetic serpentinites. Samples 03CA1601 and 04CC1401 are samples of bulk tailings. Samples 04CA0601, 04CC0703, 04CC1001, and 04CC1201 are from vertical carbonate crusts. 04CC0702 is a carbonate spire and 05CC8 is a sample containing disseminated carbonate cement. In addition, two samples from a hydromagnesite playa in Atlin, British Columbia, were analyzed as an example of natural hydrated magnesium carbonate samples lacking serpentine. The results of quantitative phase analysis are given in Table 3.

Bulk samples from Clinton Creek and Cassiar contain serpentine in excess of 80 wt% (Table 3 and Fig. 7). Where present, dolomite, magnesite, quartz, and pyroaurite constitute minor components; magnetite concentrations range from 5.1 to 8.1 wt%. Bulk geochemical data for most samples give Fe_2O_3 values in the range of 5 to 9%, which is consistent with the results from Rietveld refinement, assuming that most of the iron was partitioned into magnetite during serpentinization of the original

TABLE 2.—*EXTENDED*

ACMIX50	ACMIX70	ACMIX90	HMIX1	HMIX2	HMIX3	HMIX4	HMIX5	HMIX6	HMIX7	HMIX8	HMIX9
57.0	71.6	88.7	90.8	80.5	52.8	79.9	46.0	68.0	59.4		
7.0	1.6	1.3	0.8	0.5	2.8	0.1	1.0	2.0	0.6		
15.0	10.9	3.9				8.7	4.5	4.6	4.7		10.4
5.0	1.1	0.1				1.3	0.5	0.4	0.3		0.4
9.9	5.8	2.2						5.4	4.7	50.6	41.2
0.1	0.2	0.2						0.4	0.3	0.9	1.2
4.4	2.8	1.8						6.0	5.8	9.6	9.6
0.6	0.2	0.8						1.0	0.8	0.3	0.4
6.3	3.3	1.0								11.0	10.1
1.3	0.3	0.0								0.4	0.1
3.2	3.0	1.1	0.3	0.8	2.3	1.4	2.0	1.1	2.2	11.2	11.7
2.0	0.1	0.0	0.2	0.2	0.1	0.9	0.4	0.4	1.0	0.4	0.7
4.2	2.6	1.3	8.9	18.8	44.9	10.1	47.5	14.9	23.2	17.5	17.1
0.5	0.3	0.3	0.6	0.3	2.7	0.5	0.1	0.6	0.6	1.4	2.0
100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1.3	1.3	1.4	1.4	1.4	1.5	1.2	1.4	1.3	1.3	1.7	1.4
6.1	5.8	5.4	7.1	7.2	7.2	7.1	7.6	7.4	7.3	9.5	9.6

* χ^2 is the reduced chi-squared statistic for the least-squares fit.
† R_{wp} is the weighted pattern index, a function of the least-squares residual.
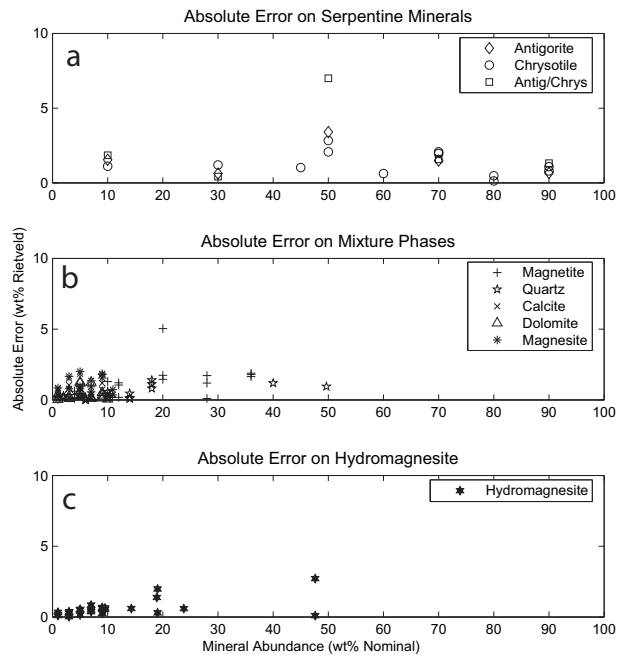
FIGURE 5. Absolute (wt%) error in estimates for all minerals vs. the abundance of that mineral in a sample. (**a**) Serpentine, (**b**) non-serpentine phases, and (**c**) hydromagnesite.

peridotite (Wicks and Whittaker 1977).

The sample of bulk tailings from Cassiar (03CA1601) contains no detectable hydrated magnesium carbonate minerals to a detection limit of 1 wt%, whereas the sample of bulk tailings from Clinton Creek (04CC1401) contains 2.2 wt% hydromagnesite. The cemented bulk tailings sample from Clinton Creek, 05CC8, contains 8.7 wt% hydromagnesite.

The crust samples (04CA0601, 04CC0703, 04CC1001, and 04CC1201) contain more than 5 wt% hydrated magnesium carbonate minerals. These crusts, grown on vertical tailings surfaces, are readily identified in the field as hydrated carbonates based on color, habit, and reaction to dilute HCl. The crust sampled from the tailings at Cassiar contains 5.5 wt% nesquehonite. Sample 04CC0703 from Clinton Creek contains 7.7 wt% hydromagnesite and 1.8 wt% nesquehonite. Analysis of the top 1 to 2 mm of sample 04CC0703 shows that it contains 47 wt% nesquehonite and 12 wt% hydromagnesite. The same trend is observed in the carbonate spire sample, 04CC0702 (and for 04CC1001 and 04CC1201); with increasing depth, below the surface of the carbonate crust or spire, hydromagnesite becomes more abundant than nesquehonite (Fig. 8). Trace dypingite (below 1 wt%) is observed in X-ray powder diffraction patterns for both carbonate samples (i.e., 04CC0702 and 04CC0703). Dypingite is a metastable mineral phase, which can be created as nesquehonite decomposes to hydromagnesite (Davies and Bubela 1973; Canterford et al. 1984).

The core samples taken from the hydromagnesite playa in Atlin, British Columbia, both contained in excess of 90 wt% hydromagnesite. A modern sample, 03ATC3-A, was taken from the top of the core at the surface of the playa. 03ATC3-I was taken from a section 50.5 cm beneath the surface. A clear trend toward decreasing magnesite abundance with depth has been observed at Atlin, with sample 03ATC3-A possessing the most magnesite in the core and 03ATC3-I having the least.

Origin of zoning

Transformation of hydrated magnesium carbonates to magnesite in mine tailings would allow CO_2 to be stored in a mineral phase that is potentially stable on a timescale of millions of years. Disposal of CO_2 in magnesite optimizes both the thermodynamic stability and amount of bound carbon: nesquehonite, lansfordite, and magnesite have a CO_2 to Mg ratio of 1 per formula unit, while dypingite and hydromagnesite have a ratio of 4/5. The stability of magnesium carbonates is known to increase from lansfordite (the least stable) through nesquehonite, dypingite, hydromagnesite, to magnesite (Langmuir 1965; Canterford et al. 1984). The zonation of hydrated magnesium carbonate phases in crusts and spires may result from decomposition of less stable phases (e.g., lansfordite and nesquehonite) forming in contact with the atmosphere to older and more stable phases at depth (e.g., dypingite and hydromagnesite). It is possible that the decomposition of magnesium carbonates could ultimately produce magnesite in the mine tailings environment.

An alternate interpretation is that the zonation of Mg-car-

TABLE 3. Results of quantitative phase analysis of natural serpentinite mine tailings renormalized to exclude 10% fluorite spike

Locality	Cassiar	Cassiar	Clinton Creek	Clinton Creek	Clinton Creek	Clinton Creek	Clinton Creek	Clinton Creek	Clinton Creek	Clinton Creek	Atlin	Atlin
Predominant serpentine phase	Chrysotile	Chrysotile	Chrysotile	Chrysotile	Chrysotile	Chrysotile	Chrysotile	Chrysotile	Chrysotile	Chrysotile	None	None
Mode	Bulk	Vertical Crust	Bulk	Spire	Spire Cap	Vertical Crust	Crust Cap	Vertical Crust	Vertical Crust	Cement	Playa	Playa
Phase	03CA1601	04CA0601	04CC1401	04CC0702	04CC0702	04CC0703	04CC0703	04CC1001	04CC1201	05CC8	03ATC3-A	03ATC3-I
Serpentine	87.6	89.4	88.4	78.0	59.5	81.3	32.3	81.1	83.3	77.3		
Palygorskite				1.6	4.4		2.8	1.2	1.5	1.5		
Magnetite	6.7	5.1	8.1	4.5	1.8	6.9	2.2	4.9	5.3	3.1		
Quartz	3.1		0.5	1.1	0.5	0.6	0.5	0.4	0.8			
Dolomite	2.6											
Magnesite			0.8			1.4		1.5	2.2	7.1	9.4	1.4
Nesquehonite	n/d‡	5.5	n/d	5.9	15.0	1.8	47.0	5.1				
Hydromagnesite	n/d	n/d	2.2	8.4	17.5	7.7	12.3	5.4	5.8	8.7	90.6	98.6
Pyroaurite			0.1	0.5	1.4	0.3	2.9	0.5		1.4		
Brucite									1.0	0.9		
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
χ^2*	1.4	1.2	1.4	1.1	1.3	1.2	1.3	1.2	1.2	1.3	2.0	2.3
R_{wp}†	8.1	6.8	7.7	6.4	7.1	6.9	6.5	7.0	7.0	7.0	8.9	9.7

* χ^2 is the reduced chi-squared statistic for the least-squares fit.
† R_{wp} is the weighted pattern index, a function of the least-squares residual.
‡ n/d means that the mineral phase was not detected above the 1 wt% limit.

FIGURE 6. Relative and absolute (wt%) error in Rietveld estimates of hydromagnesite abundance for all synthetic samples.

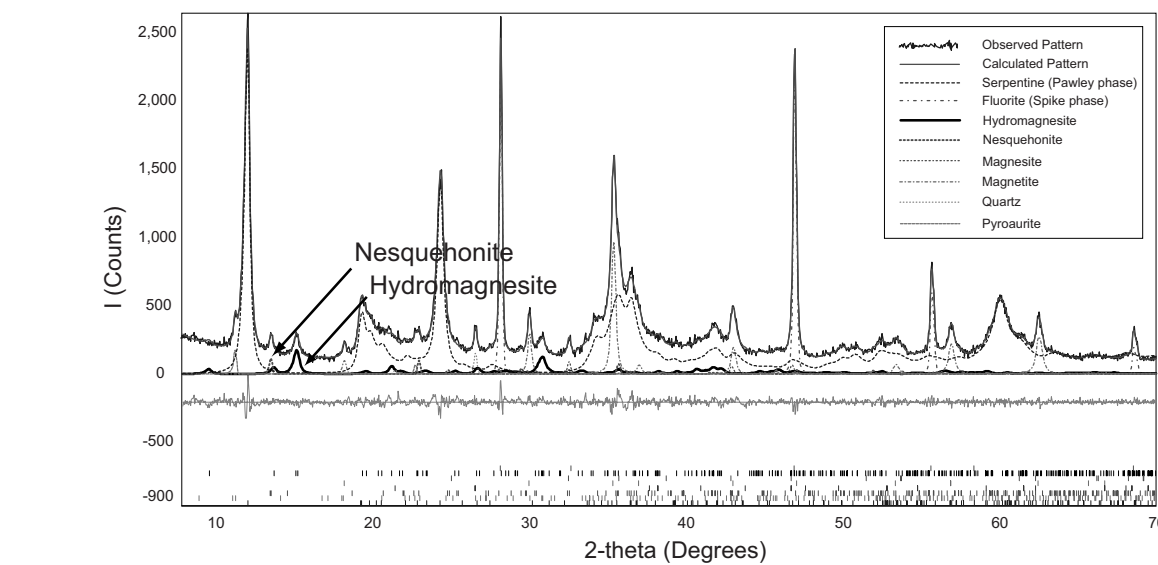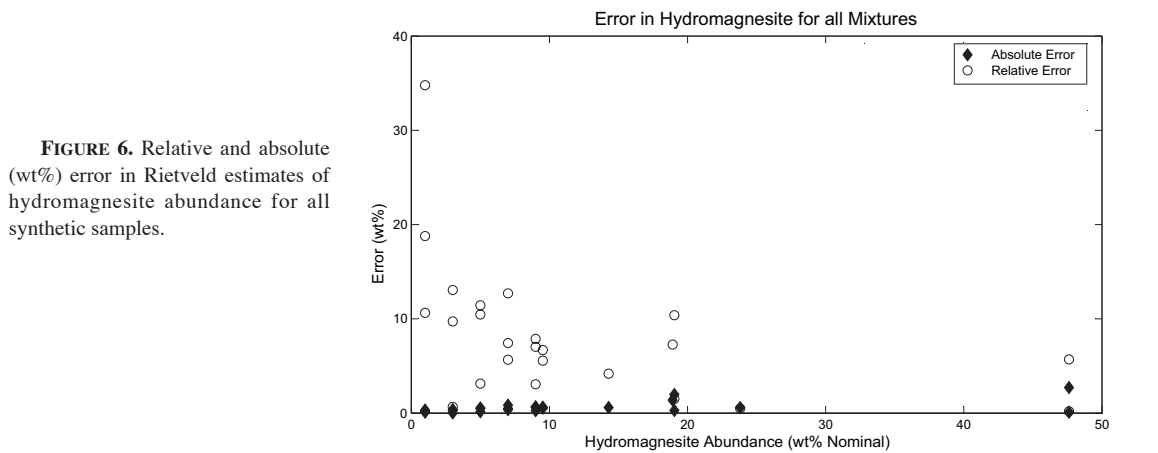**FIGURE 7.** Rietveld refinement plot of a chrysotile mine residue from Clinton Creek, Yukon Territory (04CC0703). Uppermost lines = observed data overlain by calculated pattern; black line below = residual pattern; vertical lines = positions of Bragg reflections for each phase; curves under the observed and calculated patterns = calculated patterns of each phase. Axes are intensity (counts) vs. 2θ (degrees).
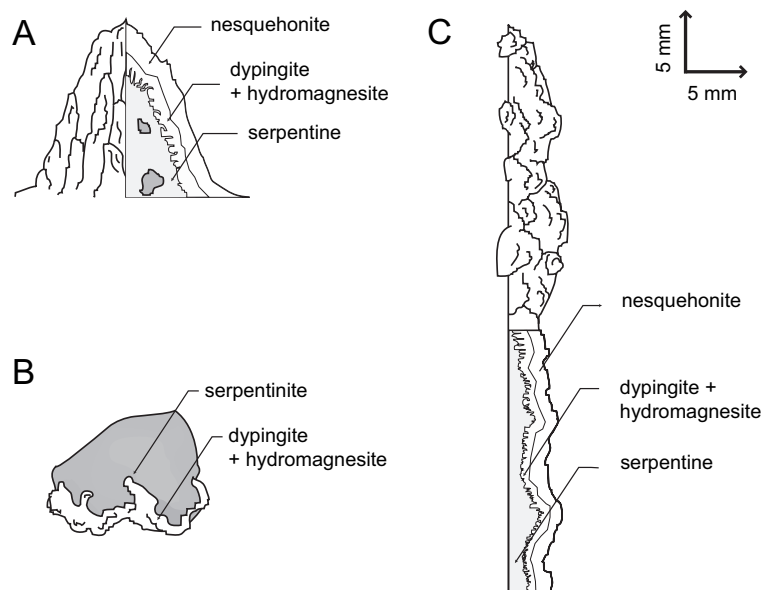
FIGURE 8. Detailed mineralogy for modal occurrences of hydrated magnesium carbonate crusts in serpentine-rich mine tailings: (A) carbonate spire from horizontal tailings surface, (B) crust on serpentinite cobble, and (C) carbonate crust from vertical tailings surface. Nesquehonite = $MgCO_3 \cdot 3H_2O$. Dypingite = $Mg_5(CO_4)(OH)_2 \cdot 5H_2O$. Hydromagnesite = $Mg_5(CO_4)(OH)_2 \cdot 4H_2O$.

TABLE 4. Estimated amounts of atmospheric CO_2 crystallographically bound in serpentinite mine tailings

Sample	Occurrence Type	CO_2 Sequestered (g/kg tailings)	CO_2 Potentially Sequestered (in tailings pile)
04CA1601*	Bulk	<3.8	<64.6 kt†
04CA0601	Vertical Crust	17.4	
04CC1401	Bulk	8.2	82.0 kt‡
04CC0702	Spire	50.5	
04CC0703	Vertical Crust	34.8	
05CC8	Bulk	32.8	328 kt‡
04CC1401 + 05CC8	Bulk	16.4	164 kt‡

* Where the upper limit on the amount of sequestration occurring in 04CA1601 has been calculated from the 1% detection limit.
† For 17 Mt of mine tailings at Cassiar, British Columbia.
‡ For 10 Mt of mine tailings at Clinton Creek, Yukon Territory.

bonate phases in crust samples from Clinton Creek and Cassiar may reflect two distinct precipitation pathways: An abiotic, atmospheric pathway for lansfordite and nesquehonite and a microbially mediated pathway for dypingite and hydromagnesite. Power and Southam (2005) have shown that dypingite and/or hydromagnesite precipitate in association with cyanobacteria in magnesium-rich water, whereas under similar yet abiotic conditions, only nesquehonite forms. Also, microbially mediated precipitation of hydromagnesite has been documented in the hydromagnesite playas at Salda Gölü, western Turkey (Braithwaite and Zedef 1996).

Hydromagnesite playas, like those found in Atlin, British Columbia represent an analog to the potential future state of mineral carbonates in serpentinite mine tailings. These natural carbon sinks provide valuable insight into the long-term stability of hydrated magnesium carbonate minerals and the environmental impact of carbon disposal in mine tailings. Playa deposits at Atlin conformably overly glacial sediments (Grant 1987), suggesting an early Holocene age. Furthermore, a decrease in ^{14}C content with depth in the Atlin playa deposits is consistent with hydromagnesite precipitation over the past several thousand years (Wilson and Dipple, unpublished data).

A series of previous studies of hydromagnesite playas located on the Cariboo Plateau, interior British Columbia, indicates that magnesite commonly becomes more abundant at depth within hydromagnesite mudflats on the periphery of alkaline playas, while magnesite dominates at the surface of modern lacustrine deposits during the summer months when the playas have desiccated (e.g., Renaut and Long 1989; Renaut 1990; Renaut and Stead 1991). The increased weight-percent abundance of magnesite at the surface of the Atlin playas (Table 3), and during the summer in the playas of the Cariboo Plateau, may be the result of decomposition of hydromagnesite in contact with the atmosphere. Morphological and isotopic similarities between modern hydromagnesite playas at Salda Gölü, western Turkey, and the Pliocene-age sedimentary magnesite deposits at Hirsizdere, Turkey, and Bela Stena, Serbia, may demonstrate large-scale diagenetic alteration of hydromagnesite to magnesite (Braithwaite and Zedef 1996; Zedef et al. 2000). Ancient sedimentary magnesite deposits like those at Hirsizdere fix carbon on a geologic time scale and may represent an analog to the final state of mineral carbonates in mine tailings.

Amount of bound carbon

The amount of atmospheric CO_2 that has been crystallographically bound in mineral form can be estimated from the Rietveld results for weight-percent abundance of hydrated magnesium carbonates (Table 4). The bulk tailings samples from Clinton Creek and Cassiar can be used to estimate the amount of CO_2 bound in hydrated magnesium carbonate minerals. Field observations indicate that the amount of carbonation in sample 04CC1401 is representative of roughly 2/3 of the tailings pile at Clinton Creek and that the heavily cemented sample (05CC8) reflects carbonation in the remaining 1/3 of the tailings. Based on this analysis, a total of 164 000 ±16 400 tons of CO_2 is bound within the tailings pile at Clinton Creek (applying 10% relative error corresponding to 4.36 wt% hydromagnesite). This high degree of accuracy cannot be readily obtained with other methods of quantitative phase analysis.

Large-scale implementation of enhanced mineral sequestra-

tion in mine tailings environments has the potential to fund remediation of historical mine sites through the trade of CO_2 credits and to provide active mining operations with a means to reduce greenhouse gas emissions. The efficacy and accuracy with which this refinement procedure can be applied to serpentine-rich samples allows for improved characterization of many tailings materials and for quantification of mineral sequestration in tailings containing a disordered mineral phase.

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Appendix A: Preparation method for synthetic serpentinites

Mixtures of pure mineral samples were prepared to simulate serpentinite mine tailings. Minerals commonly found in the tailings at Clinton Creek and Cassiar were used: kaolinite-serpentine group (antigorite and chrysotile), magnetite, quartz, calcite, dolomite, magnesite, and hydromagnesite. As sufficient amounts of pure nesquehonite, dypingite, and lansfordite (also present in the mine tailings at Clinton Creek and Cassiar) were not available, and well-crystallized, synthetic hydrated magnesium carbonates are difficult to manufacture (Davies and Bubela 1973; Kloprogge et al. 2003), hydromagnesite was used in their place. Samples of the constituent minerals were checked for purity using X-ray powder diffraction. Kaolinite-serpentine group minerals were identified positively as chrysotile and antigorite using X-ray powder diffraction and dispersive Raman microspectroscopy according the method of Rinaudo et al. (2003). All components, with the exception of hydromagnesite, were greater than 99% pure. Rietveld analysis showed that the hydromagnesite had partially decomposed to 4.8 wt% magnesite.

Three identical stock mixtures (A1, C1, and AC1) were prepared with the relevant phases exclusive of serpentine in the following abundances: magnetite (40 wt%), quartz (20 wt%), calcite (10 wt%), dolomite (10 wt%), magnesite (10 wt%), and hydromagnesite (10 wt%). Each mixture was ground under anhydrous ethanol with synthetic corundum grinding elements for 10 minutes in a McCrone mill to reduce the mean grain size and to ensure homogenization. Stock mixtures were dried at room temperature under a fume hood and were disaggregated with an agate mortar and pestle when dry. From each of the identical 6-phase mineral mixtures, series of 5 synthetic serpentinite samples were produced by adding serpentine as follows. Antigorite and chrysotile were added in amounts of 10, 30, 50, 70, and 90 wt% to mixtures A1 and C1, "AMIX" and "CMIX" series, respectively (Appendix Table). A third series ("ACMIX" series) was prepared by adding both chrysotile and antigorite to mixture AC1 in amounts 5, 15, 25, 35, and 45 wt%. A spike of annealed CaF₂ was added to each sample such that it constituted 10 wt% of the renormalized weight. Although low abundances of antigorite or chrysotile are not found in serpentinite mine tailings, they were used in this study to define the limitations of the method. The synthetic samples were ground under anhydrous ethanol in the McCrone mill for an additional 7 minutes to reduce the grain size of the serpentine phases and to homogenize the samples. The fourth, and final, series ("HMIX" series) consisted of 9 weighed mixtures, 7 of which represented more realistic mineral abundances and 2 of which contained no serpentine (Appendix Table). These samples were prepared individually, rather than from a stock mixture. As with the previous 15 samples, a 10 wt% spike of CaF₂ was added to each HMIX sample. The HMIX series samples were ground for 10 minutes in the McCrone mill. The grinding times were chosen to minimize the degradation of the serpentine structure while optimizing particle-size reduction. Samples were dried at room temperature and disaggregated with an agate mortar and pestle.

Appendix Table 1. Compositions of synthetic serpentinite mine tailings renormalized to exclude fluorite spike

Phase (wt%)	Stock mix	SERPMIX10	SERPMIX30	SERPMIX50	SERPMIX70	SERPMIX90	HMIX1	HMIX2	HMIX3	HMIX4	HMIX5	HMIX6	HMIX7	HMIX8	HMIX9
Chrysotile		10.00	30.00	50.00	70.00	90.00	90.00	80.00	50.00	80.00	45.00	70.00	60.00		
Magnetite	40.00	36.00	28.00	20.00	12.00	4.00				10.00	5.00	5.00	5.00		10.00
Quartz	20.00	18.00	14.00	10.00	6.00	2.00						5.00	5.00	49.67	40.00
Calcite	10.00	9.00	7.00	5.00	3.00	1.00						5.00	5.00	9.93	10.00
Dolomite	10.00	9.00	7.00	5.00	3.00	1.00								10.60	10.00
Magnesite	10.48	9.43	7.33	5.24	3.14	1.05	0.48	0.95	2.39	0.48	2.39	0.72	1.19	10.88	10.95
Hydro-magnesite	9.52	8.57	6.67	4.76	2.86	0.95	9.52	19.05	47.62	9.52	47.62	14.28	23.81	18.92	19.05
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00