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Microbially Mediated Mineral Carbonation: Roles of Phototrophy and Heterotrophy

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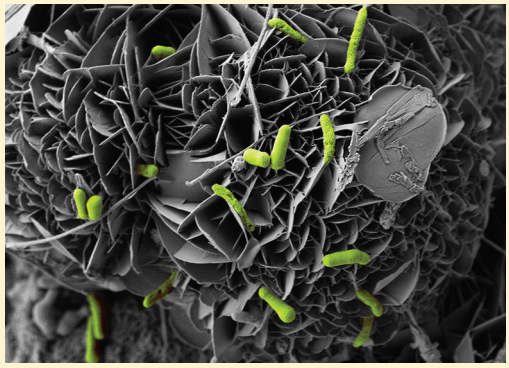
S *Supporting Information*

ABSTRACT: Ultramafic mine tailings from the Diavik Diamond Mine, Canada and the Mount Keith Nickel Mine, Western Australia are valuable feedstocks for sequestering CO_2 via mineral carbonation. In microcosm experiments, tailings were leached using various dilute acids to produce subsaline solutions at circumneutral pH that were inoculated with a phototrophic consortium that is able to induce carbonate precipitation. Geochemical modeling of the experimental solutions indicates that up to 2.5% and 16.7% of the annual emissions for Diavik and Mount Keith mines, respectively, could be sequestered as carbonate minerals and phototrophic biomass. CO_2 sequestration rates are mainly limited by cation availability and the uptake of CO_2. Abundant carbonate mineral precipitation occurred when heterotrophic oxidation of acetate acted as an alternative pathway for CO_2 delivery. These experiments highlight the importance of heterotrophy in producing sufficient DIC concentrations while phototrophy causes alkalinization of waters and produces biomass (fatty acids = 7.6 wt.%), a potential feedstock for biofuel production. Tailings storage facilities could be redesigned to promote CO_2 sequestration by directing leachate waters from tailings piles into specially designed ponds where carbonate precipitation would be mediated by both chemical and biological processes, thereby storing carbon in stable carbonate minerals and potentially valuable biomass.



INTRODUCTION

Fossil fuels account for 85% of the global energy supply and are expected to remain an important energy source as developing countries' demand for energy increases.[1] In order to reduce emissions and stabilize atmospheric CO_2 it will likely be necessary to implement carbon sequestration strategies.[2,3] Mineral carbonation involves dissolution of silicate minerals and subsequent precipitation of carbonate minerals in order to fix CO_2 in a solid form (eq 1).[1,4]

$$(\mathrm{Mg, Ca})_x\mathrm{Si}_y\mathrm{O}_{x+2y+z}\mathrm{H}_{2z}(s) + x\mathrm{CO}_2(g) \rightarrow x(\mathrm{Mg, Ca})\mathrm{CO}_3(s) + y\mathrm{SiO}_2(s) + z\mathrm{H}_2\mathrm{O} \quad (1)$$

Disposal sites for carbonate minerals require minimal monitoring because of the stability and environmental safety of these minerals.[4] An advantageous rock type for mineral carbonation is serpentinite, given its great abundance, wide availability, and high MgO content.[1,5] The rate of mineral carbonation in nature is slow, and therefore, there is a need to accelerate this process in order to use it as a viable option for CO_2 sequestration. Research on mineral carbonation has mainly focused on industrial processes involving aqueous carbonation.[5] This involves leaching or dissolution of silicate minerals, commonly using acids, and subsequent precipitation of carbonate minerals under high pressure and temperature.[1,4] Mineral acids, organic acids and ligands, and caustic soda have been used to leach serpentinite for the purpose of mineral carbonation.[1,4−6] With current technology, these processes are too expensive for CO_2 sequestration because of the high costs of mineral processing (e.g., mining and pulverization), chemical additives, and purification of CO_2.[4] The costs of mineral processing can be circumvented by using industrial waste products such as cement kiln dust, construction waste, iron and steel slag, fuel ash, and mine wastes as feedstock for mineral carbonation.[7] Mining of asbestos, nickel, diamonds, talc, and chromium produces large quantities of ultramafic tailings as a waste product.[4] Wilson et al. have documented passive mineral carbonation occurring in ultramafic tailings at historic asbestos mines as being facilitated by their high surface area.[8] The

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carbonate minerals in these tailings formed under normal mining conditions, that is, no practices were implemented to accelerate CO_2 sequestration. In the present study, ultramafic tailings are used as feedstocks from two active mines, the Diavik Diamond Mine in the Northwest Territories, Canada and Mount Keith Nickel Mine in Western Australia, which both host large stockpiles of tailings. In regards to emissions, the Diavik mine directly emitted ~162 000 tonnes of CO_2 equivalent of greenhouse gases in 2006 and in 2004, the Mount Keith mine emitted ~382 000 tonnes of CO_2 equivalent.[9,10] These two mines produce approximately 2 Mt and 11 Mt of tailings per year, respectively.[11,12] On an annual basis, complete conversion of these tailings to form magnesium carbonate minerals would allow for these mines to become zero emission facilities and carbon sinks for additional sources of CO_2. However, the bulk of the tailings are unweathered being composed of noncarbonated, silicate minerals. Therefore, there is the potential to accelerate mineral carbonation at these sites.

In nature, a variety of microorganisms can alter water chemistry in a manner that favors carbonate precipitation.[13−18] In particular, consortia with both phototrophs (e.g., cyanobacteria and microalgae) and heterotrophs have been shown to have the ability to mediate carbonate precipitation in various environments.[15,19,20] In addition, microalgae and cyanobacteria have received much attention for biotechnological applications including biofuel and nutraceutical production. These phototrophs are a very attractive feedstock for biodiesel, bio-oil, or bioethanol production because they can be grown on nonarable land such as mine sites. Many species are able to grow in saline and subsaline waters and their photosynthetic efficiencies can be several times greater than terrestrial plants leading to greater biomass production and CO_2 fixation per unit area.[21] Coupling carbonate and biomass production in an environment that is suitable for both of these processes would be a novel means of sequestering anthropogenic CO_2 and generating valuable byproducts.

In this study, we investigated combining microbial carbonate precipitation and biomass production for sequestering CO_2. The objectives were to (1) evaluate the suitability of a tailings facility that receives leachate waters as a habitat for carbonate-forming microbes, (2) elucidate the roles of phototrophs and heterotrophs in forming carbonate minerals and producing biomass from a variety of leachate waters, (3) identify limitations to this combined process, and (4) provide estimations of the CO_2 sequestration rates. In experiments, Diavik and Mount Keith tailings were leached using various dilute acids and deionized water to simulate potential leaching methods used to release cations for precipitation of carbonate minerals. Carbonate precipitation from these leachates was evaluated by microscopy, X-ray diffraction (XRD), and geochemical modeling and biofuel production was evaluated by analyzing the biochemical composition of the phototrophic consortium used in the experiments.

EXPERIMENTAL SECTION

Field Sampling. Fieldwork and sample collection were conducted at the Diavik Diamond Mine and the Mount Keith Nickel Mine (Supporting Information (SI) Figure S1). At Diavik, the majority of tailings are transported as slurry to the Fine Processed Kimberlite Containment (fine PKC) and stored in a pond of process water that is continually cycled. Grab samples of tailings with no visible evidence of secondary carbonate minerals were obtained from the fine PKC. At Mount Keith, tailings are transported as a suspension in hypersaline process water to the Tailings Storage Facility 2 (TSF2), which is a centralized discharge facility. Samples were collected with the aid of a backhoe from a depth of approximately 5 m to minimize the presence of evaporative minerals. Detailed descriptions of the Diavik tailings and the geology of the Mount Keith site are provided by others.[11,12,22] The tailings used in this study were fully characterized by determining their mineralogical and geochemical compositions, particle size distributions, neutralization potentials, and surface areas. General descriptions of the field sites and analytical methods are provided in the SI.

Microbial Carbonate Precipitation Experiments. Leaching of Diavik and Mount Keith tailings was performed using dilute solutions of acetic acid, hydrochloric acid, sulfuric acid, a mixture of nitric and phosphoric acids, and deionized water (SI Table S1). These acids were selected to represent a wide variety of acid sources such as from industrial processes (HCl, H_2SO_4),[4,5] overlying soils (CH_3COOH),[23] microbial sulfur oxidation (H_2SO_4),[24] and nutrient addition (HNO_3 and H_3PO_4) that could be used to release cations from silicate minerals. The concentrations of CH_3COOH, HCl, and H_2SO_4 used for reaction with the Diavik and Mount Keith tailings were 0.1 and 0.25 N, respectively. Acid concentrations depended upon the ability of each tailings sample to neutralize acidity during the leaching period (2 days) to a pH $\approx$ 7. Although stronger acids could be used to more aggressively leach the tailings, this would result in (1) acidic leachates that would not be suitable for growth of phototrophs and (2) result in potentially less cost-effective and less technologically viable approach to CO_2 sequestration in mine tailings. For HNO_3 and H_3PO_4 leaches, 0.018 and 0.0002 N, respectively, were used to produce similar concentrations of nitrate and phosphate that are present in growth media. Deionized water is representative of current leaching by natural carbonic acid in meteoric precipitation at the tailings facilities. Aliquots (7.0 g) of tailings were added to 125 mL Erlenmeyer flasks with 70 mL of acid solution or deionized water and allowed to react on a shaker table for 2 days. After this reaction period, the pH of each of the mixtures was measured. The mixtures were centrifuged and the supernatant was filtered (0.45 μm).

A consortium dominated by unicellular algae, cf. *Dunaliella* sp., was cultured from microbial mats collected from the hydromagnesite playas of Atlin, British Columbia, Canada. These are natural magnesium carbonate deposits in ophiolitic terrane and are a biogeochemical model for CO_2 sequestration via mineral carbonation.[25] Cultures were grown in 75 mL of BG-11 media in 125 mL Erlenmeyer flasks at room temperature (~20 °C) and in the presence of sunlight.[26]

Filtered leachate solutions were used to prepare modified BG-11 media. Given that the tailings would provide dissolved Mg, Ca and Na, the following ingredients were excluded from the media: $MgSO_4 \cdot 7H_2O$, $CaCl_2 \cdot 2H_2O$, and $Na_2CO_3(H_2O)$. In the leachate produced using nitric and phosphoric acids, $NaNO_3$ and $K_2HPO_4 \cdot 3H_2O$ were also excluded. Aliquots of 15 mL were dispensed into 20 mL sterile (autoclaved) glass vials. Media was inoculated with 100 μL of culture and incubated at room temperature and in the presence of sunlight. Abiotic controls containing only filtered leachate waters (15 mL) were also prepared. Microbial growth and pH were monitored weekly for 14 weeks. Cells and precipitates were routinely examined using light microscopy and after 12 weeks samples were collected for electron

Table 1. Major Cation Concentrations of the Leachates Produced from Reaction with Diavik and Mount Keith Tailings

	cation concentration (ppm) at $t = 0$									avg. pH, biotic/abiotic during experiment
	Ca	Fe	K	Mg	Na	Ni	P	S	Si	
Diavik										
acetic acid	529	0.3	50	235	466	0.2	7.0	10	26	9.82/9.48 (Δ = 0.34)
hydrochloric acid	504	0.3	49	263	463	0.2	7.7	12	29	8.64/7.49 (Δ = 1.15)
sulfuric acid	438	0.3	44	264	431	0.3	7.6	785	37	8.79/7.83 (Δ = 0.95)
nitric and phosphoric acids	151	0.3	29	122	10	<0.01	1.7	11	11	9.14/8.10 (Δ = 1.05)
deionized water	6	0.4	35	19	421	<0.01	5.9	12	3.2	10.2/8.54 (Δ = 1.69)
Mount Keith										
acetic acid	127	0.2	78	2952	1544	2.2	5.3	404	<0.02	9.22/8.71 (Δ = 0.51)
hydrochloric acid	125	0.2	78	2969	1502	0.8	5.3	412	5.0	9.16/7.79 (Δ = 1.37)
sulfuric acid	121	0.2	85	3024	1552	1.1	6.4	4180	4.4	8.98/7.80 (Δ = 1.19)
nitric and phosphoric acids	46	0.3	65	557	1120	<0.01	<0.1	371	<0.02	9.01/7.98 (Δ = 1.03)
deionized water	53	0.3	79	370	1578	<0.01	5.2	360	<0.02	9.26/8.04 (Δ = 1.22)

microscopy and mineralogical analyses. The SI contains further details on the analytical methods.

Biomass Production and Collection. Cultures were grown in 2 L Erlenmeyer flasks with 200 μmol of photosynthetically active radiation (PAR)/m^2/s at room temperature (~20 °C) in BG-11 media that was well mixed by bubbling with a low volume of filter sterilized air (~0.3 v/v/min). Cells were harvested by centrifugation for 15 min at 15×10^3 g using a Sorvall RC-5B refrigerated superspeed centrifuge and washed three times with 50 mL of distilled water by vortexing for 3 min at 2500 rpm. Cells were lyophilized using a Thermo Electron ModulyoD-115 with Savant Valupump VLP200 in the dark for approximately 40 h at 80 ± 20 Pa until there was no further change in mass. The SI contains methods for the biochemical analyses.

RESULTS AND DISCUSSION

Mine Tailings and Leachate Chemistry. The Diavik tailings were mainly composed of serpentine minerals (predominantly lizardite, 48.2%), high-Mg forsterite (25.2%), and vermiculite (9.8%) (SI Figure S2). Mount Keith tailings were composed primarily of antigorite and lizardite (combined 81.0%) with hydrotalcite-group minerals, which tend more toward chlorine endmembers than carbonate endmembers (SI Figure S3). Other notable minerals were calcite (3.7%) in the Diavik tailings and magnesite (3.4%), brucite (2.5%), and dolomite (0.6%) in the Mount Keith tailings. The Diavik and Mount Keith tailings had surface areas of 47.99 m^2/g and 9.35 m^2/g and average grain sizes of 0.1 mm and 0.07 mm (SI Figure S4), respectively. The surface area of the Diavik tailings was considerably higher given the amount of vermiculite, but both tailings have surface areas that are orders of magnitude greater than natural bedrock. The neutralization potentials of the Diavik and Mount Keith tailings were 370 and 352 kg/tonne of $CaCO_3$ equivalent, respectively. Although these values are nearly equal, Mount Keith tailings were able to neutralize more concentrated acid (0.25 N compared to 0.1 N for leaching of Diavik tailings) in experiments given more time (leaching time = 2 days) than what is required for determining neutralization potentials by the Sobek method. This may be due to slower reactions with dolomite or finer grained magnesium silicate minerals found in the Mount Keith tailings. The ability of a tailings sample to neutralize acidity indicates its reactivity to leaching processes. The geochemical composition of the Diavik tailings mainly consisted of SiO_2 (41.1%), MgO (32.5%), Fe_2O_3 (7.6%), CaO (3.7%), and Al_2O_3 (3.6%), whereas the Mount Keith tailings consisted primarily of MgO (40.3%), SiO_2 (31.1%), and Fe_2O_3 (6.8%). Complete data for each of the tailings are shown in SI Table S2.

The historic chrysotile tailings studied by Wilson et al. are similar to the Diavik and Mount Keith tailings in that they are ultramafic, fine grained with high surface areas; making them susceptible to carbonation. The chrysotile tailings contained hydrated magnesium carbonate minerals that precipitated in situ to store atmospheric CO_2.[8,27] Precipitation of carbonate minerals within the pore spaces of these tailings resulted from extensive evaporative concentration of dissolved magnesium and inorganic carbon released from the dissolution of magnesium silicate minerals by very weak carbonic acid, that is, meteoric precipitation. In contrast to pore waters, leachate waters from this tailings site may not precipitate carbonate minerals in the absence of evaporative concentration.

Subsaline solutions (Table 1) were produced from leaching each of the tailings and represent potential feedstocks for carbonation. The solutions of diluted acetic acid, hydrochloric acid, and sulfuric acid were equally effective at leaching both of the tailings. After the addition of nutrients (e.g., $NaNO_3$), the major cations in the Diavik solutions were Ca > Na > Mg ≫ K > Si and for the Mount Keith solutions they were Mg ≫ Na ≫ Ca > K. As expected, solutions produced by leaching tailings with less concentrated nitric and phosphoric acids and deionized water had much lower cation concentrations. In experiments, precipitation of aragonite and calcite does not represent a net sequestration of CO_2 because the only sources of dissolved calcium are carbonate minerals already present in ore prior to mining. Dissolved magnesium would have come from both the dissolution of magnesium silicate and, in the case of Mount Keith, carbonate and hydroxide minerals such as brucite, dolomite and magnesite. Precipitation of magnesite and dolomite is kinetically inhibited at ambient temperatures owing to the strong hydration of Mg^{2+} ions in solution.[28,29] Hydromagnesite may also be kinetically inhibited at ambient temperatures.[30] Therefore, the precipitation of kinetically favored magnesium carbonate minerals, such as dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot \sim 5H_2O$] and nesquehonite,

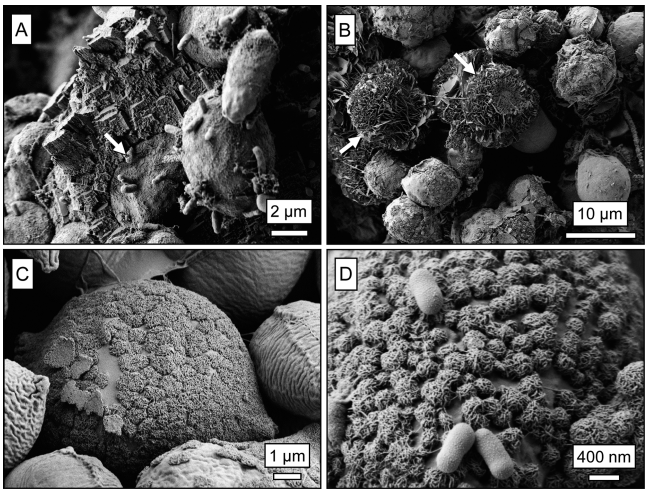

Figure 1. SEM micrographs of cells and precipitates from the experimental systems. A: Diavik acetic acid precipitate showing algal cells embedded (arrow) in a calcium carbonate aggregate; note the heterotrophic bacteria associated with algal cells. B: Cells and dypingite rosettes (arrows) formed in the Mount Keith acetic acid solution. C: An algal cell completely encrusted by fine silicate rosettes from the Diavik deionized water precipitate. D: High magnification view of silicate precipitates on an algal cell from the Mount Keith sulfuric acid precipitate.

represents the best opportunity for sequestering CO_2. Although these minerals are relatively less stable and more soluble than magnesite,[30] they are still capable of storing CO_2 on geological time scales. For example, nesquehonite and dypingite precipitate from water in a wetland that is part of a carbonate playa near Atlin, British Columbia, Canada.[25] These minerals dehydrate to form hydromagnesite, the most abundant carbonate mineral present in the playas, which are underlain by glacial till and presumably began forming soon after the last deglaciation demonstrating their stability over the Holocene epoch. The minor relief of the playas above the surrounding land further demonstrates that hydrated magnesium carbonate minerals are stable when present at near-surface conditions, especially in an alkaline environment such as an ultramafic tailings facility. In the present study, we evaluated the ability of the Atlin consortium to induce carbonate precipitation from leachate solutions that were initially undersaturated with respect to kinetically favorable carbonate minerals.

Carbonate Precipitation Experiments. The Altin consortium, dominated by cf. *Dunaliella* sp., was able to grow in all of the leachate solutions and cause alkalinization of these waters. The presence of relatively high concentrations of chlorine (HCl leach) or organics (CH_3COOH leach) did not impede growth. During the experiment, approximately 70% of the water was evaporated from the vials. In the biotic systems, the Atlin consortium was able to raise the pH value significantly in all the systems, typically by one pH unit, when compared to the abiotic controls (SI Figure S5).

Precipitation of abundant carbonate minerals occurred in solutions produced from reaction of tailings with dilute acetic acid. When examined using scanning electron microscopy (SEM), cells were seen embedded on the outside of large crystal aggregates and rod-shaped heterotrophic bacteria were associated with algal cells (Figure 1A). The Mount Keith acetic acid precipitates had rosette morphology and magnesium carbonate composition based on energy dispersive X-ray spectroscopy (EDS) (Figure 1B). Rosette precipitates of magnesium carbonate minerals, although less common, were also seen in the Diavik acetic acid precipitate. The Diavik precipitate mainly consisted of magnesium-containing calcite and minor amounts of partially dehydrated dypingite, whereas the Mount Keith precipitate mainly consisted of dypingite and halite that formed when the sample was dried (XRD patterns in SI Figure S6).

All of the Diavik solutions produced noticeable calcium carbonate over the course of the experiment. The calcium carbonate was seen as translucent crystal aggregates when viewed using light microscopy. Algal cells were entombed in the calcium carbonate along with casts of cells that had been infilled. In addition, precipitates with a silicate composition were seen directly on cells (Figure 1C). Abundant amounts of magnesium carbonate minerals did not precipitate from the Mount Keith solutions with the exception of the acetic acid solution. Similar fine grained silicate precipitates were seen in association with cells, but more commonly directly on cells with numerous cells being completely encrusted (Figure 1D). These precipitates had rosette morphology and were typically less than 0.5 μm in diameter with a magnesium and calcium silicate composition. Aragonite precipitated in some solutions after extensive evaporation. Several example micrographs of the precipitates are given in SI Figures S7 and S8.

Biomass Production. The approximate composition of the Atlin consortium showed a protein content of 44 $\pm$ 2 wt.%, which is higher than in most species of photosynthetic unicellular organisms and indicates that this consortium is a potential source of single-cell protein,[31] which could be hydrolyzed and used in fermentations as a nitrogen source, along with any carbohydrates in the biomass. The value of the proteins would depend on the amino acid composition, which was not determined. Carbohydrate content was relatively low (22 $\pm$ 1 wt.%), but at least twice the lipid content (11 $\pm$ 1 wt.%), suggesting that carbohydrates may be the preferred energy-storage medium for this culture.[31] Ash content was relatively high at 12 $\pm$ 2 wt.%. The combination of inorganics inside and outside the cells and any reduced carbon amounts to the total ash measured; however, the composition of this material was not determined. The biomass was relatively high in pigments with a low chlorophyll a (0.81 $\pm$ 0.03 wt.%) to chlorophyll b (0.32 $\pm$ 0.02 wt.%) ratio of 2.5:1 and total chlorophyll exceeding 1 wt.% of the dry biomass. This indicates acclimation to low light,[32] which is consistent with the light level used; 10% of full-strength sunlight at the Earth's surface. Carotenoid pigments were 0.045 $\pm$ 0.002 wt.% of the biomass.

Acid hydrolysis of cell biomass and excreted saccharides in the growth media (SI Table S3) showed that the total hydrolyzable carbohydrate content was 21 $\pm$ 1 wt.%, which agreed with the carbohydrate content measured by the phenol sulfuric acid method, 22 $\pm$ 1 wt.%, within experimental error (n = 3; P < 0.05). The monosaccharides in the hydrolysate of the cell biomass were 53 wt.% hexoses that are easily fermented by yeast and 47 wt.% pentoses, which cannot be fermented by standard yeast but can be fermented by other microorganisms and genetically engineered yeast.[33] The growth media contained a relatively high concentration of hydrolyzable carbohydrates, 160 mg/L or about 15 wt.% of the biomass weight. This hydrolysate contained 41 wt.% hexoses and 59 wt.% pentoses. Although the concentration of excreted saccharides is very low compared to the concentration of carbon source in a typical fermentation broth it would be possible to ferment these sugars to produce ethanol or butanol.[34]

The fatty acid content measured by gas chromatography (SI Figure S9) was significantly lower than the lipid content measured gravimetrically; 7.6 ± 0.3 wt.% versus 11 ± 1 wt.%, respectively ($n = 3$; $P > 0.05$). However most of the lipids in microalgae are often polar lipids, especially when the lipid content is low.[31] The extra weight of the nonfatty acid portions of phospholipids and other nonfatty acid lipids such as pigments may be the reason for this discrepancy. The most abundant fatty acid in the cells was α-linolenic acid, which accounted for about 37 wt.% of the total fatty acids and over 95 wt.% of the ω-3 fatty acids. Although α-linolenic acid is an essential nutrient it is not very valuable because it is present in high amounts in common foods such as flax, hemp, canola, and soya and does not have the same health benefits as eicosapentaenoic acid or docosahexaenoic acid.[35] Approximately 40 wt.% of the fatty acids had three units of unsaturation; ~13 wt.% had two units of unsaturation; ~20 wt.% had one unit of unsaturation; and ~27 wt.% were saturated. Since only the minority of fatty acids had chain lengths over eighteen or more than three double bonds the oil from this species of algae should be more suitable for biodiesel than the oil of other species such as *Nannochloropsis* sp., which is very rich in eicosapentaenoic acid.[31]

Although the lipid content was relatively low at about 11 ± 1 wt.% this was determined for late-exponential phase biomass in nutrient-sufficient cultures. It is often possible to increase lipid or carbohydrate content dramatically, often by several times, by allowing the biomass to accumulate energy storage metabolites in a second-phase of nitrate or phosphate limited growth.[31] Therefore, it may be possible to increase the oil and/or carbohydrate content of this consortium for biodiesel and/or fermentation carbon source production. If this could be achieved this consortium would be ideal for biofuel applications since it can be grown with minimal monetary and energy cost for growth media, cultivation, and harvesting from existing mine tailing ponds, while simultaneously sequestering CO_2 as biomass.

Roles of Phototrophy and Heterotrophy in Carbonate Precipitation. Field observations at Diavik suggest that mineral carbonation under some conditions for tailings disposal is limited to abiotically formed evaporative crusts (SI Figure S1C,D). The tailings at both sites are largely unweathered and therefore have tremendous potential for further carbon sequestration. In the present study, a variety of acids were used to simulate possible accelerated dissolution scenarios, but natural weathering (simulated using deionized water), although slowest, may be the most practical. Carbonate precipitation will occur if pore waters in tailings or leachate waters are sufficiently supersaturated with respect to a given carbonate mineral; however, leachate waters may often be undersaturated with respect to kinetically favorable magnesium carbonate minerals. Phototrophic and heterotrophic microbes are able to alter the geochemical conditions to cause leachate waters to become sufficiently supersaturated. The three important abiotic factors in carbonate precipitation are pH and the concentrations of cations (e.g., Ca^{2+} and Mg^{2+}) and dissolved inorganic carbon (DIC). Experimental leaching of the ultramafic tailings produced subsaline solutions rich in Mg^{2+} and Ca^{2+} ions that were then available for carbonate precipitation. Geochemical modeling of the starting solutions (Table 1) using PHREEQC showed that increasing the pH value would generally result in these solutions becoming supersaturated with respect to hydromagnesite.[36] Although dypingite has been precipitated in magnesium-rich solutions in both abiotic[37] and biotic[18] experiments, there is no thermodynamic data available for modeling its precipitation. When leachate solutions were inoculated with the Atlin consortium, phototrophs produced OH^- ions during photosynthesis while forming biomass or producing energy (eq 2).[13,38]

$$HCO_3^- + H_2O + h\nu \rightarrow CH_2O + OH^- + O_2\uparrow \quad (2)$$

This release of OH^- ions outside the cell results in alkalinization, that is, an increase in the pH value, which in turn increases the concentration of CO_3^{2-} anions. This effect is seen in the elevated pH values of the biotic systems (avg. pH 9.22), which were generally one pH unit above corresponding abiotic controls (avg. pH 8.17) (Table 1 and SI Figure S5). This can greatly increase the saturation of carbonate minerals (e.g., aragonite and dypingite), allowing for their precipitation (eq 3 and 4).

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (3)$$

$$5Mg^{2+} + 4CO_3^{2-} + 2OH^- + 5H_2O \rightarrow Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O \quad (4)$$

Heterotrophic bacteria are often associated with phototrophs in natural systems and can increase DIC concentrations, such as the acetate oxidizing, heterotrophic bacteria in this study. In natural systems, this may occur by either aerobic or anaerobic (e.g., sulfate reduction) oxidation of organics (eq 5 and 6).

$$2CHO_2^- + O_2 \rightarrow 2HCO_3^- \quad (5)$$

$$4CHO_2^- + SO_4^{2-} + H^+ \rightarrow 4HCO_3^- + HS^- \quad (6)$$

The decomposition of organic matter by heterotrophic bacteria is part of the cycling of carbon that is often first fixed by phototrophs. The acetic acid leachate solutions allowed for the growth of aerobic, acetate oxidizing bacteria that were part of the Atlin consortium. Oxidation of acetate (CH_3COO^-) produces CO_2; acting as an alternative pathway for CO_2 delivery in the experiments (eq 7).

$$CH_3COO^- + 2O_2 \rightarrow 2CO_2 + OH^- + H_2O \quad (7)$$

Acetate oxidation also increases the pH value through production of OH^-, whereas the CO_2 produced may then dissolve into solution forming CO_3^{2-} at alkaline pH. Similarly, von Knorre and Krumbein conducted calcium carbonate precipitation experiments by growing heterotrophic bacteria on agar plates in an artificial seawater medium containing 15 mM sodium acetate.[20] They found that 126 of the 128 isolates tested were able to induce carbonate precipitation, which they concluded was mainly due to physiological activities that increased carbonate alkalinity. As well, Mg carbonate and Mg-rich carbonate minerals have been precipitated with the aid of aerobic heterotrophs in batch experiments.[39]

An important observation of these microcosm experiments was the formation of magnesium and calcium silicate minerals on cell surfaces. This limits CO_2 sequestration as it removes cations from solution as precipitates that are not carbonate minerals. This observation indicates that although experiments were open to the atmosphere, uptake of CO_2 from the atmosphere was rate-limiting in the microcosms and was insufficient to allow for abundant precipitation of magnesium carbonate minerals even though solutions had high concentrations of magnesium and alkaline pH values as a result of alkalinization by phototrophs. The acetic acid systems were an exception because the oxidation of acetate acted as an alternate means of delivering CO_2.

Table 2. Estimated CO_2 Sequestration Rates (Tonnes/Year) Based on Annual Tailings Production

values are in tonnes/year	mineralized CO_2 dissolved during leach	CO_2 mineralized as carbonate minerals (ara/hmg)		CO_2 captured as biomass	total CO_2 sequestered (% in carbonate/% in biomass)		
Diavik (2 Mt tailings/year; emissions = 162 000 t CO_2 equivalent/year)							
acetic acid	1160	1290	711	422 from the PKC	4000	21%	79%
hydrochloric acid	1110	1200	0	2740 from north inlet	3250	3%	97%
sulfuric acid	962	1050	0	storage reservoir	3250	3%	97%
nitric and phosphoric acids	332	363	214		3410	7%	93%
deionized water	13	14	22	growing season: 12 weeks	3190	1%	99%
Mount Keith (11 Mt tailings/year; emissions = 382 000 t CO_2 equivalent/year)							
acetic acid	1534	1710	52 500		63 300	83%	17%
hydrochloric acid	1510	1700	51 200	10 600 from TSF2	62 000	83%	17%
sulfuric acid	1460	1580	48 400		59 100	82%	18%
nitric and phosphoric acids	556	596	8390	growing season: 52 weeks	19 000	44%	56%
deionized water	640	696	6460		17 100	38%	62%

Precipitation of dypingite from natural waters, sampled near Atlin, British Columbia, has been achieved using a phototrophic consortium; although these waters had very high alkalinities (e.g., 2661 and 4727 mg HCO_3^-/L).[18] Wilson et al. also noted that uptake of atmospheric CO_2 into brine solutions (2430 mg Mg/L) was rate-limiting for the precipitation of dypingite with initial precipitation requiring 15 days.[37] It was also noted that carbonate mineral precipitation outpaced uptake of CO_2 gas.

Additional carbon sources or more proficient means of delivering CO_2 are likely required for abundant precipitation of magnesium carbonate minerals. This differs from calcium carbonate precipitation given that the formation of magnesite is kinetically slow because of the strong hydration of Mg^{2+} ions.[28] Ferrini et al. synthesized nesquehonite at ambient temperatures by sparging CO_2 through a concentrated magnesium chloride solution at room temperature and adjusting the pH with ammonia.[40] They proposed that this process could be developed for sequestering CO_2 from point sources using waste brine solutions. Alternatively, increasing the concentration of DIC could be achieved using natural biocatalysts.[41] For example, carbonic anhydrase is a metalloenzyme that is produced by both prokaryotes and eukaryotes, which catalyzes the hydration of CO_2, that is, the dissolution of CO_2 in an aqueous form.[40,42,43] Mitchell et al. investigated bacterial ureolysis in synthetic brine solutions, which also increases carbonate alkalinity and pH to induce calcium carbonate precipitation.[42] They noted that wastewater urea sources could be utilized and that this would reduce labile carbon, thereby preventing the release of CO_2 by forming carbonate minerals. Similarly, a net sequestration of CO_2 can be achieved if the CO_2 from the oxidization of organic carbon was first fixed (from the atmosphere) by phototrophs before being precipitated as carbonate minerals.

Carbon Sequestration Strategies. Mining is an ongoing, profitable industrial activity that produces tailings with an inherent ability to sequester CO_2 through a natural weathering process. Precipitation of carbonate minerals from leachate solutions rich in magnesium and calcium is advantageous in that carbonate minerals are both benign and stable. An ideal scenario would be to have specially designed carbonate precipitation ponds with leachate waters being directed into these ponds from tailings piles. A means of accelerated leaching could be implemented post ore processing or at the tailings facility if it were deemed cost-effective. In the pond, a microbial consortium would be cultivated to induce precipitation of carbonate minerals with microbial species being selected based on their ability to mediate carbonate precipitation and the quality of their biomass. Additional nutrients and evaporative conditions would help create ideal conditions. Carbonate minerals would be deposited in these ponds while biomass would be harvested for potential use as biofuel or other valuable byproducts.

In the experiments, CO_2 was derived from uptake from the atmosphere, dissolution of tailings carbonate minerals, and microbial oxidation of acetate. Sinks of CO_2 included precipitation of secondary carbonate minerals and formation of biomass. CO_2 sequestration rates were calculated using the experimental data and have been scaled to the annual tailings production for Diavik (2 Mt/yr) and Mount Keith (11 Mt/yr) (Table 2). Tailings slurries were assumed to be approximately 50% solids by mass, thereby requiring 2 GL and 11 GL of water per year for Diavik and Mount Keith, respectively. This assumes that tailings are leached only during the year that they are produced; whereas leaching of the entire tailings storage facilities would access approximately 1 order of magnitude more material. The calculated values of mineralized CO_2 dissolved from the acid leaching were based on the Ca concentrations in the starting solutions assuming partial dissolution of calcite and dolomite in the Diavik and Mount Keith tailings. Magnesite, present in the Mount Keith tailings, was assumed unreactive as magnesite has been shown to be highly resistant to dilute acids.[43] PHREEQC modeling of the starting solutions assumed a modest evaporation of 10% and used the average pH value obtained during each of the biotic experiments (Table 1). The pH of the solutions was fixed in order to mimic experimental conditions. These conditions were generally obtained after two weeks and coincided with reaching the stationary growth phase. Aragonite and hydromagnesite (a proxy for dypingite) were allowed to precipitate and solutions were in equilibrium with atmospheric concentrations of CO_2. Net CO_2 sequestered per year as carbonate minerals for the Diavik site ranged from 23 to 841 tonnes/year (deionized water to acetic acid system), whereas for Mount Keith rates ranged from 6520 to 52 700 tonnes/year (deionized water to acetic acid system) (Table 2). Although the reacted tailings were not processed further in this study, they would still be a valuable feedstock for further leaching. The acidity of the leaching solution would need to be adjusted because primary carbonate minerals are present only in fresh tailings. Use of carbonate-free

tailings or continual leaching of carbonate-bearing tailings is preferred in comparison to the use of fresh tailings that have primary carbonate minerals. Carbonate precipitation would benefit from additional carbon sources, such as waste organics (simulated by acetic acids in experiments) and waste gas streams, or improved means of delivering CO_2 to the system as opposed to relying on uptake of CO_2 from the atmosphere. Carbonate precipitation at Mount Keith was comparably greater than Diavik given that leachate solutions contained greater concentrations of cations.

In cultures, biomass production was 1 g of dry biomass/L over 2 weeks to obtain stationary growth. We have used a conservative growth rate of half this amount (0.5 g/L) assuming nonideal conditions and accounted that 1.83 g of CO_2 is required to produce 1 g of dry biomass.[21] Biomass production will depend on the site's climate and the availability of water and nutrients (e.g., wastewater). In addition to the fine Processed Kimberlite Containment (PKC) at Diavik there is the North Inlet Water Treatment Plant, which is a reservoir in that 13 GL of water passes through each year.[44] This water is not likely suitable for carbonate precipitation as it is not associated with tailings, but may be suitable for biomass production as algal blooms have been observed at this site. Based on climate data we have estimated that suitable growing conditions at Diavik and Mount Keith are 12 and 52 weeks per year, respectively, and have therefore scaled the water available for biomass production based on the fraction of the year in which suitable growing conditions are present.[45,46] On an annual basis, CO_2 sequestered as biomass was estimated to be 422 tonnes from the PKC and 2740 tonnes from the North Inlet treatment reservoir at Diavik and 10 600 tonnes from the Tailings Storage Facility 2 (TSF2) at Mount Keith.

The Diavik and Mount Keith mines emit approximately 162 000 and 382 000 tonnes of CO_2 equivalent in the production of 2 Mt and 11 Mt of mine tailings per year, respectively. Mines are industrialized sites that provide nonarable land, large water reservoirs (e.g., tailings ponds and water treatment facilities), and abundant fine grained mine wastes that have an inherent ability to sequester CO_2. These sites could be modified to accelerate leaching of these tailings and better suit the cultivation of phototrophic microbes that are able to mediate carbonate precipitation and produce valuable biomass. From microcosm experiments, estimated sequestration rates indicate that 2.5% and 16.6% of Diavik's and Mount Keith's yearly emissions, respectively, could be sequestered. Carbonate precipitation rates will mainly depend on the availability of cations and the rate of CO_2 uptake into solutions. Heterotrophic oxidation of acetate demonstrated an alternative, effective means of accelerating CO_2 uptake in comparison to uptake of CO_2 from the atmosphere; however, it is necessary to account for the source of CO_2 in any carbon sequestration strategy. Rather than acetate oxidation, wastes organics or injection of waste gas streams with elevated partial pressures of CO_2 could provide a more efficient means of CO_2 uptake. Carbonate mineral precipitation coupled with biomass production has the potential to provide a low-energy, low-temperature, and relatively passive means of sequestering CO_2 at mine sites and possibly in other human-made environments.

■ ASSOCIATED CONTENT

Supporting Information. Details for the field sites, experimental methods, and additional figures for this study are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Alexander, G.; Maroto-Valer, M. M.; Gafarova-Aksoy, P. Evaluation of reaction variables in the dissolution of serpentine for mineral carbonation. *Fuel* **2007**, *86*, 273–281.

(2) Hoffert, M. I.; Caldeira, K.; Benford, G.; Criswell, D. R.; Green, C.; Herzog, H.; Jain, A. K.; Kheshgi, H. S.; Lackner, K. S.; Lewis, J. S.; Lightfoot, H. D.; Manheimer, W.; Mankins, J. C.; Mauel, M. E.; Perkins, L. J.; Schlesinger, M. E.; Volk, T.; Wigley, T. M. L. Advanced technology paths to global climate stability: Energy for a greenhouse planet. *Science* **2002**, *298* (5595), 981–987.

(3) Metz, B.; Davidson, O.; de Coninck, H. C.; Loos, M.; Meyer, L. A. *IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, 2005; p 442.

(4) Teir, S.; Revitzer, H.; Eloneva, S.; Fogelholm, C. J.; Zevenhoven, R. Dissolution of natural serpentinite in mineral and organic acids. *Int. J. Miner. Process.* **2007**, *83*, 36–46.

(5) Lackner, K. S.; Wendt, C. H.; Butt, D. P.; Joyce, E. L., Jr.; Sharp, D. H. Carbon dioxide disposal in carbonate minerals. *Energy* **1995**, *20* (11), 1153–1170.

(6) Maroto-Valer, M. M.; Fauth, D. J.; Kuchta, M. E.; Zhang, Y.; Andrésen, J. M. Activation of magnesium rich minerals as carbonation feedstock materials for CO_2 sequestration. *Fuel Process. Technol.* **2005**, *86*, 1627–1645.

(7) Renforth, P.; Washbourne, C. L.; Taylder, J.; Manning, D. A. C. Silicate production and availability for mineral carbonation. *Environ. Sci. Technol.* **2011**, *45* (6), 2035–2041.

(8) Wilson, S. A.; Raudsepp, M.; Dipple, G. M. Verifying and quantifying carbon fixation in minerals from serpentine-rich mine

tailings using the Rietveld method with X-ray powder diffraction data. *Am. Mineral.* **2006**, *91* (8−9), 1331–1341.

(9) *Towards Sustainable Mining Progress Report 2007: GHG Emissions and Energy Management Progress Report*; Mining Association of Canada, 2007; http://www.mining.ca/www/Towards_Sustaining_Mining/Technical_Data_and_Bulletins.php (accessed June 15, 2009).

(10) Mt Keith Nickel Operations: Environmental Data. BHP Billiton Sustainable Development Reports, BHP Billiton, 2005; http://hsecreport.bhpbilliton.com/wmc/2004/performance/mko/data/index.htm (accessed July 10, 2011).

(11) Baker, M. J.; Blowes, D. W.; Logsdon, M. J.; Jambor, J. L. Environmental geochemistry of kimberlite materials: Diavik diamonds project, Lac de Gras, Northwest Territories, Canada. *Explor. Min. Geol.* **2003**, *10*, 155–163.

(12) Grguric, B. A. Minerals of the MKD5 nickel deposit, Mount Keith, Western Australia. *Aust. J. Mineral.* **2003**, *9* (2), 55–71.

(13) Thompson, J. B.; Ferris, F. G. Cyanobacterial precipitation of gypsum, calcite, and magnesite from natural alkaline lake water. *Geology* **1990**, *18* (10), 995–998.

(14) Warthmann, R.; van Lith, Y.; Vasconcelos, C.; McKenzie, J. A.; Karpoff, A. M. Bacterially induced dolomite precipitation in anoxic culture experiments. *Geology* **2000**, *28*, 1091–1094.

(15) Riding, R. Microbial carbonates: The geological record of calcified bacterial-algal mats and biofilms. *Sedimentology* **2000**, *47* (Suppl. 1), 179–214.

(16) Wright, D. T. The role of sulphate-reducing bacteria and cyanobacteria in dolomite formation in distal ephemeral lakes of the Coorong region, South Australia. *Sediment. Geol.* **1999**, *126*, 147–157.

(17) Roberts, J. A.; Bennett, P. C.; Gonzalez, L. A.; Macpherson, G. L.; Milliken, K. L. Microbial precipitation of dolomite in methanogenic groundwater. *Geology* **2004**, *32* (4), 277–280.

(18) Power, I. M.; Wilson, S. A.; Thom, J. M.; Dipple, G. M.; Southam, G. Biologically induced mineralization of dypingite by cyanobacteria from an alkaline wetland near Atlin, British Columbia, Canada. *Geochem. Trans.* **2007**, *8*, 13.

(19) Rodriguez-Navarro, C.; Jimenez-Lopez, C.; Rodriguez-Navarro, A.; Gonzalez-Muñoz, M. T.; Rodriguez-Gallego, M. Bacterially mediated mineralization of vaterite. *Geochim. Cosmochim. Acta* **2007**, *71* (5), 1197–1213.

(20) von Knorre, H.; Krumbein, W. E. Bacterial calcification. In *Microbial Sediments*; Riding, R. E., Awramik, S. M., Eds.; Springer: Berlin, 2000; p 331.

(21) Chisti, Y. Biodiesel from microalgae. *Biotechnol. Adv.* **2007**, *25* (3), 294–306.

(22) Wilson, S. A.; Raudsepp, M.; Dipple, G. M. Quantifying carbon fixation in trace minerals from processed kimberlite: A comparative study of quantitative methods using X-ray powder diffraction data with applications to the Diavik Diamond Mine, Northwest Territories, Canada. *Appl. Geochem.* **2009**, *24* (2), 2312–2331.

(23) Bennett, P. C.; Rogers, J. R.; Choi, W. J. Silicates, silicate weathering, and microbial ecology. *Geomicrobiology Journal* **2001**, *18* (1), 3–19.

(24) Power, I. M.; Dipple, G. M.; Southam, G. Bioleaching of ultramafic tailings by *Acidithiobacillus* spp. for CO_2 sequestration. *Environ. Sci. Technol.* **2010**, *44*, 456–462.

(25) Power, I. M.; Wilson, S. A.; Thom, J. M.; Dipple, G. M.; Gabites, J. E.; Southam, G. The hydromagnesite playas of Atlin, British Columbia, Canada: A biogeochemical model for CO_2 sequestration. *Chem. Geol.* **2009**, *206*, 302−316.

(26) Stanier, R. Y.; Kunisawa, R.; Mandel, M.; Cohenbaz., G Purification and properties of unicellular blue-green algae (order *Chroococcales*). *Bacteriol. Rev.* **1971**, *35* (2), 171–205.

(27) Wilson, S. A.; Dipple, G. M.; Power, I. M.; Thom, J. M.; Anderson, R. G.; Raudsepp, M.; Gabites, J. E.; Southam, G. Carbon dioxide fixation within mine wastes of ultramafic-hosted ore deposits: Examples from the Clinton Creek and Cassiar chrysotile deposits, Canada. *Econ. Geol.* **2009**, *104* (1), 95–112.

(28) Hänchen, M.; Prigiobbe, V.; Baciocchi, R.; Mazzotti, M. Precipitation in the Mg-carbonate system—Effects of temperature and CO_2 pressure. *Chem. Eng. Sci.* **2008**, *63* (4), 1012–1028.

(29) Land, L. S. Failure to precipitate dolomite at 25C from dilute solution despite 1000-fold oversaturation after 32 years. *Aquat. Geochem.* **1998**, *4*, 361–368.

(30) Königsberger, E.; Königsberger, L.; Gamsjager, H. Low-temperature thermodynamic model for the system Na_2CO_3-$MgCO_3$-$CaCO_3$-H_2O. *Geochim. Cosmochim. Acta* **1999**, *63*, 3105–3119.

(31) Williams, P. J. L.; Laurens, L. M. L. Microalgae as biodiesel & biomass feedstocks: Review & analysis of the biochemistry, energetics & economics. *Energy Environ. Sci.* **2010**, *3* (5), 554–590.

(32) Ensminger, I.; Busch, F.; Huner, N. P. A. Photostasis and cold acclimation: Sensing low temperature through photosynthesis. *Physiol. Plant.* **2006**, *126* (1), 28–44.

(33) Hasunuma, T.; Sanda, T.; Yamada, R.; Yoshimura, K.; Ishii, J.; Kondo, A., Metabolic pathway engineering based on metabolomics confers acetic and formic acid tolerance to a recombinant xylose-fermenting strain of *Saccharomyces cerevisiae*. *Microb. Cell Fact.* **2011**, *10*.

(34) Antoni, D.; Zverlov, V. V.; Schwarz, W. H. Biofuels from microbes. *Appl. Microbiol. Biotechnol.* **2007**, *77* (1), 23–35.

(35) Williams, C. M.; Burdge, G. Long-chain *n*-3 PUFA: plant v. marine sources. *Proc. Nutr. Soc.* **2006**, *65* (1), 42–50.

(36) Parkhurst, D. L.; Appelo, C. A. J. *User's Guide to PHREEQC (Version 2) a Computer Program for Speciation, Batch Reaction, One-Dimensional Transport, And Inverse Geochemical Calculations*, Water-Resources Investigations Report 99-4259; U.S. Geological Survey: Washington, DC, 1999; p 312.

(37) Wilson, S. A.; Barker, S. L. L.; Dipple, G. M.; Atudorei, V. Isotopic disequilibrium during uptake of atmospheric CO_2 into mine process waters: Implications for CO_2 sequestration. *Environ. Sci. Technol.* **2010**, *44*, 9522–9529.

(38) Riding, R. Cyanobacterial calcification, carbon dioxide concentrating mechanisms, and Proterozoic−Cambrian changes in atmospheric composition. *Geobiology* **2006**, *4*, 299–316.

(39) Sánchez-Román, M.; Romanek, C. S.; Fernández-Remolar, D. C.; Sánchez-Navas, A.; McKenzie, J. A.; Pibernat, R. A.; Vasconcelos, C. Aerobic biomineralization of Mg-rich carbonates: Implications for natural environments. *Chem. Geol.* **2011**, *281* (3−4), 143–150.

(40) Ferrini, V.; De Vito, C.; Mignardi, S. Synthesis of nesquehonite by reaction of gaseous CO_2 with Mg chloride solution: Its potential role in the sequestration of carbon dioxide. *J. Hazard. Mater.* **2009**, *168* (2−3), 832–837.

(41) Lee, S. W.; Park, S. B.; Jeong, S. K.; Lim, K. S.; Lee, S. H.; Trachtenberg, M. C. On carbon dioxide storage based on biomineralization strategies. *Micron* **2010**, *41* (4), 273–282.

(42) Mitchell, A. C.; Dideriksen, K.; Spangler, L. H.; Cunningham, A. B.; Gerlach, R. Microbially enhanced carbon capture and storage by mineral-trapping and solubility-trapping. *Environ. Sci. Technol.* **2010**, *44* (13), 5270–5276.

(43) Alaasm, I. S.; Taylor, B. E.; South, B. Stable isotope analysis of multiple carbonate samples using selective acid-extraction. *Chem. Geol.* **1990**, *80* (2), 119–125.

(44) Rio Tinto: Diavik Diamond Mine Sustainable Development Report. 2010.

(45) Environment Canada. National Climate Archive, climate.weatheroffice.ec.gc.ca (accessed August 17, 2009).

(46) Stolberg, D. J. *Rehabilitation Studies on Tailings Storage Facilities in an Arid Hypersaline Region*; Ph.D. Thesis, The University of Queensland: Brisbane, 2005.