

# Preliminary assessment of carbon capture and storage potential of variably serpentized ultramafic rocks of the Wellgreen Project, Yukon



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## Summary

Ultramafic mine tailings can be reactive to carbon dioxide (CO<sub>2</sub>). Utilization of this waste stream therefore has the potential to reduce or eliminate the greenhouse gas (GHG) footprint of mine operations. The Wellgreen Project, contains extensive Cu-Ni mineralization within mafic to ultramafic rocks. It was assessed for its potential for carbon capture and storage based on samples provided by Nickel Creek. 45 ore pulp and 2 slurry samples were analyzed for mineral content to assess the abundance of gangue minerals that are known to be reactive to CO<sub>2</sub> in air. All 47 samples were assessed with thermogravimetric analysis (TGA) and 13 were assessed with quantitative X-ray diffraction (qXRD) analysis using the Rietveld method. qXRD results indicate that all but two of the samples are all highly serpentized ultramafic rocks. TGA indicates that brucite and/ or hydrated magnesium carbonate minerals (e.g., hydromagnesite) are present in 22 of the samples analysed.

Most of the minerals present in ultramafic rocks do not normally react with CO<sub>2</sub> in air at rates that can result in appreciable carbon storage. However, Wellgreen samples contain key magnesium-rich minerals that are known to react quickly with CO<sub>2</sub> in air such as brucite. The confirmed presence of brucite indicates that there exists significant potential for carbon mineralization within Wellgreen tailings and waste rock. Hydromagnesite is also present and may represent brucite that has reacted with CO<sub>2</sub> in air during sample storage, or could reflect low temperature bedrock alteration.

## Introduction

Most of the carbon on Earth exists in a solid mineral form where it is thermodynamically favoured and stable over geologic time (Kump et al., 2000). It is no surprise, then, that the “holy grail” of carbon sequestration is to convert the carbon dioxide (CO<sub>2</sub>) that is present in air and anthropogenic emissions into mineral carbonates (Lackner, 2003), a process referred to as *carbon mineralization*. This process proceeds naturally during chemical weathering, but at a slow rate. Increased reactive surface area in finely ground ultramafic mine tailings speeds up these reactions (Wilson et al., 2014), thus presenting an opportunity to reduce the GHG emissions of some mines. Because the capacity for carbon storage in ultramafic tailings is typically much greater than mine emissions, these mines have the potential to become sites of negative emissions, contributing towards permanent carbon removal from the atmosphere.

The reactions that sequester CO<sub>2</sub> require reactive minerals that supply divalent metal cations (typically Mg<sup>2+</sup> and Ca<sup>2+</sup>). The carbon mineralization potential of ore and tailings is therefore primarily dependent on mineral content. Ultramafic rocks are rich in Mg and can contain minerals that react

quickly with air and groundwater. They can be broadly classified as fresh igneous rocks dominated by olivine and pyroxene, as hydrated versions dominated by serpentine (serpentinites), and as carbonate-altered equivalents that contain talc, magnesite and/or quartz (ophi-carbonate, soapstone, and listwanite). Thermal metamorphism of serpentinites can further diversify the mineralogical content to include chlorite, amphibole, pyroxene, and olivine. Of these rock types, serpentinites are generally the most reactive upon exposure to CO<sub>2</sub> in air. This is because of the accessory phases, such as brucite and hydrotalcite minerals, which form during serpentinization react rapidly with CO<sub>2</sub> (Wilson et al., 2014; Turvey et al., 2018a). Serpentine group minerals can be reactive to CO<sub>2</sub> at higher concentrations such as found in flue gases from fossil fuel combustion.

Geochemical, mineralogical, and geophysical properties of rocks reflect mineral content and can all provide insights into the reactivity an ore to CO<sub>2</sub>. These data can be used to target specific ore types and samples for mineralogical analysis. If ore contains minerals known to be reactive to CO<sub>2</sub>, then lab bench reactivity testing can be used to estimate the rate and capacity for carbon mineralization of tailings. These tests include far-from-equilibrium flow through dissolution tests, batch dissolution tests, and carbonation tests. These tests are carried out under select pH conditions to assess reactivity to CO<sub>2</sub> in different concentrations depending on whether reactivity to air, flue gas, or other CO<sub>2</sub> streams is sought.

In this analysis, 47 samples were chosen based on bulk chemical content as being most likely to contain reactive minerals such as brucite. Those samples were assessed for mineral content and recommendations for further testing based on those mineralogical data are suggested.

## Methods

When investigating the mineralogy of a given rock for its carbon mineralization potential two techniques are particularly useful. Quantitative X-ray diffraction (qXRD) provides a useful bulk analysis of the samples entire mineralogy by measuring bond distances within the crystal structure. However in some samples peak overlap between different phases can obscure the presence of important minerals such as brucite. To overcome this thermogravimetric analysis is used to provide an accurate estimate of the brucite content of a sample. Thermogravimetric Analysis (TGA) is an analytical technique for identifying and quantifying mineral abundances using their thermal properties (Földvári, 2011).

## Samples

A suite of 47 samples were provided by Nickel Creek as pulps for analysis. After analysis via TGA a suite of 13 samples were chosen for analysis using qualitative and quantitative XRD. Samples were chosen based on TGA results to characterize the full range of mineralogically diverse rock types.

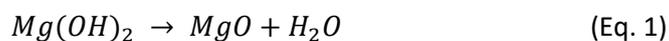
## Thermogravimetric analysis methods

### *Instrument details*

Thermogravimetric analysis was performed at the University of British Columbia using a Perkin Elmer TGA 4000 with a Polyscience chiller and an AS 6000 autosampler. Analyses used N<sub>2</sub> as an inert gas during heating at a pump rate of 19.8 ml/min. Samples were heated from room temperature to 100°C, held at 100°C for 10 minutes and then heated at a rate of 10°C/min from 100°C to 900°C with data being collected once per second (every 0.167°C). Data was processed and analysed in MATLAB R2020a (MathWorks) to produce thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for each sample as it underwent heating. The TG curve was plotted using wt.% rather than mass (mg) to allow for easy comparison between different samples. To create a smooth DTG curve every 50th data point was plotted.

### Analytical methods

TGA data is presented as TG curve that display the actual mass loss of volatile gases at different temperature values and DTG curves that show the rate of change of mass loss, allowing for better identification of different minerals within the sample. Brucite abundances can be calculated using TGA because from ~285 to 450°C (when in an inert atmosphere) pure brucite undergoes the following dehydroxylation reaction:



The size and shape of the DTG peak is dependent on the amount of brucite present in the sample as well as the rate of temperature increase (Trittschack et al 2014). The detection limit of brucite using the TGA 4000 is ~0.3 wt% brucite, any less material will result in mass loss that cannot be detected above the background mass loss that occurs when heating ultramafic rocks. If brucite is present above the detection limit the brucite content of a sample can be estimated from this mass loss using the following equation:

$$\text{Brucite (wt\%)} = (m_1 - m_2) \cdot 3.24 \quad (\text{Eq. 2})$$

Where  $m_1$  and  $m_2$  are the mass of the sample (in wt.%) at the beginning and end of the brucite peak according to the DTG curve, and 3.24 is the stoichiometric mass ratio between  $\text{Mg}(\text{OH})_2$  and  $\text{H}_2\text{O}$ . To remove any contributions made by minerals other than brucite exponential curve fitting is used on the DTG curve. The fit function in MATLAB R2020a (MathWorks) was used to fit the appropriate exponential function for each sample. The function was fitted to the data immediately before and after the brucite peak, typically from 215-285°C, and 450-525°C. The function took the form of:

$$y = a^{bx} + c^{dx} \quad (\text{Eq. 3})$$

Where  $y$  is wt.%,  $x$  is temperature and  $a$ ,  $b$ ,  $c$  and  $d$  are arbitrary constants determined by the fit function. The fitted function was then used to estimate the background mass loss from other minerals without brucite. Taking the difference between the mass loss of the fitted function at the end of the brucite peak ( $m_4$ ) and the experimental data at the same temperature ( $m_2$ ) determines the water weight percent loss due to brucite. This can be converted to brucite abundance by multiplying by the stoichiometric mass ratio, as presented below in Eq. 5.

$$\text{Brucite (wt\%)} = (m_4 - m_2) \cdot 3.24 \quad (\text{Eq. 5})$$

Furthermore, a linear correction factor of 1.18 was applied to the results to correct for consistent underestimation of brucite content.

### X-ray diffraction methods

#### Instrument details

X-ray Diffraction data was collected at the University of British Columbia Earth, Ocean and Atmospheric Sciences XRD laboratory. After milling and cation exchange samples were loaded against X00 grit sandpaper in a back-loading cavity mount to reduce preferred orientation of crystallites, before being analysed by a Bruker D8 Focus diffractometer equipped with a LynxEye detector and fine-focus Co X-ray tube operating a 35 kV and 40 mA. Data was collected over a range of 3-80° 2θ with a step size of 0.03° 2θ and a counting time of 0.07s/step.

### *Analytical methods*

Identification of minerals was performed using DIFFRAC.EVA V.X (Bruker AXS) and referencing patterns from the ICDD PDF-4+ database. Quantitative XRD analysis was performed using the Rietveld method through DIFFRAC.TOPAZ V.X (Bruker AXS) using the fundamental parameters approach (Cheary and Coelho, 1992).

### Reactivity Testing

Slurries (~500ml) were prepared by adding 500mg of each pulverized sample to 500ml of the acidic solution. Carbonic acid was introduced into the solution by continuously injecting 10% CO<sub>2</sub> compressed gas from Praxair Inc. into the solution, resulting in pH values of 4.4. The reactors (500ml conical flasks) were agitated continuously, with a V.W.R Orbital Shaker Model 1000 at speed 4.5. The slurry pH and solution chemistry were measured at regular time intervals throughout the 100-hour experimental duration. Ten aliquots of ~5 mL slurry (total 50mls) were collected per reactor to ensure the impact of solvent depletion during dissolution is minimal. Slurry aliquots were analyzed for Al, Ca, Fe, K, Mg, Na and Si concentration using ICP-OES. Solution chemistry of all liquid samples were further examined for saturation state of potential Mg-carbonate minerals (i.e. Magnesite, Nesquehonite). The saturation state of Mg-carbonate minerals were calculated using PHREEQC (Parkhurst and Appelo, 2013). Labile Mg is represented as relative % of the total Mg in the sample. Leached Ca contents were used to assess calcite content.

## Results

### TGA results

Of the 47 samples analysed using TGA 22 have visible mass loss between 285 and 400°C. This mass loss between 285 and 400°C indicates the presence of either brucite, hydrotalcites or hydrated Mg-carbonates. Detailed X-ray diffraction analysis is required to differentiate between brucite, hydrotalcites or hydrated Mg-carbonates.

### XRD Results

The qXRD results indicate that a complete spectrum from brucite-only (sample 1535163) to hydromagnesite-only samples (noplatt001112) are present. Most samples (noplatt001107, m630206, m630194) contain a mixture.

A significant number of samples from Wellgreen contain brucite and/or hydromagnesite. Hydromagnesite likely represents brucite that reacted either in low temperature bedrock systems, or during sample storage. A comparison of mineral content and whole rock chemistry indicates that these minerals can be found in rocks with wt.% Mg contents of 22 or greater.

### Leach Test Results

Leach test results on four samples, specifically Mg and Ca content, were compared to measured total inorganic carbon (TIC) and mineral content to assess the leachable Mg content (exclusive of hydromagnesite) of four samples. The TIC attributable to calcite was determined by the leached Ca content and the remaining TIC attributed to hydromagnesite. The corresponding leached Mg content attributable to hydromagnesite was deducted from total leached Mg. Finally, the leached Mg content of a sample that lacks brucite (Well 15 slurry) was used to quantify Mg leached from serpentine and this was deducted from the leached Mg content of the remaining three samples. On this basis it is estimated that all three samples (L997098, noplatt001107, L535163) contain 1-3 weight percent brucite. This represents a capacity to sequester 6 to 22 kg CO<sub>2</sub> per tonne of tailings equivalent.

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