

Characterizing Reactivity of Ultramafic Minerals and Tailings in British Columbia for Carbon Capture and Storage

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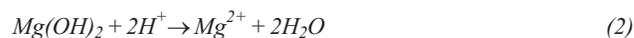
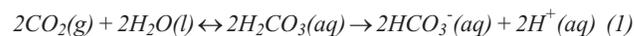
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Introduction

Climate change and rising atmospheric carbon dioxide (CO₂) levels have recently become much-debated environmental issues. One of the strategies necessary to mitigate climate change is capturing, utilizing and storing greenhouse gases such as CO₂ (Bickle, 2009). Carbon sequestration via mineral carbonation (also known as carbon mineralization) has emerged as a promising strategy to reduce net greenhouse gas emissions (Seifritz, 1990; Lackner et al., 1995; Lackner, 2003; Sipilä et al., 2008). Industrial waste materials like mine tailings are high in reactive surface area because of the crushing and grinding during mineral processing and, thus, are ideal for carbon mineralization (Uddin et al., 2012). Different tailings materials will have various sequestration capacities. Specifically, waste from mines hosted in ultramafic rocks that contain commodities such as asbestos, diamond, chromite and nickel have the highest predicted carbon sequestration capacity due to the presence of fast-reacting trace minerals such as brucite (Wilson et al., 2009, 2010, 2011; Power et al., 2011; Pronost et al., 2011; Bea et al., 2012; Harrison et al., 2013; Rozalen et al., 2014; Hamilton et al., 2020). Currently, many ultramafic mine sites around the world, such as the Mount Keith nickel mine in Western Australia and the Diavik Diamond Mine in the Northwest Territories, Canada, have documented their tailings naturally reacting with atmospheric CO₂ (Wilson et al., 2011, 2014). The province of British Columbia (BC) also represents massive carbon-capturing potential, as the area contains extensive volumes of ultramafic rock that host some of Canada's largest nickel deposits. The extraction and crushing of such rocks during mining will unlock their reactivity for ex-situ carbon mineralization.

The geochemical process of mineral carbonation in mine tailings involves incorporating CO₂ gas into inert carbonate

minerals (MgCO₃·xH₂O) through the aqueous reaction of 1) the dissolution of CO₂ into the water, producing acidity; 2) leaching of cations from the surrounding minerals; and 3) the precipitation of Mg-carbonate minerals, consuming alkalinity, as described in Equations 1 to 3, where (g) refers to gaseous phases, (l) refers to liquid phases, and (aq) refers to aqueous phases.



The current feasibility studies that are used to synthesize the capacity of mine tailings for carbon sequestration at an industrial scale include lab-scale, pilot, and field-scale testing (McGrail et al., 2003, 2006; Matter and Kelemen, 2009; Haug et al., 2011; Beerling et al., 2018; Power et al., 2021). In particular, lab-scale testing is used to study the carbon sequestration potential or the reactivity of minerals and tailings. Reaction rate and time are two dominating factors controlling mineral carbonation reactivity (Knauss and Wolery, 1988; Berg and Banwart, 2000; Pokrovsky and Schott, 2004; Harrison et al., 2013; Power et al., 2013a, b; Thom et al., 2013; Li et al., 2018; Bullock et al., 2021). Previous studies on mineral dissolution kinetics have shown that not all cations are accessible under atmospheric conditions (Snæbjörnsdóttir et al., 2018; Tutolo and Tosca, 2018; Wolff-Boenisch and Galeczka, 2018; Paulo et al., 2021). Hence, this paper uses labile Mg²⁺ (defined as Mg²⁺ that is accessible and can be rapidly leached at ambient pressure and temperature) to quantify carbon sequestration reactivity in ultramafic rocks.

Mineral dissolution in a flow-through reactor (flow-through time-resolved analysis [FT-TRA] module) was used to characterize the loosely bound, fast-reacting labile Mg²⁺ and slow-reacting non-labile Mg²⁺ (De Baere et al., 2015; Lu et al., 2022). Results show that the amount of labile Mg²⁺ is primarily controlled by the reaction rate of the mineral and time in the flow-through reactor. In other words, the amount of accessible labile Mg²⁺ will depend on the characteristics of a carbon sequestration site, particu-

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larly the length of time that the cation feedstock is exposed and can dissolve and react with CO₂ to form carbonate minerals. The lab-scale test also demonstrates that all Mg²⁺ in Mg-hydroxide minerals are labile due to their high reactivity, whereas Mg-silicate minerals contribute less due to their slow dissolution kinetics. Nonetheless, Mg-silicate minerals have the highest abundance in ultramafic rocks and, thus, represent the most significant potential source of labile Mg²⁺ for mineral carbonation.

Although the flow-through dissolution experiment has successfully characterized labile Mg²⁺, the FT-TRA module can be challenging to set up and operate (De Baere et al., 2015). Alternative experiment protocols that are easier to operate, faster and low-cost are sought for more efficient evaluation. In this study, an air carbonation test is adopted to characterize reactivity by quantifying labile Mg²⁺ carbonation. The air carbonation method treats samples under humidified CO₂ gas in a closed chamber and monitors the increase in total inorganic carbon content. Samples of typical ultramafic minerals and tailings were acquired to test the method. The air carbonation experiment is conducted with an orthogonal design to rank various factors influencing labile Mg²⁺ carbonation (Zurovac and Brown, 2012; Wu, 2013; Zhang and Ma, 2013). The details of the orthogonal experimental design and data analysis are discussed below. Overall, the air carbonation test will be evaluated as a low-cost and labour-efficient option for assessing the mineral carbonation reactivity of minerals and tailings. The results from this study will impart a better understanding of the fundamental mechanisms and chemical processes that control heterogeneity and reactivity, with implications for mineral carbonation in other processed industrial wastes, such as asbestos mine tailings, red mud and steel slag. More importantly, this research serves as a foundation to develop characterization protocols to assist CO₂ capture and storage using mine tailings in BC, and may take BC to the forefront globally in the development of carbon capture, utilization and storage.

Materials and Methods

Sample Material

Three mineral samples (brucite, serpentine and forsterite) were used to prepare samples for the air carbonation test: high-purity pulverized brucite ore was sourced from the Brucite mine (Gabbs District, Nevada, United States); serpentine samples were obtained from the Swift Creek landslide in the northwestern part of the State of Washington, United States; and forsterite grains from the Twin Sisters dunite, also in Washington, were supplied by Ward's Science (item# 470025-722).

The samples were dry-milled and dry-screened to the following particle size ranges: <53 μm, 53–106 μm, and >106 μm. All samples were characterized for their mineral-

ogical composition (using quantitative X-ray diffraction), thermal stability and fraction of volatile components (using thermogravimetric analysis [TGA]), specific surface area (using the multi-point Brunauer-Emmett-Teller [BET] method with N₂ gas absorption), and particle size distribution (using a Malvern Panalytical Mastersizer 2000 laser diffraction particle-size analyzer). Brucite abundance in the mineral samples is taken from values measured using TGA, since quantitative X-ray diffraction (qXRD) analyses often result in a high relative error for minerals at low abundance (Raudsepp et al., 1999; Washbourne et al., 2012; Tosca and Masterson, 2014; Arce et al., 2017; Turvey et al., 2018a, b, 2022). The relevant sample characterization results are summarized in Table 1.

Orthogonal Experimental Design

Orthogonal experimental design (OED) is a method of scientific testing that studies multiple factors simultaneously, and their impact level, to determine the optimal combination of factors (Zurovac and Brown, 2012; Wu, 2013). Orthogonality refers to the property of a design that ensures all the specific parameters may be estimated independently of one another. Orthogonal experimental design is often used for this purpose, because the design can effectively reduce the number of experiments needed. Variance analysis and regression analysis are commonly used to analyze the results from OED tests, and can lead to many valuable conclusions (Zhang and Ma, 2013). Thus, OED is used in this study to allow testing of multiple variables that can affect mineral carbonation reactivity of minerals and tailings.

The orthogonal table is the foundation of the orthogonal experimental design, which is formed according to the following definition:

$$L_n(m)^k,$$

where L is the table, n is the number of rows (which corresponds to the number of test cases), m is the number of col-

Table 1. Summary of relevant quantitative X-ray diffraction (qXRD) mineral abundances, thermogravimetric analyses (TGA), brucite abundance, and Brunauer-Emmett-Teller (BET) surface area values for the three mineral samples tested.

Sample name	Brucite	Serpentine (lizardite)	Forsterite
Serpentine ¹		91.9	
Brucite ²	90.0		
Diopside ¹			
Pyroaurite ²	0.2		
Forsterite ¹			94.9
Magnesite ¹	0.5		
Phlogopite ¹		3.6	
BET surface area ³	4.2	18.5	0.2

¹wt. % abundance determined by qXRD

²wt. % abundance determined by TGA

³BET (m²/g)

umns (which corresponds to the number of factors), and k is the factor level number, meaning each factor has k levels. Earlier studies investigated the controls of mineral carbonation in column experiments, and identified that water content and grain size have effects on the progress of the mineral carbonation reaction (Harrison et al., 2015, 2016). Since both brucite and Mg-silicate minerals (e.g., serpentine, olivine) were identified as important sources of reactivity, their mineralogical content may also have an impact on the carbonation process (Lu et al., 2022). Four factors that could impact labile Mg^{2+} carbonation reaction were identified for this study: 1) water content, 2) grain size, 3) brucite content, and 4) silicate mineralogy (serpentine and olivine [forsterite] content). Each of these four factors were tested at three levels (Wu, 2013). Hence, for a test of four factors and three levels, the number of independent test cases was nine, and the orthogonal table formed is defined by the expression $L_9(4^3)$, as shown in Table 2.

The three levels of water content selected for testing were 7.5 wt. % (of the sample mass), 12 wt. % and 15 wt. %. The three levels of grain size tested were $>106 \mu m$, 53–106 μm , and $<53 \mu m$. The three levels of brucite content tested were 4 wt. % (of the sample mass), 7 wt. % and 10 wt. %. The presence of forsterite and serpentine in the samples was tested by samples with forsterite only, samples with half forsterite and half serpentine, and samples with serpentine only. In this way, the combination of each line in Table 2 constitutes a test case.

Air Carbonation Tests

The set-up of the air carbonation test included a 60 L polycarbonate reaction chamber with inlet and outlet ports for gas flow, and two 4 L interconnected conical flasks (Figure 1). Compressed 10% CO_2 gas was continuously injected into the reaction chamber, using Saint-Gobain Tygon™ R-3603 tubing, at approximately 200 millilitres per minute (ml/min). Carbon dioxide gas was humidified by flowing through the two interconnected 4 L conical

flasks containing distilled water. Pulp samples of the minerals were moulded into the shape of disks with dimensions of 17.9 mm radius and 1.8 mm thickness, using a premade Perspex® glass mount and rod piston. Nine test cases representing separate combinations of the four factors were then carried out. In addition, ten subsamples of the nine test cases were made for sampling purposes, and these were taken out of the air carbonation set-up after 4, 20 and 44 days of the experiment. The temperature and humidity in the reaction chamber were stable throughout the experiment, at around $22 \pm 1^\circ C$ and $95 \pm 0.2\%$ relative humidity. Before and after the air carbonation experiments, samples were homogenized using a corundum mortar pestle and analyzed for total inorganic carbon (TIC). The content of TIC (reported as %C [grams of carbon/grams of the sample]) in the disk samples was determined using a UIC Inc. CM5130 acidification module, and the instrument was calibrated before each analysis. The carbon content in the raw sample was subtracted from the carbon content measured post-carbonation reaction, to obtain the net carbon content gained from carbonation.

Results and Discussion

Hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] with the stoichiometry of $C/Mg = 0.8$ is assumed to form from labile Mg^{2+} carbonation (Wilson et al., 2009; McCutcheon et al., 2019). Data representing TIC (g of carbon/g of the sample) is converted to grams of Mg^{2+} carbonated/grams of the sample for data analysis. The results from 4, 20 and 44 days in the experimental set-up are summarized in Table 3 and shown in Figure 2. In Figure 2, the four factors tested (A, water content; B, grain size; C, brucite content; D, silicate mineralogy) and their three levels (e.g., A1, A2, A3) are plotted on the x-axis, and the amount of Mg^{2+} carbonated is plotted on the y-axis. Data plotted in red, green and black indicate the amount of Mg^{2+} carbonated after 4 days, 20 days and 44 days, respectively, of reaction. Due to the orthogonal nature of the experimental design, the various

Table 2. The orthogonal table defined by the expression $L_9(4^3)$. The table has nine rows, representing nine test cases (i.e., nine different combinations), and the following four factors: A, water content; B, grain size; C, brucite content; D, silicate mineralogy (serpentine and olivine [forsterite] content). Each factor has three levels of variability. For factor A these levels are 7.5, 12 and 15 wt. % water; for B they are >106 , 53–106 and $<53 \mu m$ grain size; for C they are 4, 7 and 10 wt. % brucite; and for D the three levels are samples of forsterite only, samples of half forsterite and half serpentine, and samples of serpentine only.

Test case no.	A Water content (wt. %)	B Grain size (μm)	C Brucite content (wt. %)	D Silicate mineralogy
1	7.5	>106	4	Forsterite
2	7.5	53–106	7	Serpentine
3	7.5	<53	10	Forsterite + serpentine
4	12.0	>106	7	Forsterite + serpentine
5	12.0	53–106	10	Forsterite
6	12.0	<53	4	Serpentine
7	15.0	>106	10	Serpentine
8	15.0	53–106	4	Forsterite + serpentine
9	15.0	<53	7	Forsterite

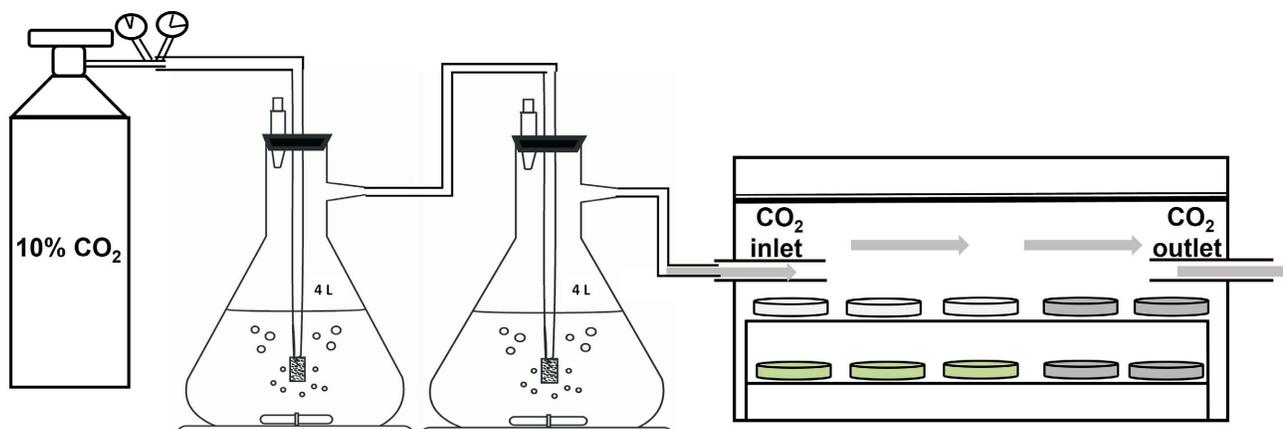


Figure 1. Schematic diagram of the air carbonation experimental set-up. As shown, 10% carbon dioxide (CO₂) gas is continuously injected into two 4 L interconnected conical flasks and then into the reaction chamber for the purpose of humidifying the gas. The colour of the disks represents samples with different mineralogy: green represents serpentine-dominated samples; grey represents forsterite-dominated samples; and white represents samples containing an equal amount of forsterite and serpentine.

levels of each factor are collocation balanced, meaning that all factors are equally tested. Since there are three levels tested, each factor is repeated three times, and the average of the results was determined for variance calculation and to reduce the test error (Table 3, Figure 3).

Variance analysis was used to analyze the impact of various factors on the net carbon gain, and to determine the optimal level of each factor. To find the variance of each factor, the average of each level within each factor is calculated, as shown in Figure 3. Next, the average is subtracted from each level and the differences are squared. The variance of each factor is determined by calculating the average of the

squared differences from each level. Equation 4 shows the calculation of variance, where \bar{x} is the mean of the levels, and n is the number of levels. The calculated variances for each factor are presented in Table 3.

$$Variance = \frac{\sum(x - \bar{x})^2}{n} \quad (4)$$

In the following sections, the effect of water content, brucite content, silicate mineralogy (serpentine and olivine [forsterite] content), and grain size on labile Mg²⁺ carbonation are discussed.

Table 3. Variance analysis of the orthogonal experiment. Grams of Mg²⁺ carbonated per gram of sample measured from day 4, day 20 and day 44 of the experiment are organized by the four factors tested: A, water content; B, grain size; C, brucite content; D, silicate mineralogy (serpentine and olivine [forsterite] content). Three levels were tested for each factor. For factor A these were 7.5, 12 and 15 wt. %; for B, >106, 53–106 and <53 μm; for C, 4, 7 and 10 wt. %; and for D, samples of forsterite only, samples of half forsterite and half serpentine, and samples of serpentine only.

	A		B		C		D	
	Water content (wt. %)	g Mg ²⁺ / g sample	Grain size (μm)	g Mg ²⁺ / g sample	Brucite content (wt. %)	g Mg ²⁺ / g sample	Silicate mineralogy	g Mg ²⁺ / g sample
44 days								
1	7.5	1.08	>106	1.17	4	0.67	Forsterite	0.91
2	12	1.02	53–106	1.05	7	1.07	Forsterite +serpentine	1.13
3	15	1.17	<53	1.06	10	1.54	Serpentine	1.24
Variance		0.01		0.01		0.19		0.03
20 days								
1	7.5	0.56	>106	0.76	4	0.39	Forsterite	0.59
2	12	0.67	53–106	0.67	7	0.65	Forsterite +serpentine	0.67
3	15	0.82	<53	0.62	10	1.01	Serpentine	0.79
Variance		0.02		0.01		0.10		0.01
4 days								
1	7.5	0.18	>106	0.39	4	0.17	Forsterite	0.28
2	12	0.3	53–106	0.33	7	0.26	Forsterite +serpentine	0.23
3	15	0.45	<53	0.21	10	0.51	Serpentine	0.42
Variance		0.02		0.01		0.03		0.01

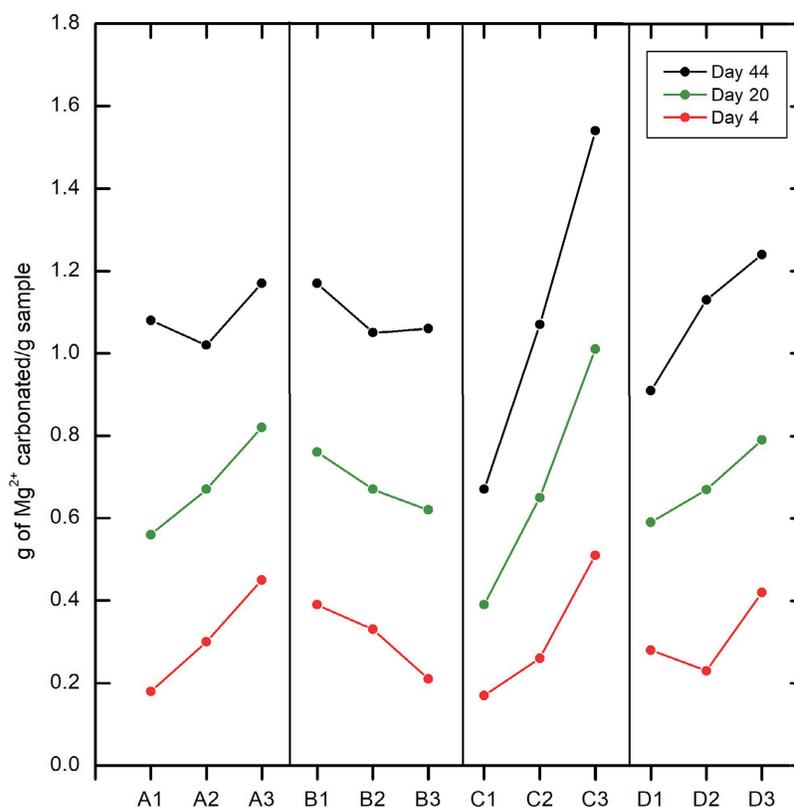


Figure 2. Plot of grams of Mg^{2+} carbonated per gram of sample versus the factors and levels tested. The x-axis shows the four factors tested (A, water content; B, grain size; C, brucite content; D, silicate mineralogy). For factor A, the three levels used were 7.5 (A1), 12 (A2) and 15 wt. % (A3); for B, >106 (B1), 53–106 (B2) and <53 μm (B3); for C, 4 (C1), 7 (C2) and 10 wt. % (C3); and for D, samples of forsterite only (D1), samples of half forsterite and half serpentine (D2), and samples of serpentine only (D3). The values of the plotted data points are also presented in Table 3. Data plotted in red, green and black represent the progression of Mg^{2+} carbonated after 4, 20 and 44 days, respectively, in the air carbonation set-up.

Effect of Water Content and Brucite Content

Three levels of moisture (water) content (7.5, 12 and 15 wt. %) and brucite content (4, 7 and 10 wt. %) were tested. As shown in Figure 2 and Table 3, the amount of Mg^{2+} carbonated is consistently higher in samples with 15 wt. % water and 10 wt. % brucite, followed by samples with 12 wt. % water, 7 wt. % brucite, and then 7.5 wt. % water, 4 wt. % brucite. The data also show a significant increase in the amount of Mg^{2+} carbonated from day 4 to day 44, which demonstrates the progress in reaction with time. Samples with the highest moisture and brucite content had the highest carbonated Mg^{2+} , demonstrating that the mineral carbonation reactivity is greater for high brucite content and moist tailings. The variances calculated in Table 3 also show that water content has lower effects on carbonation reaction during the later stages, because the reaction may become limited by the surface passivation effect and the supply of CO_2 and leachable Mg^{2+} . These findings agree with previous studies using metre-scale column experiments and reactive transport modelling (Harrison et al.,

2015, 2017). However, the air carbonation test is much easier to set up and manage.

Effect of Silicate Mineralogy and Grain Size

Samples with different serpentine and forsterite content behaved differently in the air carbonation experiment and yielded interesting results. As shown in Figure 2, the sample with only forsterite consistently reacted less than samples with serpentine. Overall, samples with only serpentine carbonated the highest amount of labile Mg^{2+} . This finding and observation agree with what was observed in the previous flow-through study (Lu et al., 2022), which is that serpentine has more labile Mg^{2+} than olivine because of the larger surface area and the longer, faster transient dissolution stage. Thus, after 44 days, samples with the highest content of serpentine carbonated the most Mg^{2+} . Moreover, the grain-size test results demonstrated that samples with the largest grain size, i.e., the largest pore space, have the highest reactivity. This agrees with the reactivity expectation of tailings based on their grain size reduction during pro-

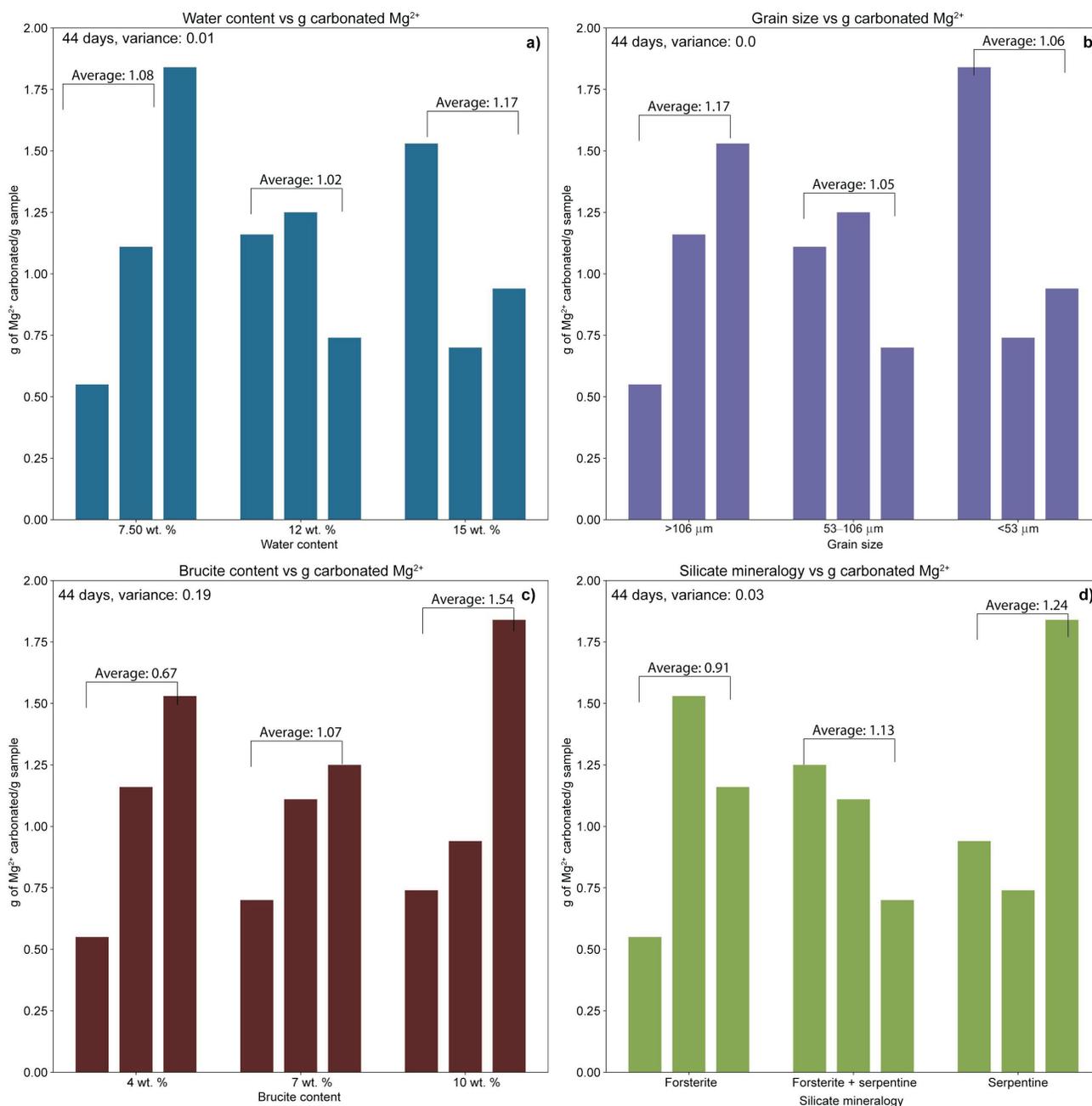


Figure 3. Bar charts showing results of the orthogonal experimental design tests (after 44 days): **a)** grams of Mg²⁺ carbonated per gram of sample versus water content (at 7.5, 12 and 15 wt. %); **b)** grams of Mg²⁺ carbonated per gram of sample versus grain size (>106, 53–106 and <53 μm); **c)** grams of Mg²⁺ carbonated per gram of sample versus brucite content (at 4, 7 and 10 wt. %); **d)** grams of Mg²⁺ carbonated per gram of sample versus mineralogy of samples (only forsterite, half forsterite and half serpentine, and only serpentine). In each subplot, the bars are grouped by level; the average carbonated Mg²⁺ of each level and the variance of each factor are also noted.

cessing. It has been well-established that mine tailings constitute gangue from crushed and ground ore, with clay- and silt- to sand-sized particles and a grain size ranging from 10 to 1000 μm (Lapakko et al., 2006; Salmon and Malmström, 2006; Power et al., 2021). Such grain size variation is highly advantageous for the rate of mineral carbonation because the smaller grain size generates large amounts of freshly exposed surfaces while the larger grain size provides sufficient space for gas, fluid and rock interaction (Pronost et

al., 2011; Vogeli et al., 2011; Bodéan et al., 2014; Li and Hitch, 2017; Li et al., 2018). In the present study, the samples were compacted to simulate mine tailings in a tailings pond. The mixture has high density, which could have deleterious effects on CO₂ diffusion and cation transportation. Larger grain size benefits the larger pore size and higher porosity, resulting in faster carbonation rates and higher CO₂-capturing ability. Therefore, samples with >106 μm grain size showed the greatest extent of carbonation throughout the

experimental duration in the present study. Grain size distribution significantly affects the CO₂-capturing ability of tailings, which makes it important.

Results from the Orthogonal Experimental Design

According to the variance analysis of OED, ranking the variance from high to low will rank factors that are the most influential to the least influential (Larson, 2008; Zhang and Ma, 2013). As shown by the results on day 44 in Table 3, brucite content is the most influential factor for labile Mg²⁺ carbonation during the air carbonation test, followed by the content of silicate minerals (i.e., serpentine and forsterite), water content and grain size. It should be noted that this order does change depending on the duration of the test. The variance of brucite content showed a consistent increase with the progression of the experiment from day 4 to day 44 (0.03 at 4 days; 0.10 at 20 days; and 0.19 at 44 days). In contrast, the effect of grain size showed a continuous decrease, leading to minimal variance values. Overall, the results from the air carbonation experiment with OED design provide valuable information, suggesting that mineralogy is the primary factor that controls the labile Mg²⁺ carbonation capacity of tailings. Water content is the second most important component, as it controls the dissolution of minerals and CO₂ gas. Grain size is also significant, as it affects the reactive mineral surface area, porosity and CO₂ mobility.

Conclusion

An improved understanding of mineral reactivity in the short and long term is critical for accurately assessing carbon sequestration capacity. Technical difficulties and financial concerns were encountered using traditional experimental methods (e.g., flow-through time-resolved analysis) and motivated the design of new experimental protocols to assess reactivity. This study proposes the use of air carbonation tests with an orthogonal experimental design to characterize the carbon sequestration reactivity of ultramafic minerals and tailings. The orthogonal design allows testing of multiple contributing factors without having to carry out numerous experiments. In addition, the air carbonation tests modelled coupled mineral dissolution–carbonation reaction in porous media and assessed labile Mg²⁺ by detecting inorganic carbon content gain in the sample. Nevertheless, the orthogonal experimental design data analysis demonstrated here is preliminary. Future work will involve in-depth data analysis and statistical calculations. Important conclusions that are drawn from this study are that 1) mineralogy, especially brucite content, is the most important controlling factor during labile Mg²⁺ carbonation; 2) water content and grain size are relatively less important, but samples with higher moisture content and larger grain size will have more reactivity; 3) controls from silicate min-

erals may prevail in the later reaction stages because stoichiometric dissolution will slow the reaction kinetics. Overall, the experimental results provide insights into controls at the pore scale. The adoption of orthogonal experimental design has implications for future experimental design when studying multiple factors and their impact level. These findings will contribute to discovering more advanced strategies to quantify reactivity and characterize the capacity of ultramafic minerals and tailings for carbon capture and storage.

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