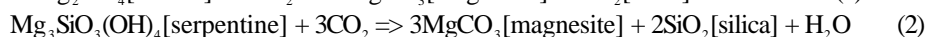
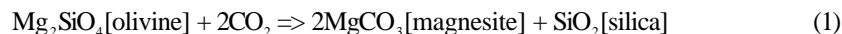


¹ M. Sc. Candidate, University of Victoria, Victoria, British Columbia, Canada, V8W 3P6² BC Geological Survey Branch, Victoria and adjunct professor at the University of Victoria, Canada³ Office of Process Development, Albany Research Center, Office of Fossil Energy, US DOE**ABSTRACT**

Given the current level of technology and projected costs per tonne of CO₂ sequestered, mineral carbonation is a "niche" method that may be applicable when a major CO₂ point source is located in proximity of ultramafic rocks and where other geological sinks are not available or can not be recommended for safety reasons. This paper presents a methodology and key parameters for the evaluation of mineral sequestration potential of a given region or specific ultramafic body. The steps are as following: a) identify areas that host ultramafic rocks and compile them into a map; b) concentrate on sectors with the potential to host large tonnages of ultramafic rocks, accessible by open cast mining and in proximity of major, stationary CO₂ point source(s); c) screen promising sites by field preliminary sampling/examinations; d) filter promising sites using petrological, mineralogical and geochemical criteria; e) submit representative samples for bench-scale carbonation testing; f) consider potential byproducts. In specific circumstances, the economics of mineral sequestration may be favourably affected by the recovery of Ni, Cr, Fe and PGE. Should precipitation of magnesite and silica take place under controlled conditions, it is possible that these reaction products could be used in industrial or construction applications.

INTRODUCTION

Various geological CO₂ sequestration methods have been proposed worldwide, including injection of CO₂ into hydrocarbon reservoirs, deep coal beds or deep saline aquifers [1]. The applicability of these methods is site specific and depends largely on tectonic and geological settings [2]. Where major CO₂ point sources are underlain by a crystalline basement or located within tectonically unstable regions, the mainstream geological CO₂ sequestration methods are not applicable. Mineral sequestration of CO₂ is one of the "niche" alternatives. It involves reacting Mg-silicates (forsteritic olivine or serpentine) with CO₂ emissions. The resulting products are magnesite (MgCO₃) and silica (equations 1 and 2).



Large quantities of Mg-silicates are needed. Magnesite (possibly hydromagnesite), and silica are stable in surface environments and could be used as open pit backfill, in industrial mineral or construction applications, without major legacy problems and needs for perpetual monitoring for CO₂ leaks [3,4]. Olivine is more reactive without the energy-intensive pre-treatment that serpentine requires [3]. However, because serpentine-rich rocks are more widespread than those rich in olivine, research into optimization of energy used in the pre-treatment of serpentine is still ongoing [3,5]. Chrysotile-containing tailings are also investigated as potential feed [6,7]. Since the serpentine in tailings has already been mined and milled, reduction in sequestration cost may be possible. The fibrous nature of this variety of serpentine, which is considered as a health concern, may be effectively destroyed by mineral carbonation, providing a major environmental benefit.

Raw Materials

Olivine- and serpentine-rich rocks are called dunites and serpentinites, respectively. These rocks are part of ultramafic complexes and are found primarily along continental margins and suture zones [8]. China, Finland, Quebec, Newfoundland, California and British Columbia are good examples. The most common types of ultramafic complexes are Alpine, Alaskan and Layered Intrusive and their geographic distribution is restricted by tectonic setting [9]. The position of the dunite and serpentinite zones, their physical and chemical characteristics and variation in mineralogy and mineral chemistry within these complexes is at least in part predictable [9]. Ultramafic rocks are commonly believed to represent nearly inexhaustible sources of raw materials for mineral sequestration [7,10], but detailed geological studies [9] indicate otherwise. Furthermore, not all ultramafic rocks can be ranked equally in terms of suitability as raw material for the mineral sequestration process. Thus far, assessments of suitable raw material have been based mainly on Mg content, size and location of the deposit [7,10,11]. However, the link between conceptual modelling and laboratory tests is lacking. There is a need to screen ultramafic deposits on the basis of mineralogy and geochemistry. The rate of dissolution of dunites and serpentinites, a limiting factor in achieving the carbonation process, is affected by the presence of impurities, such as pyroxenes, amphiboles, talc and other minerals [3]. Accessory minerals such as chromite, magnetite and platinum group elements (PGE), commonly associated with these rocks in trace amounts, may be recovered prior to the carbonation process and potentially offset part of the sequestration costs. This research is the first attempt to develop the methodology to bridge continent scale (1:10,000,000) inventory studies to bench-scale mineral sequestration tests.

IDENTIFYING ULTRAMAFIC COMPLEXES: COMPILING THE MAP

The first step in selecting favourable zones for hosting raw material for mineral sequestration of CO₂ is to identify ultramafic complexes for a given region. This information can be obtained from a provincial or federal geological survey database. Airborne EM and magnetic surveys can aid in delineating areas with ultramafic rocks for unmapped regions. To demonstrate this stage of the methodology, we focus on the province of British Columbia (BC). The distribution of ultramafic rocks in BC is presented in a map. This map was derived from the database developed for the mineral potential assessment of BC [12] and shows that ultramafic complexes are restricted to a long, narrow belt, trending from northeastern BC to southcentral BC. At this stage, the distinction between dunite and serpentinite deposits must be made. Although BC has favourable geology to host ultramafic rocks, ultramafic complexes containing dunite and/or serpentinite zones underlie less than 3% of the province. As

expected, dunite and serpentinite are commonly associated together, underlying approximately 1% of BC's surface. Ultramafic rocks containing only dunite zones underlie less than 0.5% of BC's surface and are restricted primarily to Alaskan-type complexes. In contrast, ultramafic rocks containing serpentinite, but not dunite, are more abundant, underlying about 2% of BC and are generally associated with Alpine type complexes [9].

SELECTING FAVOURABLE ZONES

From the map, dunite and serpentinite deposits may be selected for further screening. This is based on the geographic location, size and accessibility of the deposits. A map depicting locations of major (>50,000 tonnes of CO₂-equivalent per year) stationary point sources is useful in selecting proximal dunite and serpentinite deposits [2]. The deposits need to be of sufficient tonnage to supply the raw material (>30,000 t/day) for a period of 30 years [13]. They should also be easily accessible, preferably having some form of infrastructure in place (roads, railroad, pipelines). Dunite contains more reactive material per tonne; however, serpentinite is more common and is therefore more likely to be located close to a major point source than dunite. Several targets are selected from the map that meet these requirements. Further screening involves the acquisition of mineralogical and geochemical data.

EVALUATION OF SELECTED DUNITE AND SERPENTINITE DEPOSITS

Different reaction pathways for mineral carbonation have been proposed. In light of the slow conversion rate in the direct carbonation reaction and the corrosive nature of the HCl extraction process [14], most of the recent effort has focused on dissolving Mg-silicates in an aqueous medium [3]. Dissolution of the raw material, where Mg²⁺ ions become available for carbonation, is therefore an important rate-limiting step [3]. Minerals such as pyroxenes and silica are relatively insoluble. In contrast, olivine (formed at high temperatures) and serpentine dissolve easier, although olivine has a higher dissolution rate than serpentine [15]. The dunite core of the Tulameen complex, a large, easily accessible Alaskan-type ultramafic body, located in southern BC, is chosen to exemplify the mineralogical and geochemical screening process for selecting suitable raw material.

Mineralogy

Dunites are, by definition, composed of more than 90% olivine [16]. Accessory minerals may include pyroxene, amphiboles, spinel (chromite and magnetite) and silica. Alteration minerals, such as serpentine, talc, brucite and carbonates may also be present. Each of these minerals dissolves at different rates, all of them slower than olivine. Microscopic investigation can reveal the percentage of minerals, which ideally, for dunites, should be greater than 95% olivine with a trace (1-2%) of spinel. Electron microprobe analyses are used to confirm microscopic work and to determine chemical compositions of the olivine. Olivine should have forsterite (Fo) values greater than Fo 90 to ensure maximum possible conversion of olivine to magnesite in the carbonation reaction. For example, unaltered dunite from the Tulameen complex contains approximately 98% olivine with 1-2% of spinel and less than 1% carbonates. Within the Tulameen dunite core, serpentine alteration composes about 1 to 7% of the rock, except near the margins, where dunite is almost completely serpentinitized (up to 97% serpentine). Microprobe analyses of the olivine from the Tulameen dunite ranging from Fo 89 to 98, which suggest high Mg values.

Chemical Composition.

Chemical analyses are complimentary to mineralogy in the screening of raw materials for mineral sequestration. Lost on ignition (LOI) indicates presence of volatiles and is related to the proportion of hydrous phases (serpentine, chlorite, brucite, palygorskite). High LOI in combination with high CO₂ content indicates presence of carbonates. CaO content may be indicative of pyroxene, amphibole and carbonate minerals. Thus, dunites with high MgO and low Fe₂O₃, CaO, water and LOI values are the most promising. Serpentinite rocks have similar requirements, except that lower MgO and higher LOI values are expected. Ranges of chemical compositions of dunites and serpentinites from the Tulameen Complex provide good examples: Dunites consist of MgO (44-48%), Fe₂O₃ (10-12%), LOI (<1-6%) and CaO (0.30-0.75%). Serpentinites range from MgO (38-43%), Fe₂O₃ (9-11%), LOI (7-14%) and CaO (0.10-1.20%). Trace element analyses are informative because they indicate accessory mineral phases that could potentially interfere with reactions during mineral carbonation. However, minor elements may also indicate the presence of potentially marketable ores [9].

Magnetic Susceptibility and Density Analysis

Ultramafic rocks have typically higher magnetic susceptibility (MS) than surrounding rocks and their MS increases with degree of serpentinitization [17]. The iron in the dunites occurs mainly as Fe²⁺ in the olivine crystal structure, whereas in serpentinites, the iron is found as magnetite and ferritchromite. MS could be used to characterize dunite targets for CO₂ sequestration. For example, dunites from the Nahlin ultramafic body, northwestern BC, have mean MS of approximately 14x10⁻³ SI, whereas intensely serpentinitized samples yield values in excess of 200x10⁻³ SI [17]. On the deposit scale, unaltered dunites from Tulameen have MS ranging from 7.45 to 60.6x10⁻³ SI, with a mean of 36.4x10⁻³ SI, whereas MS of their highly serpentinitized equivalents ranges from 57.9 to 106x10⁻³ SI, with a mean value of 88.3x10⁻³ SI. Although results from the Nahlin study present a poor linear relationship between LOI and MS [17], ongoing work of the Tulameen dunite suggests that the relationship between LOI and MS may be effective on the deposit scale to evaluate a degree of serpentinitization. Serpentinization of dunite is a hydration reaction which results in volume increase and density decrease. Thus, density can also be used to distinguish between fresh and serpentinitized dunites and to delineate highly serpentinitized areas [18].

Laboratory and Bench-scale Tests

Bench-scale carbonation tests and related experimental research are taking place at the Albany Research Centre, Arizona State University and Princeton University. Carbonation tests provide a reality check on the characterization of raw materials based on petrology, mineralogy and chemistry. It can also present objective ranking of materials, permit to gauge technical achievements made in optimization of the mineral carbonation on bench scale, supply reaction products for market testing and constrain the cost estimates for CO₂ sequestration.

POTENTIAL BY-PRODUCTS

Ultramafic rocks contain a variety of metallic and industrial mineral deposits [8] and in some cases the host rock may be suitable for mineral CO₂ sequestration. Chromite, magnetite and Ni, Co, Au and PGE are commonly present in sub-economic concentrations. Under favourable circumstances, some of these commodities could be separated before Mg-silicates reach the reactor. Metals locked into olivine's crystal structure, such as Ni (up to 0.5%), could be liberated during the carbonation process. There may also be a market for silica and magnesite (or hydromagnesite), the products of the mineral carbonation process. The construction industry currently uses wastes with pozzolanic properties to reduce CO₂ in cement manufacture and fine grain silica products may be very reactive [19]. The magnesite market is well documented [20] and if it is possible to crystallize magnesite under controlled conditions, it is likely that the product could be marketed. For example, hydromagnesite has applications as a natural fire retardant in plastics [21]. Should it prove to be impossible to separate magnesite and silica, the mixture could be used as low-cost functional filler in carpet backings or in the construction industry.

SUMMARY

Mineral CO₂ sequestration is a "niche" method in an early phase of development. Dunite, serpentinite and chrysotile tailings are the most promising materials for this process. Raw material assessment for the carbonation reaction should proceed in stages: Compilation of ultramafic rocks in a map, selection of targets based on location relative to major CO₂ sources, type of material (dunite or serpentinite) and tonnage. Mineralogical investigation in combination with chemical analyses of selected material will provide insight into the presence of unwanted minerals that interfere with the carbonation reaction. Most suitable raw materials are those with high MgO and low FeO, CaO, LOI, CO₂ and low H₂O content. Density and magnetic susceptibility tests may effectively indicate the degree of serpentinization of dunite deposits. Magnetite, chromite, Ni, Cr, Co and PGE are potential by-products. Magnesite and silica may have industrial applications.

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