

# **Carbon Dioxide Sequestration Options for British Columbia and Mineral Carbonation Potential of the Tulameen Ultramafic Complex**

By

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We accept this thesis as conforming  
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## **Abstract**

In an effort to lower atmospheric carbon dioxide (CO<sub>2</sub>) levels, a number of sequestration methods, including geological storage, ocean storage and mineral carbonation of CO<sub>2</sub> have been proposed for British Columbia. The selection of a suitable sink depends largely on the geology available for a given region. A methodology for assessment of suitable raw material for the mineral carbonation process has been proposed. The Tulameen ultramafic complex is selected as a promising site for providing the raw feed for mineral CO<sub>2</sub> sequestration and representative dunites have been collected and examined. Carbonation tests of these dunites took place at the Albany Research Center in Oregon and CO<sub>2</sub> analyses in reaction products (up to 29.4 wt%) suggest 48-56% conversion to magnesite and silica for the dunites, and 18% conversion for a serpentinized dunite. Based on these results, one tonne of Tulameen dunite could potentially sequester up to 0.4 tonnes of CO<sub>2</sub>.

Examiners:

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# 1. Introduction and Objectives

## 1.1 Statement of Problem

Canada has officially ratified the Kyoto Protocol on greenhouse gases (GHG). Of the six GHGs covered by the Protocol, carbon dioxide (CO<sub>2</sub>) is the greatest contributor. In an effort to lower atmospheric CO<sub>2</sub> levels, a number of sequestration methods, including geological storage, ocean storage and mineral carbonation of CO<sub>2</sub> have been proposed worldwide. These methods all involve some form of capture of CO<sub>2</sub> from a major point source, its transportation and subsequent storage into a sink. The selection of a suitable sink depends largely on the geology available for a given region. When a major stationary CO<sub>2</sub> emission point source is located within or near a sedimentary basin, then options for storing CO<sub>2</sub> would include injection of the gas into deep geological formations, such as hydrocarbon reservoirs, saline aquifers or coal beds. When CO<sub>2</sub> sources are located along continental margins, such as the Canadian Cordillera, where the geology is relatively complex, other methods need to be considered. Mineral CO<sub>2</sub> sequestration is one of the "niche" alternatives and involves reacting Mg-silicates (forsteritic olivine and serpentine) *ex situ* with CO<sub>2</sub> to form stable carbonates. This study attempts to assess British Columbia (BC)'s potential for providing the raw material necessary for mineral CO<sub>2</sub> sequestration.

## 1.2 Objectives

Primary objectives of this study were:

- To identify BC's major (>50 kt /yr) stationary point sources of CO<sub>2</sub>.
- To examine the province's CO<sub>2</sub> sequestration options.
- To establish a methodology for the assessment of mineral CO<sub>2</sub> sequestration potential for a given region or deposit.
- To assess BC's distribution of ultramafic hosted Mg-silicate deposits.
- To estimate the mineral CO<sub>2</sub> sequestration potential of the Tulameen dunite core.

In order to meet these primary objectives, the following secondary objectives were set:

- A review of geological, mineral and ocean CO<sub>2</sub> sequestration methods, based in large part on proceedings from the 2002 6<sup>th</sup> Greenhouse Gas Technologies (GHGT6) conference in Kyoto, provided the necessary background information. The major stationary point sources of CO<sub>2</sub> for the province were identified and a map showing their geographical distribution was published. The potential for utilizing the geology directly surrounding some of the larger point sources for sequestering CO<sub>2</sub> was investigated in terms of political limitations and public perception.
- The geographical distribution of dunite and/or serpentinite-bearing ultramafic complexes is delineated utilizing an existing mineral potential database for the province of British Columbia. These zones are presented in a map, which may also serve as a metallotect for exploration of ultramafic-hosted metal, mineral, gemstone and industrial mineral deposits.
- Out of the aforementioned ultramafic zones, the dunite core of the Tulameen ultramafic complex near Princeton, southern BC, was selected as a potential candidate and is evaluated for its mineral carbonation reactivity by petrological, mineralogical and geochemical means. Percent conversion of dunite to magnesite and silica was quantified based on results of tests run at the Albany Research Centre/ Department of Energy (DOE) in Oregon.

### **1.3 Outline of Thesis**

The following five chapters are written as stand-alone papers. After these chapters a short summary will follow with recommendations for future research.

*Chapter 2* is a review paper that defines CO<sub>2</sub> sequestration and describes the different methods for geological, mineral and ocean CO<sub>2</sub> sequestration that are currently considered for the reduction of greenhouse gas (GHG) emissions. This study was presented at the *GAC-MAC Conference* in Vancouver, 2003 and was published in *Geoscience Canada* in 2004.

**Chapter 3** presents the geographical distribution of BC's major stationary point sources of CO<sub>2</sub> (greater than fifty kilotonnes of CO<sub>2</sub> per year) and discusses the different CO<sub>2</sub> sequestration options that are potentially available for reducing these emissions to the atmosphere. The results of this study were presented at the 7<sup>th</sup> GHGT Conference in Vancouver, 2004. The CO<sub>2</sub> point source data was published as *BC Ministry of Energy and Mines Geofile 2003-11*. From these methods, mineral sequestration of CO<sub>2</sub> is selected for further study.

**Chapter 4** presents a methodology for the evaluation of mineral sequestration potential using Mg-silicates, for a given region or deposit. The first half of this chapter focuses on how to select favourable zones for the mineral carbonation process. The second half of this chapter describes how to evaluate the potential of the selected deposits for the mineral carbonation process. This material was presented, in poster format, at the 7<sup>th</sup> GHGT Conference in Vancouver, 2004 and published as *BC Ministry of Energy and Mines Geofile 2004-13*.

**Chapter 5** applies the methodology of chapter 4 to compile a map for BC that delineates dunite and serpentinite-bearing ultramafic complexes. This map also has applications for mineral exploration and can therefore be used as a metallotect. This study was published in *BC Ministry of Energy and Mines Energy-Resource Development and Geoscience Branch Summary of Activities 2004* and presented as *BC Ministry of Energy and Mines Geofile 2004-1*.

**Chapter 6** describes the mineral carbonation tests run on selected rock samples from the Tulameen dunite core. Mineral carbonation by aqueous dissolution was selected as the option for the Tulameen dunite and samples were run at the ARC in collaboration with the US DOE in Albany, Oregon. Petrology, mineralogy and geochemical information is presented and used to assess its theoretical carbonation potential. Percent conversion of dunite to magnesite and silica is calculated based on increased CO<sub>2</sub> content in the reaction products. Methodology of the experiments and results from the tests are presented and discussed. This paper will be submitted to *Canadian Institute of Mining (CIM) Bulletin*.

There is some overlap between the different chapters, in particular Canada and BC's commitments to the Kyoto Protocol, the definition of CO<sub>2</sub> sequestration and the description of the mineral sequestration reactions. However, each chapter takes its own focus.

## **2. Geological, Ocean and Mineral CO<sub>2</sub> Sequestration Options: A Technical Review**

By: Danae A. Voormeij<sup>1</sup> and George J. Simandl<sup>2</sup>

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### **2.1 Summary**

Of the six greenhouse gases (GHG) covered by the Kyoto protocol, carbon dioxide (CO<sub>2</sub>) is the greatest contributor to Canada's total GHG emissions. Fossil fuel combustion is the main source of anthropogenic CO<sub>2</sub> and it currently supplies over 85% of the global energy demand. Worldwide, an effort for reduction of CO<sub>2</sub> emissions aims at increased efficiency of fossil energy usage, development of energy sources with lower carbon content and increased reliability on alternative energy sources such as wind, solar, geothermal and nuclear. However, to meet the objectives of the Kyoto agreement, CO<sub>2</sub> sequestration methods may be needed. The methods that we will cover in this review are: storage in oil and gas reservoirs, in deep coal seams, in deep saline aquifers, in deep ocean, in salt caverns and mineral carbonation. Each of these methods has its weaknesses and strengths.

### **2.2 Introduction**

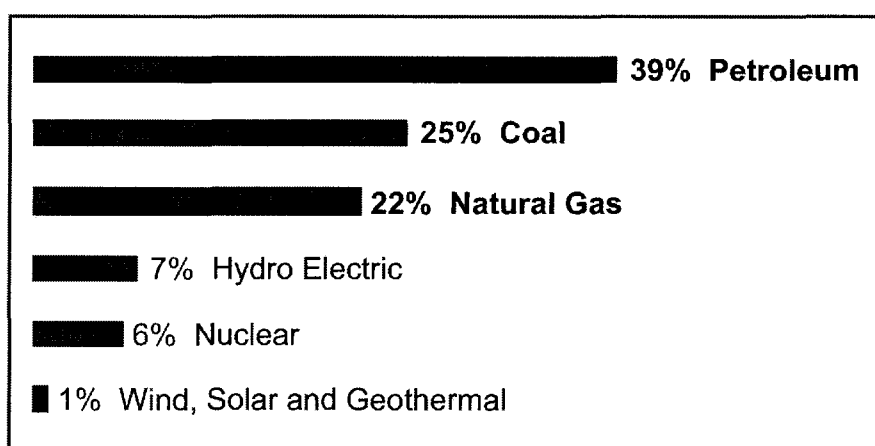
Canada's Kyoto commitments are to reduce its annual greenhouse gas (GHG) emissions level by 6% relative to its 1990 level, which was estimated by Environment Canada (2002) at 601 Megatonnes (Mt). Although Canada contributes only about 2% of total global GHG emissions (Table 2.1), it is one of the highest per capita emitters (23.6 tonne CO<sub>2</sub> equivalent per year), largely due to its resource-based economy, cool climate (i.e. heating) and travel distances (Environment Canada, 2002). Of the six GHGs covered by the Kyoto protocol, CO<sub>2</sub> is the greatest contributor to Canada's total GHG emissions (Table 2.2). Fossil fuel combustion is the

main source of anthropogenic CO<sub>2</sub>, and it currently supplies over 85% of global energy demand (Figure 2.1).

The main engineering effort for reduction of CO<sub>2</sub> emissions is aimed at increased efficiency of fossil energy usage, development of energy sources with lower carbon content and increased reliability on alternative energy sources such as wind, solar, geothermal and nuclear. It is not likely that the reduction of CO<sub>2</sub> emissions required to meet targets set by the Kyoto agreement could be met using these measures alone. Thus a need for geological, mineral or deep ocean sequestration of carbon dioxide (CO<sub>2</sub>) may arise.

CO <sub>2</sub> EMISSIONS	Mt	%		CO <sub>2</sub> EMISSIONS	Mt	%
World total (1999)	23900.00	100.00		Nova Scotia	21.50	0.09
Canada total (1990)	601.00	2.51		Manitoba	21.40	0.09
Canada total (2000)	726.00	3.04		New Brunswick	20.20	0.08
Alberta	223.00	0.93		Newfoundland	8.80	0.04
Ontario	207.00	0.87		Prince Edward Island	2.10	0.01
Quebec	90.40	0.38		North West Territories and Nunavut	1.80	0.01
British Columbia	65.90	0.28		Yukon	0.53	0.00
Saskatchewan	61.80	0.26		Nova Scotia	21.50	0.09

**Table 2.1** Canada's total CO<sub>2</sub> emissions for 2000 as compared to global emission estimates. Numbers for emission levels are in Megatonnes (Mt) of CO<sub>2</sub> equivalent (source: Environment Canada, 2002).



**Figure 2.1** Global energy demand: Fossil fuels supply over 85% of the world's energy. (McKee, 2002).

<b>CANADA'S GREENHOUSE GAS EMISSIONS (2000)</b>	
<b>Carbon Dioxide (CO<sub>2</sub>)</b>	78.90%
<b>Methane</b>	12.40%
<b>Nitrous Oxide</b>	7.40%
<b>Other (HFCs<sup>+</sup>, PFCs<sup>+</sup> and SF<sub>6</sub>s<sup>x</sup>)</b>	1.30%

**Table 2.2** Canadian greenhouse gas emissions. Carbon dioxide (CO<sub>2</sub>) is the main contributor to Canada's total greenhouse gas emissions (source: Environment Canada, 2002). \*Hydrofluorocarbons; <sup>+</sup>Perfluorocarbons; <sup>x</sup>Sulphur hexafluorides

For the purpose of this paper, the term "CO<sub>2</sub> sequestration" refers to the capture, separation, transportation and storage of CO<sub>2</sub>. The storage is expected to be permanent (i.e. on the order of thousands to millions of years). Methods of sequestration that are currently considered by industrialized countries include enhancement of terrestrial carbon sinks (not covered in this study) as well as geological, ocean and mineral sequestration. Each method has its weaknesses and strengths. The methods that we will cover in this review are:

1. Storage in Oil and Gas Reservoirs
2. Storage in Deep Coal Seams
3. Storage in Deep Saline Aquifers
4. Storage in Deep Ocean
5. Storage in Salt Caverns
6. Mineral Carbonation

Geographic relationships between the main stationary point CO<sub>2</sub> sources and sinks are an essential piece of the puzzle for CO<sub>2</sub> sequestration planning since transportation of the CO<sub>2</sub> is one of the most important cost factors. Voormeij and Simandl (2003) and Bachu (2001) have identified the main stationary point sources of CO<sub>2</sub> emissions and the main potential carbon or CO<sub>2</sub> sinks for British Columbia and Alberta, respectively.

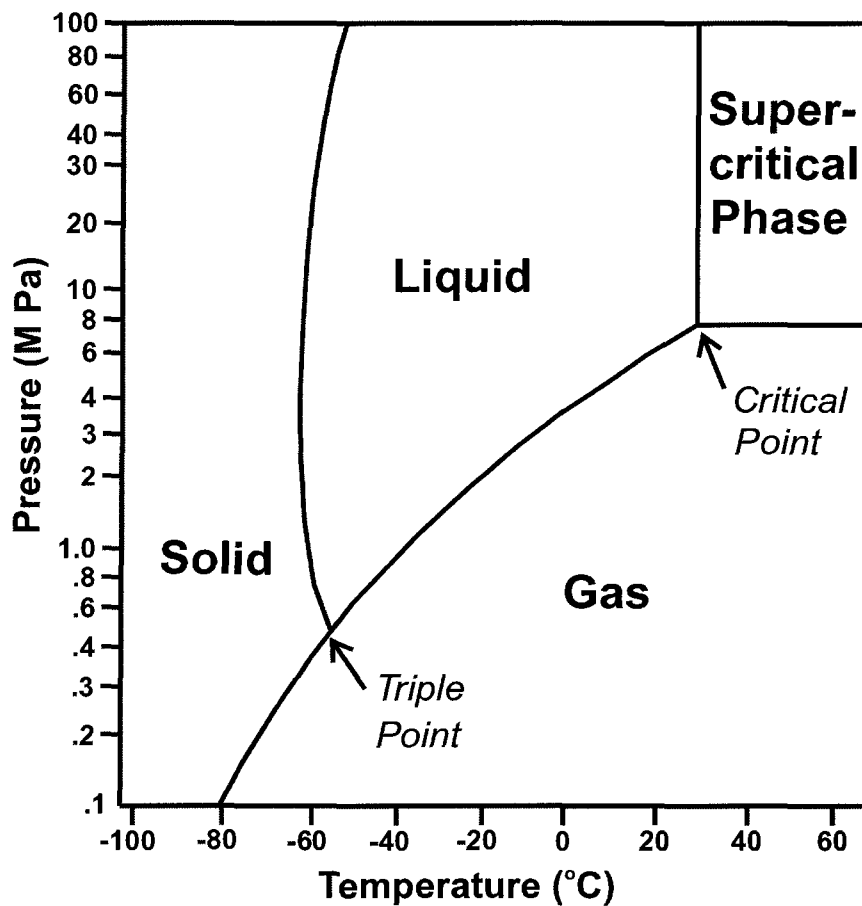
### **2.2.1 Physical Properties of Carbon Dioxide**

It is important to know the main properties of carbon dioxide to understand the different sequestration methods. CO<sub>2</sub> is an odourless, colourless gas that occurs naturally in the



atmosphere at current ambient concentrations of around 370 ppm (0.037%). The effects of high concentrations of CO<sub>2</sub> on humans and other life forms are beyond the scope of this paper and are summarized by Benson *et al.* (2002).

Depending on pressure and temperature, CO<sub>2</sub> can take on three separate phases (Figure 2.2). CO<sub>2</sub> is in a supercritical phase at temperatures greater than 31.1°C and pressures greater than 7.38 MPa (critical point). Below these temperature and pressure conditions, CO<sub>2</sub> will be either a gas, liquid or a solid. Depending on in situ temperature and pressure, CO<sub>2</sub> can be stored as a compressed gas or liquid, or in a supercritical (dense) phase.



**Figure 2.2** Carbon dioxide phase diagram. The critical point for CO<sub>2</sub>, when it reaches supercritical state, is 31.1°C and 7.38 MPa. (Adapted from Koide *et al.*, 1996). 100 MPa=1 kbar.

## **2.3 CO<sub>2</sub> Storage in Oil and Gas Reservoirs**

Both depleted and active fossil fuel reservoirs are potential storage spaces for CO<sub>2</sub> in underground formations. For the purpose of this paper, the term "depleted fossil fuel reservoirs" refers to abandoned oil or gas reservoirs. These reservoirs have undergone primary and secondary recoveries and CO<sub>2</sub>-enhanced oil recovery is not currently envisaged to generate positive cashflow. Thus CO<sub>2</sub> may be injected directly into a depleted or inactive hydrocarbon reservoir without expectation of any further oil or gas production, resulting in the permanent storage of CO<sub>2</sub>. CO<sub>2</sub> may also be injected into producing oil and gas reservoirs, where CO<sub>2</sub>-enhanced oil recovery (EOR) and CO<sub>2</sub>-enhanced gas recovery (EGR) will offer an economic benefit. Alberta currently has about 26,000 gas pools and more than 8,500 oil pools in various stages of production and completion (Thambimuthu *et al.*, 2003). CO<sub>2</sub> storage capacity in these reservoirs is estimated at 637 Megatonnes of CO<sub>2</sub> in depleted oil pools; 2.2 Gigatonnes of CO<sub>2</sub> in gas caps of approximately 5,000 oil reservoirs and 9.8 Gigatonnes of CO<sub>2</sub> storage capacity in gas reservoirs that are not associated with oil pools (Thambimuthu *et al.*, 2003). Of the more than 8,500 oil pools in Alberta, 4,273 reservoirs were identified as suitable for CO<sub>2</sub>- EOR.

Typically, oil reservoirs have undergone a variety of production and injection processes during primary and secondary recovery (e.g. gas, water or steam injection), as described by Jimenez and Chalaturnyk (2003). As a tertiary recovery process, CO<sub>2</sub> can be injected into the reservoir to improve the mobility of the remaining oil, thereby extending the production life of the reservoir. Injection of CO<sub>2</sub> into producing gas reservoirs for EGR was previously believed to risk contaminating the natural gas reserve (Stevens *et al.*, 2000). However, recent studies by Oldenburg *et al.* (2001) and Oldenburg and Benson (2002) suggest that mixing of the CO<sub>2</sub> and methane (CH<sub>4</sub>) in a gas reservoir would be limited due to the high density and viscosity of CO<sub>2</sub> relative to the natural gas. Furthermore, significant quantities of natural gas can be produced by re-pressurization of the reservoir. It is possible that improved gas recovery could more than offset the cost of CO<sub>2</sub> capture and injection (Davison *et al.*, 2001).

### **2.3.1 Depleted Oil and Gas Reservoirs**

Following more than a century of intensive petroleum exploitation, thousands of oil and gas fields are approaching the ends of their economically productive lives (Davison *et al.*, 2001). Some of these exhausted fields are potential sites for CO<sub>2</sub> sequestration. The concept of CO<sub>2</sub> disposal in depleted oil and gas reservoirs is that the hydrogeological conditions that allowed

the hydrocarbons to accumulate in the first place will also permit the accumulation and trapping of CO<sub>2</sub> in the space vacated by the produced hydrocarbons (Hitchon *et al.*, 1999; Gentzis, 2000). The caprock that prevented the escape of oil and gas over geological time, should retain the sequestered CO<sub>2</sub> for thousands of years (Bachu, 2001a), as long as it is not damaged as a result of overpressure during the CO<sub>2</sub> injection (van der Meer, 1993), or by the presence of unsealed, improperly completed or abandoned wells (Hitchon *et al.*, 1999). Depleted hydrocarbon reservoirs that are filled with connate water (fully water-saturated reservoirs) offer limited storage capacity. Storage of CO<sub>2</sub> in water-saturated reservoirs would in practice amount to aquifer storage (Bachu, 2000; van der Meer, 2003).

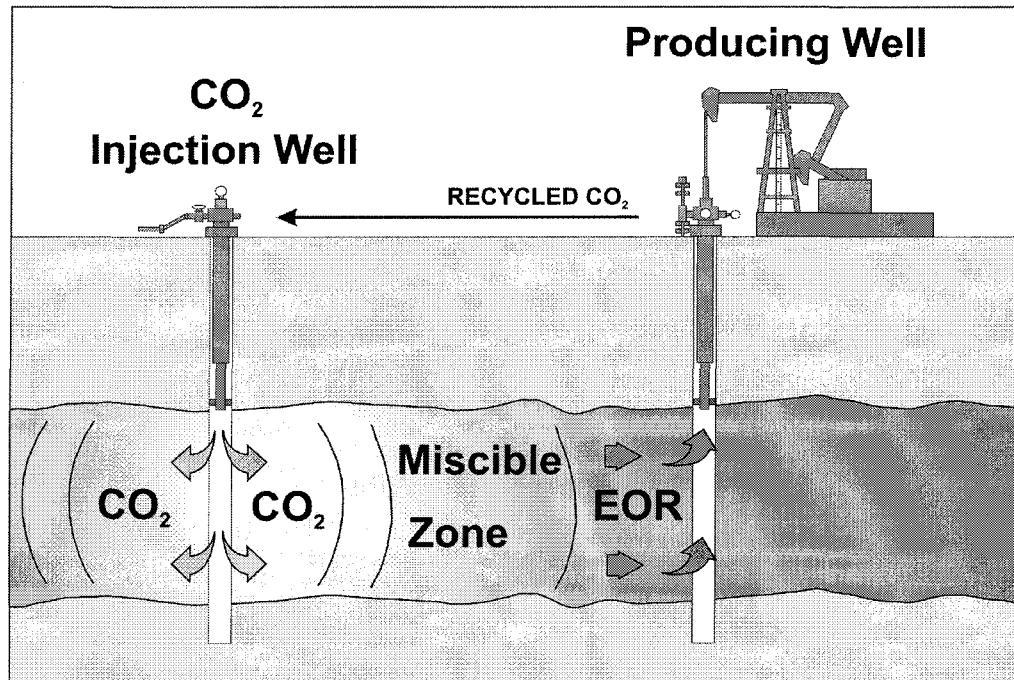
Closed, underpressured, depleted gas reservoirs are excellent geological traps for CO<sub>2</sub> storage. Firstly, primary recovery of gas fields usually removes as much as 95% of the original gas in place (Bachu, 2001a), creating large storage potential. Secondly, the injected CO<sub>2</sub> can be used to restore the reservoir to its original pressure (Bachu *et al.*, 2000), thereby preventing possible collapse or man-induced subsidence. Thirdly, the trapping mechanism that retained hydrocarbons in the first place should ensure that CO<sub>2</sub> does not reach the surface. And lastly, the existing surface and down-hole infrastructure used for production of gas may be modified for transportation and injection of supercritical CO<sub>2</sub>. About 80% of the world's hydrocarbon fields are at depths greater than 800 m (IEA, website), thus meeting the pressure and temperature requirements needed to store CO<sub>2</sub> as a supercritical fluid (van der Meer, 1993). Spatial association between hydrocarbon production and the presence of reservoirs suitable for CO<sub>2</sub> sequestration may result in shared infrastructure and reduction of transportation costs. Furthermore, depleted hydrocarbon fields commonly have an established geological database and as such, reservoir characteristics are well known. Currently, the petroleum industry is reluctant to consider storage of CO<sub>2</sub> in depleted hydrocarbon reservoirs, because abandoned fields will still contain oil and gas resources (US Dept of Energy, 2002), which potentially have economic value if oil prices were to rise enough or new EOR technologies were developed in the future (Davison *et al.*, 2001; Bachu *et al.*, 2000).

Acid gas injection operations in the Western Canada sedimentary basin are a useful small-scale analogue for storage of CO<sub>2</sub> into depleted oil or gas reservoirs. Acid gas is a product of oil and gas processing and consists of a combination of CO<sub>2</sub> and hydrogen sulphide (H<sub>2</sub>S). It is either injected into depleted hydrocarbon reservoirs or into saline aquifers for the purpose of

reducing atmospheric  $\text{H}_2\text{S}$  emissions. The technology used in acid gas injection in terms of transportation, injection and storage may be comparable to that of geological sequestration of  $\text{CO}_2$  (Bachu and Gunter, 2003).

### 2.3.2 Active Oil Reservoirs

The petroleum industry has been injecting  $\text{CO}_2$  into underground formations for several decades (Gentzis, 2000) to improve oil recovery from light and medium oil reservoirs, even before climate change became an issue (Bachu, 2000).  $\text{CO}_2$  injected into suitable oil reservoirs can improve oil recovery by 10-15% of the original oil in place in the reservoir (Davison *et al.*, 2001). When  $\text{CO}_2$  is injected into a reservoir above its critical point (typically a reservoir depth greater than 800 m), the fluid acts as a powerful solvent. If the pressure is high enough and the oil gravity is greater than  $25^\circ$  API, the  $\text{CO}_2$  and oil become completely miscible (Bachu, 2001a). According to Aycaguer *et al.* (2001), the miscible flood reduces the oil's viscosity thereby enabling the oil to migrate more readily to the producing wells (Figure 2.3). At lower pressures  $\text{CO}_2$  and oil are not completely miscible, and only a fraction of the  $\text{CO}_2$  will dissolve in the oil. This is known as immiscible displacement and it also enhances oil recovery.  $\text{CO}_2$  enhanced oil recovery is now considered as a mature technology (Gentzis, 2000).



**Figure 2.3** Simplified diagram showing a  $\text{CO}_2$ -enhanced oil recovery (EOR) operation. (Modified from IEA R&D Programme, 2001).

Much of the CO<sub>2</sub> will remain stored in the reservoir, but a significant part ultimately breaks through at the producing well, together with the recovered oil. As a result, the residence time is relatively small, on the order of months to several years (Bachu, 2000). If EOR is the main objective of CO<sub>2</sub> injection, then the operation is optimized to minimize the cost of CO<sub>2</sub> used and maximize the oil recovery. An example of this is Penn West Petroleum's Joffre Viking EOR field in Alberta. However, CO<sub>2</sub> sequestration differs from CO<sub>2</sub>-EOR; its main objective is to sequester as much CO<sub>2</sub> in the reservoir as possible and to keep it underground for thousands if not millions years (van der Meer, 2003; Benson, 2000).

A life cycle assessment study on EOR with injection of CO<sub>2</sub> in the Permian Basin of West Texas (Aycaguer *et al.*, 2001) suggests that the amount of CO<sub>2</sub> injected, not including recycled CO<sub>2</sub>, may balance the amount of CO<sub>2</sub> in emissions that ultimately are produced by combustion of the extracted hydrocarbon product. Most of the existing CO<sub>2</sub>-EOR projects in the world use naturally occurring sources. CO<sub>2</sub> from natural carbon dioxide reservoirs, where the infrastructure for distribution is already present, provide delivery without major capital costs (Aycaguer *et al.*, 2001) and without processing (Smith, 1998). To help mitigate the release of CO<sub>2</sub> to the atmosphere, the source of CO<sub>2</sub> for EOR should come from anthropogenic (man-made) sources. A Canadian study done by Tontiwachwuthikul *et al.* (1998) on the economics of CO<sub>2</sub> production from coal-fired power plants concluded that flue gas extraction could be an economically viable CO<sub>2</sub> supply source for CO<sub>2</sub>-EOR projects in Western Canada, should oil prices increase substantially.

Canada is the forerunner in the technology of using anthropogenic CO<sub>2</sub> emissions in a large-scale EOR project at the Weyburn oil field in Saskatchewan. The ongoing project aims at implementing a guideline for geological storage of anthropogenic CO<sub>2</sub> by EOR (Moberg, 2001; Whittaker and Rostron, 2003). Although natural sources can supply CO<sub>2</sub> at a lower cost (Bachu, 2000), if available, anthropogenic sources are also used. CO<sub>2</sub> is captured from the Great Plains coal-gasification plant at Beulah, North Dakota, USA and transported through a 320 km pipeline to the Weyburn Pool. The injected CO<sub>2</sub> is 95% pure and initial injection rates are 5000 tons/day (Moberg *et al.*, 2003). The reservoir is located within the Williston Basin and has temperatures near 65°C and pressures around 14.5 Mpa, which indicate that the injected CO<sub>2</sub> will likely exist as a supercritical fluid (Whittaker and Rostron, 2003). The CO<sub>2</sub> from the produced oil will be captured and re-injected into the reservoir so that most of the

anthropogenic CO<sub>2</sub> used for EOR will ultimately be sequestered (Whittaker and Rostron, 2003). An estimated 20 Megatonnes of CO<sub>2</sub> will be injected over the project life (Moberg *et al.*, 2003). Potential future sources of CO<sub>2</sub> include the purified flue gas from Saskatchewan coal-fired thermal plants, such as those at Boundary Dam, Poplar River and Shank (Huang, 2001).

## **2.4 CO<sub>2</sub> Storage in Coal Seams**

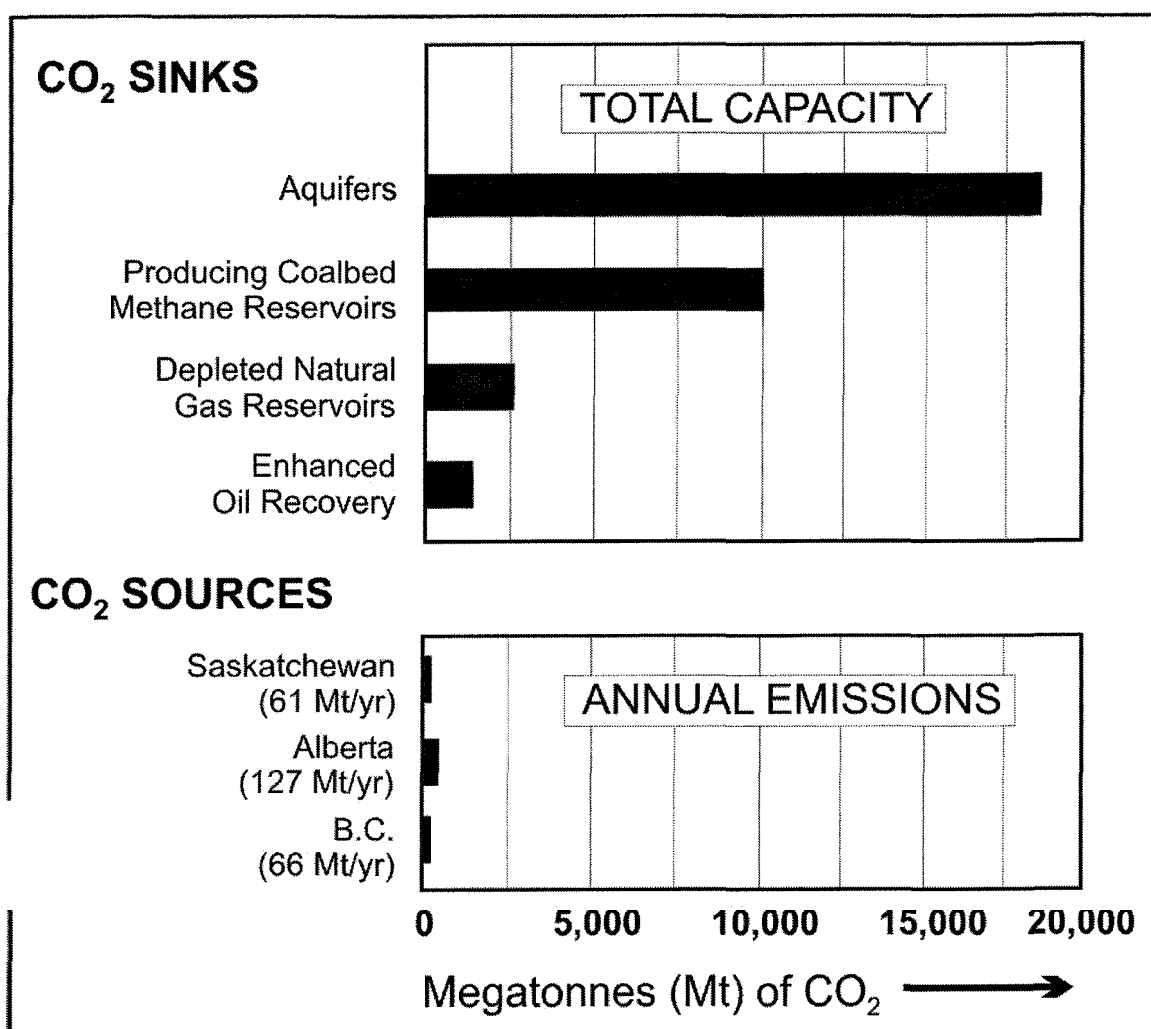
Coalbeds are a potential storage medium for CO<sub>2</sub>. Canada has abundant coal resources; some of them lie at depths too great to be considered for conventional mining. CO<sub>2</sub> can be injected into suitable coal seams where it will be adsorbed onto the coal and stored in the pore matrix of the coal seams for geologic time. Since flue gas, a mixture of CO<sub>2</sub> and nitrogen (N<sub>2</sub>) accounts for 80% of CO<sub>2</sub> emissions in western Canada (Reeve, 2000), an alternative to CO<sub>2</sub>-only storage is injection of flue gas into coalbeds, which may avoid the high cost of CO<sub>2</sub> separation (Law *et al.*, 2003).

### **2.4.1 CO<sub>2</sub>-Enhanced Coalbed Methane Recovery**

CO<sub>2</sub> sequestration in coal seams has the potential to generate cash flow through enhanced coalbed methane (CBM) recovery, a process similar to the practice of CO<sub>2</sub>-EOR. Recovery of CBM is a relatively well-established technology used in several coalfields around the world (Schraufnagel, 1993; Ivory *et al.*, 2000). A number of companies are looking at producing CBM in Western Canada. Primary CBM recovers about 20-60% of the gas in place (Gentzis, 2000; van Bergen and Pagnier, 2001); some of the remaining CBM may be further recovered by CO<sub>2</sub> enhanced CBM recovery. A study done on the Alberta Sedimentary Basin estimate a potential capacity for CO<sub>2</sub> sequestration by enhanced CBM recovery at nearly 10,000 Mt (Figure 2.4). To put this storage capacity into perspective, CO<sub>2</sub>-enhanced CBM recovery could potentially sequester Metropolitan Toronto's CO<sub>2</sub> emissions (City of Toronto, 1991) for more than 300 years.

The disposal of CO<sub>2</sub> in methane-rich coalbeds, where applicable, is expected to increase drive pressure and the CBM recovery rate (Hitchon *et al.*, 1999). Thus, injection of CO<sub>2</sub> should enable more CBM to be extracted, while at the same time sequestering CO<sub>2</sub>. CO<sub>2</sub> has a higher affinity with coal, about twice that of methane (Figure 2.5), depending on coal rank, just below

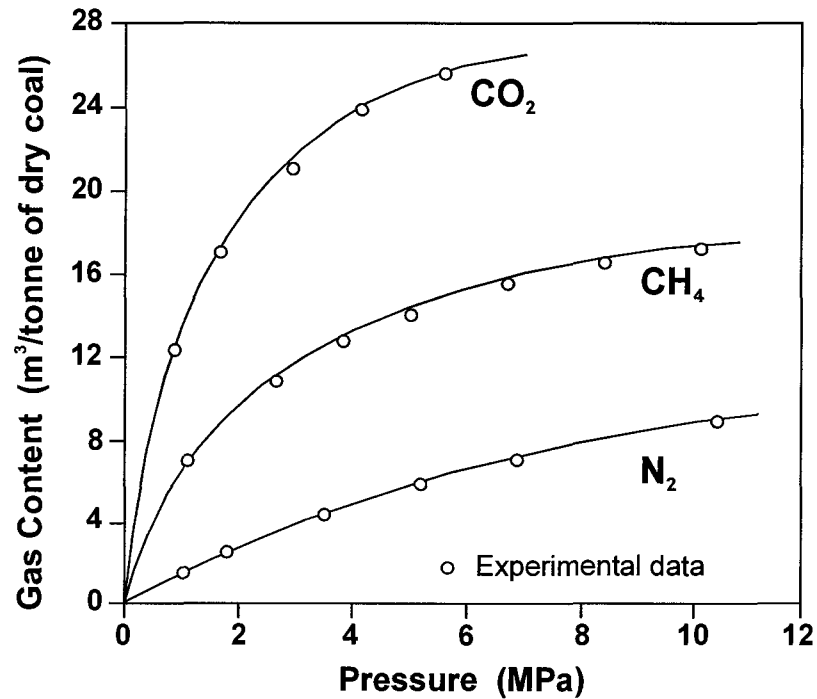
the critical point ( $\sim 7.38$  MPa). In theory, injected  $\text{CO}_2$  molecules displace the adsorbed methane molecules (Wong *et al.*, 2001; Ivory *et al.*, 2000; Hitchon *et al.*, 1999), which desorb from the coal matrix into the cleats (Figure 2.6) and flow to the production wells. However, limited data at pressures exceeding the critical point of  $\text{CO}_2$  indicate that the extrapolation of the  $\text{CO}_2$  adsorption curve above 7.38 MPa is not justified (Krooss *et al.* 2002) and that we do not really know what is happening above this pressure.



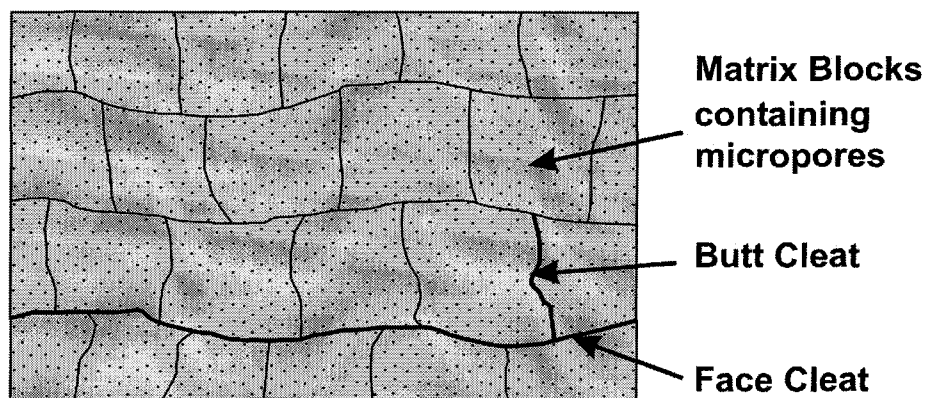
*Figure 2.4 Total CO<sub>2</sub> sink capacity for the Alberta Sedimentary Basin and annual CO<sub>2</sub> emissions for provinces near the basin (modified from Gentzis, 2000).*

$\text{CO}_2$ -enhanced CBM production could be achieved by drilling wells into the coal deposits, typically a five-spot pattern, with the centre well as the injector and the four corner wells as the

producing wells (Wong *et al.*, 2001). After discharging formation waters from the coal, CO<sub>2</sub> is injected into the coal seam. CO<sub>2</sub> enhanced CBM extraction may achieve up to 72% recovery (Wong *et al.*, 2000). A CO<sub>2</sub> enhanced CBM production project terminates at CO<sub>2</sub> breakthrough in one or more of the production wells (Wong *et al.*, 2001).



**Figure 2.5** Adsorption isotherms for carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and nitrogen (N<sub>2</sub>) on coal (adapted from Arri *et al.*, 1992). Limited data is available for CO<sub>2</sub> adsorption at pressures in excess of 7.38 MPa (Krooss *et al.*, 2002).



**Figure 2.6** Coalbeds contain both primary and secondary porosity systems. The coal matrix (primary porosity system) contains the vast majority of the gas-in-place volume, while the cleats (secondary porosity system) provide the conduits for mass transfer to production wells. (Adapted from Rice *et al.*, 1993)



Flue gas injection may enhance methane production to a greater degree than CO<sub>2</sub> alone (Ivory *et al.*, 2000). However, N<sub>2</sub> has a lower affinity for coal than CO<sub>2</sub> or methane (Figure 2.5). Therefore, injection of flue gas or CO<sub>2</sub>-enriched flue gas will probably result in rapid nitrogen breakthrough at the producing wells (Macdonald *et al.*, 2003; Law *et al.*, 2003). In such cases, N<sub>2</sub> waste could be recycled and reinjected into the coal seam (Wong and Gunter, 1999).

Sequestration of CO<sub>2</sub> in coal seams, while enhancing CBM recovery, is an attractive option, but the most suitable physical characteristics of the coals for the purpose of CO<sub>2</sub>-enhanced coalbed methane recovery (ECBM) are largely unknown. Recent studies (Fokker and van der Meer, 2003; Reeves, 2003) have shown that continued injection of CO<sub>2</sub> in coalbeds induces a decrease in the permeability of the cleat system surrounding the injection well area. In general, desorption of methane induces shrinkage of the coal matrix that result in widening of the cleats, thereby allowing the CO<sub>2</sub> injection rate to increase and methane to flow to the producing well. However, replacement of the methane by the injected CO<sub>2</sub> is believed to cause the coal matrix to swell. This swelling will partially close the cleat system and reduce permeability. The fracturing and swelling of the coal have opposite effects on the CO<sub>2</sub> injectivity (Fokker and van der Meer, 2003). One possible solution to achieve an acceptable CO<sub>2</sub> injection rate would be to allow the gas pressure in the cleat system to exceed the hydraulic fracturing pressure (Fokker and van der Meer, 2003; Shi *et al.*, 2002), essentially fracturing the coal bed in the vicinity of the injection well to enhance permeability. However, if repeated hydraulic fracturing is necessary to maintain connectivity between the well bore and the permeable areas of the coal seam, this may result in over/under burden fracturing (Gale, 2003), and subsequent CO<sub>2</sub> leakage.

The Alberta Research Council (ARC) has done extensive applied research in the field of CBM and some of the outstanding contributions were published by Wong *et al.* (2000), Law *et al.* (2003), and Mavor *et al.* (2002). There are currently several CO<sub>2</sub>-ECBM recovery field projects studying sequestration of CO<sub>2</sub> and flue gas in deep coal seams. These projects range in depth from 760 to 1100 metres:

- Alberta Research Council under an international project, facilitated by the IEA Greenhouse gas R&D Programme, has established a pilot site at Fenn-Big Valley, Alberta, Canada (Figure 2.7). The project is looking at the enhancement of CBM

production rates in low permeability CBM reservoirs using mixtures of CO<sub>2</sub> and N<sub>2</sub> while sequestering CO<sub>2</sub> into coalbeds (Law *et al.*, 2003; Reeve, 2000; Ivory *et al.*, 2000).

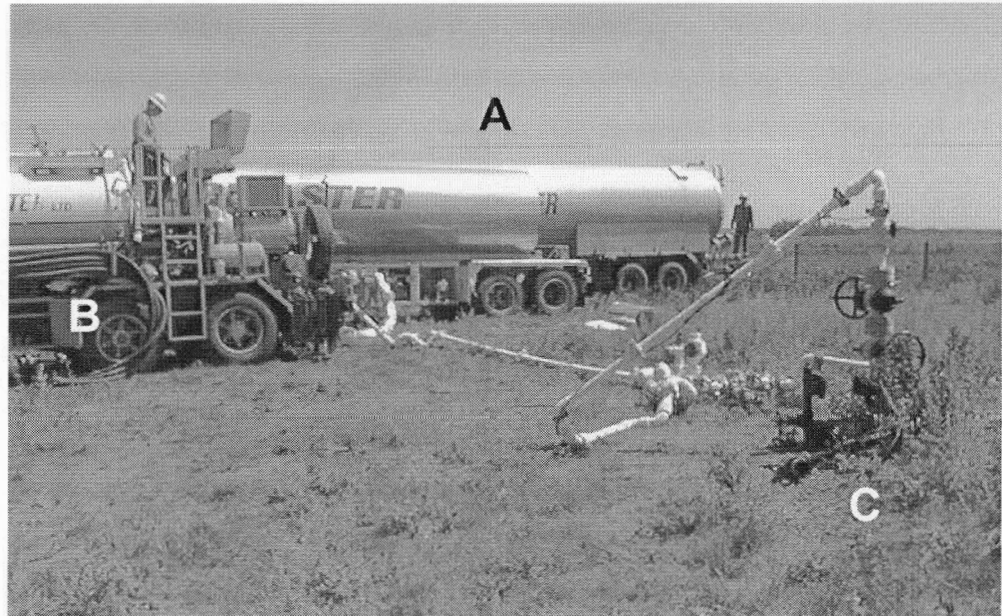


Figure 2.7 Carbon dioxide injection test into a coalbed, central Alberta, 1998. A= CO<sub>2</sub> cisterns, B= compressor and C= injection well. (Courtesy of Bernice Kadatz, Alberta Research Council)

- In October 2000 a three-year government-industry project in the San Juan Basin (USA), known as the Coal-Seq project, was launched. The project studies the feasibility of CO<sub>2</sub>-sequestration in deep, unmineable coal seams using enhanced CBM recovery technology (Reeves, 2003).
- In November 2001, the RECOPOL project (Reduction of CO<sub>2</sub> emission by means of CO<sub>2</sub> storage in coal seams in the Silesian Coal Basin of Poland), funded by the European Commission, aims to develop the first European field demonstration of CO<sub>2</sub> sequestration in subsurface coal seams (van Bergen *et al.*, 2003).

The industrial and scientific community will carefully scrutinize the results from these deep field tests, particularly since they may provide empirical data on CO<sub>2</sub> adsorption behaviour above its critical point (7.38 MPa).

## 2.5 CO<sub>2</sub> Storage in Deep Aquifers

Worldwide, deep saline aquifers have larger geological storage capacity than hydrocarbon reservoirs and deep coal seams (Table 2.3). Deep aquifers are found in most of the sedimentary basins around the world (Bachu, 2001a) and typically contain high-salinity connate water that is not suitable for human consumption or agricultural use.

STORAGE OPTION	GLOBAL CAPACITY	
	Gigatonnes CO <sub>2</sub>	% of Emissions to 2050
Depleted Oil and Gas Fields	920	45
Deep Saline Aquifers	400-10,000	20-500
Unmineable Coal Seams	>15	>1

**Table 2.3** Global CO<sub>2</sub> storage capacity of geological reservoirs (source: IEA Greenhouse Gas R&D Programme, 2001).

Deep saline aquifers have been used for injection of hazardous and nonhazardous liquid waste (Bachu *et al.*, 2000) and as such provide viable options for CO<sub>2</sub> sequestration. Approximately 2% of the total effective volume in a deep aquifer can be made available for CO<sub>2</sub> storage (van der Meer, 2003; 1993). Thus, from a capacity perspective, deep saline aquifers offer a significant potential for CO<sub>2</sub> storage (Gale, 2003).

Suitable aquifers must be capped by a regional aquitard (e.g. shale), which should not contain any fractures or uncompleted wells (Bachu *et al.*, 1994). The top of the aquifer must be located at a minimum depth of 800 meters (van der Meer, 2003), ensuring that the injected CO<sub>2</sub> will be stored in supercritical state. A suitable aquifer should have high permeability locally, for injection purposes, but regional-scale permeability should be low, to ensure long-term disposal of CO<sub>2</sub> (Bachu *et al.*, 1994). When the CO<sub>2</sub> is injected into an aquifer it will rise up due to buoyancy effects and gradually spread out forming a layer of CO<sub>2</sub> under the cap rock (Gale, 2003). In the early stages of geochemical reactions, dissolution of CO<sub>2</sub> into formation water is expected to be the predominant process (Gunter *et al.*, 1997). The surface area of CO<sub>2</sub> in contact with the formation water will control the rate of dissolution. It is believed that during an

injection period of 25 years, between 10 and 25% of the CO<sub>2</sub> will be dissolved (Gale, 2003). The undissolved portion of the injected CO<sub>2</sub> will segregate and form a plume at the top of the aquifer as a result of density differences (Bachu, 2001a). The CO<sub>2</sub> plume will be driven by both hydrodynamic flow and by its buoyancy (Bachu *et al.*, 2000).

The greater the density and viscosity differences between CO<sub>2</sub> and the formation fluid, the faster the undissolved CO<sub>2</sub> will separate and flow upwards in the aquifer in a process similar to oil and gas migration (Bachu, 2001a). Thus, CO<sub>2</sub> should be injected under high pressures to ensure high density of the CO<sub>2</sub> and high CO<sub>2</sub> solubility rate in formation water.

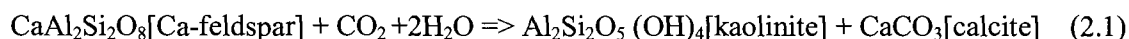
Injection of CO<sub>2</sub> into deep, saline aquifers relies on existing technology. Since 1996, Statoil injects about 1 Mt of CO<sub>2</sub> per year into a deep aquifer offshore Norway (Chadwick *et al.*, 2003). Sequestration of the CO<sub>2</sub> waste, a by-product of natural gas production, saves the company from paying a Norwegian CO<sub>2</sub> tax (Gentzis, 2000).

### **2.5.1 Hydrodynamic Trapping**

Studies done on the Alberta Basin suggests that outside the radius of influence of the injection well, both dissolved and immiscible CO<sub>2</sub> will travel at the same velocity as the formation water (Gunter *et al.*, 1997), termed hydrodynamic trapping. Regionally, the velocities of formation water in deep aquifers are expected to be around 1 to 10cm/year (Bachu *et al.*, 1994), suggesting a basinal residence time for CO<sub>2</sub> of tens to hundreds of thousands of years (Gunter *et al.*, 1997).

### **2.5.2 Mineral Trapping**

The injected CO<sub>2</sub> may be sequestered permanently by undergoing geochemical reactions with silicate minerals, resulting in carbonate production whereby CO<sub>2</sub> is fixed as a carbonate mineral (e.g. calcite, dolomite or siderite). This is known as mineral trapping (Bachu *et al.*, 1994; Gunter *et al.*, 2003) and is based on a similar rock-weathering reaction as mineral carbonation, which will be discussed in the last section of this paper. The following chemical reaction is an example of mineral trapping of CO<sub>2</sub>:



Experiments carried out to test the validity of mineral trapping of CO<sub>2</sub>, by Gunter *et al* (1997), concluded that these reactions are expected to take hundreds of years or more to complete. Due to the long residence time of CO<sub>2</sub>-charged formation waters within the aquifer, these reactions may eventually trap over 90% of the injected CO<sub>2</sub> if enough basic aluminum silicates are present in the aquifer (Gunter *et al.*, 1997). Mineral trapping will not greatly increase the CO<sub>2</sub> storage capacity of the aquifer; rather its advantage in the permanent nature of CO<sub>2</sub> disposal (Bachu *et al.*, 1994).

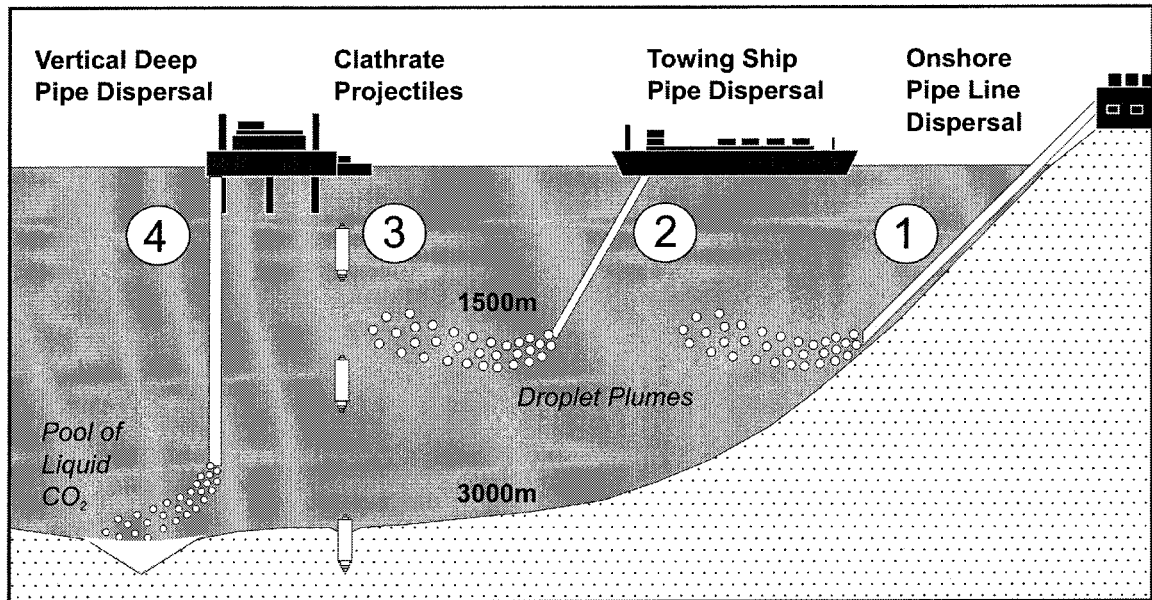
## **2.6 Deep Ocean Disposal of CO<sub>2</sub>**

The ocean is the largest sink available for disposal of CO<sub>2</sub> with a residence time of four to five hundred years (Gentzis, 2000). The oceans contain a stratified thermocline, which is located between the surface layer and the deep ocean. Its waters circulate between surface and deep layers on varying time scales from 250yrs in the Atlantic Ocean to 1000yrs for parts of the Pacific Ocean (Mignone *et al.*, 2003; Ormerod *et al.*, 2002). The atmosphere and the ocean are in contact over 70% of the globe and there is a continuous exchange of inorganic carbon between them. Oceans are, at present time, removing about six Gt CO<sub>2</sub>/year from the atmosphere (Ormerod *et al.*, 2002). Disposing anthropogenic CO<sub>2</sub> in the deep ocean would accelerate a natural process. CO<sub>2</sub> could be injected as a liquid below the thermocline at depths greater than 1500 metres and be sequestered either by dissolution in the water column or by formation of CO<sub>2</sub> hydrates (Figure 2.8).

### **2.6.1. Storing CO<sub>2</sub> by Dissolution**

One approach involves transporting liquid CO<sub>2</sub> from shore by pipeline and then discharging it from a manifold lying on the ocean bottom, forming a **droplet plume**. Since liquid CO<sub>2</sub> is less dense than seawater, the CO<sub>2</sub> droplets will rise until they are dissolved into the seawater and the CO<sub>2</sub>-charged solution spreads laterally into the (stratified) surrounding seawater. The dissolved CO<sub>2</sub> may travel in the thermocline, and eventually (after hundreds of years) circulate back into the atmosphere. The deeper the CO<sub>2</sub> is injected, the more effectively it is sequestered, but injecting deeper requires more advanced technologies (Ormerod *et al.*, 2002). The oil and gas industry have established technologies to construct vertical risers in deep water and to lay

seabed oil and gas pipelines at depths down to 1600 metres (Ormerod et al., 2002), suggesting that this method is technically feasible.



**Figure 2.8** Compilation diagram of proposed methods for ocean disposal of CO<sub>2</sub>. Methods 1 and 2 dispose of CO<sub>2</sub> by injecting a droplet plume below 1500m depth, either through onshore pipeline or via a pipe towing behind a ship. The buoyant CO<sub>2</sub> droplets dissolve into the water column before reaching the surface. Methods 3 and 4 involve sequestration of CO<sub>2</sub> as clathrate hydrates, which are denser than the surrounding seawater and either penetrate into the seabed as streamlined blocks (3) or generate a dense pool on the ocean floor or filling a trench (4).

Alternatively, liquid CO<sub>2</sub> could be transported by a tanker and discharged from a pipe towed by a moving ship. The Japanese R&D program for ocean sequestration of CO<sub>2</sub> is currently in phase II of a large-scale "moving-ship" scheme in the western North Pacific to assess environmental impact and CO<sub>2</sub>-plume behaviour (Murai et al., 2003). Studies by Ozaki et al. (2001) have shown that CO<sub>2</sub> injection would be most effective at relatively slower rates (larger droplet size) and at depths greater than 1500 metres. Such a depth is well within the capability of present day subsea pipeline technology and CO<sub>2</sub> could be transported by tankers, similar to those used for transportation of liquid petroleum gas (Ormerod et al., 2002).

### 2.6.2 Storing CO<sub>2</sub> as Clathrates

Another method for ocean disposal of CO<sub>2</sub> involves sequestration of CO<sub>2</sub> at depths in excess of 3000 metres. At these depths, due to the high pressure and low temperatures, CO<sub>2</sub> exists in the

form of a *clathrate hydrate*, an ice-like combination of CO<sub>2</sub> and water (Brewer et al., 2000). Pure CO<sub>2</sub>-hydrate is denser than seawater and will generate a sinking plume, settling on the bottom of the ocean (Brewer et al., 2000). CO<sub>2</sub> sequestered in this way would accumulate in hollows or trenches in the deep sea. Dissolution of CO<sub>2</sub> into the overlying seawater would be reduced significantly due to formation of the CO<sub>2</sub>-hydrates. Direct disposal of CO<sub>2</sub> at great depths is currently not technically feasible, however, it may be possible to send cold CO<sub>2</sub> (dry ice) from mid-depth to the ocean floor (Aya et al., 2003). With a density greater than seawater, cold CO<sub>2</sub> will sink to the ocean bottom and be effectively stored.

The Monterey Bay Aquarium Research Institute (MBARI) has recently conducted a series of controlled experiments that involve release of cold CO<sub>2</sub> slurry at depths of 350-500m (Aya et al., 2003). Yet another method proposes disposal of CO<sub>2</sub> as *clathrate blocks*. Studies on this disposal method confirm that streamlined blocks have higher terminal velocity and thus reach the seabed faster than equidimensional blocks (Guever et al., 1996). As large as 1000 tonnes and shaped like a projectile, these blocks could penetrate into the deep seabed where the solid CO<sub>2</sub> would physically and chemically interact with the sediments before reacting with the ocean water. The retention times could, therefore, be significantly increased as compared to the gaseous or liquid CO<sub>2</sub> disposal methods (Guever et al., 1996). According to the IEA this method is currently not economically feasible (Ormerod et al., 2002).

Further studies on ocean disposal of CO<sub>2</sub> include *fertilising the oceans* with additional nutrients to increase draw-down of CO<sub>2</sub> from the atmosphere (Ormerod et al., 2002). Addition of nutrients such as nitrates and phosphates or iron may increase production of biological material, thereby drawing down additional CO<sub>2</sub> from the atmosphere through photosynthesis of the phytoplankton. Should this method prove to be feasible, the fishing industries may benefit from the resulting increase in the fish population, with atmospheric CO<sub>2</sub> sequestration as a secondary benefit, however the overall impact on the marine ecosystem is not well understood.

All the above described ocean disposal methods could potentially cause at least a local change in pH of the ocean water. Marine populations are, in general, intolerant to changes in the pH. Thus, due to environmental impacts on the marine ecosystem and associated public disapproval, ocean sequestration of CO<sub>2</sub> is not currently considered as an attractive option.

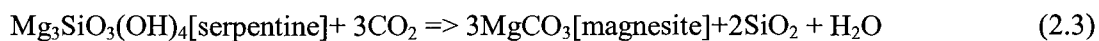
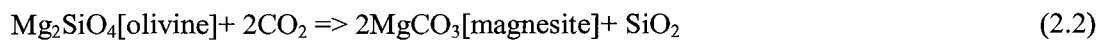
## **2.7 Storage in Salt Caverns**

Salt can be found as evaporite beds or as intrusive (domal or ridge) deposits whereby salt from a major underlying source has been forced up into overlying formations. The Western Canada Sedimentary Basin contains several regionally-extensive salt deposits, contained primarily within strata of the Devonian Elk Point Group (Grobe, 2000). Large cavities are created by solution mining, whereby water is injected into a salt bed or dome and the brine solution is pumped out. These caverns can be up to  $5 \times 10^5 \text{ m}^3$  in volume (Bachu, 2000), and since salt is highly impermeable (Murck et al., 1996) these spaces could provide a long-term solution to  $\text{CO}_2$  sequestration. The technology has been developed and applied for salt mining and underground storage of liquid petroleum gas (LPG), compressed air and petrochemicals (Bachu, 2000; Crossley, 1998; Istvan, 1983). Solid  $\text{CO}_2$  (dry ice) could also be stored in these repositories, surrounded by thermal insulation to minimise heat transfer and loss of  $\text{CO}_2$  gas (Davison et al., 2001). Although salt and rock caverns theoretically have a large storage capacity, the associated costs are very high and the environmental problems relating to the mined rock and disposal of large amounts of brine are significant (Kolkas-Mossbah and Friedman, 1997). Based on current technology, storage of  $\text{CO}_2$  in underground salt caverns is uneconomical.

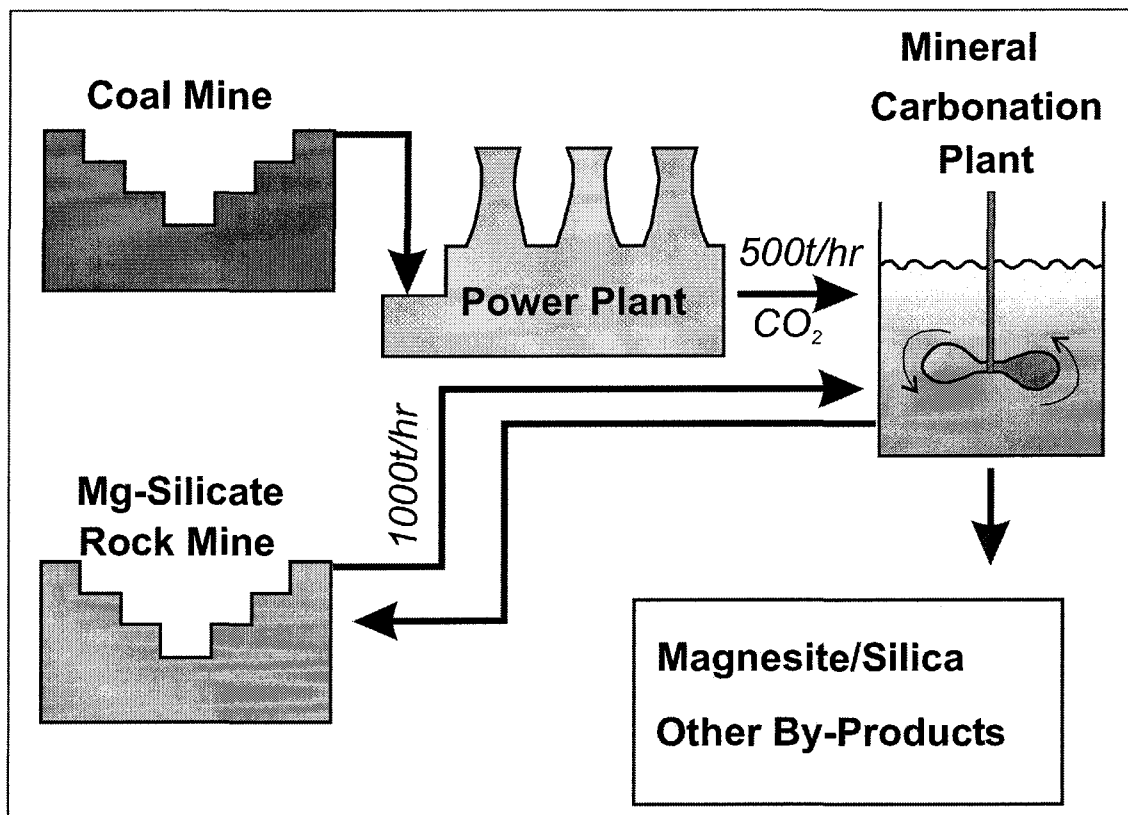
## **2.8 Mineral Carbonation**

Based on a natural rock-weathering reaction, mineral carbonation is a sequestration concept whereby  $\text{CO}_2$  is chemically combined in an exothermic reaction with readily available Mg or Ca-silicate minerals to form carbonates (Lackner et al., 1997; O'Connor et al., 2000; Gerdemann et al., 2003). The products are stable on a geologic time-scale, potentially storing  $\text{CO}_2$  for millions of years. Mg-silicates are favoured relative to Ca-silicates because they are more widespread, form larger bodies and contain more reactive material per tonne of rock (Lackner et al., 1997; Kohlmann et al., 2002). Wide variety of Mg-bearing materials, such as enstatite, fly ash and other industrial residues were investigated as potential starting materials for the industrial carbonation process. Recent laboratory tests however, indicate that olivine  $[(\text{Mg,Fe})\text{SiO}_4]$  and serpentine  $[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$  are the most promising raw material (e.g. Lackner et al., 1997; O'Connor et al., 2000). The two reactions below illustrate the basic  $\text{CO}_2$  carbonation principle using olivine and serpentine as examples:





In nature, carbonation reactions involving silicates are slow (Kohlmann and Zevenhoven, 2001). A sequestration plant can be visualized as a blender operating at high temperature and pressure conditions (Figure 2.9).



**Figure 2.9** Idealized view of a mineral carbonation plant. Envision the coal mined for energy, and the waste  $\text{CO}_2$  emissions combined with finely ground Mg-silicates in a temperature and pressure controlled slurry. The resulting carbonate and silica may have industrial applications. Other by-products may include strategic minerals typically associated with serpentinite and dunite deposits, such as Ni, Co, Cr, Fe and Mn. (Modified from Bauer, 2001).

For industrial  $\text{CO}_2$  sequestration applications, carbonation reactions have to be accelerated. This can be achieved by increasing the surface area of the Mg-silicate (crushing and milling), agitating the slurry (O'Connor et al., 1999; Dahlin et al, 2000) and by adding catalysts (for

example, NaCl and NaHCO<sub>3</sub> and HCl) to the solution/slurry prior to the carbonation process (Dahlin et al., 2000; Goldberg and Walters, 2003; Jia and Anthony, 2003; Fauth and Soong, 2001; Lackner et al., 1998). Optimization of the carbonation process by controlling temperature and partial pressure of CO<sub>2</sub> (P<sub>CO2</sub>) may be also a major factor (O'Connor et al., 1999; Dahlin et al., 2000). In the case of serpentine, an energy-intensive heat pre-treatment (activation-destabilization of the crystal structures) at temperatures of 600-650°C is required (O'Connor et al., 2000). Such pre-treatment removes chemically bound water and increases overall porosity (Gerdemann et al., 2003; Kohlmann et al., 2002; Goldberg and Walters, 2003), thereby enhancing its mineral carbonation potential.

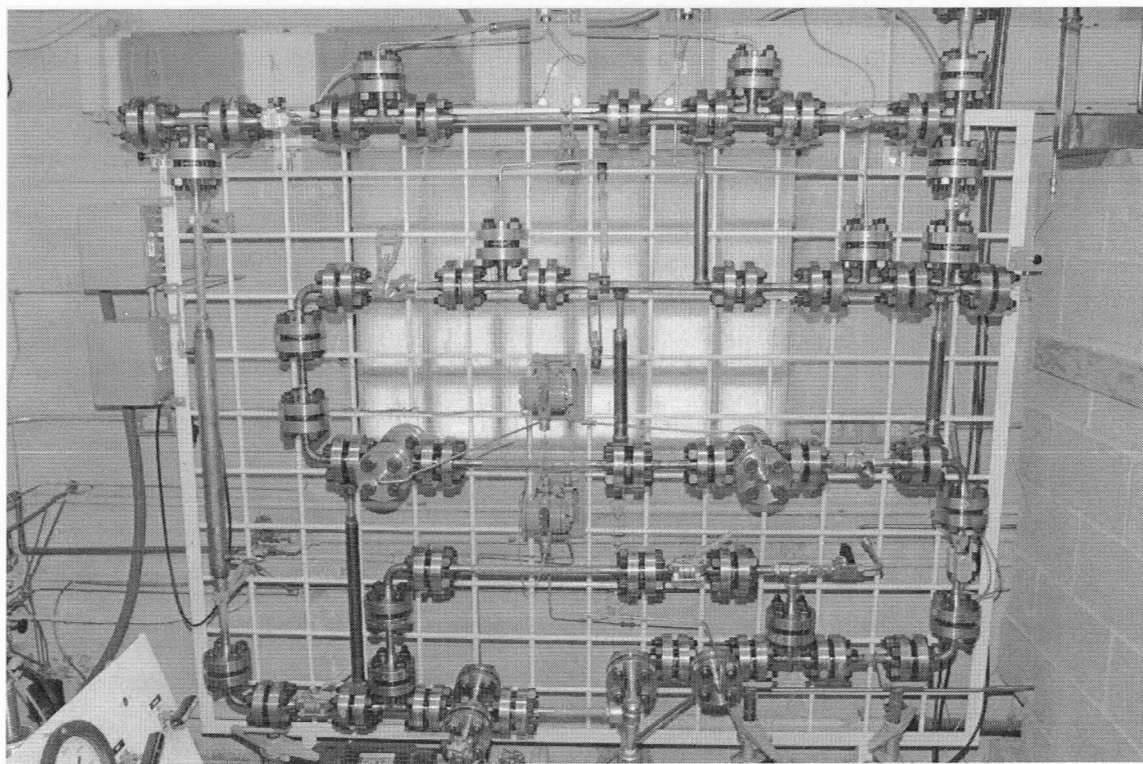
There is currently no mineral sequestration plant in operation, however members of the Mineral Sequestration Working Group, a multi-laboratory team managed by the National Energy Technology Laboratory (NETL) of the Department of Energy (DOE) are developing pilot-scale mineral carbonation units and according to their plan a 10 MW demonstration plant will be operational by 2008 (Goldberg and Walters, 2003). Their current research includes the design and operation of a first prototype high temperature-high pressure (HTHP) flow loop reactor by the Albany Research Center (Figure 2.10), with the aim to develop a transition from batch experiments to continuous operation.

The mineral sequestration concept is currently incorporated into the design of the coal-fuel electricity generating plant of the Zero Emission Coal Alliance (ZECA), an international consortium of utilities, mining companies, engineering firms and government laboratories; however it may be also applied elsewhere.

### ***2.8.1 Advantages of Mineral Carbonation***

Serpentine and Olivine are the two most likely silicates that could be used as starting materials in mineral sequestration. Olivine is favoured because it reacts better without the energy-intensive pre-treatment that serpentine requires. In contrast to the previously described methods, once the CO<sub>2</sub> is locked into a carbonate (a mineral stable on geological time scale), there is no possibility for an accidental release of CO<sub>2</sub>. As well, direct carbonation does not lead to problematic by-products (Lackner et al., 1998). Furthermore, should fibrous serpentine tailings (chrysotile) be considered as raw material for the process (e.g. Huot et al., 2003), then mineral

sequestration would help dispose of unwanted asbestos waste. Mineral carbonation may, therefore, benefit from public acceptance.



**Figure 2.10** Flow loop test-bench reactor at Albany Research Centre used for mineral carbonation tests. The apparatus is 2 meters high by 2 meters wide, with an ~1.25 cm diameter stainless steel pipe and rated to 150 atm at 200°C. (Photo is the courtesy of Thermal Treatment Technology Division; Albany Research Center; Office of Fossil Energy, US DOE)."

The costs of the CO<sub>2</sub> disposal could be higher than for the injection of CO<sub>2</sub> into oil and gas reservoirs or deep coal seams, for example. However, these costs may be reduced if the potential for industrial applications of the product (depending on acceptable purity, form, grain size, particle shape and chemical properties). Magnesite has a wide variety of industrial applications (Simandl, 2002) and the same applies for silica. The carbonation process may also become a new source of Fe, Mn, Co, Cr and Ni recovered during the breakdown of Mg silicate's crystal structure (Haywood et al., 2001; O'Connor et al., 2000).

Large-scale CO<sub>2</sub> sequestration as mineral carbonates will require enormous amounts of mineral (Kohlmann et al., 2002). For a typical power plant, the mass flows of fuel and

carbonated mineral will be of the same order of magnitude. For example, studies suggests that for a single 500 MW coal-fired power plant, generating approximately 10 000 tons CO<sub>2</sub> per day, over 23 000 to 30 000 tons per day of Mg-silicate ore would be required (Dahlin et al., 2000; O'Connor et al., 2000). Thus, under ideal conditions, coal and Mg-silicate mines should be located close to each other. No shortage of starting material is likely to occur if mineral sequestration becomes a reality and serpentine becomes a workhorse of mineral CO<sub>2</sub> sequestration (Goff et al., 1997). However, if forsterite (Mg-end member of olivine) is used as starting material, supplies are limited and geographically constrained. In most cases, serpentine is an unwanted by-product of metal and chrysotile mining, but in some locations, this waste may become a sought after commodity when its potential for CO<sub>2</sub> sequestration is realized. Should mineral sequestration of CO<sub>2</sub> become an established technology, then new opportunities will arise for potential producers of magnesium silicates and owners of magnesium silicate-rich tailings.

## **2.9 Conclusions**

This review concentrated on the description of the main geological, ocean and mineral CO<sub>2</sub> sequestration methods that are currently the focus of intensive research by industrialized nations worldwide. At first glance, the most technologically mature methods are storage in active and depleted oil and gas fields, though most of the emphasis lies on maximizing oil and gas recovery rather than sequestration potential. Research relating to injection of CO<sub>2</sub> into deep coal seams is rapidly advancing, with CO<sub>2</sub>-enhanced CBM recovery potentially offsetting sequestration costs. Saline aquifers provide huge storage potential in terms of volume for CO<sub>2</sub> sequestration, but they are much more difficult and expensive to characterize than hydrocarbon reservoirs due to the lack of an existing exploration database.

The methods that currently will encounter the most resistance from the public are storage in salt caverns and ocean sequestration. Mineral sequestration is the only method that truly disposes of CO<sub>2</sub> on geological time scale, with a minimum risk for an accidental CO<sub>2</sub> release.

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### **3. Options for Sequestration of CO<sub>2</sub> from Major Stationary Point Sources, British Columbia, Canada**

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#### **3.1 Abstract**

This study presents a conceptual overview of the major CO<sub>2</sub> point sources for British Columbia (BC) and suggests potential geological sinks for the disposal of these emissions. In BC, stationary sources of CO<sub>2</sub> (>50,000 t/yr) include operations in aluminium and glass manufacturing; cement, chemical and smelting industries; oil and gas processing, coal operations; waste incinerators, pulp and paper mills, and potentially thermal power plants. These point sources total approximately 17 Mt of CO<sub>2</sub> equivalent for 2003, which is about 26% of BC's total estimated GHG emissions. Currently, BC does not have any coal-fired power plants. Major single stationary points sources or clusters of smaller stationary sources with combined emissions in excess of 500 kt/yr are located in the Vancouver area, Fort Nelson (northeastern BC), Campbell River (Vancouver Island), Kitimat (west coast of central BC), Fort St. John (northeastern BC), and Elkford (southeastern BC).

BC is located on a tectonically active continental margin, which consists of a variety of sedimentary, igneous and metamorphic lithologies underlain by a crystalline basement. CO<sub>2</sub> sequestration potential in sedimentary basins similar to that in Alberta is applicable only in the northeastern area of BC. Alternate options need to be considered for the remainder of BC, including injection of CO<sub>2</sub> into deep coal seams, ocean disposal and mineral carbonation. Matching large stationary point sources to suitable sinks suggests that northeastern BC has potential for injection into deep saline aquifers, depleted gas reservoirs and coal beds; Vancouver Island and southeastern BC are also partly underlain by deep coalbeds; and large tracts of ultramafic rocks bearing magnesium silicates indicate that the raw material necessary for the mineral sequestration process exists in sufficient amounts to sequester CO<sub>2</sub> emissions

from point sources in the Vancouver and Prince George regions. Offshore sedimentary basins are under a moratorium, which limits sequestration planning for stationary CO<sub>2</sub> emission sources located along the west coast.

This study shows that BC has few major stationary CO<sub>2</sub> point sources. Although sequestration of CO<sub>2</sub> emissions from several selected major stationary point sources in BC would significantly reduce emissions to the atmosphere, BC will have to combine this effort with usage of renewable energy resources, cleaner fuel (natural gas), as well as increased car-pooling for metropolitan areas. Only a combination of these efforts would bring BC to the reduction required by the Kyoto agreement.

### **3.2 Introduction**

Canada has officially ratified the Kyoto Protocol on greenhouse gases (GHGs). Under the accord, Canada has until 2012 to lower its GHG emissions to 6% below 1990 levels. Of the six GHGs covered by the Protocol, carbon dioxide (CO<sub>2</sub>) is the greatest contributor (85%) to Canada's total GHG emissions (UNFCCC, 2003). GHG emission numbers are therefore typically reported as CO<sub>2</sub> equivalent (CO<sub>2</sub>-e). Canada's GHG emissions for 1990 were estimated at 601 million tonnes (Mt) of CO<sub>2</sub>-e/yr; current levels are estimated at 726 Mt (Table 3.1). British Columbia's (BC) emissions for 1990 were estimated at 52.7 Mt and current levels are estimated at about 65.9 Mt (Table 3.1), of which 82.4% results from the combustion of fuels (Environment Canada, 2002).

Total reduction (6% below 1990) of CO<sub>2</sub> emissions for BC is estimated at 16 Mt CO<sub>2</sub>-e/yr, or approximately a 25% decrease of current CO<sub>2</sub> levels. Nearly all CO<sub>2</sub> emissions growth can be attributed to increased usage of light-duty gasoline trucks, including sport utility vehicles and minivans (Environment Canada, 2002). Sequestering CO<sub>2</sub> from mobile sources is not technically feasible at this time. Significant reduction of CO<sub>2</sub> emissions can be achieved by use of more efficient technology such as use of energy fuels with lower carbon content and increased use of alternative sources, including wind, solar, geothermal and nuclear power. It is unlikely that the reduction of CO<sub>2</sub> emissions, required to meet the Kyoto agreement, could be achieved by these measures alone. CO<sub>2</sub> sequestration, which involves the capture and extraction

of CO<sub>2</sub> from industrial streams, transportation of CO<sub>2</sub> and its subsequent disposal in an appropriate geological sink, will likely be needed.

<b>PROVINCE</b>	<b>CO<sub>2</sub>-e in Million Tonnes</b>	<b>Tonnes of CO<sub>2</sub> /person/yr</b>
<b>Alberta</b>	223.00	74
<b>Ontario</b>	207.00	18
<b>Quebec</b>	90.40	12
<b>British Columbia</b>	65.90	16
<b>Saskatchewan</b>	61.80	61
<b>Nova Scotia</b>	21.50	23
<b>Manitoba</b>	21.40	19
<b>New Brunswick</b>	20.20	27
<b>Newfoundland</b>	8.80	17
<b>PEI and Labrador</b>	2.10	15
<b>NWT</b>	1.80	26
<b>Yukon</b>	0.53	17
<b>Canada total (2000)</b>	726	24

**Table 3.1** CO<sub>2</sub>-equivalent emission numbers for Canada and her provinces in million tonnes for 2000 (Environment Canada, 2002). British Columbia ranks 4<sup>th</sup> in total CO<sub>2</sub> release for the province, but it ranks 10<sup>th</sup> in terms of tonnes of CO<sub>2</sub> per capita (Statistics Canada, 2003).

Major stationary point sources of CO<sub>2</sub> or flue gas (a mixture of CO<sub>2</sub> and other GHGs) represent prime targets for sequestration efforts, largely due to economy of scale. CO<sub>2</sub> sequestration planning involves investigation of both the CO<sub>2</sub> sources and the geological sinks within which the emissions are to be disposed of. The present study begins with the identification of BC's major stationary point sources. Candidates with large emission sources and high concentration of CO<sub>2</sub> are selected. Distance from source to sink should be limited, since transportation of CO<sub>2</sub> to a sink is a significant cost factor, estimated at \$1-\$3 per tonne of CO<sub>2</sub> per 100 km pipeline, which is on the same order as the cost of the actual storage of CO<sub>2</sub> into a depleted hydrocarbon reservoir or deep saline aquifer (Davison et al., 2001). Investigation of the geology surrounding a major CO<sub>2</sub> point source is an important component in matching sources to sinks, since the local geology dictates the possible method(s) for sequestering the CO<sub>2</sub> emissions. Most of the methods for CO<sub>2</sub> sequestration in geological media that are currently being developed are described by Voormeij and Simandl (2004a).

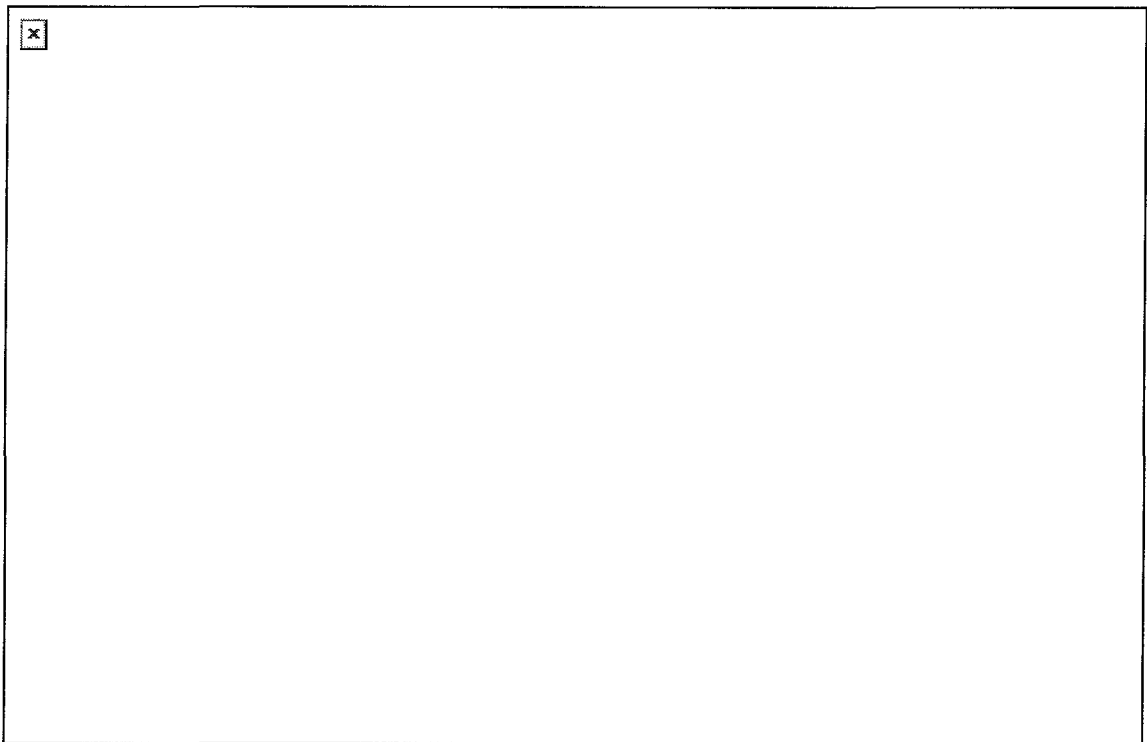
The methodology of matching sources to sinks on a global and country (Australia) scale has been initiated (Van Bergen et al., 2003; Bradshaw et al., 2003). On a more regional scale, Alberta's major stationary point sources of CO<sub>2</sub> emissions have been identified and the CO<sub>2</sub> sequestration potential of the Western Canadian Sedimentary (WCS) basin has been investigated in terms of injection into depleted or active hydrocarbon reservoirs, into deep coal beds and injection into deep saline aquifers (Bachu and Stewart, 2002). The WCS basin extends into NE corner of BC; therefore extrapolation from Alberta is applicable to this region. However, most of BC is located on an active continental margin, where the geology is complex. Furthermore, exploration for oil and gas in other sedimentary basins has not been sufficient to allow for an adequate evaluation of their suitability for geological sequestration. Thus, alternate methods of sequestering CO<sub>2</sub> need to be considered for this province. This study attempts a preliminary overview of the major CO<sub>2</sub> point sources for BC and provides the groundwork for selecting potential geological sinks.

### ***3.3 Identifying BC's Major CO<sub>2</sub> Point Sources***

Presently, there are no regulations in Canada stating that individual plants or facilities have to measure or report their CO<sub>2</sub> emissions. Because most major emitters of NO<sub>x</sub> and SO<sub>x</sub> also emit significant amounts of CO<sub>2</sub>, a list of these facilities provides the starting point for identifying BC's major stationary point sources of CO<sub>2</sub>. Next, CO<sub>2</sub> emission levels for each facility were screened to limit the list to stationary point sources emitting more than fifty kilotonnes of CO<sub>2</sub> to the atmosphere per year. The 50 kt CO<sub>2</sub>/yr threshold chosen is substantially lower than the one set in neighbouring Alberta (Bachu and Stewart, 2002), because BC doesn't have very many large stationary CO<sub>2</sub> point sources. The conservative cut-off provides an option to consider clusters of smaller point sources in addition to the single large sources. Identification of facilities with CO<sub>2</sub> emissions in excess of 50 kt/yr inferred from NO<sub>x</sub> and SO<sub>x</sub> emissions was corroborated in large part by use of reports from the Volunteer Challenge Registry (VCR) website and contacts with the industry. The VCR registry is useful for CO<sub>2</sub> sequestration planning, as many companies submit reports on their facilities' CO<sub>2</sub> emission levels. Not all companies submit reports, however, and out of those that do, few companies actually provide direct CO<sub>2</sub> emission numbers for individual facilities. Instead, CO<sub>2</sub> emission numbers are typically submitted as a company total. Several BC companies that did register with VCR

reported CO<sub>2</sub> emission data for a total of 44 single facilities in BC, of which 13 are probably in excess of 50 kt CO<sub>2</sub>/yr.

Additional information was utilized from the VCR reports including emission factors (EF) for individual facilities. The amount of CO<sub>2</sub> released to the atmosphere from each point source is not directly measured, but rather is estimated based on general or specific emission factors that take into account the type and amount of energy (fuel) consumed for production. Thus, the EFs are often listed as number of tonnes or kilograms of CO<sub>2</sub> per tonne of product, whether the product is paper, aluminum, cement, clean coal, etc. Further EFs were obtained from the BC Pollution Prevention and Remediation Branch, Environmental Effects Monitoring, which supplied EFs for individual pulp and paper plants, a major industry in BC. Production numbers were acquired from VCR reports as well as from companies' websites and from the Council of Forest Industries. Note that production numbers are often a capacity or maximum possible production for a facility, therefore the resulting CO<sub>2</sub> emission levels calculated from these numbers should be considered a maximum; actual CO<sub>2</sub> emission are most likely a little less.



**Figure 3.1** Geographical distribution of major (>50 kt CO<sub>2</sub>/yr) stationary point sources for British Columbia (source: Voormeij and Simandl, 2003).

### **3.3.1 Results**

Stationary sources with estimated emissions of CO<sub>2</sub> in excess of 50 kt/yr are shown in Figure 3.1. These include operations in aluminium and glass manufacturing; cement, chemical and smelting industries; oil and gas processing, coal operations; waste incinerators, pulp and paper mills, and thermal power plants (during low water level years). Due to confidentiality agreements with some of the industry contacts, individual numbers and operations are not listed. BC's point sources with CO<sub>2</sub> emissions over 50 kt/yr total approximately 17 Mt CO<sub>2</sub> for 2002.

## **3.4 Options for Geological CO<sub>2</sub> Sequestration in BC**

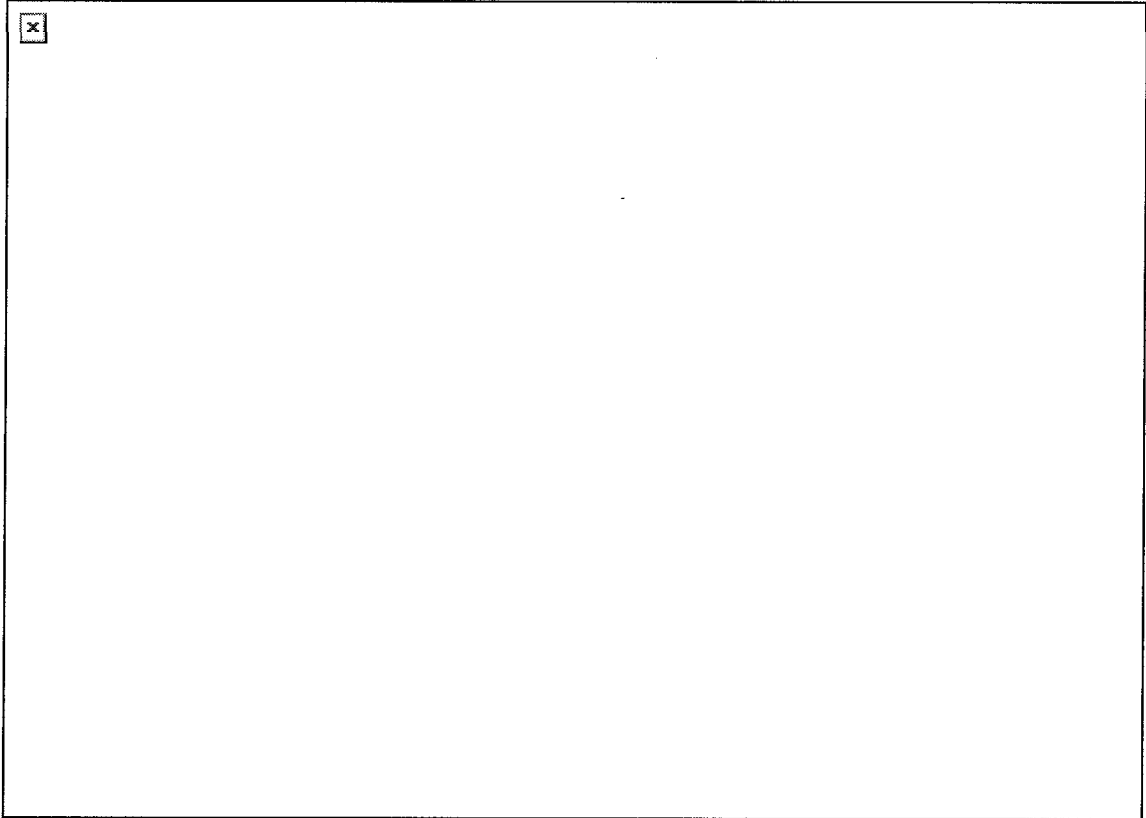
British Columbia has been situated on an active, west-facing margin of continental North America for the last 530 million years and part of a subduction zone (accretionary) tectonic setting for the last 390 million years (Monger, 1997). Several parts of the province contain young sedimentary basins that show potential for CO<sub>2</sub> sequestration by injection into depleted gas reservoirs, deep saline aquifers, and coalbeds. BC also contains belts of ultramafic rocks that are rich in magnesium silicates, the raw material necessary for reacting with CO<sub>2</sub> emissions in a process known as mineral sequestration (Voormeij and Simandl, 2004b). This section investigates the geology in BC in terms of its suitability for CO<sub>2</sub> sequestration.

### **3.4.1 Injection into Sedimentary Basins: Depleted Oil and Gas Reservoirs**

Nine hydrocarbon basins and two sedimentary troughs with hydrocarbon potential are identified for BC (Figure 3.2). These include the Western Canada Basin in the northeast, the Bowser Basin and the Nechako Basin in the central interior of the province, the Fernie Basin in the southeast and the Queen Charlotte (QC), Winona, Tofino and Georgia basins off the west coast of the province. BC is a major natural gas producer and is currently producing commercial quantities of gas in the northeast of the province, a western extent of the WCS basin, which is assessed as being suitable for sequestering CO<sub>2</sub> in depleted oil and gas reservoirs and deep carbonate aquifers (Bachu and Stewart, 2002; Bachu and Gunter, 1999). Under normal conditions, primary gas recovery is followed by a secondary recovery method that repressurizes the reservoir by allowing the water table to rise (Oldenburg and Benson, 2001). As a result, large depleted, or partially depleted water-saturated gas reservoirs do exist that could be utilized for sequestering CO<sub>2</sub>. Currently, BP's In Salah Gas demonstration project in Algeria (Riddiford



et al., 2002; Knott, 2004) is testing the hypothesis that CO<sub>2</sub> could be sequestered, while at the same time recovering more natural gas, by injecting the CO<sub>2</sub> in the aquifer zone of a gas reservoir. Depending on the results from this project, CO<sub>2</sub>-enhanced gas recovery (EGR) may become applicable in BC.



**Figure 3.2** Map of British Columbia's sedimentary basins, pipelines and acid gas injection sites. 1-Western Canada Basin, 2-Bowser Basin, 3-Nechako Basin, 4-Fernie Basin, 5-Queen Charlotte Basin, 6-Winona Basin, 7-Tofino Basin, 8-Georgia Basin, 9-Whitehorse Trough, 10-Quesnel Trough, 11-Rocky Mountain Trench (Hannigan et al., unpublished).

### **3.4.2 Injection into Sedimentary Basins: Acid Gas**

Gas processing facilities worldwide produce an emission stream that is a combination of CO<sub>2</sub> and hydrogen sulphide (H<sub>2</sub>S) known as acid gas. In 1988, sulphur emission limits changed from 10 ton of sulphur per day to 1 ton per day (Wichert and Royan, 1997). As a result, acid gas was commonly desulphurized, which involves the extraction of sulphur and the release of a CO<sub>2</sub> stream to the atmosphere. A new industry trend is to bypass the sulphur extraction and inject the acid gas directly into the subsurface. There are seven acid gas injection sites in northeastern BC

(Figure 3.2). West Stoddart is the largest to date with a licensed capacity of 391,000 m<sup>3</sup>/d and is currently operating at 280,000 m<sup>3</sup>/d. At this site, 340 t/d of H<sub>2</sub>S and 78 t/d of CO<sub>2</sub> are injected through two wells some 4.5 km apart. Thus, fairly significant amounts of CO<sub>2</sub> are being sequestered through acid gas injection. Monitoring the behaviour of the injected gases may provide useful information for future CO<sub>2</sub> sequestration planning.

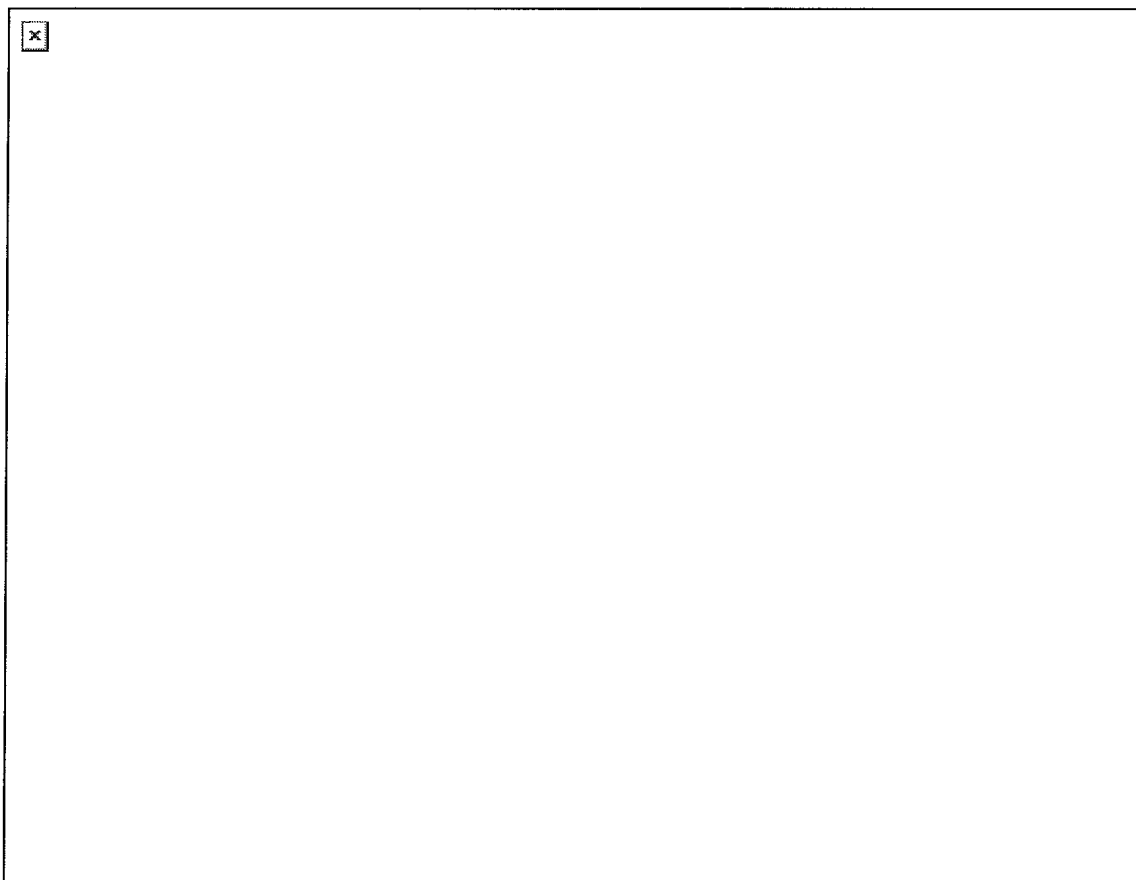
### ***3.4.3 Offshore BC: Injection into Deep Saline Aquifers and Ocean Disposal***

Although great potential for hydrocarbon exploration does exist in the four sedimentary basins along the west coast of BC (Hannigan et al., 2001), there are two moratoria imposed on these basins. Ownership of the four basins, unresolved First Nations negotiations and the discovery of unique fauna in the Hecate Strait (glass sponge reefs) make CO<sub>2</sub> sequestration planning for this region complicated. In addition, with the moratorium being imposed primarily due to fear of environmental impacts on these regions, ocean disposal or injection of CO<sub>2</sub> into these basins is unlikely to receive strong public support. There are no producing or depleted hydrocarbon reservoirs offshore and there are less than 50 exploratory wells. Therefore, deep-lying aquifers offshore BC are poorly constrained. Currently, the provincial government is attempting to lift the moratoria. If offshore hydrocarbon exploration goes ahead and is successful, it will be imperative to educate the public on the environmental merits of sequestering CO<sub>2</sub> from potential offshore hydrocarbon processing facilities.

### ***3.4.4 Injection into Deep Coal Beds***

BC has abundant coal resources (Figure 3.3), some of them lie at depths too great to be considered for conventional mining. CO<sub>2</sub> can be injected into suitable coal seams where it adsorbs onto the coal and is stored in the pore matrix of the coal seams and in solution within the cleats (Ryan and Richardson, 2004). Coalbed methane (CBM) can be found in almost every coalfield across the province (BC MEM, 2003). Thus, CO<sub>2</sub> sequestration in coal seams has the potential to generate cash flow through enhanced coalbed methane recovery (ECBMR). CO<sub>2</sub>-ECBMR technology is still in its infancy stage and little is known about the behaviour of CO<sub>2</sub> in coal above pressures of 7.38 Mpa (Krooss et al., 2001). Currently, there are active CBM exploratory projects under way in southeast BC, where seventeen wells have been drilled to date (Ryan and Richardson, 2004) as well as around Fort St. John.

The most recent study on coal sequestration potential of BC (Ryan and Richardson, 2004) includes results of CO<sub>2</sub> adsorption data for different coal samples collected throughout BC (Figure 3.3). Candidates with the best potential for CO<sub>2</sub> sequestration include low ranking coals such as lignite, sub-bituminous and bituminous coal at depths of 500 to 900m (Ryan and Richardson, 2004). CO<sub>2</sub> should either be injected into coalbeds that are undersaturated with respect to methane (abandoned CBM wells), or CO<sub>2</sub> sequestration should be accompanied with CBM production to minimize the risk that displaced methane molecules escape to the surface (Ryan and Richardson, 2004). Methane is an even more powerful GHG than CO<sub>2</sub>.

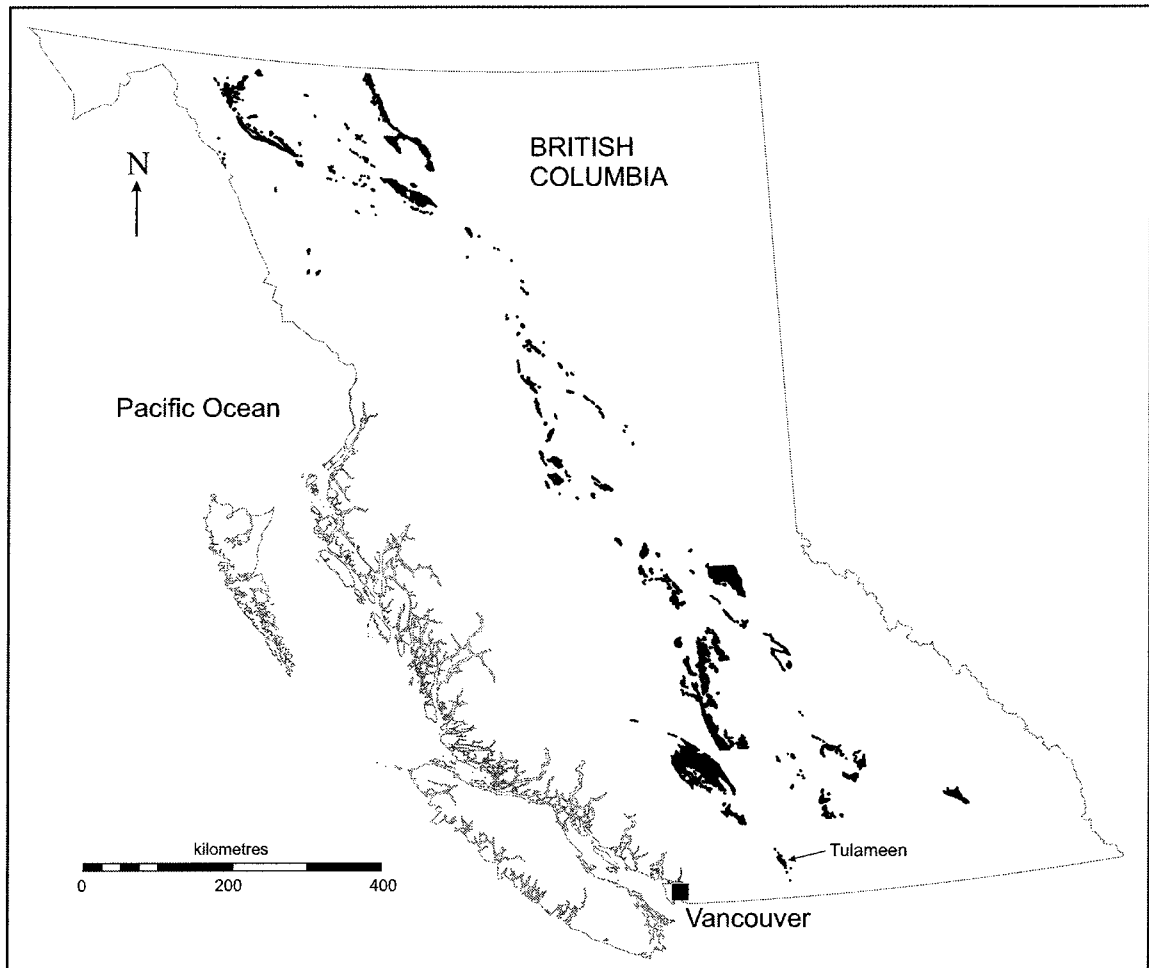


**Figure 3.3** Coal beds in British Columbia above 2000m depth (Owsiacki and Payie, 2000). Samples of low-ranking coalbeds with potential for CO<sub>2</sub> sequestration were collected from 1-Willow Creek (Gething Fm), 2-Bullmoose (Gates Fm), 3-Quinsam (Comox Fm), 4-Princeton Coal Basin (Allenby Fm) and 5-Elkview (Mist Mountain Fm).

### 3.4.5 Mineral Carbonation

Mineral sequestration of CO<sub>2</sub> by mineral carbonation involves mining of large amounts of Mg-silicates (forsteritic olivine or serpentine minerals) and reacting these minerals *ex situ* with CO<sub>2</sub>

emissions. The resulting products are the thermodynamically stable magnesite ( $\text{MgCO}_3$ ) and silica ( $\text{SiO}_2$ ). Mg-silicates are typically associated with ultramafic rocks, which are found in tracts parallel to the continental margin (Figure 3.4). The Tulameen Complex (Figure 3.4) is a promising dunite deposit (rock composed of more than 90% forsteritic olivine), which is currently undergoing assessment for its  $\text{CO}_2$  sequestration potential (Voormeij et al., 2004).



**Figure 3.4** Distribution of dunite (olivine-rich) and/or serpentinite-bearing ultramafic rocks in British Columbia (Voormeij and Simandl, 2004b).

Some selected chrysotile-bearing stockpiles sites may also have promise as raw material, thereby simultaneously disposing of unwanted asbestos waste (Huot et al., 2003). Although mineral carbonation is not considered, at this time, cost-competitive with other disposal methods, it is the only method that disposes of  $\text{CO}_2$  in a solid form on a geological time scale, without a risk of release back to the atmosphere (O'Connor et al., 2000). It is possible that in

very specific cases, assuming that produced magnesite and silica finds industrial applications (see section 4.5.5), this method could be cost effective.

### ***3.5 Matching Sources to Sinks***

British Columbia has a variety of potential sinks for geological sequestration of CO<sub>2</sub>, including injection into depleted gas reservoirs, possibly combined with EGR, and injection into deep saline aquifers in the WCS basin in northeastern BC. Further sinks include deep coal beds, with the potential for ECBMR, in southeastern, northeast and southern interior of BC, as well as in the Comox area on Vancouver Island. Mg-silicate-bearing ultramafic rocks underlie large tracts of land, indicating a promising resource for the mineral CO<sub>2</sub> sequestration process. The technologies associated with these methods are not at the same level of development. The most mature methods (acid gas injection and injection into depleted gas reservoirs) will be implemented first and the use of less mature methods (injection into deep coalbeds and mineral sequestration) will depend on results of active demonstration projects and bench scale tests worldwide.

#### ***3.5.1 Screening Major Point Sources for CO<sub>2</sub> Sequestration***

Selection of ideal candidates for CO<sub>2</sub> sequestration should be based on the amount of CO<sub>2</sub> released per year (>500 kt/yr), high purity of emission stream (>90% CO<sub>2</sub>), lifespan (>10 years) and associated infrastructure in place (pipelines, roads, etc.), to keep the sequestration costs to a minimum. Stationary point sources or clusters of smaller stationary sources in excess of 500 kt CO<sub>2</sub>/yr are located in the Vancouver area (southwestern BC), Fort Nelson, Pine River, Fort St. John (northeastern BC), Campbell River (Vancouver Island), Kitimat (west coast of central BC) and Elkford regions (southeastern BC). Emission sources with low CO<sub>2</sub> concentration require advances in technology to reduce the cost of capture and separation, thus high purity sources of CO<sub>2</sub> should be selected for sequestration. Pure sources of CO<sub>2</sub> (>90%) include industrial plants producing hydrogen, ammonia or ethylene-oxide (Van Bergen et al., 2003; Gale, 2003; Kuuskraa, 2003). Other candidates that could have high purity CO<sub>2</sub> streams, depending on the technology, include thermal power plants (Gale, 2003; Analysisworks, 2002) and gas-processing facilities (Kuuskraa, 2003). Gas processing facilities have associated gas pipelines in place that may be converted to transport CO<sub>2</sub> gas.

In summary, BC has a number of promising candidates that could be targeted for CO<sub>2</sub> sequestration. The Fort Nelson and Pine River gas processing sites are located in a region containing relatively well-defined depleted gas reservoirs and deep saline aquifers. Furthermore, they are situated in an area that is already actively injecting acid-gas into the subsurface. The chemical complex in Kitimat constitutes a good candidate, as it is tentatively identified as a large source with high purity CO<sub>2</sub> emissions. Technically, nearby sinks, including ocean disposal and injection into local offshore sedimentary basins are possible options, however, these options would currently meet with public opposition. Similarly, large point sources along the west coast and on Vancouver Island at this time cannot utilize the offshore sedimentary basins as sinks due to the moratoria placed on them. The future of CO<sub>2</sub> disposal in coalbeds will be further enhanced if CO<sub>2</sub>-ECBMR proves to be viable. In the Fernie basin, southeastern BC, large stationary point sources associated with coal mining operations can be matched with local deep coalbed sinks. Depending on developing technology, mineral sequestration of CO<sub>2</sub> may be applied to large point sources or clusters of point sources in the Vancouver and Prince George regions.

### **3.6 Conclusions**

BC's inventoried stationary point sources (>50 kt/yr) total approximately 17 Mt CO<sub>2</sub>/yr. It is impossible for BC to sequester all these sources. A more realistic approach, to reduce BC's CO<sub>2</sub> emissions, is to target several of the major, high-concentration point sources or clusters of point sources and combine a CO<sub>2</sub> sequestration effort with increased usage of renewable energy resources (wind power, hydro-power), more public transportation and increased usage of hybrid vehicles.

The CO<sub>2</sub> sequestration methods potentially applicable to the selected large point sources of CO<sub>2</sub> in BC are (1) injection into depleted and water-saturated gas reservoirs, (2) deep saline aquifers in northeastern BC, (3) injection into deep coalbeds in northeastern, southeastern BC and parts of Vancouver Island, and (4) mineral carbonation in southwest and central BC. Actual quantification of the amount of CO<sub>2</sub> that can potentially be stored in individual sinks is not addressed and will require much further research. The method of sequestering acid gas into deep saline aquifers is most advanced and therefore the first sequestration projects in BC will

most likely be based on this technology. However, rapid technological advances may change this view and other CO<sub>2</sub> sequestration methods may become applicable.

### 3.7 Acknowledgements

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## **4. A Systematic Assessment of Ultramafic Rocks and Their Suitability for Mineral Sequestration of CO<sub>2</sub>**

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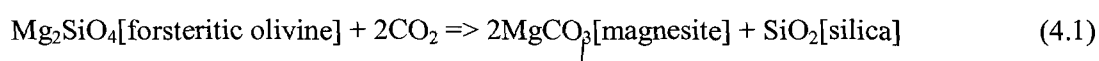
### **4.1 Abstract**

Given the current level of technology and projected costs per tonne of CO<sub>2</sub> sequestered, mineral carbonation is a "niche" method that may be applicable when a major CO<sub>2</sub> 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 ultramafic rocks. 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 CO<sub>2</sub> point source(s); c) screen promising sites by field preliminary sampling/examinations; d) filter selected 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.

### **4.2 Introduction**

Various geological CO<sub>2</sub> sequestration methods have been proposed worldwide, including injection of CO<sub>2</sub> into hydrocarbon reservoirs, deep coal beds or deep saline aquifers (Voormeij and Simandl, 2004a). The applicability of these methods is site specific and depends largely on

tectonic and geological settings (Voormeij and Simandl, 2004b). Where major CO<sub>2</sub> point sources are underlain by a crystalline basement or located within tectonically unstable regions, the mainstream geological CO<sub>2</sub> sequestration methods are not applicable. Mineral sequestration of CO<sub>2</sub> is one of the "niche" alternatives. It can involve reacting a variety of Ca-, Fe<sup>2+</sup> and Mg-silicates and waste materials with CO<sub>2</sub> emissions (O'Connor et al., 2000; Lackner et al., 1997; Kakizawa et al., 2002; Fauth and Song, 2001). Mg-silicates have the best potential in terms of reaction efficiency (Lackner et al., 1997), quantity of material needed per unit CO<sub>2</sub> sequestered, and are the focus of this paper. The resulting products are magnesite and silica (equations 4.1 and 4.2).



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 CO<sub>2</sub> leaks (O'Connor et al., 2000; Lackner et al., 1997). Olivine is more reactive without the energy-intensive pre-treatment (heat treatment and/or attrition grinding) that serpentine requires (O'Connor et al., 2000). 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 (O'Connor et al., 2000; McKelvy et al., 2002). Chrysotile-containing tailings are also investigated as potential feed (Huot et al., 2003; Goff et al., 1997). 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.

#### **4.2.1 Raw Materials**

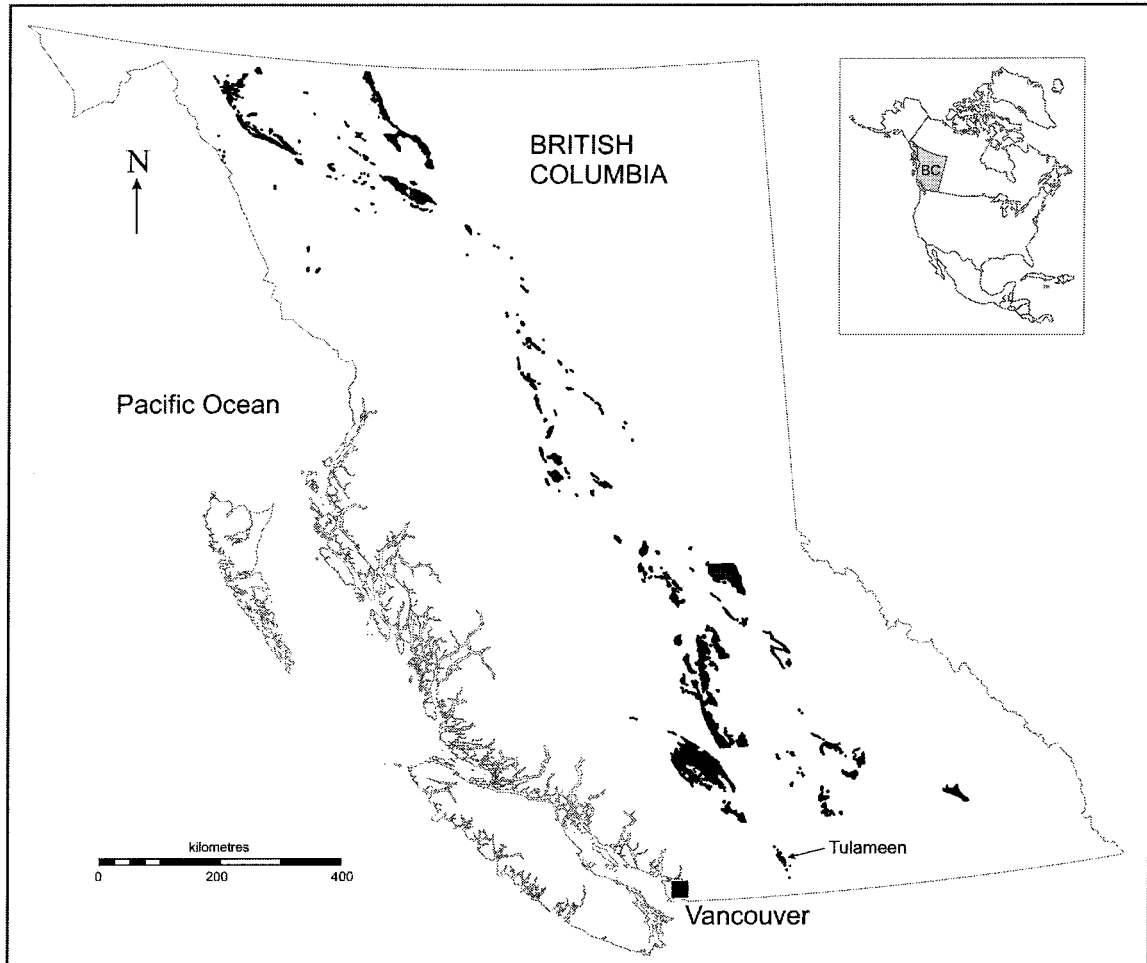
Olivine- and serpentine-rich rocks are called dunites and serpentinites, respectively. These rocks are part of ultramafic complexes and are found primarily along continental margins and suture zones (Coleman, 1997). The most common types of ultramafic complexes are Alpine, Alaskan and Layered Intrusive and their geographic distribution varies with tectonic setting (Voormeij and Simandl, 2004c). 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 (Voormeij and Simandl, 2004c). Ultramafic rocks are commonly believed to represent nearly inexhaustible sources of raw materials for mineral sequestration (Goff et al., 1997; Goff and Lackner, 1998), but detailed geological studies (Voormeij and Simandl, 2004c) indicate that this may not be the case. 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 (Goff et al., 1997; Goff and Lackner, 1998; Kohlmann and Zevenhoven, 2001). However, the link between conceptual modelling and laboratory studies 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 less soluble minerals, such as pyroxenes, amphiboles, talc and other minerals (O'Connor et al., 2000). 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.

### ***4.3 Identifying Ultramafic Complexes: Compiling the Map***

The first step in selecting favourable zones for hosting raw material for mineral sequestration of CO<sub>2</sub> 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 (Figure 4.1). This map was derived from the database developed for the mineral potential assessment of BC (Kilby, 1994) 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 (Voormeij and Simandl, 2004c).



**Figure 4.1** Distribution of ultramafic rocks in BC (Voormeij and Simandl, 2004c).

#### **4.4 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 CO<sub>2</sub>-equivalent per year) stationary point sources is

useful in selecting proximal dunite and serpentinite deposits (Voormeij and Simandl, 2004b). The deposits need to be of sufficient tonnage to supply the raw material (>30,000 t/day) for a period of 30 years (Goldberg et al., 2001). 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 mineral and geochemical data.

## ***4.5 Evaluation of Selected Dunite and Serpentinite Deposits***

Different reaction pathways for mineral carbonation have been proposed (Appendix I). In light of the slow conversion rate in the direct carbonation reaction and the corrosive nature of the hydrochloric acid extraction process (Guthrie et al., 2001), most of the recent effort has focused on dissolving Mg-silicates in an aqueous medium (O'Connor et al., 2000). Dissolution of the raw material, where  $\text{Mg}^{2+}$  ions become available for carbonation, is therefore an important rate-limiting step (O'Connor et al., 2000), however, Ca and  $\text{Fe}^{2+}$  cations may also significantly contribute to the carbonation reaction. Minerals such as pyroxenes and talc are relatively insoluble when compared to olivine and serpentine (Benner et al., 2001). 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.

### ***4.5.1 Mineralogy***

Dunites are, by definition, composed of more than 90% olivine (LeMaitre, 1989). 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 by definition, 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. Forsteritic olivine is preferred because it has a higher reaction efficiency than other Mg-silicates when

converting to magnesite. Similarly, fayalitic olivine converts to siderite, but its reaction efficiency is lower and the quantity of rock needed to carbonate a mass of CO<sub>2</sub> is higher (O'Connor et al., 2004). As an example, unaltered dunite from the Tulameen complex contains approximately 98% olivine (Fo 89 to 98) 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 serpentinized (up to 97% serpentine).

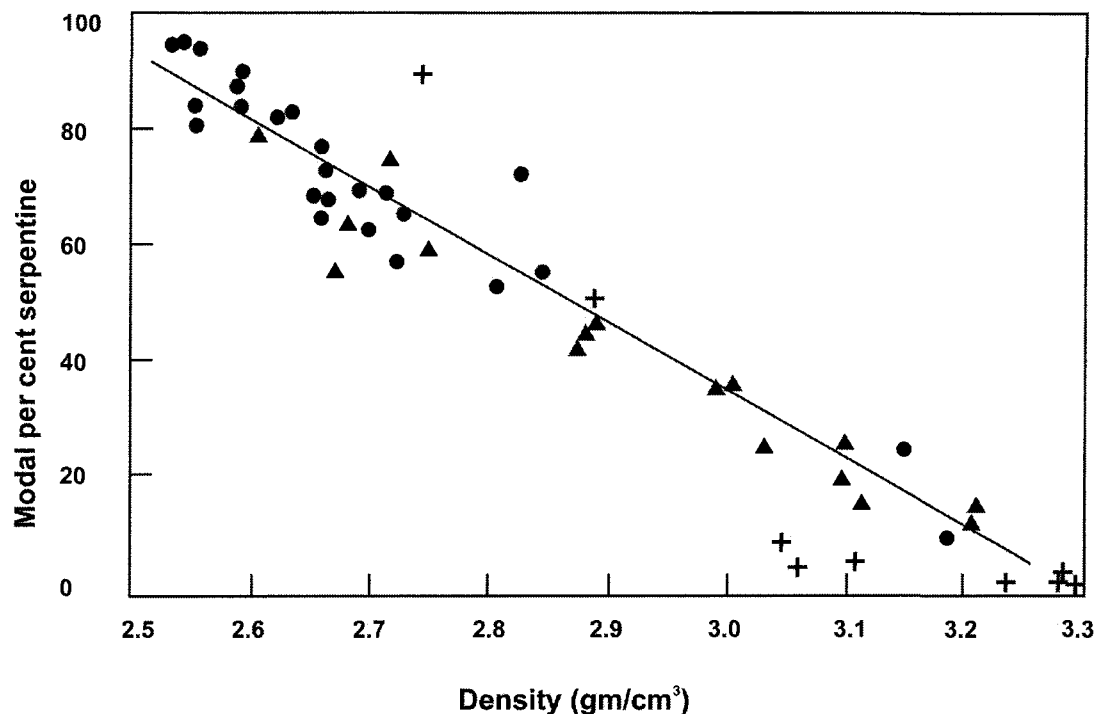
#### **4.5.2 Chemical Composition**

Whole rock chemical analyses are complementary 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 CO<sub>2</sub> content indicates presence of carbonates. CaO content may be indicative of pyroxene, amphibole and carbonate minerals. Thus, dunites with high MgO and low Fe<sub>2</sub>O<sub>3</sub>, 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%), Fe<sub>2</sub>O<sub>3</sub> (10-12%), LOI (<1-6%) and CaO (0.30-0.75%). Serpentinites range from MgO (38-43%), Fe<sub>2</sub>O<sub>3</sub> (9-11%), LOI (7-14%) and CaO (0.10-1.20%). Trace element analyses are informative because they may indicate accessory mineral phases that could interfere with reactions during mineral carbonation and may also indicate the presence of potentially marketable ores (Voormeij and Simandl, 2004c).

#### **4.5.3 Magnetic Susceptibility and Density Analysis**

Ultramafic rocks have typically higher magnetic susceptibility (MS) than surrounding rocks and their MS increases with degree of serpentinization (Lowe et al., 2003). The iron in the dunites occurs mainly as Fe<sup>2+</sup> in the olivine crystal structure, whereas in serpentinites, the iron is found mainly as magnetite and ferritchromite. MS could be used to characterize dunite targets for CO<sub>2</sub> sequestration. For example, dunites from the Nahlin ultramafic body, northwestern BC, have mean MS of approximately  $14 \times 10^{-3}$  SI (système internationale), whereas intensely serpentinized samples yield values in excess of  $200 \times 10^{-3}$  SI (Lowe et al., 2003). On the deposit scale, unaltered dunites from Tulameen have MS ranging from 7.45 to  $58.8 \times 10^{-3}$  SI, with a mean of  $36.4 \times 10^{-3}$  SI, whereas MS of their highly serpentinized equivalents ranges from 60.6 to  $123 \times 10^{-3}$

SI, with a mean value of  $88.3 \times 10^{-3}$  SI (see Appendix II). Although results from the Nahlin study present a poor linear relationship between LOI and MS (Lowe et al., 2003), 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 serpentinization. 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 serpentinized dunites and to delineate highly serpentinized areas (Findlay, 1963). Figure 4.2 shows the linear relationship between density and degree of serpentine alteration. Appendix III presents the raw data obtained for this study (plus symbols).



**Figure 4.2** Density vs. degree of serpentinization graph. Existing data are density measurements by Findlay (1963) on Tulameen dunites and serpentinites (circles) and Mt. Albert dunites and serpentinites (triangles). Density measurements from Tulameen dunites and serpentinized equivalents selected for this study (plus symbols) were performed on a stereo pycnometer. Percent serpentinization on selected samples for this study was done by means of microscopic investigations on polished thin sections.

#### 4.5.4 Laboratory and Bench-Scale Tests

Bench-scale carbonation tests and related experimental research are taking place at the Albany Research Centre (O'Connor et al., 2000), Arizona State University (McKelvy et al., 2002) and Los Alamos National Laboratory (Lackner et al., 1997). Carbonation tests provide validation on the characterization of raw materials based on petrology, mineralogy and chemistry. Lab



experiments can also present objective ranking of materials, permit to evaluate technical achievements made in optimization of the mineral carbonation on bench scale, supply reaction products for market testing and constrain the cost estimates for CO<sub>2</sub> sequestration.

#### **4.5.5 Potential By-Products**

Ultramafic rocks contain a variety of metallic and industrial mineral deposits (Coleman, 1977) and in some cases the host rock may be suitable for mineral CO<sub>2</sub> 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. In a number of cases, chromite has magnetite overgrowths (Voormeij and Simandl, 2004d), and can be removed by magnetic separation. Metals locked into olivine's crystal structure, such as Ni (up to 0.5%), could potentially 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 CO<sub>2</sub> in cement manufacture and fine grain silica products may be very reactive (Simandl, 2003). The magnesite market is well documented (Simandl and Ogden, 1999) 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 (Simandl et al., 2001). 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.

### **4.6 Summary**

Mineral CO<sub>2</sub> sequestration is a "niche" method in an early phase of development. Dunite, serpentinite and chrysotile tailings are the most promising ultramafic 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 CO<sub>2</sub> sources, type of material (dunite or serpentinite) and tonnage. Mineralogical investigation in combination with whole rock chemical analyses of selected material will provide insight into the presence of unwanted minerals that interfere with the carbonation reaction. Most suitable raw materials covered by this paper are those with high MgO and low FeO, CaO, LOI, CO<sub>2</sub> and

low H<sub>2</sub>O 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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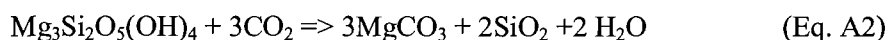
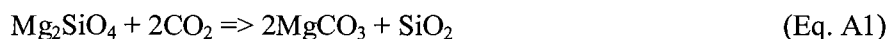
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## **Appendix I: Mineral Carbonation Pathways**

There are three major pathways that have been proposed as potential routes for industrial carbonation of ultramafic rocks. The reaction rates in the natural processes are exothermic and thermodynamically favoured, but extremely slow. Optimizing of the reaction rate and degree of completion is tested by increasing the surface area of the silicates (grinding and milling the raw material), increasing pressure and temperature to the reaction, heat pretreatment of serpentine and by addition of catalysts. Following is a brief summary of the three main methods proposed for the mineral CO<sub>2</sub> sequestration reaction.

### **Direct Solid-Gas Carbonation**

This method involves direct carbonation of Mg-silicate minerals in the solid state, using CO<sub>2</sub> typically under supercritical conditions. For example, exposing forsterite (Eq. A1) or serpentine (Eq. A2) to CO<sub>2</sub> produces magnesite and silica.



Lackner *et al.* (1997) carbonated serpentine samples of 100 µm radius with CO<sub>2</sub> to about 25% completion at pressures of 34 MPa (supercritical phase for CO<sub>2</sub>) and temperatures of 500°C within 2 hours. Reaction rates were found to be slow even when operated at higher temperatures. Kakizawa *et al.* (2001) examined the direct reaction of CO<sub>2</sub> with CaSiO<sub>3</sub>

(wollastonite) and also found that the rate of this reaction was too slow for practical use. Much faster kinetics can be obtained by first dissolving the minerals in solution.

### **Multi-Step Carbonation with Hydrochloric Acid Extraction**

The dissolution of peridotite and serpentinite in HCl was studied around the turn of the century and there had been considerable work done in this area during and right after WW II when the US experienced a magnesium shortage (Houston, 1945; Gee *et al.*, 1946). Considerable technological progress in this field has been achieved during the recent development of the billion-dollar Magnolia magnesia plant in Quebec (Ficara *et al.*, 2000). For the purpose of sequestering CO<sub>2</sub> emissions, Lackner *et al.* (1997) suggests a multi-step magnesium hydroxide process that uses HCl to dissolve magnesium silicates. They were able to obtain nearly complete carbonation in less than 30 minutes at 5 MPa (gas phase for CO<sub>2</sub>) and 550°C. This method involves three major steps:

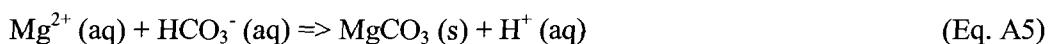
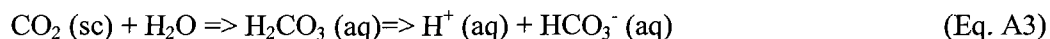
1. Magnesium is obtained as MgCl<sub>2</sub> in an acidic extraction step.
2. Hydrolysis of MgCl<sub>2</sub>. The HCl used in the extraction is recovered, subsequently leaving behind magnesium hydroxide, Mg(OH)<sub>2</sub>.
3. The hydroxide, in turn, is carbonated in a solid-gas reaction at 500-550°C, resulting in precipitation of MgCO<sub>3</sub> (magnesite).

Although serpentine dissolves readily in acid, the amount of water that needs to be evaporated in the HCl recovery is too large for this process to be economically viable (Haywood *et al.*, 2001). To get around this problem, Wendt *et al.* (1998) suggest dissolving serpentine in molten MgCl<sub>2</sub> salts. The CO<sub>2</sub> can be added to the solution to produce magnesite and the molten salts can be recycled. However, for this process to approach environmental acceptability, operational difficulties due to the corrosive nature of this process and the huge volumes of HCl required (Haywood *et al.*, 2001) need to be overcome.

### **Direct Aqueous Carbonation**

It is known that in rock weathering the rate is greatly improved by the presence of water. A natural analog would be exposure of a rock to rainwater plus atmospheric CO<sub>2</sub>. The Albany Research Centre in Oregon applies the direct aqueous carbonation route for mineral sequestration of CO<sub>2</sub> (O'Connor *et al.*, 2000). Supercritical CO<sub>2</sub> is mixed in a slurry of water

containing finely milled magnesium silicate particles. The CO<sub>2</sub> dissolves in the water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which in turn dissociates to H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> (Eq. A3). The H<sup>+</sup> ions hydrolyse the mineral grains, liberating Mg<sup>2+</sup> cations and forming silicic acid or free silica and water (Eq. A4). The free Mg<sup>2+</sup> cations react with the bicarbonate ions and precipitate as magnesite (Eq. A5). 24 Hour tests were conducted at 34 MPa and 400°C resulting in up to 89% conversion (O'Connor *et al.*, 2000).



Addition of heat to the carbonation reaction increases mineral dissolution rates, but it is energy-intensive and decreases the solubility of the CO<sub>2</sub> (Gerdemann *et al.*, 2002). Addition of salts to the solution, such as NaCl, Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> have been found beneficial in dissolving serpentine (O'Connor *et al.*, 2000).

## ***Appendix II: Magnetic Susceptibility of Tulameen Rocks***

Magnetic susceptibility is a measure of how magnetizable a substance can become in the presence of a magnetic field. Measurements of selected dunites and variably serpentinized dunites from the Tulameen ultramafic complex were performed on an Exploranium Kappameter KT-9 at the Pacific Geoscience Center (PGC) in Sidney, BC, under supervision of Dr. Carmel Lowe. Table 4A.1 presents the data.

<b>Trial #</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>Average</b>
<b>Tu-03-13G</b>	7.29	7.37	7.61	7.12	7.75	7.56	7.20	7.60	7.61	7.56	<b>7.47</b>
<b>Tu-03-13D</b>	12.60	15.40	15.30	16.40	14.70	14.70	15.60	15.40	15.50	15.20	<b>15.08</b>
<b>Tu-03-13E</b>	23.40	24.20	24.90	23.80	24.20	23.40	23.10	23.30	24.50	23.80	<b>23.86</b>
<b>Tu-03-13I</b>	32.60	33.80	35.80	33.20	33.30	33.20	33.20	33.70	32.90	35.20	<b>33.69</b>
<b>Tu-03-08</b>	39.80	44.00	44.10	41.40	34.80	40.20	35.40	37.70	37.70	38.30	<b>39.34</b>
<b>Tu-03-13C</b>	37.50	36.20	32.10	39.80	41.50	42.60	38.90	41.50	42.30	41.60	<b>39.40</b>
<b>Tu-03-09</b>	60.30	59.70	57.60	59.40	57.90	56.50	58.80	60.10	59.60	58.30	<b>58.82</b>
<b>Tu-03-10</b>	59.00	59.20	60.60	62.00	60.20	61.40	60.40	62.50	60.70	60.30	<b>60.63</b>
<b>Tu-03-13A</b>	94.80	90.60	96.10	87.20	120.00	95.30	111.00	103.00	114.00	84.70	<b>99.67</b>
<b>Tu-03-12A</b>	132.00	123.00	106.00	108.00	102.00	94.90	81.60	79.40	129.00	118.00	<b>107.39</b>
<b>Tu-03-13B</b>	114.00	108.00	113.00	110.00	115.00	113.00	153.00	138.00	133.00	140.00	<b>123.70</b>

*Table 4A.1 Magnetic susceptibility data for Tulameen dunites and serpentized equivalents. Sample numbers Tu-03-13G, 13D, 13E, 13I, 13C and 09 are fresh, relatively unaltered dunites. Sample Tu-03-08 is a dunite breccia and samples Tu-03-10, 13A, 12A and 13B are serpentized dunites.*

### **Appendix III: Density Measurements of Tulameen Dunites**

Density measurements of selected dunites and variably serpentized dunites from the Tulameen ultramafic complex were performed on a Quantachrome Corporation steropycnometer at the Albany Research Center (ARC) in Oregon. This instrument is specifically designed to measure the volume of solid objects by employing Archimedes principle of fluid displacement to determine the volume. The displaced fluid, in this case, is helium because its small atomic dimension assures penetration into crevices and pores approaching one Angstrom in dimension. In addition, its behaviour as an ideal gas is also desirable. Particle density is determined by placing a crushed rock sample in the pycnometer sample cell chamber and degassing it by purging it with helium gas. The analysis is performed by pressurizing the sample cell with helium to approximately 19 psi and recording the value. A valve is then rotated so that the helium expands into the adjoining chamber and the subsequent lower pressure is recorded. From these two readings, the sample's solid volume can be calculated by the following formula:

$$V_s = (V_c + V_a) / (1 - (P_2/P_3)) \quad (\text{Eq. A5})$$

Where  $V_s$  is the volume of solid sample;  $V_c$  is the volume of the cell holder;  $V_a$  is the added volume,  $P_2$  is the pressure reading after pressurizing the cell and  $P_3$  is the pressure reading after adding  $V_a$ . The solid particle density is then determined by the following formula:

$$\rho = Wt_s / V_s \quad (\text{Eq. A6})$$

Where  $\rho$  is the solid particle density,  $Wt_s$  is the weight of the sample in air and  $V_s$  is the volume of the sample derived from Equation 4A.1. A known standard was used to calibrate the instrument and results were accurate within 0.2%. Samples were run through the pycnometer four times and the density was calculated and averaged on the last three runs. Table 4A.1 presents the density data used for Figure 4.2.

Sample #	Sample wt (g)	Density (g/cm <sup>3</sup> ) run 1	Density (g/cm <sup>3</sup> ) run 2	Density (g/cm <sup>3</sup> ) run 3	Density (g/cm <sup>3</sup> ) run 4	Average Density (g/cm <sup>3</sup> )
Tu-03-08	112.3	2.884	2.882	2.885	2.884	2.88
Tu-03-10	155.6	3.105	3.107	3.108	3.106	3.11
Tu-03-13A	111.8	2.743	2.740	2.744	2.744	2.74
Tu-03-13B	122.6	3.043	3.043	3.046	3.047	3.05
Tu-03-13D	148.0	3.067	3.065	3.066	3.065	3.07
Tu-03-13E	163.7	3.264	3.271	3.270	3.269	3.27
Tu-03-13G	115.6	3.279	3.297	3.293	3.295	3.30
Tu-03-13I	127.8	3.275	3.284	3.285	3.282	3.28
Tu-03-23	126.2	3.210	3.228	3.232	3.247	3.24

**Table 4A.2** Density data for Tulameen dunites and variably serpentinized dunites.



## 5. Ultramafic Rocks in British Columbia: Delineating Targets for Mineral Sequestration of CO<sub>2</sub>

By: Danae A. Voormeij<sup>1</sup> and George J. Simandl<sup>2</sup>

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### 5.1 Summary

British Columbia has favourable geology and excellent exploration potential to host the raw materials suitable for CO<sub>2</sub> mineral carbonation, one of the methods considered for lowering greenhouse gas levels. British Columbia has been situated on the active, west-facing Pacific convergent margin of continental North America for at least the last 530 million years. Due to its tectonic history, British Columbia contains numerous Alpine-type and several Alaskan-type complexes, both of which are rich in Mg-silicates. Dunite zones within these complexes are currently considered as the most promising sources of raw materials for the mineral sequestration process, since they contain the most Mg by weight, the component necessary for binding with CO<sub>2</sub> to form stable carbonates. In addition, stockpiles containing short fibre chrysotile mined from serpentine-rich zones in ultramafic complexes may provide a source of starting material, thereby simultaneously disposing of CO<sub>2</sub> as well as potentially hazardous materials.

British Columbia's ultramafic rocks were studied previously as possible hosts of base metals, precious metals and gemstones. This study draws relevant information from that research and utilizes the database originally designed to evaluate mineral potential for the province. From this database a map depicting dunite- and serpentinite-bearing ultramafic rocks has been produced. Several targets have been selected, relying on preliminary data including mineralogy, geochemistry, potential size of the resource, accessibility and proximity to major CO<sub>2</sub> point sources. These include the dunite zone of the Alaskan-type Tulameen Complex near Princeton

and the Cassiar Chrysotile tailings in northern British Columbia. These targets are the subject of current detailed research (Voormeij and Simandl, 2004).

## 5.2 Introduction

A number of carbon dioxide (CO<sub>2</sub>) sequestration methods, including geological storage, ocean storage and mineral sequestration have been proposed worldwide, and methods conceivably applicable to British Columbia (BC) were listed and reviewed by Voormeij and Simandl (2003a). Mineral carbonation is considered to be the only method that truly disposes of CO<sub>2</sub> on a geologic time-scale and with minimum risk of leakage (Lackner *et al.*, 1997; O'Connor *et al.*, 2000). Although Ca-silicates (e.g. wollastonite) may also have potential for mineral carbonation (Wu *et al.*, 2001; Kakizawa *et al.*, 2001), Mg-silicates are more common in high concentrations and as large deposits (Goff and Lackner, 1998). Mg-silicates also contain more reactive material per tonne than Ca-silicates (Lackner *et al.*, 1997). The mineral carbonation concept is based on the natural weathering process of Mg-olivine (forsterite) and serpentine, which carbonate by the following reactions:



This process is thermodynamically favoured in near surface environments and its products are stable on a geological time scale. The concept was first proposed by Seifritz (1990) and considered in more details by Lackner *et al.* (1997), O'Connor *et al.* (1999; 2000) and Kohlmann and Zevenhoeven (2001; 2002).

The mineral carbonation process, as considered in this paper, is envisioned in an industrial setting (*ex situ*). Geographical location, proximity to infrastructure, the size of dunite and serpentinite resources and their physical and chemical properties are some of the important factors determining the potential viability of mineral sequestration in BC. Ideal sites should be located close to both the Mg-silicate deposit and a major CO<sub>2</sub> emission point source to minimize transportation costs of the CO<sub>2</sub> and raw materials. Geographic distribution of major

stationary CO<sub>2</sub> point sources in BC has been completed (Voormeij and Simandl, 2003b). In order to match sinks to these point sources, areas with the potential to host raw material for mineral CO<sub>2</sub> sequestration need to be identified. Dunite zones of ultramafic complexes are preferred over the serpentinite zones, since they contain the most magnesium by weight. Serpentinite zones are more common and for this reason are also considered as candidates. Detailed methodology proposed for systematic evaluation of the ultramafic materials for use in mineral carbonation is outside of the scope of this study and is covered by Voormeij and Simandl (Chapter 4).

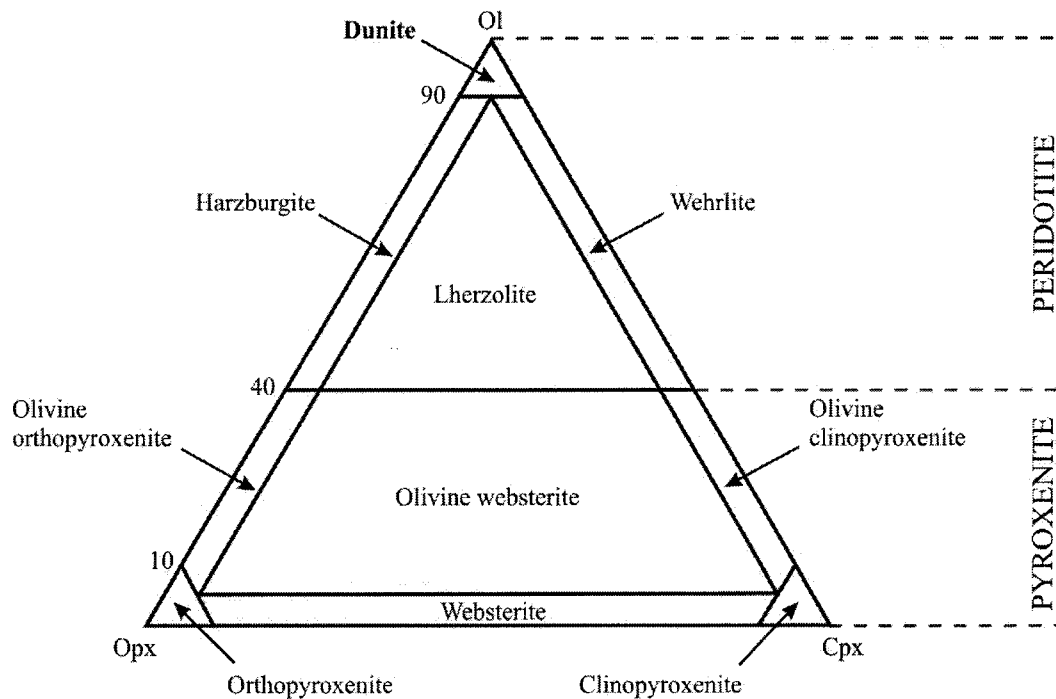
### **5.3 Ultramafic Rocks: Petrology and Mineralogy**

Serpentine and forsteritic olivine are common silicates with high magnesium contents. There are three principal forms of serpentine: lizardite, antigorite and chrysotile (Deer, Howie and Zussman, 1978), all with the approximate composition  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . The most abundant is lizardite, whereas the fibrous chrysotile is relatively rare. The latter is perhaps best known since it had many industrial applications including fireproofing insulation, specialty paints, brake pads, gaskets, etc. (Virta and Mann, 1994). It has also been used extensively in construction materials such as cements and tiles. However, the use of chrysotile was curtailed due to health regulations associated with its use (Hamel, 1998) and banned in several European countries.

Olivine exists as a solid solution series between the  $\text{Mg}_2\text{SiO}_4$  (forsterite) and  $\text{Fe}_2\text{SiO}_4$  (fayalite) end members. The monomineralic rock of olivine is called dunite (Figure 5.1). Forsteritic olivine is currently the favoured mineral for the carbonation process because it does not require the energy-intensive pre-treatment (high heat and high-energy attrition grinding) that serpentine needs (Lackner *et al.*, 1997; O'Connor *et al.*, 2000). However, research into optimization of energy used in the pre-treatment of serpentine is still ongoing (McKelvy *et al.*, 2002; O'Connor *et al.*, 2000). Furthermore, serpentine-rich rocks are more widespread than those rich in olivine. Thus both have to be considered. Some selected chrysotile-bearing stockpiles sites are also investigated because in addition to sequestering CO<sub>2</sub>, the mineral carbonation method may also aid in the disposal of unwanted asbestos waste (Huot *et al.*, 2003).

## 5.4 Ultramafic Complexes

Ultramafic complexes can be divided into three major categories: Alpine, Alaskan and Layered intrusive types. Their geographic distribution is restricted by tectonic setting, which also indirectly influences the physical and chemical characteristics of dunite and serpentinite rocks within these complexes. These characteristics include relative position of the dunite and serpentinite bodies, structural control, variation in mineralogy, and mineral composition. Table 5.1 lists well-documented examples of these categories and describes their geological setting.



**Figure 5.1** IUGS classification scheme for ultramafic rocks (after Le Maitre, 1989). Ol-olivine; Opx-orthopyroxene; Cpx-clinopyroxene. The general term "peridotite" is used when the olivine content is 40-100%, whereas "pyroxenite" refers to an olivine content of 0-40%. For example, "dunite" is a peridotite containing 90-100% olivine.

### 5.4.1 Alpine-Type Complexes

Alpine-type ultramafics are the most voluminous and widespread of all ultramafic bodies (Coleman, 1977) and are interpreted as forming the basal part of an ophiolitic suite (Dewey, 1976 and Moores, 1982; 2002). A complete ophiolite sequence, tectonically emplaced over

crystalline basement (Figure 5.2), consists of (from bottom to top): tectonic mélange, metamorphic sole, deformed mantle tectonite, cumulate peridotite (alternately layered olivine and pyroxene), cumulate gabbros grading upwards into massive gabbros and plagiogranites, overlain and partially intruded by sheeted dike swarms, followed by pillow basalts, capped by deep-sea and/or pelagic or, in some cases, volcanoclastic turbidites, all overlain by shallow water sediments. This sequence is thought to represent an analogue for oceanic crust formed at fast spreading centres as exemplified by the Juan de Fuca Ridge situated off the coast of BC.

Geological Setting	Complex Type	Description	Distribution of dunite and/or serpentinite zones	Examples
Syn-orogenic ultramafic bodies	<i>Alpine-Type</i>	Tectonically emplaced ultramafic complex that makes up the basal section of an ophiolite (ocean-crust) sequence	Mantle tectonite section contains pods of dunite. Cumulate section contains layers of dunite. Dunite variably serpentinized. Tectonic melange is typically rich in serpentinite.	Nahlin UMF Complex (BC); Cache Creek UMF complex (BC); Shulaps UMF Complex (BC)
	<i>Alaskan-Type</i>	Podiform intrusions of mafic to ultramafic magmas into accreted island arcs.	Concentrically zoned. Successive zones of wehrlite, clinopyroxenite and orthopyroxenite around a dunite core. Dunite variably serpentinized, increasing outwards from core.	Duke Island (Alaska); Polaris (BC); Tulameen (BC); Turnagain (BC)
Intracratonic	<i>Layered Intrusion-Type</i>	Large, often funnel-shaped sill-like intrusions. Layering formed partly as a result of fractional crystallization of the primary melt	Laterally extensive, alternating layers of dunite/peridotite and pyroxenite.	Muskox (NWT), Bushveld (RSA), Great Dyke (Zimbabwe), Stillwater (MT), Windemurra (AUS)

**Table 5.1** Characteristics of the three main types of ultramafic complexes containing significant deposits of dunite and/or serpentinite.

Dunitic rocks of ophiolitic sequences are divided into two broad categories based upon their texture and petrography, tectonite and cumulate. Dunites within the tectonite section generally occur as lenses within harzburgite or lherzolite, ranging from 1 metre to hundreds of meters in size. In most cases the tectonite is gradational into the cumulate sequence, where forsteritic olivine is the dominant cumulate phase (Coleman, 1977; Moores, 2002). Podiform chromitite is commonly associated with the tectonite zone; stratiform or thin chromitite accumulations are

typical of the cumulate zone (Coleman, 1977). During the serpentinization of the alpine peridotites, fibrous chrysotile veins and stockworks may be formed. Where chrysotile-filled fractures constituted 3-10 % of the rock and formed long fibres of high quality, it was economically mined (Hora, 1999).

#### **5.4.2 Alaskan-Type Complexes**

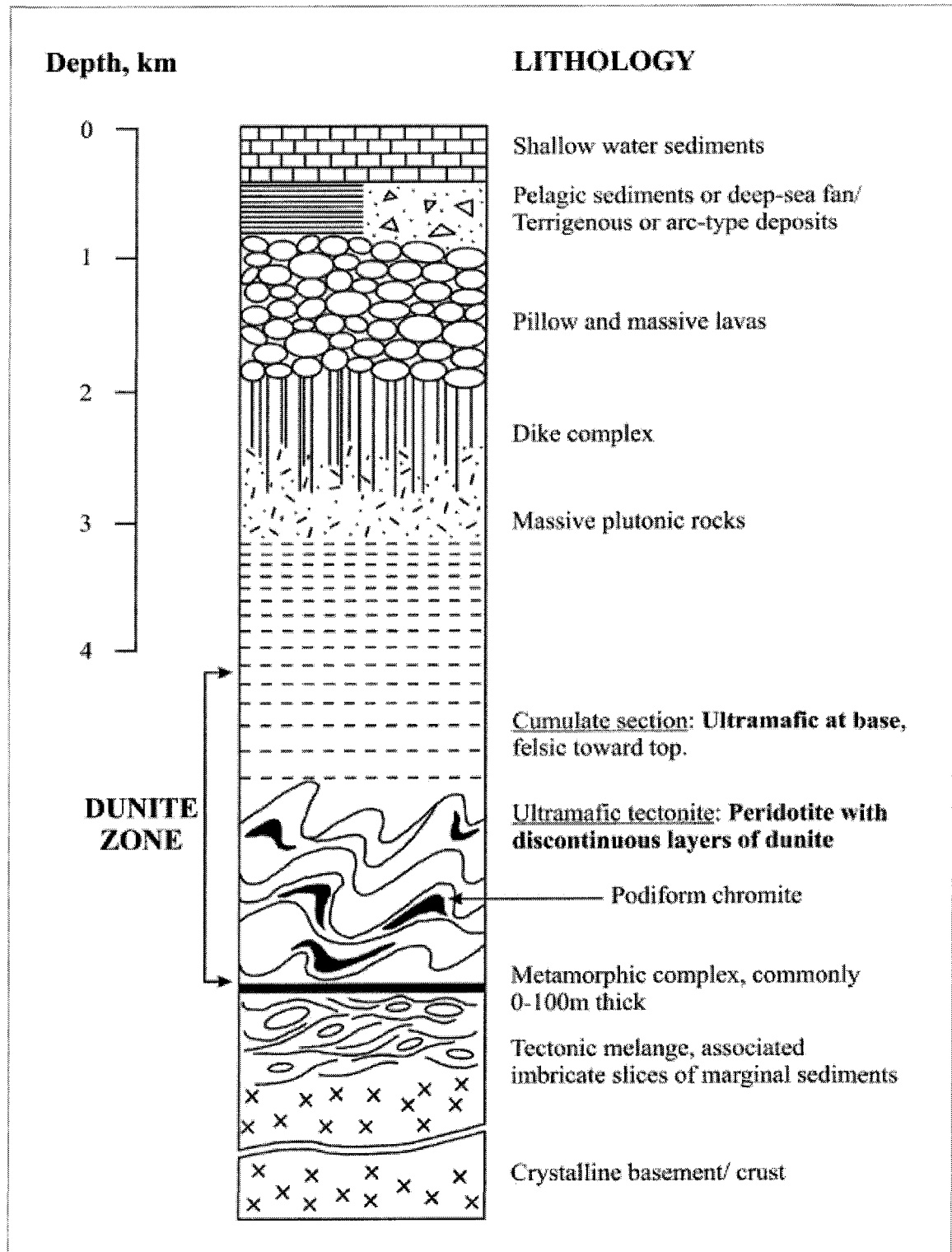
Alaskan-type complexes (also called Alaskan-Ural, Uralian and concentric or zoned complexes) are mafic and ultramafic intrusions. Their type locations are in a narrow, northerly trending belt, 600 kilometres long, in southeastern Alaska (Irvine, 1967). Similar ultramafic bodies are found in belts along the central Ural Mountains of Russia (Irvine, 1987) and through the interior of BC (Findlay, 1963, Irvine, 1976, Clark, 1980 and Nixon, 1990).

Idealized Alaskan-type complexes are characterized by the crude zonation of successive wehrlite, clinopyroxenite and hornblende-rich lithologies around a dunite core (Irvine, 1987). In many of the well-documented examples any one of these zones may be missing or discontinuous (Nixon, 1990). Massive dunite cores, consisting primarily of forsteritic olivine (Irvine, 1987), may be exposed over large areas and in many cases dunite is well preserved.

#### **5.4.3 Layered Intrusive Complexes**

Layered mafic-ultramafic intrusions are either sill-like (e.g. Stillwater) or funnel shaped (e.g. Skaergaard and Great Dyke). They are typically intruded into rifted cratons and may be associated with tholeiitic flood basalt provinces. A good example of this is the Muskox intrusion, which is intimately associated with Coppermine River basalts (Baragar, 1969, Kerans, 1983).

As magma crystallizes and differentiates, cyclically layered sequences form. An ideal cycle consists of basal dunite followed upward by a harzburgite and an uppermost orthopyroxene layer (Naslund and McBirney, 1996). These cyclic units vary in thickness. For example, in the Bushveld complex they are present on a millimetre scale (Eales and Cawthorn, 1996), at Great Dyke on centimetre scale (Naslund and McBirney, 1996) and at Muskox intrusion on metre scale (Irvine and Smith, 1967). Olivine composition in a typical layered ultramafic intrusion trends from forsterite-rich olivine towards fayalitic olivine upwards in succession (Table 5.2).



**Figure 5.2** Cross-section of a "complete" ophiolite complex. Few ophiolite complexes contain all of these units; most contain only part(s) of the entire complex (source: Moores, 2002).

Name, locality	Olivine composition in lower zone	Olivine composition in upper zone	References
Bjerkreim-Sokndal, Norway	Fo77-74	Fo50-19	Wilson <i>et al.</i> (1996)
Bushveld, RSA	Fo85-88	Fo63-35	Eales and Cawthorn (1996)
Great Dyke, Zimbabwe	Fo92	Fo91-87	Wilson (1996)
Skaergaard, Greenland	Fo74-68	Fo10-5	McBirney (1996)
Windimurra, Australia	Fo90-50	Fo35	Mathison and Ahmat (1996)

**Table 5.2** Olivine composition changes from Mg-rich (*forsterite*) to Fe-rich (*fayalite*) from lower to upper zones within layered intrusive complexes.

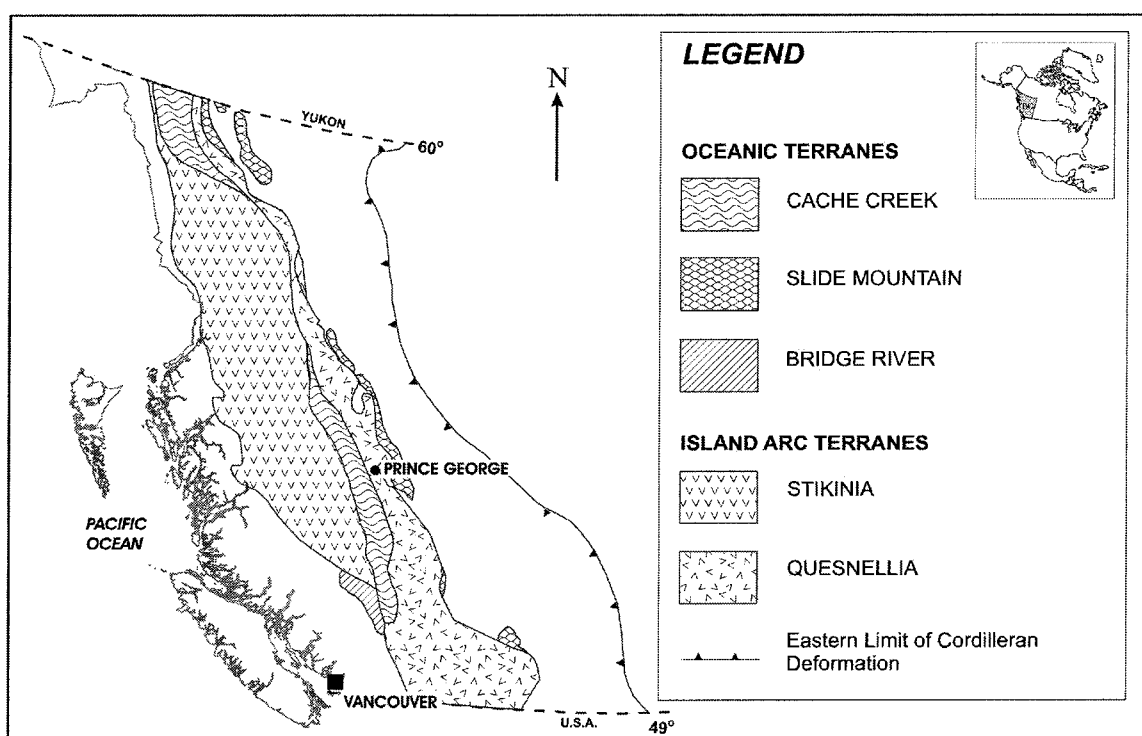
The layering is commonly laterally continuous for hundreds of square kilometres (Eales and Cawthorn, 1996) and the ultramafic sequence can be up to several kilometres in thickness. For example, the Windimurra Complex has a 0.5 kilometre thick ultramafic section (Mathison and Ahmat, 1996), the Muskox Intrusion has ultramafic layers that total 1.5 kilometres in thickness (Irvine and Smith, 1967) and the Great Dyke has an ultramafic sequence several kilometres in thickness (Wilson, 1996).

## 5.5 Tectonic Setting of British Columbia

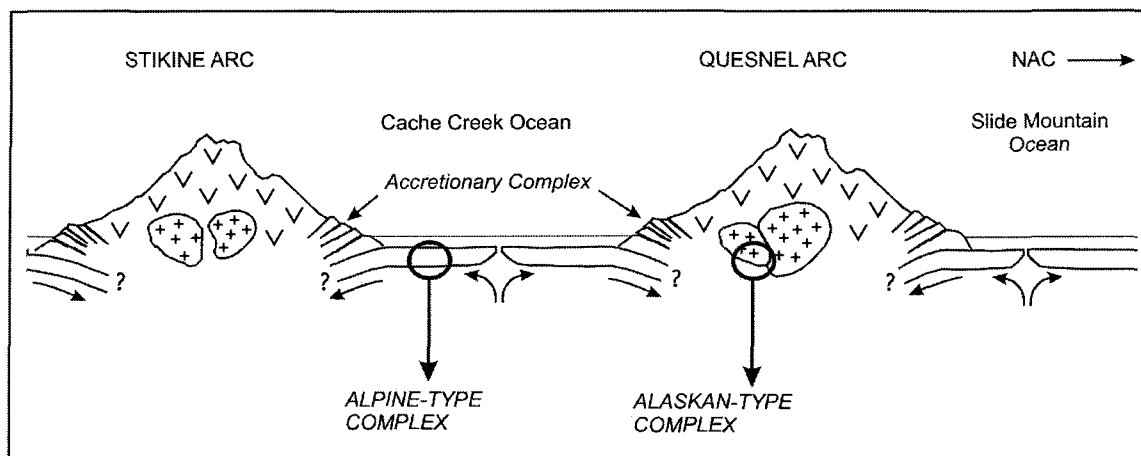
Since the breakup of the Rodinia supercontinent, British Columbia has been located on a continent-ocean boundary for at least 530 million years (Monger, 1997). As a result of subduction-related activity, which started approximately 390 million years ago, the Canadian Cordillera is commonly described as an orogenic collage made up of intra-oceanic arc and subduction complexes accreted to the craton margin, and of arcs emplaced in and on the accreted bodies. The Canadian Cordillera has been subdivided into 'terrane' (Figure 5.3), each consisting of characteristic assemblages (Monger and Berg, 1984).



Assemblages within the *Slide Mountain*, *Cache Creek* and *Bridge River* terranes (Figure 5.3) are of oceanic affinity, representing the deformed sequences of ocean basins that closed in the Mesozoic during the accretion of offshore island arcs to the North American Craton. The *Slide Mountain* terrane is composed of ultramafic rocks, gabbro, pillow basalt and chert, which formed in a back-arc ocean basin (Figure 5.4). The ultramafic rocks in the *Cache Creek* and *Bridge River* terranes are associated with a *mélange* of marine sediments with blocks, lenses and slivers of ophiolitic origin, often in a serpentine matrix, representing an accretionary/subduction complex (Figure 5.4). These oceanic affiliated terranes contain numerous Alpine-type complexes (Evenchick *et al.*, 1986). The *Stikinia* and *Quesnellia* terranes are composed of arc-related volcanic and sedimentary rocks and coeval intrusions (Evenchick *et al.*, 1986). BC's Alaskan-type complexes are found in these terranes (Figure 5.4) and represent the high-level magma chambers of Late Triassic to Middle Jurassic arc volcanoes (Nixon, 1990). There are no large layered intrusive ultramafic complexes known in British Columbia, as they are believed to be restricted to an intra-cratonic tectonic setting.



**Figure 5.3** Distribution of major ultramafic-bearing terranes in British Columbia (based on Gabrielse *et al.*, 1991). The Alpine-type ultramafic complexes are confined primarily to the Cache Creek, Slide Mountain and Bridge River oceanic-affiliated terranes, whereas the Alaskan-type ultramafic bodies are associated with the Stikinia and Quesnellia island-arc terranes.



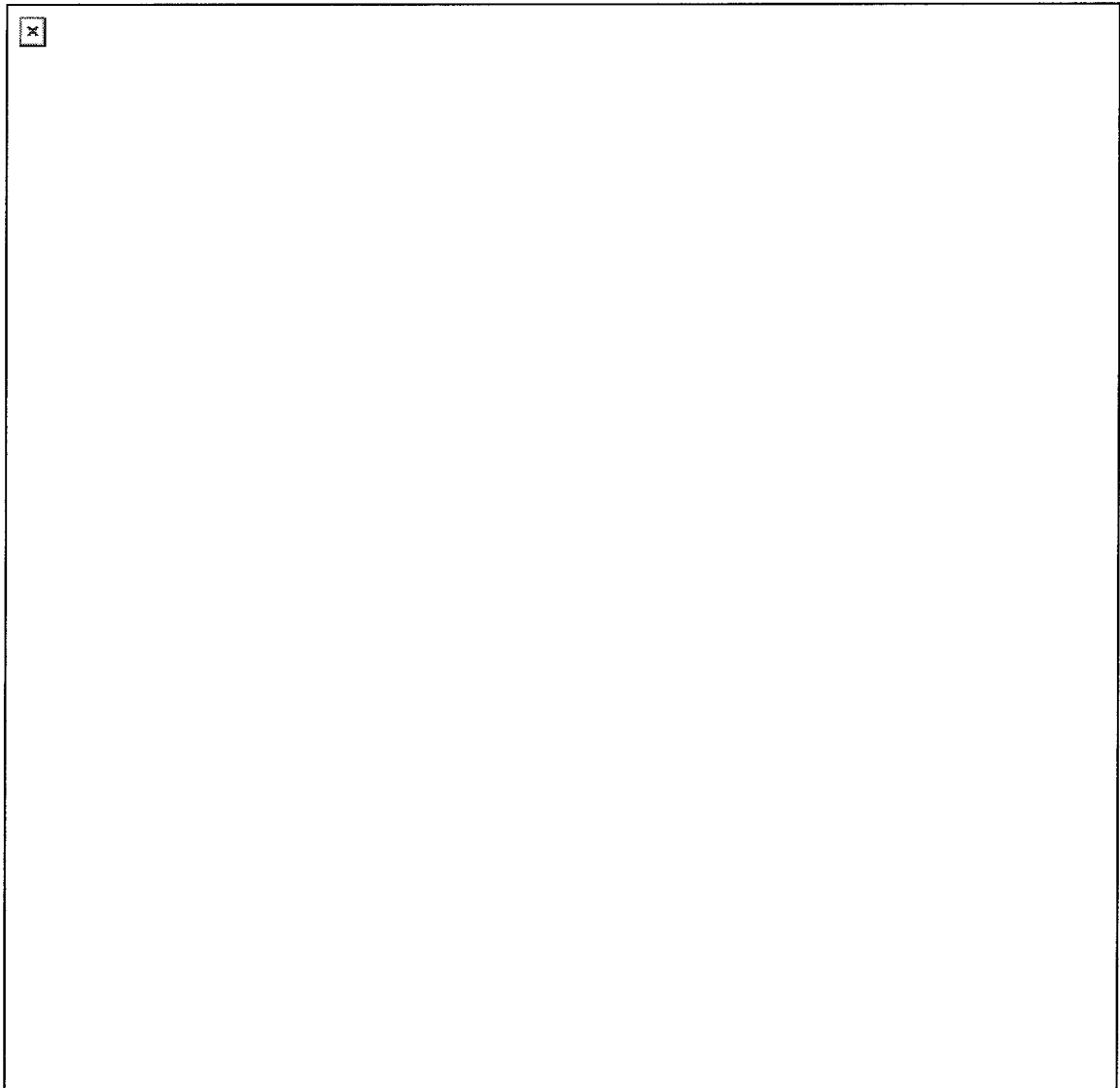
**Figure 5.4** Simplified diagram depicting the different tectonic settings for the oceanic affiliated, subduction-related and island arc terranes in British Columbia and the origin of their ultramafic complexes (based on Monger and Journeay, 1994). NAC= North American Continent.

## 5.6 Ultramafic Rocks in British Columbia

The geographic distribution of ultramafic rocks in British Columbia, with emphasis on those Alpine and Alaskan-type complexes, which contain known dunite and/or serpentinite zones, are depicted in Figure 5.5. This map was derived from the database developed for the mineral potential assessment of British Columbia (Kilby, 1994) and was originally introduced in a Geofile (Voormeij and Simandl, 2004). The compiled geology used in Figure 5.5 has been captured in digital form at a scale of 1:250,000, by means of GSB Open File series releases (Massey, 1994); (Schiarizza *et al.*, 1994); (Höy *et al.*, 1994); (MacIntyre *et al.*, 1994); (Bellefontaine and Alldrick, 1994); (MacIntyre *et al.*, 1995); (Bellefontaine *et al.*, 1995); (Mihalynuk *et al.*, 1996) and (Schiarizza and Church., 1996). From this electronic database, units containing the words "dunite" and "serpent-" were extracted, thereby assembling a digital file of zones that contain the words "dunite", "serpentinite", "serpentinized", or "serpentine" in their original description. Figure 5.5 shows the resulting zones.

Extraction of areas that contain the terms "dunite" and "serpent-" from the database does not discriminate between minor and major amounts of dunite and/or serpentinite present. Thus, most of the zones are overestimates of actual area underlain by dunites and/or serpentinites. For example, Figure 5.5 shows a zone in southeastern BC, ~120 km north of Nelson. This area appears approximately 100 km long by 50 km wide on the map. However, a more detailed map

(Figure 5.5, Inset 1) shows the presence of serpentine-magnesite-talc related rocks only a few km across (source: Read and Wheeler, 1977). Although the approach used to construct Figure 5.5 results in overestimating the areas underlain by ultramafic rocks, it is a preferred preliminary approach because large portions of BC have not been mapped in detail and may contain more ultramafic rocks than expected.

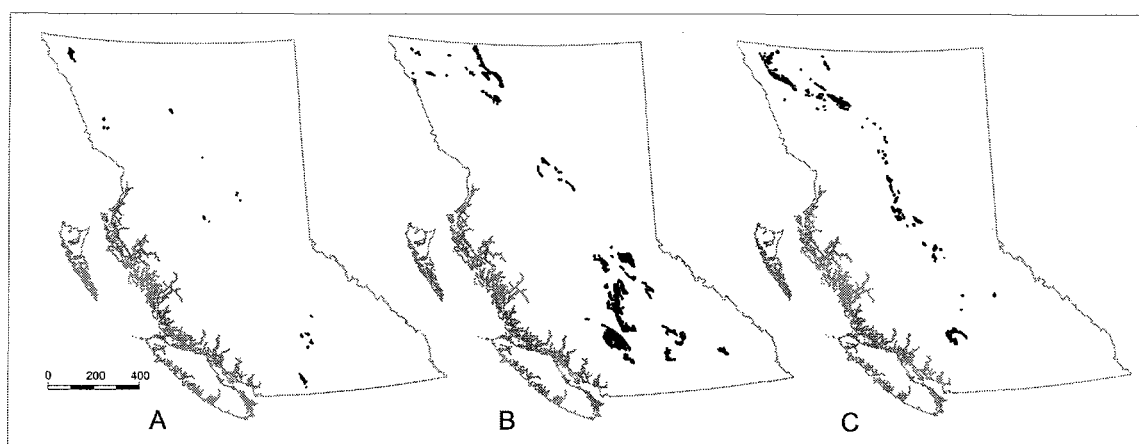


**Figure 5.5** Distribution of dunite and serpentinite-bearing rocks in British Columbia. Alpine-type ultramafic complexes include: 1. Cogburn Emory Zone, 2. Coquihalla Serpentine Belt, 3. Bralorne-East Liza, 4. Bridge River Complex, 5. Shulaps, 6. Chapperon Group, 7. Mount Ida Assemblage, 8. Southern Cache Creek Complex, 9. Crooked Amphibolite, 10. Antler Formation, 11. Central Cache Creek Complex, 12. Manson Lake Complex, 13. Blue Dome Fault Zone, 14. Sylvester Allochthon, 15. Cassiar and McDame, 16. Zus Mountain, 17. Northern Cache Creek Complex (includes Atlin and Nahlin complexes). Alaskan-type ultramafic complexes include: 18. Tulameen, 19. Polaris, 20. Wrede, 21. Hickman, 22. Lunar Creek, 23. Turnagain.

Several potential dunite and serpentinite tracts shown on this map are abruptly terminated along straight lines that correspond to map boundaries. This happens where a geological unit extends across two or more 1:250 000 map sheets. This unit may have the same name on several of the mapsheets, but ultramafic rocks are not present in all of them.

Our approach also delineated areas that contain ultramafic xenoliths. For example, numerous zones within central BC correlate to spinel peridotite xenoliths described by Canil *et al.* (1987), many of which are hosted in the alkali basalts typical of the Chilcotin Group plateau-lavas (Dostal *et al.*, 1996). The olivine-rich xenoliths are not significant as a potential source of raw material for the *ex situ* mineral carbonation process. However, recent studies have shown the mineral trapping potential of injected CO<sub>2</sub> into deep saline aquifers located within thick sequences of flood basalt provinces (O'Connor *et al.*, 2003). For this reason, the distribution of British Columbia's flood basalts that contain olivine xenocrysts and dunite xenoliths is included in Figure 5.5.

Ultramafic rocks containing dunite zones but not serpentinite (Figure 5.6a) are not common. These zones are mostly restricted to Alaskan-type complexes. In contrast, ultramafic rocks containing serpentine but not dunite, are relatively abundant (Figure 5.6b). As expected from the distribution of ultramafic rocks in Alpine-type complexes, dunite and serpentinite are commonly associated together (Figure 5.6c).



**Figure 5.6** Separating out the dunite and serpentinite zones associated with ultramafic rocks: A. Areas where ultramafic rocks are reported to contain dunite only. B. Serpentinite only. C. Dunite and serpentinite are reported together.

### 5.6.1 Alpine-Type Complexes in BC

Most of BC's Alpine-type complexes are located within the *Cache Creek*, *Slide Mountain* and *Bridge River* terranes. The *Cache Creek* terrane forms a long narrow tract that extends within the Intermontane belt from southern BC to central Yukon Territory (Figure 5.3). The larger complexes of the *Cache Creek* terrane include the Southern Cache Creek Ultramafic Assemblage in southwestern BC and the Nahlin Ultramafic Complex near Atlin, northwestern BC (Figure 5.5). The *Slide Mountain* terrane forms a narrow, discontinuous belt extending 2000 km from southeastern BC to northwestern Yukon Territory (Figure 5.3). Alpine-type ultramafics are located in the Antler Formation in central BC, the Redfern and Crooked Amphibolite in east-central BC and the Sylvester Allochthon in north-central BC (Figure 5.5). The Cassiar and McDame asbestos deposits are located in Sylvester serpentinites (Figure 5.5). Zus Mountain, located in the Sylvester Allochthon, is known to contain intact oceanic upper mantle and ultramafic cumulate material (Nelson and Bradford, 1993). *Bridge River* is a small terrane, situated near latitude 52°N, just west of the *Cache Creek* terrane. The Bridge River Complex, with the associated Shulaps and Bralorne-East Liza complexes (Figure 5.5), the Coquihalla Serpentine Belt and the Cogburn body are probably the southern extent of the Cache Creek terrane (Schiarizza *et al.*, 1997).

### 5.6.2 Alaskan-Type Complexes in BC

In British Columbia, Alaskan-type complexes are found in the *Stikinia* and *Quesnellia* terranes. However, only those with a recognized dunite zone are discussed and their geographical distribution is given in Figure 5.5. Table 5.3 gives the major Alaskan-type complexes for BC that contain known dunite cores. *Stikinia* is the largest terrane in the Canadian Cordillera. It extends more than 1700 km from eastern Alaska to south-central BC (Figure 5.3). The Hickman complex is an Alaskan-type ultramafic within *Stikinia*. The Lunar Creek Complex is located on the boundary between *Quesnellia* and *Stikinia* terranes (Figure 5.5). *Quesnellia* forms an orogen-parallel belt that extends from south-central BC into the Yukon Territories (Figure 5.3). Complexes of the Alaskan type that are located in this terrane include the Tulameen (Figure 5.2), Polaris, Wrede and Turnagain complexes. Tulameen is the largest Alaskan-type body in BC (Table 5.3).

Complex Name	Terrane	Aerial Extent of Complex	Surface Area of Dunite zone	References
Hickman	ST	~11 km <sup>2</sup>	< 1 km <sup>2</sup>	Nixon <i>et al.</i> (1997)
Lunar Creek	QN	~45 km <sup>2</sup>	~ 1.5 km <sup>2</sup>	Nixon <i>et al.</i> (1997)
Polaris	QN	~50 km <sup>2</sup>	~8-9 km <sup>2</sup>	Nixon <i>et al.</i> (1997)
Tulameen	QN	~ 60 km <sup>2</sup>	~ 6 km <sup>2</sup>	Findlay (1963); Nixon <i>et al.</i> (1997)
Turnagain	QN	~25 km <sup>2</sup>	~ 5 km <sup>2</sup>	Clark (1980); Gabrielse
Wrede	QN	~10 km <sup>2</sup>	~ 5km <sup>2</sup>	Hammack <i>et al.</i> (1990)

**Table 5.3** Surface areas of dunite zones in Alaskan-type complexes. Arc-related tectonostratigraphic terranes within which these complexes are located: QN= Quesnellia; ST= Stikinia.

### 5.6.3 Economic Potential of Ultramafic Rocks in BC

Up to now, BC's ultramafic complexes were primarily of interest to economic geologists in terms of associated metals, traditional industrial mineral deposits and gemstones. These complexes are known to host Cyprus-type massive sulphide (Höy, 1995), Au-quartz veins (Ash and Alldrick, 1996), silica-carbonate mercury deposits (Ash, 1996a), podiform chromite (Ash, 1996b), stratiform chromite (Nixon *et al.*, 1997), talc and magnesite (Simandl and Ogden, 1999), chrysotile asbestos (Hora, 1999), nephrite jade (Simandl *et al.*, 2000), vermiculite (Simandl *et al.*, 1999a), emeralds (Simandl *et al.*, 1999b) and corundum group gemstones (Simandl and Paradis, 1999). Also, they are known to host platinum group elements (Ruble, 1986; Evenchick *et al.*, 1986; Nixon, 1990; Nixon, 1996; Nixon *et al.*, 1997), Ti and Fe oxide deposits (Gross *et al.*, 1999) and nickel (Hancock, 1990). Olivine may be used as a foundry and blasting sand (White, 1987) as well as a raw material in the manufacture of refractories (Henning, 1994). In the past, most of the complexes were assessed with these commodities in mind, however, should mineral sequestration of CO<sub>2</sub> emissions become a reality, then these complexes will also become essential as sources of high magnesia silicates. The synergy between the development of some of the traditional metal, industrial mineral and gemstone commodities and magnesium silicates for CO<sub>2</sub> sequestration may be possible.

## 5.7 Targets for Mineral Sequestration of CO<sub>2</sub>

Figure 5.5 also marks the following specific areas considered for detailed study as part of the M.Sc. Thesis of the senior author: The Tulameen site was chosen because it contains a well-exposed, large (6 km<sup>2</sup>), relatively unserpentinized dunite body, and is located within the vicinity of several major point sources of CO<sub>2</sub> (Voormeij and Simandl, 2003b). Cassiar Asbestos tailings, currently owned by Cassiar Resources Inc., are investigated because the waste piles have potential as raw material for the mineral carbonation process, since the serpentine has already been milled and therefore may lower the sequestration costs. The site contains 5,457,000 tonnes of broken rock, 17,021,000 tonnes of tailings and 48 millions of tonnes of *in situ* serpentine-rich rock (Budinski, 2000). The fibrous nature of this variety of serpentine, which is considered a health concern (Hamel, 1998), may be effectively destroyed during the mineral carbonation process.

## 5.8 Conclusions

Should the mineral carbonation process be considered as a form of sequestering CO<sub>2</sub> emissions in British Columbia, an overview of locations of raw material within the vicinity of major CO<sub>2</sub> point sources is an important parameter in conceptual modeling. The distribution of ultramafic rocks in BC, with emphasis on those complexes containing dunite and/or serpentinite zones is depicted in Figure 5.5. Based on this map, less than 3% of BC's surface is underlain by ultramafic rocks containing dunite and/or serpentinite. Of this 3%, less than 0.5% corresponds to areas where dunite is reported without serpentinite, approximately 2% is related to areas where serpentinite occurs without dunite and ~1% of BC is underlain by ultramafic rocks where dunite and serpentinite are reported together. Because of the methodology used to construct the map, surface areas corresponding to ultramafic rocks are overestimates.

Due to the subduction-related tectonic setting, Alpine-type and Alaskan-type ultramafic complexes are more common along the western margin of North America than, for example, in areas located on the stable craton or passive margin. With this in mind, claims made by Goff et al. (1997) and Goff and Lackner (1998), in which they state that "abundant resources of Mg-rich peridotite [dunite] and serpentinite exist within the United states and many other countries" should be questioned and follow-up is needed.

Ultramafic complexes may host a wide variety of economic minerals. Thus, the geographic distribution of dunites and serpentinites can be used as a metallotect in exploration for a variety of metallic, industrial mineral and gemstone deposits. In a number of specific cases, serpentine- and olivine-bearing rocks contain chromite, Ni, Co and platinum group elements. If these commodities can be recovered at profit as a by-product of mineral sequestration, then costs of the CO<sub>2</sub> disposal may be substantially reduced.

## 5.9 Acknowledgements

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## 6. Mineral CO<sub>2</sub> Sequestration of the Tulameen Dunite

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### 6.1 Abstract

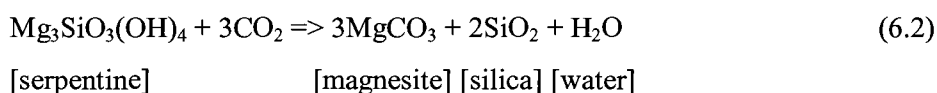
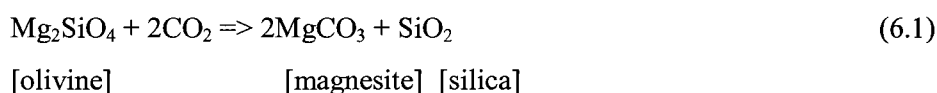
The Tulameen ultramafic complex in south-central British Columbia was selected for the first *ex situ* CO<sub>2</sub> sequestration study in Canada. Representative dunites, dunitic breccia and serpentinized dunites were collected and examined by means of microscopic investigation, geochemical analysis (including major oxides, LOI and trace elements) and electron microprobe analysis. Theoretical carbonation potential of the rocks,  $R_{CO_2}$ , was calculated and compared with that of rocks in US studies. Rock samples were tested for their mineral carbonation potential at the U.S. Department of Energy's Albany Research Center. Autoclave conditions were 150 atm (15 MPa) partial pressure of CO<sub>2</sub> ( $P_{CO_2}$ ) and 185°C, and samples were carbonated in 15% solids slurry with 0.64M NaCO<sub>3</sub>, 1.0M NaCl carbonation solution for one hour. CO<sub>2</sub> analyses in reaction products (up to 29.4 wt%) suggest 48-56% conversion of magnesium silicates to magnesite and silica for the dunites, and 18% conversion for a serpentinized dunite. As expected, feed with highest MgO and lowest LOI content, indicative of a low level of impurities and minimum degree of serpentinization, shows the highest conversion. Based on carbonation test results, one tonne of Tulameen dunite could potentially sequester up to 0.4 tonne of CO<sub>2</sub>. Recovery of strategic metals, in particular chromium, may offset part of the sequestration costs.

### 6.2 Introduction

In an effort to lower atmospheric carbon dioxide (CO<sub>2</sub>) levels, a number of sequestration methods, including geological storage, ocean storage and mineral carbonation of CO<sub>2</sub> have been

proposed worldwide (Voormeij and Simandl, 2004). Mineral sequestration is based on the natural weathering reaction of Mg, Fe and Ca silicates with CO<sub>2</sub> to form carbonates and silica. Once the CO<sub>2</sub> is locked into a carbonate (a thermodynamically stable product), there is no possibility for an accidental release of CO<sub>2</sub>. This concept is described in detail by Lackner *et al.* (1997), O'Connor *et al.* (1999; 2000), Kohlmann and Zevenhoven (2001; 2002) and others. Mineral carbonation does not lead to problematic by-products or require expensive monitoring for potential leaks, and is therefore considered to be the only method that safely disposes of CO<sub>2</sub> on a geologic time-scale (Lackner *et al.*, 1997; O'Connor *et al.*, 2000). This method is still in the laboratory and bench-scale level of development, and its commercial application will depend largely on results from ongoing laboratory studies, results of pilot plant tests, and the economics of this method in relation to other sequestration methods. Mineral CO<sub>2</sub> sequestration is currently more costly than other methods discussed by Voormeij and Simandl (2004). The most expensive aspect of *ex situ* sequestration by mineral carbonation is the need to produce a particle size fine enough to achieve an acceptable rate of reaction. This can be reported in terms of a work index (Wi) for the grinding required. Future research should cover grinding optimization and cost minimization.

Mg-silicates (olivine and serpentine) are considered the favoured raw materials for mineral carbonation (equations 6.1 and 6.2), because they are available worldwide in large amounts (Goff and Lackner, 1998) and contain more reactive material per tonne of rock than the Ca-based minerals (Lackner *et al.*, 1997). Other sources of feedstock for the carbonation process that are or have been considered include Ca-silicates (Kakizawa *et al.*, 2002), industrial wastes such as coal fly ash (Fauth and Soong, 2001) and asbestos tailings (Huot *et al.*, 2003).

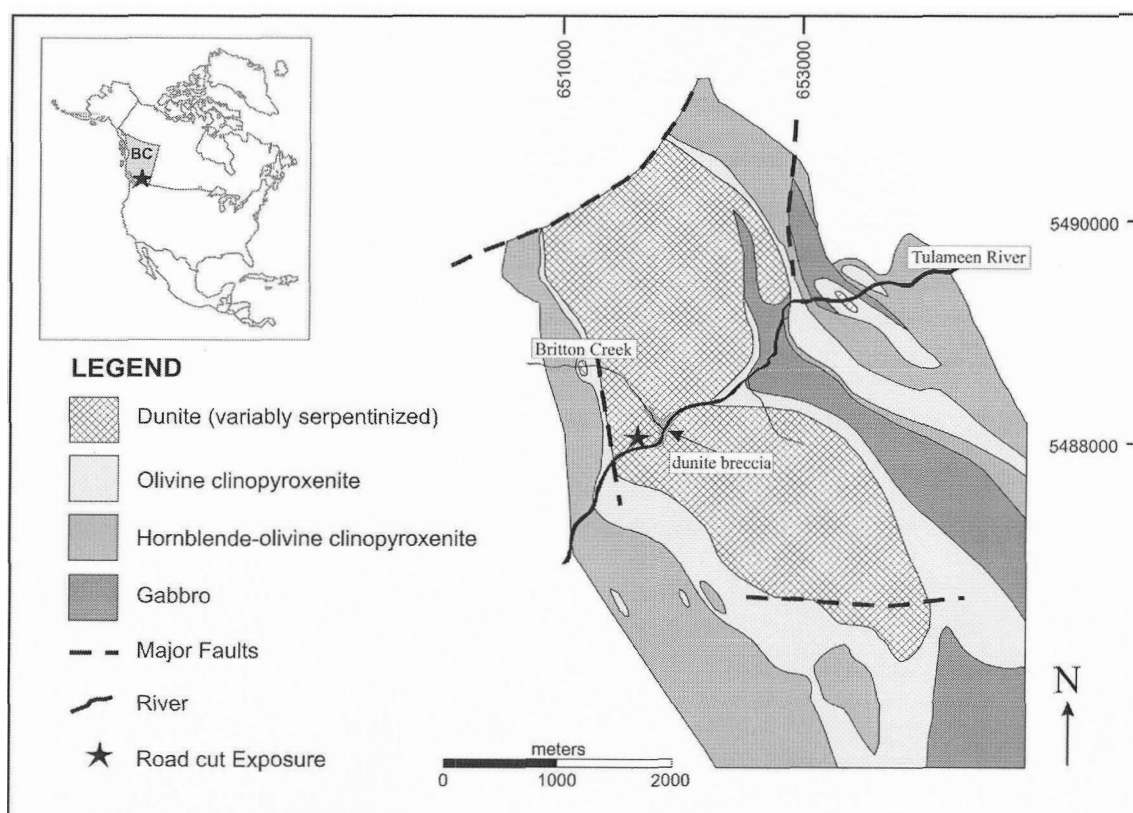


Olivine is a solid solution (Fe,Mg)<sub>2</sub>SiO<sub>4</sub>, which ranges in composition from iron-rich (fayalite) to magnesium-rich (forsterite) end members. There are three principal polymorphs of serpentine: lizardite, antigorite and chrysotile (Deer, *et al.*, 1963). The monomineralic rocks of

olivine and serpentine are dunite (>90% olivine) and serpentinite (>80% serpentine), respectively. Dunite is the preferred raw material over serpentinite, because it contains more magnesium by weight (~44-51 wt% MgO) than serpentinite (~32-38 wt% MgO). In addition, serpentine requires an energy-intensive heat treatment prior to the carbonation process to achieve a significant extent of reaction (O'Connor *et al.*, 2000). However, because dunite is less common than serpentinite, both should be considered as potential sources of raw material for the CO<sub>2</sub> sequestration process.

### 6.3 Tulameen Ultramafic Complex

The Tulameen site, an Alaskan-type (intrusive) ultramafic complex located in south-central British Columbia (Figure 6.1), was selected because it is easily accessible, contains a well-exposed, large (6 km<sup>2</sup>), unusually well preserved dunite core, and is located relatively close to several major point sources of CO<sub>2</sub> emissions (Voormeij and Simandl, 2003).



**Figure 6.1** Northern Section of the Tulameen ultramafic complex (modified from Nixon *et al.*, 1997).



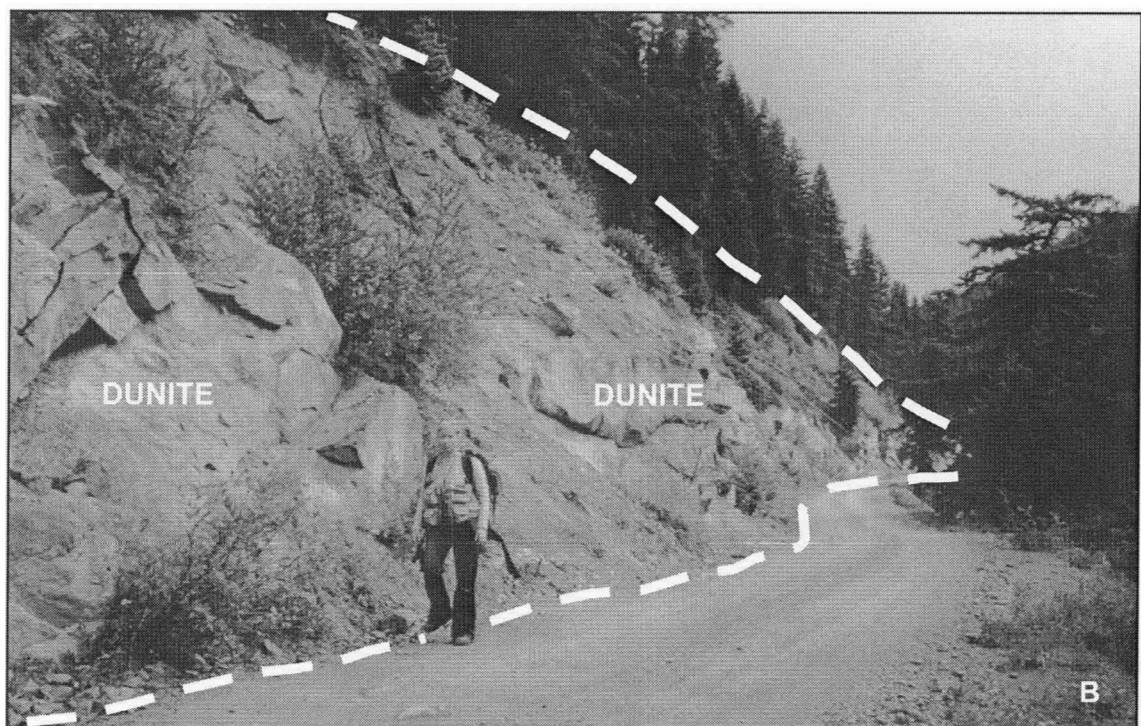
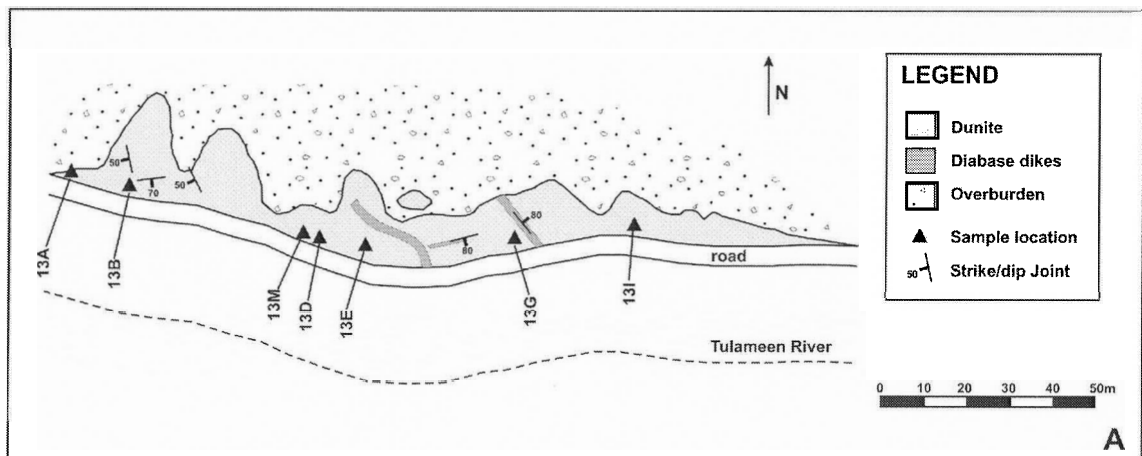
The principal ultramafic rocks of the Tulameen Complex (using the classification according to Le Maitre, 1989) are dunite, olivine-pyroxenite, and hornblende pyroxenite. Dunite forms the core of the intrusion in the northern part of the ultramafic complex (Findlay, 1963; Nixon *et al.*, 1997), which is enclosed by successively pyroxene- and hornblende-rich lithologies (Figure 6.1).

#### **6.4 Petrography and Mineralogy of the Dunite Body**

The core of the Tulameen Complex is composed primarily of massive chromite-bearing dunite. Dunitic breccia is found along the water-worn outcrops in the Tulameen River bed just downstream from the mouth of Britton Creek (Figure 6.1) and continues up Britton Creek for another 80 m. The breccia may represent a lower vertical extent for the dunite body. Minor amounts of serpentine are almost always present in dunite, even in the freshest rocks. The degree of serpentinization of the dunite core is highly variable (Findlay, 1969), ranging from fresh dunite (less than 1% serpentine) to heavily serpentinized dunite. A roadcut exposure, approximately 190 m in length and up to 12 m in height, 470 m west of Britton Creek (Figure 6.1) was selected for detailed investigation of the least serpentinized dunite (Figure 6.2).

The dunite has a buff to pale grey weathering surface, with weathering rinds that range from a few millimetres to several centimetres in thickness. The fresh surface is medium to dark grey to black. It has an even appearance, both on weathered and fresh surfaces. Layering is absent. The dunite is characterized by a well-developed joint system, with blocks ranging from about 20 cm to greater than 1 m in size. Three diabase dikes cut through the roadcut exposure (Figure 6.2a). The primary mineralogy of the dunite consists of forsteritic olivine (98%), chromite (1 to 2%) and rare diopside (one 3-mm bright green crystal was found in a hand sample [13M]; none were seen in thin section). Secondary minerals include serpentine (ranging from 1 to 90%), magnetite (1 to 25%), minor carbonate (about 1% of either dolomite or magnesite) and trace sulphides (pyrite and pyrrhotite). Five dunite samples (Tu-03-13B, D, E, G and I) and one heavily serpentinized dunite sample (Tu-03-13A) were collected from the roadcut outcrop for carbonation tests.

One sample of dunitic breccia (Tu-03-08) was selected for carbonation tests, because the breccia may underlie the dunite deposit. The breccia consists of angular to sub-rounded dunite fragments (from less than 1 cm to less than 1 m) in a matrix of black and waxy green serpentine. The dunite fragments vary from relatively unaltered dunite (less than 3% serpentine) to highly serpentinized dunite (more than 85% serpentine). A summary of mineral features is presented in Table 6.1 and Appendix I gives detailed microscopic descriptions.



**Figure 6.2** A) Schematic of roadcut exposure of nearly homogeneous dunite outcrop along Tulameen River, with sample locations plotted. B) Photo of roadcut showing continuous dunite outcrop exposure.

Sample #	Rock Name	Serpentine Alteration (%)	Olivine (%)	Olivine Grain Size (mm)			Spinel (%)	Chromite Grain Size (mm)		
				Min	Max	Ave		Min	Max	Ave
				Olivine megacrysts				First generation chromite		
				Olivine neoblasts				Second generation chromite		
Tu-03-13B	Dunite	7	90	<1 -	4 -	1.5 -	3	<0.01 <0.10	0.05 0.60	0.02 0.20
Tu-03-13D	Dunite	4	93	<0.1 -	1 -	0.3 -	2	<0.03 <0.10	0.1 0.3	0.05 0.15
Tu-03-13E	Dunite	2	96	<1.0 <0.25	5 1	2 0.5	1	<0.05 -	0.3 -	0.2 -
Tu-03-13G	Dunite	1	98	<0.5 <0.2	5 1	1 0.4	1	<0.01 <0.07	0.1 0.7	0.05 0.3
Tu-03-13I	Dunite	3	96	<0.5 <0.25	2 1	1 0.5	1	<0.01 <0.05	0.1 0.5	0.05 0.2
Tu-03-08	Serpentinized Dunite Breccia	50-65	3-20	n/v	n/v	n/v	33	<0.05 -	0.5 -	0.1 -
Tu-03-13A	Chromitiferous Serpentinite	90	4	<0.5 -	2 -	1 -	5	<0.1 -	0.9 -	0.4 -

**Table 6.1** Microscopic observations of selected samples from Tulameen Complex. Silicates and alteration products were examined under plane-polarized light and crossed polars. Spinel (chromite, ferritchromite and magnetite) and sulphides were studied using a reflecting microscope. Percentages (%) are visual estimates. For Sample 13A, original olivine grain boundaries are not visible (n/v) due to intense serpentinization.

## 6.5 Tulameen Dunite Geochemistry

The compositional variation of the Tulameen dunite core was studied by employing several analytical techniques for determining bulk rock and mineral composition. Mineral chemistry and whole-rock chemical composition are described below. See Appendix II for lab procedures.

### 6.5.1 Mineral Chemistry

Forsterite (Fo) content of olivine can be estimated by the ratio  $[Mg^{2+}/(Mg^{2+}+Fe^{2+})]$ . The higher the Fo number, the closer the olivine is to its forsterite end member. Table 6.2 lists averaged electron microprobe analyses for olivine in some representative rocks from the Tulameen dunite core and clearly indicate a bimodal distribution in forsterite content. One group of olivines (from fresh dunites and serpentinized dunites) ranges from Fo 89 to 91, and another group (dunitic breccia and one dunite) ranges from Fo 93 to 96, with individual analyses up to Fo 98 (Tu-03-13B). Microprobe analysis was also used to confirm microscopic studies: the carbonates are primarily dolomite and magnesite (Table 6.3), and the spinel-group minerals are dominantly chromite, ferritchromite and magnetite.

	<b>Tu-03-04</b>	<b>Tu-03-07A</b>	<b>Tu-03-12A</b>	<b>Tu-03-13B</b>	<b>Tu-03-13G</b>	<b>Tu-03-23</b>
<b>SiO<sub>2</sub></b>	40.89	41.25	40.80	41.19	39.96	39.88
<b>FeO*</b>	9.44	6.84	8.42	3.90	8.86	10.34
<b>MnO</b>	0.20	0.16	0.21	0.23	0.20	0.21
<b>MgO</b>	48.99	51.16	50.33	53.99	49.82	48.31
<b>NiO</b>	0.19	0.29	0.15	0.12	0.14	0.15
<b>CaO</b>	0.20	0.17	0.20	0.01	0.21	0.22
<b>Total</b>	99.91	99.86	100.11	99.45	99.19	99.11
<b>Numbers of ions on the basis of 4 oxygens</b>						
<b>Si</b>	1.00	1.00	0.99	0.99	0.99	0.99
<b>Fe</b>	0.19	0.14	0.17	0.08	0.18	0.21
<b>Mn</b>	0.00	0.00	0.00	0.00	0.00	0.00
<b>Mg</b>	1.79	1.85	1.83	1.93	1.83	1.79
<b>Ni</b>	0.00	0.01	0.00	0.00	0.00	0.00
<b>Ca</b>	0.01	0.00	0.01	0.00	0.01	0.01
<b>Total</b>	3.00	3.00	3.01	3.01	3.01	3.01
<b>Fo</b>	<b>90.2</b>	<b>93.0</b>	<b>91.4</b>	<b>96.1</b>	<b>90.9</b>	<b>89.3</b>

\* All Fe as FeO

**Table 6.2** Microprobe analysis results for olivine grains averaged for each sample. Composition of olivine in Tulameen dunites (13B, 13G and 23) is averaged from 10, 9 and 12 analyses, respectively. Dunite breccia (07A) averaged from 5 analyses and serpentinites (04 and 12A) averaged from 3 and 12 analyses, respectively.

<b>Sample #</b>	<b>CO<sub>2</sub></b>	<b>MgO</b>	<b>CaO</b>	<b>MnO</b>	<b>FeO</b>	<b>Total</b>	<b>Carbonate</b>
13G-1	47.37	24.41	27.06	0.18	0.98	100.00	dolomite
13G-2	47.72	21.73	29.75	0.22	0.58	100.00	dolomite
13G-3	48.37	20.97	29.90	0.13	0.62	100.00	dolomite
13G-4	48.05	20.43	30.68	0.28	0.56	100.00	dolomite
23-4	48.82	20.37	29.77	0.19	0.85	100.00	dolomite
12A-1	47.64	21.08	30.43	0.20	0.65	100.00	dolomite
12A-2	47.87	21.35	29.97	0.22	0.59	100.00	dolomite
23-1	44.23	53.27	0.27	0.20	2.02	100.00	magnesite
23-2	51.59	41.73	2.24	0.71	3.73	100.00	magnesite
23-3	51.68	43.99	0.41	0.59	3.33	100.00	magnesite

**Table 6.3** Microprobe analysis results for carbonates in Tulameen dunites. CO<sub>2</sub> is calculated by difference.

### 6.5.2 Bulk Rock Chemistry

The main constituents of the Tulameen dunite are MgO (44-48 wt%), SiO<sub>2</sub> (38-40 wt%) and Fe<sub>2</sub>O<sub>3</sub> (9-11 wt%). Table 6.4 gives major oxides and loss-on-ignition (LOI) values for samples selected for mineral carbonation tests. Fresh dunites and serpentinized equivalents can be readily distinguished by their water content (Table 6.4). The difference between the crystalline water content and the LOI is very minor, suggesting that carbonate content is minimal as confirmed by microscopic investigation.

Sample #	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> *	MnO	MgO	CaO	LOI	Total	H <sub>2</sub> O <sup>-</sup>	H <sub>2</sub> O <sup>+</sup>
Tu-03-13A	35.31	0.02	0.18	11.01	0.15	38.63	0.31	13.35	98.96	0.32	13.47
Tu-03-08	36.93	0.03	0.23	8.80	0.15	43.27	0.46	9.09	98.96	0.55	8.42
Tu-03-13B	38.02	0.01	0.07	10.06	0.20	44.63	0.28	5.88	99.15	0.31	5.19
Tu-03-13D	38.00	0.01	0.11	10.02	0.17	44.04	0.76	6.19	99.30	0.15	4.99
Tu-03-13E	40.00	0.01	0.07	9.57	0.15	47.90	0.38	1.21	99.29	0.14	1.07
Tu-03-13G	39.70	0.01	0.10	10.46	0.17	47.50	0.28	0.95	99.17	0.16	1.00
Tu-03-13I	39.38	0.01	0.07	11.43	0.20	46.75	0.30	1.39	99.53	0.19	1.29

**Table 6.4** Whole rock compositions and loss-on-ignition values (LOI) of dunites (13B, D, E, G and I), dunitic breccia (08) and serpentinized dunite (13A) in weight percent (wt%). \*Total iron as Fe<sub>2</sub>O<sub>3</sub>.

### 6.6 Theoretical Carbonation Potential

The carbonation potential of minerals and rocks is defined as the unit mass of rock or mineral necessary to convert a unit mass of CO<sub>2</sub> to solid carbonate (Goff *et al.*, 2000). With this approach, the molar concentration of Mg in a sample (Table 6.4) is used to determine the theoretical number of moles of CO<sub>2</sub> that could be converted to magnesite in a carbonation reaction. The carbonation potential, R<sub>CO<sub>2</sub></sub>, is calculated as follows (Equation 6.3), where MW<sub>CO<sub>2</sub></sub> is the molecular weight of CO<sub>2</sub>:

$$R_{CO_2} = \frac{100}{[Mg^{2+}]MW_{CO_2}} \quad (6.3)$$

When iron and calcium silicates are present in the feed, this formula can be modified to include the cations Fe<sup>2+</sup> and Ca<sup>2+</sup> (O'Connor *et al.*, 2004). However, based largely on microscopic examinations and microprobe analysis of the Tulameen rocks, we chose not to include the other cations. The Ca cations originate mostly from carbonates (Table 6.3) and

would therefore not be available for the carbonation reaction. The calcium in the olivine is minor (Table 6.2) and therefore has a negligible effect on the carbonation results. In addition, a large proportion of the ferrous iron in these rocks is contained within magnetite and ferritchromite. Magnetite ( $\text{Fe}_3\text{O}_4$ ) has an extremely low reaction efficiency (8%), one-tenth that of forsteritic olivine (O'Connor *et al.*, 2004). As a first approximation, the ferrous iron in olivine (Table 6.2) does not contribute significantly to the carbonation reaction. Table 6.5 shows the theoretical carbonation potential of the Tulameen rocks. The dunites (13B, E, G, and I), as expected, have the best carbonation potential ( $R_{\text{CO}_2} = 1.9$  to 2.0), and the serpentinized equivalent (13A) has  $R_{\text{CO}_2} = 2.4$ . These numbers are comparable to those for dunites (Goff *et al.* 2000) from Day Book and Buck Creek in western North Carolina ( $R_{\text{CO}_2} = 2.0$ ), dunites from Belvidere Mountain, East Dover, and Mad River, Vermont ( $R_{\text{CO}_2} = 2.1$ , 2.1 and 2.5, respectively), and serpentinites from State Line and Rockville Quarry, Maryland ( $R_{\text{CO}_2} = 2.3$  and 2.4, respectively). Overall, the Tulameen dunites and serpentinized equivalent have comparable or slightly better  $\text{CO}_2$  sequestration potential than those examined by Goff *et al.* Interestingly, the dunitic breccia (Tu-03-08) has a  $R_{\text{CO}_2}$  comparable to that of some of the dunites (Tu-03-13D).

<i>Sample #</i>	<i>MgO</i>	<i>Mg<sup>2+</sup></i>	<i>[Mg]</i>	<i>R<sub>CO2</sub></i>
<b>Tu-03-13A</b>	38.63	23.29	0.96	2.37
<b>Tu-03-08</b>	43.27	26.09	1.07	2.12
<b>Tu-03-13B</b>	44.63	26.91	1.11	2.05
<b>Tu-03-13D</b>	44.04	26.55	1.09	2.08
<b>Tu-03-13E</b>	47.90	28.88	1.19	1.91
<b>Tu-03-13G</b>	47.50	28.64	1.18	1.93
<b>Tu-03-13I</b>	46.75	28.19	1.16	1.96

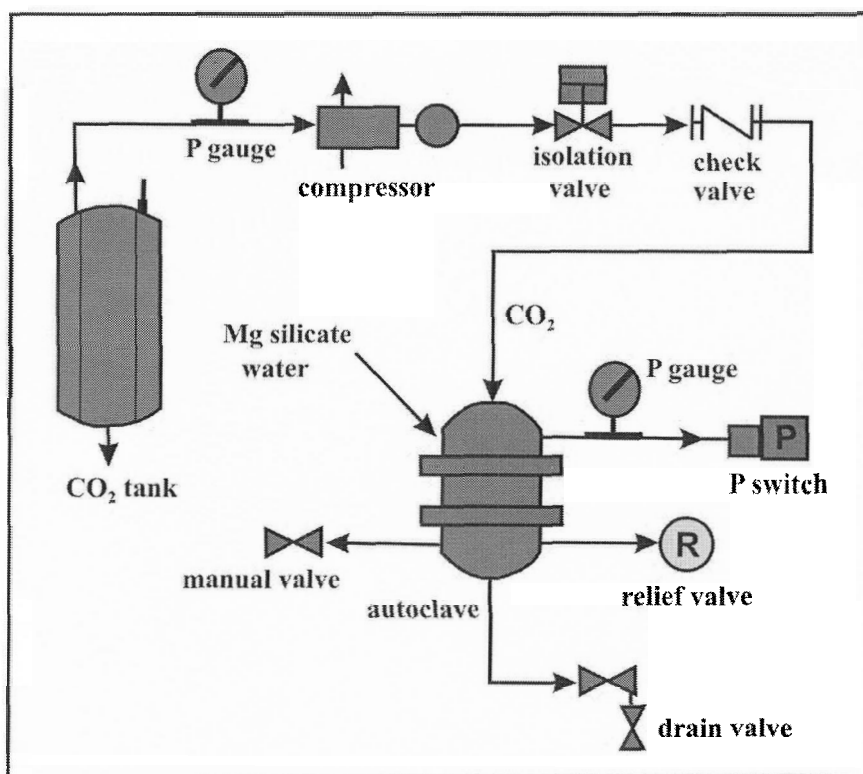
**Table 6.5** Theoretical carbonation potential ( $R_{\text{CO}_2}$ ) for Tulameen dunites (13B, D, E, G and I), dunitic breccia (08) and serpentinized dunite (13A).  $\text{MgO}$  and  $\text{Mg}^{2+}$  are in wt%,  $[\text{Mg}]$  is molar concentration of magnesium in mol%. Lower  $R_{\text{CO}_2}$  numbers correspond to better carbonation potential.

## 6.7 Mineral Carbonation Tests

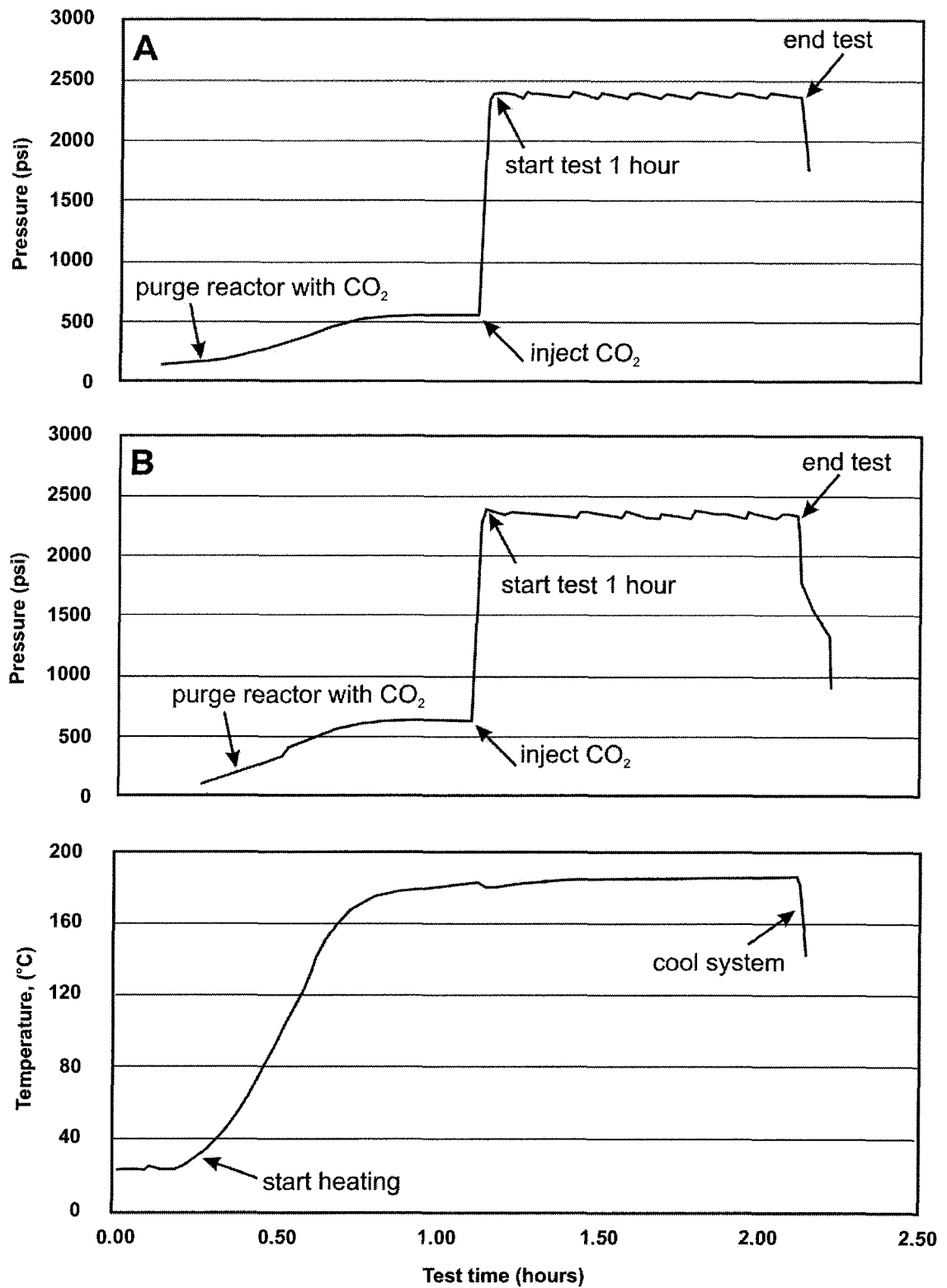
The procedure adopted for mineral carbonation of selected Tulameen samples was developed at the Albany Research Center (ARC) and described by O'Connor *et al.* (2004). Sample

preparation specific to this study is described in Appendix II. The tests were conducted at the ARC in an autoclave with a gas-dispersion agitator that allows for three-phase mixing in the reactor (Figure 6.3). Feed material was a slurry consisting of 167 g of minus 400-mesh rock sample mixed with 950 g of 0.64M  $\text{NaCO}_3$ , 1.0 M  $\text{NaCl}$  carbonation solution, which had an initial pH of 7.51 at 23.6°C.

Initial autoclave conditions were 28°C and  $P_{\text{CO}_2}$  of 10 atm after purging the system with  $\text{CO}_2$ . The autoclave was heated to approximately 185°C in one hour, after which  $\text{CO}_2$  was injected into the autoclave to a  $P_{\text{CO}_2}$  of 150 atm. These pressure and temperature conditions were maintained for 60 minutes. As  $\text{CO}_2$  reacts with Mg silicates to form magnesite and silica, the pressure in the autoclave drops, and additional  $\text{CO}_2$  is injected to maintain system pressure. This results in a "saw-tooth" pattern in the time vs. pressure graph. Under normal test conditions, the frequency of the saw-tooth pattern decreases over time (Figure 6.4a) as the surface area of the feed available for reaction decreases. Highly serpentinized samples, which should not carbonate as readily as the dunites, have saw-tooth patterns with lower frequency than dunites (Figure 6.4b).



**Figure 6.3** Schematic of ARC's batch autoclave used for carbonation tests on the Tulameen samples (O'Connor et al., 2004).



**Figure 6.4** Pressure and temperature conditions in the autoclave before, during and after test for (A) fresh dunite and (B) serpentinized dunite sample.



## 6.8 Results of Carbonation Tests

The weight difference between the reaction product and reactant gives a first approximation of the success of the carbonation reaction. Theoretically, with 100% stoichiometric conversion of 100g of pure forsteritic olivine to magnesite and silica (Equation 6.1), the reaction products will weigh 162.6g. However, weight change can be affected by loss of solids, which can lead to weight loss, or residual moisture in the filter cake. Therefore, weight gain provides a first estimate only and should not be used to estimate percent conversion. Table 6.6 lists the initial feed and product weights for each sample.

The preferred method for determining the percent conversion is to calculate it based on the cations available to carbonate in the feed (e.g. Mg, Ca, and  $\text{Fe}^{2+}$ ; in this case the Ca and Fe cations are negligible) and the difference in  $\text{CO}_2$  content between the feed and the reactant product. Table 6.6 lists the  $\text{CO}_2$  content of head and product; the increase is due to  $\text{CO}_2$  sequestered during the carbonation reaction.

<i>Sample #</i>	<i>Weight Reaction Product (g)</i>	<i>Head Mg<sup>2+</sup> (wt%)</i>	<i>Head CO<sub>2</sub> (wt%)</i>	<i>Reaction Product CO<sub>2</sub> (wt%)</i>	<i>ε<sub>A</sub> (%)</i>	<i>R<sub>x</sub> (%)</i>
<b>Tu-03-13B</b>	216.2	26.92	0.55	23.60	48.19	<b>48.1</b>
<b>Tu-03-13D</b>	220.1	26.56	1.31	25.40	46.78	<b>51.8</b>
<b>Tu-03-13D<sub>R</sub></b>	218.0	26.56	1.32	25.20	46.77	<b>51.3</b>
<b>Tu-03-13E</b>	236.8	28.89	0.37	29.40	51.94	<b>56.2</b>
<b>Tu-03-13G</b>	231.9	28.65	0.21	27.90	51.67	<b>53.9</b>
<b>Tu-03-13I</b>	225.7	28.20	0.35	26.00	50.71	<b>50.8</b>
<b>Tu-03-13I<sub>R</sub></b>	203.6	28.20	0.37	18.40	50.69	<b>35.7</b>
<b>Tu-03-08</b>	211.6	26.10	0.70	21.40	46.56	<b>44.7</b>
<b>Tu-03-13A</b>	148.9	23.30	0.62	8.19	41.57	<b>18.2</b>

**Table 6.6** Results of carbonation reactions of dunites (13B, D, E, G and I), dunitic breccia (08) and serpentinized dunite (13A). 13D<sub>R</sub> is a repeat of 13D under the same P-T conditions; 13I<sub>R</sub> is a repeat of 13I under the same P-T conditions, but feed was only milled for 30 minutes. ε<sub>A</sub> is the weight gain in percent assuming 100% stoichiometric conversion of Mg-silicates to carbonates. R<sub>x</sub> is the percent conversion of Mg-silicate to magnesite and silica.

Assuming only Mg cations are reacting with CO<sub>2</sub> we can calculate % conversion, or reaction efficiency  $R_x$ , by the following equation:

$$R_x = \frac{X_{CO_2}}{\varepsilon_A (1 - X_{CO_2})} \quad (6.3)$$

Where  $X_{CO_2}$  is the difference in CO<sub>2</sub> concentration in wt% (product minus head) and  $\varepsilon_A$  is the weight gain (%) assuming 100% stoichiometric conversion of Mg-silicates to carbonates (O'Connor et al., 2004). Based on carbonation test results, Tulameen dunites carbonated over one hour (following standard procedure) have reaction efficiencies ranging from 48 to 56%. The serpentinized dunite from Tulameen has a 18% conversion, this is relatively high, considering it did not undergo heat-treatment or high-energy attrition grinding.

## **6.9 Strategic Metals: Offsetting Sequestration Costs**

The purpose of analyzing the Tulameen rocks for trace elements is to estimate the theoretical potential for offsetting sequestration costs by the recovery of valuable by-products, in this case, chromium, nickel, copper and even platinum group elements (PGE). These elements are commonly found in ultramafic rocks in sub-economic concentrations. Overall, the serpentinites appear to have higher Cr content than the fresh dunites (Table 6.7). Anomalous copper concentrations are found only in the dunitic breccia. Au and Pd values are near detection limit, however, one sample contains 356 ppb platinum (Pt), which is not surprising since the Tulameen Complex was previously considered for its PGE potential (Nixon, 1990). Based on microscopic investigation, second generation chromite grains range from 50  $\mu$ m to just under 1 mm (Table 6.1) and have thin to thick magnetite rims (Appendix I). Wet magnetic separation of a serpentinized dunite prior to carbonation recovered 4.2wt%. Geochemical analysis will have to confirm the quality of chromite contained in the magnetic fraction that was recovered.

Sample #	Cr	Co	Ni	Cu	Au	Pt	Pd
	ppm	ppm	ppm	ppm	ppb	ppb	ppb
Tu-03-13A	5660	131	959	11	-	-	-
Tu-03-08	2480	131	1290	656	2	88	<2
Tu-03-13B	3180	153	990	16	3	356	2
Tu-03-13D	3440	142	1060	6	3	16	<2
Tu-03-13E	2130	144	1220	8	-	-	-
Tu-03-13G	4780	155	1060	4	<2	94	<2
Tu-03-13I	1620	167	920	23	-	-	-
Detection limit:	4	10	2	1	2	2	2

**Table 6.7** Trace-element and precious-metal concentrations for dunites (13B, D, E, G and I), dunitic breccia (08) and serpentized dunite (13A). Cobalt concentrations are primarily due to contamination from tungsten-carbide mill used for preparing samples for analysis (see Appendix II).

## 6.10 Grinding Work Index

A grinding work index (Wi) can be calculated to estimate the energy required to achieve a particle size desired for mineral carbonation reaction. Appendix III shows work-index calculations based on size analysis of the crushed raw material and ground feed for carbonation tests. Of particular interest are samples 13I, fresh dunite ground for 2 hours, and 13I<sub>R</sub>, the same material ground only 30 minutes (Table 6A.2). The Wi for 13I<sub>R</sub> is one-quarter (12.7 kW-hr/t) that of 13I (41.9 kW-hr/t), but the percent conversion (Table 6.6) in the subsequent carbonation test on 13I<sub>R</sub> (35.7%) is more than half that of 13I (50.8%). Based on these work-index results, optimization of the particle size for reaction appears to be possible.

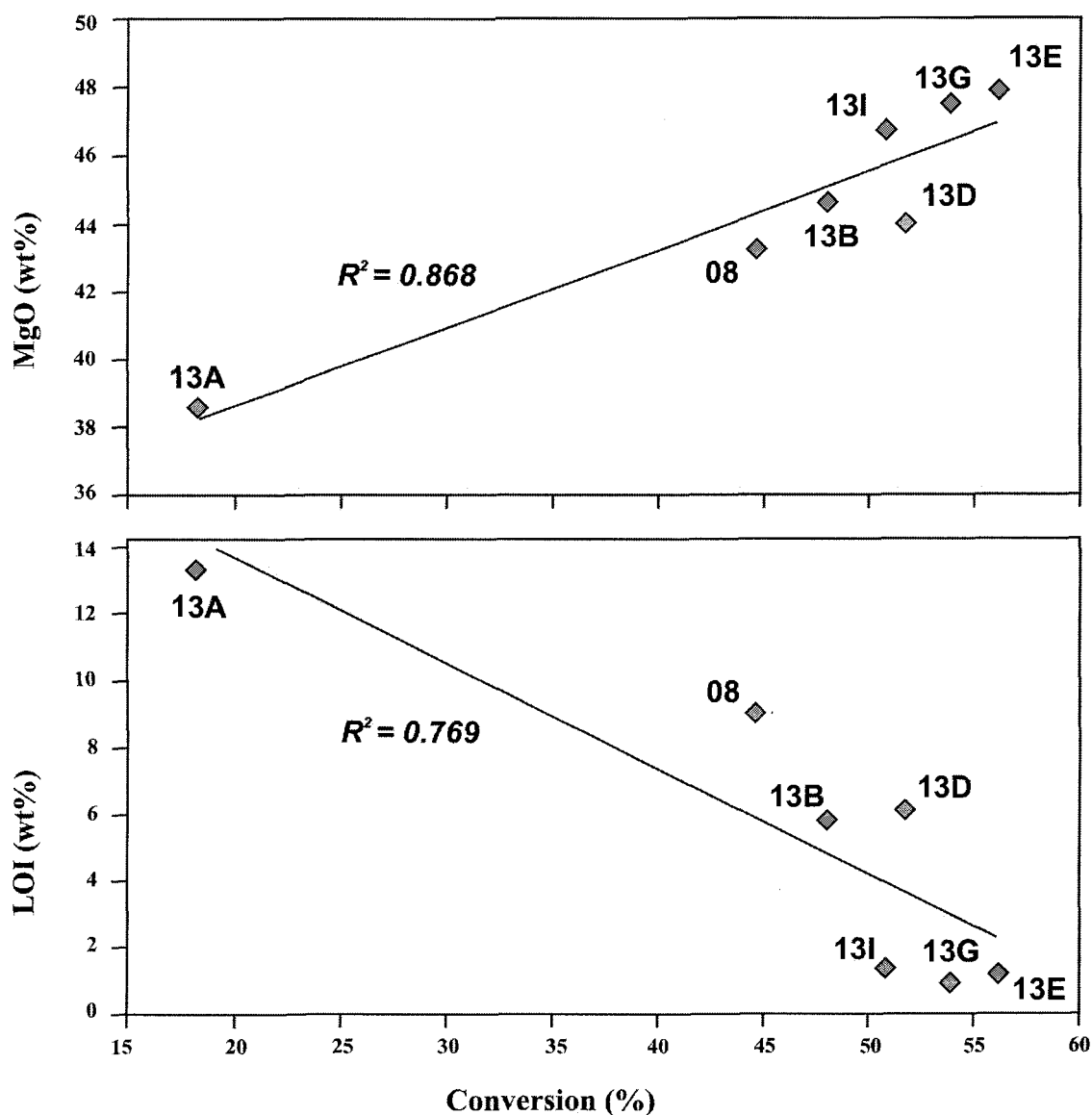
## 6.11 Discussion and Summary

Based on CO<sub>2</sub> content in reaction products, one-hour carbonation tests of the Tulameen dunites resulted in 48 to 56% conversion to magnesite and silica. There is a good correspondence ( $r = 0.94$ ) between the theoretical carbonation potential,  $R_{CO_2}$ , and the reaction efficiency,  $R_x$  (see

Tables 6.5 and 6.6). The  $R_{CO_2}$  factor as defined by Goff *et al.* (2000) is useful in assessing the carbonation potential of the Tulameen dunites, however it is based solely on Mg content and does not take into account the presence of Mg-silicates other than olivine. Pyroxenes, for example, are commonly found in peridotites and have a lower carbonation potential ( $R_{CO_2} = 2.7$ ) than forsteritic olivine (O'Connor *et al.*, 2004). Because the Tulameen dunites are composed primarily of highly forsteritic olivine, the  $R_{CO_2}$  factor as defined by Goff *et al.* (2000) was used effectively to approximate the reaction potential for this deposit. It is therefore essential to have a good knowledge of the mineralogy and the mineral chemistry of the rocks before applying the  $R_{CO_2}$  factor. Should Ca- and/or Fe-silicates be present, then the modified  $R_{CO_2}$  factor, per O'Connor *et al.* (2004), should be applied.

As expected, there is a strong correlation between percent conversion and MgO content of raw feed; conversely there is a negative correlation between percent conversion and LOI content of feed (Figure 6.5). Interestingly, the highly serpentinized dunite (Tu-03-13A), with an LOI of 13.35 wt%, had a surprising 18% conversion, even though serpentinites are reported to carbonate poorly, if at all, without heat pretreatment to drive off the chemically bound water (O'Connor *et al.*, 2000). High energy-attrition grinding has been used in other studies to activate serpentinite (McKelvy *et al.*, 2002), but it is possible that the Tulameen serpentinites may not need these energy-intensive treatments. The relatively high theoretical carbonation potential ( $R_{CO_2} = 2.1$ ) and conversion (45%) for the dunite breccia suggests that it may be included when considering the Tulameen dunite core as a source of raw material for the mineral  $CO_2$  sequestration process.

Based on results from laboratory work, one tonne of Tulameen dunite could potentially sequester up to 0.4 tonne of  $CO_2$ . The recovery of strategic metals, in particular Cr, is theoretically possible and may partially offset sequestration costs. Optimization of feed size necessary for carbonation reaction, based on work-index calculations, appears possible. More work is needed to see if the reaction products have desirable qualities for industrial-mineral or construction applications.



**Figure 6.5** Percent conversion of raw feed, based on  $\text{CO}_2$  content in reaction products after 1 hour carbonation, versus MgO and Loss on Ignition (LOI) content of feed.

## 6.12 Acknowledgements

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## **APPENDIX I: Sample Descriptions**

Following are detailed descriptions of selected samples from the Tulameen Complex. Presence of antigorite in sample 13D and brucite in sample 13A were confirmed by X-ray diffraction. Carbonates are primarily dolomite and magnesite as identified by electron microprobe analysis.

Tu-03-13B: Equigranular olivine grains display granoblastic polygonal to interlobate texture. Olivine grains occur as mosaic of small (ave: 0.05mm) anhedral grains in subparallel crystallographic orientations. Serpentinization is limited to olivine grain boundaries and fractures. Serpentine veinlets are approximately 0.5 mm thick, 0.10 to 2.5mm apart and are lined with dusty magnetite. First generation chromite are subhedral to anhedral and sparsely disseminated within olivine grains. Second generation chromites are euhedral to subhedral, slightly fractured, located primarily along olivine grain boundaries and fractures; chromite has

been partially replaced by magnetite, leaving rounded chromite grains with thick magnetite rims, which are partially resorbed. Trace of sulphides (<0.05mm), which are enclosed by anhedral magnetite.

Tu-03-13D: Olivine grains display a granoblastic polygonal texture. Serpentinization is limited to olivine grain boundaries. Laths of serpentine (antigorite?) cut into olivine grain boundaries at right angles, grain size min: <0.05mm, max: 0.25mm, ave: 1.0mm. First generation chromite grains are euhedral, located within olivine grains and have no magnetite rims. Second generation chromite are euhedral to anhedral, located along olivine grain boundaries and fractures and have thick magnetite rims. Trace (<0.5%) dusty magnetite located along olivine grain boundaries and fractures. Late carbonate vein, approximately 1mm wide cuts across sample.

Tu-03-13E: Olivine megacrysts display well developed kink banding. Olivine neoblasts have a granoblastic polygonal texture. Serpentinization is restricted to olivine grain boundaries, with serpentine laths (antigorite?) located at right angles to olivine grains, grain size min: <0.05mm, max: 0.2mm, ave: 0.1mm. Euhedral chromite grains are disseminated as well as in thin stringers, located primarily along olivine grain boundaries and fractures, with thick magnetite rims that are partially resorbed. Fine-grained (<0.01mm) chromite grains are sparsely disseminated within olivine grains and lack magnetite rims.

Tu-03-13G: Olivine megacrysts are anhedral, display undulatory extinction and kink banding and contain fine annealing fractures with fluid inclusions. Olivine neoblasts are mainly euhedral, located in patches along olivine megacrysts' grain boundaries, have triple junctions and some show idioblastic textures. All olivine grains have clear, distinct crystal boundaries. Serpentine is limited to filling of hairline fractures, which are oriented along granoblastic fabric of olivine grains. First generation chromite is subhedral to anhedral and is sparsely disseminated within olivine megacrysts, lacking magnetite rims. Second generation chromite forms stringers of euhedral grains, oriented along same direction as serpentine veinlets and also lacks magnetite rims.

Tu-03-13I: Olivine megacrysts are anhedral and display undulatory extinction and some have distinct kink banding. Olivine neoblasts are abundant, subhedral to euhedral and form large



patches surrounding olivine megacrysts. Serpentinization is minor and restricted to olivine grain boundaries. First generation chromite grains are euhedral to anhedral, sparsely disseminated within megacrysts and have no magnetite rims. Second generation chromite are euhedral to subhedral, located along megacrysts' grain boundaries and fractures, as well as within neoblasts, with thin, partially resorbed magnetite rims grown onto chromite grain boundaries.

Tu-03-08: Breccia is clast supported. Clasts are serpentinized dunite and are subangular to rounded, up to 5cm across. Chromite grains are subhedral to anhedral, have thick magnetite rims and are partially replaced by magnetite. Serpentine alteration started along olivine grain boundaries and along fractures, moving inwards leaving xenomorphic islands of olivine (ave size: 0.10mm) with communal extinction angles. Dusty magnetite lines fractures and all serpentinized regions (up to 30%), resulting in the thin section being nearly completely opaque and making it difficult to assess grain size of original olivine. Minor (<0.5%) sulphides present within serpentine matrix.

Tu-03-13A: Original olivine grain morphology and texture is not recognizable due to intense serpentinization of the dunite. Serpentinization commenced along olivine grain boundaries and fractures, moving inwards into olivine grains, creating a mesh texture with micrometer-scale xenomorphic islands of olivine with individual extinction angles. Serpentine vein, approximately 0.5 mm thick is lined by dusty magnetite. Chromite grains are euhedral and have thick magnetite rims grown onto chromite grain boundaries. Chromite grains may be located along relict olivine grain boundaries and fractures and are crosscut by serpentine vein. Carbonate minerals fill a 0.15mm fracture completely and form patches within serpentine vein. Fibrous mineral filling fracture, possibly brucite. Minor sulphide (<0.5%) within and near serpentine vein.

## ***APPENDIX II: Laboratory Procedures***

### ***Mineral Chemistry***

Electron-probe microanalyses were carried out on polished thin sections of dunite, dunite breccia and serpentinized dunites. Olivine (6 samples, 43 analyses) and serpentine (6 samples, 15 analyses) were analyzed on a fully automated CAMECA SX-50 instrument, at the Department of Earth and Ocean Sciences, University of British Columbia. The following

operating conditions were used: excitation voltage, 15 kV; beam current, 20 nA; peak count time, 20 s; background count-time, 10 s; and 5  $\mu\text{m}$  spot diameter. Data reduction for improved quantitative microanalysis was done using the 'PAP'  $\phi(\rho Z)$  method (Pouchou & Pichoir 1985). Previously published analyses for this deposit include mineral analyses by Findlay, 1963; Nixon *et al.*, 1990; and Rublee, 1994.

#### ***Major Oxides and LOI Analysis***

Whole-rock analysis included major-oxide and loss on ignition (LOI) determinations by X-ray fluorescence (XRF) done by Global Discovery Labs, Vancouver, BC. Previously published analyses include whole-rock major-element compositions by Camsell, 1913; Findlay, 1969; and Rublee, 1994).

#### ***Trace Element Analysis***

Trace elements were determined by XRF and water content by IR spectroscopy at Geoscience Laboratories, Sudbury, Ontario. Au, Pt and Pd (6 samples only) analysis were done by fire assay by Global Discovery Labs, Vancouver, BC.

Cobalt values are most likely from contamination of the tungsten-carbide mill used to prepare the samples at the BC Geological Survey Branch. This mill introduced approximately 100-200 ppm of Co to each ground sample. Dunites have slightly higher Co values than the serpentized samples, because the dunites are more abrasive than the serpentized equivalents, thereby incorporating slightly more Co from the mill into the sample. The tungsten-carbide mill was used, because the regular mill would have contaminated the samples with Cr, which is a major trace element in dunites. Blank milling tests using crushed quartzite gave contamination values of 110, 280 and 180 ppm Co (Ray Lett, BCMEM Geological Survey Branch, personal communication).

#### ***Sample Preparation for Carbonation Reaction***

Selected rock samples were crushed at the British Columbia Geological Survey Branch laboratory in Victoria in a jaw crusher until 80% passed 0.3 cm (determined by sieve analysis). Samples were further processed at ARC to produce feed materials for the carbonation reaction tests.

Following is a description of the sample preparation before and after carbonation: A 500-gram (g) sample of crushed rock was split by a cone-and-quartering method, and it was then added with 500 millilitres of tap water to a ball mill to produce a 50% solids slurry. The ball mill has a 2-litre capacity, an inside diameter of 7", and is rated at  $\frac{1}{2}$  horsepower (0.36 kW) at 3 amps (A) and 120 volts (V). Thirty-three 1- $\frac{1}{4}$ " and one hundred and forty-seven  $\frac{3}{4}$ " steel balls (initial combined weight of 8235g) were used to grind the samples. Grinding time for each sample was two hours, except for one sample (Tu-03-13I<sub>R</sub>) that was ground for 30 minutes.

The first two samples of ball-mill products were wet-sieved through 400 mesh (38 $\mu$ m), and it was determined that less than 1% was coarser than 400 mesh. For the subsequent samples, it was assumed that after two hours of grinding, the sample was essentially 100% minus 400 mesh (38 $\mu$ m). Size analysis of the feeds indicated that two hours of grinding produced a feed with  $D_{80} = \sim 19\mu$ m, and that 30 minutes of grinding (sample 13I<sub>R</sub>) produced feed with  $D_{80} = 38\mu$ m.

The ground product was removed from the ball mill with a stream of water and filtered. The filter used pressurized air to remove excess water and produced a filtered cake for each sample. The cake was then dried overnight (16 to 24 hours) in an oven at 103°C. The dried cake was weighed and compared to the initial sample weight (500g). On average, the samples gained 6 to 8 grams, of which 3 to 4g was due to abrasion of the steel balls (determined by weighing the balls before and after each grind). Additional weight was gained from the mill liner, but absolute numbers were not determined, because minor product loss during recovery and filtering of the milled sample is inevitable, and the ball mill itself was not weighed between the grinds.

After weighing, the dried cake was rolled with a steel rolling pin and passed through a 35-mesh (500 $\mu$ m) screen to break lumps caused by drying. The screened product was then blended, and a 167g sample was split for the carbonation test. The remaining product was blended again, and a 25g sample was taken, passed through an 80-mesh screen (177 $\mu$ m), and submitted for chemical and X-ray-diffraction (XRD) analyses to identify serpentine polymorphs and accessory minerals.

The 167g of feed was mixed with 950g of 0.64M NaCO<sub>3</sub>, 1.0 M NaCl carbonation solution, which had an initial pH of 7.51 @ 23.6°C. The prepared slurry (15% solids) was poured into the

autoclave and the autoclave was sealed, covered with insulating material and purged with CO<sub>2</sub>. After the one-hour test time at the predetermined temperature and CO<sub>2</sub> pressure, the autoclave was cooled, the pressure was bled off, the slurry was removed, and the autoclave was rinsed to recover additional solids. The recovered slurry and rinse solids were filtered in a pressure filter. The volume of liquid was measured, and a sample of the liquid was submitted for chemical analysis. Table 6A.1 shows analyses of carbonation solutions before and after tests. The wet cake was weighed and put into the oven overnight to dry at 103°C. The following morning, the dried cake was weighed, rolled with a steel rolling pin and passed through a 35-mesh screen to break lumps caused by drying. The product was then blended, and a 25g sample was submitted for chemical and XRD analyses.

	Cl	Cr	Fe	Mg	Ni	K	Si	Na	CO <sub>2</sub>	HCO <sub>3</sub>	pH
<b>Initial Solution*</b>	35.1	<0.0005	0.0003	0.0006	<0.0005	0.0021	0.0031	32.0	26.7	34.3	7.51
<b>After test</b>	Cl	Cr	Fe	Mg	Ni	K	Si	Na	CO <sub>2</sub>	HCO <sub>3</sub>	pH
<b>Tu-03-13E</b>	34.6	<0.0005	0.0003	0.0393	<0.0005	0.0046	0.0654	30.0	25.4	31.6	7.87
<b>Tu-03-13G</b>	35.1	<0.0005	0.0004	0.0354	<0.0005	0.0045	0.0578	32.1	26.3	33.4	7.92
<b>Tu-03-13I</b>	35.7	<0.0005	0.0002	0.0476	<0.0005	0.0053	0.0590	30.6	25.7	32.7	7.78
<b>Tu-03-23</b>	35.7	<0.0005	0.0003	0.0204	0.0005	0.0032	0.0644	31.7	26.5	33.0	7.81
<b>Tu-03-13B</b>	34.7	<0.0005	0.0003	0.0324	<0.0005	0.0052	0.0770	30.0	25.5	32.2	7.83
<b>Tu-03-12A</b>	33.7	<0.0005	0.0003	0.0204	<0.0005	0.0040	0.0771	30.7	24.6	30.8	7.93
<b>Tu-03-12A<sub>2</sub></b>	34.4	<0.0005	0.0003	0.0192	<0.0005	0.0040	0.0764	29.9	25.2	32.2	7.91
<b>Tu-03-13D</b>	35.2	<0.0005	0.0003	0.0256	<0.0005	0.0040	0.0712	30.2	24.5	30.5	7.91
<b>Tu-03-13F</b>	36.3	<0.0005	0.0003	0.0352	<0.0005	0.0036	0.0490	30.2	27.1	34.3	7.83
<b>Tu-03-13A</b>	36.3	<0.0005	0.0003	0.0222	<0.0005	0.0042	0.0540	31.9	26.9	33.9	7.75
<b>Tu-03-08</b>	36.2	<0.0005	0.0003	0.0163	<0.0005	0.0059	0.0666	30.5	26.3	32.9	7.87

**Table 6A.1** Solution analysis before and after each carbonation test in grams per Litre (g/L). \*Initial solution is identical for each tests run. Uncertainty is +/- 2%. Analysis were performed at the ARC laboratory; Fe, Mg, K, Si and Na analysis were done by atomic adsorption; Cr and Ni by ICP analysis; HCO<sub>3</sub> and Cl by volumetric titration and CO<sub>2</sub> content was measured by an absorption/gravimetric method. Note that Mg and Si contents increase, whereas contents of other species remain relatively constant. Metals do not appear to enter into solution and solution appears to be buffered.

### **APPENDIX III: Calculating the Work Index (Wi) for Grinding**

Pilot-plant grinding tests are designed to produce an accurate measure of the work required (in kilowatt hours per ton) to grind a feed material to the desired product size (Weiss, 1985). Although the samples for this initial investigation were too small for the scale of testing usually done to establish work-index data and the mill dimensions are not exactly those utilized for the

established methods, the following calculations provide a first estimate of the energy necessary to grind the Tulameen samples.

In this investigation, the feed was the minus 1/4" crushed rock that was prepared at the BCGSB laboratory, and the grinding product was the material that was fed into the carbonation reactor. To calculate the work index (Wi) for the grinding process, several variables need to be identified (Weiss, 1985):

- $P_t$  Mill power operated empty (no balls or feed in the mill while operating)
- $P_g$  Gross mill power for grinding (with balls and feed in mill)
- $Q$  Grinding rate (tons per hour)
- $F_{80}$  Feed size (in micrometers)
- $P_{80}$  Product size (in micrometers)
- $E_1$  Motor efficiency factor at a given load (in percent)
- $D$  Mill diameter inside (in feet)

The net power demand,  $P$ , for grinding is expressed as

$$P = P_g E_1 - P_t E_1 \quad (\text{Eq. A1})$$

The net work done in grinding is expressed as

$$W = \frac{P}{Q} \quad (\text{Eq. A2})$$

The mill-diameter correction factor to an 8-ft diameter reference mill is

$$\left( \frac{8}{D} \right)^{0.2} \quad (\text{Eq. A3})$$

The fineness-of-grind correction factor for grinds finer than  $P_{80} < 70\mu\text{m}$  is expressed as

$$A_1 = \frac{P_{80} + 10.3}{1.145 P_{80}} \quad (\text{Maximum value of } A_1 = 5) \quad (\text{Eq. A4})$$

The work index (Wi) is calculated as follows:

$$Wi = \frac{WA_1 \left( \frac{8}{D} \right)^{0.2}}{\frac{10}{\sqrt{P_{80}}} - \frac{10}{\sqrt{F_{80}}}} \quad (\text{Eq. A5})$$

The following illustrates the calculation of Wi for fresh dunite (Tu-03-13I) ground for 2 hours in the ARC mill:

Mill data

$$D = 0.583 \text{ ft}; E_1 = 0.90 (90\%); P_t = 3.2A @ 120V = 384W = 0.384kW$$

Test data

$$P_g = 3.3A @ 120V = 396W = 0.396kW;$$

$$Q = 500g \text{ in } 2 \text{ hours} = 250g/hr = 2.76E-04 \text{ tons/hr};$$

$$F_{80} = 3100\mu m; P_{80} = 18.26\mu m$$

Then net power at mill (Eq. A1):

$$P = 0.396kW(0.90) - 0.384kW(0.90)$$

$$\underline{P = 0.0108kW}$$

Net work done in grinding (Eq. A2):

$$W = 0.0108kW/2.76E-04tons/hr$$

$$\underline{W = 39.13kW-hr \text{ per ton}}$$

Mill diameter correction factor (Eq. A3):

$$(8/0.583ft)^{0.2} = \underline{1.69}$$

Fineness of grind correction factor (Eq. A4):

$$A_1 = ((18.26\mu m) + 10.3)/(1.145(18.26\mu m))$$

$$\underline{A_1 = 1.37}$$

Calculating Wi corrected to an 8-ft diameter reference mill (Eq. A5):

$$Wi = ((39.13kW-hr/ton)(1.37)(1.69))/(10/(18.26\mu m)^{0.5}) - (10/(3100\mu m)^{0.5}))$$

$$\underline{Wi = 41.93kW-hr/ton}$$

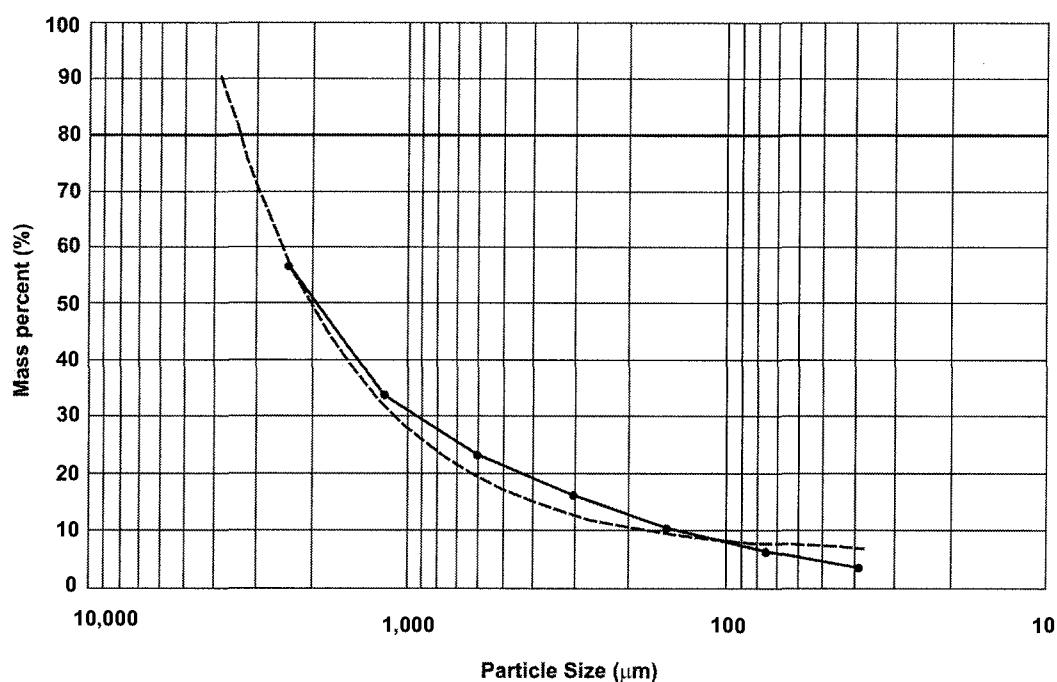
Calculated  $W_i$  values for the samples in this investigation are shown in Table 6A.2.

### **$D_{80}$ for Feed**

A necessary component in calculating  $W_i$  is the  $D_{80}$  of each sample before and after grinding. The  $D_{80}$  of a sample is the particle size at which 80% of the material is finer. Similarly,  $D_{10}$  and  $D_{50}$  values represent the size of particle at which 10% and 50% pass, respectively.  $D_{10}$  and  $D_{50}$  values were determined from percent of material retained on a standard sieve series (Table 6A.3). Trend lines were used to extrapolate the data in order to obtain the  $D_{80}$  (Figure 6A.1). The  $D_{10}$  for the samples used as feed to the ball mill at ARC ranged from 85 to 300 $\mu\text{m}$ ,  $D_{50}$  ranged from 1600 to 2300 $\mu\text{m}$ , and  $D_{80}$  ranged from 2800 to 3800 $\mu\text{m}$ .

### **$D_{80}$ for Product**

A sample of each ground product was sized in a Micromeritics Model 5100 Sedigraph to determine the  $D_{10}$ ,  $D_{50}$  and most importantly, the  $D_{80}$ . Each sample was run twice and the  $D_{80}$  used for  $W_i$  calculations is an average of the two runs (Table 6A.2).



**Figure 6A.1** Particle size of feed prior to grinding in ball mill versus material passing in percent. For example,  $D_{10}$  is the size at which 10% of the feed passes; in this case (Tu-03-13D),  $D_{10}$  is 160 $\mu\text{m}$ ; similarly,  $D_{50}$  is 2000 $\mu\text{m}$ . To obtain the  $D_{80}$ , the variable necessary for calculating  $W_i$  for grinding the feed, a trend line (dashed line) was passed through the data points and extrapolated past 80 mass percent

(heavy line); for this sample,  $D_{80}$  is estimated at  $3400\mu\text{m}$ .  $R^2$  for this trend line is 0.9778.  $R^2$  values for all of the trend lines are listed in Table 6A.1.

<i>Sample #</i>	<i>ARC #</i>	<i>R<sup>2</sup></i>	<i>Feed D<sub>80</sub> (μm)</i>	<i>Product D<sub>80</sub> (μm)</i>	<i>Work Index (kW-hr/ton)</i>
<b>Tu-03-13B</b>	SC-636	0.979	3000	19.14	42.4
<b>Tu-03-13D</b>	SC-639	0.978	3400	20.52	42.7
<b>Tu-03-13G</b>	SC-633	0.922	2800	19.40	42.6
<b>Tu-03-13I</b>	SC-634	0.934	3100	18.26	41.9
<b>Tu-03-13I<sub>R</sub></b>	SC-642	0.934	3100	37.41	12.7
<b>Tu-03-08</b>	SC-641	0.958	3000	15.07	40.7

**Table 6A.2** Work Index (Wi) of selected Tulameen samples ground for 2 hours (except as noted) that were used in the carbonation tests.  $R^2$  values are for trend lines extrapolated from sieve analyses to obtain feed  $D_{80}$  sizes. Product  $D_{80}$  is an average of two runs of milled products in a Micromeritics 5100 Sedigraph. Note that sample Tu-03-13I<sub>R</sub> is a repeat grind of sample Tu-03-13I for 30 minutes, which explains the coarser size fractions and lower Wi.



**Weight distribution of jaw crush product retained on different sieve sizes for each sample**

Sieve No. <sup>1</sup>	Opening (µm)	Tu-03-13G		Tu-03-13I		Tu-03-13B		Tu-03-13D		Tu-03-13A		Tu-03-08	
		wt (g)	wt (%)	wt (g)	wt (%)	wt (g)	wt (%)	wt (g)	wt (%)	wt (g)	wt (%)	wt (g)	wt (%)
+8	+2,360	259.7	36.23	198.6	39.77	186.5	37.40	219.9	43.52	243.8	48.92	193.6	37.78
8 x 16	2,360 x 1,180	143.9	20.07	103.4	20.70	119.5	23.96	115.1	22.78	113.8	22.83	115.1	22.46
16 x 30	1,180 x 600	76.8	10.71	46.9	9.39	58.2	11.67	52.9	10.47	53.8	10.79	57.2	11.16
30 x 50	600 x 300	85.2	11.88	44.6	8.93	39.7	7.96	36.9	7.30	34.6	6.94	40.4	7.88
50 x 100	300 x 150	71.2	9.93	42.4	8.49	27.8	5.57	28.5	5.64	22.4	4.49	34.4	6.71
100 x 200	150 x 75	40.9	5.71	29.8	5.97	20.7	4.15	21.3	4.22	13.6	2.73	29.4	5.74
200 x 400	75 x 38	21.8	3.04	17.5	3.50	18.2	3.65	14.1	2.79	8.1	1.63	21.0	4.10
-400	-38	17.4	2.43	16.2	3.24	28.1	5.63	16.6	3.29	8.3	1.67	21.4	4.18
Total		716.9	100	499.4	100	498.7	100	505.3	100	498.4	100	512.5	100

<sup>1</sup> U.S. Standard sieve series.

**Cumulative weight percent finer for each sample**

Sieve No. <sup>1</sup>	Opening (µm)	wt % finer		wt % finer		wt % finer		wt % finer		wt % finer		wt % finer	
		wt (g)	wt % finer	wt (g)	wt % finer	wt (g)	wt % finer	wt (g)	wt % finer	wt (g)	wt % finer	wt (g)	wt % finer
8	2360	457.2	63.77	300.8	60.23	312.2	62.60	285.4	56.48	254.6	51.08	318.9	62.22
16	1180	313.3	43.70	197.4	39.53	192.7	38.64	170.3	33.70	140.8	28.25	203.8	39.77
30	600	236.5	32.99	150.5	30.14	134.5	26.97	117.4	23.23	87.0	17.46	146.6	28.60
50	300	151.3	21.10	105.9	21.21	94.8	19.01	80.5	15.93	52.4	10.51	106.2	20.72
100	150	80.1	11.17	63.5	12.72	67.0	13.43	52.0	10.29	30.0	6.02	71.8	14.01
200	75	39.2	5.47	33.7	6.75	46.3	9.28	30.7	6.08	16.4	3.29	42.4	8.27
400	38	17.4	2.43	16.2	3.24	28.1	5.63	16.6	3.29	8.3	1.67	21.4	4.18

<sup>1</sup> U.S. Standard sieve series.

**Table 6A.3 Results from sieve analysis.**

## 7. Summary

Summarizing the key points from the preceding five chapters:

### ***7.1 British Columbia's Stationary Point Sources of CO<sub>2</sub> Emissions***

In British Columbia (BC), stationary point sources of CO<sub>2</sub> (>50,000 t/yr) include operations in aluminium and glass manufacturing; cement, chemical and smelting industries; oil and gas processing, coal operations; waste incinerators, pulp and paper mills, and potentially thermal power plants. These point sources total approximately 17 Mt of CO<sub>2</sub> equivalent for 2003, which is about 26% of BC's total estimated greenhouse gas emissions. Major single stationary points sources or clusters of smaller stationary sources with combined emissions in excess of 500 kt/yr are located in the Vancouver area, Fort Nelson (northeastern BC), Campbell River (Vancouver Island), Kitimat (west coast of central BC), Fort St. John (northeastern BC), and Elkford (southeastern BC).

### ***7.2 Matching Sources to Sinks***

British Columbia has a variety of potential sinks for geological sequestration of CO<sub>2</sub>, including injection into depleted gas reservoirs, possibly combined with enhanced gas recovery, and injection into deep saline aquifers in the Western Canadian Sedimentary Basin in northeastern BC. Further sinks that should be considered include deep coal beds, with the potential for enhanced coalbed methane recovery, in southeastern, northeast and southern interior of BC, as well as in the Comox area on Vancouver Island. Mg-silicate-bearing ultramafic rocks underlie large tracts of land, indicating a promising resource for the mineral CO<sub>2</sub> sequestration process. The technologies associated with these methods are not at the same level of development. The most mature methods (acid gas injection and injection into depleted gas reservoirs) will most likely be implemented first and the use of less mature methods (injection into deep coalbeds and mineral sequestration) will depend on results of active demonstration projects and bench scale tests worldwide.

### ***7.3 Methodology for Assessing Mineral CO<sub>2</sub> Sequestration Potential***

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 CO<sub>2</sub> sources, type of material (dunite or serpentinite) and tonnage. Mineralogical investigation in

combination with whole rock chemical analyses of selected material will provide insight into the presence of unwanted minerals that interfere with the carbonation reaction. Most suitable raw materials covered by this study are those with high MgO and low FeO, CaO, LOI, CO<sub>2</sub> and low H<sub>2</sub>O 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, the reaction products of the mineral carbonation process, may have industrial applications.

#### ***7.4 British Columbia's Distribution of Ultramafic Complexes***

Dunites and serpentinites, rocks composed primarily of Mg-silicates, are considered the most suitable raw material for the mineral CO<sub>2</sub> sequestration process. These rock types are found primarily within ultramafic complexes. Their geographical distribution in BC is restricted to a long, narrow belt, trending from northeastern BC to southcentral BC, which is intimately associated with accreted Mesozoic ocean basins and island arc terranes. 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. Based on this map, less than 3% of BC's surface is underlain by ultramafic rocks containing dunite and/or serpentinite.

#### ***7.5 Mineral Carbonation Potential of Tulameen Dunite Core***

The Tulameen ultramafic complex in southcentral British Columbia was selected for potential source of raw material for mineral CO<sub>2</sub> sequestration. Representative dunites, dunitic breccia and serpentinized dunites were collected and examined by means of microscopic investigation, geochemical (including major oxides, LOI, water and trace elements) and microprobe analysis. Theoretical carbonation potential, R<sub>CO<sub>2</sub></sub>, was calculated and compared with US studies. Rock samples were prepared and carbonated for one hour in an autoclave at the Albany Research Center, Oregon. CO<sub>2</sub> analysis in reaction products (up to 29.4 wt%) suggests 48 to 56% conversion for the dunites and 18% for a serpentinized dunite. As expected, feed with highest MgO and lowest LOI content, indicative of low level of impurities and minimum degree of serpentinization, reaches highest conversion rates. Based on carbonation test results, one tonne of Tulameen dunite could potentially sequester up to 0.4 tonnes of CO<sub>2</sub>. Recovery of chromium by magnetic separation may offset part of the sequestration costs.

## 7.6 Future Recommendations

Recommendations for future study includes the following:

- Examination of reaction products from carbonation tests by means of scanning electron microscopy could reveal whether magnesite and silica have suitable quality for industrial or construction applications.
- Analysis of magnetic fraction recovered from feed prior to carbonation will give an indication of percent and quality of chromite. This will be important when considering recovery of chromium to offset part of sequestration costs.
- Optimization of particle size for carbonation tests is still possible and should be investigated further, as grinding of raw feed is one of the major costs involved in the *ex situ* mineral CO<sub>2</sub> sequestration process.