

## MINERAL CARBONATION AS A POTENTIAL CARBON DIOXIDE STORAGE OPTION FOR THE REGION OF WESTERN MACEDONIA, GREECE

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### Abstract

*The long-term storage of the greenhouse gas CO<sub>2</sub> generated by fossil fuel-fired power plants in the form of stable mineral carbonates appears to be a promising option for reducing global CO<sub>2</sub> emissions. In the case of mineral carbonation captured gaseous CO<sub>2</sub> is chemically stored in an exothermic reaction by the carbonation of magnesium or calcium silicate minerals, forming environmentally benign and thermodynamically stable products. The purpose of this paper is to give an overview of the carbon dioxide storage by mineral carbonation and to examine the feasibility of this sequestration option in the region of Western Macedonia. The main candidate minerals for carbonation and their sequestration capacity are presented. Furthermore, the most promising mineral carbonation process routes as well as the thermodynamics and kinetics of carbonation reaction are addressed, based on a review on the published literature. In Greece abundant magnesium-rich ultramafic rocks exist that probably could support the national CO<sub>2</sub> emissions abatement policy. The attractiveness stems from the favourable geographical relationship between large stationary CO<sub>2</sub> emission sources and potential magnesium silicate deposits. Thus, a roughly description of the olivine deposits and their quality in the region of Western Macedonia will be provided.*

**Keywords:** chemical fixation, reaction kinetics, olivine, Vourinos ophiolites.

### Περίληψη

*Η μακροπρόθεσμη αποθήκευση του διοξειδίου του άνθρακα, του κυριότερου αερίου του θερμοκηπίου που εκλύεται από την καύση ορυκτών καυσίμων στους ηλεκτροπαραγωγικούς σταθμούς, υπό τη μορφή στερεών ανθρακικών ορυκτών αποτελεί μια πολλά υποσχόμενη μέθοδο για την μείωση των εκπομπών CO<sub>2</sub> σε παγκόσμιο επίπεδο. Στην περίπτωση της ορυκτοποίησης (mineralization) το δεσμευμένο αέριο CO<sub>2</sub> αποθηκεύεται χημικά αντιδρώντας με πυριτικά ορυκτά πλούσια σε μαγνήσιο ή ασβέστιο. Από την εξώθερμη αυτή αντίδραση σχηματίζονται φιλικά προς το περιβάλλον και θερμοδυναμικά σταθερά προϊόντα. Η συγκεκριμένη εργασία στοχεύει σε μια προεπισκόπηση της μεθόδου αποθήκευσης του διοξειδίου του άνθρακα υπό μορφή ανθρακικών ορυκτών αλλά και σε μια αρχική διερεύνηση της εφικτότητας αυτής της τεχνολογίας στην περιφέρεια της Δυτικής Μακεδονίας. Θα παρουσιαστούν*

οι κυριότερες ομάδες υπερβασικών πετρωμάτων κατάλληλων για ορυκτοποίηση καθώς και η αποθηκευτική τους ικανότητα. Επίσης θα αναφερθούν οι διεργασίες της μεθόδου με τις μεγαλύτερες προοπτικές καθώς και η θερμοδυναμική και κινητική της αντίδρασης του διοξειδίου του άνθρακα με τα πυριτικά ορυκτά με βάση μια βιβλιογραφική ανασκόπηση. Στην Ελλάδα υπάρχουν άφθονα υπερβασικά πετρώματα πλούσια σε μαγνήσιο που θα μπορούσαν πιθανόν να συμβάλλουν σημαντικά στην εθνική προσπάθεια εξάλειψης των εκπομπών διοξειδίου του άνθρακα. Η ελκυστικότητα αυτής της μεθόδου σε εθνικό επίπεδο απορρέει από την ευνοϊκή γεωγραφική θέση σημαντικών κοιτασμάτων πυριτικών ορυκτών πλούσιων σε μαγνήσιο σε σχέση με μεγάλες σημειακές πηγές εκπομπών CO<sub>2</sub>. Για αυτό το λόγο θα γίνει μια πρωταρχική προσέγγιση του δυναμικού και της ποιότητας των ολιβινικών αποθεμάτων στην περιφέρεια της Δυτικής Μακεδονίας.

**Λέξεις κλειδιά:** χημική δέσμευση, κινητική αντίδρασης, ολιβίνης, οφειόλιθοι Βούρινου.

## 1. Introduction

Fossil fuel combustion produces CO<sub>2</sub>, the main anthropogenic greenhouse gas, which when released into the atmosphere is responsible for enhancing the greenhouse effect leading to global warming. Fossil fuels are the main energy source and will continue to dominate global energy use. By 2030 it is projected that more than 80 % of the world primary energy will be met by fossil fuels. The increased global demand for energy will in turn result in CO<sub>2</sub> emissions increasing by about 62 % (A Strategy for Developing Carbon Abatement Technologies for Fossil Fuel Use, Carbon Abatement Technologies Programme, *Department of Trade and Industry (DTI), Department for Environment Food and Rural Affairs (DEFRA), June 2005, UK*). In order to reduce the CO<sub>2</sub> emissions from fossil fuel-fired power plants effective mitigation actions should be undertaken including higher efficiency conversion processes, fuel switching to low carbon or carbon-free energy sources and CO<sub>2</sub> capture and storage methods (CCS). CCS technologies offer a great potential in reducing the CO<sub>2</sub> emission (up to 85 %) from fossil fuel power plants (A Strategy for Developing Carbon Abatement Technologies for Fossil Fuel Use, Carbon Abatement Technologies Programme, June 2005, UK). The paper focuses only on carbon dioxide sequestration not capture, since different capture processes could be integrated. Potential technical storage methods are: geological storage (in underground permeable and porous rock formations), ocean storage (direct release into the ocean water column or onto the deep seafloor) and industrial fixation of CO<sub>2</sub> into mineral carbonates (IPCC 2005).

**Table 1 - Main Power Plants in Western Macedonia Region and CO<sub>2</sub> emissions in 2005**

Power Plant	Installed capacity	Emissions (kt CO <sub>2</sub> /yr)
PPC S.A., TPS Ag. Dimitriou	1595 MW	13,629
PPC S.A., TPS Kardias	1250 MW	9,815
PPC S.A., TPS Ptolemaidas	620 MW	3,488
PPC S.A., TPS Amyndaiou	600 MW	5,124
PPC S.A., TPS Florinas	330 MW	1,956
PPC S.A., TPS Liptol	43 MW	358
Total		34,371

Mineral carbon dioxide sequestration has three positive attributes compared to the rest storage options. First the carbonation reaction is exothermic and can theoretically produce energy as the

formed mineral carbonates represent a lower energy state than CO<sub>2</sub>. Secondly, the sequestration capacity is large since the magnesium and calcium silicate deposits are available worldwide in quantities greater than the known fossil fuel reserves. Finally, the products of mineral carbonation occur naturally as stable solids because they are thermodynamically favoured. Their formation is due to natural CO<sub>2</sub>-rich fluids percolating through mineral deposits. Therefore, the storage of carbon dioxide is permanent and safe, eliminating the need to monitor the storage sites (Goff and Lackner 1998, Lackner *et al.* 1995).

Greece, as the second largest producer of lignite within the European Union, generates almost 93% of its electrical power requirements from fossil fuels with lignite accounting for about 64% of the total. There are two lignite centres, Ptolemais-Amynteo (LCPA) in the region of Western Macedonia and Megalopolis (LCM) in the southern region of Peloponnese. The proven lignite reserves of LCPA are 4.3 billion tons, corresponding to the 2/3 of the total lignite deposits of Greece, with an annual production reaching 50 million tons (Koukouzas 1998). The largest Public Power Corporation's lignite-fired power plants in LCPA, representing 70 % of the total electricity production are located in the region of Western Macedonia. As a result, 80 % of the total annual CO<sub>2</sub> emissions from the Greek lignite-fired electricity generation sector (43,041 kt/ yr CO<sub>2</sub>) derive from this region, as illustrated in Table 1 (Psomas 2006).

The disposal of carbon dioxide via the creation of magnesium or calcium carbonate solids as a sequestration option to mitigate climate change could enable lignite, Greece's only indigenous energy carrier, to stay competitive assuring the national energy security, the economic development as well as the environmental protection.

## 2. Selection of minerals for the chemical fixation of carbon dioxide

Calcium and magnesium oxides are generally selected for mineral CO<sub>2</sub> sequestration purposes and are bound as a chemical combination with other oxides in the form of a silicate matrix. These silicate minerals are capable of being carbonated because the stronger carbonic acid is exchanged with the weaker silicic acid (H<sub>4</sub>SiO<sub>4</sub>) (Huijgen and Comans 2003). These oxides are found in large quantities in ultramafic igneous rocks within large ophiolite complexes, exceeding the amount required for binding the carbon dioxide generated by fossil fuels combustion (Lackner *et al.* 1997). Although carbonation of calcium oxide is easier, the use of magnesium-based minerals (dunites, peridotites, and serpentinites) is favoured because they are available worldwide in large amounts and in relatively high purity (Huijgen and Comans 2003). The amount of oxide required to bind carbon dioxide from burning one ton of carbon, additionally, favours magnesium oxide at 3.3 tons compared to 4.7 tons of calcium oxide (Lackner *et al.* 1995). The composition of Mg-bearing rocks and their specific CO<sub>2</sub> sequestration capacity are listed in table 2. (Lackner *et al.* 1995, Huijgen and Comans 2003).

**Table 2 - Composition of peridotites, serpentinites and their carbon dioxide sequestration capacity. R<sub>c</sub> =mass ratio of rock needed for CO<sub>2</sub> fixation to carbon burned. R<sub>CO2</sub> = corresponding mass ratio of rock to CO<sub>2</sub>**

Rock	MgO [wt%]	CaO [wt%]	R <sub>c</sub> [kg/kg]	R <sub>CO2</sub> [kg/kg]
Peridotites				
Dunite	49.5	0.3	6.8	1.8
Harzburgite	45.4	0.7	7.3	2.0
Lherzolite	28.1	7.3	10.1	2.7
Serpentinite	~40	0	~8.4	~2.3

### 3. Thermodynamics and kinetics of carbonation reaction

The carbonation reactions of pure magnesium and calcium oxides are quite exothermic. The heat released can be compared to that one from the coal combustion (394 kJ/mol) (Lackner *et al.* 1997):



Respectively, the carbonation reactions of calcium and magnesium oxides occurring as silicate minerals are still exothermic though to a lesser extent (Lackner *et al.* 1997):



Actually, the carbonation reaction proceeds very slowly at room temperature and pressure. At ambient temperatures and 1 bar of CO<sub>2</sub> pressure, the Gibbs free energy of the reaction favours the formation of carbonates (below 200 °C). Although the temperature increase would overcome any activation energy barrier and improve the reaction kinetics, the chemical equilibrium favours gaseous CO<sub>2</sub> over the carbonates at high temperatures due to entropy effects (Huijgen and Comans 2003). At 1 bar of CO<sub>2</sub> pressure, the temperature limit is 900 °C for calcium carbonate and 410 °C for magnesium carbonate (Lackner *et al.* 1997).

### 4. Mineral Carbonation Process Routes

Two approaches for the carbonation of calcium and magnesium oxides can be distinguished:

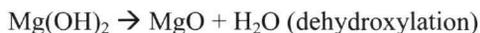
- Direct carbonation, where the mineral is carbonated in one step either in a direct dry gas-solid reaction or in an aqueous solution.
- Indirect carbonation, in which the reactive component is first extracted from the mineral structure by using various agents and then carbonated in a separate step at elevated pressure and temperature.

#### 4.1. Mineral pre-treatment options

Many of the mineral carbonation processes include a pre-treatment option such as size reduction (crushing, grinding and milling), magnetic separation extraction of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and thermal treatment in order to accelerate the slow carbonation reaction kinetics. This is achieved by activating the reactive surface which in turn will speed up the metal oxide extraction from the mineral feedstock. However, the improved carbonation reactivity achieved by these pre-treatment activations is counteracted by the high energy requirements.

#### 4.2. Direct gas-solid carbonation at high temperatures

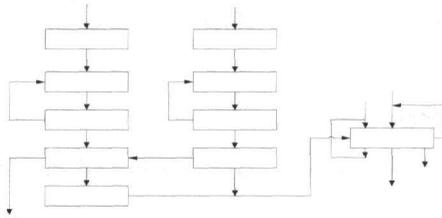
The direct reaction of gaseous CO<sub>2</sub> with Mg-bearing silicate minerals (olivine or serpentine) in the solid state at suitable temperature and pressure levels is the simplest process. Moreover, the heat is released at elevated temperatures with minimum dilution. Since this process takes place too slowly at room temperatures, higher temperatures are required. However, if the temperature exceeds the calcination point, the chemical equilibrium shifts and the carbonation will not occur. Carbonation at atmospheric pressure and various temperatures (140 to 300 °C) was insignificant even when the experiments lasted for days (Lackner *et al.* 1995). Therefore, the direct carbonation requires high CO<sub>2</sub> pressures or pre-treatment activation in order to obtain adequate reaction rates. However, as currently understood, this method does not appear to have a potential to become an industrially viable process. On the other hand, the carbonation rate of Mg(OH)<sub>2</sub> appears to have a practical interest and proceeds in two steps occurring simultaneously (Huijgen and Comans 2003).



The optimum temperature reported is 375°C (Huijgen and Comans 2003). During the dehydroxylation of the hydroxide, fractures are formed into the crystal structure providing a greater reactive surface and thus a higher reactivity of Mg (OH)<sub>2</sub> compared to MgO (Lackner *et al.* 1997). The steam may also play a catalytic role.

### 4.3. Aqueous direct carbonation route

From natural serpentinization reaction of ultramafic minerals, it is known that the presence of water induces reactions. Based on this principle, aqueous direct carbonation route refers to a process which utilizes a slurry of fine particle sized mineral in water with solid concentration from 15 to 30 %, at elevated temperature (below 200 °C) and high CO<sub>2</sub> pressure. A process flow diagram of the aqueous process route is illustrated in Figure 1 (Goldberg 2001). Optimal conversions reported are 91 % in 6 hours for olivine at 185 °C and 34 % in 6 hours for serpentine at 155 °C (80 % of minerals ground to <37 μm and P<sub>CO2</sub> of 150 atm) (O'Connor *et al.* 2005).



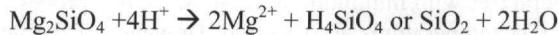
**Figure 1 - Process flow diagram of the aqueous direct carbonation route**

The aqueous mineral CO<sub>2</sub> sequestration is conducted via three reactions that take place simultaneously in one reactor (O'Connor *et al.* 2005):

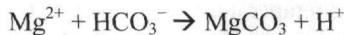
First, CO<sub>2</sub> is dissolved in distilled water to form carbonic acid which dissociates to bicarbonate and H<sup>+</sup>:



Then, mineral hydrolysis liberates Mg<sup>2+</sup> cations from the olivine matrix with co-production of silica acid or free silica and water:



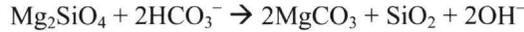
Finally, the Mg<sup>2+</sup> cations react with bicarbonate ions to form magnesite:



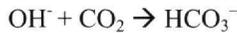
In aqueous carbonation the rate-limiting step appears to be the dissolution rate of the minerals, although the formation of carbonic acid also plays an important limiting role. Since dissolution is surface-controlled, the formation of silica or carbonates layers on the dissolving mineral particles tends to hinder further carbonation (Huijgen and Comans 2003, IPCC 2001). The operating parameters such as mineral particle size, CO<sub>2</sub> pressure and temperature determine the dissolution extent. The use of high CO<sub>2</sub> pressure and the mineral pre-treatment (fine grinding, heat treatment of serpentine) are energy consuming. On the other side, the temperature raise improves the

dissolution kinetics but the carbonate precipitation slows down due to reduced solubility of carbon dioxide and the change in the available free energy (O'Connor *et al.* 2005).

In order to further improve the reaction extent, a bicarbonate/salt mixture (NaHCO<sub>3</sub>/NaCl) in water with concentrations 1 M NaCl and 0.5-0.64 M NaHCO<sub>3</sub> can be used. The NaHCO<sub>3</sub> addition increases the HCO<sub>3</sub><sup>-</sup> concentration favouring the carbonate precipitation. An increase of 0.5-1.0 g/l CO<sub>2</sub> in distilled water to 20 g/l CO<sub>2</sub> in a NaHCO<sub>3</sub>/NaCl-solution has been reported (Huijgen and Comans 2003). Conversion of nearly 80 % was achieved for olivine in 30 minutes in test conditions of 155 °C and 185 atm P<sub>CO<sub>2</sub></sub>. The solution is buffered at pH 7.7 to 8.0 and the reaction sequence is modified to (O'Connor *et al.* 2005):



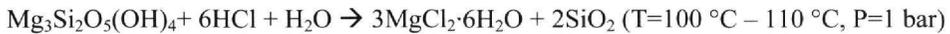
The bicarbonate is almost immediately regenerated due to the reaction of the hydroxyl ion with gaseous carbon dioxide:



Thus, the addition of NaCl increases the ionic strength of the solution, lowering the magnesium activity. Furthermore, the Mg<sup>2+</sup> cations solubility is enhanced by creating soluble complexes (MgCl<sub>2</sub>, MgCl<sub>3</sub><sup>-</sup>, MgCl<sub>4</sub><sup>2-</sup>, etc.), (Huijgen and Comans 2003).

#### 4.4. Carbonation route by hydrochloric acid extraction

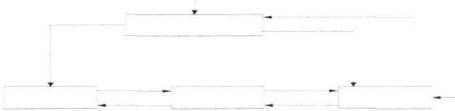
Serpentine or forsterite dissolve in a solution containing about 20% hydrochloric acid forming hydrated magnesium chloride and silica gel (Fig. 2), (Lackner *et al.* 1997). Consequently, the magnesium content is extracted. Silica precipitates simultaneously with the iron oxide content of the feedstock (8 to 10 %), after raising the pH of the solution by neutralizing the solution with MgCl(OH), which is generated in another step of the process. For serpentine the process steps are (Lackner *et al.* 1997):



Consecutively, the MgCl<sub>2</sub>·6H<sub>2</sub>O is hydrolyzed at 200 to 250°C. Initially, the associated water is removed, resulting in MgCl<sub>2</sub>·H<sub>2</sub>O and finally, the hydrochloric acid is recovered by further heating. The acid recovery is the only endothermic stage of the process. The temperature increase during this step enables the hydrogen chloride and the water to be removed as vapour:

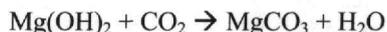


Then, Mg(OH)Cl disassociates in an aqueous solution into magnesium hydroxide and magnesium chloride, according to the following reaction:



**Figure 2 - Process flow diagram for Mg carbonation route by HCl extraction. The mass flows correspond to CO<sub>2</sub> emissions of a 1GW power plant with 33% conversion efficiency**

Finally, the precipitated  $\text{Mg}(\text{OH})_2$  is nearly completely carbonated in thirty minutes, at elevated temperatures (500-600 °C) and pressures of 50 bar enabling the better use of the heat released by the exothermic reaction:



The hydrochloric acid should be effectively regenerated after dissolving the magnesium component of the rock. All chlorides are passed on to the acid recovery step in the form of magnesium chloride and thus, great losses of hydrochloric acid could be caused by the formation of alkali metal chlorides. Fortunately, typical serpentine or peridotite are essentially free of alkali metals (<0.5 wt-%) (Lackner *et al.* 1997).

## 5. Comparison of process routes

Besides the straightforward design, the main advantage of the direct dry routes is that the heat released during the carbonation reaction is available at high temperatures and thus, can be applied in other parts of the process. Nonetheless, the reaction rate is too low at thermodynamically allowed temperatures and the  $\text{CO}_2$  pressure needed is higher compared to indirect process routes (Huijgen and Comans 2003).

Despite the fact that aqueous mineral carbonation has achieved acceptable conversion rates, the current need for energy-intensive heat treatment leads to high process costs. Moreover, due to the high degree of dilution into a large amount of water and the lower reaction temperature, the heat of the reaction is not practically useful. Another possible disadvantage of the aqueous route with modified solution chemistry is the need for additional chemicals in the case of their incomplete recovery (IPCC 2001).

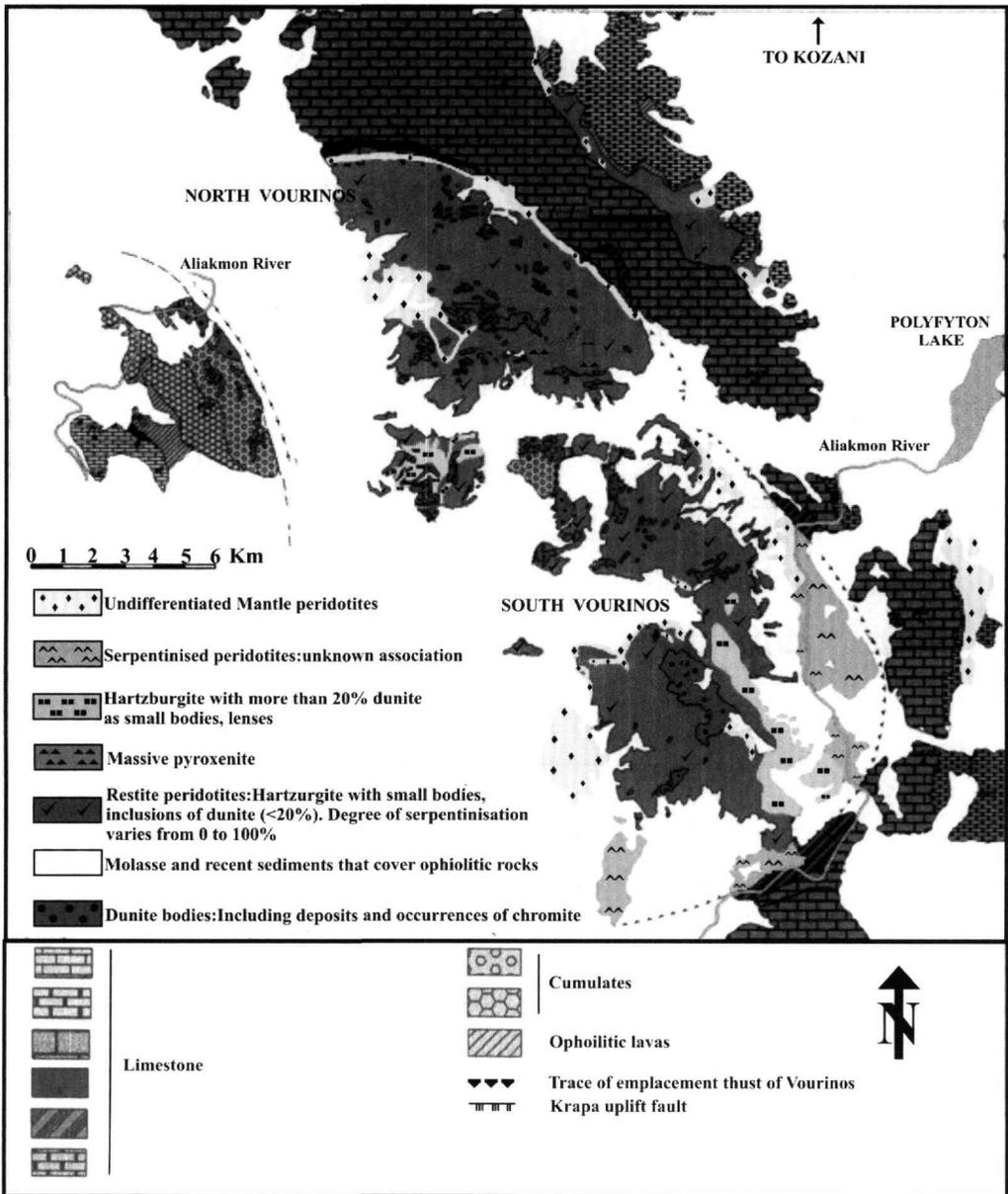
In contrast, the hydrochloric acid extraction route requires a net energy input for the regeneration of the acid due to the fact that water evaporation and condensation steps occur at temperatures higher than the exothermic steps (Lackner *et al.* 1997). Another preoccupation appears to be the costs associated with the use of hydrochloric acid owing to its highly corrosive nature and the excessive make-up needs (Haywood *et al.* 2001).

## 6. Magnesium silicates in Western Macedonia

There are three ophiolitic belts of late Jurassic age occurring in West Macedonia. The eastern is a series of tectonic fragments, serpentinised ultramafic mantle rocks, at the borders of West Macedonia and Veria city (mountain Vermion). The major ophiolitic belts are those exposed at Mount Vourinos and the mountain chain of Pindos.

The Pindos ophiolite complex of NW Greece is located in the Subpelagonian Zone and covers an area of about 2000  $\text{Km}^2$ . Peridotites extend over at least 600  $\text{Km}^2$  (Dabitzias and Rassios 2000). This complex is composed of several tectonic units. The uppermost tectonic unit is the Pindos Ophiolite Group. The Ophiolite Group is divided into three sub-units (from top to bottom): i) the Dramala Complex consists of locally serpentinized, depleted mantle harzburgite, dunite, pyroxenite, and assorted ultramafic cumulates that directly overlie ii) the Loumnitsa Unit which is the metamorphic sole of the ophiolite; iii) the Aspropotamos Complex is an ophiolitic horizon containing dismembered ultramafic cumulates, intrusives, and mafic extrusives.

The Vourinos Ophiolite Complex was emplaced on the Western margin of the Pelagonian zone during Late Jurassic-Early Cretaceous times (Mountrakis 1983, Mountrakis 1986, Smith 1979). The Vourinos Ophiolite Complex (Fig. 3, Margaras and Vacondios 1996) with minimal stratigraphic disruption, is exposed over an area of about 30 km by 15 km at an estimated thickness of 10 km, 30 km SW of the city of Kozani (Brunn *et al.* 2004, Ross *et al.* 1980).



**Figure 3 – Simplified Geological map with Magnesium silicate deposits of Vourinos Ophiolite Complex**

Hartzburgites with interlaminated dunites in equal proportions comprise about 85 % of Vourinos Complex (Ross *et al.* 1980). In addition, mafic and ultramafic cumulates, diorites, sheeted dikes, pillow lavas, amphibolites and metamorphic sediments parts of the sole are present (Moore 1969, Rassios *et al.* 1983) while a layer of a Late Jurassic calcipionellid limestones lies on the ophiolites (Mavrides *et al.* 1977). Within the northern block of Vourinos Ophiolite Complex, the thickness of the individual unserpentinized ultramafic rocks layers varies from a few centimetres to several meters while layers of dunite vary in thickness from 10 m to 200 m with higher degree of serpentinization within the southern block, (Ross *et al.* 1980). However, the largest dunite deposits of Vourinos Complex are those of Xerolivado whose lengths are greater than 5 km (Dabitzias and Rassios 2000). In addition, fresh slightly serpentinized dunites and hartzburgites occur in a belt

20 km long and 0.5 to 1 km thickness, between the basal thrust sole of the ophiolite and the zone of chromites (Dabitzias and Rassios 2000).

## 7. Investigation of mineral carbonation's potential in Western Macedonia

According to chemical analyses carried out by the Institute Of Geology & Mineral Exploration, olivine, chromite, and orthopyroxene (average content 8 %) are the main mineralogical phases of these deposits. The range of the major elements' concentration is listed in Table 3. (Institute of Geology & Mineral Exploration, Greece). These Mg-rich silicate minerals with an average MgO content ~ 45 wt-percent and little pyroxene represent desirable ores for the chemical fixation of carbon dioxide (Lackner *et al.* 1997).

**Table 3 - The range of the chemical composition (in wt- %) of ultramafic rocks from Vourinos Complex**

SiO <sub>2</sub>	40.64 - 42.78
Al <sub>2</sub> O <sub>3</sub>	0.38 - 0.57
Fe <sub>2</sub> O <sub>3</sub>	8.00 - 8.72
CaO	0.28 - 0.98
MgO	43.52 - 46.52
K <sub>2</sub> O	0.01
Na <sub>2</sub> O	0.03
MnO	0.10 - 0.13
TiO <sub>2</sub>	0.01
Cr <sub>2</sub> O <sub>3</sub>	0.34 - 1.59
NiO	0.31 - 0.34
LOI	1.50 - 3.37

TPS AG. DIMITRIOU and TPS KARDIAS, the largest power plants in the region, are located at the favourable distance of 50 km from the potential mineral resources of the Vourinos Complex (Fig. 3). Due to their proximity, an integrated concept of mineral carbonation and carbon dioxide capture should be considered. Based on the average MgO content (45 % by wt) in the regional silicate ores (Table 3), it has been estimated that for the sequestration of 1t CO<sub>2</sub>, 2.82 t of ultramafic ore should be mined and processed, assuming 90 % ore recovery and 80 % conversion in the carbonation reaction. In addition, about 99 Mt/yr of ore will be needed to fix all the carbon dioxide output of the regional power plants, requiring a deposit with an estimated volume of at least 0.03 km<sup>3</sup> (average peridotites density ~3.3 g/cm<sup>3</sup>, Goff and Lackner 1998). Considering only the serpentinized dunites and harzburgites body at Xerolivado (20 km long, 0.5 km thick and assumed 0.5 km wide), it could be concluded that this deposit alone could dispose of all the carbon dioxide emissions of the region for over one hundred years. Nonetheless, these values represent only a rough estimate. For this reason, a more detailed evaluation of the available silicate resources should be made so as to assess with higher certainty the sequestration reactivity for the regional mineral deposits. Furthermore, the disposal of carbonate waste, due to large chrome mining activities conducted in the past, could probably fill the large open pits left accelerating the landscape reclamation in Vourinos Complex.

Intensive research activities related to the further development of the carbonation process are currently carried out by the DOE-funded Mineral Carbonation Research Cluster which consists of Los Alamos National Laboratory, Albany Research Center, Arizona State University, National Energy Research Laboratory, and Science Applications International Corporation. It is worth mentioning that a bilateral collaboration of CERTH/ISFTA (Centre for Research & Technology Hellas / Institute for Solid Fuel Technology & Applications) in Greece and LANL (Los Alamos

National Laboratory) has recently started in the field of mineral carbonation. The aim of this project is to provide some basic information concerning the implementation's feasibility of this concept to fossil fuel-fired power plants located in the region of Western Macedonia.

Within this project the composition and quality of various samples from regional silicate deposits will be characterised through a series of mineralogy and chemical analyses. In addition, laboratory carbonation tests will be carried out in order to get some basic data about the carbonation reactivity of these samples in a range of different temperatures and pressures.

In the case that the results of the experiments show promise further studies will then be focused on:

- Assessing the actual scale of the minerals required for an industrial-scale operation in order to identify the location of the mineral carbonation plant at the mineral site or at the fossil fuel-fired power plant.
- Evaluating the economic feasibility of CO<sub>2</sub> sequestration by mineral carbonation in the Region of Western Macedonia taking into account the energy requirements as well as the production of value-added by-products, such as silicon, chrome bound as chromite etc. that may offset the carbonation costs.
- Addressing the potential environmental issues related to mineral carbonation such as the large-scale open pit mining impact, the extra emissions due to the increased energy consumption, and the disposal of tailings.

## 8. Conclusions

On the whole, sequestration of carbon dioxide in mineral form appears to be an attractive option due to many fundamental advantages such as:

- Long term stability since the products of mineral carbonation occur naturally as stable solids due to natural CO<sub>2</sub>-rich fluids percolating through mineral deposits. In addition the formed are thermodynamically stable providing a permanent and safe storage of carbon dioxide and thus, eliminating the monitoring requirements.
- Vast capacity of ultramafic rocks suitable to fix carbon dioxide far exceeding the known fossil fuel reserves.
- Potential to be economically viable owing to the exothermic nature of the carbonation reaction.

Currently, the main challenge is the development of faster carbonation reaction rates in a cost-effective and energetically acceptable way so as to maximize the competitive advantages of this concept.

At national level, mineral carbonation merits further investigation as a promising technology for carbon dioxide abatement. At first glance, the sequestration potential of Western Macedonia appears considerable. The basic geology of Vourinos Complex is well-known and the distribution and volume of Mg-rich rocks is significant. In addition, the proximity of the mineral deposits to large CO<sub>2</sub> sources is another positive attribute. However, a more detailed mapping and evaluation of the magnesium silicate mineral resources is recommended in line with the results generated by the laboratory tests in order to determine the scale of application for mineral carbonation.

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