

## A REVIEW OF MINERAL CARBONATION BY ENHANCED WEATHERING

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### Abstract

Climate change mitigation efforts have so far failed to achieve rapid rates of de-carbonisation. A technical possibility can still be realised. However, the long residence time of CO<sub>2</sub> in the atmosphere would continue the warming trend for the foreseeable future even if emissions were immediately cut to zero. Geoengineering methods provide a useful complement to mitigation and adaptation. The emission of CO<sub>2</sub> from power stations operating on fossil fuel and other sources can be handled by only three types of storage technologies including: (1) ocean storage, (2) geological storage (geosequestration), and (3) CO<sub>2</sub> mineralization or mineral carbonation (geomimicry). This last option provides a permanent solution to storing CO<sub>2</sub> safely on a geological time scale. The high cost and elevated energy requirements are preventing this technology from reaching industrial scale. Ultramafic complexes and serpentinite bodies are major sources of magnesium-rich minerals like olivine and serpentine, which can be carbonated by using CO<sub>2</sub>. The ultramafic rocks of the Great Serpentinite Belt (GSB), northern New South Wales, Australia, have been identified as a high-potential feedstock for mineral carbonation. These deposits indicate variable degrees of carbonation. The source of carbon in ultramafic rocks hosted magnesite veins and deposits are still under debate but agreement appears to be emerging on their near surface formation at low temperature pressure condition. The petrographic and geochemical studies on serpentinite and magnesite have revealed the possibilities of finding the agent/catalyst that could enhance the process of carbonation by using the atmospheric CO<sub>2</sub>.

The list of advantages for Mineral Carbonation over alternative methods for large scale CO<sub>2</sub> sequestration is quite long and the fact that Pakistan has substantial amount of serpentinite, for example, in Taleri Mohammad Jan village near Hindubagh, opens up the opportunities to carry forward the study on Mineral Carbonation in Pakistan and this could reveal highly effective results.

**Keywords:** Mineral carbonation, Geosequestration, Serpentinite, Pakistan.

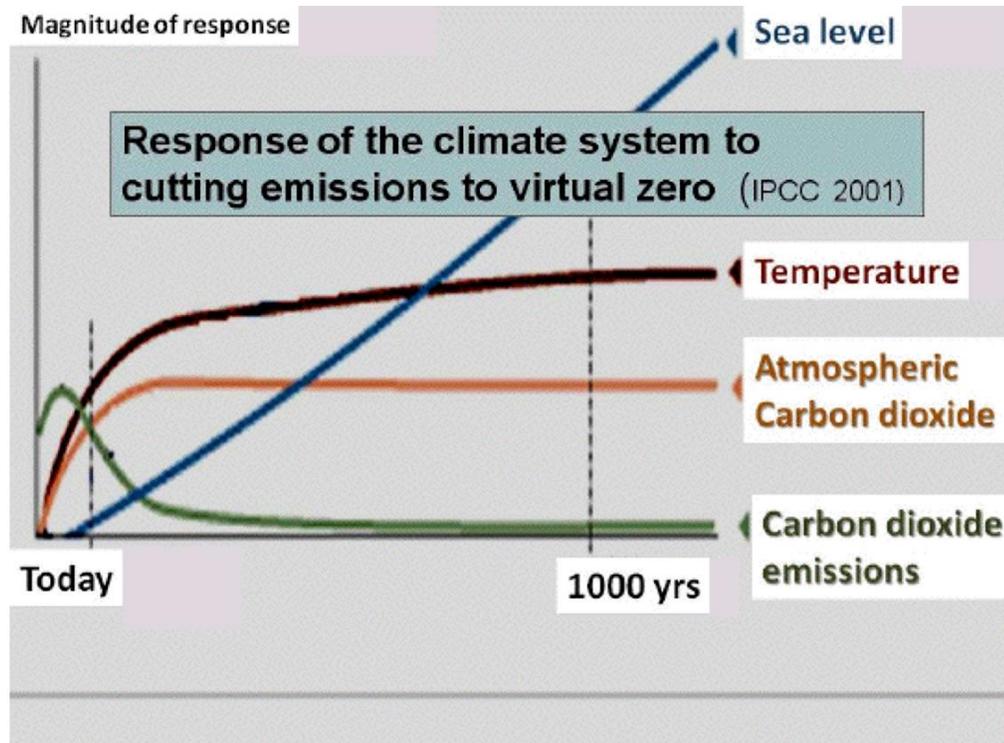
### Introduction

The effects of climate change induced by humans have become severe and it is damaging not just because of the magnitude but also because of its potential irreversibility. It has been demonstrated that the increase in carbon dioxide concentration in atmosphere that causes climate change is largely irreversible for 1,000 years (Figure 1, Solomon et al., 2009) and if carbon dioxide increases with the current rate, levels will peak to 450-600 ppm in the coming century and sea level will rise to 0.4m-1.0m with a drastic increase in global temperature (IPCC, 2010).

To stabilise the carbon dioxide concentration in the atmosphere, Erich Roeckner from Max-Planck Institute, Germany, and the leader of the team for IPCC for the future Fifth IPCC Assessment Report says that the emission has to be cut down to 56% by the year 2050 and approach zero by the end of the century. However, new numbers have shown the extent to which the international climate change policy has failed (<http://www.spiegel.de/international/world/0,1518,795978,00.html>). The concentration of Carbon Dioxide in the atmosphere was 360ppm in 1992 when the first "Earth Summit" in Rio de

Janeiro took place and after 20 years, it has risen to 390 ppm and there is no end in sight to the rising trend. It has to be considered that most of the CO<sub>2</sub> emission inventories and environmental studies excluded CO<sub>2</sub> emission from biomass combustion because biomass has been categorised as a renewable energy source and considered safe for the environment whereas Cherubini et al. (2011) have proposed that the CO<sub>2</sub> emission from biomass combustion for

bioenergy should also be included in the Life Cycle Assessment studies because combustion of biomass also plays a role in CO<sub>2</sub> emission. All these facts indicate that in order to reduce the present and future impact of drastically changing climate due to increasing CO<sub>2</sub> and greenhouse gases in the atmosphere, the world should concentrate on carbon capturing, storing technologies and their applications.



**Fig. 1.** To cut the CO<sub>2</sub> emission to zero now would still need 1,000 years for CO<sub>2</sub> in atmosphere to stabilise (IPCC, 2001).

One of the technologies for carbon capturing and storing it permanently, which is considered to be safe and effective, is called mineral carbonation. This is a geoengineering method in which silicate minerals are converted to carbonate minerals by the process of chemical weathering. This exothermic process, which uses up the CO<sub>2</sub> in this conversion, occurs very slowly in nature. Therefore by enhancing the process using catalysts or other means would increase the rate of the conversion substantially, hence capturing the CO<sub>2</sub> and locking it up for good. A number of research findings related to this carbon capturing technology already exist and have been published

in different journals as reports but a method that is cheap enough to be used commercially has not yet been found. One of the aims of this paper is to highlight the possibilities of achieving this target of developing a technology which can be used on industrial level.

The need for such technology has become crucial now because climate change has strongly impacted the already serious challenges against the fights for extreme poverty and diseases, especially in developing countries where drought, floods, water scarcity and increased health challenges like malnutrition are already in critical forms.

### Mineral Carbonation: Geoengineering method

Rapidly advancing scientific consensus is emphasising the need for a massive and rapid reduction of anthropogenic emissions of carbon dioxide, the most abundant “greenhouse gas”. Carbon dioxide from energy generation accounts for about 57% of the total anthropogenic emissions.

<http://www.edo.org.au/edonsw/site/pdf/casesum/>. It is the most obvious target for strategies aimed at reducing emissions. The current approach to controlling these emissions relies on demonstrating the suitability of existing technologies to capture large quantities of CO<sub>2</sub> usually in the order of 100 kt to 1 Mt per year at a single facility. Several technological options exist for capturing CO<sub>2</sub>, with demonstration plants in design or under construction in Australia and overseas. However, there is no point in capturing CO<sub>2</sub> without an effective strategy for storing what is captured and the technology for CO<sub>2</sub> storage lags far behind the carbon-capture technology. The permanent, risk-free storage of anthropogenic CO<sub>2</sub> remains an international and national problem.

Only three types of storage technologies have the capacity to handle CO<sub>2</sub> streams as large as the emissions from power stations operating on fossil fuels. The two most discussed are: (i) ocean storage, in which CO<sub>2</sub> is pumped to depths of at least 3000m, and (ii) geological storage, which involves injecting CO<sub>2</sub> into porous rocks “geosequestration”. However, neither the

geosequestration nor ocean storage provides a permanent solution. Carbon dioxide injected into the deep ocean may find its way back into the atmosphere (Haugan and Joos, 2004) and models show that 1% per year leakage from geological or ocean storage translates into zero reduction in atmospheric concentrations of CO<sub>2</sub> (Masao and Takashi, 2005). Furthermore, the location of geological basins does not coincide with the global distribution of CO<sub>2</sub> sources. This is especially evident in Asia (e.g., China and Japan) and in Northern New South Wales, Australia. Thus, the present reliance on geosequestration as the sole solution for storing CO<sub>2</sub> has important drawbacks.

The third option is mineral carbonation or CO<sub>2</sub> mineralisation in which the CO<sub>2</sub> is reacted with suitable rock materials. This technology is called “geomimicry” because it mimics the natural weathering of magnesium-rich silicate rocks to form stable magnesium carbonates (Figure 2); it is the only option that provides a permanent solution to storing CO<sub>2</sub> safely on a geological time scale (Goldberg et al., 2001; O’Connor et al., 2001; Guthrie et al., 2001; Blok et al., 1992; Lackner et al., 1995). At present, CO<sub>2</sub> mineralisation technologies suffer from high cost and elevated energy penalties because of the substantial kinetic barriers involved in starting the chemical reactions. These barriers have prevented the geomimicry technologies from proceeding to demonstration projects at industrial scale pilot plants.



Fig. 2. Magnesium silicate (green) in Oman naturally absorbed CO<sub>2</sub> to form magnesium carbonate, in white (Krevor, 2009).

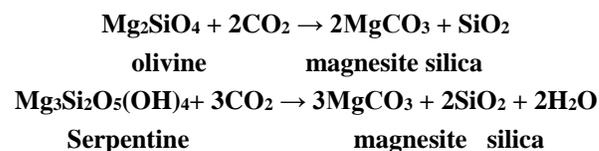
### Enhance Weathering

There are no fundamental reasons why other geomimicking pathways, in addition to those known today, should not exist. In particular, the free energy change of the transformation of magnesium silicates to carbonates (e.g.,  $\text{MgSiO}_3 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{SiO}_2$ ) is significantly negative and hence the products, carbonates and silica, are thermodynamically more stable than the reactants. The resources of magnesium silicate rocks are substantial, exceeding by hundreds of times the amount needed to sequester  $\text{CO}_2$  produced from burning all fossil fuels (Goldberg et al., 2001; Goff et al., 1997). These resources are also more evenly distributed around the world, with a particularly good share in Pakistan. However, breakthroughs in our knowledge of reaction kinetics, solid state diffusion and the geochemistry of ultramafic (mantle) rocks are needed to decrease the kinetic barriers and develop technologies for permanent storage of  $\text{CO}_2$  for their urgent deployment.

Invention of new processes and optimising the existing aqueous Albany Research Council (O'Connor et al., 2005) process for reacting  $\text{CO}_2$  with ultramafic rocks, especially with serpentinites, which constitute most of the world deposits of magnesium silicates (Goff et al., 1997; Goff and Lackner, 1998; Goff et al., 2000; Hunter, 1941), is the prime focus of today for the  $\text{CO}_2$  sequestration. With respect to serpentinite, the goal will be to circumvent the need for the thermal activation of these rocks and to decrease the pressure and temperature severity of the process by using chelates and moving the operating pH window to higher values. An attempt to invent pathways for an integrated process that combines  $\text{CO}_2$  capture from flue gases with  $\text{CO}_2$  storage and to investigate carbonation reactions in non-aqueous solvents are the two focus points.

Schuilung et al. (1986) have developed a process by which industrial waste acids are neutralised by reaction with olivine. Liefertink (1997) and Jonckbloedt (1997) described the products and process in more detail. Goldberg et al. (2001) proposed a similar approach which indicates that under right, conditions ground olivine reacts with compressed  $\text{CO}_2$  in autoclaves in a matter of hours in the presence of a suitable catalyst. Lackner et al. (1997) also reviewed the

sequestration of fossil carbon as carbonate and follow the simple reaction for this:



To establish ways of accelerating the kinetics of the complex reaction of  $\text{CO}_2$  with various silicates (serpentinites, especially lizardite and antigorite and single-chain inosilicate pyroxenes, especially enstatite) to form carbonates (and silica) needs a program that achieve this by making use of computational methods in order to gain a detailed understanding of how these minerals are put together chemically and specifically and also how they react with  $\text{CO}_2$  under various conditions of heat transfer, pressure, water,  $\text{H}^+$  availability and structural amorphisation. The 'parameter set' in this problem of reaction of silicates with  $\text{CO}_2$  is exceedingly large. It is simply not feasible to address it experimentally alone. Computational materials science has now matured to the extent that it can effectively guide the experimentation. The computational research program will identify smart strategies for 'exposing' the  $\text{Mg}^{2+}$  ions in these silicate structures according to imposed conditions. This is the key to accelerating the overall reaction kinetics. The computational methods of *ab initio*, molecular dynamics, molecular statics, kinetic Monte Carlo and finite element and various multi-scale hybrids can be employed.

### Attunga Magnesite Deposits NSW, Australia

It is now established that ultramafic complexes and serpentinite bodies are major sources of magnesium rich minerals like olivine and serpentine and  $\text{CO}_2$  can be used to carbonate these rocks. In Northern New South Wales, Australia, the Great Serpentine Belt (GSB) has been identified as a high-potential feedstock for mineral carbonation. It has also been generally accepted that the serpentinite of GSB are the host rocks for Attunga magnesite deposits and that they have been formed by the decomposition of serpentinite. These deposits occur as irregular veins and pockets of compact, nodular, high purity magnesite in the altered host rocks and indicate variable degrees of carbonation. The

sources of carbon in ultramafic rocks hosting magnesite deposits are debatable but agreement appears to be emerging on their near surface formation.

The research based on oxygen stable isotope signatures of the Attunga magnesite carried out by Oskierski et al. (2010) indicates a near-surface formation at low temperatures from meteoric waters but according to them, the pathway of carbon into the magnesite is still controversial because the very low carbon isotope signature indicates a source of carbon from organic material enriched in  $^{12}\text{C}$  during C3 photosynthesis. In the Great Serpentine Belt, the isotopic compositions of other carbonate rocks are significantly different and interpreted to be derived from sources that may not be the source for Attunga magnesite.

The rate of dissolution reactions, which release divalent metal cations into solution and the rate of precipitation reactions that combine injected  $\text{CO}_2$  with divalent cations to form stable carbonate minerals are important for finding the degree to which  $\text{CO}_2$  is incorporated into carbonate rocks. The key to create the stable carbon storage in carbonate minerals may be to identify the catalysts playing an important role in the formation of these minerals at low temperatures and inhibiting the formation of secondary silicate minerals. The research already done on Attunga magnesite identified the alteration of serpentinised olivine mesh cells as the primary mechanism of progressive magnesite vein formation in the early stages of carbonation and the inferred crystallisation sequence is used to interpret fluid evolution. The study of elemental concentration in a sequence from the host rocks serpentinite into the altered olivine mesh cells and the magnesite veins deposits that are present at GSB might lead to the identification of the catalysts. Instruments such as Neutron Activation Analysis (NAA) together with the High-Resolution Powder Diffractometer and Laue Diffractometer for single-crystal diffraction would allow such an investigation in detail.

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

The advantages of mineral carbonation include: the overall process of mineral carbonation is exothermic in nature and, hence, has the potential to be economically viable. The compounds of carbonate and residual silicate or

alumino-silicates formed in the process are thermodynamically stable, environmentally benign and weakly soluble in meteoric water. In addition, its potential to produce value added by products during the carbonation process may further compensate its costs. Carbonate rocks are good for enhancing the productivity of soil for agricultural use by reducing acidity and increasing moisture content. These rocks can be combined with stone to strengthen roadbeds. Magnesite can be used to prevent some weeds.

Furthermore, the raw materials needed for this process can be found in large quantities around the world. The fact that this method is the only form of carbon sequestration that is “permanent” also adds value to it. The other major proposed sequestration options like terrestrial, geologic and oceanic have the potential for leakage over time. Leakage can make the sequestration ineffective if the  $\text{CO}_2$  returns too quickly to the atmosphere. In addition, leaks may present other environmental, health, or safety issues. Mineral sequestration has none of these concerns.

Application of the mineral carbonation technology would result in the formation of carbonate rocks in the parts of the world where acid rain is a constant problem. This would benefit the soil and help in the growth of forests instead of being damaged due to the acid rain.

#### **Serpentinite Deposits of Pakistan**

Literature and research/field work by the Pakistani geologists and scientists have revealed that serpentinite and ultramafic deposits are wide spread in Pakistan as outcrop and within the rock successions in Talari Mohammad Jan area (Bilgrami, 1960), Ahingaro serpentinite zone in Kohistan arc complex, Swat (Dipietro and Ahmad, 1995) and Karakoram, Kohistan Hindu Bagh (Heuberger, 2004) amongst others.

The presence of these rocks in Pakistan has made Pakistan a source to provide raw material for future application of Mineral Carbonation technology to other parts of the world where such rocks are not available. Pakistan can also use these rocks for its own fossil fuel outlets by capturing the  $\text{CO}_2$  emission from them and storing it in the form of mineral carbonates, hence participating in the global issue of climate change by cutting its  $\text{CO}_2$  emission substantially whilst

still utilising its fossil fuel energy and helping other countries in doing the same.

### Conclusions

Chemical weathering of the rocks and subsequent precipitation of calcium and magnesium carbonates may be the main mechanism by which the CO<sub>2</sub> levels of the atmosphere can be controlled.

Point sources of CO<sub>2</sub> can be treated by a reaction with reactive magnesium or calcium-silicates in autoclaves. The products, magnesium-carbonate or calcium-carbonate and precipitated silica, can be used for different purposes, e.g., in construction materials and in agriculture, in order to make this process economically more attractive.

It is also possible to use the concept of enhanced weathering by applying powdered olivine or crushed basalt to farmland and woodland that are threatened by acid rain; this is probably the cheapest way to sequester large volumes of CO<sub>2</sub>, since it provides at the same time an effective way of counteracting the effect of acid rain on forests and improving the quality of the forest soil.

The presence of ultramafic rocks, especially serpentinite, in Pakistan, has given advantage to Pakistan over other countries lacking these rocks. Therefore research related to the details with in the mineral carbonation process can be conducted in Pakistan more economically.

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