



CATO – CO₂ capture, transport and storage
towards a clean use of fossil fuels in the energy economy



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**Coastal spreading of olivine to reduce
atmospheric CO₂ concentrations:
a preliminary evaluation**

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Abstract

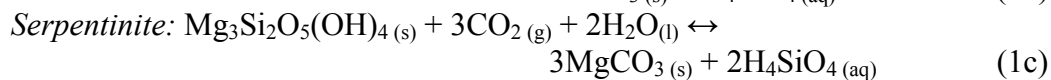
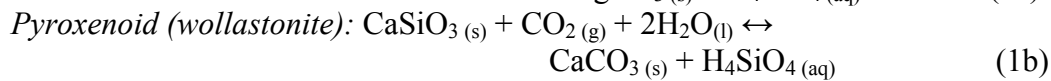
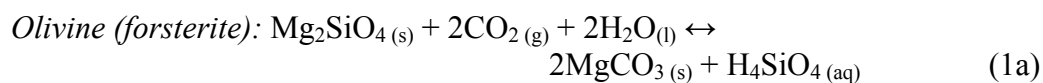
In the Dutch media, it has recently been proposed (by Prof. R.D. Schuiling) to reduce atmospheric CO₂ concentrations by spreading ground, sand-grade olivine along large portions of the Earth's coastlines. This paper provides a preliminary evaluation of this proposal, and has been carried out as part of CATO, the national Dutch CCS program. The feasibility of beach weathering of olivine depends on factors such as the rate of olivine dissolution, the sequestration capacity of the dominant reaction, and process efficiency including olivine mining, crushing, grinding, and transportation. Offsetting 25% of the current worldwide CO₂ emission of 28 Gt/yr by beach spreading of olivine requires the distribution of 5.6 Gt of olivine per year on the world's beaches. For seawater temperatures of 15 to 25°C, olivine sand of 300 µm takes approximately 700 to 2100 years, to reach a steady state sequestration rate and is of little practical value for sequestration. To obtain useful, steady state CO₂ uptake rates by 2020 requires grain sizes of < 10 µm. The transportation and deposition of such quantities poses major infrastructural transport, environmental, and public health questions. The practicality of CO₂ sequestration by coastal spreading of olivine is therefore questionable. Some modest contribution may be feasible in special situations, but more research is needed to evaluate this. Much more promising is the possibility of land weathering of olivine in tropical regions.

Keywords: CO₂ sequestration, olivine, mineralisation, beach spreading



1. Introduction

Carbon dioxide capture and storage (CCS) is now widely seen as an essential strategy for reducing CO₂ emissions at large point sources. One of the methods considered involves capture at source followed by direct, industrial carbonation of Ca- and Mg-rich silicate minerals at elevated pressure and temperature. Suitable minerals include olivine (particularly the Mg-rich end member), pyroxenes (or pyroxenoids), and serpentinite rock (see Gerdemann et al., 2007; Jia and Anthony, 2002; O'Connor et al., 2005). The corresponding reactions generally anticipated can be represented as:



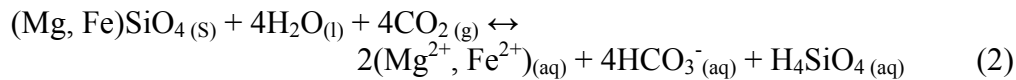
where CO₂(g) represents CO₂ in either gas or supercritical fluid form, depending of the pressure and temperature conditions under which reaction takes place.

The ultimate products of these reactions are solid carbonate and silica, which can be used as secondary raw materials. However, the reactions are slow. To accelerate them to rates appropriate for an industrial process, the rock or mineral feedstock must be crushed to a fine grain size (high surface area) (Gerdemann et al., 2002; Gerdemann et al., 2007; Kakizawa et al., 2000; Kojima et al., 1997; O'Connor et al., 2000) and reacted at 100 - 185°C and 4 - 15 MPa CO₂ partial pressure, P_{CO₂} (Gerdemann et al., 2007). Such treatments consume energy and produce CO₂, leading to low efficiency and high costs (Huijgen et al., 2006). An alternative approach involves pre-treatment of the crushed feedstock with acid to extract Ca²⁺, Mg²⁺ and Fe²⁺ (Goff and Lackner, 1998; Haywood et al., 2001; Kakizawa et al., 2000), but these methods use large quantities of acid, and are even less favourable (Haywood et al., 2001). A further possibility is reaction of the above minerals with CO₂ at ambient P_{CO₂} and temperature conditions, i.e. at Earth surface conditions, in a process akin to natural weathering. Following earlier articles in the scientific literature (Schuiling, 2006; Schuiling and Krijgsman, 2006), a highly appealing idea, based on the concept of natural olivine weathering, has recently been proposed by Utrecht University Emeritus, Prof. R. D. Schuiling, via the Dutch media (Biersma, 2007; Eshuis, 2007). Vast amounts of olivine are available in ultramafic rocks around the world (e.g. in Greenland, Norway and Turkey). Schuiling's "Green Beaches" proposal is to spread finely ground olivine along large parts of the Earth's coastlines, above the wave base, in an attempt to fix atmospheric CO₂ into bicarbonates, via weathering reactions. It is suggested that crushed olivine "sand" (grain size $d \approx 300 \mu\text{m}$) will be completely converted into bicarbonate salts within several decades. It should be noted that this concept does not lead to CO₂ emissions reductions but is envisaged to offset emissions by removing carbon dioxide directly from the atmosphere. Alternatives put forward by Schuiling include land weathering of crushed



olivine, both in developed countries or, more effectively, in developing (sub)tropical countries.

It is proposed by Schuiling (Schuiling and Krijgsman, 2006; see also Olsen, 2007), that the relevant ‘weathering’ reaction of olivine with CO₂ in coastline and surface environments is



The total CO₂ uptake capacity of this reaction is 1.25 ton of CO₂ per ton of Mg-olivine, comparable with 0.625 ton of CO₂ per ton of Mg-olivine for Reaction (1a). The slowest step of the overall reaction is the dissolution reaction of olivine. This itself involves H⁺-Mg²⁺ exchange by the adsorption of 0.5 H⁺ per forsterite ≡Mg₂SiO₄(surface) site, as well as adsorption of one proton on two polymerised silica tetrahedra (Pokrovsky and Schott, 2000). The removal of protons from solution, increases pH and alkalinity and results in an increase in the dissolved inorganic carbon (DIC) content, i.e. in HCO₃⁻ and CO₂ concentrations (Schulz et al., 2006). Of the various serial reaction steps involved in dissolution, adsorption of H⁺ is the slowest, and is hence rate-controlling for dissolution (Pokrovsky and Schott, 2000).

This paper analyses the latest data on the dissolution and reaction rate of Mg-rich olivine exposed to CO₂ and water under Earth surface conditions and considers the feasibility of using large-scale coastal mineralisation of olivine to significantly offset CO₂ emissions within the next 15 years. Aspects of land-based weathering are also considered but it is evident that much more work is needed on this before its feasibility can be reliably assessed.

2. Dissolution of olivine under Earth surface conditions

Regardless of the detailed reaction, the rate-limiting step in the process of reacting olivine with water and CO₂ to form either bicarbonates (Reaction (2)) or carbonates (e.g. Reaction (1a)) is expected to be the dissolution of olivine (Baines and Worden, 2000; Zerai et al., 2006). In the following we consider the available data in the kinetics of olivine dissolution, as a basis for estimating CO₂ uptake rates through engineered weathering.

2.1. Dissolution rate of olivine: Effect of pH and temperature

In acidic to slightly basic environments (1 < pH < 8.5), the dissolution rate of forsterite olivine (FO₈₉-FO₁₀₀) is proportional to the square root of the hydrogen ion concentration in solution (Blum and Lasaga, 1988; Golubev et al., 2005; Hänchen et al., 2006; Oelkers, 2001; Pokrovsky and Schott, 2000; Wogelius and Walther, 1991, 1992). The most recent data available on the dissolution rate coefficient (R_{diss}) in solutions with controlled pH at 25°C are summarised in Figure 1. At Earth surface pH values (pH 4.0-8.2), the mean rate coefficient lies in the range $1.58 \cdot 10^{-10} \pm 1.40 \cdot 10^{-10}$ mol/m² s to $3.79 \cdot 10^{-9} \pm 2.85 \cdot 10^{-9}$ mol/m² s (Fig.1). The activation energy for the dissolution process has been determined to be 79.5 ± 10.5 kJ/mol in the temperature range 25 to 65°C, at a



pH of 1.8 to 9.8 (Wogelius and Walther, 1992), and 52.9 ± 6.9 kJ/mol in the temperature range 90-150°C at pH 2 to 8.5 (Hänchen et al., 2006). Thus, taking the activation energy for olivine dissolution determined by Wogelius and Walther (1992), i.e. 79.5 ± 10.5 kJ/mol, and a pH range of 1.8 to 9.8, increasing the temperature from 25°C to 30°C (tropical seawater) or 40°C (terrestrial tropics) will increase mean dissolution rate by a factor of 1.6-3.8 (30°C) or of 1.8-5.7 (40°C). It should be noted, however, that while 25°C may be a reasonable seawater temperature at low to intermediate latitudes (45°S-45°N), at higher latitudes, such as those of Western Europe, a typical seawater temperature of 15°C is more likely. Lowering the seawater temperature from 25 to 15 degrees decreases the dissolution rate of olivine by a factor of 2.6 to 3.5. Compared to the dissolution rates of other minerals with a suitable composition for CO₂ trapping, such as Ca-rich aluminosilicates like anorthite and bytownite, the dissolution rate of olivine is 1 to 2.5 orders of magnitude faster (Amrhein and Suarez, 1992; Oxburgh et al., 1994), at 25°C and a typical seawater pH of ~ 8.2 (Krauskopf and Bird, 1995; Millero et al., 1993). It should be noted, however, that the dissolution rate of olivine is still very low.

2.2. Effect of fluid composition on dissolution rate

Aside from effects of pH through acid addition, relatively little research has been done on the effect of solution composition, i.e. of other dissolved components, on the dissolution rate of olivine. Recent dissolution experiments performed on olivine in electrolyte solutions (i.e. MgSO₄, Na₂SO₄, Mg(NO₃)₂, and KNO₃) in the pH range 2 to 4 and of varying ionic strength ($I < 12$ M) show that this has no effect on the dissolution rate (Olsen, 2007), except at high I -values where the dissolution rate is slightly reduced, most likely due to the lowering of the activity of water (Olsen, 2007). We could find no data on the effect of NaCl or seawater on the dissolution rate of olivine, but, on the basis of the lack of effect of other electrolytes, any effects of NaCl are likely to be small.

Independently of direct activity effects, it has been observed in various studies that the presence of Mg or Si in solution does not affect the reaction rate coefficient R_{diss} (Oelkers, 2001; Olsen, 2007; Pokrovsky and Schott, 2000). It has also been shown that sulphate ions in solution do not affect the dissolution rate of olivine (Olsen, 2007). The effect of carbonate ions is less clear. A study by Pokrovsky and Schott (2000) showed that in alkaline solutions with $\text{pH} > 8$, olivine dissolution is strongly inhibited when the activity of carbonate ions ($a(\text{CO}_3^{2-})$) exceeds 10^{-4} M. However, in a more recent study by Golubev et al. (2005) it was shown that neither HCO₃⁻ nor CO₃²⁻ in solution has an effect on the olivine dissolution rates in the pH range 1-12 at 25°C. Golubev et al. (2005) noted that in the study of Pokrovsky and Schott (2000) both pH and CO₃²⁻ concentration were subjected to large uncertainties, which made it difficult to differentiate independently between the effects of pH and CO₂ on dissolution rates. On this basis, we assumed that the dissolution rate coefficient R_{diss} for olivine at 25°C and $4 \leq \text{pH} \leq 9$ (Fig. 1), hence at Earth surface conditions, is probably not affected by the presence of bicarbonate or carbonate ions in solution, and is probably insensitive to common salts.

In contrast, at temperatures in the range 25-150°C, organic acids, like citric acid, potassium hydrogen phthalate (KHP), and ascorbic acid (ASC), significantly enhance olivine dissolution rates, compared to rates measured in the same pH range in the



absence of organics. The effect of organics is largest in the near-neutral pH range, $5 < \text{pH} < 7$, due to the formation of surface complexes (Hänchen et al., 2006; Wogelius and Walther, 1991), and can constitute an acceleration of a half to one orders of magnitude. Such acids are particularly important in soils, so are of interest in relation to the possibility of ‘land’ carbonation of olivine (Jonckbloedt, 1997). We could find no data on the effects of organic acids in seawater, but in view of the relatively high pH of seawater (~ 8), it seems reasonable to suppose that any effects are minor.

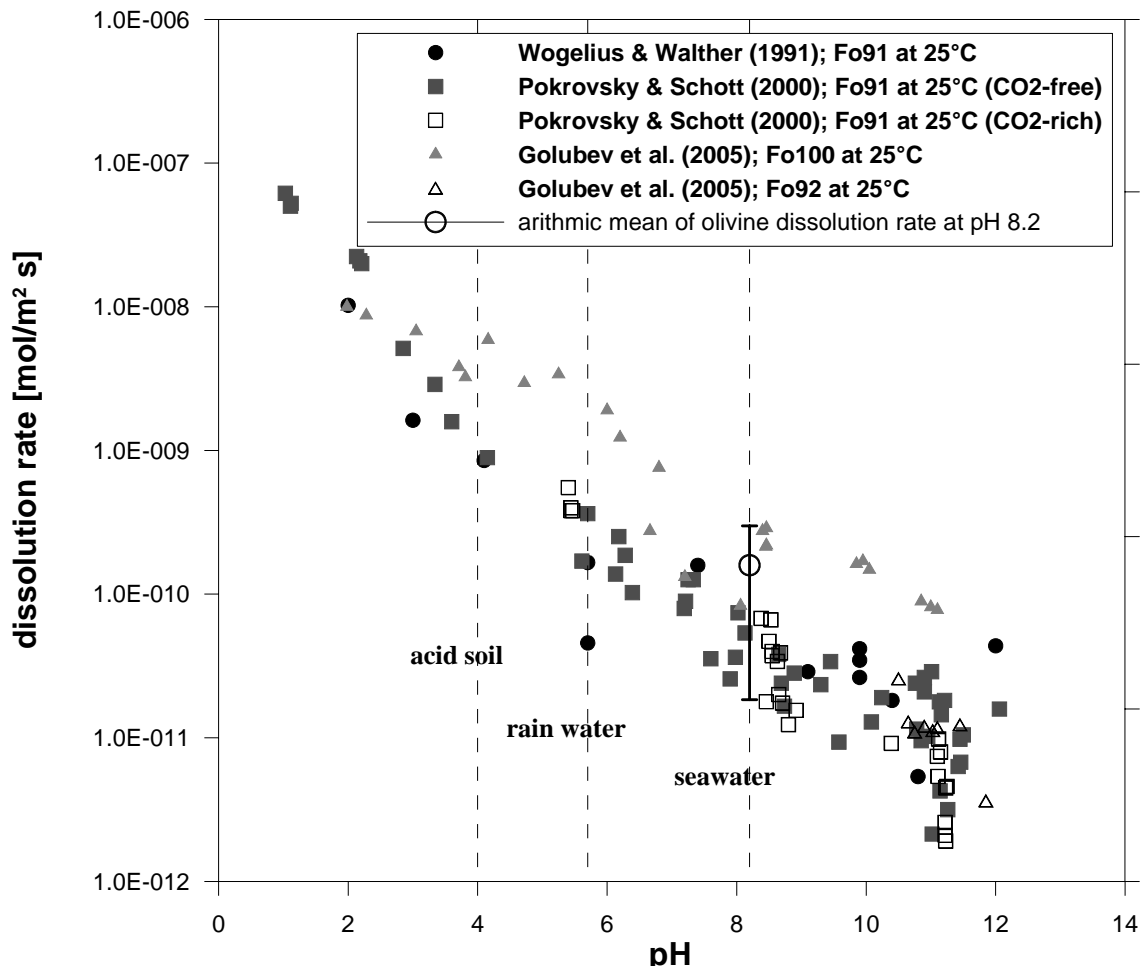


Fig. 1 Available data on the dissolution rate coefficient R_{diss} ($\text{mol}/\text{m}^2 \text{ s}$) of olivine (Fo_{91} - Fo_{100}) in water as a function of pH at 25°C (after Wogelius & Walther, 1991; Pokrovsky & Schott, 2000; Golubev et al., 2005). The dissolution rate range representing seawater conditions, at a pH of ~ 8.2 , is indicated and is given as $1.58 \cdot 10^{-10} \pm 1.40 \cdot 10^{-10} \text{ mol}/\text{m}^2 \text{ s}$ (see \circ and error bar). Thus one order of magnitude variability is present in the data at these conditions. Decreasing pH to 5.7 (rain water pH) and 4.0 (acid soil pH) increases the dissolution rate by approximately one and two orders of magnitude, respectively.

2.3. Effects at the dissolving olivine surface

Many silicates, like feldspars, micas and olivines, show the progressive formation of secondary coatings (Hodson, 2003; McKelvy et al., 2005; Murakami et al., 1998) or cation-depleted layers (Hellmann et al., 2003; Inskeep et al., 1991; Kalinowski and



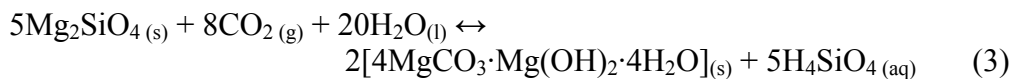
Schweda, 1996; McKelvy et al., 2005) on dissolving surfaces. We have already mentioned evidence for the formation of a Mg(OH)₂-like layer on the surface of olivine in solutions of pH > 8 or 9, which can inhibit olivine dissolution. At lower pH a Mg-depleted surface layer develops with time (Wogelius and Walther, 1991, 1992). These Si-rich or Mg(OH)₂-like layers may progressively limit the dissolution rate, as diffusion of ions from the mineral surface through the depleted layer into solution will eventually become rate controlling. In a situation where olivine sand is distributed on beaches, it is likely that wave motion will abrade the grains, hence removing any Si-rich surface layer (McKelvy et al., 2005).

2.4. Practical estimates of R_{diss}

We have shown above that the dissolution kinetics of olivine in the pH range relevant for seawater (pH 7.9-8.4 (Millero et al., 1993)) is likely to be insensitive to the chemical components present. Grain abrasion in coastal environments further implies that surface coating effects will be minimised. We accordingly assume that the free surface dissolution rate coefficient R_{diss} (Figure 1), with activation energy of 79.5 kJ/mol (Wogelius and Walther, 1992), gives a reasonable upper bound for the dissolution rate of olivine in the pH range relevant to coastal spreading of olivine. For land spreading of olivine in the tropics, at T = 40°C, pH = 4, no organics considered, these data predict olivine dissolution rates some 200 to 600 times higher. Note, however, that the formation of surface coatings and the absence of grain abrading processes may inhibit olivine dissolution kinetics in terrestrial environments.

3. Reaction of CO₂ with olivine and associated sequestration capacity

From an emissions reduction perspective, trapping of carbon dioxide at point sources, in the form of carbonate minerals such as magnesite (MgCO₃) is attractive as it fixes CO₂ in a stable solid form. Research on industrial carbonation of olivine has focused on Reaction (1a), whereby the optimum pressure and temperature conditions for magnesite precipitation are around 185°C and 15 MPa CO₂ partial pressure (Gerdemann et al., 2002; Gerdemann et al., 2007), which is far removed from surface conditions of present interest. At temperatures below 100°C, and at slightly elevated CO₂ pressures (P_{CO2} = ~ 1 MPa), not magnesite but hydromagnesite is observed to precipitate (O'Connor et al., 2002), via the reaction

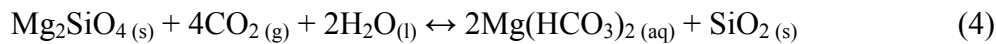


Under ambient conditions (15-25°C, P_{CO2} = 10^{-5.0}-10^{-2.5} MPa), however, neither magnesite nor hydromagnesite generally precipitate, even at high supersaturation (Hostetler, 1964). Suggested explanations for this include nucleation and growth barriers related to ionic substitution in the precipitate, to very fine precipitated grain size (high surface energy), and to the presence of defects or dislocations in the precipitate (Hostetler, 1964). On the other hand, in some highly saline (evaporitic) environments and soils, magnesite and hydromagnesite precipitation has been reported (Hostetler,

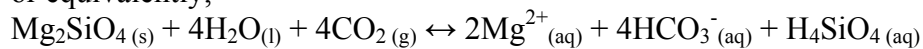


1964). On balance, it seems unlikely that magnesite and hydromagnesite will form in Earth surface environments via Reactions (1a) and (3), except where strong evaporation occurs (e.g. hot terrestrial environments).

In seawater under ambient conditions, it has been recently proposed (Lackner, 2005) that reaction of olivine with CO₂ leads to the formation of soluble bicarbonates through the following reaction



or equivalently,



as put forward in (2) for (Mg,Fe)-olivine by Schuiling for surface environments in general (Schuiling and Krijgsman, 2006). Sequestering CO₂ in the form of bicarbonates via Reaction (2), or its equivalent (4), requires only 1 ton of Mg-olivine to fix 1.25 ton of CO₂. If the products remain stable, this makes this reaction much more efficient than mineralisation forming hydromagnesite or magnesite via Reactions (1a) or (3), which can sequester only 0.5 and 0.625 tons of CO₂ per ton of olivine, respectively.

The recent proposal by Schuiling to spread olivine on beaches to trap CO₂ (Biersma, 2007) is based on the assumption that Reaction (2) will indeed occur and that bicarbonate salts will be formed and remain stable in solution in the marine environment, rather than re-releasing CO₂ to form carbonates in a manner ultimately equivalent to Reactions (1a) and (3). This assumption is reasonable, but still needs to be confirmed by experiments.

To gain insight into the maximum possible effect of olivine dissolution, via Reaction (2), on the pH and alkalinity of the marine geochemical environment, we performed a simple geochemical calculation on an idealised coastal marine system, consisting of seawater and olivine, in equilibrium with atmospheric CO₂. Our calculation assumes that the transport of species from the coastal marine regime to the deep ocean is slow compared to reaction, i.e. we treated the coastal environment as a closed system. In the most extreme case, equilibrium will ultimately be established within the system, and the seawater will be saturated with dissolved olivine components. All further details and assumptions used to explore this scenario are described in the Appendix. Our calculations show that seawater pH can increase from 8.2 to a maximum of 9.0, as a result of the dissolution of olivine, which consumes H⁺. At the same time, seawater alkalinity and dissolved inorganic carbon (DIC) content concomitantly increase, causing more CO₂ to dissolve into the seawater, in the form of bicarbonate and carbonate ions, reaching equilibrium concentrations of 2.23·10⁻² and 7.47·10⁻² mol/l, respectively. The concentrations of other species in solution (e.g. Mg²⁺, MgCO₃⁰, and MgHCO₃⁺) change only slightly.

The above mechanism of increasing seawater alkalinity to enhance marine CO₂ sequestration capacity has been suggested previously in the literature, either by the addition of artificial alkali, in the form of NaOH (House et al., 2007), or by enhanced limestone weathering (Rau et al., 2007). However, it should be noted that local changes in alkalinity, as well as dissolved inorganic carbon (DIC) content, will probably affect the marine ecosystem. As far as we can determine, little seems to be known about this. Viewed overall, we infer that to properly assess the effects of olivine reaction on



beaches, and the fate of reacted CO₂, it is important to study not only Reaction (2) but also the effects of changes in alkalinity and DIC on the retention of CO₂ in bicarbonate form in the marine system, and the effect on the ecosystem.

4. Reaction progress with time and effect of grain size

In light of our analysis of olivine dissolution rates the total rate at which atmospheric CO₂ can be taken up by seawater through olivine deposition on beaches, via Reaction (2), depends on the amount of olivine deposited and on the fundamental dissolution rate of olivine (Fig. 1). We now proceed to apply the dissolution rate data presented in Figure 1 to calculate how dissolution of a batch of olivine sand will proceed in terms of reacted mass vs. time. This provides a (upperbound) basis for assessing CO₂ uptake rates and whether the process is fast enough to be useful for CO₂ sequestration purposes in the coming decades.

Assuming that olivine sand is composed of spherical particles, which dissolve according to a shrinking core model, the extent of dissolution of a batch of deposited olivine, and hence the fraction of reacted material, can be expressed as

$$X_{\text{olivine}} = \frac{d_0^3 - d(t)^3}{d_0^3} \times 100\% \quad (5a)$$

$$\text{where } d(t) = d_0 - 2R_{\text{diss}}\Omega t \quad (5b)$$

where X_{olivine} is the extent of olivine reaction [vol%], d_0 is the initial grain size [m], d is the grain size at time t [m], R_{diss} is the dissolution rate coefficient of olivine [mol/m² s], Ω is the molar volume of olivine [43.02·10⁻⁶ m³/mol], and t is time [s]. As can be seen from Figure 1, at a solution pH of 8.2, as expected in natural seawater, the dissolution rate R_{diss} has an average value of $1.58 \cdot 10^{-10} \pm 1.40 \cdot 10^{-10}$ mol/m² s at 25°C. At 15°C, the dissolution rate of olivine will be 2.6-3.5 times slower, i.e. $5.93 \cdot 10^{-11} \pm 5.42 \cdot 10^{-11}$ mol/m² s. Progressive dissolution of olivine will increase coastal seawater pH, as mentioned in Section 3. However, this will only lower the dissolution rate slightly (see Figure 1), and this effect is therefore neglected in our calculations.

In these calculations we used the above dissolution rate data plus equations 5a and b to construct Figure 2, assuming a seawater temperature of 25°C (Fig. 2a) and 15°C (Fig. 2b), and neglecting any (probably minor) effects of NaCl or any deceleration of dissolution due to the formation of surface layers. Figure 2 shows the progress of the olivine reaction and of CO₂ uptake versus time after deposition, for a range of initial olivine grain sizes. As seen from Figure 2, reaction times (the time to react 50-100%) of granular olivine are long even at grain sizes smaller than 300 μm. Even at an average temperature of 25°C, it takes on average 50 years to half react, and approximately 230 years to fully react, a mass of olivine powder ground down to 100 μm grain size. Given the range of olivine dissolution rates at these conditions, the stated reaction times are only averages, hence half reaction of 100 μm grain size olivine may take between 25 and 410 years, while full reaction may take between 125 and 2005 years. Decreasing the grain size rapidly decreases reaction time, but will also require more energy for the grinding process. Olivine sand (grain size 300 μm), of the type proposed by Schuiling in



the Dutch media, would take on average approximately 145 years (75-1240 yr) to half react and 700 years (370-6010 yr) to fully react. Corresponding times taken to trap 10, 25, 50 and 100% of the maximum amount of CO₂ that can be sequestered per ton of olivine, through seawater uptake of bicarbonates (Reaction (2)) via beach weathering at 25°C, are also visible in Figure 2 and are listed in Table 1. At a lower temperature of 15°C, reaction times are three times longer, as a result of the decrease in olivine dissolution rate.

To gain further insight into the progress of olivine reaction and marine CO₂ uptake via Reaction (2) under practical conditions, we have examined the situation where olivine of a given grain size d_0 is deposited as a constant rate of S ton/yr. For a constant olivine supply scenario of this type, it is easily shown from (5) that the total rate of reaction of olivine at any point t in time after initiation of olivine deposition is given by

$$\dot{M} = \frac{S}{100} \int_0^t \frac{\partial X_{\text{olivine}}}{\partial t} dt = \frac{S}{100} X_{\text{olivine}}(t) \quad (6)$$

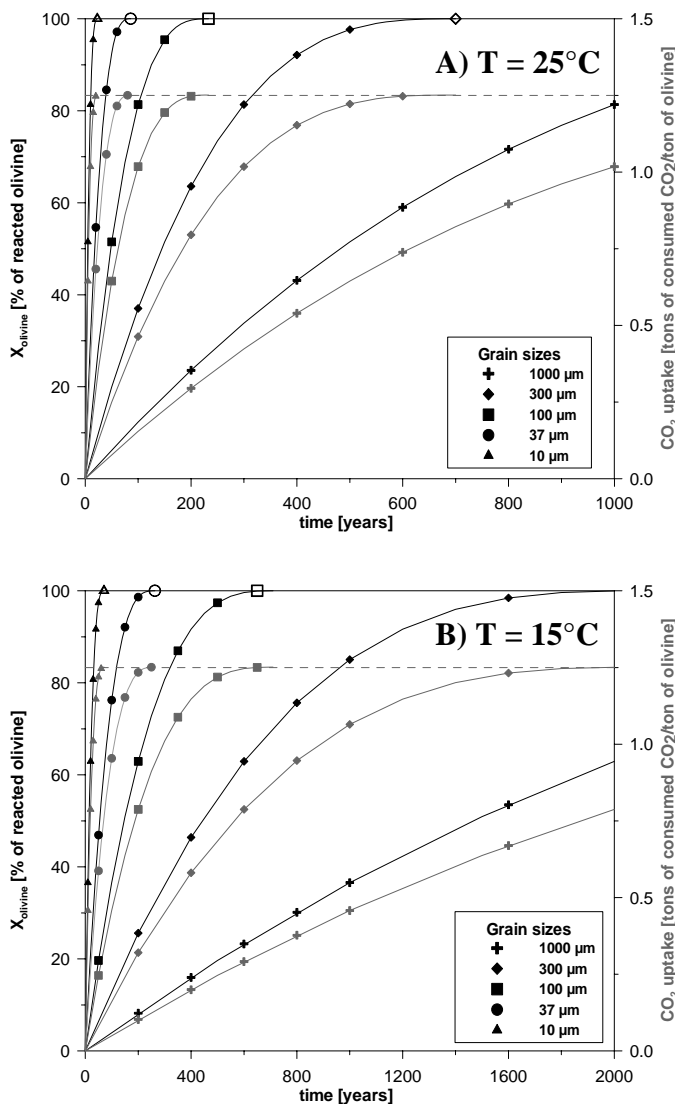


Fig. 2 The extent of granular olivine reaction as a function of time. Solid lines show the extent of olivine dissolution reaction in terms of reacted mass-fraction (%) of deposited olivine, while dashed lines show the amount of CO₂ sequestered per ton of dissolved olivine. Open symbols indicate reaction times to reach steady state reaction, at constant olivine supply rate. It was assumed that dissolution of the olivine grains occurred by a shrinking spherical core model. The amount of CO₂ sequestered per ton of olivine was calculated assuming Reaction (2), which results in the formation of soluble magnesium bicarbonate salts. A) Reaction progress at 25°C, assuming that the dissolution rate of olivine is $1.58 \cdot 10^{-10}$ mol/m² s (see Fig. 1). B) Reaction progress at 15°C, with the olivine dissolution rate being $5.19 \cdot 10^{-11}$ mol/m² s (calculated using the dissolution rate at 25°C and an activation energy of 79.5 kJ/mol, following Wogelius and Walther (1992)).



where \dot{M} is the total mass of olivine reacting per time unit at any instant [tons/yr]. This demonstrates that when the rate of reaction \dot{M} attains a value equal to the supply rate of olivine S , a steady state situation is reached at which the olivine first deposited has been completely consumed ($X_{\text{olivine}} = 100\%$). From (5), it is seen that this steady state is reached at $t = d_0/2R_{\text{diss}}\Omega$ after deposition starts.

Comparison of equation (6) with (5) now shows that when olivine is supplied at fixed rates, the total rate of olivine reaction \dot{M} evolves with time as depicted in Figure 2 (Eq. (5)) but with the vertical axis scaled by the constant factor $S/100$. Similarly, the steady state situation ($\dot{M} = S$) attained at $t = d_0/2R_{\text{diss}}\Omega$ is seen to correspond to the point in Figure 2 at which X_{olivine} , for individual grain sizes, attains the value of 100%.

On this basis, we can see from equation (6) and Figure 2, that to attain a steady state olivine consumption rate $\dot{M} = S$, and corresponding CO₂ uptake rate $\dot{C} = 1.25\dot{M}$ for Reaction (2), at 25°C, takes 700, 233, and 23 years for grain sizes 300, 100, and 10 μm , respectively. At 15°C, these times are increased by a factor of approximately 3.

5. CO₂ production due to mining and grinding

From the above, it is evident that grain size reduction to values $< 10\text{-}50 \mu\text{m}$ is crucial to accelerating the dissolution rate of olivine to levels that can contribute significantly to CO₂ sequestration by beach reaction in the next 15 years. Overall, the efficiency of CO₂ sequestration depends on the amount of carbon dioxide produced during the mining, grinding and transportation of the material. In this section, an attempt will be made to estimate the amount of CO₂ that is emitted during the various steps of the process.

The estimates presented in this study are based on a study performed by the Canadian Industry Program for Energy Conservation in 2005, on 7 open-pit gold and iron ore mines in Canada. Since gold and iron ore is generally associated with (ultra)mafic rocks (Nurmi, 1991; Stendal and Ünlü, 1991), these values are taken as representative for the mining of dunite and olivine peridotite – the principal sources of relatively pure olivine (60-90%). In our calculations, only energy consumption and hence CO₂ production during drilling, blasting, excavating, and transport (or hauling) to a crusher, are taken into account. Additional costs may be incurred in mine dewatering and in providing mine support equipment and services (CIPEC, 2005). On average, drilling consumes 0.35 kWh of energy per ton ($1.26 \cdot 10^6$ J/ton) of material produced, though upscaling of drilling operations will lower energy consumption per ton of material. In addition, approximately 0.44 kWh ($1.58 \cdot 10^6$ J/ton) per ton of material is consumed by blasting, 0.95 kWh/ton ($3.42 \cdot 10^6$ J/ton) during excavation, and 3.49 kWh/ton ($1.8 \cdot 10^6$ J/ton) during transport. These costs remain fairly constant regardless of the size of the pit. So in total, the energy consumption during mining per ton of material is approximately 5 kWh ($1.8 \cdot 10^6$ J/ton). CO₂ emission rates for pulverised coal, coal gasification and natural gas power plants are reported to be 0.795 kg CO₂/kWh, 0.757 kg CO₂/kWh, and 0.358 kg CO₂/kWh, respectively (Rubin et al., 2004). Taking these emission rates, CO₂ production during olivine mining would be 4.0 kg CO₂/ton material, 3.8 kg CO₂/ton material, and 1.8 kg CO₂/ton material, for those types of power



Table 1 Summary of the reaction time, grinding energy and costs for crushed olivine of various grain sizes (assuming beach reaction at 25°C)

grain size [μm]	Time for 10% dissol. ^a [years]	Time for 25% dissol. ^a [years]	Time for 50% dissol. ^a [years]	Time for 100% dissol. ^a [years]	grinding energy [kWh/ton olivine]	CO ₂ emission ^b [kg CO ₂ /ton CO ₂ sequestered]			Costs ^{b,c} [€/ton CO ₂ avoided]		
						(1)	(2)	(3)	(1)	(2)	(3)
1000	80 (43-692) ^d	213 (113-1832) ^d	481 (255-4134) ^d	2333 (1235-20039) ^d	10.17	6.5	6.2	2.9	0.49	0.49	0.49
300	24 (13-207) ^d	64 (34-550) ^d	144 (76-1240) ^d	700 (371-6012) ^d	13.40	8.5	8.1	3.8	0.65	0.65	0.65
100	8 (4-69) ^d	21 (11-183) ^d	48 (25-413) ^d	233 (124-2004) ^d	18.63	11.9	11.3	5.3	0.91	0.90	0.90
37	3 (2-26) ^d	8 (4-68) ^d	18 (9-153) ^d	86 (46-741) ^d	28.94	18.4	17.5	8.2	1.42	1.41	1.40
10	1 (0.4-7) ^d	2 (1-18) ^d	5 (3-41) ^d	23 (12-200) ^d	178.94	113.8	108.4	51.2	9.69	9.63	9.05
CO₂ uptake [ton CO₂/ton olivine]	0.125	0.313	0.625	1.25							

^a dissolution of the olivine is assumed to follow a shrinking core model (Eq. 5); dissolution of olivine will increase seawater alkalinity resulting in increased oceanic uptake of CO₂, resulting in the sequestration of 1.25 ton of CO₂ per ton of olivine, according to Reaction (2). Reaction time scales are calculated assuming the dissolution rate of olivine to be $1.58 \cdot 10^{-10} \pm 1.40 \cdot 10^{-10} \text{ mol/m}^2 \text{ s}$ at 25°C and pH = 8.2.

^b (1) powdered coal; (2) coal gasification; (3) natural gas power plant.

^c energy costs are assumed to be €0.06/kWh.

^d Time scale range for the range of dissolution rates applying to beach reaction at 25°C ($1.58 \cdot 10^{-10} \pm 1.40 \cdot 10^{-10} \text{ mol/m}^2 \text{ s}$ – see a).



plants, respectively. Typical olivine rocks (peridotites) usually consist of more than 60% olivine, while dunites generally consist of more than 90% olivine. However, we assume the olivine to be 100% ore grade, following previous studies on olivine mining (Gerdemann et al., 2007; O'Connor et al., 2005), and, hence, no beneficiation of the material is considered. The use of peridotites with only 60% olivine, instead of pure olivine, would mean roughly a doubling of the mass of material that has to be mined.

After the mining procedure, primary in-pit crushing, performed by jaw or gyratory crushers (Guimaraes et al., 2007), reduces the mined material to a grain size of approximately 1 to 300 mm (TKRI, 2004), and requires roughly 1.3 kWh/ton ($4.68 \cdot 10^6$ J/ton) of gold or iron ore produced (CIPEC, 2005). This is similar to the 2.0 kWh/ton ($7.2 \cdot 10^6$ J/ton) determined for the crushing of olivine, serpentinite and wollastonite, based on data from the U.S. Bureau of Mining (O'Connor et al., 2005). In terms of CO₂ emissions, crushing of the feedstock would thus lead to the production of 1.0 kg CO₂/ton ore, 0.98 kg CO₂/ton ore, and 0.5 kg CO₂/ton ore, respectively, depending on the energy source (Rubin et al., 2004).

The energy consumption W during the secondary and tertiary crushing and grinding stage to a reactable grain size of around 37-100 μm can be calculated using Bond's Equation (Morrel, 2004; Perry and Green, 1987). This assumes grain size reduction from a feedstock with an 80% passing size of d_∞ to a product with an 80% passing size of d μm . This is written as

$$W = 10 W_i \left(\frac{1}{\sqrt{d}} - \frac{1}{\sqrt{d_\infty}} \right) \quad (6)$$

where W is the energy [kWh/ton] required to reduced the feedstock to the desired grain size, W_i is an empirical work index of the feedstock material [kWh/ton], d_∞ is the grain size of the feedstock with 80% passing size [μm], and d is the desired grain size with 80% passing size [μm]. The work index of olivine has been taken to be the average of those found for Fe₂O₃ (8.6 kWh/ton) and silica sand (16.46 kWh/ton), i.e. 12.38 kWh/ton (Perry and Green, 1987). In case of a tertiary grinding step to a final grain size in the range 37-70 μm , Perry and Green (1987) added a multiplying factor F to equation (6), written as

$$F = \frac{10.3 + d}{1.145d} \quad (7)$$

Ultra-fine grinding, from 37 μm down to 10 μm , using a scalable stirred media detritor (SMD) mill has been shown, by direct measurement, to consume ~ 150 kWh/ton for olivine, wollastonite and serpentinite (O'Connor et al., 2005).

The total CO₂ emissions produced by mining, crushing, and grinding one ton of olivine, or per ton of sequestered CO₂, calculated as a function of grain size, using the above data and relationships, are depicted in Figure 3. The initial mined feedstock grain size has been set at 200 mm, and grinding has been treated as a four-step process, including primary in-pit crushing, secondary grinding to 75 μm , tertiary grinding to 37 μm and ultra-fine grinding down to 10 μm . It is clear from Figure 3 that carbon dioxide



emissions increase with decreasing final grain size. At a final grain size of 10 μm , CO₂ emissions as a result of mining, crushing and grinding constitutes between 5 and 11% of the total amount of sequestered CO₂.

Carbon dioxide emissions derived from the olivine mining, crushing and grinding process may therefore seriously reduce the efficiency of coastal weathering of olivine. However, for final grain sizes larger than approximately 40 μm carbon dioxide sequestration efficiency is reduced by less than 2%. Note that a reduction in CO₂ sequestration efficiency by a few per cent requires an increase of the amount of olivine deployed by the same percentage, in order to maintain the desired offset in CO₂ emissions. Setting the cost of electricity at €0.06/kWh (DACE, 2005), the total costs of mining, crushing and grinding of olivine, per ton of CO₂ avoided, can be calculated. A summary of the reaction time, grinding energy, CO₂ emission per ton CO₂ sequestered, and costs is shown in Table 1. If peridotites with only 60% olivine content were to be used instead of pure olivine, the consumed energy and CO₂ emissions per ton CO₂ sequestered would of course almost double.

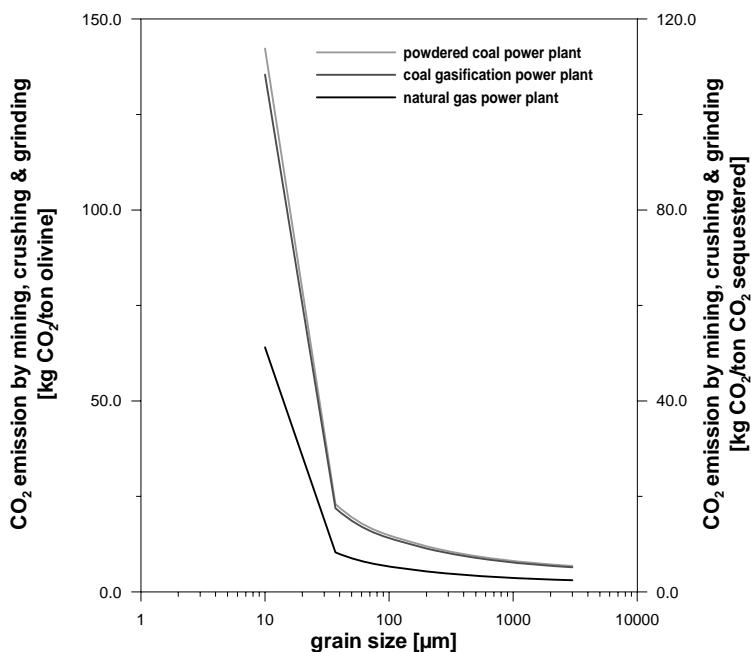


Fig. 3 Estimates of CO₂ emissions produced during mining, crushing and grinding of one ton of pure olivine feedstock (grain size 200 mm) to a given grain size, assuming a four-stage process for the finest grain size (10 μm).

Note that the calculations presented here do not include any energy consumption concerning transport from the mine to the location of deposition. In general, the means of transportation may include ships, trains and trucks. A British study on CO₂ emissions from freight transport (McKinnon, 2006) has shown that per ton of transported material CO₂ emissions are 30 g/km for inland or coastal ships, 20 g/km for trains, and 138 g/km for trucks. So, per 100 km of transport of one ton of olivine by ship, train, or truck the efficiency of CO₂ sequestration by olivine weathering is reduced by only 0.2, 0.1, and 1% respectively. CO₂ costs associated with building the extra transport facilities needed to move large amounts of olivine will reduce sequestration efficiency further – this needs further research.



6. Feasibility of sequestration via coastal spreading of olivine

In order to assess the feasibility of coastal spreading of olivine all of the factors discussed above have to be taken into account - the reactions, the olivine dissolution rate, grinding, mining and transportation energy, and the amount of olivine required. We assume that Reaction (2) is the most favourable and will be the one that will actually occur. This along with the “upperbound” mean value of R_{diss} used in our calculations and assumption of pure olivine, means that our analysis likely overestimates the effectiveness and efficiency of beach reaction of olivine. As reference cases only, we apply our calculations to examine uptake of 100% and of 25% of world and Dutch CO₂ emissions by olivine reaction.

Considering the fact that in 2004 the world’s yearly CO₂ emission, resulting from the burning of fossil fuels, was approximately 28 Gt (Bernstein et al., 2007), complete sequestration through olivine weathering via Reaction (2) would consume approximately 22.4 Gt of refined olivine on a yearly basis, or 5.6 Gt per year to achieve an equivalent of a 25% reduction in worldwide CO₂ emissions. The mass needed for industrial mineralisation via Reactions (1a) or (3) would be approximately twice this amount. From Figure 2 (equations 5 and 6) and our result that the time to reach steady

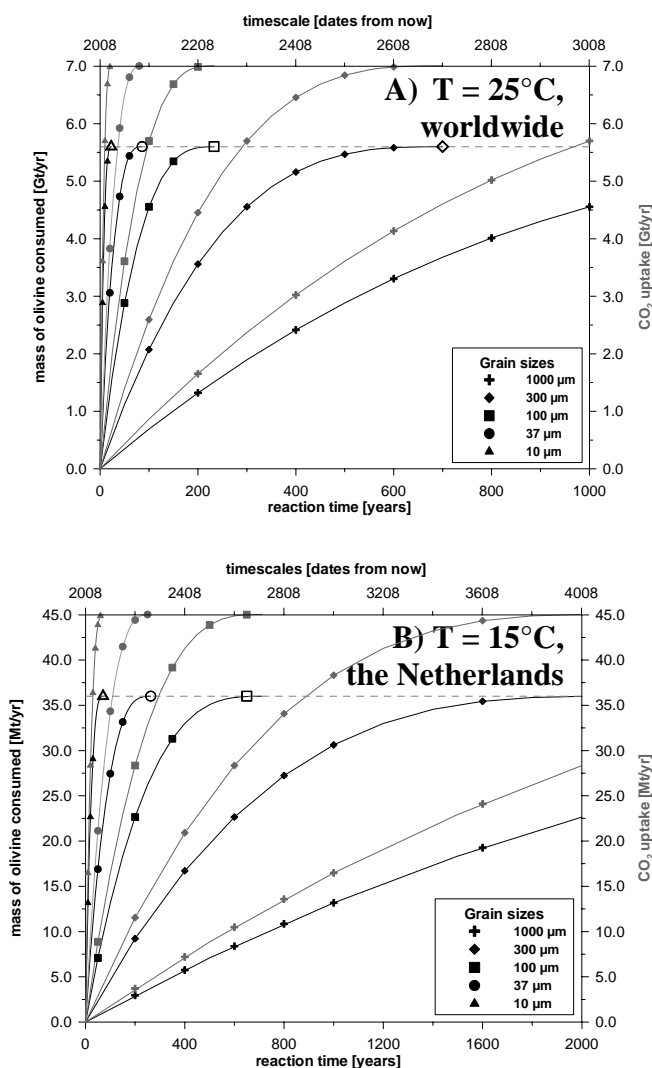


Fig. 4 The amount of granular olivine reacting per year (black lines) and the equivalent amount of CO₂ consumed per year (grey lines) as a function of time, at a constant olivine supply rates. Open symbols indicate reaction times to reach steady state reaction (rate of olivine reaction balances rate of supply). It was assumed that dissolution of the olivine grains occurred by a shrinking spherical core model. The amount of CO₂ sequestered per year was calculated assuming Reaction (2), which results in the formation of soluble magnesium bicarbonate salts. A) $S = 5.6$ Gt/yr, equivalent to a 25% reduction in worldwide CO₂ emissions. The dissolution rate of olivine was set at $1.58 \cdot 10^{-10}$ mol/m² s, assuming seawater temperature is 25°C (see Fig. 1). B) $S = 36$ Mt/yr, equivalent to a 25% reduction in Dutch CO₂ emissions. Seawater temperature was assumed to be 15°C with the dissolution rate of olivine being $5.19 \cdot 10^{-11}$ mol/m² s (calculated using the dissolution rate at 25°C and an activation energy of 79.5 kJ/mol, following Wogelius and Walther (1992)).



state is $t = d_0/2R_{\text{diss}}\Omega$ at constant supply rate, it follows that using coastal weathering of olivine to sequester CO₂ will require material with a grain size of less than 10 μm, in order to reach a steady state sequestration rate within roughly 15 years - assuming a dissolution rate in seawater of $1.58 \cdot 10^{-10}$ mol/m² s, at 25°C.

Now, to illustrate the amount of olivine reacted, and equivalently the amount of CO₂ consumed, per year at a constant olivine supply rate of 5.6 Gt/yr (equivalent to a 25% reduction in worldwide CO₂ emissions), we constructed Figure 4a, using equations 5 and 6. From Figure 4a it can be seen that at a constant supply rate of $S = 5.6$ Gt/yr it would take 233 years to reach a steady state olivine consumption rate at a grain size of $d_0 = 100$ μm and a seawater temperature of 25°C. To achieve a steady state reduction in 15 years, at a constant supply of 5.6 Gt of olivine per year, would require a grain size of approximately 6 μm. Since the extent of olivine consumption scales linearly with grain size (equation 5), using olivine grain sizes greater than ~ 6 μm would require proportionally larger supplies of olivine, to achieve the same offset in atmospheric CO₂ concentrations in the same time. When the desired sequestration rate is reached, the amount of olivine supplied per year could then be decreased until steady state is reached, after which a constant supply rate has to be maintained. In colder regions, i.e. at 15°C, steady state sequestration rates take approximately three times longer to reach, so the supply of olivine needed has to be tripled, or else three times smaller grain sizes are required, to maintain sequestration within similar time scales. Coastal spreading of olivine in warmer areas will improve reaction times by 1.7 times if the temperature is raised to 30°C, and even by 4.6 times if temperature increases to 40°C. In these cases, grain sizes of 30 μm could be used to reach equivalent steady state reduction rates in 15 years.

The above-mentioned contributions to global emission reduction by olivine weathering would make a major impact if 5.6 Gt/yr, or more, of fine olivine powder could be handled and transported and if the environmental impact is acceptable. It should not be forgotten here that finely crushed peridotite might pose a health risk, especially if the material contains serpentinite minerals (asbestos). Transport towards the location of deposition could be achieved by means of truck or ship. A truck can typically transport 50 ton, while the most commonly used cargo ship, a so-called Handysize, can carry 25 kt on average. This would mean that complete CO₂ sequestration (100% uptake of present CO₂ output) through enhanced coastal weathering would require the movement of roughly 448 million trucks or 896,000 Handysize ships, on a yearly basis. On a weekly basis it would come down to 8.6 million truckloads or 17,200 ship cargoes. The current worldwide Handysize fleet in comprised of less than 2000 units, which is approximately one third of the entire world fleet. By comparison, sequestration levels equivalent to a 25% reduction in current worldwide carbon dioxide emissions levels, which is the EU target for 2020 (CotEU, 2007), would mean 112 million trucks, or 224,000 cargo ships, transporting olivine on a yearly basis, and 2.2 million trucks, or 4300 cargo ships, on a weekly basis. The practicality of sequestration by coastal spreading to reach global CO₂ uptake target levels is therefore questionable. Nonetheless, assuming that the entire Handysize fleet is available solely for olivine transportation – i.e. for 2000 25-kt cargoes per week (2.6 Gt/yr) – coastal weathering of olivine could result in worldwide uptake of atmospheric CO₂ equivalent to a 10% reduction in emissions.



We now consider what the above would all mean for an industrialised country, like the Netherlands, assuming emission trading is not possible. In 2004 the Dutch CO₂ emission rate was 180 Mt/yr (Brandes et al., 2006). Assuming a constant olivine supply rate of 36 Mt/yr (equivalent to a 25% reduction in Dutch CO₂ emissions) and a seawater temperature of 15°C ($R_{\text{diss}} = 5.19 \cdot 10^{-11} \text{ mol/m}^2 \text{ s}$) the amount of reacted olivine, and consumed CO₂, per year is depicted in Figure 4b. From the underlying equations (5 and 6), it is clear that in order to achieve an equivalent of a 25% steady state reduction in CO₂ emissions by 2020 (i.e. within 12 years), by olivine weathering, a maximum grain size of 2 μm is required. This approaches the theoretical limit of grain size reduction and would be highly energy/ CO₂ inefficient in practice. Moreover, to achieve the constant supply of olivine of 36 Mt/yr, an equivalent of 720,000 truckloads, or 1440 Handysize ship cargoes, of ground olivine would have to be imported every year. This in turn implies the movement of approximately 0.7 Mt of olivine per week, that is 13,850 50-t olivine trucks on the Dutch transport network, or the passing of 28 Handysize ships along the coast, on a weekly basis. Bearing in mind that the Netherlands imports 10⁷ m³ of sand per year, to maintain coastal defence, Schuiling (Biersma, 2007) suggests replacing the sand by olivine. Importing a similar volume of olivine (33.2 Mt/yr) would generate a CO₂ uptake capacity of approximately 20% per year at steady state. However, it would also require a 30% increase in freight transport capacity, as olivine is 30% heavier than (quartz) sand. When importing the same mass of olivine per year as sand (26 Mt/yr), it would be possible to reach equivalent emission reduction levels of 15%. A more modest target for reduction of say 5% through olivine weathering would be more feasible, but still a major undertaking, with many questions still to be answered. In particular, the very fine particle size of ~2 μm required, to achieve useful reaction rates is particularly problematic, being highly inefficient and raising a wide range of public health (dust) issues. Sand grade olivine (300 μm) will simply react too slowly to be useful in feasible amounts, requiring roughly 48 times the mass of sand to be imported. On the other hand, with emissions trading possibilities, coastal weathering of olivine could be performed in hotter (sub)tropical areas, or closer to areas where the olivine will be mined. This offers improved possibilities and costs, which do warrant further investigation.

7. Coastal vs. land spreading

In addition to the ‘Green Beaches’ concept, the proposal by Schuiling to trap CO₂ from the atmosphere by spreading olivine on acidified soils (Biersma, 2007; Eshuis, 2007; Schuiling and Krijgsman, 2006) also assumes Reaction (2) and is expected to be controlled by olivine dissolution kinetics. However, it is possible that, as a result of high evaporation rates, magnesite or hydromagnesite may be formed instead, following Reactions (1a) and (3), hence reducing CO₂ uptake.

We have shown above that coastal weathering is relatively slow and probably impractical, certainly at levels beyond approximately 5-10% equivalent CO₂ emissions reduction. However, land spreading has several advantages over coastal spreading of olivine, as soils generally have a lower pH, typically around pH 4 (Schuiling and Krijgsman, 2006). This will enhance olivine dissolution rates by approximately two



orders of magnitude compared to dissolution in seawater, as depicted in Figure 1. Various studies have already shown that the presence of organic acids, found in soils (Fox and Comerford, 1990), further increases the dissolution rate of olivine (Olsen, 2007; Wogelius and Walther, 1991), adding perhaps half to one order, depending on the concentration of organic acid. Moreover, when spreading olivine in (sub)tropical areas it is possible to benefit from the higher temperatures, which will enhance dissolution rates further. In (sub)tropical areas, mean temperatures are generally perhaps 15°C higher than the figure of 25°C, which we assumed for beaches. If mean temperatures increase to 40°C, olivine dissolution rates increase with a factor 1.6 to 5.7, assuming an activation energy of 79.5 ± 10.5 kJ/mol (Hänchen et al., 2006; Wogelius and Walther, 1991). This all means that reaction rates for olivine spread on land could be up to 200-600 times faster than for beaches. Though land spreading of olivine will most likely encounter similar transport and infrastructural problems as coastal spreading, and while the possible impact upon agriculture, environment, ecology and human or animal health (fine olivine) remains to be clarified, it is certainly worth looking into its possibilities. Through shorter transport paths and lower costs, olivine spreading on land in developing (sub)tropical countries clearly has greater potential than in the developed world.

8. Conclusions

It has recently been proposed in the Dutch media, by Prof. R.D. Schuiling, to spread finely ground olivine along the coastlines of the world, in an attempt reduce atmospheric CO₂ concentrations, through weathering reactions. In this study, we have reviewed available data on the type and rate of relevant weathering reactions, and have considered the feasibility of such an undertaking in broad terms. The most important CO₂ uptake mechanism likely involves the formation of bicarbonate ions as olivine dissolves at a rate controlled by its dissolution kinetics. CO₂ sequestration by the weathering of olivine, resulting in the formation of bicarbonate ions, has a sequestration capacity of 1.25 tons of carbon dioxide per ton of olivine. However, the dissolution rate of olivine is very slow under Earth surface conditions, i.e. at temperatures of 15-25°C and pH range of 4.0 to 8.2, being of the order of $1.6 \cdot 10^{-10} \pm 1.4 \cdot 10^{-10}$ mol/m² s to $3.8 \cdot 10^{-9} \pm 2.9 \cdot 10^{-9}$ mol/m² s. Increasing temperature, from 25°C to 30°C (tropical seawater) or 40°C (tropics, land), will improve olivine dissolution rates up to about half an order of magnitude (factor 1.6 to 5.7). For fixed rates of olivine supply, the available data on olivine reaction rate demonstrate that beach weathering of olivine with an initial grain size d_0 of 10, 100 and 300 µm requires 23, 233, and 700 to reach steady state, at 25°C and three times longer at 15°C (i.e. 71, 710, and 2130 years).

To sequester the world's CO₂ emissions, i.e. 28 Gt/yr, or even 25% thereof, by beach reaction with olivine would require mining, crushing and movement of vast amounts of olivine (at least 22.4 and 5.6 Gt/yr, respectively) over large distances. Our estimates show that for sequestration of current entire CO₂ emissions through controlled weathering of olivine, reaching a steady state situation in roughly 15 years, the grain size of the reacting olivine must be small, ≤ 10 µm, at assumed seawater temperatures of 15 to 25°C. The grinding process to obtain 10 µm material from 200 mm feedstock



material will generate 50-110 kg of CO₂ per ton of ground olivine, equivalent to 5 to 11 per cent of the amount of CO₂ sequestered. This means that per ton of CO₂ avoided 5-11% of the sequestered CO₂ is actually produced during mining, crushing and grinding, and has to be compensated for. Costs for mining and grinding would be on the order of €10/ton CO₂ avoided. Moreover, vast transportation and infrastructural changes could be needed to implement the process on a useful scale, so its feasibility is unclear.

Aiming for an equivalent of a (EU) target of 25% steady state emissions reduction by 2020 would require coastal spreading of 5.6 Gt of 2 to 6 µm grain size olivine per year, depending on seawater temperature (15-25°C). Such large quantities of dust-grade mineral material (including asbestos-related serpentinite minerals) may have health consequences. Using larger grain sizes, such as 100 to 300 µm, lowers the costs for mining and grinding to roughly €1-4/ton CO₂ avoided. Sequestration efficiency for such grain sizes is approximately 95%, not including transportation, which will reduce efficiency. However, it would also require the transportation of amounts larger than 5.6 Gt/yr (89-267 Gt/yr). More research quantifying sequestration efficiency, supply rates and possible health or ecological impact of using fine olivine is necessary.

For a country like the Netherlands, in order to implement an equivalent 25% reduction in emissions by 2020, 0.7 Mt of 2 µm olivine has to be imported on a weekly basis – i.e. something like 13,850 truckloads of 50 tons each, or 28 cargo ships of 25kt each per week. This is probably not practical and may carry health risks. Beach reaction of sand grade olivine, as suggested in the media, would require 2130 years to reach a steady state sequestration rate, and is not a feasible solution.

On this basis, we infer that the spreading of olivine on beaches alone cannot provide a single solution to reach equivalent emissions reduction targets for the Netherlands or worldwide. However, it could contribute perhaps 5% equivalent reduction, and the appeal the idea has to the public should not be neglected. More research on costs, logistics and seawater reaction rates is needed to clarify the possible contribution. Spreading of olivine on land in tropical areas is much more promising, especially on land with acidic soils. More research is needed on this.

9. Recommendations and suggestions for future research

Surface weathering of ground olivine rock can potentially contribute to reducing atmospheric concentrations of CO₂. However, the extent to which it can contribute and the feasibility of the necessary production and transport infrastructure is not yet clear and spreading of olivine in (sub)tropical regions seems more promising than coastal reaction, which requires distribution of vast amounts of fine olivine to have an impact in the coming decades. In order to get fuller insight into the feasibility and possible role of using olivine beach or land weathering for CO₂ sequestration under Earth surface conditions, additional research is required. Here we summarise the further research that we feel is needed.

- For both coastal and land spreading it is important to verify which weathering reactions will control CO₂ sequestration when using olivine, as these control carbon dioxide uptake capacity. Uptake in the form of dissolved bicarbonate (Reaction (2) of this paper) seems the most likely process, though this has not been validated.



Notably, for spreading on land in hot climates it may be possible for magnesite or hydromagnesite precipitation to occur, especially in periods of high evaporation, reducing CO₂ uptake. Spectroscopic measurements to determine the reaction of finely ground olivine, with water or brine appear to offer a promising method (Wolf et al., 2004) for investigating and validating the relevant reactions. Using this method it should be possible not only to confirm the reaction but also to get an estimate of reaction rates under these conditions.

- As the dissolution of olivine is likely to be rate controlling for uptake of CO₂ via beach weathering reactions, insight into the effect of salinity on this rate is required. The lack of a need for such data in industrial process mineralisation means that little data is available. However, for the implementation of the idea of reacting olivine on beaches, or in soils, this information is important. Both conventional geochemistry and spectroscopic methods offer possibilities here.
- Relevant for the beach option is the effect of changes in local seawater chemistry (especially alkalinity) on the marine environment, particularly the ecosystem. In addition, modelling efforts on the sedimentological regime are needed to provide insight into transport and sedimentation rates of olivine spread on beaches, and into any possible coastline impact. This does not seem to have been considered to date.
- For the land option, it is also important to investigate the effect of the released Mg-ions on agriculture. The addition of magnesium to soils is often beneficial (El-Wahab and Mohamed, 2007; Ende and Zöttl, 1991). However, at higher concentrations this may no longer be the case.
- For the beach and land weathering options, the supply rate of olivine per year depends on the desired sequestration levels, as well as on the grain size of the supplied material. A numerical study of the necessary evolution of olivine supply rate, as a function of grain size and time to optimise sequestration growth, should be made. This can be done on the basis of equations 5 and 6.
- The efficiency of CO₂ sequestration by beach and land methods depends on CO₂ production during the mining, grinding and transportation stages. Energy consumption, CO₂ production, and costs during the mining, grinding, and transportation stages require much more thorough investigation, as does the environmental and infrastructural feasibility of transporting the vast quantities of olivine that must be moved to take up significant amounts of atmospheric CO₂. An advanced system modelling approach is needed here.
- If technically feasible even on a moderate scale, public acceptability also needs investigating, as do legal and economic measures to facilitate implementation internationally. Possible health impacts of spreading very fine olivine dust also need investigation.

Acknowledgements

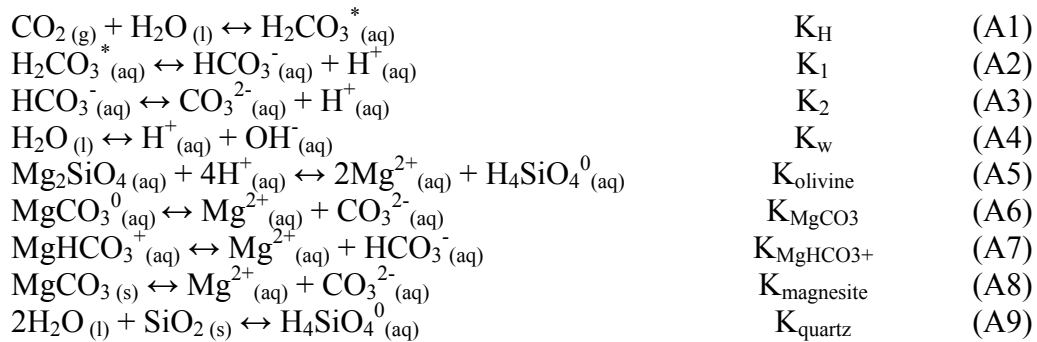
This research was financed by Shell International Exploration and Production (contract number 4600002284) and by the Dutch National Research Programme CATO (CO₂ capture, transport and storage) as part of WorkPackage 4 on Mineralisation. The motivation to conduct the work arose as a result of numerous questions raised in the



Netherlands after media attention for the issue. Prof. Dr. R.D. Schuiling and Erik Lysen are thanked for their comments on earlier versions of this manuscript, which helped improve it.

Appendix

Geochemical calculations have been performed on a very simplified olivine-seawater-CO₂ system. It was assumed that transport from the coastal waters to the deep sea was slow, and olivine supply was assumed to be infinite, which would ultimately lead in the extreme case to saturation of the coastal seawater with respect to olivine. Atmospheric CO₂ partial pressure was kept constant at the present value, 10^{-3.4} bar. It was also assumed that the calcite system would not be affected by any chemical changes. Magnesium was allowed to form carbonate and bicarbonate complexes, as these are considered to be the most prominent in marine environments (Langmuir, 1997), as well as to precipitate magnesite. The set of reactions associated with the olivine-seawater-CO₂ system thus considered are as follows



Equilibrium constants (K) for the various reactions are given as follows:

Henry's constant (Weiss, 1974):

$$\ln K_{\text{H}} = -60.2409 + 93.4517(100/T) + 23.3585(T/100) \\
 + S(0.023517 - 0.023656(T/100) + 0.0047036(T/100)^2)$$

Dissociation constants of CO₂ (Dickson and Millero, 1987):

$$-\log K_1 = 62.008 + 3670.7/T + 9.7944\ln(T) - 0.01118S + 0.000116S^2 \\
 -\log K_2 = 4.777 + 1394.7/T - 0.0184S + 0.000118S^2$$

Dissociation constant of water (Millero, 1995):

$$-\ln K_{\text{w}} = 148.96502 - 13847.26/T - 23.6521\ln(T) \\
 + S^{1/2}(-5.977 + 118.67/T + 1.0495\ln(T)) - 0.01615S$$

where, T is absolute temperature [K] and S is salinity on the practical salinity scale [-]. In seawater at 25°C and with a salinity of 35 the constants become $K_{\text{H}} = 10^{-1.55}$, $K_1 = 10^{-5.84}$, $K_2 = 10^{-8.96}$, and $K_{\text{w}} = 10^{-13.21}$. The solubility product for the dissolution of olivine is taken to be $K_{\text{olivine}} = 10^{28.67}$ (Stefánsson, 2001). The equilibrium constants for the



formation of the Mg-complexes are taken from Langmuir (1997) $K_{MgCO_3} = 10^{-2.98}$ and $K_{MgHCO_3^+} = 10^{-1.07}$. The solubility product for magnesite dissolution is $K_{magnesite} = 10^{-7.93}$ (Langmuir, 1997). The solubility product of quartz (Rimstidt and Barnes, 1980) is taken to be $K_{quartz} = 10^{-3.96}$.

The charge balance for the system is as follows

$$a(H^+) + 2a(Mg^{2+}) + a(MgHCO_3^+) = 2a(CO_3^{2-}) + a(HCO_3^-) \quad (A10)$$

Taking into account equations A1-A10, one can solve the problem. We corrected the concentrations of the species in solution, for the ionic strength of solution, $I = 0.66$, using their activity coefficients. All activity coefficients were calculated using the Debye-Hückel equation. We calculated the concentrations of all species in solutions at the point when equilibrium was reached, i.e. at saturation of the seawater with respect to olivine. Present day seawater concentrations and calculated concentrations are shown in Table A1. The calculation shows that seawater pH will go up from approximately 8.2 to 8.9, when equilibrium is reached. The calculated pH increase results in an increase in alkalinity and dissolved inorganic carbon (DIC) content, defined as

$$\begin{aligned} \text{Alk} &= a(OH^-) + a(HCO_3^-) + 2a(CO_3^{2-}) + a(MgCO_3^0) + a(MgHCO_3^+) - a(H^+) \\ \text{DIC} &= a(H_2CO_3^*) + a(HCO_3^-) + a(CO_3^{2-}) + a(MgCO_3^0) + a(MgHCO_3^+) \end{aligned}$$

Table A1 Calculated activity coefficients of species in a simplified coastal system, present day seawater concentrations, and concentrations for seawater in equilibrium with olivine

species in solution	activity coefficient f^- ^a	present day concentration [M] ^b	concentration, seawater in equilibrium with olivine [M]
H^+	0.76	$6.03 \cdot 10^{-9}$	$1.37 \cdot 10^{-9}$
OH^-	0.65	$3.00 \cdot 10^{-6}$	$8.94 \cdot 10^{-6}$
$H_2CO_3^*$	1.00	$1.30 \cdot 10^{-5}$	$1.12 \cdot 10^{-5}$
HCO_3^-	0.70	$1.54 \cdot 10^{-3}$	$2.23 \cdot 10^{-2}$
CO_3^{2-}	0.22	$3.80 \cdot 10^{-5}$	$7.47 \cdot 10^{-2}$
Mg^{2+}	0.29	$4.72 \cdot 10^{-2}$	$7.79 \cdot 10^{-2}$
$MgCO_3^0$	1.00	$1.10 \cdot 10^{-4}$	$1.12 \cdot 10^{-5}$
$MgHCO_3^+$	0.65	$2.50 \cdot 10^{-4}$	$6.73 \cdot 10^{-3}$
$H_4SiO_4^0$	1.14	$4.60 \cdot 10^{-5}$	$9.19 \cdot 10^{-5}$
pH		8.2	9.0

^a activity coefficients are calculated using the Debye-Hückel equation (Kielland, 1937). Following the literature the activity coefficient of $H_4SiO_4^0$ was set to 1.14 (Marshall and Chen, 1982) and of water to 0.98 (Krauskopf and Bird, 1995).

^b concentrations taken from the literature, assuming $T = 25^\circ\text{C}$, $I = 0.66$ and $a(H_2O) = 0.98$ (Krauskopf and Bird, 1995).



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