Coastal spreading of olivine to control atmospheric CO_2 concentrations: A critical analysis of viability

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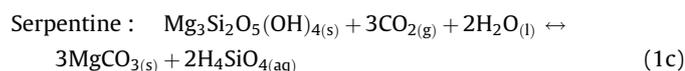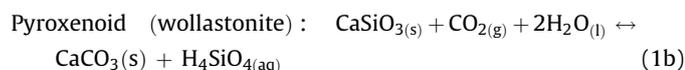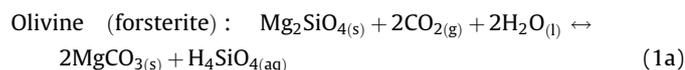
ABSTRACT

Qualitative proposals to control atmospheric CO_2 concentrations by spreading crushed olivine rock along the Earth's coastlines, thereby accelerating weathering reactions, are presently attracting considerable attention. This paper provides a critical evaluation of the concept, demonstrating quantitatively whether or not it can contribute significantly to CO_2 sequestration. The feasibility of the concept depends on the rate of olivine dissolution, the sequestration capacity of the dominant reaction, and its CO_2 footprint. Kinetics calculations show that offsetting 30% of worldwide 1990 CO_2 emissions by beach weathering means distributing of 5.0 Gt of olivine per year. For mean seawater temperatures of 15–25 °C, olivine sand (300 μm grain size) takes 700–2100 years to reach the necessary steady state sequestration rate and is therefore of little practical value. To obtain useful, steady state CO_2 uptake rates within 15–20 years requires grain sizes <10 μm. However, the preparation and movement of the required material poses major economic, infrastructural and public health questions. We conclude that coastal spreading of olivine is not a viable method of CO_2 sequestration on the scale needed. The method certainly cannot replace CCS technologies as a means of controlling atmospheric CO_2 concentrations.

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1. Introduction

Carbon dioxide capture and storage (CCS) is now widely seen as an essential strategy for reducing CO_2 emissions. One of the methods investigated to date involves CO_2 capture at source followed by industrial-scale reaction with naturally occurring Ca- or Mg-rich silicate minerals to form stable carbonates plus silica. Candidate minerals include *olivine* (particularly the more common Mg-rich end member, forsterite), *pyroxenes* (or pyroxenoids), and *serpentine* (see Gerdemann et al., 2007; Jia and Anthony, 2002; O'Connor et al., 2005). The corresponding reactions generally anticipated can be represented as:

Olivine (forsterite) : $Mg_2SiO_{4(s)} + 2CO_{2(g)} + 2H_2O_{(l)} \leftrightarrow$
$2MgCO_{3(s)} + H_4SiO_{4(aq)}$ (1a)

Pyroxenoid (wollastonite) : $CaSiO_{3(s)} + CO_{2(g)} + 2H_2O_{(l)} \leftrightarrow$
$CaCO_3(s) + H_4SiO_{4(aq)}$ (1b)

Serpentine : $Mg_3Si_2O_5(OH)_{4(s)} + 3CO_{2(g)} + 2H_2O_{(l)} \leftrightarrow$
$3MgCO_{3(s)} + 2H_4SiO_{4(aq)}$ (1c)

where $CO_{2(g)}$ represents CO_2 in either gas or supercritical fluid form, depending on pressure and temperature. However, these reactions are slow under atmospheric conditions. 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, 2007; Kakizawa et al., 2001; Kojima et al., 1997; O'Connor et al., 2000a) or pre-treated with large quantities of acid (Goff and Lackner, 1998; Haywood et al., 2001; Kakizawa et al., 2001). In addition, temperature and CO_2 pressures of 100–185 °C and 4–15 MPa are needed for optimum results (Gerdemann et al., 2007). The associated energy consumption, environmental impact and costs are therefore high and have placed industrial mineralisation low on the list of CCS options (Huijgen et al., 2006).

A possible alternative may be to react the above minerals with CO_2 at ambient conditions, i.e. through natural weathering reactions at Earth surface conditions (Wogelius and Walther, 1991, 1992). Following earlier articles in the scientific literature (Schuiling, 2006; Schuiling and Krijgsman, 2006), a superficially appealing idea, based on the concept of beach weathering of crushed natural olivine, was recently proposed by Schuiling, via the Dutch media (Biersma, 2007; Eshuis, 2007). This "Green Beaches" proposal entails the spreading of crushed olivine rock along large parts of the Earth's coastlines, above the wave base, using coastal dumper-barges and/or beach bulldozing equipment. The notion put forward by Schuiling is that dissolution of
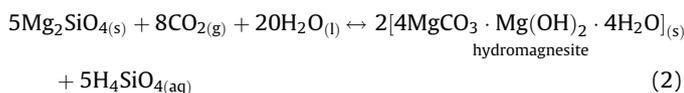
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sand-grade olivine (grain size 300 μm) will promote natural bicarbonate production, and hence oceanic uptake of CO_2 to rates that produce a significant sequestration effect over several decades. The concept does not lead to CO_2 emissions reduction but is envisaged to offset emissions by removing carbon dioxide directly from the atmosphere and has been profiled in the media as offering a cheap, natural alternative to CCS technologies. Other alternatives put forward by Schuiling (Schuiling and Krijgsman, 2006) include terrestrial weathering of crushed olivine, notably in developing (sub)tropical countries. For all such ideas, it is argued that olivine supplies are more than adequate but must be mined and transported from the relatively localised major ultramafic occurrences, such as ophiolite complexes, found around the world, i.e. in regions such as Norway, Turkey and North America (see for example the ophiolite distribution map in Coleman, 1977).

The perceived low risk, low cost and green character of olivine beach weathering have led to much political and popular attention for the proposed method in the Netherlands and within international web-based fora (e.g. http://www.realclimate.org/index.php/ archives/2008/03/air-capture/). However, the green beaches concept has not yet been quantitatively evaluated. Moreover, because weathering is a slow process (Chen et al., 2006; Kakizawa et al., 2001; Lackner et al., 1995; O'Connor et al., 2000b) much scepticism exists in the scientific community regarding CO_2 sequestration by weathering approaches.

This paper critically analyses the concept of beach weathering of crushed olivine, with the aim of demonstrating quantitatively whether or not it can contribute significantly to CO_2 sequestration targets. We do this by first reviewing the available data on the type and rate of the relevant olivine dissolution and CO_2 uptake reactions, and the effects upon these of environmental variables, such as temperature, pH and salinity. We go on to construct a simple model predicting the progress of beach olivine reaction and CO_2 uptake as a function of grain size and time. Finally, we consider the overall CO_2 footprint of the method itself, and the feasibility of using it to offset CO_2 emissions significantly by 2020 (Commission of the European Union, 2007), compared with the EU reduction target of 20–30%. Aspects of land-based weathering are also considered but much more work is needed on this before its feasibility can be reliably assessed.

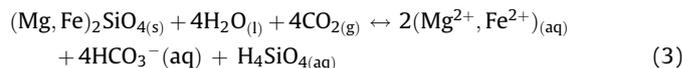## 2. Reaction of CO_2 with olivine and associated sequestration capacity

Key to coastal weathering of olivine is the sequestration capacity of the dominant sequestering reaction. At temperatures below 100 °C and at slightly elevated CO_2 pressures ($P_{CO_2} = \sim 1$ MPa), experimental studies have shown that reaction (1a), seen in high pressure mineralisation experiments, is replaced by the reaction

$$5Mg_2SiO_{4(s)} + 8CO_{2(g)} + 20H_2O_{(l)} \leftrightarrow 2[4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O]_{(s)}$$
$$\underset{\text{hydromagnesite}}{}$$
$$+ 5H_4SiO_{4(aq)} \qquad (2)$$

whereby, hydromagnesite precipitates instead of magnesite ($MgCO_3$) (O'Connor et al., 2002). On the other hand, analysis of natural waters (ground waters in contact with carbonates or ultramafics and surface waters from alkaline soda lakes) shows that, under ambient conditions (15–25 °C, $P_{CO_2} = 10^{-5.0}$ to $10^{-2.5}$ MPa), neither magnesite nor hydromagnesite generally precipitates, even at high supersaturation (Hostetler, 1964). This is because carbonate minerals formed at ambient conditions are in a high free-energy state as a result of fine grain size, metastable ionic substitution, and crystal defect content (Hostetler, 1964). Indeed, available evidence suggests that magnesite and hydromagnesite

form in Earth surface environments via reactions (1a) and (2) only when strong evaporation occurs (e.g. in evaporitic or hot terrestrial soil environments).

Instead, natural mineral weathering processes generally remove CO_2 from the atmosphere via carbonic acid neutralisation to form soluble bicarbonates. In the case of olivine of typical natural composition (Mg:Fe ratio >90%), reaction with water and atmospheric CO_2 leads to the formation of soluble bicarbonates through the reaction (Lackner, 2002; Schuiling and Krijgsman, 2006)

$$(Mg, Fe)_2SiO_{4(s)} + 4H_2O_{(l)} + 4CO_{2(g)} \leftrightarrow 2(Mg^{2+}, Fe^{2+})_{(aq)}$$
$$+ 4HCO_3^-(aq) + H_4SiO_{4(aq)} \qquad (3)$$

Sequestering CO_2 in the form of bicarbonates via this reaction requires only 1 tonne of pure Mg–olivine to fix 1.25 t of CO_2 (CO_2:olivine uptake ratio Q = 1.25). If the products remain stable, this makes the reaction much more efficient than mineralisation via reaction (1a) or (2), which can sequester only 0.625 and 0.5 t of CO_2 per tonne of olivine, in magnesite and hydromagnesite, respectively.

Extensive data on dissolution/precipitation kinetics in geomaterials in aqueous environments indicate that the rate limiting step of CO_2 mineralisation (reactions (1) and (2)), and of weathering reactions such as (3), is the dissolution rate of the reacting silicate minerals rather than the dissolution rate of CO_2 in solution or the precipitation of secondary phases (see these references and others therein: Amrhein and Suarez, 1992; Köhler et al., 2003; Lebrón and Suarez, 1998; Pokrovsky and Schott, 2000; Tödheide and Franck, 1963). Dissolution of olivine is controlled by the adsorption of H^+ on the olivine surface, exchanging Mg^{2+} ions for protons. The removal of protons from solution, increases pH and alkalinity and results in an increase in the dissolved inorganic carbon (DIC) content of the fluid phase, i.e. in aqueous HCO_3^-, CO_3^{2-} and CO_2 concentrations (Schulz et al., 2006). This is the basic sequestration mechanism proposed by Schuiling.

Similar mechanisms of increasing seawater alkalinity to enhance marine CO_2 sequestration capacity have been suggested previously in the literature, notably via the addition of artificial alkali in the form of NaOH (House et al., 2007), or by enhanced weathering of alkaline minerals, such as calcite (Archer et al., 1997; Kheshgi, 1995; Rau and Caldeira, 1999; Rau et al., 2007), sodium carbonate (Kheshgi, 1995; Lackner, 2002), and (ultra)mafic rocks (Lackner, 2002). It is recognised by the authors, however, that such approaches may affect marine life and to date neither of these methods have been applied.

3. Dissolution of olivine under Earth surface conditions

In the following, we consider the available data on the kinetics of olivine dissolution and on the effects of solution composition and dissolution progress, as a basis for estimating CO_2 uptake rates through coastal weathering of crushed olivine.

3.1. Dissolution rate of olivine: effect of pH and temperature

At pH values in the range 1 < pH < 8.5, it is well-established that the steady state dissolution rate of forsteritic olivine (i.e. Fo_{89}–Fo_{100}, with Mg:Fe ratios of 89–100%) is proportional to the square root of the hydrogen ion concentration (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 parameter R_{diss} (mol/m^2 s) in solutions with controlled pH at 25 °C are summarised in Fig. 1. At Earth surface pH values (pH 4.0–8.2, see for example Millero et al., 1993; Motavalli et al., 1995), the mean values of R_{diss} lies in the range $(1.58 \pm 1.40) \times 10^{-10}$ to
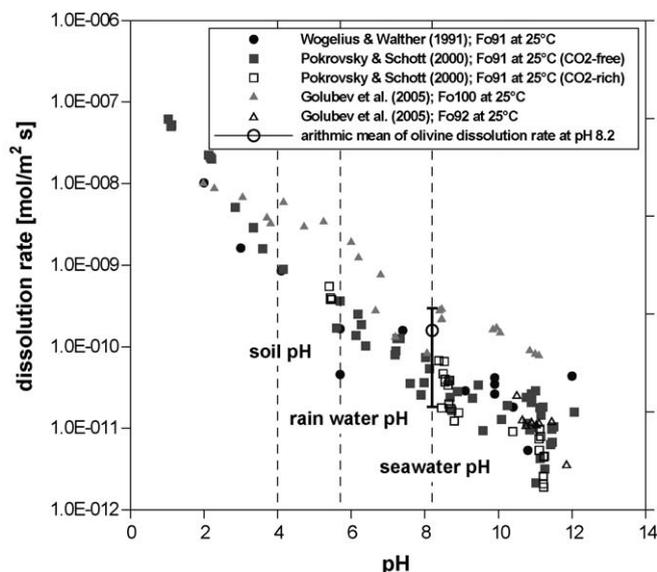
Fig. 1. Available data on the dissolution rate R_{diss} (mol/m^2 s) of olivine (Fo$_{91}$–Fo$_{100}$) in water as a function of pH at 25 °C (after Golubev et al., 2005; Pokrovsky and Schott, 2000; Wogelius and Walther, 1991). The dissolution rate range representing seawater conditions, at a pH of ~8.2, is indicated and is given as $(1.58 \pm 1.40) \times 10^{-10}$ mol/m^2 s (see ○ 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.

$(3.79 \pm 2.85) \times 10^{-9}$ mol/m^2 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 25–65 °C, at a pH of 1.8–9.8 (Wogelius and Walther, 1992), and 52.9 ± 6.9 kJ/mol in the temperature range 90–150 °C at pH 2–8.5 (Hänchen et al., 2006). Thus, taking the activation energy of 79.5 ± 10.5 kJ/mol for olivine dissolution determined by Wogelius and Walther (1992), increasing the temperature from 25 °C to 30 °C (tropical seawater) or 40 °C (terrestrial tropics) will increase the mean dissolution rate by a factor of 1.6–3.8 (30 °C) or of 1.8–5.7 (40 °C). However, while 25 °C may be a reasonable mean seawater temperature at low to intermediate latitudes (45°S to 45°N), at higher latitudes, such as those of Western Europe, a typical mean seawater temperature of 15 °C is more likely. Lowering the seawater temperature from 25° to 15° decreases the dissolution rate of olivine by a factor of 2.6–3.5. Compared to the dissolution rates of other minerals with a suitable composition for CO$_2$ trapping, such as Ca-rich feldspars, the dissolution rate of olivine is 1–2.5 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.

3.2. Effect of fluid composition on dissolution rate

Aside from effects of pH through acid or alkali addition, relatively little research has been done on the effect of solution composition on the dissolution rate of olivine. In experiments performed at 25–65 °C, atmospheric pressure and pH 1–12, it has been observed that the presence of aqueous magnesium or silica in solution at concentrations up to 4 M, does not affect the dissolution rate R_{diss} (Oelkers, 2001; Olsen, 2007; Pokrovsky and Schott, 2000). This is because olivine is highly unstable under such conditions and very far from equilibrium. Recent dissolution experiments performed on olivine in single electrolyte solutions containing MgSO$_4$, Na$_2$SO$_4$, Mg(NO$_3$)$_2$, or KNO$_3$, in the pH range 2–4 and of varying ionic strength ($I < 12$ M), show that these components

likewise have no significant effect on dissolution rate at ambient pressure and temperature (Olsen, 2007).

Accelerated olivine dissolution and reaction rates with CO$_2$ have been achieved at elevated pressure and temperature (8–15 MPa P_{CO_2}, 115–185 °C) by the use of bicarbonate/salt solutions with a composition of 1 M NaCl and 0.5–0.64 M NaHCO$_3$ (Gerdemann et al., 2007; O'Connor et al., 2005, 2000a,b). O'Connor et al. (2000a) observed an increase in reaction rate by a factor of about four. This was attributed to the formation of intermediate magnesium chloride complexes, which reduce the activity of Mg^{2+} in solution, and hence increase the solubility of olivine (O'Connor et al., 2000a). On the other hand, McKelvy et al. (2005) claim little effect of NaCl but a substantial increase in reactivity (conditions: 185 °C, 15 MPa P_{CO_2}) due to the joint effect of HCO$_3^-$ and CO$_{2(aq)}$. Prigiobbe et al. (2009) also observed no significant effect of NaCl (<1 M) on the dissolution rate of olivine at elevated temperatures. It remains difficult to extrapolate results on the effects of NaCl obtained at elevated temperature and pressure to weathering conditions, so more uncertainty remains here. Nonetheless, a major effect of NaCl on olivine dissolution rate at ambient conditions seems unlikely.

The effect of carbonate ions in solution is unclear. Pokrovsky and Schott (2000) report that in alkaline solutions with pH > 8, olivine dissolution is strongly inhibited when the activity of carbonate ions ($a(CO_3^{2-})$) exceeds 10^{-4} M. However, in a more recent study by Golubev et al. (2005) it was shown that neither HCO$_3^-$ nor CO$_3^{2-}$ 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 CO$_3^{2-}$ concentrations were subject to large uncertainties, which made it difficult to differentiate independently between the effects of pH and CO$_2$ on dissolution rates.

On the basis of all this, we assume that the dissolution rate parameter R_{diss} for olivine at 25 °C and $4 \le pH \le 9$ (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 organic acids is largest in the near-neutral pH range, $5 < pH < 7$, due to the formation of surface complexes (Hänchen et al., 2006; Prigiobbe et al., 2009; Wogelius and Walther, 1991), and can constitute an acceleration of a half to one order of magnitude. Such acids are particularly important in soils, so are of interest in relation to the possibility of terrestrial 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 is reasonable to suppose that organic acids will be of minor importance in a marine environment.

3.3. Effects at the dissolving olivine surface

Many silicates, like feldspars, micas and olivine, 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. Pokrovsky and Schott (2000) suggested that preferential release of Si at pH > 9 could lead to the formation of an Si-depleted, Mg(OH)$_2$-like layer on the surface of olivine in solutions of pH > 9, which can inhibit olivine dissolution. At the lower pHs expected in Earth surface environments, an Mg-depleted surface layer develops with time (Wogelius and Walther, 1991, 1992). Such 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. However, in a situation where olivine sand is distributed on beaches, it is likely that wave motion will abrade the grains, reducing any tendency to build up thick surface layers (McKelvy et al., 2005). Retarding effects of surface layer formation on dissolution rate are therefore expected to be minimal.

3.4. 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, see Millero et al., 1993) are insensitive to the presence of most salts and to the concentrations of Mg^{2+} and Si. Grain abrasion in coastal environments further implies that surface coating effects will be minimised. Additional processes, such as autogenous grinding of the grains in the surf zone, enhancing uptake rates, or the removal of material from the beach by wind and water influences, reducing uptake rates, are not taken into account, as these effects are site specific (Martens, 1931; McBride et al., 1996). We accordingly assume that the steady state dissolution rate parameter R_{diss} (Fig. 1), with an 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 terrestrial spreading of olivine in the tropics, at 40 °C and a soil pH of ~4, no organics considered, the same steady state data predict olivine dissolution rates some 200–600 times higher. Note, however, that the formation of surface coatings and the absence of grain abrading processes may strongly inhibit olivine dissolution in terrestrial environments.

4. Reaction progress with time and effect of grain size: a simple model

Applying the dissolution rate data presented in Fig. 1, it is now possible to construct a model predicting how dissolution of a batch of olivine sand will proceed in a beach environment, in terms of dissolved mass or volume vs. time. This provides an upper bound basis for assessing CO_2 uptake rates via reaction (3) and whether or not the process is fast enough to be useful for CO_2 sequestration purposes in the coming decades. We assume that olivine sand is composed of spherical particles, which dissolve according to a shrinking core model with external mass removal of dissolved material. This is reasonable considering the washing effect of seawater on a beach. On this basis, the extent of dissolution of a single, instantaneously deposited batch of olivine, i.e. the fraction of reacted material as a function of time, can be expressed as

$$X_{\text{olivine}}(t) = \frac{d_0^3 - d(t)^3}{d_0^3} \times 100\% \tag{4a}$$

with $\quad d(t) = d_0 - 2R_{diss}\Omega t \tag{4b}$

where X_{olivine} is the amount of olivine to have dissolved [vol%], t is elapsed time since deposition [s], d_0 is the initial grain size [m], d is the grain size at time t [m], R_{diss} is the dissolution rate of olivine [mol/m² s] and Ω is the molar volume of olivine [43.02×10^{-6} m³/mol]. As can be seen from Fig. 1, at a solution pH of 8.2, as expected in natural seawater, the dissolution rate R_{diss} has an average value of $(1.58 \pm 1.40) \times 10^{-10}$ mol/m² s at 25 °C. At 15 °C, the dissolution rate of olivine will be 2.6–3.5 times slower, i.e. $(5.93 \pm 5.42) \times 10^{-11}$ mol/m² s.

The progress of the olivine reaction and of CO_2 uptake versus time after deposition, calculated from Eq. (4) and reaction (3) for a range of initial olivine grain sizes and for seawater temperatures of 25 °C and 15 °C, are shown in Fig. 2. Recall here that 1 tonne of
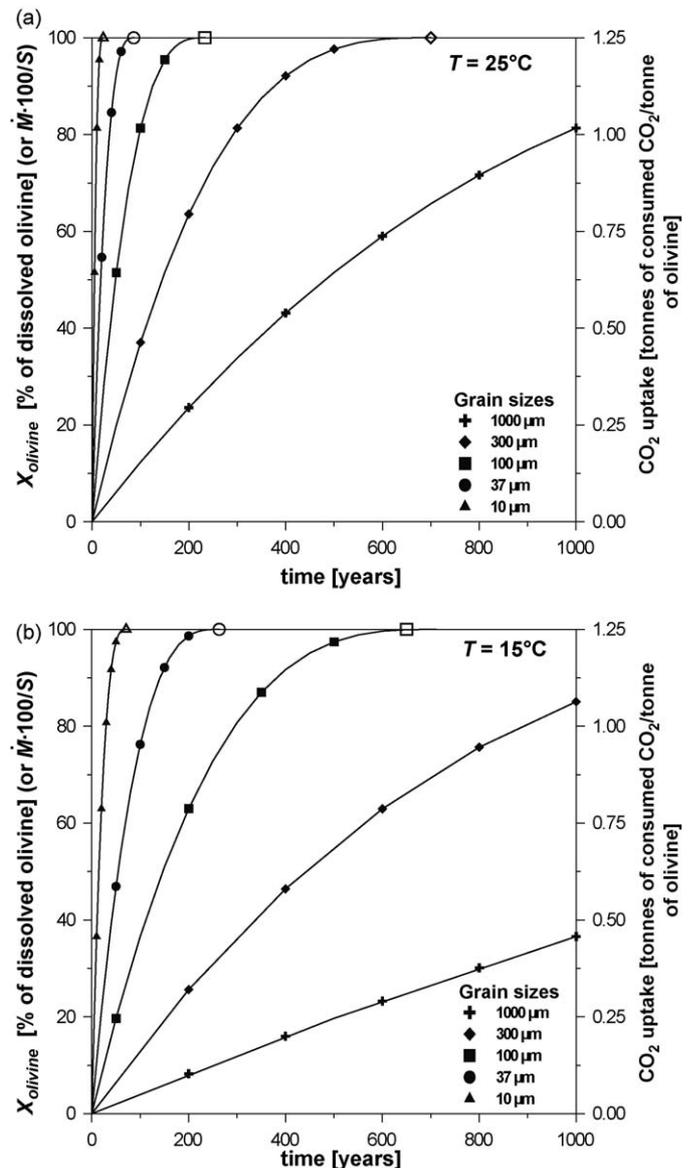

Fig. 2. The extent of granular olivine dissolution X_{olivine} as a function of time. The left axis shows the extent of olivine dissolution reaction in terms of reacted mass-fraction (%) of deposited olivine, while the right axis shows the amount of CO_2 sequestered per tonne of dissolved olivine. The left axis also shows in %, the total normalised rate of olivine reaction $\dot{M} \cdot (100/S)$ where $\dot{M}$ is the total rate of reaction of olivine at time t in t/year at a constant olivine supply rate of S t/year. 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 core model. The amount of CO_2 sequestered per tonne of olivine was calculated assuming reaction (3), which results in the formation of soluble magnesium bicarbonate salts and CO_2:olivine uptake ratio of 1.25 t CO_2 per tonne olivine. (a) Reaction progress at 25 °C, assuming that the dissolution rate of olivine is 1.58×10^{-10} mol/m² s (see Fig. 1). (b) Reaction progress at 15 °C, with the olivine dissolution rate being 5.19×10^{-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).

dissolved olivine traps 1.25 t of CO_2 (CO_2:olivine uptake ratio $Q = 1.25$). Reaction times (defined here as the time to dissolve 50–100%) of granular olivine are long even at grain sizes smaller than 300 μm. At 25 °C for example (Fig. 2a), olivine sand (grain size 300 μm), of the type proposed by Schuiling via the Dutch media, would take approximately 145 years to dissolve by half and 700 years to dissolve completely. Given the range of olivine dissolution rates at these conditions, the stated reaction times are only averages, since 50% dissolution of 300 μm grain size olivine may

Table 1
Summary of reaction times and CO_2 uptake for crushed olivine of various grain sizes (assuming beach reaction at 25 °C).

Grain size [μm]	Time for 10% dissol. [years]	Time for 25% dissol. [years]	Time for 50% dissol. [years]	Time for 100% dissol. [years]
1000	80 (43–692)	213 (113–1832)	481 (255–4134)	2333 (1235–20039)
300	24 (13–207)	64 (34–550)	144 (76–1240)	700 (371–6012)
100	8 (4–69)	21 (11–183)	48 (25–413)	233 (124–2004)
37	3 (2–26)	8 (4–68)	18 (9–153)	86 (46–741)
10	1 (0.4–7)	2 (1–18)	5 (3–41)	23 (12–200)
CO_2 uptake [t CO_2/tonne olivine]	0.125	0.313	0.625	1.25

Dissolution of the olivine is assumed to follow a shrinking core model (Eq. (4)). This will increase seawater alkalinity resulting in increased oceanic uptake of CO_2, and the sequestration of 1.25 t of CO_2 per tonne of olivine, according to reaction (3). Reaction time scales are calculated assuming the dissolution rate of olivine to be $(1.58 \pm 1.40) \times 10^{-10}$ mol/m^2 s at 25 °C and pH 8.2. Bracketed quantities represent the time scale range for the range of dissolution rates applying to beach reaction at 25 °C $((1.58 \pm 1.40) \pm 10^{-10}$ mol/m^2 s).

take between 75 and 1240 years, while complete dissolution may take between 370 and 6010 years. Decreasing the grain size strongly decreases reaction time, but will also require more energy for the grinding process. The corresponding times taken to trap 10, 25, 50 and 100% of the maximum amount of CO_2 that can be sequestered per tonne of olivine, through reaction (3) at 25 °C, are also visible in Fig. 2 and are listed in Table 1. Note that at 15 °C (Fig. 2b), reaction times are about three times longer, as a result of the decrease in olivine dissolution rate. Thus on Western European coasts, 50% dissolution of sand grade olivine (300 μm) will take on average about 450 years (225–3720 years). Clearly, grain size reduction to values <10 μm is needed to accelerate the dissolution rate of olivine to levels that can contribute significantly to CO_2 sequestration in the next 15 years (Fig. 2, Table 1).

To gain further insight into the progress of olivine dissolution and marine CO_2 uptake via reaction (3) under practical conditions, i.e. at a constant and continuous olivine supply rate, we have examined the situation where olivine of a given grain size d_0 is deposited at a steady, constant rate of S t/year. For a constant, steady olivine supply scenario of this type, the rate of dissolution of a mass increment of olivine Sdt, at time t since deposition, is given by differentiation of (4) with respect to t to yield $\partial X_{olivine}/\partial t$. The total rate of dissolution and hence reaction of olivine ($\dot{M}$) at any point τ in time, after *initiation* of olivine deposition, is then given by

$$\dot{M} = \frac{S}{100} \int_0^\tau \frac{\partial X_{olinine}(t)}{\partial t}\, dt = \frac{S}{100} X_{olinine}(\tau) \qquad (5)$$

where $\dot{M}$ is measured in [t/year] and t is time measured since deposition starts. This along with (4) demonstrates (a) that $\dot{M}$ increases monotonically from zero with time and (b) that when the rate of reaction $\dot{M}$ attains a value equal to the supply rate of olivine S, a steady state situation is attained at which the olivine first deposited has been completely consumed ($X_{olivine}$ = 100%, d(t) = 0). From (4b), it is seen that this steady state is reached at a time t after deposition starts, given

$$t = \frac{d_0}{2 R_{diss} \Omega} \qquad (6)$$

From Eqs. (4) and (5), it thus emerges that when olivine is supplied at a fixed rate S, the total normalised rate of olivine reaction $\dot{M}(100/S)$ evolves with time exactly as depicted for $X_{olivine}$ in Fig. 2 (Eq. (5)). Similarly, the steady state situation ($\dot{M} = S$), attained at $t = d_0/2R_{diss}\Omega$ is seen to correspond to the point in Fig. 2 at which $X_{olivine}$, for individual grain sizes, attains the value of 100%. On this basis, we can see from Eq. (5) and Fig. 2a, that to attain a steady state olivine consumption rate $\dot{M} = S$, and corresponding CO_2 uptake rate $\dot{C} = Q\dot{M} = 1.25\dot{M}$ for reaction (3), at 25 °C, takes 700, 233, and 23 years for grain sizes of 300, 100, and 10 μm respectively. At 15 °C, these times are increased by a factor of approximately 3.

It also emerges from (5) and from the relation $\dot{C} = 1.25\dot{M}$ that constant total reaction and sequestration rates $\dot{M}$ and $\dot{C}$ can be achieved by varying the olivine supply rate S such that the product $S X_{olivine}(t)/100$ is constant, i.e. by varying S with time according to the relation $S = (100\dot{M}/X_{olivine}(t))$ or $(S/\dot{M}) = (100/X_{olivine}(t))$. However, this requires very large quantities of olivine to be deposited per year during the early stages of beach spreading (high S values), while smaller amounts of olivine (lower S values) will suffice as the steady state condition $\dot{M} = S$ is approached (see Fig. 3). At 15 °C for example (Fig. 3b), the supply rate S of 300 μm grade olivine sand would have to be more than 10 times the target reaction rate $\dot{M}$ (hence more than 8 times the target CO_2 uptake rate $\dot{C} = 1.25\dot{M}$) for the first 80 years or so of olivine deposition. In addition, one should realise that once the method of coastal olivine weathering is applied on a large scale, the process itself cannot be stopped until all deposited olivine is consumed. It is safe to say that it is undesirable to create processes that keep absorbing CO_2 for decades or centuries to come.

5. CO_2 production due to mining and grinding

We have shown in Fig. 2 and Table 1 that grain size reduction to values <10–50 μm is needed to accelerate the dissolution rate of olivine to levels that can contribute significantly to CO_2 sequestration by beach reaction in the next 15 years. However, the overall efficiency of CO_2 sequestration depends on the amount of carbon dioxide produced during mining, grinding and transportation of the material. Though olivine-rich rocks are found in several major massifs around the world, they are very resistant to grinding, they are heavy (dense) and the source regions are often remote from the world's coastlines. The mining, crushing/grinding and transportation steps of beach weathering must therefore be considered carefully. For example, importing olivine to the Netherlands from the nearest source in Norway implies ~1000 km transportation. In this section, an attempt will be made to estimate the amount of CO_2 that is emitted during these various steps.

The estimates presented here are based on a study performed (CIPEC, 2005) by the Canadian Industry Program for Energy Conservation, on 7 open-pit gold and iron ore mines in Canada. Since the gold and iron ore in question is associated with (ultra)mafic rocks (Nurmi, 1991; Stendal and Ünlü, 1991) or materials of similar hardness, the data reported by CIPEC can be considered reasonably representative for the mining of olivine-rich rocks such as peridotite and dunite. Though the pure olivine content of peridotites and dunites generally varies between 60 and 90%, we assume these olivine sources to be 100% ore grade, following previous studies on olivine mining (Gerdemann et al., 2007; O'Connor et al., 2005). Therefore, no beneficiation (i.e. ore quality improvement by separating ore from waste material) is considered. The use of peridotites with only 60% olivine, instead of pure olivine, would clearly mean almost a doubling of the mass of
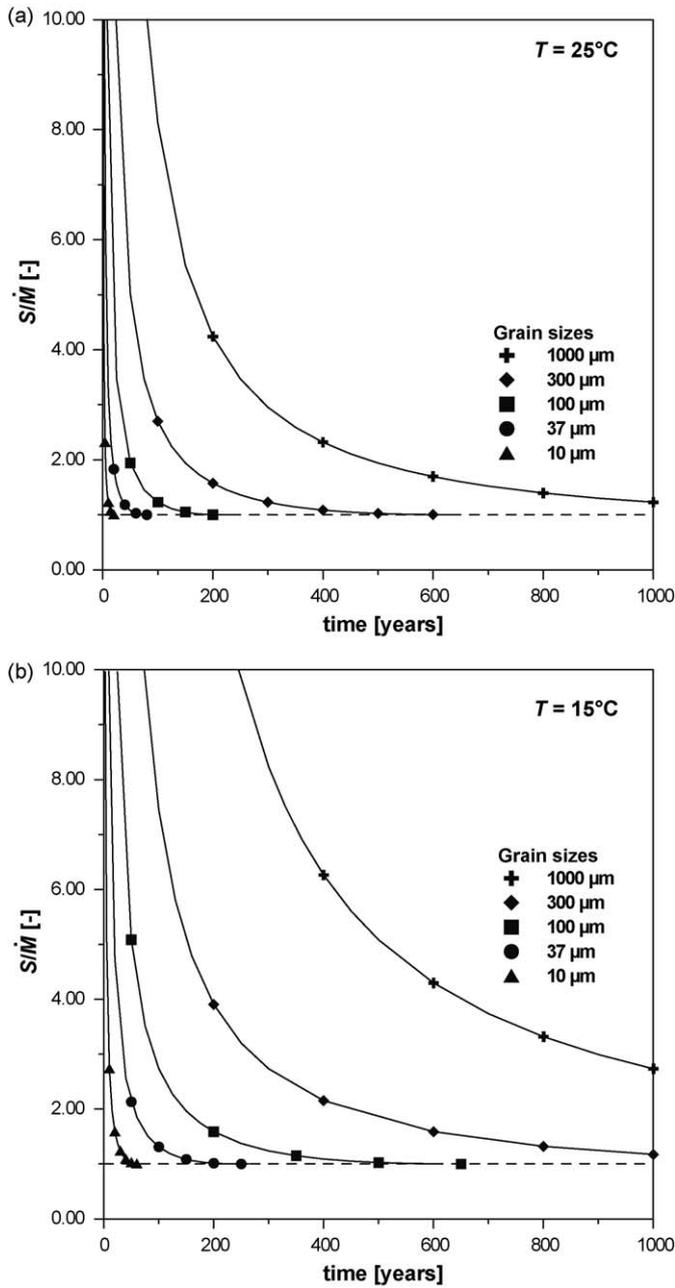
Fig. 3. Ratio of olivine supply rate S (t/year) to total olivine dissolution or reaction rate $\dot{M}$ (t/year) as a function of time. The graphs illustrate how supply rate S should vary with time to maintain a constant olivine consumption rate $\dot{M}$ and hence constant CO_2 uptake rate of $\dot{C} = 1.25\dot{M}$. Calculations were made with the same assumptions used in Fig. 2, and using the relation $(S/\dot{M}) = (100/X_{olivine}(t))$. The plots show that very large quantities of olivine are required in the early stages of deposition, while smaller amounts will suffice as steady state is approached. (a) Supply rate to dissolution rate ratio at 25 °C. (b) Supply rate to dissolution rate ratio at 15 °C.

material that has to be mined and processed, so a doubling of the associated CO_2 footprint.

In the following mining calculations, only energy consumption and hence CO_2 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). As can be seen in Table 2, the total energy consumption estimated for olivine mining is ~5 kWh/tonne. CO_2 emission rates for pulverised coal, coal gasification and natural gas power plants are reported to

be 0.795, 0.757, and 0.358 kg CO_2/kWh, respectively (Rubin et al., 2004). Taking these emission rates, CO_2 production during olivine mining would fall in the range 1.5–3.3 kg CO_2/tonne CO_2 sequestered (Table 2).

After mining, a series of crushing and grinding procedures have to be performed to produce olivine of a suitable grain size distribution (Table 2). Firstly, primary in-pit crushing, performed by jaw or gyratory crushers (Guimaraes et al., 2007), reduces the mined material to a grain size of approximately 1–300 mm (TKRI, 2004). For gold or iron ore, this requires roughly 1.3 kWh/tonne of ore produced (CIPEC, 2005). This value is similar to the 2.0 kWh/tonne 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 CO_2 emissions, primary crushing would thus lead to the production of 0.37–0.82 kg CO_2/tonne CO_2 sequestered (Rubin et al., 2004).

Primary crushing is followed by secondary grinding. The energy consumption W during this can be calculated using Bond's Equation (Morrel, 2004; Perry and Green, 1987). This equation 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, and is written as

$$W = 10W_i\left(\frac{1}{\sqrt{d}} - \frac{1}{\sqrt{d_\infty}}\right) \tag{7}$$

where W is the energy [kWh/tonne] required to reduced the feedstock to the desired grain size and W_i is an empirical work index of the feedstock material [kWh/tonne]. The work index for olivine has been taken to be the average of those found for Fe_2O_3 (8.6 kWh/tonne) and silica sand (16.46 kWh/tonne) which have similar hardness, i.e. 12.38 kWh/tonne (Perry and Green, 1987). For final grain sizes in the range 37–70 μm, Perry and Green (1987) added an empirical multiplying factor F to Eq. (7), given as $F = (10.3 + d/1.145d)$. Tertiary 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/tonne for olivine, wollastonite and serpentinite (O'Connor et al., 2005). Assuming a typical average feedstock grain size of 200 mm, the grinding energy and CO_2 production values implied for various final grain sizes are shown in Table 2.
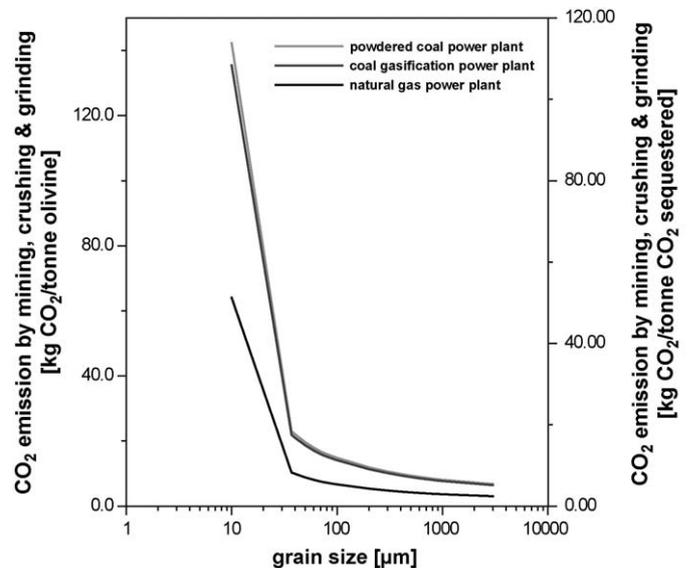

Fig. 4. Estimates of CO_2 emissions produced during mining, crushing and grinding of one tonne of pure olivine feedstock (grain size 200 mm) to a given grain size, assuming a four-stage process for the finest grain size (10 μm).

Table 2
Energy consumption and CO_2 production during olivine mining, crushing, grinding and transportation.

Mining procedures	Energy consumption during mining [kWh/tonne olivine][a]	CO_2 emission[b] [kg CO_2/tonne CO_2 sequestered]		
		(1)	(2)	(3)
Drilling	0.35	0.22	0.21	0.10
Blasting	0.44	0.28	0.26	0.13
Excavation	0.95	0.61	0.58	0.27
Transport/hauling	3.49	2.22	2.11	1.00
Total	5.23	3.33	3.16	1.50

Crushing and grinding: grain size [μm]	Energy consumption during crushing/grinding procedures [kWh/tonne olivine][c]				Total CO_2 emission[b] [kg CO_2/tonne CO_2 sequestered]		
	(A)	(B)	(C)	Total (A + B + C)	(1)	(2)	(3)
1000	1.3	3.64		4.94	3.14	2.99	1.42
300	1.3	6.87		8.17	5.20	4.94	2.34
100	1.3	12.10		13.40	8.52	8.11	3.84
37	1.3	22.41		23.71	15.08	14.36	6.79
10	1.3	22.41	150	173.71	110.48	105.20	49.75

Transport	CO_2 emission [g CO_2/tonne olivine]	CO_2 emission [kg CO_2/100 km/tonne CO_2 sequestered]
Inland/coastal ships	30	2.4
Freight train	20	1.6
Trucks	138	11.0

[a] Note that 1 kWh = 3.6×10^6 J. Estimates based on gold/iron mining; see text.
[b] (1) Powdered coal; (2) coal gasification; (3) natural gas power plant.
[c] (A) Primary in-pit crushing; (B) secondary grinding (to 37 μm); (C) tertiary grinding (ultra-fine grinding, 10 μm).

For synoptic purposes, the total CO_2 emissions produced by mining, crushing, and grinding 1 tonne of olivine, or per tonne CO_2 avoided, calculated as a function of grain size, are depicted in Fig. 4. The pure olivine feedstock grain size has been set at 200 mm. It is clear from Fig. 4 that carbon dioxide emissions (and of course costs) increase with decreasing final grain size. For final grain sizes larger than approximately 40 μm, carbon dioxide sequestration efficiency is reduced by less than 2% (<20 kg/tonne CO_2 sequestered). However, at a final grain size of 10 μm, CO_2 emissions as a result of mining, crushing and grinding constitute between 5 and 11% of the total amount of sequestered CO_2.

The calculations presented so far do not include energy consumption associated with 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 CO_2 emissions from freight transport (McKinnon, 2006) has shown that CO_2 emissions per tonne of transported material are 30 g/km for inland or coastal ships, 20 g/km for trains, and 138 g/km for trucks. This will result in an additional efficiency reduction of 1.6–11.0 kg CO_2/100 km/tonne CO_2 sequestered or of 0.1–1% (Table 2). Hence, for an 1000–4000 km boat haul to import crushed olivine from the nearest sources in Norway, Greenland or Turkey to Western Europe, an additional CO_2 output of at least 24–96 kg CO_2/tonne CO_2 sequestered would be generated.

This all means that the efficiency reduction of olivine beach sequestration would be around 10–20% for locations that are remote from the olivine sources (like Western Europe) and up to 10% for locations near source (e.g. coast of Turkey). Since most olivine-rich rocks are ~60% olivine, more realistic figures are probably 15–30% and up to 15%, respectively. In addition, CO_2 costs associated with building the extra production and transport facilities needed to mine and move large amounts of olivine will reduce sequestration efficiency further still, but this needs more research.

6. Feasibility of CO_2 sequestration via coastal spreading of olivine

In order to assess the feasibility of coastal spreading of olivine as sequestration method, all of the factors discussed above have to be taken into account—the relevant reaction, the olivine dissolution rate, the reaction progress, the grinding, mining and transportation energies and the amount of olivine required. Our starting point is our reaction progress model for olivine "sand" embodied in Eqs. (4) and (5). The assumption that reaction (3) will occur with a CO_2:olivine uptake rate Q of 1.25, the "upper bound" mean value of R_{diss} used and the assumption of pure olivine, mean that the model likely overestimates the effectiveness of beach reaction of olivine.

In the following, we apply our model to examine the feasibility of beach weathering of olivine to offset CO_2 emissions in two reference scenarios. To date no consensus has been reached on the required CO_2 emissions reductions. Within the EU it has been proposed that CO_2 emissions reductions of up to 30% of 1990 levels are required by 2020, and up to 80% by 2050 (Commission of the European Union, 2007). Schuiling has suggested that coastal weathering of olivine can replace technological solutions, such as CCS, to achieve such targets (Biersma, 2007; Eshuis, 2007). Our first reference scenario therefore involves offsetting 30% of global CO_2 emissions through coastal weathering of olivine by 2020, while the second scenario involves offsetting 30% of Dutch CO_2 emissions by 2020 (all percentages are of 1990 levels).

6.1. Global scenario

In 1990 the world's yearly CO_2 emission, resulting from the burning of fossil fuels, was approximately 21 Gt (Bernstein et al., 2007). Offsetting worldwide CO_2 emissions by 30% of 1990 levels through olivine weathering according to reaction (3) with Q = 1.25 would thus consume approximately 5.0 Gt of olivine per year. The mass needed for industrial mineralisation via reactions (1a) or (2) would be approximately twice this amount.

To illustrate the amount of olivine reacting $\dot{M}$, and the amount of CO_2 being consumed $\dot{C}$ per year, at a constant olivine supply rate of S = 5.0 Gt/year, we constructed Fig. 5a, using our reaction progress model (Eqs. (4) and (5)) applied for a mean global seawater temperature of 25 °C and a dissolution rate in seawater of 1.58×10^{-10} mol/m^2 s (Fig. 1). From Fig. 5a (see also Fig. 2a), it can be seen that at this supply rate it would take 700 years to reach the desired steady state olivine consumption and CO_2 uptake rates at a
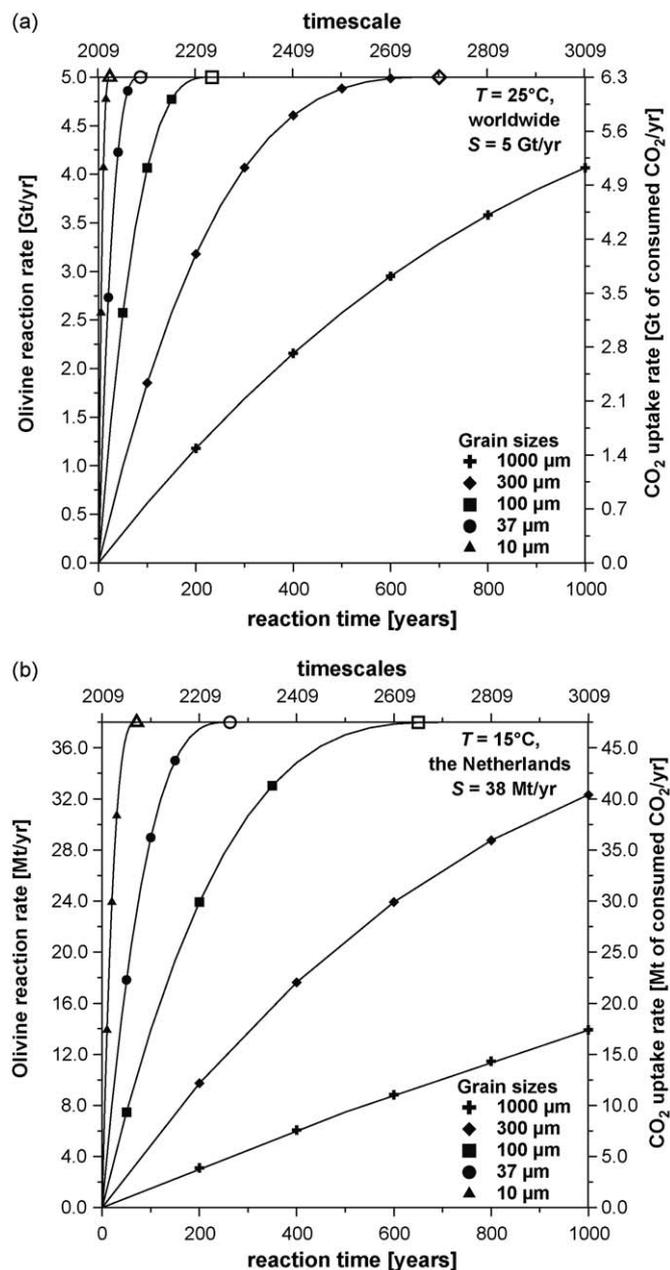
(a)

(b)

Fig. 5. The amount of granular olivine reacting per year ($\dot{M}$, left axis) and the equivalent amount of CO_2 consumed per year ($\dot{C}$, right axis) as a function of time, at constant olivine supply rates S. 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 core model. The amount of CO_2 sequestered per year was calculated assuming reaction (3), which results in the formation of soluble magnesium bicarbonate salts and a CO_2:olivine uptake ratio of 1.25 t CO_2 per tonne olivine. (a) S = 5 Gt/year, equivalent to a 30% reduction in worldwide CO_2 emissions. The dissolution rate of olivine was set at 1.58×10^{-10} mol/m^2 s, assuming seawater temperature is 25 °C (see Fig. 1). (b) S = 38 Mt/year, equivalent to a 10% reduction in Dutch CO_2 emissions. Seawater temperature was assumed to be 15 °C with the dissolution rate of olivine being 5.19×10^{-11} mol/m^2 s (calculated using the dissolution rate at 25 °C and an activation energy of 79.5 kJ/mol, following Wogelius and Walther, 1992).

grain size of d_0 = 300 μm and a seawater temperature of 25 °C. Similarly, at a grain size of d_0 of 100 μm or 10 μm it would take 230 and 23 years, respectively (see also Section 4). To achieve a steady state emissions rate offset of 30% in 15 years (i.e. by 2024) at 25 °C, Eq. (6) shows a grain size of approximately 6 μm would be required. Since the instantaneous rate of olivine consumption $\dot{M}$ scales linearly with supply rate (Eq. (5)), using olivine grain sizes

greater than ~6 μm would require proportionally larger supplies of olivine (>5.0 Gt/year), to achieve the same offset in atmospheric CO_2 concentrations in the same time. The (vast) magnitude of the increased olivine supply rates S needed are predicted by Fig. 3, setting $\dot{M}$ at the steady state values $\dot{M} = S = 5.0$ Gt/year.

In colder regions, i.e. at 15 °C, steady state sequestration rates take approximately three times longer to reach than at 25 °C (Fig. 2b), so the supply rate of olivine needed has to be tripled (15.0 Gt/yr), or else, following (6), three times smaller grain sizes are required (e.g. 2 μm), to achieve the same sequestration target within a given time scale (e.g. 15 years). Coastal spreading of olivine in warmer areas will decrease reaction times by a factor of 1.7 times if the temperature is raised to 30 °C, and even by 4.6 times if temperature increases to 40 °C. In this case of 40 °C, equation (6) shows that grain sizes of 30 μm could be used to reach equivalent steady state reduction rates of 5.0 Gt/year in 15 years.

The above shows that to offset global CO_2 emissions by 30% within a timescale of 15–20 years, by beach weathering alone, requires 5.0 Gt/year, or more of fine (10 μm grade) olivine powder to be mined, handled, transported and spread. We have already shown that the CO_2 cost of such operations will be of the order of 15% of the CO_2 removed from the atmosphere. Assuming that the broader environmental impact is acceptable, the question remains as to whether the transportation of such vast solid masses is feasible. A truck can typically transport 50 t, while the most commonly used cargo ship, the so-called Handysize, can carry 25 kt on average. Sequestration levels equivalent to an approximate 30% reduction in 1990-level worldwide carbon dioxide emissions (i.e. 6.25 Gt/year) would therefore mean moving 100 million truckloads, or 200,000 shiploads of olivine on a yearly basis, that is 1.9 million truckloads, or 3800 shiploads, on a weekly basis. Given that the entire worldwide fleet of Handysize cargo ships is around 2000 vessels, and assuming a roughly 1-week round trip for each vessel, this means that it would be necessary to roughly double the fleet within a few years, to reach the desired CO_2 uptake targets. While this neglects road transport aspects, it nonetheless illustrates the magnitude of the mass transport problem. Though it may be possible to expand the current fleet, the large ship building expenses will bring about a significant increase in the costs of the proposed method and will affect the "cheap" character it has been given in the media. Given the current world fleet, we infer that transporting 5.0 Gt of olivine per year is an impractical task and we suggest that the maximum achievable haulage would be between 5 and 10% of this figure. This implies that the maximum possible CO_2 uptake by beach reaction of olivine would be between 1.5 and 2.8% of 1990-level emission rates, neglecting the additional CO_2 costs of expanding the transport fleet to cope.

6.2. The Dutch scenario

We now consider what the above would all mean for an industrialised Northern hemisphere country, like the Netherlands, in a situation where emissions trading is not possible. In 1990, the Dutch CO_2 emission rate was 158 Mt/yr (Brandes et al., 2006). A 30% reduction in this amounts to ~47 Mt/year. Assuming a constant olivine supply rate of S = 38 Mt/year (equivalent to a 30% reduction in CO_2 emissions by olivine weathering at steady state) and a mean seawater temperature of 15 °C (R_{diss} = 5.19 × 10^{-11} mol/m^2 s), our reaction progress model predicts the evolution of olivine reaction rate $\dot{M}$, and the CO_2 uptake rate $\dot{C}$ per year, depicted in Fig. 5b. From this figure and the underlying Eqs. (4)–(6), it is clear that sand grade olivine (100–300 μm) will simply react too slowly to have a significant impact in the coming decades, achieving CO_2 uptake rates of just 2–4 Mt/year, which is equivalent to only 1–3% of 1990 Dutch emissions. In order to achieve an

equivalent of a 30% steady state reduction in CO_2 emissions in approximately 15 years by olivine beach weathering, Eq. (6) shows that a grain size of 2 μm or less is required. This value approaches the theoretical limit of grain size reduction and would be highly energy/CO_2 inefficient in practice (Fig. 4). In addition, the haulage of 38 Mt of olivine per year, that is 0.7 Mt per week, implies the movement of 14,600 50-t olivine trucks on the already choked Dutch road network, or the passing of 29 Handysize ships or dumper-vessels along the coast, on a weekly basis. On a yearly basis, the corresponding volume of olivine sand or powder deposited on Dutch beaches would be 16–32 Mm^3 (assuming 40% porosity, 50–100% olivine) equivalent to a strip of 10 m high, 100 m wide and 16–32 km long. As demonstrated by Fig. 3b, to achieve a 30% equivalent emissions reduction ($\dot{C} = 43$ Mt CO_2 per year, $\dot{M} = 38$ Mt olivine per year) in the coming 15 years, using sand grade (100–300 μm) olivine, would require an olivine deposition or supply rate S many tens or even hundreds of times greater, which is entirely impractical.

6.3. Synthesis

Our calculations for both the global (25 °C) and Dutch (15 °C) scenarios show that very fine-grained olivine (2–6 μm) is required to achieve significant steady state CO_2 uptake rates within a few decades. This makes beach spreading of olivine inefficient. In addition, impractically large amounts of olivine must be transported to achieve a significant impact in terms of CO_2 uptake. Moreover, it should not be forgotten that finely crushed olivine rock might very well pose a (wind-born) health risk, especially if the material contains fibrous serpentine minerals (asbestos), which it often does. Landward wind borne transport of such fine olivine powder could in itself pose problems. It is our conclusion that beach reaction is not a practical option for Northern hemisphere countries with mean coastal seawater temperatures of 15 °C or less. On the other hand, given suitable emissions trading regulations, coastal weathering of olivine in hot, (sub)tropical areas, close to sites where olivine can be mined, could perhaps contribute to offsetting global emissions at the 0.1–1% level. Such areas offer improved possibilities and costs, which may warrant further investigation from a niche market perspective. Clearly, coastal weathering of olivine cannot offer a stand-alone solution for CO_2 control and cannot replace CO_2 mitigation technologies, such as CO_2 capture and storage (CCS).

7. Coastal vs. land spreading

In addition to the 'Green Beaches' concept, the proposal by Schuiling to trap CO_2 from the atmosphere by terrestrial spreading olivine on acidified soils (Biersma, 2007; Eshuis, 2007; Schuiling and Krijgsman, 2006) also assumes reaction (3) and is expected to be controlled by olivine dissolution kinetics. We have shown above that coastal weathering is relatively slow and largely impractical. However, terrestrial spreading has several possible advantages over coastal spreading of olivine, as soils generally have a lower pH, typically around pH 4 and are rich in organic acids. These factors could potentially enhance olivine dissolution rates by a total of perhaps two orders of magnitude compared to dissolution in seawater (cf. Fig. 1). In addition, terrestrial spreading of olivine in (sub)tropical areas would benefit from the higher temperatures, which will enhance dissolution rates further (up to 600 times at 40 °C compared to 25 °C). On the other hand, evaporation effects may lead to magnesite or hydromagnesite formation (reactions (1a) and (2) instead of (3)) reducing CO_2 uptake rates by up to a factor of 2. This all means that reaction rates for olivine spread on land in the tropics could be up to 200–600 times faster than for beaches. Though terrestrial spreading of olivine will encounter

similar transport and infrastructural problems to coastal spreading, and while the possible impact upon agriculture, environment, ecology and human or animal health (fine olivine) remains to be clarified, it is inherently more promising and deserves further research.

8. Conclusions

This evaluation of the proposal to spread olivine sand (300 μm) along the coastlines of the world, in an attempt to reduce atmospheric CO_2 concentrations through weathering reactions, has led to the following conclusions:

(1) From the literature, we deduced that the dominant reaction is most likely $(Mg,Fe)_2SiO_{4(S)} + 4H_2O_{(l)} + 4CO_{2(g)} \leftrightarrow 2(Mg^{2+}, Fe^{2+})_{(aq)} + 4HCO_3^-{}_{(aq)} + H_4SiO_{4(aq)}$, which has an uptake capacity of 1.25 t of CO_2 per tonne of olivine. Dissolution of olivine will be rate controlling, though verification of both the nature and rate of the dominant reaction is still required.

(2) At temperatures of 15–25 °C and pHs in the range 4.0–8.2, the dissolution rate of olivine is of the order of $(1.6 \pm 1.4) \times 10^{-10}$ to $(3.8 \pm 2.9) \times 10^{-9}$ mol/m^2 s. Increasing temperature, from 25 to 30 °C (tropical seawater) or 40 °C (tropics, land), will increase olivine dissolution rates by up to about half an order of magnitude (factor 1.6–5.7).

(3) For fixed rates of olivine supply, beach weathering of olivine with an initial grain size d_0 of 300 μm requires 700 years to reach a steady state CO_2 uptake rate at 25 °C, and three times longer at 15 °C (i.e. 2130 years). This is too slow to make a useful impact on atmospheric CO_2 levels in the coming decades. Grain size reduction to micrometer levels is needed on this timescale.

(4) Mining, crushing and grinding of olivine to a grain size of less than 10 μm will reduce process efficiency by 5–11% for pure olivine and by 10–20% for typical olivine rock. An additional 0.1–1% efficiency reduction will be generated per 100 km of transport of 1 tonne of crushed olivine rock by ship, train, or truck. Typical transport distances in Europe would be ~1000 km.

(5) Aiming for an equivalent of a global target of 30% steady state emissions reduction by 2020 would require coastal spreading of 5.0 Gt of 6 μm grain size (i.e. dust-grade) olivine per year, depending on seawater temperature (15–25 °C). This is not feasible given the current global capacity of trucks and Handysize cargo ships. A 1.5–2.8% equivalent reduction might be feasible. It should be noted, however, that the necessary quantities of dust-grade mineral material (including asbestos-related serpentine minerals) may pose public health risks.

(6) For an industrialised, Northern hemisphere country such as the Netherlands, with a mean seawater temperature of ~15 °C, coastal olivine weathering would be very impractical. An equivalent target of 30% steady state emissions reduction by 2020 would require coastal spreading of 47 Mt of 2 μm, dust-grade olivine per year. This implies a vast increase in transport capacity, and again possible asbestos-related health risks. Spreading of 100–300 μm sized crushed olivine could result in a 1–3% offset in CO_2 emissions in the coming few decades.

(7) We infer that coastal spreading of olivine is not a stand-alone solution for CO_2 sequestration and cannot replace technological options, such as CCS. However, beach weathering could contribute perhaps a 1% equivalent reduction as a niche activity, particularly in tropical regions where reaction rates are accelerated. More research on costs, logistics and seawater reaction rates is needed to clarify the possible contribution.

(8) The biggest uncertainty in our calculations for beach weathering probably resides in the effect of seawater salt content, and other solute content, on the dissolution rate of olivine. Available data suggest no effect of such solutes, but there is a possibility that Cl^- complexation may accelerate olivine dissolution to some minor extent. This needs further experimental investigation, but even if a doubling or tripling is observed, the rate of olivine dissolution in seawater will still be insufficient to render beach weathering a forefront CO_2 uptake method.

(9) Terrestrial spreading of crushed olivine in tropical areas is more promising than beach reaction, especially on land with acidic soils. More research is needed on this, particularly on the reaction capacity and effect of the released Mg-ions on agriculture.

Acknowledgements

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