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Enhanced weathering of olivine in seawater: The efficiency as revealed by thermodynamic scenario analysis

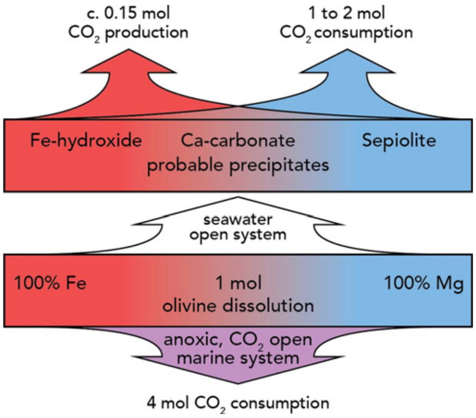
Jasper Griffioen

TNO Geological Survey of the Netherlands, P.O. Box 80015, 3508 TA Utrecht, The Netherlands
Copernicus Institute of Sustainable Development, Utrecht University, P.O. Box 80115, 3508 TC Utrecht, The Netherlands

HIGHLIGHTS

- Measures may be needed to lower the atmospheric CO_2 level and combat climate change as well as ocean acidification
- Enhanced weathering of olivine in marine environment is such a measure
- The efficiency of olivine weathering depends on the Mg/Fe fractions of olivine and precipitation of secondary minerals or not
- For Fe-rich olivine, CO_2 may be released to the atmosphere and ocean pH might decrease during oxic olivine weathering

GRAPHICAL ABSTRACT



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ABSTRACT

Enhanced weathering of olivine has been suggested as a measure to lower the atmospheric CO_2 level and it might also mitigate ocean acidification. This study aimed to characterise how olivine can weather in seawater, to elucidate the role of secondary precipitation and to ascertain the efficiency in terms of molar CO_2 removal per mole of olivine dissolution. Geochemical thermodynamic equilibrium modelling was used, which considered both the variable mineralogical composition of olivine and the kinds of secondary precipitates that may be formed. The advantage is that such an approach is independent from local or regional factors as temperature, related kinetics, mineralogy, etc. The results show that the efficiency falls when secondary precipitates are formed. When Fe-bearing olivine undergoes weathering in an oxic environment, Fe(III) hydroxides will inevitably be formed, and as a result of this acidifying process, CO_2 could be released to the atmosphere. This might also enhance ocean acidification when Fe-rich olivine becomes used. Ocean alkalinisation only happens when more than 1 mol/kg_{H2O} Mg-rich olivine weathers. Maintenance of supersaturation for calcite or aragonite as holds in seawater reduces the efficiency by about a factor of two compared to the efficiency without secondary precipitation. Precipitation of sepiolite as Mg silicate reduces the efficiency even more. Magnesite precipitation has a similar effect to Ca carbonate precipitation, but according to the literature magnesite precipitation is improbable at ambient conditions and relatively low supersaturation. When less than 0.05 mmol olivine/kg(seawater) weathers the efficiency is slightly different than at higher intensities, due to strong buffering by seawater alkalinity.

E-mail address: jasper.griffioen@tno.nl.

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1. Introduction

One mitigating measure that has attracted attention to halt rising atmospheric concentrations of CO_2 is enhanced weathering: anthropogenically induced weathering resulting from introducing relatively rapidly weathering minerals, such as olivine, into the environment (Seifritz, 1990; Lackner, 2003; Lenton and Britton, 2006; Schuiling and Krijgsman, 2006; Köhler et al., 2010; Hartmann et al., 2013; Williamson, 2016). In principle, enhanced weathering can take place in terrestrial and marine environments (Hartmann et al., 2013). A similar measure is 'mineral carbonation', which is the accelerated weathering of easily weatherable rocks or minerals under high temperature and pressure; this can take place in geological formations or aboveground (e.g. Béarat et al., 2006; Alfredsson et al., 2008; Kelemen and Matter, 2008). The socio-scientific interest in these topics has stimulated research on the temperature dependence of weathering rates and the related formation of secondary products.

An idea proposed in the case of the marine environment is to scatter olivine grains on the open ocean, which will have largely dissolved before they disappear out of the surface mixed layer which is averagely 64 m thick (Köhler et al., 2013); it has also been proposed to scatter crushed olivine in shallow seawater (Schuiling and De Boer, 2011). Articles in the Dutch press led Hangx and Spiers (2009) to question whether the second idea is feasible geochemically and in terms of environmental economics. The rationale behind the idea of spreading olivine in shallow seawater is that in this water, and especially in coastal seawater, the grains undergo frequent agitation, which results in abrasion of the grains and in any coatings on the grains being rubbed off. These coatings are undesirable because they can retard or even prevent weathering, as a result of the limited exchange between CO_2 in the air and interface with the olivine crystal (e.g. Olsson et al., 2012; Wang and Giammar, 2012).

Weathering reactions are often alkalising. Enhanced weathering of olivine in marine environment may then not only mitigate rising atmospheric concentrations of CO_2 but also mitigate the associated CO_2 problem of ocean acidification. Ocean acidification causes the risk that biologically controlled calcium carbonate precipitation will no longer be able to take place, and this is potentially damaging for marine ecosystems such as coral reefs (e.g. Atkinson and Cuet, 2008; Artioli et al., 2012; Feely et al., 2012). Addition of limestone or quicklime has been proposed to raise the ocean alkalinity initially in order to capture atmospheric CO_2 in the ocean and later on to combat ocean acidification as well (Kheshgi, 1995; Rau and Caldeira, 1999; Caldeira and Rau, 2000; Harvey, 2008; Ilyina et al., 2013): more anthropogenic carbon would be adsorbed by the ocean while buffering the acidifying effect of CO_2 on ocean pH. A substantial CO_2 release happens in producing quicklime from limestone which must be dealt with as well (Paquay and Zeebe, 2013; Renforth et al., 2013). Ocean liming and enhanced weathering of olivine in marine environment are thus comparable mitigating measures compared to alternatives as geological disposal of CO_2.

Mg-rich and Fe-rich olivine occur often in nature, in a range of mixtures between the end-members forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) (e.g. Deer et al., 2013). Huang (1989) noted that the most frequently occurring olivine appears to contain 30–50% Fe, which is the typical Fe fraction of olivine in gabbros (Deer et al., 2013). Ultramafic rocks such as dunite and peridotite contain much Mg and correspondingly contain the highest content of Mg-rich olivine (Krauskopf, 1982; Deer et al., 2013). The percentage of Mg in dunite-olivine varies: in regular dunites the range is 88–93% (Su et al., 2016) and in Fe-rich dunites it is 80–88% (Rehfeldt et al., 2007; Ackerman et al., 2009). Enhanced weathering of olivine is routinely described as a dissociation reaction of olivine (Schuiling and Krijgsman, 2006; Olsson et al., 2012; Schuiling and De Boer, 2011; Köhler et al., 2013; Hauck et al., 2016):

$$(\mathrm{Mg,Fe})_2\mathrm{SiO_4} + 4\ \mathrm{CO_2} + 4\ \mathrm{H_2O} \rightarrow 2\ \left(\mathrm{Mg^{2+}}/\mathrm{Fe^{2+}}\right) + 4\ \mathrm{HCO_3}^- + \mathrm{H_4SiO_4} \tag{1}$$

Moosdorf et al. (2014) assumed pure forsterite. Such reaction equations pay no attention to which secondary products might be formed. For example, dissolved Fe^{2+} is not stable in an oxic environment and so will be oxidised to Fe oxyhydroxide, which is an acid-producing reaction. Béarat et al. (2006) and Hartmann et al. (2013) also presented the subsequent reaction for pure forsterite with $MgCO_3$ precipitation:

$$\mathrm{Mg_2SiO_4} + 2\ \mathrm{CO_2} + 2\ \mathrm{H_2O} \rightarrow 2\ \mathrm{MgCO_3} + \mathrm{H_4SiO_4} \tag{2}$$

Note that the molar ratio of olivine to CO_2 differs between these two reaction equations by a factor of 2. Mineral carbonation of olivine is mainly written as a weathering reaction of forsterite to $MgCO_3$ (Béarat et al., 2006; Mani et al., 2008; Wang and Giammar, 2012; Johnson et al., 2014; Lafay et al., 2014). Köhler et al. (2010) noted that enhanced weathering of olivine in the marine environment will have an impact on the carbon cycle and the alkalinity, but did not elaborate further. It should be noted that in contrast to rainwater, seawater has a strong weathering signature, with high concentrations of Mg, SiO_2, and alkalinity and also a fairly high pH. The degree of undersaturation will therefore be more limited than in slightly acid rainwater, and this can limit olivine weathering in this marine environment.

The research described here had three aims: to characterise how olivine can weather in seawater, to elucidate the role of secondary precipitation and to ascertain the related efficiency in terms of molar CO_2 removal per mole of olivine dissolution. The key questions addressed were:

- What is the difference in the weathering of forsterite, fayalite and a compound crystal that is a mixture of Mg_xFe_{1-x} olivine?
- What is the influence of equilibrium or non-equilibrium with atmospheric CO_2?
- What is the influence of maintaining or not maintaining equilibrium with Ca carbonate and/or Mg carbonate and, more specifically, with or without precipitation of magnesite, $MgCO_3$?
- What is the influence of precipitation or non-precipitation of sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$) as a weathering product?

The first question is relevant because different olivine minerals occur in different rock types. The second and third questions are relevant because marine environments vary in the extent to which they may be closed to CO_2 exchange, with the beach zone having relatively good exchange with the air; also, marine environments do not have a thermodynamic equilibrium with pure carbonate materials such as calcite, dolomite, magnesite and aragonite. A multicomponent geochemical modelling approach based on thermodynamic equilibrium was followed. The study therefore focused on achieving an end stage in the weathering and not on how rapidly this was achieved or the factors also determining this. This implies that the outcome has a general, global meaning and is not limited by local or regional boundary conditions such as temperature, reaction kinetics, mineralogical composition of the seabed or suspended matter, etc.

2. Model set-up

The calculations were performed with the multicomponent geochemical model code PHREEQC (Parkhurst and Appelo, 2013), which is standardly equipped with several thermodynamic databases that can be used. In this research the LLNL database was used because it includes the solution reactions of fayalite and forsterite. Two olivine solid solutions were added:

$$\mathrm{Mg_{1.6}Fe_{0.4}SiO_4} + 4.0\ \mathrm{H^+} = 1.0\ \mathrm{SiO_2} + 2.0\ \mathrm{H_2O} + 1.6\ \mathrm{Mg^{2+}} + 0.4\ \mathrm{Fe^{2+}}$$
$$\text{with}\ \log K = 25.9126 \tag{3}$$

and

$$Mg_{0.86}Fe_{1.14}SiO_4 + 4.0\ H^+ = 1.0\ SiO_2 + 2.0\ H_2O + 0.86\ Mg^{2+} + 1.14\ Fe^{2+} \quad \text{with}\ \log K = 22.6126 \tag{4}$$

Thermodynamic properties for these two solid solutions were explicitly established by Stefansson (2001) and their compositions are relevant compared to the common range in natural olivine solid solutions (as discussed in the Introduction). Therefore, these solid solutions serve as examples in the calculations. The dissolution products of these solid solutions as derived from Stefansson (2001) had to be adjusted for the LLNL database because Stefansson's values were based on the thermodynamic database of Robie and Hemingway (1995), and individual thermodynamic constants are not interchangeable among databases. For the transformation, we opted to interpolate the logK for solid solutions between the logK values of fayalite and forsterite, thus maintaining the mutual difference in logK values. Note that solid solutions of this type are nowadays indicated in a notation with the percentage of the most frequently occurring end-member, which in this case is Fo_{80} and Fa_{57}.

The composition of seawater was taken from Hem (1985; Table 1). The saturation index (SI) is defined as the log value of the ratio of the ion activity product (IAP) and the solubility constant (K). The pH of seawater was set at 8.2 but it varies between 7.5 and 8.4 (Marion et al., 2011). This has a direct repercussion on the saturation index for carbonate minerals: each time the pH changes by 0.1, there is a near-identical change in the saturation indices for calcite, aragonite and magnesite for this pH range. All model calculations were made at a reference temperature of 25 °C. They were done for different thermodynamic boundary conditions:

1. closed or open to O_2 or to CO_2, assuming that in open systems P_{O2} is equal to the value for air ($10^{-0.7}$atm) and P_{CO2} is equal to the value for seawater ($10^{-3.4}$ atm);
2. system with and without carbonate mineral equilibrium (calcite, aragonite and/or magnesite);
3. system with and without sepiolite equilibrium.

There is all kinds of evidence from laboratory and field experiments that Ca carbonate precipitation to total thermodynamic equilibrium (SI = 0) does not occur in marine systems but that some supersaturation remains, with the precipitation rate being a function of the degree of supersaturation (e.g. Sabbides et al., 1992; Langdon et al., 2000; Broecker et al., 2001). With regard to the second boundary condition, it may be assumed that seawater supersaturation is maintained and that as soon as the saturation index exceeds that of seawater through olivine weathering, carbonate precipitation occurs down to seawater supersaturation, i.e. not until thermodynamic equilibrium is attained (see further under Discussion). The calculations assumed the occurrence of calcite precipitation, but it does not matter whether it is assumed that the seawater saturation maintained is with calcite ($SI_{calcite}$ is 0.7) or with aragonite, because as a result of the constant difference in thermodynamic solubility constant at a given temperature, there is a constant systematic difference of 0.15 in the SI values of these two minerals. With regard to this boundary condition, note that any other assumption would imply that olivine weathering triggers the attainment of a carbonate saturation state that differs from the one that now generally occurs in seawater. This is unrealistic, as it would mean that under the usual marine conditions there would also be a different thermodynamic equilibrium with Ca carbonate and Mg carbonate.

Table 1
Composition (in mg/l for the ions with alkalinity based on HCO_3) for seawater according to Hem (1985) with saturation indices for different phases as calculated with the LLNL database.

Cl	Na	SO_4	Mg	Ca	K	Alkalinity	SiO_2
19,000	10,500	2700	1350	400	380	142	6,4
Saturation Indices							
pH	Calcite	Aragonite	Magnesite	Sepiolite	$SiO_{2(am)}$	$P(CO_2)$	
8,2	0,70	0,55	1,03	3,46	−1,32	−3,4	

Another assumption is that equilibrium with amorphous SiO_2 establishes itself if supersaturation with this SiO_2 occurs because intensive weathering has resulted in large amounts of dissolved SiO_2. In normal seawater there is undersaturation with amorphous SiO_2 that is also maintained if during olivine weathering the saturation index remains negative.

3. Results

3.1. Weathering reactions

Before presenting the model calculations, it is insightful to simply characterise the weathering reactions in terms of molar CO_2 consumption. The dissociation reaction has already been given (Eq. (1)). Table 2 gives the weathering reactions for fayalite, forsterite, Fo_{80} and Fa_{57} in which representative secondary precipitation reactions occur. When fayalite weathers in an oxic environment, Fe(II) in olivine oxidises to Fe(III) that will precipitate as Fe oxyhydroxide. This is an acid-producing reaction, as OH^- is incorporated into the Fe hydroxide. Note that the result of this is that no CO_2 is consumed, i.e. this reaction has no immediate influence on the CO_2 regime (as was also noted by Bakker et al., 2012). There is indirect influence, however, via dissolved silica as a weak acid, as will be illustrated in the next section. During weathering under anaerobic conditions, Fe^{2+} is released and may go on to react to form siderite (Neubeck et al., 2014) or possibly Fe sulphides such as pyrite. This will not be considered further, because – as will be explained later – anoxic weathering is not effective for CO_2 sequestration.

Reactions B and C in Table 2 show the weathering reactions of pure forsterite in a marine environment in which carbonate precipitation occurs. Note that the two carbonate reactions have a 1:2 mol ratio of olivine to CO_2 whereas the mole ratio for the dissociation reaction (1) is 1:4. Thus in terms of CO_2 consumption the dissociation ratio is twice as effective (Hangx and Spiers, 2009). Reaction D is the weathering reaction in which sepiolite is formed as a secondary Mg silicate. The mole ratio between olivine and CO_2 is now 3:8, which is in between the two ratios mentioned earlier. Generally speaking, therefore, the production of a secondary product is unfavourable with regard to the CO_2 consumption per unit olivine in favour of less weathering products dissolved in water.

When an olivine solid solution weathers under oxic conditions, this leads to a situation that is between that of pure forsterite and fayalite: oxic weathering of a solid solution will combine the acid production during fayalite weathering with the CO_2 consumption during forsterite weathering. The net result depends on the Fe:Mg ratio. Reaction E in Table 2 indicates that for Fo_{80} the mole ratio of olivine to CO_2 is 1:3.2 (instead of 1:4 in the case of pure forsterite). In the case of maintenance of equilibrium with Ca or Mg carbonate, this ratio is twice as low: 1:1.6 (Table 2). Reactions J and K show that a similar pattern holds for Fa_{57}. During weathering to sepiolite, however, the ratio is for Fo_{80} not 0.8 times that for pure forsterite (i.e. 3:6.4) but is lower (3:5.6) and thus less favourable.

In nature, serpentinisation of olivine-containing rocks may also occur. Serpentine ($Mg_3Si_2O_5(OH)_4$) is a sheet silicate, like the clay minerals. One of the forms of serpentine is chrysotile, which is the most important source of commercial asbestos. Olivine is converted to serpentine in the following reaction:

$$2\ MgSiO_4 + 3\ H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 \tag{5}$$

Table 2
Relevant weathering reactions of olivine with secondary precipitation.

Fayalite	
$Fe_2SiO_4 + 0.5\ O_2 + 5.0\ H_2O \rightarrow 2\ Fe(OH)_3 + H_4SiO_4$	A
Forsterite	
$Mg_2SiO_4 + 2\ CO_2 + 2\ Ca^{2+} + 2\ H_2O \rightarrow 2\ Mg^{2+} + H_4SiO_4 + 2\ CaCO_3$	B
$Mg_2SiO_4 + 2\ CO_2 + 2\ H_2O \rightarrow 2\ MgCO_3 + H_4SiO_4$	C
$3\ Mg_2SiO_4 + 8\ CO_2 + 7½\ H_2O \rightarrow ½\ Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O + 4\ Mg^{2+} + 8\ HCO_3^-$	D
Fo_{80}	
$Mg_{1\cdot6}Fe_{0.4}SiO_4 + 3.2\ CO_2 + 0.1\ O_2 + 4.2\ H_2O \rightarrow 1.6\ Mg^{2+} + 0.4\ Fe(OH)_3 + H_4SiO_4 + 3.2\ HCO_3^-$	E
$Mg_{1\cdot6}Fe_{0.4}SiO_4 + 1.6\ CO_2 + 0.1\ O_2 + 1.6\ Ca^{2+} + 2.6\ H_2O \rightarrow 1.6\ Mg^{2+} + 0.4\ Fe(OH)_3 + H_4SiO_4 + 1.6\ CaCO_3$	F
$Mg_{1\cdot6}Fe_{0.4}SiO_4 + 1.6\ CO_2 + 0.1\ O_2 + 2.6\ H_2O \rightarrow 1.6\ MgCO_3 + 0.4\ Fe(OH)_3 + H_4SiO_4$	G
$3\ Mg_{1\cdot6}Fe_{0.4}SiO_4 + 5.6\ CO_2 + 0.3\ O_2 + 8.1\ H_2O \rightarrow ½\ Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O + 2.8\ Mg^{2+} + 1.2\ Fe(OH)_3 + 5.6\ HCO_3^-$	H
Fa_{57}	
$Mg_{0\cdot86}Fe_{1.14}SiO_4 + 1.72\ CO_2 + 0.285\ O_2 + 4.57\ H_2O \rightarrow 0.86\ Mg^{2+} + 1.14\ Fe(OH)_3 + H_4SiO_4 + 1.72\ HCO_3^-$	J
$Mg_{0\cdot86}Fe_{1.14}SiO_4 + 0.86\ CO_2 + 0.285\ O_2 + 0.86\ Ca^{2+} + 3.71\ H_2O \rightarrow 0.86\ Mg^{2+} + 1.14\ Fe(OH)_3 + H_4SiO_4 + 0.86\ CaCO_3$	K

or

$$3\ Mg_2SiO_4 + 4\ H_2O + SiO_2 \rightarrow 2\ Mg_3Si_2O_5(OH)_4 \tag{6}$$

or

$$2\ Mg_2SiO_4 + 2\ H_2O + CO_2 \rightarrow Mg_3Si_2O_5(OH)_4 + MgCO_3 \tag{7}$$

In reaction (5) brucite ($Mg(OH)_2$) is also formed, and in reaction (7) magnesite is also formed. The various Mg minerals do indeed also co-occur as products of hydrothermal weathering (Deer et al., 2013; Boschi et al., 2009). Serpentine minerals form during hydrothermal weathering of ultramafic rocks, although they may also be formed in a marine environment at temperatures of 0–40 °C, but then in combination with sulphate reduction (Alt et al., 2012). Only in reaction (7) is CO_2 consumed in a molar olivine to CO_2 ratio of 2 or 1, which is less favourable than in many of the reactions considered earlier. Kinetically, however, no magnesite is directly formed out of solution under the conditions normally found at the Earth's surface and thus under ambient conditions in the field, reaction (7) can be considered to be impossible (except when hydrated Mg carbonates can be formed as intermediate product; see Discussion). If aiming to sequester CO_2 by weathering olivine, it is therefore undesirable for serpentisation to occur during the first or second reaction equation.

The first conclusion is that it matters greatly whether precipitation of carbonates or of sepiolite occurs during the weathering of Mg-rich olivine in a marine environment, because this causes the effectiveness to vary by a factor of two. Another relevant conclusion that has so far received little attention is that no CO_2 is consumed during 1. oxic weathering of Fe-rich olivine, or 2. serpentisation of olivine with or without related production of brucite.

3.2. Modelling results

Tables 3–5 give the results of the various model calculations performed. Table 3 shows that for fayalite no more than 0.53 or 0.46 mmol fayalite/kg$_w$ can dissolve with or without siderite precipitation, respectively, if there is a closed system for O_2, i.e. in the absence of O_2 supply. The difference between these two scenarios is rather small, so siderite precipitation does not play an important role. If oxygen is supplied, then unlimited olivine can dissolve because the reaction is one in which no dissolved ions are involved according to which solubility can be limited (compare reaction A in Table 2). As expected, the pH usually falls as a result of hydroxide consumption by the precipitation of $Fe(OH)_3$ and because dissolved SiO_2 is a weak acid that is increasingly dissociated under basic pH (the reaction shown is the one implemented in the LLNL database):

$$SiO_2{}^0{}_{(aq)} + H_2O \leftrightarrow HSiO_3{}^-{}_{(aq)} + H^+ \quad \log K = 9.9525 \tag{8}$$

The CO_2 partial pressure increases correspondingly when the pH falls, because the carbonate species equilibrium shifts towards $H_2CO_3^*$ or CO_2 escapes to the air if the CO_2 partial pressure of seawater is maintained (scenarios 3.4 and 3.5 in Table 3). In the absence of an equilibrium with carbonate minerals, the saturation indices of calcite and magnesite fall in relation to those for seawater, but remain positive

Table 3
Modelling results for fayalite weathering under different scenarios with 1 mmol olivine/kg$_w$ present initially. Dissolved compounds in mmol/kg$_w$, alkalinity in meq/kg$_w$. F indicates the flux in mmol/kg$_w$ in which a positive value indicates flux in the water (i.e. dissolving of mineral or from the air) and a negative value indicates leaving the water (i.e. precipitation of mineral or release to the air). Cells shaded orange show the equilibrium preconditions imposed.

Scenario	pH	Alkalinity	SiO_2	F olivine	F CO_2	F calcite	F siderite	SI-fayalite	SI SiO_2(am)	SI calcite	SI magnesite	SI siderite	SI $Fe(OH)_3$(am)	Log $P(O_2)$	Log $P(CO_2)$
	Fayalite														
3.1a CO_2/O_2closed	8.17	2.50	0.57	0.46	0	0	0	0	-0.60	0.67	1.01	0.22	0	-53.23	-3.37
3.1b CO_2/O_2closed + siderite	8.34	2.45	0.65	0.53	0	0	0.17	0	-0.59	0.79	1.13	0	0	-53.21	-3.59
3.2 O_2open + CO_2 closed	7.87	2.41	1.11	1	0	0	0	-25.93	-0.27	0.39	0.72	-12.59	0	-0.7	-3.05
3.3 O_2open + CO_2 closed + Ca-carb-eqm.	8.15	2.80	1.11	1	0	0.19	0	-25.97	-0.31	0.7	1.03	-12.85	0	-0.7	-3.31
3.4 CO_2/O_2open	8.17	2.41	1.11	1	-0.18	0	0	-25.98	-0.31	0.63	0.97	-12.94	0	-0.7	-3.4
3.5 CO_2/O_2open + Ca-carb-eqm.	8.20	2.61	1.11	1	-0.12	0.10	0	-25.98	-0.32	0.7	1.03	-12.94	0	-0.7	-3.4

Ca-carb= calcite or aragonite

Table 4
Modelling results for forsterite weathering under different scenarios with 1 mmol olivine/kg_w present initially. Set-up and legend as in Table 3.

Scenario	pH	Alkalinity	SiO_2	F olivine	F CO_2	F calcite	F magnesite	F sepiolite	SI forsterite	SI SiO_2(am)	SI calcite	SI magnesite	SI sepiolite	Log P(CO_2)
	Forsterite													
4.1 Closed CO_2	8.87	3.02	0.26	0.15	0	0	0	0	0	-1.20	1.26	1.60	9.56	-4.18
4.2 Closed + Ca-carb-eqm.	8.78	1.30	0.53	0.42	0	-1.40	0	0	0	-0.84	0.7	1.10	11.00	-4.49
4.3 Closed + cc/mg-eqm.	8.78	1.14	0.57	0.46	0	0.59	-2.14	0	0	-0.82	0.7	1	11.10	-4.58
4.4 Open CO_2	8.53	6.41	1.11	1	2.97	0	0	0	-0.55	-0.42	1.36	1.71	11.61	-3.4
4.5 Open + Ca-carb-eqm.	8.24	2.91	1.11	1	1.98	-1.75	0	0	-1.62	-0.33	0.7	1.13	9.82	-3.4
4.6 Open + cc/mg-eqm.	8.19	2.53	1.11	1	1.86	0.70	-2.64	0	-1.86	-0.32	0.7	1	9.38	-3.4
4.7 Open + Ca-carb-eqm. + sepio	8.23	2.58	0.10	1	1.39	-1.24	0	-0.17	-2.72	-1.37	0.7	1.10	3.46	-3.4
4.8 Open + sepio	8.47	5.01	0.06	1	2.17	0	0	-0.18	-2.08	-1.69	1.23	1.58	3.46	-3.4

cc = calcite, mg = magnesite, sepio = sepiolite

(scenarios 3.1, 3.2 and 3.4). The dissolution of calcite in scenarios 3.3 and 3.5 is also questionable, given that the starting situation is already supersaturation (cf. scenarios 3.2 and 3.4). Thus no carbonate precipitation reactions are expected. The notation that CO_2 can escape to the atmosphere during intensive weathering of fayalite, instead of being removed from the atmosphere, is important. Scenario 3.4 indicates this; it is also the most realistic scenario, as there are no precipitation/dissolution reactions of Ca carbonate. The scenario of fayalite weathering in an open, marine environment is thus an acid-producing process with possible emission of CO_2 towards the atmosphere. This runs counter to achieving that olivine weathering is a measure to mitigate the increase of CO_2 in the atmosphere.

The model's results for forsterite are summarised in Table 4. Now iron does not play a role and thus it is irrelevant whether this reaction takes

Table 5
Modelling results for weathering of olivine solid solutions Fo_{80} and Fa_{57} under different scenarios with 1 mmol olivine/kg_w present initially and all scenarios open to O_2 except for the first row in a series (shaded grey). Set-up and legend as in Tables 3 and 4.

scenario	pH	Alkalinity	SiO_2	F oli	F CO_2	F calc.	F magnesite	F sepiolite	SI olivine sol.sol.	SI SiO_2(am)	SI calcite	SI magnesite	SI sepiolite	Log P(CO_2)
	Fo80													
5.1 Closed CO_2/O_2	10.08	5.61	1.11	1	0	0	0	0	−1.69	−1.55	1.73	2.08	17.10	−6.10
5.2 Closed CO_2	10.08	5.61	1.11	1	0	0	0	0	−1.72	−1.55	1.73	2.08	17.10	−6.10
5.3 Open CO_2	8.49	5.61	1.11	1	2.36	0	0	0	−5.65	−0.40	1.26	1.61	11.32	−3.4
5.4 Closed CO_2 + Ca–carb–eqm.	9.91	1.69	1.11	1	0	−1.96	0	0	−2.08	−1.40	0.7	1.14	16.75	−6.72
5.5 Open CO_2 + Ca–carb–eqm.	8.23	2.84	1.11	1	1.56	−1.39	0	0	−6.38	−0.33	0.7	1.11	9.75	−3.4
5.6 ClosedCO_2 + cc/mg–eqm.	9.90	1.57	1.11	1	0	0.62	−2.64	0	−2.12	−1.39	0.7	1	16.66	−6.83
5.7 Open CO_2 + cc/mg–eqm.	8.19	2.53	1.11	1	1.46	0.70	−2.24	0	−6.54	−0.32	0.7	1	9.38	−3.4
5.8 Open CO_2 + Ca–carb–eqm. + sepio–eqm.	8.22	2.53	0.10	1	0.97	−0.87	0	−0.17	−7.45	−1.35	0.7	1.08	3.46	−3.4
5.9 Open CO_2+ sepio–eqm.	8.41	4.22	0.07	1	1.53	0	0	−0.17	−7.10	−1.61	1.11	1.45	3.46	−3.4
	Fa57													
5.10 Closed CO_2/O_2	9.10	3.75	0.89	1	0	0	0	0	0	−0.81	1.41	1.75	13.69	−4.48
5.11 Open CO_2	8.38	4.13	1.11	1	1.20	0	0	0	−15.12	−0.36	1.04	1.38	10.63	−3.4
5.12 Open CO_2 + Ca–carb–eqm.	8.22	2.73	1.11	1	0.78	−0.70	0	0	−15.35	−0.32	0.7	1.07	9.62	−3.4
5.13 Open CO_2 + Ca–carb–eqm. + sepio–eqm.	8.21	2.43	0.11	1	0.20	−0.18	0	−0.17	−16.38	−1.33	0.7	1.04	+3.46	−3.4
5.14 Open CO_2 + sepio–eqm.	8.26	2.78	0.10	1	0.32	0	0	−0.17	−16.36	−1.40	0.81	1.14	+3.46	−3.4

sol.sol. = solid solution

place in oxic or anoxic conditions. The alkalinity changes appreciably, decreasing in the closed CO_2 system plus carbonate precipitation (scenarios 4.2 and 4.3 in Table 4) but increasing in the other scenarios. Additional calculations show that 1.6 mmol/kg_w can dissolve in the open CO_2 scenario without precipitation of other minerals, and in the other open CO_2 scenarios more than 10 mmol/kg_w can dissolve. In all open CO_2 scenarios (scenarios 4.4–4.8) CO_2 is taken up by the seawater but the molar ratio between olivine and CO_2 is larger than the ratio according to the theoretical reaction equations. This is related to the shifts in the alkalinity that result from shifts in the pH. If saturation with calcite continues to be maintained, with no role for magnesite, calcite is precipitated. If magnesite can also precipitate, this precipitates thermodynamically, with some transformation of calcite to magnesite. In the scenarios with sepiolite, 0.17–0.18 mmol sepiolite/kg_w is precipitated, with or without calcite precipitation (scenarios 4.7 and 4.8, respectively). The molar amount of Mg in sepiolite is double that in olivine and thus 0.28 to 0.36 mmol olivine/kg_w is converted into the secondary mineral and the remainder disappears in solution. In the scenario with forsterite weathering, CO_2 is taken from the air, but the amount is less than that suggested by the simple reaction equations. The assumptions relating to equilibrium with Ca/Mg carbonates have a great influence on the compound fluxes that may occur, as well as on the changes in pH and alkalinity.

The modelling results for the two solid solutions are shown in Table 5. In view of the presence of Fe(II) in the solid solution, it is again relevant to compare systems in terms of whether they are open or closed to O_2. The first two scenarios indicate that in both situations, 1 mmol of Fo_{80} can totally dissolve and that a pH of 10.08 is reached. This pH is much higher than for the situation with the two end-members of olivine. The alkalinity also rises steeply to 5.61 meq/kg_w. No difference is observed because the initial seawater solution contains dissolved oxygen and the released Fe(II) is insufficient to consume all dissolved oxygen when oxidised to Fe(III). The difference in outcome for the comparable scenarios 5.10 and 5.11 point out that all oxygen becomes consumed in a closed O_2 system when 1 mmol of Fa_{57} is involved. When the remaining scenarios for Fo_{80} are compared with the scenario for forsterite (Table 4), it is striking that for comparable scenarios the differences are slight for the carbonate scenarios with an open system for CO_2: the CO_2 uptake and the carbonate precipitation are somewhat less, whereas the pH and alkalinity are very similar. The lower CO_2 uptake per mole olivine therefore means that this solid solution is less effective to use than pure forsterite. The differences between the two olivine minerals are substantial for the scenarios with closed CO_2 system and carbonate equilibrium. The solubility of Fo_{80} is slightly more than 1 mmol/kg_w for these scenarios (i.e. approximately 4 mmol/kg_w, as indicated by additional calculations). By comparison with forsterite, the pH is much higher, and the alkalinity and amount of calcite precipitated are also higher. The scenarios with sepiolite precipitation are fairly similar to those for pure forsterite. The pH values and alkalinity are virtually identical, except for the alkalinity when only sepiolite is precipitated. In comparison, for the two sepiolite scenarios it holds that the CO_2 uptake is again less favourable, the amount of sepiolite precipitated is the same, and the amount of calcite precipitated is less. The scenarios show that the situation for Fo_{80} is generally less favourable than for pure forsterite: under the same geochemical preconditions approximately 20% less CO_2 is taken up per mole olivine and in some scenarios considerably higher pH values and alkalinity are reached. The scenarios for Fa_{57} show that the CO_2 uptake is even less favourable when the Mg content in olivine is further reduced (Table 5). The pH and alkalinity are intermediate for these scenarios compared to the scenarios for the other olivine minerals. As expected, the efficiency is lower than for the other two Mg-containing olivine minerals but still positive. The two scenarios with sepiolite precipitation (scenarios 5.13 and 5.14) have olivine to CO_2 ratios of 1 to 0.20–0.32 which is more than 10 times lower than the ratio of 1 to 4 for the dissociation reaction. These figures also deviate more strongly than those for only carbonate precipitation compared to the other two Mg-containing olivine minerals, which is due to the low Mg to Si ratio in this olivine.

4. Discussion and conclusions

In the preceding section the modelling results were presented for four types of olivine under different scenarios with different geochemical boundary conditions. In this section the plausibility of these boundary conditions will be discussed further. The plausibility of the occurrence of serpentisation of olivine was already discussed.

4.1. Plausibility of the geochemical boundary conditions

At normal temperatures and CO_2 pressures, formation of magnesite is rare: the minimal temperature for magnesite precipitation is generally considered to be 60–100 °C (e.g. Hanchen et al., 2008; Hopkinson et al., 2012; Swanson et al., 2014; Qafoku et al., 2014) although it has been synthesised at 40 °C under ambient pressures (Deelman, 1999; Alves dos Anjos et al., 2011) or at 35–50 °C under water-saturated supercritical CO_2 pressure of 90 atm (Felmy et al., 2012). Magnesite has been found in playa-type settings where it is supposed to be formed at ambient, subaerial conditions with hydrated Mg-carbonate as precursor (Rahimpour-Bonab and Abdi, 2012; Detriche et al., 2013; Power et al., 2014) as well as in marine algae (Nash et al., 2011). Its genesis is still enigmatic and it has been suggested that desiccation of hydrated Mg-carbonate is responsible (Renaut and Stead, 1990) or alternations of dissolution and precipitation of hydrated and unhydrated Mg-carbonate due to e.g. changes in pH (Deelman, 1999, 2012; Alves dos Anjos et al., 2011). Nesquehonite, a hydrated Mg carbonate with the formula $MgCO_3 \cdot 3H_2O$, is able to precipitate at a temperature of 25 °C and when the CO_2 partial pressures are not too high (Hanchen et al., 2008). The logK value of nesquehonite at 25 °C is 3.02 units higher than that of magnesite, i.e. it is 1000 times more soluble than magnesite. This also means that supersaturation with nesquehonite occurs only when the saturation index for magnesite exceeds 3.02. This was not the case in any of the model runs (cf. Tables 3–5). This means that precipitation of Mg carbonate will not occur under ambient temperature and CO_2 pressure conditions for the states in magnesite supersaturation reached. The underlying reason is that magnesite precipitation is hampered kinetically by the slow dehydration kinetics of the Mg^{2+} ion (Saldi et al., 2009; Gautier et al., 2014); instead, magnesite or hydromagnesite is formed by reprecipitation from dissolving more soluble, hydrated Mg carbonates as suggested from experiments at elevated CO_2 pressures and/or temperatures (Davies and Bubela, 1973; Qafoku et al., 2015). In practical terms, therefore, the insights from the modelling are probably not relevant. This would also mean that no Mg carbonate coating will be deposited on olivine and thus influence the solution kinetics of olivine.

In a marine environment, calcium carbonate can be precipitated as calcite and aragonite and may or may not be biologically controlled. It is usually supposed that precipitation that is biologically controlled (e.g. by algae or shellfish) is more rapid than abiological precipitation (Carpenter and Lohmann, 1992). Aragonite precipitates chemically in seawater because calcite precipitation is hampered by the high Mg:Ca ratio in seawater (Rushdi et al., 1992; Sabbides et al., 1992). With regard to carbonate precipitation in relation to olivine weathering, whether carbonate precipitates and, if it does, to which saturation index, is more important than the mechanism and the mineral precipitated. Calcium carbonate precipitation from supersaturation above that of seawater is observed to last days to years; many studies have been done on corals with biologically controlled precipitation (Langdon et al., 2000; Broecker et al., 2001; Pandolfi et al., 2011). This has led to the conclusion that calcium carbonate precipitation down to seawater supersaturation is a plausible assumption in relation to weathering of Mg-rich olivine in a marine environment.

In addition, if the calcium carbonate supersaturation as a result of fayalite weathering decreases to less than seawater supersaturation, there is a risk that biologically controlled calcium carbonate precipitation will no longer be able to take place, and this is potentially damaging for marine ecosystems. This is currently an important research topic in the context of rising CO_2 concentrations and is referred to as sea acidification or ocean acidification (e.g. Atkinson and Cuet, 2008; Artioli et al., 2012; Feely et al., 2012). Table 3 shows that at weathering of 1 mmol fayalite/kg_w in a system open to O_2 but closed to CO_2 (scenario 3.2), the pH falls to 7.87 and the associated SI(calcite) falls to 0.39. Note too that calcite must dissolve if seawater supersaturation is maintained in the modelled scenarios, but this is thermodynamically impossible from an supersaturated solution. Thus these two scenarios are also unrealistic, although the relationship between biologically controlled precipitation and saturation state is far from simple (Atkinson and Cuet, 2008; Pandolfi et al., 2011).

The only Mg silicate mineral that in the absence of Al can be precipitated directly out of seawater is sepiolite (Wollast et al., 1968). Sepiolite also occurs in saline alkaline conditions where evaporation plays a role, such as in saline lakes in closed basins with no outlet to the sea (Wollast et al., 1968; Stoessell and Hay, 1978). If there is sepiolite supersaturation of groundwater, precipitation of sepiolite is slow compared with carbonate precipitation reactions. Under marine conditions, enhanced concentrations of silica without the availability of Al are necessary, as otherwise it is more likely that chlorite will form. This condition can arise during olivine weathering in a marine environment. Sepiolite is also found in marine environments with ultramafic rocks that are typically rich in olivine (Bonatti et al., 1983). Thus formation of sepiolite appears to be possible if there is sufficient olivine weathering in a marine environment.

4.2. The most realistic scenarios for olivine weathering in the marine environment

The preceding discussion indicates which secondary reaction products will probably accompany olivine weathering in a marine environment under normal temperature and pressure. Precipitation of Ca carbonate and sepiolite is very likely, precipitation of magnesite is impossible, and serpentisation is very unlikely under aerobic conditions. It is unrealistic to expect carbonate precipitation until thermodynamic equilibrium, but it is possible that it will occur down to seawater supersaturation. The carbonate chemistry will be further complicated by additional processes such as evaporation of seawater, photosynthesis and decomposition of organic matter. The silicate chemistry can also be complicated by biotic reactions, such as the growth of diatoms, etc. But this was beyond the scope of this study. Further, for mitigation of CO_2 rise in the atmosphere, a precondition for enhanced weathering is actually that the system is open to CO_2, because otherwise there will be no CO_2 flux from the

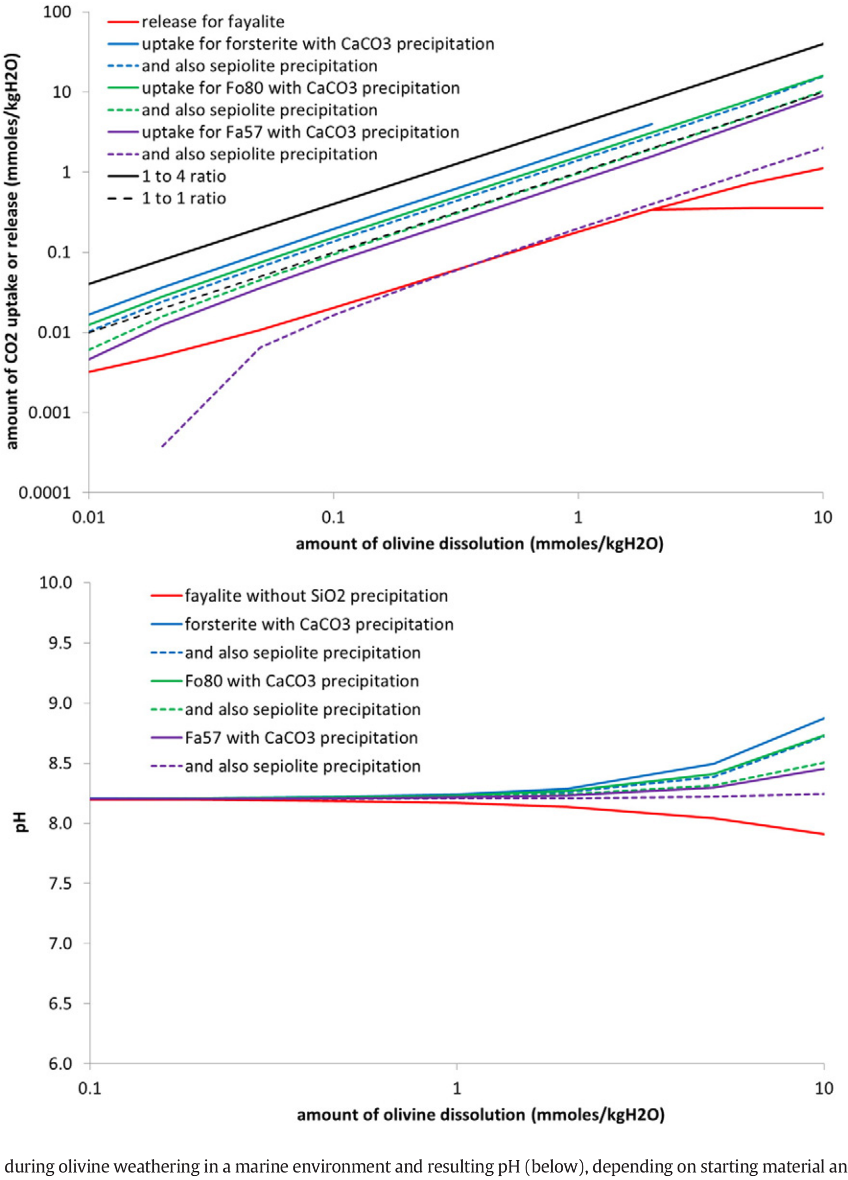

Fig. 1. CO_2 uptake or release (above) during olivine weathering in a marine environment and resulting pH (below), depending on starting material and plausible secondary precipitation reactions in the case of Mg olivine. The CO_2 released (in red) diverges above the 1 mmol fayalite weathering depending on whether at supersaturation precipitation of amorphous SiO_2 occurs (lower line) or is absent (upper line).

air to the seawater. In conclusion, the following reaction scenarios are the most plausible for olivine weathering in an open, marine environment:

- weathering of fayalite to Fe hydroxide with decreasing supersaturation for aragonite and calcite compared to seawater;
- weathering of forsterite with precipitation of aragonite or calcite until seawater supersaturation, and possible sepiolite precipitation;
- weathering of an olivine solid solution with precipitation of Fe hydroxide, precipitation of aragonite or calcite until seawater supersaturation, and possible sepiolite precipitation.

These are five possible scenarios, which are also presented in Tables 3–5 as scenarios 3.4, 4.5, 4.7, 5.5 and 5.8 (or 5.12 and 5.13).

It is interesting to look at which molar ratios of olivine to CO_2 are typical for these scenarios. Fig. 1 presents the amount of olivine weathering versus the CO_2 uptake from the air, or the release to the air for each of the five scenarios. As reference, the maximal 1:4 ratio is also given, and the 1:1 ratio. The end of the line on the graph marks where solubility has been reached: it is noteworthy that for most scenarios the solubility exceeds 10 mmol/kg_w despite the high weathering signature of seawater. This value has been taken as the maximum, but will not be reached in practice because of the slow absolute weathering rate of olivine. Conversely, the lowest value of 0.01 mmol weathering appears to be negligible within the complicated CO_2 system of seawater (cf. Mostofa et al., 2016).

As indicated earlier, in the case of fayalite, what occurs is the opposite of what is desired during enhanced weathering: CO_2 goes from the seawater into the atmosphere. The ratio between olivine weathering and CO_2 release falls from 1 to 0.3 at 0.01 mmol/kg_w weathering to 1 to 0.1 (or even less if amorphous SiO_2 is also precipitated) at 10 mmol/kg_w weathering. As demonstrated theoretically in section 3.1, the olivine to CO_2 ratio is higher for forsterite than for Fo_{80}. The ratio rises from 1.7 to 2.0 for the first situation and from 1.2 to 1.6 for the second situation. The theoretical ratios are thus achieved only at high intensities of olivine weathering: when weathering exceeds 0.2 mmol/kg_w the deviation from the theoretical ratio is less than 0.05. Further, the figure shows that the combination of sepiolite and calcium carbonate precipitation results in a ratio that is more unfavourable than when there is only calcium carbonate precipitation. The ratio now rises from 1.0 to 1.6 for forsterite and from 0.6 to 1.0 for Fo_{80}. The latter is four times lower than the theoretical maximum applied, which is 1:4. Köhler et al. (2010) found a slightly lower ratio of 1 to 0.8 for the situation in which olivine weathering takes place on land and the resulting alkalinity reaches the marine system via rivers. In both situations the ratio is thus appreciably lower than according to the theoretical solution reaction without taking account of secondary reactions and the buffer action of the alkalinity of seawater.

4.3. Implication for engineering potential

Several studies addressed the engineering potential of enhanced weathering of olivine (Hangx and Spiers, 2009; Hartmann et al., 2013; Köhler et al., 2013) or ocean liming (Ilyina et al., 2013; Paquay and Zeebe, 2013; Renforth et al., 2013) at the global scale. These studies make clear that huge mineral volumes are needed in order to raise an impact at the global scale. Hangx and Spiers (2009) and Köhler et al. (2010) also emphasize that olivine grains in the order of 1–10 μm are needed to be effective within the coming decades, which raises questions to the environmental-economic feasibility. Ilyina et al. (2013) pointed out that smaller-scale alkalinization could counteract ocean acidification at a subregional scale whereas global measures are needed to lower atmospheric CO_2 levels. The presented results add the following insights to these findings.

First, the composition of olivine plays an important role in trapping atmospheric CO_2 and modifying ocean pH. Most olivine is Mg-rich (Huang, 1989) which makes enhanced weathering of olivine a potentially feasible option. However, use of Fe-rich olivine may cause adverse effects. Note that a similar conclusion holds for any other Fe(II)-rich silicate as may be present in basalt and other rock types. The thermodynamic calculations for the most realistic scenarios show that more than 1 mmol/kg_w of olivine must weather in order to change the pH with more than 0.05 units (Fig. 1). Here, the pH decreases for fayalite as starting material and rises for the other olivines.

Second, mixing of ocean water plays a role as it may attenuate the efficiency of CO_2 sequestration: the efficiency in terms of molar ratio between CO_2 uptake and olivine dissolution is less with decreasing amount of olivine dissolution per volume ocean water (Fig. 1). This finding emphasizes that in order to be effective at the global scale huge mineral volumes are needed or the measure must be applied in combination with other mitigating measures to halt rising CO_2 levels. Here, one may realise that the amount of olivine dissolution as variable presented can be interpreted as a mixing effect under the condition of thermodynamic equilibrium. It equally expresses a large amount of dissolution in a small volume that becomes mixed with a large volume or a small amount of dissolution in a large volume. This assumption does, however, not hold as soon as kinetics is involved for in particular the secondary precipitation processes, when their rates are controlled by the degree of supersaturation. Dilution by mixing will also diminish the impact of enhanced weathering compared to other biogeochemical processes that influence ocean pH and carbonate chemistry.

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