

Deriving Nickel (Ni(II)) and Chromium (Cr(III)) Based Environmentally Safe Olivine Guidelines for Coastal Enhanced Silicate Weathering

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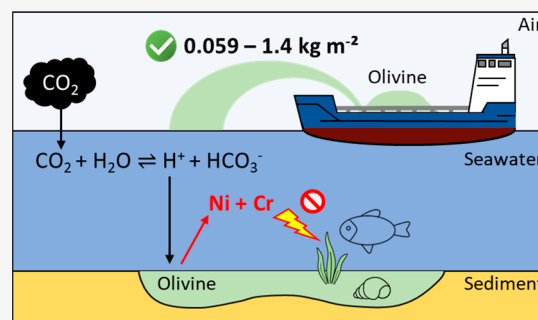


Supporting Information

ABSTRACT: Enhanced silicate weathering (ESW) by spreading finely ground silicate rock along the coastal zone to remove atmospheric carbon dioxide (CO₂) is a proposed climate change mitigation technique. The abundant and fast-dissolving mineral olivine has received the most attention for this application. However, olivine contains nickel (Ni) and chromium (Cr), which may pose a risk to marine biota during a gigaton-scale ESW application. Herein we derive a first guideline for coastal olivine dispersal based on existing marine environmental quality standards (EQS) for Ni and Cr. Results show that benthic biota are at the highest risk when olivine and its associated trace metals are mixed in the surface sediment. Specifically, depending on local sedimentary Ni concentrations, 0.059–1.4 kg of olivine m⁻² of seabed could be supplied without posing risks for benthic biota.

Accordingly, globally coastal ESW could safely sequester only 0.51–37 Gt of CO₂ in the 21st century. On the basis of current EQS, we conclude that adverse environmental impacts from Ni and Cr release could reduce the applicability of olivine in coastal ESW. Our findings call for more in-depth studies on the potential toxicity of olivine toward benthic marine biota, especially in regard to bioavailability and metal mixture toxicity.

KEYWORDS: negative CO₂ emissions, coastal enhanced silicate weathering, climate change mitigation, environmental risk assessment, nickel, chromium, olivine, ocean alkalization



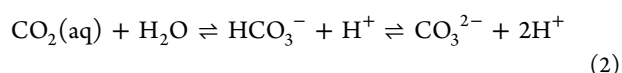
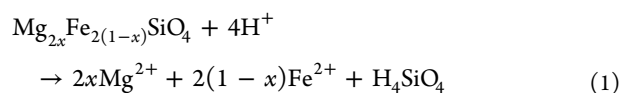
INTRODUCTION

Achieving the goals set in the 2015 Paris agreement to limit global warming to well below 2 °C will require drastic reductions in anthropogenic greenhouse gas emissions during the coming decades.¹ Additionally, carbon dioxide (CO₂) will also need to be captured from the atmosphere by so-called negative emission technologies (NETs).² These NETs are needed to be able to achieve net zero CO₂ emissions by the year 2050 and net negative CO₂ emissions during the second half of the 21st century.^{3,4} One of the proposed NETs is coastal enhanced silicate weathering (ESW). This technique aims to artificially speed up the natural CO₂-consuming chemical weathering of a silicate mineral by supplying gigatons of finely ground ground source rock to the dynamic coastal environment.⁵

The mineral olivine (Mg_{2x}Fe_{2(1-x)}SiO₄) is a prime candidate for coastal ESW because of its relatively fast dissolution rate and widespread abundance.^{5–7} Billions of tonnes of olivine are globally present in mafic and ultramafic igneous rocks, and each year approximately 8 Mt is mined from dunite (rock containing >90% olivine) or serpentinite (metamorphosed olivine-rich ultramafic rock) deposits for metallurgical use.^{8–10} Relatively low energy costs and low CO₂ emissions associated with grinding olivine source rock to 100 μm particles make this a desirable grain size for use in coastal ESW.⁶ However, several

studies indicate that grain sizes of 10 μm or smaller might be needed to ensure significant olivine dissolution and CO₂ uptake in the coming decades.^{6,7,11}

During olivine dissolution, protons are consumed (eq 1), which leads to a shift in the equilibrium of the acid–base reactions of the seawater–carbonate system (eq 2) to the right. Consequently, seawater total alkalinity (TA) will increase, and additional CO₂ can be taken up from the atmosphere (eq 3).⁵ This artificial seawater TA increase to drive atmospheric CO₂ removal is called ocean alkalization (OA) or ocean alkalinity enhancement (OAE).^{12,13}



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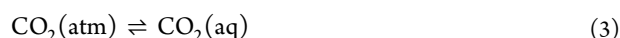


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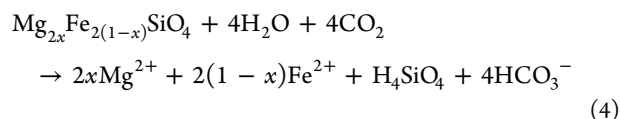
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Combining these reactions gives the overall dissolution reaction of olivine (eq 4), from which we can derive that theoretically 4 mol of CO_2 is sequestered in the form of bicarbonate (HCO_3^-) per mole of dissolved olivine.¹⁴



In addition to CO_2 sequestration, the proton consumption during dissolution could counteract ocean acidification. Furthermore, the released iron (Fe) and silicon (Si) are necessary nutrients for phytoplankton growth and could therefore result in additional atmospheric CO_2 uptake and increased abundance of silicifiers (e.g., diatoms), but these aspects remain to be investigated.^{5,13} In contrast to these associated benefits, olivine also contains chromium (Cr) and nickel (Ni), which are toxic to marine organisms above certain threshold concentrations.^{5,15}

Nickel is a transition metal that is mainly used in the production of stainless steel and other Ni alloys.¹⁶ In the crystal structure of olivine, Ni^{2+} is homogeneously distributed in the M1 octahedral binding sites, substituting for other divalent cations such as Mg^{2+} or Fe^{2+} , thereby forming a nickel silicate (Ni_2SiO_4).^{17,18} The Ni content in olivine ranges from 2.4 to 12 mmol of Ni mol^{-1} of olivine depending on the site of origin.^{14,18,19} Nickel is an essential component of nine enzymes associated with carbon, nitrogen, and oxygen cycling in marine microorganisms.^{20,21} However, for other marine biota Ni essentiality has not been recognized and the uptake mechanisms are not well-known.²² Exposure to elevated concentrations of Ni can lead to toxicological effects as a consequence of three main toxicity mechanisms: (1) ionoregulatory disruption (mainly Ca^{2+} , Mg^{2+} , and $\text{Fe}^{2+/3+}$), (2) respiratory toxicity as a result of an allergic type reaction of respiratory epithelia, and (3) reactive oxygen species induced oxidative stress.^{16,22} However, the relative importance of the different toxicity mechanisms is not well-known for marine organisms.²²

In contrast to nickel, chromium is not homogeneously distributed in olivine, but rather is present in iron (Fe)-rich areas, likely as Cr^{3+} in the form of water-insoluble chromite (FeCr_2O_4).¹⁸ Reported Cr concentrations in olivine from the Norwegian Åheim mine (the largest exploited olivine source) vary considerably, ranging from 0.19 mmol mol^{-1} of olivine to 6.6 mmol mol^{-1} of olivine.^{14,18,19,23,24} In the marine environment Cr occurs in two stable oxidation states, Cr^{3+} and Cr^{6+} , which differ significantly in their environmental and biological behaviors.²⁵ Hexavalent Cr occurs as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anions in aquatic systems, which can easily cross biological membranes via nonspecific anion channels and are therefore considered highly bioavailable and potentially very toxic.^{25–27} After entering the cell, Cr(VI) is reduced to Cr(III) . This reduction is accompanied by the production of reactive oxygen species (ROS) which can damage cell membranes, proteins, and DNA when in excess of antioxidant molecules.^{27,28} By contrast, trivalent chromium is predominantly present as Cr(OH)_3 or Cr(OH)_2^+ in the marine environment, which are chemical species of less ecotoxic-

logical concern compared to Cr(VI) species due to their low aqueous solubilities.^{25,29}

A body of literature is available on the acute and chronic toxicities of Ni^{2+} and $\text{Cr}^{3+}/\text{Cr}^{6+}$ toward marine biota.^{30–37} Most of the data have been derived from laboratory studies that exposed single biological species to single metal ions (e.g., Ni^{2+} or Cr^{3+}) under optimal conditions (e.g., constant pH and temperature). With the use of various approaches, e.g., species sensitivity distributions (SSDs), these data are used to derive marine metal environmental quality standards (EQS), which are threshold metal concentrations in seawater or sediment that are considered to be sufficiently protective for the aquatic environment.³⁸ These EQS are used by industries, the government, and environmental agencies as a guidance tool in the setting of regulations.³⁹

It has been predicted that, depending on the weathering rate and the water residence time, ESW may cause accumulation of Cr and Ni in coastal waters to levels that are well above the background.^{5,15} Currently, possible negative ecosystem impacts of coastal ESW are unknown since no marine toxicity tests have yet been conducted with olivine. However, for Ni and Cr considered individually, marine EQS do exist. Therefore, this study aimed to derive a maximum amount of olivine that could be supplied to the coastal seas without exceedance of the Ni or Cr EQS. This olivine guideline provides a first indication of the environmental safety and applicability of the mineral for employment in global-scale coastal ESW.

MATERIALS AND METHODS

All calculations were performed in Microsoft Excel (2016), and figures were constructed in GraphPad Prism version 9.01 for Windows (GraphPad Software, La Jolla, CA, USA).

Global Coastal Ni and Cr Concentrations. Data on Ni and Cr concentrations in coastal seawater and sediment were compiled from primary literature. Coastal waters were defined as those with a water depth up to 200 m, located on continental or insular shelves.⁴⁰ Data were included when the water depth at the sampling location was ≤ 200 m or when it was specified that the sampling was conducted in bays, lagoons, estuaries, near-shore banks, harbors, or coastal zones.⁴⁰ For Ni and Cr in seawater, only data on dissolved metal concentrations (meaning water samples filtered through $\leq 0.45 \mu\text{m}$ pore size filters) were collected. For sediment, metal concentrations on a dry weight (dry wt) basis measured after microwave-assisted acid mixture digestion of sieved or unsieved sediment were included. Data collected on a transect along a coastline (e.g., on a cruise or along an expected pollution gradient) or at different time points or depths on the same location were summarized using descriptive statistics (Tables S4–S7 and Figures S1–S4). The mean concentrations for each location were then summarized in the same way to derive median values and percentiles of Ni and Cr in a coastal environment around the globe.

Deriving a Ni-Based Guideline for Olivine Application in Coastal Systems. The occurrence of most Cr in olivine as water-insoluble FeCr_2O_4 implies low bioavailability and lower ecotoxicological concern compared to Ni.¹⁸ Therefore, the following calculations were made under the assumption that Ni release from olivine weathering is the factor of highest concern for the health of marine biota during a gigaton-scale olivine application in the world's coastal seas.^{5,7} The corresponding calculations for Cr are given and discussed in the [Supporting Information](#).

On the basis of the environmental quality standards for Ni in marine water and sediment, the expected maximum amount of olivine that could be supplied to the coastal zone without adverse effects for marine biota was calculated. Calculations were made assuming the two limiting application scenarios where that all metals released during weathering end up in either the water column or the sediment.

All Ni Ends Up in the Water Column. The maximum amount of olivine, m_{app} , that could be applied per square meter of seabed (kg m^{-2}) without exceeding the Ni marine EQS was calculated from

$$m_{app} = \frac{c_{max} V_w}{k_{diss} A t} \quad (5)$$

where c_{max} is the maximum allowed concentration of olivine (mol L^{-1}) based on the European seawater Ni EQS ($0.147 \mu\text{mol L}^{-1}$),⁴¹ V_w is the water volume per square meter of seabed (L m^{-2}), A is the reactive surface area of olivine ($\text{m}^2 \text{kg}^{-1}$), t is the water residence time (s), and k_{diss} is the olivine dissolution rate constant ($\text{mol m}^{-2} \text{s}^{-1}$). The dissolution of olivine was modeled for two grain sizes, 100 and 10 μm grain diameters, for both temperate (15°C) and tropical (25°C) coastal systems. For all further calculations, the dissolution rate constants for olivine were considered to be 5.19×10^{-11} and $1.58 \times 10^{-10} \text{ mol m}^{-2} \text{s}^{-1}$ for the 15 and 25°C scenarios, respectively as derived by Hangx and Spiers.⁶ A more detailed description of how seawater Ni EQS based olivine guidelines were derived is provided in the [Supporting Information](#).

All Ni Remains in the Sediment. For sediment, the maximum amount of olivine, m_{app} , that could be supplied per square meter of seabed (kg m^{-2}) without exceeding the marine Ni EQS for sediment was calculated from

$$m_{app} = C_{max} V_s \rho_s (1 - \Phi) M_{olivine} \quad (6)$$

where C_{max} is the maximum allowed amount of olivine (mmol kg^{-1} dry wt) based on a sediment Ni EQS ($0.729 \text{ mmol kg}^{-1}$ dry wt),⁴² V_s is the volume of the sediment in which olivine is mixed per square meter of seabed ($\text{m}^3 \text{m}^{-2}$ seabed), ρ_s is the specific density of marine sediment (2650 kg m^{-3}), $M_{olivine}$ is the molecular weight of olivine (kg mol^{-1}), and Φ is the porosity of the sediment. The application of common forsterite olivine with a molar Mg-to-Fe ratio of 0.94:0.06 ($\text{Mg}_{1.88}\text{Fe}_{0.12}\text{SiO}_4$) was assumed, resulting in a molecular weight of $0.144 \text{ kg mol}^{-1}$.¹⁴ The porosity of marine surface sediment was assumed to be 0.60 based on the predicted global coastal sediment porosity ranging from approximately 0.50 to 0.85.⁴³ To estimate the global maximum amount of olivine that could be distributed, the global continental shelf was assumed to have a surface area of $28 \times 10^6 \text{ km}^2$ for all further calculations.⁴⁰

Implications of the Olivine Guideline for CO_2 Sequestration Potential. Based on the derived olivine guideline value for coastal ESW, the associated CO_2 uptake during the 21st century was calculated to investigate if Ni release could limit the potential of coastal enhanced olivine weathering as a NET. Under the assumption that olivine grains are spherical, olivine is expected not to dissolve linearly over the coming decades, but to dissolve according to a shrinking core model.⁶ The volume fraction of dissolved olivine $X(t)$ at time t can be expressed as

$$X(t) = \frac{d_0^3 - (d_0 - 2k_{diss} V_m t)^3}{d_0^3} \quad (7)$$

where d_0 is the starting olivine grain diameter (m); k_{diss} is the dissolution rate constant of olivine ($\text{mol m}^{-2} \text{s}^{-1}$), and V_m is the molar volume of olivine ($4.38 \times 10^{-5} \text{ m}^3 \text{mol}^{-1}$). The dissolution of olivine was modeled for two grain sizes, 100 and 10 μm grain diameters, for both temperate (15°C) and tropical (25°C) coastal systems. A weekly application of 9.615 Mt of olivine along the global continental shelf was assumed. This would equate to 500 Mt of olivine spread along the coast every year, which was estimated to be logistically feasible by Hangx and Spiers⁶ assuming significant expansion of the cargo ship fleet size and olivine mining industry. The amount of olivine dissolved as a function of time is calculated from

$$m_{oa} = \sum_{t=0}^n X(t) S \quad (8)$$

with n = duration of olivine application (weeks)

where m_{oa} is the amount of olivine (Mt) weathered at time t (weeks), $X(t)$ is the fraction of olivine dissolved at time t (weeks), and S is the supply rate of olivine ($9.615 \text{ Mt week}^{-1}$) for an n -week application. In a typical application scenario, the olivine supply will be stopped after n weeks, i.e., once the global continental shelf has been covered in olivine and the expected maximum environmentally safe amount of olivine has been reached. The weekly amount of dissolved olivine for the next $4160 - n$ weeks (i.e., after olivine application has stopped) can then be expressed as

$$m_{os} = \sum_{i=1}^{4160-n} \sum_{t=0}^n X(t+i) S \quad (9)$$

with n = duration of olivine application (weeks)

where m_{os} is the amount of olivine weathered (Mt) at time $t+i$ (weeks) from the moment olivine supply was halted onward, i is the index for each week after olivine supply was stopped, $X(t+i)$ is the fraction of olivine dissolved at time $t+i$ (weeks), and S is the supply rate of olivine ($9.615 \text{ Mt week}^{-1}$), for an n -week application. Subsequently, the associated weekly CO_2 uptake was calculated from

$$m_{\text{CO}_2} = \gamma_{\text{CO}_2} m_{oa/os} \quad (10)$$

where m_{CO_2} is the amount of CO_2 sequestered via olivine dissolution (Mt), γ_{CO_2} is the net CO_2 -sequestration efficiency, which represents the net amount of CO_2 that is withdrawn from the atmosphere upon dissolution of 1 kg of olivine, which was taken to be 1 kg of CO_2 based on upper limits of expected values.^{5,14} Finally, $m_{oa/os}$ is the amount of olivine dissolved during the period of application (m_{oa}) or after the olivine supply was stopped (m_{os}), respectively.

RESULTS AND DISCUSSION

Global Coastal Ni Concentrations. A literature search was conducted to obtain globally occurring coastal Ni and Cr concentrations for the derivation of an olivine application guideline. A summary of the Ni concentrations globally occurring in coastal waters and sediment is shown in [Table 1](#). A summary for Cr and data from individual studies are shown in [Tables S1 and S4–S7](#) and [Figures S1–S4](#). The

Table 1. Summary of Dissolved ($\leq 0.45 \mu\text{m}$) Nickel (Ni) Concentrations (nmol L^{-1}) in Seawater and Total Ni Concentrations (mmol kg^{-1} dry wt) in Sediment for Coastal Systems (Water Depth ≤ 200 m) around the World^a

	dissolved seawater [Ni] (nmol L^{-1}) ($n = 30$)	total sediment [Ni] (mmol kg^{-1} dry wt) ($n = 50$)
median	3.92	0.52
P25–P75	2.81–36.2	0.29–0.70
P5–P95	1.24–373	0.14–3.46
min–max	0.92–5290	0.06–5.44

^aNumber of locations (n), median, percentiles (P), and range (min–max) are provided to illustrate the distribution of the data. Results for Cr and mean data of the individual locations are provided in Tables S1 and S4–S7.

median dissolved Ni concentration in seawater for the 30 coastal locations was 3.92 nmol L^{-1} . This value is similar to the reported dissolved Ni concentration in open ocean seawater of the Southern Ocean ($6.2 \pm 0.3 \text{ nmol L}^{-1}$)⁴⁴ and total Ni concentrations offshore in the Northeast Atlantic Ocean ($3.9 \pm 1.6 \text{ nmol L}^{-1}$).⁴⁵ Dissolved Ni concentrations ranged from 0.92 nmol L^{-1} in 2002 in the Bay of Bengal in India to 5290 nmol L^{-1} in 2003 at the Alang–Sosiya ship scrapping yard in the Gulf of Cambay, India.^{46,47} Generally, human-impacted coastal waters and sediments tend to have elevated and more

variable Ni concentrations than offshore locations due to nearshore mining or industrial activities.^{48,49}

Total recoverable Ni concentrations in 50 coastal sediments ranged from $0.06 \text{ mmol kg}^{-1}$ dry wt measured along the eastern Gulf of Mexico, USA,⁵⁰ to $5.44 \text{ mmol kg}^{-1}$ dry wt around the thermal power plant on the Tuticorin coast in India.⁵¹ The median sediment Ni concentration was $0.52 \text{ mmol kg}^{-1}$ dry wt. These concentrations are a lot higher than concentrations in water, showing that the sediment serves as a sink for metals in the marine environment.⁵²

Deriving a Ni-Based Guideline for Olivine Application in Coastal Systems. The expected maximum amount of olivine that can be supplied to the coastal zone without exceedance of existing marine Ni EQS was derived for the two limiting olivine application scenarios in which all Ni released during olivine weathering ends up in either the water column or the sediment.

All Ni Ends Up in the Water Column. The maximum amount of olivine that can be distributed in coastal waters without exceedance of the European Ni EQS for seawater ($0.147 \mu\text{M}$)⁴¹ assuming an olivine Ni concentration of $7.5 \text{ mmol mol}^{-1}$ of olivine is shown in Figure 1. A seawater Ni background concentration of 3.92 nmol L^{-1} was considered. As indicated by the study of Hangx and Spiers,⁶ based on the Arrhenius equation and an olivine dissolution activation energy of 79.5 kJ mol^{-1} in seawater conditions,⁵³ the dissolution rate of olivine is expected to be approximately 3 times higher in

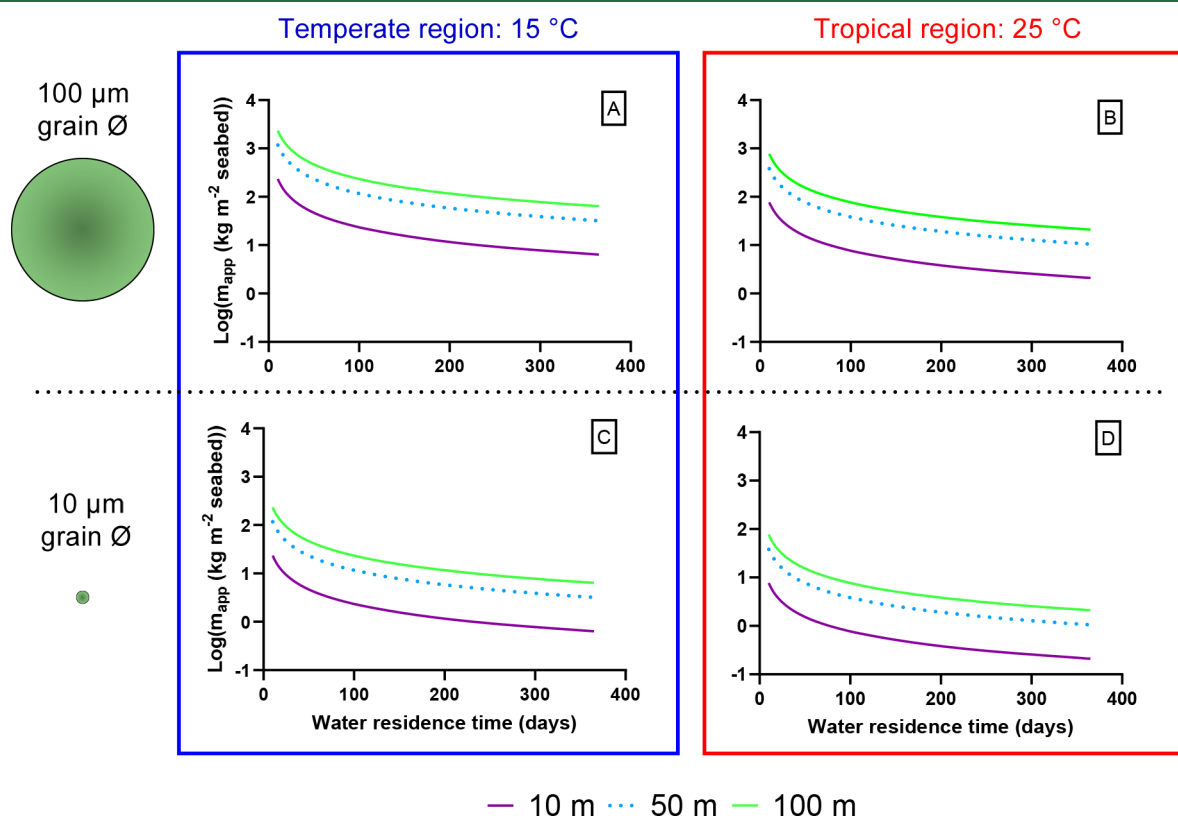


Figure 1. Maximum amount of olivine (kg m^{-2} seabed) on a logarithmic scale that can be distributed without exceedance of the European nickel (Ni) environmental quality standard ($0.147 \mu\text{M}$) as a function of coastal water residence time (days). Scenarios for coastal waters with an average water depth of 10, 50, or 100 m located in a 15°C temperate region (A, C) or a 25°C tropical region (B, D) are shown. The maximum application of olivine with a uniform grain diameter of 100 (A, B) or $10 \mu\text{m}$ (C, D) is given. A seawater Ni background concentration of 3.92 nmol L^{-1} and a Ni concentration in olivine of $7.5 \text{ mmol mol}^{-1}$ of olivine were assumed. As derived by Hangx and Spiers,⁶ olivine dissolution rate constants of 5.19×10^{-11} and $1.58 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ were used for the temperate (15°C) and tropical (25°C) scenarios, respectively.

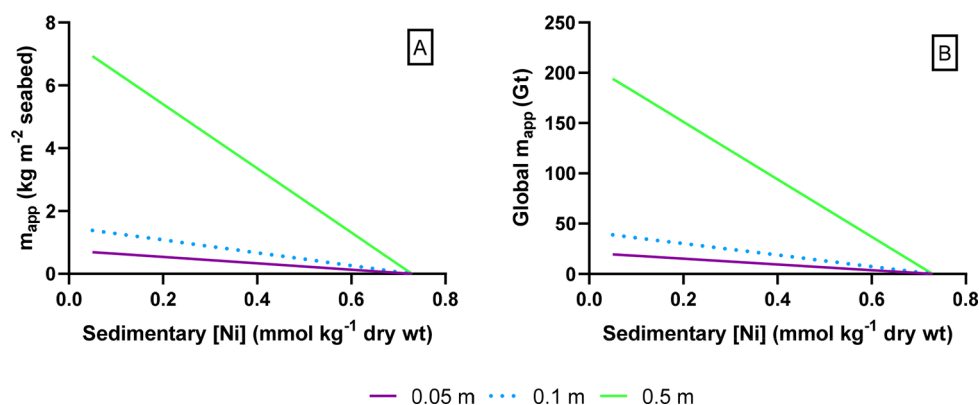


Figure 2. Maximum amount of olivine, m_{app} , that can locally (A) or globally (B) be distributed without exceedance of the nickel (Ni) probable effect level (PEL) for marine biota (0.729 mmol kg⁻¹ dry wt) as a function of sedimentary Ni concentrations (mmol kg⁻¹ dry wt) for different olivine mixing depths (0.05, 0.1, and 0.5 m). The global continental shelf was assumed to have a surface area of 28×10^6 km², and the olivine was assumed to have a nickel concentration of 7.5 mmol of Ni mol⁻¹ of olivine. The worst-case scenario is shown for which all the nickel released from olivine weathering is assumed to stay inside the sediment.

tropical (25 °C) compared to temperate (15 °C) coastal waters.⁶ Furthermore, assuming that the olivine grains are spherical, grains with a diameter of 10 μ m are expected to dissolve approximately 10 times faster than grains with a diameter of 100 μ m according to basic geometry (see eq 4 in the Supporting Information).⁶ If all Ni released during olivine weathering is being homogeneously mixed in the overlying water, then Ni concentrations will be 10 times lower at a location with a water depth of 100 m compared to a location with a 10 m water depth with the same water residence time.

From these assumptions, we can derive that for continental shelf seas with a short water residence time of 2 weeks, such as the East Brazil shelf in the South Atlantic Ocean or the California Current in the Pacific Ocean,⁵⁴ relatively high quantities of olivine (on the order of $5\text{--}1.7 \times 10^3$ kg m⁻² depending on water depth, temperature, and olivine grain size) can be distributed without exceedance of the European Ni EQS. For coastal waters with a relatively long residence time of approximately 1 year, such as the North Sea or the East China Sea,⁵⁴ the amount of olivine that can be distributed is approximately 26 times lower than that for seas with a residence time of 2 weeks assuming total coverage of the continental shelf with olivine.

We note that these results were derived from average, laboratory-based olivine dissolution rate constants for seawater.⁶ However, when supplied to the coastal zone, the rate and extent of olivine dissolution could be enhanced or reduced by several biotic (e.g., bioturbation) and abiotic (e.g., wave induced pore water flushing or burial by sediment) processes.⁵ Furthermore, in deeper parts of continental shelf seas, released trace metals might not be homogeneously mixed in the water column due to the presence of seasonal or permanent pycnoclines (boundaries between two water layers of different density) or other oceanic processes.⁵⁵ Moreover, an olivine Ni concentration of 7.5 mmol mol⁻¹ of olivine was assumed,¹⁴ while concentrations can vary from 2.4 to 12 mmol of Ni mol⁻¹ of olivine depending on the origin of the source rock.¹⁸ Additionally, a low Ni background concentration (3.92 nmol L⁻¹) was considered, while concentrations of up to 3 orders of magnitude higher have been observed.⁴⁶ Finally, the European seawater Ni EQS of 0.147 μ mol L⁻¹ was used to derive the olivine guideline, but different EQS values are implemented in other regions (see Table S2) and Ni concentrations as low as

0.102 μ mol L⁻¹ have been recently recommended to ensure protection of marine biota.⁵⁶

These sources of variation can significantly affect the olivine application guideline and should therefore be taken into account in the best way possible on a local scale when determining the amount of olivine that can be supplied to a specific coastal area. Especially the *in situ* olivine dissolution and metal release rate remain unknown and require additional research efforts.⁵

All Ni Ends Up in the Sediment. In addition to Ni EQS for seawater, there are also sediment Ni EQS values, of which the threshold effect level (TEL) and probable effect level (PEL) derived by the Florida Department of Environmental Protection (FDEP) (Table S3) are among the most widely used.^{42,57} The TEL was derived to represent the pollutant concentration below which adverse biological effects rarely occur, while the PEL corresponds to the pollutant concentrations above which adverse biological effects are frequently expected. In the context of coastal ESW, a conservative approach would be to halt olivine deposition when future Ni release is expected to exceed the TEL.^{42,57} However, 76% of the collected coastal sedimentary Ni concentrations are above the TEL of 0.271 mmol of Ni kg⁻¹ dry wt. Furthermore, in the biological effects database for sediments (BEDS), adverse biological effects were only observed in 9.4% of cases where sedimentary Ni concentrations exceeded the PEL, whereas for other metals these percentages were much higher (e.g., 56% for copper).⁴² Moreover, Chapman et al. and Bakke et al. derived sediment Ni EQS at which biological effects were unlikely of 0.68 and 0.78 mmol kg⁻¹ dry wt, respectively.^{58,59} Therefore, the PEL of 0.729 mmol Ni kg⁻¹ dry wt is a more suitable threshold concentration for deriving an olivine application guideline.

The maximum amount of olivine that can be distributed in coastal waters without future exceedance of the PEL derived for Florida coastal sediments (0.729 mmol kg⁻¹ dry wt) is shown in Figure 2. For the scenario where olivine remains in the upper 5 cm of the sediment, a maximum amount of 0.69 kg m⁻² and minimum amount of 0.029 kg m⁻² seabed can be dispersed without exceedance of the PEL if sedimentary Ni concentrations are 0.05 and 0.7 mmol of Ni kg⁻¹ dry wt, respectively (Figure 2A). In case the olivine gets mixed to greater depths by wave action or bioturbation in a site with an

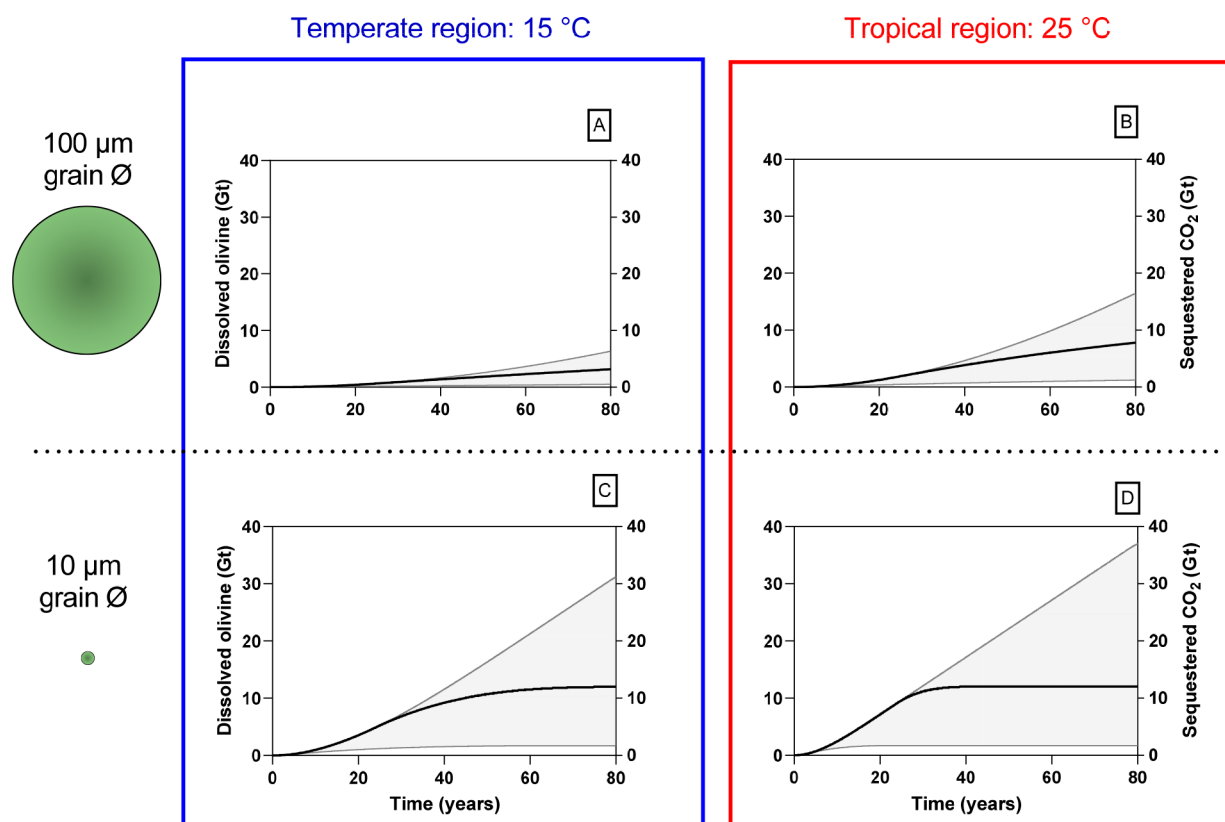


Figure 3. Amount of dissolved olivine (Gt) and associated CO₂ sequestration (Gt) as a function of time (years) for a 1.7–39 Gt global coastal enhanced olivine weathering scenario. A constant olivine supply rate (S) of 9.615 Mt week⁻¹ for a period of 3.4–78 years was assumed based on a sedimentary Ni concentration of 0.05–0.7 mmol kg⁻¹ dry wt. The solid black line shows the scenario where 12 Gt of olivine is supplied to an average coastal sediment (0.52 mmol of Ni kg⁻¹ dry wt) for a period of 24 years. Scenarios for a 15 °C temperate region (A, C) and a 25 °C tropical region (B, D) are shown for olivine with a uniform grain diameter of 100 (A, B) or 10 μm (C, D). Olivine dissolution was assumed to occur according to a shrinking core model with olivine dissolution rate constants of 5.19×10^{-11} and 1.58×10^{-10} mol m⁻² s⁻¹ and an activation energy of 79.5 kJ mol⁻¹¹⁵³ for the 15 and 25 °C scenarios, respectively. The CO₂-sequestration efficiency was taken to be 1 ton of CO₂ sequestered for each ton of dispersed olivine.

average sedimentary Ni concentration of 0.52 mmol of Ni kg⁻¹ dry wt, double (0.42 kg m⁻²) or 10 times (2.1 kg m⁻²) the amount of olivine can be spread out on the seafloor for a 10 or 50 cm mixing depth scenario (Figure 2A).

Importantly, in these calculations the sediment Ni EQS derived for Florida waters were used while guidelines for a range of locations have been derived in the past ~30 years ranging from 0.27 to 0.75 mmol kg⁻¹ dry wt to protect local marine biota.⁶⁰ Furthermore, marine sediments were considered a static sink for metals, while in reality metals are constantly exchanged between the sediment and the overlying water column.⁶¹ Metal efflux from the sediment is mainly driven by molecular diffusion, but it can be significantly enhanced by bioturbation and advection.^{61–63} To take these metal effluxes into consideration when deriving an olivine application guideline, accurate data on local biological and physicochemical processes in the sediment would be required. However, in the literature these data are scarce and can show significant temporal and spatial variations.^{61,64} Furthermore, the olivine mixing depth and weathering rate as a function of sediment depth and time need to be well-defined, since they would have a large effect on the magnitude of the metal influx and efflux. Currently these data are lacking.⁵ Therefore, olivine sediment EQS based guidelines were only derived under the conservative assumption that all trace metals released during olivine weathering remain in the sediment.

Collectively, the calculations show that benthic marine biota are at highest risk from Ni release during a large-scale coastal olivine application in the case where all the released Ni stays in the sediment. Assuming a mixing depth of 10 cm and a sedimentary Ni concentration of 0.52 mmol kg⁻¹ dry wt, the maximum amount of olivine that can be distributed without future exceedance of the Ni guidelines is 0.42 kg m⁻². When comparing this amount to the amount needed to surpass the Ni water quality guidelines, only in the case where very fine-grained olivine (10 μm grain diameter) is dispersed in tropical (25 °C) or shallow temperate (15 °C, 10 m water depth) coastal areas with a water residence time of more than half a year (>181 days), Ni water quality guidelines can be exceeded by dispersing lower amounts of olivine (Figure 1D). Therefore, for most locations around the world the maximum amount of olivine that can be dispersed should be based on the local sedimentary Ni concentrations.

Implications of the Olivine Guideline for CO₂ Sequestration Potential. To investigate the potential of coastal ESW as an NET in the 21st century, the dissolution of an environmentally safe amount of olivine derived from the FDEP sediment Ni EQS and associated CO₂ sequestration are shown in Figure 3. A CO₂-sequestration efficiency of 1 ton of CO₂/ton of supplied olivine was assumed.¹⁴ A conservative environmentally safe olivine application of 1.7–39 Gt, spread over a period of 3.4–78 years, was calculated based on an

olivine mixing depth of 10 cm and the assumption that all trace metals released during weathering remain in the sediment (Figure 2B). This mixing depth was based on the zone in the sediment where most benthic fauna is present.^{64,65} For the larger 100 μm olivine grains, 0.51 (~30%) to 6.4 Gt (~16%) of the supplied olivine would have dissolved by the end of the 21st century in a temperate (15 °C) region (Figure 3A) and 1.2 (~71%) to 16 Gt (~42%) would have dissolved in a tropical (25 °C) region (Figure 3B). Alternatively, if 10 μm grain size olivine would be distributed, 1.7 (100%) to 31 Gt (~80%) and 1.7 (100%) to 37 Gt (~95%) of the supplied olivine would be dissolved at the end of the 21st century for temperate and tropical zones, respectively (Figure 3C,D). These results highlight that olivine would have to be ground to very small grain sizes to dissolve fast enough to achieve significant CO_2 withdrawal from the atmosphere during the coming decades.^{6,11}

Based on the environmentally safe amount of olivine that could be applied to the global continental shelf, a maximum net amount of ~0.51–37 Gt of CO_2 could be removed from the atmosphere during the 21st century using coastal enhanced olivine weathering. Narrowing this result based on the median coastal sedimentary Ni concentration (0.52 mmol kg^{-1} dry wt), 3.2–12 Gt of CO_2 could be sequestered in the coming 80 years depending on the olivine grain size, application location, and net CO_2 -sequestration efficiency. The latter is estimated to vary between 0.50 and 1.0 ton of CO_2 sequestered per ton of dispersed olivine.^{5,66} The net CO_2 -sequestration efficiency is dependent on the mineral composition of the source rock, potential secondary mineral formation during olivine dissolution, and CO_2 emissions from mining, grinding, and transportation of the olivine from its source to the coastal zone.^{5,6,11,66}

To keep global warming below 1.5 °C, all NETs would need to collectively capture approximately 150–1180 Gt of CO_2 during the 21st century, depending on the rate of conventional mitigation.⁶⁷ Therefore, a total CO_2 capture potential of 0.51–37 Gt via coastal enhanced olivine weathering is relatively low. Hence, this first olivine application guideline shows that additional research on the environmental safety of the technique is needed.

Future Perspectives: The Need for Site-Specific Olivine Guidelines. Overall, our results show that Ni and Cr release could limit the potential safe usage of the mineral olivine in coastal enhanced silicate weathering on a global scale. As explained in more detail in the [Supporting Information](#), the release of Cr is expected to be of lower concern compared to Ni. However, the potential of some released Cr^{3+} to be oxidized to Cr^{6+} , which forms anionic complexes in seawater that are highly bioavailable and potentially synergistically toxic with Ni^{2+} , implies that Cr^{3+} release during olivine weathering cannot be disregarded in the risk assessment of coastal ESW.^{25,27,29,68}

Ecological risk assessment of olivine in coastal ESW is still at a very early stage. Data on olivine toxicity in marine environments and accurate predictions on *in situ* olivine dissolution rates and mixing depths are still lacking.⁵ In a coastal environment, organisms will be exposed to Ni and Cr released in the water (porewater or overlying water) or in their gastrointestinal tracts after ingestion of sediment particles and/or contaminated food.⁶⁹ The degree of metal uptake will depend on the exposure concentration and duration, metal speciation, competition with other ions for uptake, abiotic

variables (such as temperature, pH, and organic carbon), and the organism's physiology.^{69,70} Toxicological effects will occur when metal concentrations in an organism's biologically active metal compartments exceed certain threshold values.⁶⁹

Biotic ligand models (BLMs) have been used to account for site- and species-specific metal bioavailability in the derivation of the European freshwater Ni EQS and have been recently validated for Australian freshwater species.^{71,72} However, for marine systems additional research on the interactions between seawater chemistry, Ni bioavailability, and toxicity is needed to derive bioavailability based EQS.^{22,73}

Differences in biogeochemical processes among coastal sites necessitate the derivation of site-specific olivine application guidelines. The risk assessment should be based on multiple lines of evidence (laboratory toxicity testing and field-based studies) to determine implications of coastal olivine spreading for ecosystem health.⁶⁵ Potential benefits (counteracting ocean acidification and global warming) of olivine spreading should also be considered to decide how much olivine will ultimately be dispersed in a specific coastal sea.⁵

To conclude, we recommend that future studies try to fill in the data gap on olivine toxicity to marine biota and *in situ* olivine dissolution rates by (I) conducting laboratory flume experiments, (II) performing olivine toxicity tests for a range of (benthic) marine organisms (algae, invertebrates, and fish), and (III) conducting monitoring campaigns at natural olivine beaches (e.g., Papakōlea Beach, Hawaii) before starting large-scale field trials. Our work provides a first conservative coastal olivine application guideline and highlights the need for additional research to perform an accurate site-specific risk assessment of coastal enhanced olivine weathering.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.1c02974>.

More detailed description on how the olivine guidelines were derived based on seawater EQS for Ni and Cr; globally occurring Cr concentrations in coastal seawater and sediment; literature data used to derive a summary on global coastal Ni and Cr concentrations; Cr EQS based olivine guidelines ([PDF](#))

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Notes

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