

1 **Phytoplankton Response to Increased Nickel in the Context of** 2 **Ocean Alkalinity Enhancement**

3 Xiaoke Xin, Giulia Faucher, Ulf Riebesell

4 GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

5 *Correspondence to:* Xiaoke Xin (xxin@geomar.de)

6 **Abstract**

7 Ocean alkalinity enhancement (OAE) is considered one of the most promising approaches to
8 actively remove carbon dioxide (CO₂) from the atmosphere by accelerating the natural process
9 of rock weathering. This approach involves introducing alkaline substances sourced from
10 natural mineral deposits such as olivine, basalt, and carbonates or obtained from industrial
11 waste products such as steel slags, into seawater and dispersing them over coastal areas. Some
12 of these natural and industrial substances contain trace metals, which would be released into
13 the oceans along with the alkalinity enhancement. The trace metals could serve as
14 micronutrients for marine organisms at low concentrations, but could potentially become toxic
15 at high concentrations, adversely affecting marine biota. To comprehensively assess the
16 feasibility of OAE, it is crucial to understand how the phytoplankton, which forms the base of
17 marine food webs, responds to ocean alkalization and associated trace metal perturbations.
18 As one of the most abundant metals in OAE source materials, understanding the impacts of
19 nickel (Ni) on the phytoplankton is critical for OAE assessment. In this study, we investigated
20 the influence of nickel (Ni) on three representative phytoplankton species over a gradient of
21 nine Ni concentrations (from 0 to 100 $\mu\text{mol L}^{-1}$ with 12 $\mu\text{mol L}^{-1}$ synthetic organic ligand). The
22 impacts of elevated Ni varied among the tested phytoplankton species. The coccolithophore
23 *Emiliana huxleyi* and the dinoflagellate *Amphidinium carterae* exhibited a growth rate
24 inhibition of about 30% and 20%, respectively, at the highest Ni concentrations. The half
25 maximal inhibitory concentration (IC₅₀, at which the growth rate is inhibited by 50%) of both
26 species exceeded the tested range of Ni. This suggests that both species were only mildly
27 affected by the elevated Ni concentrations. In contrast, the diatom *Thalassiosira weissflogii*
28 displayed a considerably higher sensitivity to Ni, with a 60% growth rate inhibition at the
29 highest Ni concentration and an IC₅₀ value of 63.9 $\mu\text{mol L}^{-1}$. In conclusion, the variability in
30 phytoplankton sensitivity to Ni exposure suggests that for OAE applications with Ni-rich
31 materials caution is required and critical toxic thresholds for Ni must be avoided.

32 **1 Introduction**

33 The progressive release of anthropogenic carbon dioxide (CO₂) into the atmosphere since the
34 industrial revolution resulted in a multitude of environmental challenges, including global
35 warming, ocean acidification, ecosystem alteration, increasing frequency of extreme climatic
36 events, and food insecurity (Pörtner et al., 2022). To keep the effects of climate change within
37 acceptable limits, about 1 to 15 GtCO₂ yr⁻¹ must be captured by 2100 (Rogelj et al., 2018).
38 Carbon capture activities, known as negative emission technologies (NETs), have moved to
39 the limelight of discussion as they will need to be implemented over the next two decades to
40 meet the climate targets and limit global warming to < 2°C (Shepherd, 2009; Allan et al., 2021).
41 One of the promising NETs is to accelerate natural rock weathering by introducing finely
42 ground alkaline products on land (Enhanced Weathering, EW) or into the surface ocean (Ocean
43 Alkalinity Enhancement, OAE) to remove CO₂ from the atmosphere (Minx et al., 2018; Bach
44 et al., 2019). OAE, in addition to enhancing the buffering capacity of seawater, has the co-
45 benefit of mitigating ocean acidification at the deployment sites (Köhler et al., 2010). Natural
46 alkaline minerals, as well as by-products from industrial activity, are potential candidates for
47 EW and OAE (Taylor et al., 2016; Renforth, 2019). Among the most recognized alkaline
48 minerals, olivine rocks have gained considerable attention due to their relatively fast
49 weathering rate, wide availability, and low cost (Schuiling and Krijgsman, 2006; Hartmann et
50 al., 2013). These rocks contain high amounts of trace metals, e.g., nickel (Ni) and chromium
51 (Cr) (Montserrat et al., 2017; Amann et al., 2020) that through OAE could affect coastal and
52 off-shore systems, possibly influencing marine communities (Gaillardet et al., 2003).

53 In seawater, Ni is present at low concentrations (Donat et al., 1994; Mackey et al., 2002; Saito
54 et al., 2004) and acts as a micronutrient when urea serves as the nitrogen source (Muysen et
55 al., 2004; Egleston and Morel, 2008). However, this metal at elevated concentrations may
56 emerge as a concern to marine ecosystems, due to its toxicity, bioaccumulation, and
57 biogeochemical cycling (Sclater et al., 1976; Hall and Anderson, 1995; Horvatić and Peršić,
58 2007; Debelius et al., 2011; DeForest and Schlegel, 2013; Martínez-Ruiz and Martínez-
59 Jerónimo, 2015; Karthikeyan et al., 2018). In olivine-based OAE scenarios, Ni concentrations
60 could rapidly rise above critical levels that become harmful to marine organisms (Montserrat
61 et al., 2017; Hartmann et al., 2023). To date, studies on high Ni concentrations are scarce. In
62 this study, we examined the impacts of Ni on three representative marine phytoplankton species:
63 the diatom *Thalassiosira weissflogii*, the dinoflagellate *Amphidinium carterae*, and the
64 coccolithophore *Emiliania huxleyi*. These species were selected as they represent three

65 dominant functional groups of phytoplankton. This research aimed to (1) investigate how
66 different phytoplankton species respond to a gradient of Ni concentrations and (2) compare the
67 inter-species differences in Ni sensitivity.

68 **2 Materials and methods**

69 **2.1 Strain and culture conditions**

70 Experiments were conducted with cultures of the marine diatom *Emiliana huxleyi* B92/11
71 (Plymouth Marine Laboratory), the dinoflagellate *Amphidinium carterae* CCAP1102
72 (University of Oldenburg), and the coccolithophore *Thalassiosira weissflogii* CCMP1336
73 (Bigelow Laboratory for Ocean Sciences). Algae were cultivated in sterile-filtered (0.2 μm) f/2
74 media prepared with artificial seawater (Guillard and Ryther, 1962; Kester et al., 1967). Media
75 were enriched with essential trace metals buffered by ethylenediaminetetraacetic acid (EDTA,
76 12 $\mu\text{mol L}^{-1}$). Cells grew at 18°C with a 12:12h light and dark cycle under 200 $\mu\text{mol photons}$
77 $\text{m}^{-2} \text{s}^{-1}$ of photosynthetically active radiation (PAR). Media were acclimated to the incubation
78 temperature prior to inoculation from the precultures to avoid a potential thermal shock.

79 **2.2 Experimental setup**

80 To determine the toxicity of nickel, a stock solution (as $\text{NiCl}_2 \times 6\text{H}_2\text{O}$) was prepared, with a
81 nominal value of 50 mmol L^{-1} . All bottles were soaked with 10 % HCl (Fisher) for 24 h and
82 rinsed with Milli-Q water before the experiment. Stock solutions of Ni were added to the algal
83 media for different Ni concentration treatments (0.01, 0.1, 1, 5, 10, 20, 50, and 100 $\mu\text{mol L}^{-1}$)
84 and the control with exclusive f/2 medium. Experiments were performed in triplicate
85 independent 75 mL falcon flasks for each concentration. All cultures were gently turned by
86 hand twice a day to avoid cells from settling. Samples were always collected at the same time
87 of day between 9:00 a.m. and 10:00 a.m. to avoid an effect of the photocycle. Samples (1 mL)
88 of each flask were collected into sterile 2 mL microtubes. The cell density was determined
89 daily with a flow cytometer (BD Accuri™ C6). To minimize the impact of changes in the
90 carbonate chemistry of the medium induced by cellular metabolism, the phytoplankton biomass
91 at the harvest time should consume less than 5% of the total dissolved inorganic carbon
92 (Zondervan et al., 2002). The maximum density was determined based on the cell carbon quota
93 of the tested species. Accordingly, the maximum cell densities of *A. carterae*, *T. weissflogii*,
94 and *E. huxleyi* never exceeded 12000 cells mL^{-1} , 15000 cells mL^{-1} , and 130000 cells mL^{-1} ,
95 respectively (Zondervan et al., 2002; Olenina et al., 2006).

96 **2.3 Growth rate and IC50 value determination**

97 Growth rates (μ ; d^{-1}) were calculated from cell density following:

98
$$\mu = \frac{\ln(c_f) - \ln(c_0)}{d}, \quad (1)$$

99 where c_0 and c_f are the cell densities at the beginning and end of the experiment,
100 respectively; d is the duration of the experiment.

101 The toxic response was expressed as:

102
$$I = \left(1 - \frac{\mu_{inhibited}}{\mu_{control}}\right) \times 100\%, \quad (2)$$

103 where I is the growth inhibition and μ is the growth rate.

104 Dose-response curves were constructed for growth rate following Stephenson et al. (2000).

105 Nonlinear regression models were determined by the least square method. Model equations
106 were chosen based on scatter plots of the growth rates of the different species. The sigmoidal
107 model was applied as:

108
$$Y = \frac{t}{1 + \left(\frac{C}{u}\right)^B}, \quad (3)$$

109 where Y is the growth rate and C is the Ni concentration. The parameter t is the control response,
110 and u and B define the location and shape of the equation, respectively. The half maximal
111 inhibitory concentration (IC50), at which the growth rate is inhibited by 50%, was determined
112 from the dose-response curve.

113 **2.4 Nickel measurement**

114 At the end of the growth experiment, 30 mL media of each sample were filtered with 0.2 μ m
115 sterile disc filters to remove the algae. The filtered media were collected for Ni measurements.
116 The total nickel concentrations were measured with ThermoFisher Scientific ElementXR to
117 ensure that the target concentrations were reached. The measured Ni concentrations were used
118 as input data for the program Visual Minteq 3.1 (Gustafsson, 2013). The software utilizes a
119 chemical equilibrium model to calculate metal speciation and obtain the concentrations of free
120 Ni^{2+} .

121 **2.5 Statistical analysis**

122 Data represent means \pm standard deviations ($N = 3$). ANOVA was performed on the cell density
123 and growth rates to assess the effect of Ni concentrations. Differences among treatments were
124 tested with Tukey's HSD ANOVA test. Significant differences were reported at the 95 %

125 confidence level. All statistics were conducted in the Rstudio environment (R packages
 126 “tidyverse” and “ggplot2”; Posit team, 2023; R Core Team, 2023).

127 3 Result

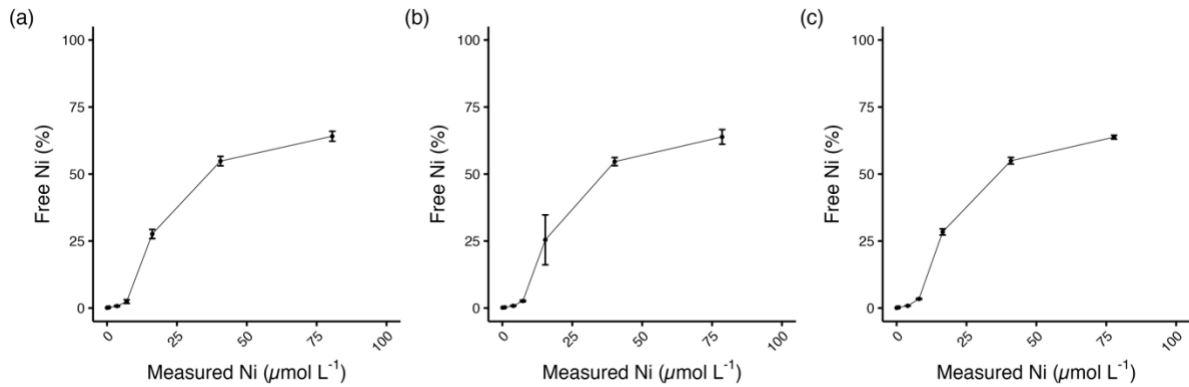
128 3.1 Ni concentrations

129 Table 1. Target, measured, and free concentrations of Ni for the different phytoplankton cultures at the end of the experiment.
 130 SD standard deviation.

	Target Ni concentration ($\mu\text{mol/L}$)	Measured Ni concentration ($\mu\text{mol/L}$)	Measured Ni SD ($\mu\text{mol/L}$)	Free Ni ²⁺ concentration ($\mu\text{mol/L}$)	Free Ni ²⁺ SD ($\mu\text{mol/L}$)
Stock	5×10^4	4.16×10^4			
	0	0.00	0	0	0
	0.01	0.01	3.45×10^{-3}	8.0×10^{-6}	7.83×10^{-6}
	0.1	0.05	0.02	7.94×10^{-5}	2.87×10^{-5}
	1	0.70	0.02	1.61×10^{-3}	7.60×10^{-5}
<i>A. carterae</i>	5	3.59	0.41	0.03	6.95×10^{-3}
	10	7.04	0.54	0.17	0.05
	20	16.19	0.39	4.47	0.28
	50	40.59	0.97	22.26	0.71
	100	80.57	2.03	51.64	1.49
	0	0.00	0	0	0
	0.01	/	/	/	/
	0.1	0.12	0.02	9.17×10^{-5}	2.56×10^{-5}
	1	0.88	0.07	2.21×10^{-3}	2.53×10^{-4}
<i>E. huxleyi</i>	5	3.89	0.31	0.03	5.71×10^{-3}
	10	7.32	0.21	0.19	0.02
	20	15.34	2.09	3.90	1.43
	50	40.17	0.83	21.95	0.61
	100	78.60	2.92	50.19	2.14
	0	0.00	0	0	0
	0.01	0.07	/	3.03×10^{-6}	/
	0.1	0.07	1.36×10^{-3}	9.31×10^{-5}	2.19×10^{-6}
	1	0.77	3.99×10^{-3}	1.81×10^{-3}	1.33×10^{-5}
<i>T. weissflogii</i>	5	3.99	0.13	0.03	2.42×10^{-3}
	10	8.01	0.13	0.27	0.02
	20	16.50	0.27	4.68	0.19
	50	40.91	0.68	22.48	0.50
	100	77.80	0.76	49.60	0.56

131 The stock solution was not acidified to avoid pH changes in the culture media. For this reason,
 132 nickel carbonate precipitation occurred in the stock solution and approximately 80 % of the
 133 target Ni concentrations were achieved (Table 1, Fig. S1; Gad 2023). Free Ni²⁺ was chelated
 134 by ligand at low concentrations but concentrations of free Ni²⁺ increased with elevated total Ni
 135 (Table 1, Fig. 1). Ligand chelated more Ni²⁺ with elevated total Ni concentration, while the

136 binding ability decreased. More than 60 % free Ni²⁺ were beyond ligand binding capacity at
 137 the highest Ni concentration.

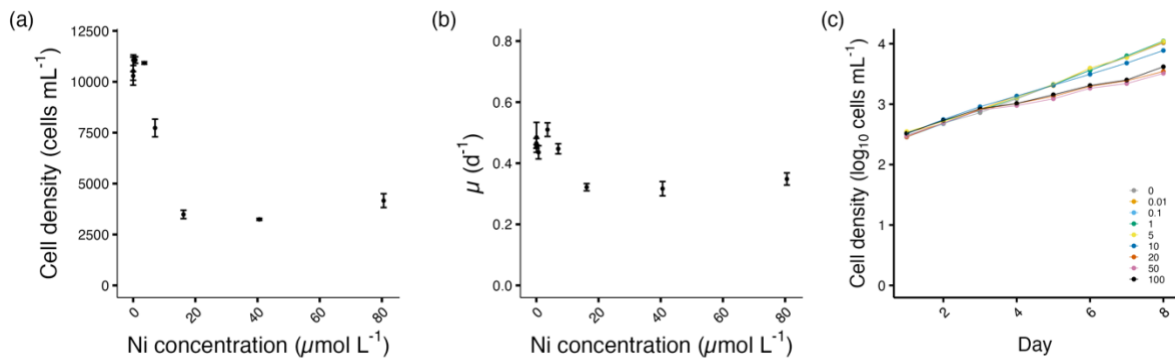


138
 139 Fig. 1. Percentage of free Ni²⁺ in (a) *A. carterae*, (b) *E. huxleyi*, and (c) *T. weissflogii* cultures at the end of the experiment.
 140 Error bars denote standard deviations (N = 3).

141 **3.2 Growth response and cell density accumulation**

142 All three species survived the highest tested concentrations. With increasing Ni, the cell
 143 densities and growth rates of the three species decreased, albeit differently.

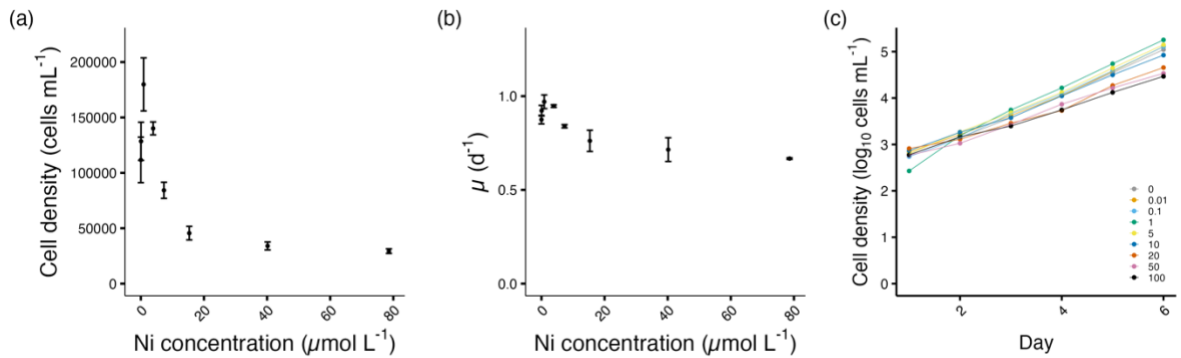
144 **3.2.1 *Amphidinium carterae***



145
 146 Fig. 2. Growth performance of *A. carterae*. (a) Cell densities (cells mL⁻¹), and (b) Growth rates (d⁻¹) plotted against measured
 147 Ni concentrations on the final experimental day. (c) Log-transformed cell densities plotted against time (day) to indicate
 148 the time of response; target Ni concentrations (μmol L⁻¹) used for clarity. Error bars denote standard deviations (N = 3). If not
 149 visible, error bars are smaller than symbols.

150 The cell densities of *A. carterae* decreased significantly from 7.1 μmol L⁻¹ and the growth rates
 151 from 16.2 μmol L⁻¹ Ni concentrations ($p < 0.05$; Fig. 2a, Fig. 2b). Growth was not inhibited
 152 until day 4 after the exposure to Ni (Fig. 2c). From 16.2 to 80.6 μmol L⁻¹ Ni concentrations, we
 153 observed the maximum decrease in cell density of about 59–66 %, with the growth rate
 154 decreasing up to 30 % at the highest Ni concentration compared to the control (Fig. 2a, Fig. 2b,
 155 Table S1).

156 **3.2.2 *Emiliania huxleyi***

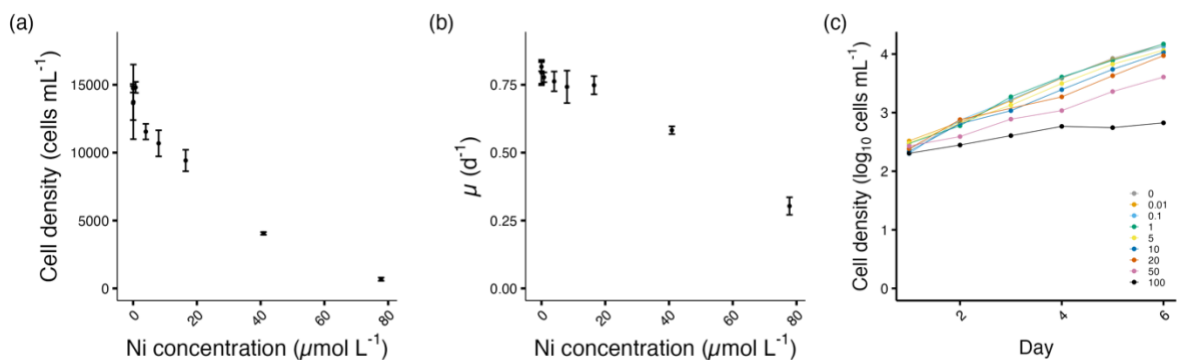


157
 158 Fig. 3. Growth performance of *E. huxleyi*. (a) Cell densities (cells mL⁻¹), and (b) Growth rates (d⁻¹) plotted against measured
 159 Ni concentrations on the final experimental day. (c) Log-transformed cell densities plotted against time (day) to indicate the
 160 time of response; target Ni concentrations (μmol L⁻¹) were used for clarity. Error bars denote standard deviations (N = 3). Note
 161 that the data point at 0.01 μmol L⁻¹ was excluded in (a) and (b) due to technical measurement error. If not visible, error bars
 162 are smaller than symbols.

163
 164 The cell densities and growth rates of *E. huxleyi* increased with the addition of Ni up to 3.89
 165 μmol L⁻¹. At 0.9 μmol L⁻¹ Ni, the maximum cell density with a 63 % increase was observed (p
 166 < 0.01). The growth rate increased by about 11 % but this value is not statistically significant
 167 ($p = 0.07$).

168 From 15.3 to 78.6 μmol L⁻¹, the cell densities decreased significantly between 57–72 %
 169 compared to the control ($p < 0.05$; Fig. 3a, Table S1). The decrease in growth rate reached up
 170 to 24 % at the highest Ni concentration compared to the control (Fig. 3b, Table S1). The growth
 171 variance of *E. huxleyi* started on day 3 after being exposed to Ni (Fig. 3c).

172 **3.2.3 *Thalassiosira weissflogii***

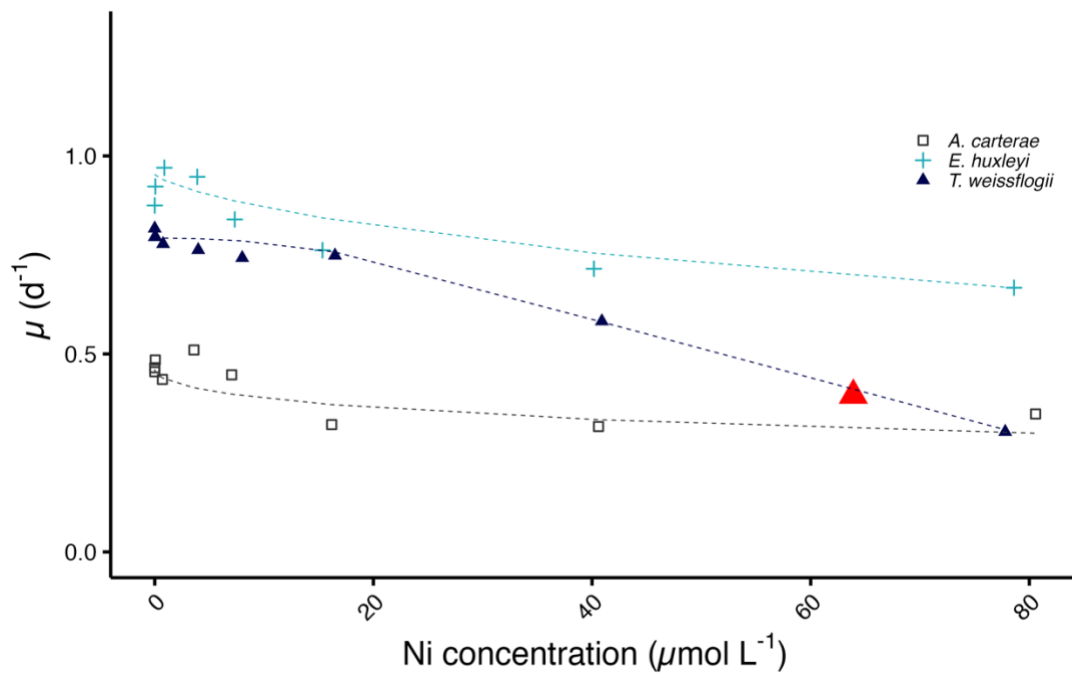


173
 174 Fig. 4. Growth performance of *T. weissflogii*. (a) Cell densities (cells mL⁻¹), and (b) Growth rates (d⁻¹) plotted against measured
 175 Ni concentrations on the final experimental day. (c) Log-transformed cell densities plotted against time (day) to indicate the
 176 time of response; target Ni concentrations (μmol L⁻¹) used for clarity. Error bars denote standard deviations (N = 3). If not
 177 visible, error bars are smaller than symbols.

178

179 The cell densities of *T. weissflogii* remained relatively stable until $8.0 \mu\text{mol L}^{-1}$ Ni, above which
 180 the densities started to decrease significantly ($p < 0.05$; Fig. 4a, Table S1). Similarly, the growth
 181 rates of *T. weissflogii* remained relatively stable until $40.9 \mu\text{mol L}^{-1}$ Ni, above which the growth
 182 rates started to decrease significantly ($p < 0.05$; Fig. 4b, Table S1). After being exposed to Ni,
 183 *T. weissflogii* reacted immediately from day 2 onwards (Fig. 4c).

184 3.3 Determination of IC50



185
 186 Fig. 5. Predicted growth curves plotted against measured Ni concentrations. The red triangle denotes the IC50 value of *T.*
 187 *weissflogii*. Note that the predicted IC50 values of *A. carterae* and *E. huxleyi* are not shown as they exceed the highest tested
 188 Ni concentration.

189 The diatom *T. weissflogii* has the lowest IC50 value with a concentration of $63.9 \mu\text{mol L}^{-1}$
 190 while the IC50 values for *A. carterae*, and *E. huxleyi* exceed the highest tested Ni concentration
 191 (Fig. 5).

192 4 Discussion

193 4.1 Effects of Ni on marine plankton

194 Trace metals are required by phytoplankton for numerous physiological processes and
 195 biochemical reactions; however, it is difficult to disentangle the distinct role of each element.
 196 Ni, for example, is widely recognized to be “bio-required” in several species when urea is
 197 utilized as a nitrogen source (Bartha and Ordal, 1965; Pederson et al., 1986; Price and Morel,
 198 1991). However, to our knowledge, no studies have reported that phytoplankton could benefit
 199 from supplemented Ni when cultivated in nitrate-enriched media while only a few studies have

200 documented the tolerances of different taxa to progressively increased (possibly toxic) Ni
201 concentrations (Horvatić and Peršić, 2007; DeForest and Schlegel, 2013; Martínez-Ruiz and
202 Martínez-Jerónimo, 2015; Panneerselvam et al., 2018).

203 Nickel in natural seawater has a concentration lower than 10 nmol L⁻¹ (Gerringa et al., 2021;
204 John et al., 2022), and exists mainly in the form of free Ni²⁺ (Donat et al., 1994; Achterberg
205 and Van Den Berg, 1997; Saito et al., 2004). Basic and ultrabasic rocks, which are widely
206 recognized source minerals for OAE, would introduce high amounts of Ni into seawater during
207 mineral dissolution (Renforth, 2019). A wide range of Ni content in olivine (0-0.44 wt%)
208 suggests that the Ni release is source-dependent (Simkin and Smith, 1970). In a previous batch
209 reaction experiment using forsterite olivine sand with 0.26 wt% Ni, an increase of 100 μmol
210 L⁻¹ alkalinity was associated with a parallel increase of approximately 3 μmol L⁻¹ dissolved Ni
211 during the non-stoichiometric dissolution process (Montserrat et al., 2017). According to these
212 results, the concentration of released Ni could potentially reach the highest concentration tested
213 in this study with a doubling of the current ocean alkalinity level, e.g. at the point source of
214 alkalinity release. In real-world applications, the release of alkaline solutions at discrete
215 locations could potentially lead to “hotspots” of alkalinity and associated increases of Ni in
216 seawater (Bach et al., 2019; Caserini et al., 2021). Alkalinity enhancement modelling studies
217 suggest that the phytoplankton may be impacted by the cumulative effects of alkalinity and
218 released trace metals from recurring local addition (Ilyina et al., 2013, Feng et al., 2017).

219 In this study, we focused on the impacts of a gradient of Ni concentrations on three key species
220 that belong to different phytoplankton groups. The results showed that while the three tested
221 species were able to survive in all treatments, they displayed adverse responses to high Ni
222 concentrations. The diatom species *T. weissflogii* was the most sensitive species, with an instant
223 reaction to the exposure of Ni and a decrease in cell density when Ni increased to 4.0 μmol L⁻¹.
224 At the highest Ni concentration, its growth rate was reduced by 60 %. The dinoflagellate *A.*
225 *carterae* and coccolithophore *E. huxleyi* are more tolerant to Ni enrichment, with less inhibition
226 in growth rate. The growth rates of *A. carterae* and *E. huxleyi* remained relatively constant
227 beyond a certain threshold and the IC50 values of these two species exceeded the highest tested
228 Ni concentration. The cell densities of *E. huxleyi* were even enhanced when Ni was supplied
229 at low concentrations. Considering the high tolerance of *E. huxleyi* to several other trace metals
230 such as copper and cadmium (Brand et al., 1986), it is not surprising that this species was found
231 to be mostly unaffected by Ni in our study. For example, to counteract high Cu concentrations,
232 *E. huxleyi*, regardless of the needs of the cells, can continuously produce organic Cu-ligand
233 (Echeveste et al., 2018). Another study postulates that *E. huxleyi* survives the Cu stress through

234 an efficient efflux system by exporting intracellular metals (Walsh and Ahner, 2014). We
235 speculate that *E. huxleyi* may apply analogous strategies to grow at high nickel concentrations.
236 Furthermore, Ni was shown to interact with Ca²⁺ and Mg²⁺ transport systems; the uptake of
237 Ca²⁺ and Mg²⁺ may compete with Ni for the transport pathways and reduce the uptake of Ni in
238 *E. huxleyi* (Deleebeeck et al., 2009). Interestingly, we observed an enhancement in the cell
239 densities of *E. huxleyi* at low Ni concentrations. Ni serves as a necessary micronutrient to the
240 Ni-containing enzyme urease in phytoplankton when the primary nitrogen source is urea (Price
241 and Morel, 1991). However, this does not apply to our study. To the best of our knowledge,
242 there are no reports indicating the positive effects of nickel as a nutrient when nitrate serves as
243 the nitrogen source. One possible explanation might be that the introduction of low-dose toxins
244 prompted an increased rate of cell division, a phenomenon known as hormesis. Studies on
245 various phytoplankton groups revealed a similar dose-response pattern, where low doses
246 exhibited beneficial effects and high doses led to toxicity. In these investigations, hormesis was
247 attributed to low increased levels of Cd (Brand et al., 1986) and Cu (Brand et al., 1986; Pérez
248 et al., 2006; Yang et al., 2019). This interpretation differs from the notion of metal limitation.
249 Considering Ni, a slight increase in concentrations positively impacted multiple chlorophyll
250 fluorescence parameters associated with photosynthesis in terrestrial plants, which was
251 explained as a hormetic response (Moustakas et al., 2022). Another potential explanation is
252 that Ni may, to some extent, contribute to the functionality of superoxide dismutase enzymes
253 which are vital components in an organism's defense against oxidative stress (Sunda 2012).
254 Either way, this growth alteration should not be dismissed, as it could indirectly impact the
255 competitive dynamics within ecosystems containing multiple phytoplankton species. Similar
256 strategies to counteract metal stress were observed in the other species. The dinoflagellate *A.*
257 *carterae* produces strong ligands to reduce free metal levels (Croot et al., 2000). The growth
258 rates of *T. weissflogii* were unperturbed about 40 µmol/L and dropped rapidly beyond this
259 threshold. Production of metal chelators was also reported in diatoms and green algae under
260 metal stress (Gerringa et al., 1995; Gonzalez-Davila et al., 1995). The release of phytochelatin-
261 metal complex probably is a detoxification mechanism of the diatom *T. weissflogii* (Lee et al.,
262 1996). Sequestering metals into a vacuole or storage complexes or binding metals with small
263 chaperones are also adaptive strategies to buffer the uptake of metals (Blaby-Haas and
264 Merchant, 2012).

265 Due to the increasing interest in olivine-based alkalization applications, recent studies
266 investigated the effects of Ni on marine phytoplankton in the context of OAE. In the study by
267 Guo et al. (2022), most of the tested phytoplankton species did not exhibit growth inhibition in

268 response to the tested Ni concentrations, ranging between 0 and 50 $\mu\text{mol L}^{-1}$. The inconsistency
269 between our results and those of Guo et al. (2022) could be attributed to the different amounts
270 of bio-available Ni. Guo et al. (2022) utilized a chelator at a high concentration (100 $\mu\text{mol L}^{-1}$
271 EDTA), while in our experiment 12 $\mu\text{mol L}^{-1}$ EDTA was added. EDTA can chelate free trace
272 metal ions, forming metal-EDTA complexes. The ligand serves as a buffer by increasing trace
273 metal availability when trace metal concentrations are low and decreasing trace metal reactivity
274 at excess levels (Van den Berg and Nimmo, 1987). Several studies documented that
275 phytoplankton is sensitive to free Ni^{2+} rather than total dissolved Ni (Canterford and Canterford,
276 1980; Morel et al., 1991; Dupont et al., 2010). Indeed, the lower amount of EDTA employed
277 in our study led to five orders of magnitude higher concentration of free Ni^{2+} at the target
278 concentration of 50 $\mu\text{mol L}^{-1}$, compared to that of Guo et al. (2022). We presume that the
279 variance in the growth inhibition between this study and that of Guo et al. (2022) arises from
280 the discrepancy of free Ni^{2+} determined by the different amounts of EDTA used in the two
281 studies. Contrarily, Hutchins et al. (2023) showed that most phytoplankton taxa were
282 irresponsive to Ni independent of the concentrations of Ni species and EDTA. However, the
283 study was conducted in a coastal enhanced weathering scenario where the Ni-release process
284 would be gradual (i.e., years) and the olivine utilized for the experiment contained a low
285 amount of Ni, measuring 0.13 $\mu\text{mol L}^{-1}$ at the highest concentration. Thus, the synthetic olivine
286 dissolution yielded lower Ni concentrations, possibly without reaching threshold values of
287 toxicity compared to those tested in our experiment.

288 Several studies investigated the impact of Ni at high concentrations on various marine
289 organisms, albeit outside the specific context of OAE. These studies showed a range of
290 sensitivities to Ni among different plankton. For example, certain diatom species with low IC50
291 and copepod species with LC50 (concentration expected to be lethal to 50 % of the tested
292 organisms) could potentially be vulnerable to the nickel released in the context of OAE. On
293 the contrary, the lethal concentration of Ni for the dinoflagellate *Prorocentrum donghaiense*
294 and the diatom *Skeletonema costatum* was found to be 1.7 mmol L^{-1} (Huang et al., 2016), which
295 is unlikely to be encountered during the process of OAE.

296 DeForest and Schlegel (2013) suggested a threshold of 20.9 $\mu\text{g L}^{-1}$ Ni (0.35 $\mu\text{mol L}^{-1}$) as the
297 Predicted No Effect Concentration (PNEC) for chronic Ni toxicity in marine organisms. In a
298 coastal OAE scenario, with a short water residence time, the low Ni released from alkaline
299 particles is unlikely to impact the ecosystem due to the slow dissolution rate (Hutchins et al.
300 2023; Table 2). In the open ocean, olivine must be ground to a very small size (less than 1 μm)
301 before sinking out of the surface mixed layer (Köhler et al. 2013; Meysman and Montserrat,

2017). Thus, olivine has the potential to release a high quantity of Ni above the IC50 and LC50 values reported in Table 2 for most species. The perturbation could be minimal if the mixing with surrounding waters could rapidly dilute the alkaline solution before impacts in plankton species occur. Therefore, the deployment of alkalinity enhancement in zones with high mixing dynamics could meet the PNEC requirement. Taken together, the introduction of Ni through olivine-based OAE has the potential to shift the taxonomic composition of natural phytoplankton communities. Hence, the observed species-specific sensitivities towards the release of Ni underline that caution is needed in terms of magnitude and temporal mode (e.g., weekly, monthly, seasonal, and annual release) of ocean alkalization to alleviate the cumulative effects of Ni.

Table 2. IC50 and LC50 values ($\mu\text{mol L}^{-1}$) of different marine organisms. LC50 is the concentration of a material expected to be lethal to 50 % of the tested organisms.

Taxa	Species	Time (h)	Test water	Ni	IC50 ($\mu\text{mol L}^{-1}$)	LC50 ($\mu\text{mol L}^{-1}$)	EDTA ($\mu\text{mol L}^{-1}$)	Reference
Diatom	<i>Odontella mobiliensis</i>	96	Natural	-	5.28		/	(Karthikeyan et al., 2018)
Diatom	<i>Coscinodiscus centralis</i>	96	Natural	-	10.56		/	(Karthikeyan et al., 2018)
Diatom	<i>Skeletonema costatum</i>	72	Natural	-	154		/	(Huang et al., 2016)
Diatom	<i>Phaeodactylum tricorutum</i>	72	Natural	-	124.04		/	(Horvatić and Peršić, 2007)
Diatom	<i>Thalassiosira weissflogii</i>	120	Synthetic	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	63.9		12	this study
Dinophyta	<i>Prorocentrum donghaiense</i>	96	Natural	-	185		/	(Huang et al., 2016)
Dinophyta	<i>Amphidinium carterae</i>	120	Synthetic	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	>100		12	this study
Coccolithophore	<i>Emiliana huxleyi</i>	96	Synthetic	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	>100		12	this study
Copepod	<i>Oithona similis</i>	96	Natural	-	47.37		/	(Karthikeyan et al., 2018)
Copepod	<i>Acartia danae</i>	96	Natural	-	39.87		/	(Karthikeyan et al., 2018)
Copepod	<i>Amphiascus tenuiremis</i>	96	Natural	-		11.76	/	(Hagopian-Schlekat et al., 2001)
Copepod	<i>Tigriopus brevicornis</i>	96	Natural	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$		3.41	/	(Barka et al., 2001)
Copepod	<i>Tisbe holothuriae</i>	48	Synthetic	$\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$		44.30	/	(Verriopoulos and Dimas, 1988)

4.2 Implication for the deployment of ocean alkalinity enhancement

To prevent the potential ecological impacts of Ni in the process of OAE, Ni could be removed during the preparation of alkaline solutions. Numerous techniques that have been employed to remove Ni from wastewater could provide insights into the removal of Ni in olivine (Kadirvelu et al., 2001; Kim et al., 2002; Kalyani et al., 2004; Papadopoulos et al., 2004; Fu et al., 2007; Decostere et al., 2009). For example, chemical precipitation is an effective and the most widely used method in the industry. Though varying success has been achieved, these methods are

321 associated with high costs, operational drawbacks, and the potential for secondary pollution
322 (Fu and Wang, 2011). Nowadays Ni is a highly demanded metal resource for battery
323 manufacture (Turcheniuk et al., 2021). A novel approach has been proposed to recover Ni for
324 enhancing the supply of critical battery metals (Wang et al., 2018; Wang and Dreisinger, 2023).
325 This technique could be useful in the context of OAE, contributing to the mitigation of
326 ecological impacts on the one hand and reducing the costs of OAE application on the other.
327 For OAE applications, minerals containing less heavy metals, such as quicklime produced from
328 limestone, could also be considered (Gabe and Rodella, 1999; Šiler et al, 2018). These minerals
329 could provide a viable option for the required application with less harmful elements
330 introduced into the ocean (Bach et al., 2019; Caserini et al., 2022). The limestone is abundantly
331 available and could meet the requirement for large-scale deployment of OAE. In addition, its
332 economic costs for extraction and transportation are relatively low, and the duration required
333 for dissolution is shorter compared to olivine (Caserini et al., 2022; Fuhr et al., 2022). However,
334 it is essential to acknowledge that the calcination of limestone demands a substantial amount
335 of energy and necessitates proper capture and storage of the released CO₂. To comprehensively
336 assess the applicability and scalability of various material deployments, further investigation
337 and research are warranted.

338 **5 Conclusions**

339 The goal of this study was to examine the response of three phytoplankton species
340 representative for different taxonomic groups to the exposure of elevated Ni, which may occur
341 in the process of OAE. The results demonstrated that the tested phytoplankton species exhibited
342 varying responses to excess Ni. The diatom *T. weissflogii* displayed a high sensitivity to
343 elevated Ni, evident from its rapid growth inhibition response, high growth inhibition, and low
344 IC50 value. In contrast, the low growth inhibition and high IC50 values of *A. carterae* and *E.*
345 *huxleyi* indicate that these two species are more tolerant to excess Ni. The variability in
346 sensitivity to Ni among different species highlights the importance of avoiding critical toxic
347 thresholds of Ni concentrations. The recovery of Ni from Ni-rich materials and the usage of
348 alternative clean minerals would avoid adverse impacts on the phytoplankton community,
349 enhancing the feasibility and scalability of ocean alkalization. In summary, the varying
350 responses to Ni among different species make it clear that the impacts of Ni cannot be neglected,
351 and that caution is needed in setting the threshold for Ni in OAE applications with Ni-rich
352 materials. Future studies focusing on the taxonomical shift in natural communities and on
353 incorporation and potential bioaccumulation of Ni in different plankton species are foreseen to

354 provide a more comprehensive understanding of the potential effects and risks of metal release
355 associated with OAE.

356 *Data availability.* The raw data will be made available by the authors, without undue
357 reservation. The data will be submitted to Pangaea, <https://www.pangaea.de/>.

358 *Author contributions.* XX and UR designed the experiment and XX carried them out. XX
359 conducted statistical analyses and prepared the manuscript with contributions from all authors.

360 *Competing interests.* The contact author has declared that none of the authors has any
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