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Impact of ferromanganese ore pollution on phytoplankton CO_2 fixation in the surface ocean

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Abstract

Because ferromanganese polymetallic crusts can become a global resource of valuable elements the ecological impact of seafloor crust mining requires evaluation. Whilst the detrimental impact on deep-ocean benthos is established, experimental evidence about the mining hazard to surface-ocean is sparse. When retrieved, mined crusts can leach elements potentially harmfull to the core oceanic CO_2-fixers – phytoplankton. To directly assess the magnitude of this potential hazard at ocean-basin scale, we examine the impact of ore slurry on phytoplankton CO_2 fixation along a meridional transect through the South Atlantic Ocean. Within 12~~ hours~~h crust slurry additions caused a 25% decrease of CO_2 fixation in the subtropical region and 15% in the temperate-polar region. Such moderate susceptibility of phytoplankton indicates limited release of harmful elements from tested polymetallic powder. Although this implies that environmentally sustainable seafloor mining could be feasible, longer-term complex studies of the mining impact on the surface ocean are required.

Keywords: Ferromanganese polymetallic crust; ~~d~~Deep-sea mining; ~~o~~Oceanic phytoplankton; ~~p~~Primary production

~~1.~~1 Introduction

Commercial interest in the deep-ocean ferromanganese polymetallic crusts and nodules (Fe-Mn deposits) is growing owing to constantly increasing industrial demand for specific elements, *e.g.* Co, Li, Cu, Te, Mo and rare-earth elements, many of which are considered critical to low-carbon energy technologies. Oceanic Fe-Mn deposits, particularly deep-ocean crusts, are especially enriched in these valued elements (Hein et al., 2013) and modern technological advances make it economically feasible to mine these deposits for metal extraction (Lusty and Murton, 2018). To date, the generally accepted mining procedure will involve crushing and excavation Fe-Mn deposits using remotely operated mining equipment, vertical transport of the resulting deep seawater-ore slurry from the seafloor to a vessel on the ocean surface, separation of ore and waste material on-board the mining vessel and disposal of the separated waste rock and seawater back to the ocean (Weaver et al., 2018). These activities, even in their normal mode of operation and especially in non-standard situations, have the possibility to perturb both the deep and surface ocean.

Owing to global spatial distribution of deep-ocean Fe-Mn crusts, their mining will affect mostly pristine, pollution-intolerant surface waters of the open ocean (Weaver et al., 2018). Negative effects of mining on the seafloor benthic bottom-dwelling biota are unavoidable but locally restricted (Gollner et al., 2017; Jones et al., 2017). Potential effects of mining on the surface ocean biota can, however, be extensive and hence should be controlled (Vare et al., 2018). Despite the long-standing belief of the potential of Fe-Mn deposit mining hazard to surface ocean plankton (e.g. through spillages or managed discharge of ore slurry or waste water, separated from the bulk Fe-Mn crusts), the paucity of experimental evidence about this hazard continues to reignite debate (Amos et al., 1977; Maxmen, 2018). This is especially important as policy is being developed for the commercial extraction of these deposits, and hence the urgent need for scientific evidence upon which to inform these decisions.

Previously, a unique study of environmental effects of simulated Fe-Mn nodule-mining at a site in the Equatorial Pacific (Burns, 1980) showed only limited phytoplankton shading by the surface plume of discharged waste water and sediment. In Fe-Mn crust mining, however, phytoplankton shading is a secondary problem because bioactive ions, leached from the crushed ore, could directly harm phytoplankton. The negative effects of specific elemental ions, commonly present in Fe-Mn crusts, on phytoplankton are well documented (for a comprehensive list of studies see the EPA~~’~~'s ECOTOX database: https://cfpub.epa.gov/ecotox/). Environmentally relevant concentrations of Mn, Cu, Zn, Mo, V, Ni, and Pb ions were reported to trigger adverse ~~responcees~~responses in marine phytoplankton, when tested on both cultured species and natural assemblages (Rajendran et al., 1978; Christensen et al., 1979; Østgaard et al., 1982; Mann et al., 2002; Wei et al., 2013; Hauton et al., 2017). These responses included decrease in CO_2 fixation, growth rates and size of algal cells. Furthermore, by inducing Fe deficiency, Mn and Co ions were shown to specifically inhibit synthesis of chlorophyll precursors in cyanobacteria (Csatorday et al., 1983). Cyanobacteria were reported to be particularly sensitive to Cu (Brand et al., 1986): whilst 10 ppb of Cu were required to inhibit CO_2 fixation of eukaryotic algae (Wilson and Freeberg, 1980), growth of open ocean cyanobacteria was significantly reduced by only 0.6 ppb of Cu (Stuart et al., 2009). At present, the actual susceptibility of oceanic phytoplankton to Fe-Mn crust slurries is unknown (Verlaan, 2018) because the release of ionic species in slurries could differ from controlled addition of the particular elements. Moreover, combinations of elements can cause either synergistic or antagonistic effects (Christensen et al., 1979; Wei et al., 2013), further complicating direct predictions of their effect on marine phytoplankton.

Therefore, to inform the debate and help frame future policy about the potential hazard of Fe-Mn crust mining on the surface ocean, we conducted a series of slurry-test experiments in the broadest range of ~~prestine~~pristine oceanic provinces. Our objective was to assess the acute, short-term effects of crushed polymetallic Fe-Mn crust ore pollution on oceanic phytoplankton growth by measuring CO_2 fixation – the key biological process that maintains the habitability of our planet (Falkowski et al., 1998).

We collected Fe-Mn crust samples from Tropic Seamount in the NE Atlantic (see ~~Figure 1~~Fig. 1, Methods, Supplementary Table 1) and chose this material for testing because its elemental composition is representative of deep-ocean Fe-Mn polymetallic crusts in general (Lusty et al., 2018). The Fe-Mn crust contains elements (Supplementary Table 1) which, if leached to seawater as ions, could suppress phytoplankton growth (Rajendran et al., 1978; Christensen et al., 1979; Wilson and Freeberg, 1980; Østgaard et al., 1982; Csatorday et al., 1983; Brand et al., 1986; Mann et al., 2002; Stuart et al., 2009; Wei et al., 2013; Hauton et al., 2017). On the other hand, low concentrations of some of these elements can stimulate phytoplankton growth owing to their role as essential cofactors in metalloenzymes (Sunda, 1989; Shcolnick and Keren, 2006). For instance, artificial release of Fe^{3+} into surface waters of the polar Southern Ocean increased CO_2 fixation rates and triggered a massive phytoplankton bloom, sustained by Fe^{3+} recycling, that was large enough to be monitored from space over a period of several months (Boyd et al., 2000). ~~Similarly~~Similarly, deep-water rich with nutrients (e. g. NH_4^+, NO_3~~$^-$~~$^{-}$, PO_4^3~~$^-$~~$^{-}$) could stimulate phytoplankton growth and cause blooms, if delivered to the surface with Fe-Mn crust slurry. Because phytoplankton sensitivity to the solubilized crust ions likely depends on phytoplankton species composition, and because the leached ions and deep-water nutrients could affect phytoplankton growth both negatively and positively, an experimental *in vivo* assessment is the most informative. To test the effects of polymetallic Fe-Mn crust leachate on the broadest range of oceanic, pollution-intolerant phytoplankton we conducted the basin-scale study across the Atlantic, which covered oligotrophic, frontal, temperate and sub-polar regions (~~Figure 1~~Fig. 1).

~~Figure 1.~~Fig. 1

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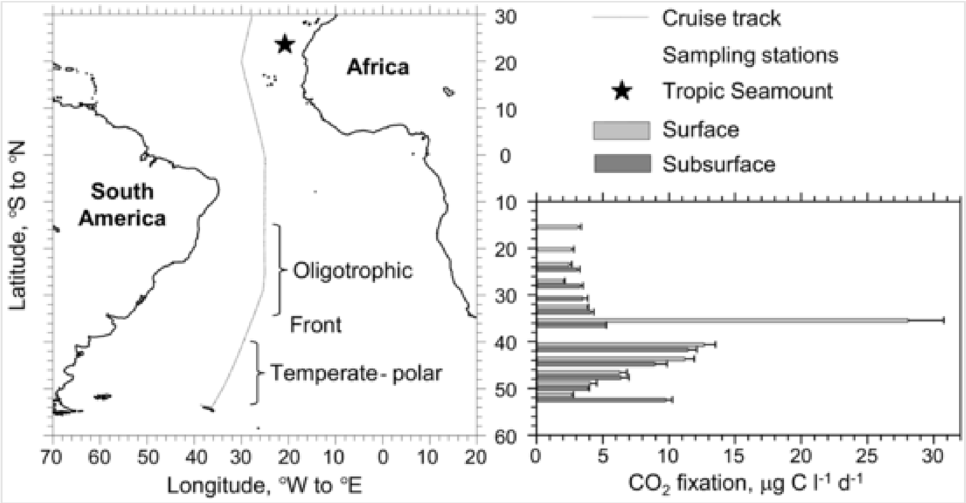

Location of the crust collection site, sampling stations and rates of CO_2 fixation in surface and subsurface seawaters of the South Atlantic Ocean along a meridional transect. Data are mean ± single standard deviation.

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~~2.~~2 Materials and ~~M~~methods

~~2.1.~~2.1 Sampling

The study was carried out on board the Royal Research Ship (RRS) *Discovery*, on cruise DY084, during the Atlantic Meridional Transect (AMT27) during 17th~~-~~–30th October~~,~~ 2017 (~~Figure 1~~Fig. 1). At predawn stations, seawater samples from 20 m (surface), 5 m above the deep chlorophyll maximum or at 1% light depth (subsurface), and 500 m (deep) were collected using a rosette of 24 Niskin bottles (20 ~~L~~l) on a conductivity-temperature-depth (CTD) profiler. The experiments were setup within 2~~ hours~~h after sample collection. Before coming into contact with the samples, all plastic-ware and clear borosilicate glass incubations bottles were soaked in 10% HCl, and consecutively rinsed with deionized water and re-rinsed with freshly sampled seawater.

~~2.2.~~2.2 Phytoplankton CO_2 fixation experiments with Fe-Mn crust

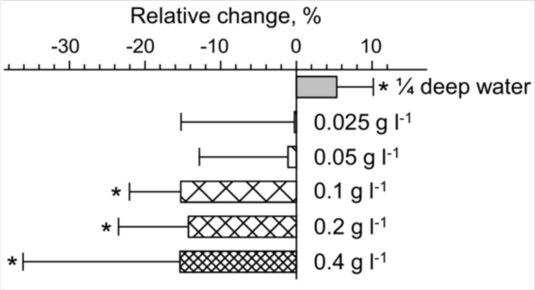
Bedrock-free Fe-Mn crust samples, collected by a remotely operated vehicle from the slopes of Tropic Seamount (Fig. 1), were dried and ground to a fine powder to maximize surface area and optimise mineral dissolution when the powder was mixed with tested seawater to form slurry. The fine ground powder of the Fe-Mn reference crust, with well characterized elemental composition (British Geological Survey UCAS ID 14051-0093, Supplementary Table 1), was pre-weighed ashore. Slurry was prepared by suspending 0.1 g of the powder in 10 ml of tested surface or subsurface seawater (Supplementary Fig~~ure~~. 1, left) and was left for 40 ~~minutes~~min to settle the coarser fraction and to solubilize crust materials (Supplementary Fig~~ure~~. 1, right). Then, 0.25~~-~~–4.0 ml of slurry extract was withdrawn without agitation and added to seawater samples to get the final volume of 50 ml. The settled coarser fraction was found to comprise ~50% of the original powdered material, such that the final crust slurry concentrations ranged between 0.025 and 0.4 g l~~-~~$^{-1}$. Deep seawater was mixed with the surface water samples at a ratio of 1 to 3.

Rates of CO_2 fixation in seawater samples were determined as described in detail previously by Zubkov (2014). In brief, 50 ml samples were spiked with 140 ± 10 KBq of $NaH^{14}CO_3$ (4.81 GBq mol~~-~~$^{-1}$, American Radiolabeled Chemicals). By using bottom-domed incubation bottles, illuminated from below, we designed the experiments to preferentially assess the biological effect of solubilized ions whilst minimizing the shading effect caused by settling of fine Fe-Mn crust particles resulting in minimal light obstruction. The experimental bottles were placed in a custom-made incubator to maintain a constant *in situ* temperature and incubated at 300 μmol photons m~~-~~$^{-1}$ s~~-~~$^{-1}$ for 12~~ hours~~h, mimicking the average *in situ* light conditions at 20 m depth in the subtropical oceanic waters in spring. The constant light output was used to allow direct comparison of CO_2 fixation rates determined in experiments with seawater samples collected at different latitudes (~~Figure 1~~Fig. 1). Incubated samples were then fixed with paraformaldehyde (1% w/v final concentration), filtered onto polycarbonate membranes with 0.2 μm pore size (Whatman) and washed twice with 5 ml of deionized water. Filters were radio-assayed using Tri-Carb 3180 TR/SL liquid scintillation analyser (PerkinElmer).

~~2.3.~~2.3 Statistical analyses

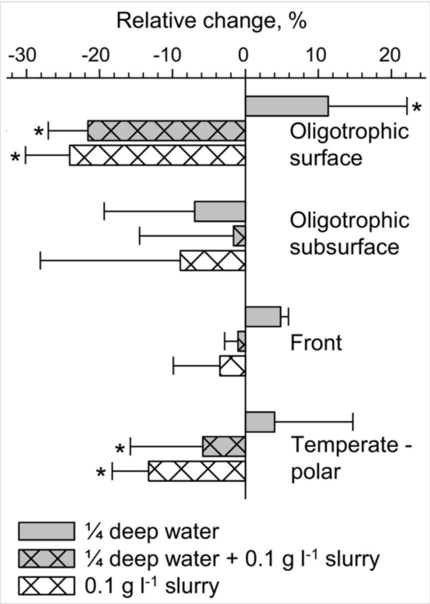
The CO_2 fixation rates in untreated samples were used as the main experimental controls, against which changes for all other treatments were measured. The results, and their statistical analyses, are shown on Figs. 2–3 and summarized in Supplementary Tables 1~~-~~–4.

~~Figure 2.~~Fig. 2



Change in CO_2 fixation upon addition of a range of concentrations (0.025~~-~~–0.4 g l~~-~~$^{-1}$) of crust slurry and a nutrient-rich deep water relative to an untreated control. Data are mean ± single standard deviation. *, statistically significant difference from the untreated control (*t*-test, $p < 0.05$, Supplementary Table 2).

~~Figure 3.~~Fig. 3



Change in rates of CO_2 fixation in sampled seawater upon dilution with deep seawater, addition of deep seawater and 0.1 g l~~-~~$^{-1}$ of slurry, addition of the slurry. Data are mean ± s.d. *, statistically significant difference when compared to the untreated control (*t*-test, $p < 0.05$, Supplementary Table 4).

~~3.~~3 Results and ~~D~~discussion

Phytoplankton samples, collected along a latitudinal transect from the centre of the South Atlantic subtropical gyre to South Georgia Island during austral spring, maximized the range of tested phytoplankton from oligotrophic (most pollution-intolerant), to frontal, to temperate-polar (Zubkov et al., 2000) at various stages of the spring bloom. The corresponding >10 fold range of CO_2 fixation rates with the frontal surface maximum (~~Figure 1~~Fig. 1) ensured comprehensive testing of the effects of Fe-Mn crust slurry on CO_2 fixation.

The earlier *in situ* case study (Burns, 1980) demonstrated that the shading effect of suspended sediment is short-lived, owing to rapid sinking of sediment particles. Our experimental design minimized this shading effect and hence preferentially assessed the biological effect of solubilized ions (see Methods). The impact of five different concentration levels of the slurry on the rate of CO_2 fixation in the water samples were compared with the untreated control sample (~~Figure 2~~Fig. 2, Supplementary Table 2). In addition, a ¼ dilution with nutrient-rich deep-water, collected from 500 m, significantly stimulated CO_2 fixation and served as a positive control.[Instruction: Insert Fig. 2 here, please.
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Whilst the effect of the two lowest slurry concentrations differed insignificantly from the untreated control, the negative impact of the three higher concentrations was found to be statistically significant~~ly~~ (~~Figure 2~~Fig. 2, Supplementary Table 2). These comparisons show that the measurable effect of the slurry on CO_2 fixation has a threshold of between 0.05 and 0.1 g l~~-~~$^{-1}$. To ensure measurable effects of slurry on CO_2 fixation, we chose the higher concentration slurry for our basin-scale experiments. All of these tested the effect of slurry combined with nutrient-rich deep-water, which represents a more realistic scenario of mining Fe-Mn deposits from the deep ocean floor. Results of these treatments were also compared to the untreated control sample,

whilst the deep-water dilution continued to serve as the positive control (Fig. 3, Supplementary Tables 3 and 4).[Instruction: Insert Fig. 3 here, please.
]

The experimental results revealed that, in the temperate-polar region, phytoplankton CO_2 fixation in the surface and the subsurface waters reacted similarly to the slurry treated samples (Supplementary Table 3) and are presented together (~~Figure 3~~Fig. 3). None of the treatments had a significant effect on CO_2 fixation in the oligotrophic subsurface waters or in the frontal waters, compared with the control samples. The negative effects of the treatments on CO_2 fixation in the oligotrophic surface and temperate-polar surface/subsurface waters showed a similar pattern but were more pronounced in the oligotrophic region (~~Figure 3~~Fig. 3, Supplementary Table 5). Stimulation of CO_2 fixation by deep-water dilution was marginally significant in the oligotrophic surface waters and insignificant in the temperate-polar waters, but the addition of slurry leachate reduced CO_2 fixation in both regions (Supplementary Table 4). The negative effect caused by slurry addition was significantly more pronounced in the oligotrophic than in the temperate-polar region, and it was not alleviated by the deep-water dilution (~~Figure 3~~Fig. 3).

In our short-term experiments, the addition of nutritious deep-water moderately stimulated CO_2 fixation by ambient phytoplankton (<20% within 12 ~~hours~~h, ~~Figure 3~~Fig. 3). However, the longer term enrichment of oligotrophic waters by deep-water dilution will initiate blooms of opportunistic phytoplankton, reminiscent of those in oceanic upwelling regions. Therefore, exposure of phytoplankton to deep-ocean water should be minimized to control artificial phytoplankton blooms.

In the oligotrophic waters, where Fe-Mn crust mining is most likely (Hein et al., 2013), addition of slurry leachate reduced CO_2 fixation by 25% (~~Figure 3~~Fig. 3), demonstrating vulnerability of their phytoplankton. On the other hand, the immediate effect of sizable addition (0.1 g crust l~~-~~$^{-1}$) of slurry extract diluted with deep-water (the most realistic scenario for mining) on CO_2 fixation in the frontal phytoplankton-blooming waters and the temperate-polar waters was found to be only moderate (~~Figure 3~~Fig. 3). Such differential response of phytoplankton to polymetallic Fe-Mn crust leachate could be explained by differences in the composition of phytoplankton community (Zubkov et al., 2000; Zubkov, 2014). Whereas oligotrophic waters are dominated by cyanobacteria, frontal and temperate-polar waters harbour numerous eukaryotic algae which are more resilient to potentially harmfull cations (*e.g.* Cu^{2+}, Supplementary Table 1) compared to cyanobacteria (Wilson and Freeberg, 1980; Mann et al., 2002; Stuart et al., 2009). The considerable general resilience of phytoplankton to crust slurry pollution further suggests that harmfull cations do not readily leach from particles of the crushed ore. Instead, insolubility of trace-metal cations is probably a result of ferromanganese crust minerology; when Fe-Mn crusts form, trace-metal cations are trapped and remain bound within the ore-forming Fe-Mn oxyhydroxide crystal structure (Saratovsky et al., 2006; Villalobos et al., 2005) rather than leach into seawater.

~~4.~~4 Conclusions

In a short term, CO_2 fixation of oceanic phytoplankton is moderately reduced by the release of crashed polymetallic deep-sea Fe-Mn crust, with phytoplankton of the oligotrophic open ocean being most susceptible. These results suggest that discharge of coarse-grained ore materials, which is more realistic for mining operations, is of lower potential effect due to its settling and low surface area reactivity. However, to develop comprehensive guidance for an environmentally acceptable Fe-Mn crust mining, the effects of long-term exposure of the entire plankton community to the crust ~~lechate~~leachate and nutrient-rich deep water~~s~~ require further research.

Data accessibility

The datasets are available from the corresponding author on request.

Author~~’~~'s contributions

M.Z. and N.K. conceived the experimental study, A.D. conducted the experiments, A.D. and M.Z. analysed the results, M.Z. and B.M. secured funding and all authors wrote and reviewed the manuscript.

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Declaration of Competing Interest

We declare we have no competing interests.

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~~Appendix A.~~Appendix A Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2019.07.062.

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Highlights

- Slurry of mined deep-ocean crust can inhibit CO_2 fixation at the ocean surface.
- Addition of nutrient-rich deep water to the slurry does not alleviate the inhibition.
- CO_2-fixers of nutrient-poor tropical ocean are most susceptible to the slurry.
- Blooming phytoplankton is least susceptible to the slurry.
- The impact of the slurry on CO_2 fixation within 12~~ hours~~h is moderate.

~~Appendix A.~~Appendix A Supplementary data

Multimedia Component 1

Supplementary material

Queries and Answers

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Answer: The capital L (in 20 L) was replace with l. Thank you.

Query: Have we correctly interpreted the following funding source(s) and country names you cited in your article: "Natural Environment Research Council".

Answer: Yes

Query: Supplementary caption was not provided. Please check the suggested data if appropriate, and correct if necessary.

Answer: We agree with the suggested caption. Thank you.