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Short communication

Proposing a potential strategy concerning Mineral-enhanced Biological Pump (MeBP) for improving Ocean Iron Fertilization (OIF)

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ABSTRACT

Ocean iron fertilization (OIF) is a geoengineering strategy aimed at mitigating global warming by reducing the amount of atmospheric CO_2. However, the efficacy by which OIF vertically exports organic carbon of bloomed phytoplankton (mostly, diatoms) to the deep sea is low because of the remineralization of organic carbon during the sinking of diatomaceous silica (BSi). To address the low efficiency of the vertical C export of OIF, a potential strategy for enhancing oceanic biological pump using clay minerals, so-called mineral-enhanced biological pump (MeBP), is proposed herein. Under ideal operation of MeBP, the purposefully added clay minerals are supposed to agglomerate with BSi, facilitating an increase in the quantity of BSi settling and a decrease of organic carbon loss. Meanwhile, the structural Al of clay minerals would be assimilated by diatoms due to the biological dissolution of the clays, inhibiting the dissolution of BSi during its sinking. The abovementioned effects would significantly improve the efficiency of the vertical C export of OIF. The preliminary evidence and arguments in support of MeBP are presented.

Addressing the threats posed by global climate change to human existence and development, especially reducing the amount of greenhouse gases such as carbon dioxide in the atmosphere, is currently one of the most important research goals of the scientific community. This demand has become even more urgent than ever after the Paris Agreement, which was signed by more than 170 countries as contracting parties in 2016.

Ocean iron fertilization (OIF) is a geoengineering strategy aimed at mitigating global warming through human intervention. It is based on the reasoning that adding iron to iron-limited regions of the ocean will lead to phytoplankton blooms and mass sinking of organic matter, ultimately leading to the sequestration of significant amounts of atmospheric carbon dioxide (CO_2) in the deep sea and sediments (Smetacek and Naqvi, 2008). The theoretical basis of OIF is the famous “iron hypothesis” proposed by John Martin in 1990 (Martin, 1990). This hypothesis suggests that iron availability may be an important player in strengthening the biological pump (BP), and evidence for the iron hypothesis has been continuing to mount since its emergence. Currently, evidence has convincingly shown that iron fertilization in the Southern Ocean was indeed a leading actor in this global climate feedback, as summarized by Stoll (2020) in her paper commemorating the 30th anniversary of the proposition of the iron hypothesis.

Since 1993, at least 13 OIF experiments have been conducted over time and space scales of weeks and kilometres in polar, subpolar and tropical areas of the oceans featuring high nutrients and low chlorophyll, so-called HNLC areas (Secretariat of the Convention on Biological Diversity, 2009). These OIF experiments have led to a good understanding of the role of iron in regulating marine ecosystems and have confirmed that the iron supply exerts key controls on the dynamics of phytoplankton blooms, such as diatom blooms, which in turn affect the biogeochemical cycling of elements such as carbon (Boyd et al., 2007). The mesoscale OIF experiments clearly showed that diatom blooms were accompanied by CO_2 drawdown (Smetacek and Naqvi, 2008), which is in accordance with the iron hypothesis and shows the potential of OIF in influencing the Earth’s climate system.

However, OIF as an effective carbon control strategy is not adequately supported. Most OIF experiments were not specifically designed to test the fate of iron-induced blooms of biomass, such as diatoms (Smetacek and Naqvi, 2008), so there are no adequate data from in-depth analyses on the vertical export of organic carbon to the

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deep sea. In several of the OIF experiments concerning C export fluxes (Coale et al., 2004; Boyd et al., 2005; Buesseler et al., 2005), it was found that iron fertilization did not significantly strengthen the vertical C export to the deep sea and thereby the sequestration of CO_2. The reason is that much of the carbon is released again in the following processes that include the consumption of diatoms by zooplankton, microbial remineralization, and the dissolution of diatomaceous biogenic silica (BSi), as well documented (Martin et al., 2013; Lemaitre et al., 2016). In other words, the efficacy by which OIF vertically exports organic carbon associated with diatom blooms to the deep sea remains constrained due to the remineralization and loss of organic carbon during the sinking of BSi.

Given the C of diatom comes from the organic content within the cell that is encapsulated in a diatom frustule, the C release during the sinking of BSi is highly dependent on a variety of chemical, physical, and biological factors (*e.g.*, biodegradation and grazing by zooplankton) that together determine the efficiency of the export of organic carbon to the deep sea. Therefore, in the next generation of OIF experiments purposefully designed for addressing the low efficiency of the vertical export of bloomed phytoplankton such as diatoms induced by iron fertilization, a possible strategy for reducing the loss of organic carbon during the sinking of biomass should be devised.

Among the physicochemical factors determining the C and Si fluxes to the deep ocean during diatom blooms, the aggregation of diatom frustules and the dissolution of frustules have proven to be key factors. Aggregation of diatoms is beneficial to the flux because of several consequences, such as the enhanced sinking velocities of aggregated frustules (Moriceau et al., 2007; Seebah et al., 2014). The dissolution extent of diatom frustules is mainly controlled by the physicochemical properties of both the BSi itself (*e.g.*, Al incorporation in the silica) and the aqueous medium (Dixit et al., 2001), such as the salinity and pH. Therefore, from a physicochemical perspective, measures of either enhancing the aggregation or inhibiting the dissolution of frustules should be developed and adopted in the next generation of OIF experiments as potentially effective strategies for mitigating global warming.

Recently, a noticeable dissolution–inhibition effect of Al-bearing lake BSi was found in our previous study (Liu et al., 2019). This dissolution–inhibition effect is caused by the high content of Al incorporation in the structure of the lake BSi, which was identified using comprehensive microscopic and spectroscopic characterizations. The mechanism of the abovementioned Al-induced effect of BSi has been ascribed to the production of negative charges by Al incorporation in BSi, which repels OH^- and thereby retards the dissolution of silica (Dixit et al., 2001). The much higher Al/Si atomic ratio of lake BSi than of marine BSi results from lakes having significantly higher concentrations (μM scale) of dissolved Al than oceans. The results of the abovementioned study suggest that increasing the Al proportion in the structure of BSi by creating an Al-rich environment for the growth of diatoms might be used in OIF experiments to inhibit the dissolution of BSi, which may address the low efficiency of the vertical C export. However, direct addition of Al ions to the ocean is apparently infeasible because of the toxicity of Al. Instead, naturally occurring and environmentally safe Al-rich minerals could be a suitable alternative as an Al source for addition to an environment where diatoms grow.

In this regard, we hypothesize that clay minerals, with characteristically high contents of Al and Si, might be good ingredients for addition in OIF experiments to enhance the efficiency of the vertical C export of BP. This mineral-aided process could be called a mineral-enhanced biological pump (MeBP hereafter) or a clay-enhanced biological pump (CeBP). It has several potential advantages that may facilitate increasing the efficiency of organic carbon preservation during the sinking of BSi not only *via* the dissolution–inhibition effect caused by a high content of Al incorporation in BSi but also *via* other effects, such as aggregation between clays and BSi.

The prerequisite for the MeBP strategy is that the structural Al in clay minerals can be assimilated by diatoms, just like the intake of Al ions by diatoms previously reported (Liu et al., 2019). This point is evidenced by the result of a culture experiment (see Supplementary data for details) with diatom *Thalassiosira weissflogii* (*T. weissflogii*) in the presence of montmorillonite (Mt), which was used as a model clay mineral.

Fig. 1a-c shows the morphological and structural feature of a diatom frustule and a Mt particle reclaimed from a mixture of cultured diatoms and clay particles. The homogeneous Al incorporation in the internal structure of BSi (the elemental mapping result in Fig. 1b) is clearly indicated by energy-dispersive X-ray spectroscopy (EDS) mapping analysis on a nanosized slice of the diatom frustule prepared by using focused ion beam (FIB) milling (schematically illustrated in top left of Fig. 1b). In contrast, no Al was detected in the internal structure of diatoms in the control experiment, where clay minerals were absent during the culturing of the diatoms. In addition, the Mt particles recovered from the clay-diatom mixture showed poor crystallinity, indicated by that the transmission electron microscope (TEM) image of Mt particle lost typical feature of the well-distinguished ordered stacking layers (Fig. 1c) and by the broad and isotropic halos in the selected area electron diffraction (SAED) image (the inset in Fig. 1c).

This evidence diagnostically indicates that, as the diatoms were cultured in the presence of Mt particles, diatom-induced biological dissolution of Mt particles occurred, and the Al released from the structure of Mt was assimilated by diatoms. Therefore, it is very possible that the addition of clay minerals in OIF experiments could create locally high-Al environments, leading to Al incorporation in the structure of BSi and thereby having the potential to inhibit the dissolution of BSi. Furthermore, the biological dissolution of clay minerals would release their structural Si and Fe, which are nutrients required for the growth of diatoms, and thereby could support the sustainable blooming of diatoms desirable for OIF.

Another prominent effect of the addition of clay minerals to the growth environment of diatoms is that coaggregation between diatoms and clays readily occurred, as indicated by the scanning electron microscope (SEM) images of the particles collected from the diatom-montmorillonite system. Fig. 2a shows that the diatom frustules were tightly agglomerated with clay particles in the collected particles. Indicated by the SEM image of a diatom frustule (Fig. 2b), the fragments of clay were closely adhered to the surface of the frustule, of which the compositional feature of the clay fragment was determined by the EDS analysis (Fig. 2b). It is noteworthy that the observation regarding diatoms-clays coaggregation is not new because interactive aggregation between diatoms and lithogenic materials had been observed and discussed in many reports (Hamm, 2002; De La Rocha and Passow, 2007). The implications of the complex interactions between diatom aggregates and minerals (*e.g.*, carbonate, opal, and clay minerals) for the ballast hypothesis, which proposes that fluxes of ballast minerals determine the deep-water fluxes of particulate organic carbon (Armstrong et al., 2002), had also been studied (De La Rocha et al., 2008). The underlying mechanism of the clay-diatom coaggregation is likely due to the attraction between the surface groups of clays and organic groups such as –COOH or $–NH_2$ groups in the transparent exopolymeric particles (TEP) secreted by diatom cells (Passow et al., 2003). In addition, the consequences of diatoms aggregation that may benefit the preservation of BSi and the reduction of its dissolution during its sinking to the ocean floor were discussed (Alldredge and Cohen, 1987; Alldredge and Silver, 1988; Moriceau et al., 2007; Seebah et al., 2014).

From a technical perspective, apart from the aggregation between diatoms and the particles of clay minerals, other types of coaggregation could be postulated and used for the design of OIF experiments; *i.e.*, other finely grained mineral particles (*e.g.*, iron oxide minerals) or metal ions (*e.g.*, iron ions) and the combination of these materials could be used to enhance the aggregation of diatoms. For example, the surface of iron oxide could be partially positively charged in seawater because of its high isoelectric point (Cornell and Schwertmann, 2003), which may bridge clays and diatoms and enhance coaggregation. In addition, the coaggregation between iron oxides with high density and BSi will have a

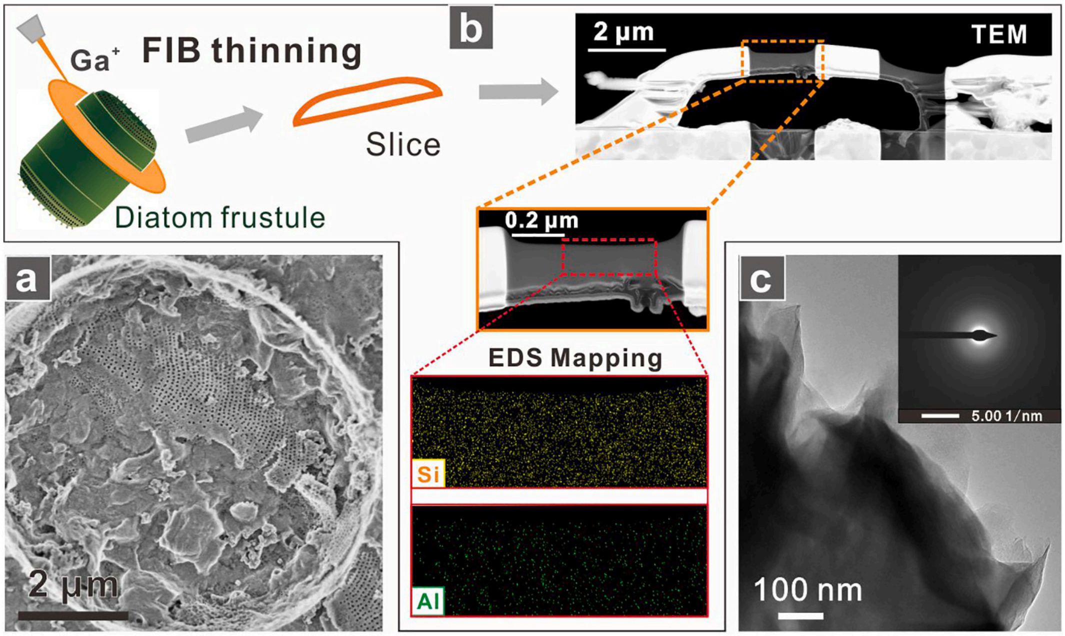

Fig. 1. (a) The scanning electron microscope (SEM) image of a diatom of *T. weissflogii* cultured in the presence of montmorillonite (Mt) samples; (b) Schematic representation of the steps of the treatment of focused ion beam (FIB) thinning (top left of Fig. 1b); the high-angle annular dark field (HAADF) transmission electron microscope (TEM) image of a sliced frustule fragment after FIB treatment (top right of Fig. 1b); the image of the selected area (marked by the orange rectangle) of the select (middle of Fig. 1b); the Si and Al distribution (middle bottom of Fig. 1b) in the selected area (marked by the red rectangle), determined by the energy-dispersive X-ray spectroscopy (EDS) elemental mapping; (c) The TEM image of a Mt particle recovered from the montmorillonite-diatom mixture; the inset is the selected area electron diffraction (SAED) pattern of the Mt particle.

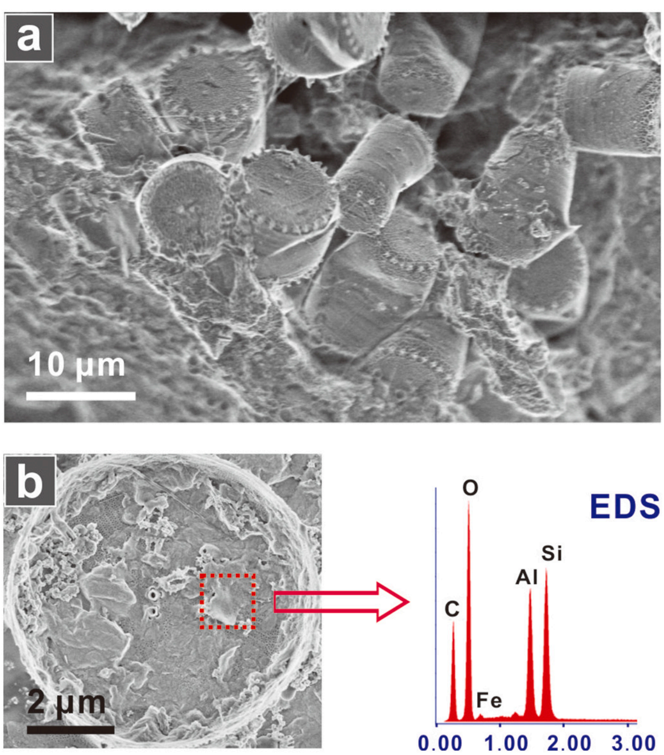

Fig. 2. (a) The SEM image of a coaggregate of the frustules of *T. weissflogii* and clay particles; (b) the SEM image (left part) of a diatom frustule coated with fragments of clay particles; the EDS analysis (right part) of a selected area (marked by the red square) of the fragment of a particle on the surface of the frustule.

ballasting effect (Iversen and Ploug, 2010), which may help to increase the sinking speed of the aggregates.

Fig. 3 shows a schematic representation of the proposed MeBP in next-generation OIF experiments and its idealized mechanism. In short, under ideal operation conditions, the particles of purposefully added clay minerals or other suitable fine minerals agglomerate with BSi, and the resulting coaggregation facilitates an increase in the quantity of BSi settling and a decrease of organic carbon loss. Synergistically, Al incorporation into the structure of BSi helps to inhibit the dissolution of BSi during its sinking. These dual effects, if exerted to an optimized extent, would significantly improve the efficiency of the vertical C export by diatom-driven BP.

To realize OIF experiments that adopt MeBP, comprehensive fundamental research at the laboratory scale should be conducted to look for suitable additives as well as the proper combination of these materials and the ways, orders and dynamics of the addition. Based on those results, mesoscale experiments should be performed to obtain parameters useful for optimizing the geoengineering techniques of OIF. Notably, the possible effects of the composition of diatom assemblage on the efficiency of the carbon sequestration need to be considered in the mesoscale experiments in HNLC areas because there are large differences in the capacity of different diatoms to export carbon to the deep sea (Assmy et al., 2013; Rigual-Hernández et al., 2015). For example, the heavily silicified (thick-shelled) diatom, *Fragilaripsis kerguelensis*, abundant in the Southern Ocean (Assmy et al., 2013), may display large physiological and ecological differences with *T. weissflogii*. Therefore, the actual diatom assemblage of the sea where OIF will be conducted must be considered as an important variable in the MeBP experiments. In addition, technical difficulties, such as how to maintain the desirable concentration of the Al released from clay minerals in the open ocean environments, also need to be tackled. Apart from these investigations, consequences such as the possible environmental risks of MeBP-based OIF experiments must be carefully assessed. Also, all future OIF experiments should be conducted under the request of international agreements (*e.g.*, the London Convention; see details from the official website

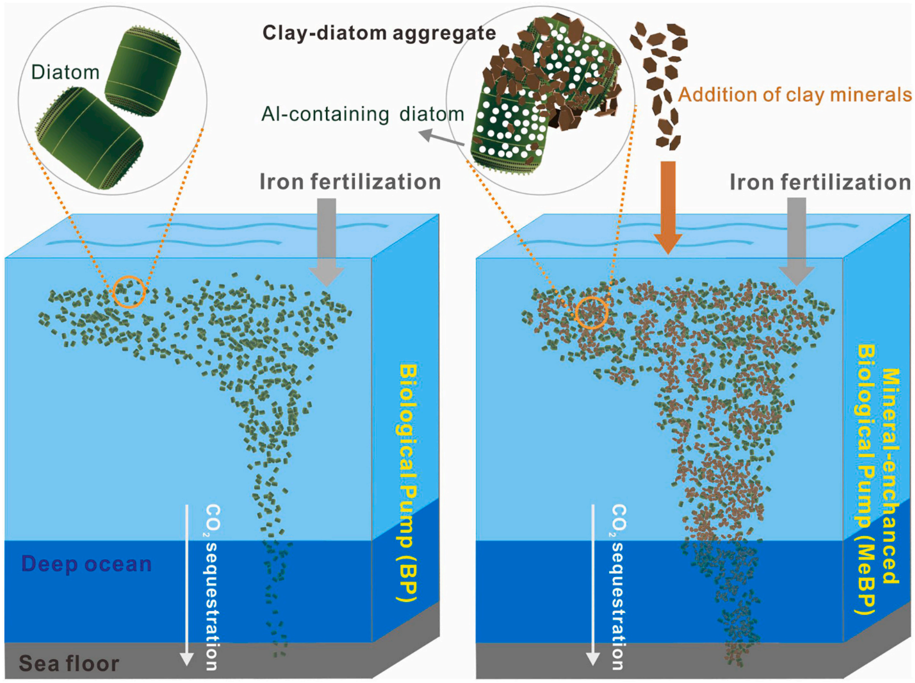

Fig. 3. Schematic representation of the idealized mechanisms of biological pump (BP; the left) and mineral-enhanced biological pump (MeBP; the right).

of International Maritime Organization) in compliance with their provisions.

In summary, we propose a strategy for enhancing biological carbon pump using minerals such as clay minerals, so-called mineral-enhanced biological pump (MeBP) or clay-enhanced biological pump (CeBP). The preliminary evidence supporting the hypothesized MeBP strategy includes (i) the diatom-induced microbial dissolution of clay minerals that results in Al incorporation into the structure of diatomaceous silica (BSi) and (ii) the occurrence of coaggregation between BSi and clays resulting from the addition of clay particles. The abovementioned mechanisms both help to inhibit the dissolution of BSi and thereby have the potential to increase the flux of carbon contained in BSi to the bottom of the ocean. Based on the MeBP hypothesis, novel methods aimed at CO_2 sequestration could be developed and used in the next generation of ocean iron fertilization (OIF) experiments. Testing the MeBP strategy and developing new geoengineering techniques associated with OIF experiments to realize effective carbon sequestration will require multidisciplinary fundamental research that will lay a foundation for future mesoscale field OIF experiments or practical geoengineering methods for oceanic CO_2 sequestration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2021.106096.

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