Short communication

Evidence of intensified biogenic silica recycling in the Black Sea after 1970

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ABSTRACT

The Black Sea has been subject to increased levels of nitrogen and phosphorus loading and a decrease in silicate input after around 1970. Changes in phytoplankton community composition from diatoms to non-diatom groups have been attributed to the decrease in silicate. However, a discrepancy between the decreasing silicate input and the increasing silicate pool in the deep sea reported elsewhere implies that another silicate source exists which challenges the current paradigm of widespread silicate limitation. In this study, we investigate changes in the dissolution state of siliceous protists over the last 140 years and show that siliceous protists became significantly more dissolved after the late 1960s indicating a reduction of the silicate pool preserved in the deep sea sediment. We hypothesize that the decline in the dissolution state is caused by increased recycling of biogenic silica in the water column due to an increased annual production driven by nitrogen enrichment.

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1. Introduction

The Black Sea has been subject to extensive human induced nutrient enrichment which has led to increased eutrophication with several effects being noted both in the coastal and open ocean ecosystems (Mee, 1992; Oguz, 2005a; Yunev et al., 2005). However, while concentrations of dissolved inorganic nitrogen (N) and phosphate (P) have increased in the entire basin, dissolved silicate (DSi) has shown a decrease after the 1970s (Cociasu et al., 1996; Konovalov and Murray, 2001) (Fig. 1A, B).

Humborg et al. (1997) reported a shift in the dominating bloom forming group after 1970 from diatoms to non-diatom species, and argued that extreme change in the DSi:N ratio (from 42 to 2.8) was the primary forcing factor. Other researchers have drawn similar conclusions on the effects of decreasing DSi concentrations; e.g. changes in the phytoplankton community composition towards non-siliceous species (Bodeanu, 1993), increasing dinoflagellate diversity vs. diatom diversity (Eker-Develi and Kideys, 2003) and changes in the diatom community composition from large to small diatoms (Mousing et al., 2013). These patterns have led to the current understanding that the productivity of silicate utilizing protists became severely DSi limited after 1970.

However, even though the decreasing DSi concentration in the upper layers of the Black Sea correlates with the reduced discharge of DSi, a discrepancy exists. Konovalov et al. (1999) and Konovalov and Murray, (2001) reported a two-fold increase in the DSi concentration in the deep anoxic waters (Fig. 1B). This increase was surprisingly high relative to the riverine discharge reported by Humborg et al. (1997) and was also surprising as a decrease in the surface DSi concentration should lead to a decreased downward flux of DSi and biogenic silica (BSi). This discrepancy raises several questions relating to the underlying mechanisms driving the increased DSi concentration in the deep layer and to the apparently missing DSi source in an environment where DSi input, in general, was decreasing.

The primary source of DSi in aquatic systems is terrestrially derived from weathering of silica-containing minerals transported to the oceans via rivers (Tréguer and De La Rocha, 2013). However, recent studies suggest that BSi recycling as a significant DSi source should also be considered (Ragueneau et al., 2010). In the Black Sea, Ragueneau et al. (2002) investigated biogeochemical transformations of the major inorganic nutrients on the north-western shelf and found evidence of intense recycling of BSi with

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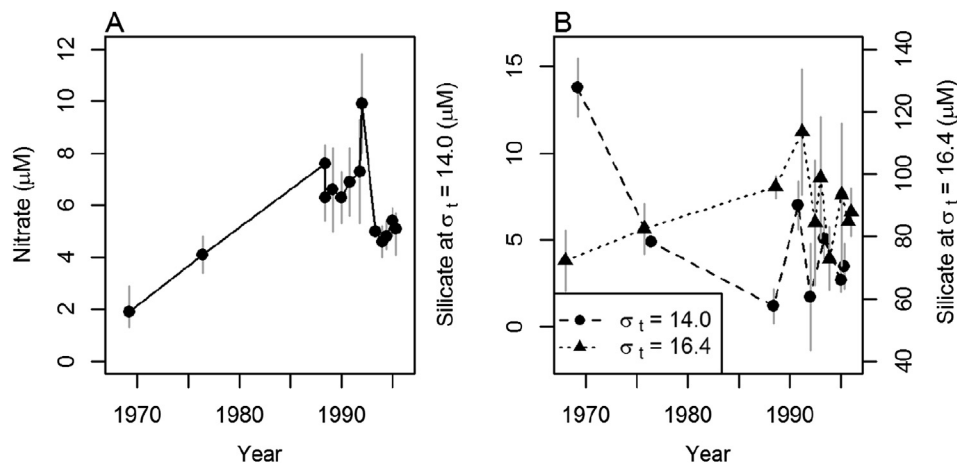*E-mail address:* eamousing@snm.ku.dk (E.A. Mousing).

Fig. 1. Temporal patterns in the concentrations of nitrate in the upper ocean (A) and silicate at the surface (at $\sigma_t = 14.0$) and the deep sea (immediately below the permanent pycnocline at $\sigma_t = 16.4$) (B). Data are redrawn from Konovalov and Murray (2001) and represents average concentrations measured at 14 cruises in the period 1969 to 1995.

dissolution taking place both in the water column and in the sediments. Other studies have shown a similar importance of BSi recycling when other sources were limited (Adjou et al., 2011; Beucher et al., 2004).

Konovalov and Murray (2001) found an increase in the sulfide concentration in the deep Black Sea after around 1970 indicating increased primary productivity and downward flux of particulate organic matter (POM). The concomitant increase in DSi the deep sea suggested increased sinking of BSi in the form of diatom-generated POM. This would, however, imply an activation of the silicate utilizing protists rather than limitation after 1970. Although part of DSi could originate from coastal shelf sediments (Konovalov and Murray, 2001; Friedl et al., 1998), a decreasing DSi concentration in the open euphotic part of the Black Sea would also lead to increased dissolution and potential recycling of BSi in the water column. It is thus possible that some of the DSi in the deep sea could originate from the water column because a larger percentage of BSi did not reach the sea floor.

Thus, in this study we hypothesize that the increase in DSi concentration in the deep layers of the Black Sea originates from increased dissolution of sinking BSi, and to investigate this we examine the dissolution state of siliceous protists in two sediment cores from the southern open Black Sea.

2. Materials and methods

Two sediment cores (22-MUC-1 and 25-MUC-1) were collected with a multiple corer in the southern Black Sea on board the RV Meteor (cruise M72-3b) in March 2007 (Fig. 1 in Mousing et al., 2013). The uppermost 10 cm of the cores were removed, cut into samples of 0.5 cm width (depth), and freeze dried for 96 h (Heto FD5-66). The core was dated using ^{210}Pb-dating and CRS-modeling (Constant Rate of Supply) (Appleby, 2001).

Permanent slides preserving the siliceous protists (microfossils) were prepared following the method of Renberg (1990) and enumerated using phase contrast at 1000x on an Olympus BH-2 light microscope. Changes in the species abundance and composition as well as a detailed description of the methodology are described in Mousing et al. (2013).

While enumerating, microfossils were categorized as being either 'pristine' (showing no signs of dissolution; Fig. 2A, C) or 'dissolute' (showing signs of dissolution; Fig. 2B, D). At least 200 microfossils were evaluated in each sample resulting in more than

2400 individual assessment of dissolution state. From these assessments, the dissolution state of each sample was estimated by calculating the Dissolution Index (F_i) (Flower and Likhoshway, 1993; Ryves et al., 2001) following Equation (1):

$$F_i = \sum_j^m x_{ij} \left/ \sum_j^m X_{ij}, \right.$$

(1)

where x_{ij} is the count of pristine microfossils of species j (of m) in sample i and X_{ij} is the total count of microfossils of species j (of m) in sample i. The equation produces a number between 1 and 0 where 1 describes a perfectly preserved sample without any signs of dissolution and 0 describes a very badly preserved sample where all observed microfossils show signs of dissolution.

Ryves et al. (2001) found that F_i was strongly correlated to the percentage of dissolved biogenic silicate (DBSi%) in relation to the original content (i.e. before the beginning of the dissolution experiment). Thus, F_i can provide insight into BSi recycling. In order to quantify the temporal changes in DBSi% we first modeled F_i as a function of time (year) using a Generalized Additive Model (GAM: Wood, 2006). Using this model, we calculated yearly values of F_i on which we applied the empirical relationship suggested by Ryves et al. (2001) following Equation (2):

$$DBSi\% = (0.97 - F_i)*100\%; (F_i < 0.97)$$

(2)

3. Results and discussion

The dissolution index (F_i) shows the same temporal pattern in both cores (Fig. 3A): From the 1860s to around 1950 there is a gradual increase in F_i from ca. 0 to 0.5. After the late 1960s, however, the pattern is reversed showing a decrease in F_i until around 2000. Together, the development in F_i in both cores clearly reflects a shift in the dissolution state of the siliceous protists from general improvement through time before the 1960 to degradation after the 1960s. By calculating the temporal changes in percentage dissolved BSi (DBSi%) (Fig. 3B) we estimate the relative change in the BSi pool preserved in the sediment. The pattern shows a decrease in the DBSi% from ca. 95 %–50 % in the period prior to around 1950 indicating a rapid increase BSi preserved in the sediment. After the late 1960s, however, the DBSi% increases indicating a decrease in the BSi inventory in the sediment. This decrease in the BSi
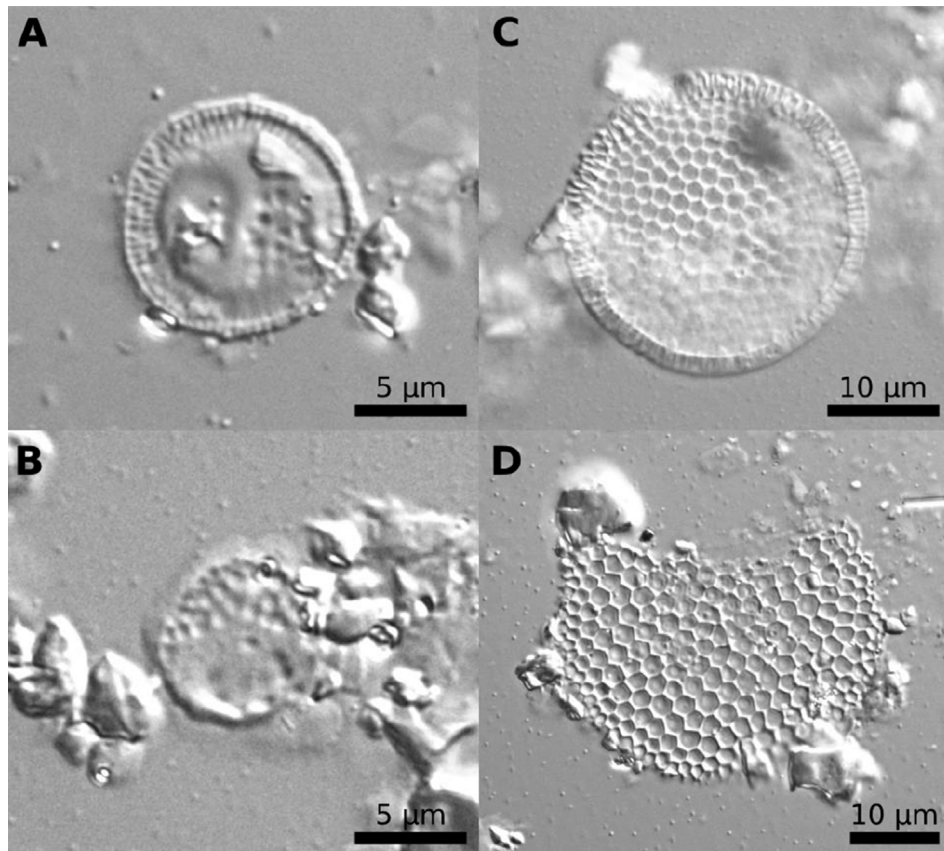
Fig. 2. Example micrographs of dissolution state: "pristine microfossils" (A, C) and "dissolute microfossils" (B, D); *Cyclotella choctawhatcheeana* (A, B) and *Thalassiosira oestrupii* (C, D).

inventory in the sediment after the late 1960s strongly suggest a change in one or more of the factors affecting the dissolution of BSi.

The dissolution rate of BSi is primarily affected by temperature, ambient dissolved silica concentrations (DSi), exposure time and pH (Rickert et al., 2002; Van Cappellen et al., 2002; Kamatani and Riley, 1979; Lewin, 1961). The Black Sea has experienced only minor temperature changes (<1 °C) over the last 100 years (Oguz, 2005b) which would seem unlikely to have had a major impact on the dissolution rate of BSi. In addition, no significant pH change in the Black Sea that could affect the rate of BSi dissolution has been reported in the literature. Furthermore, although we have no information on changes in the DSi concentration in the sediment pore
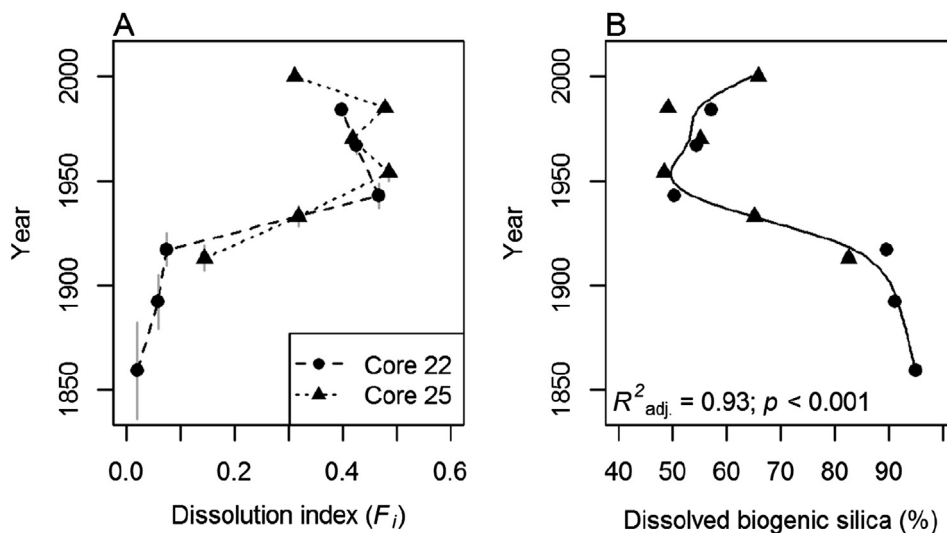

Fig. 3. Temporal patterns in dissolution state of siliceous protists: Dissolution index (F_i) through time in both cores (A); Estimated percentage dissolved biogenic silica (DBSi%) through time modeled using a generalized additive model and the empirical F_i-DBSi% relationship reported in Ryves et al. (2001) (B).

water, it is unlikely that intrinsic changes in the sediment should be responsible for the pattern documented here (see below).

Dissolution in the sediment usually takes place in the upper 5 cm and as about 100 years were reached in the upper about 3.5 cm (Mousing et al., 2013) the dissolution pattern could potentially be driven by a dissolution front within the core top. However, there are several reasons why this is unlikely to be the case in the open Black Sea. First of all, the existence of a permanent pycnocline significantly limits water mixing between the deep and euphotic layers which reduces the upwards flux of DSi. The cores studied here were collected at 842 m and 418 m (the average depth of the open Black Sea is 1250) and while a flux from the sediments to the euphotic zone is in theory possible, depth alone should serve as an efficient barrier for DSi diffusion. Furthermore, a flux from the sediments to the euphotic zone would depend on a decreased DSi concentration in the entire water column from the sediment to the depth where DSi is assimilated which is in conflict with the increase in deep sea DSi (Fig. 1B; Konovalov and Murray, 2001).

Considering the well documented decrease in DSi in the upper water masses after around 1970 (Fig. 1B; Konovalov and Murray, 2001; Cociasu et al., 1996), it seems much more likely that the decline in the dissolution state (Fig. 3A) and, thus, the BSi inventory (Fig. 3B) beginning in the late 1960s was caused by increased dissolution of BSi in the water column. However, although the increasing DSi concentration in the deep sea (Konovalov and Murray, 2001), in theory, can be explained by a decrease in the BSi inventory in the sediment, the mechanism behind this pattern is not straight forward. If a decrease in the DSi input was the primary factor resulting in increased dissolution of BSi in the water column after 1970, then we would expect similar changes in the DSi inventories in both the upper and lower water layers as well as in the sediment. As this is not the case, there must be other mechanisms responsible for the accumulation of DSi in the deep layer.

One possible explanation which accounts for the observed pattern is increased dissolution of siliceous remains in the water column due to BSi recycling. Diatoms are known to be very efficient at removing DSi as long as other macronutrients are available (Egge and Aksnes, 1992) and DSi dependent production can, therefore, be high despite low levels of DSi if a high rate of BSi recycling is assumed (Ragueneau et al., 2002). Interestingly, both the number of diatom blooms (Humborg et al., 1997) and the total abundance of diatoms increased after 1970 (Mousing et al., 2013), indicating an increased DSi dependent production despite the documented decrease in DSi input. Here we hypothesize that the increase in DSi in the deep water of the Black Sea after the late 1960s is caused by an increased DSi dependent production supported by increased availability of N (and P) coupled with intense recycling of BSi. In the following two paragraphs, we describe the hypothesis in detail.

3.1. Before the 1970s

In the beginning of spring, concentrations of N, P and DSi were relatively high due to light limitation during the winter. When the water column stabilized, diatoms bloomed until the DSi concentration became limiting (Sorokin, 1983). During the summer, the biomass of phytoplankton was generally low due to N limitation above the pycnocline and the dominant groups were comprised of different flagellates. In autumn, following slightly increased mixing, a second bloom formed, usually dominated by Coccolithophores (Sorokin, 1983). Eventually, wind induced mixing would result in deepening of the mixed layer leading to light limitation, and thus restarting the production cycle. Before 1970, then, the primary limiting nutrient over the year was N and DSi only became limiting for a short period following the spring bloom. Under N limitation, any increase in DSi would not support new DSi dependent

production which would lead to accumulation of DSi in the upper layers and counteract BSi dissolution. Therefore, siliceous protists that sink out of the water column would arrive in a relatively pristine condition on the sediment floor (Fig. 2A,C).

3.2. After the 1970s

In the beginning of spring, concentrations of N and P were higher than in the previous period (pre-1970) due to increased nutrient loading and low primary production during winter (Cociasu et al., 1996). The DSi concentration would be reduced compared to the period before 1970 but DSi would still be available at non-limiting concentrations ($\gg 2$ μM (Egge and Aksnes, 1992; Ragueneau et al., 2002)). When the water column stabilized, a spring bloom would form primarily dominated by diatoms but now other groups (e.g. dinoflagellates) were more common compared to the period before 1970 (Bodeanu, 1993). As a result of the spring bloom DSi became depleted but compared to the period before 1970, there was no concomitant depletion of N which would remain high and support additional blooms of dinoflagellates and coccolithophores during summer and autumn (Bodeanu, 1993; Humborg et al., 1997). Although the DSi concentration was too low to support additional large diatom blooms, siliceous protists could maintain a high production due to high N and recycled DSi (from the dissolution of BSi). Thus, in the after the 1970s scenario, N did not become limiting following the spring bloom and the siliceous protists were, therefore, able to recycle the DSi released from the dissolution of BSi. This situation was maintained throughout the summer and autumn and would result in an increased annual flux of BSi and DSi to the deep layers compared to before 1970 as well as an decreased dissolution state for the siliceous protists reaching the sediment floor (Fig. 2B, D).

Our hypothesis thus implies activation and increased productivity of the silicate utilizing protists after around 1970 rather than the current understanding of widespread DSi limitation. Activation of the siliceous protists after 1970 was also suggested by Konovalov and Murray (2001) but their explanation relied on DSi fluxes from coastal shelf sediments. Our study indicates that increased BSi dissolution and recycling in the water column of the open Black Sea can also contribute significantly to increase annual DSi dependent production.

Support for the hypothesis of increased silicate utilizing production can be found in Mousing et al. (2013) where we reported a fourfold increase in the abundance of siliceous protists after 1970. The increase was accompanied by a change in the diatom community composition from dominance of relatively large diatoms (especially *Thalassiosira oestrupii*) in 1930–1950 to relatively small diatoms (especially *Cyclotella choctawhatcheeana*) in 1970–1990. While the study could not differentiate to what extend the changes were caused by an increased N and P and/or a decreased DSi concentration, it can provide insight as to how a high DSi dependent production can be maintained at relatively low DSi concentrations. According to resource competition theory, a small diffusive boundary layer and a large surface to volume ratio would give smaller species an advantage relative to larger species at low nutrient concentrations (Kiørboe, 1993; Tilman et al., 1982). Furthermore, sinking rate decreases rapidly with decreasing cell size (Finkel et al., 2010; Kiørboe, 1993) potentially increasing BSi dissolution in the water column by increasing the exposure time. Therefore, assuming that the compositional change reported in Mousing et al. (2013) is a general pattern in the open Black Sea, then a change from large to small diatom species after the spring bloom would increase the efficiency of DSi uptake under the low concentration which would be the results of a gradual supply from the dissolution of BSi.

Our results support and extend upon the work of Konovalov et al. (1999), Konovalov and Murray, (2001) and Ragueneau et al. (2002) and indicate that diatoms (and other siliceous protists) in the Black Sea, in terms of annual production, were probably not as limited by the decrease in DSi after the late 1960s as has been suggested. Instead, if the hypothesis proposed in this study is accurate, then it would imply that the major forcing factor for the observed structural changes in the Black Sea after the late 1960s was general nutrient enrichment (N and P), with the concomitant decrease in DSi probably playing a minor role.

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