



Stockholm
University

Master Thesis

Degree Project in
Geochemistry 45 hp

An Investigation of Early Silica Diagenesis Using Silicon Isotopes: Evidence of Reverse Weathering?

Wanjiao Kong



Stockholm 2018

Department of Geological Sciences
Stockholm University
SE-106 91 Stockholm

Abstract

Silica early diagenesis is a substantial part for understanding global biogeochemical cycle. It is tied tightly with carbon budget, with reverse weathering acting as a key parameter in controlling ocean-atmospheric carbon turnovers and the chemistry of seawater. However, its impacts on stable silicon isotope are still unrevealed. The aim of this study is to investigate silicon isotope variations during silica early diagenesis (i.e., silica reconstitution, dissolution and reprecipitation) and the capability for them to indicate reverse weathering in the context of biogeochemical redox reaction sequence.

This study is performed using sediment cores collected in the Trosa archipelago of the Baltic Sea. One core (80 cm) was used for porewater extraction at 5 cm intervals ($n=15$), to analyze concentrations of total alkalinity (Alk_T), silicic acid (DSi), with diffusion fluxes of DSi and alkalinity modeled based on Fick's first law. Another core (70 cm) was sliced and subsampled every 5 cm interval ($n=15$). For each section, reactive iron (Fe_{reactive}) contents were determined, and biogenic silica (BSi) were extracted by a strictly time controlled wet-alkaline leach method, with two groups of non-biogenic silica (NonBSi_A, NonBSi_B-A) further leached during specific time durations (i.e., 5 hrs and 21 hrs, respectively). Meanwhile, three multicores retrieved from the same site were incubated, for determining dissolved silicon flux (J_{DSi}) and associated $\delta^{30}\text{Si}$ variations in their bottom water ($n=10$). Stable silicon isotope compositions were analyzed using MC-ICP-MS in porewater samples ($n=14$), incubated bottom water samples and all these solid phase silicon samples (i.e., BSi, NonBSi_A and NonBSi_B-A) that were extracted in form of silicic acid (DSi) ($n=45$).

Gross decreases of Alk_T and DSi concentration in porewater, and consumptions of BSi and Fe_{reactive} in solid phase sediments are of the theoretical consequences of reverse weathering, leading to transforms of authigenic silicates. On one hand, silicon isotope signatures in DSi of porewater, BSi, NonBSi_A and NonBSi_B-A appear to coincide with trends in these conventional parameters at 5-30, 50 and 60 cmbsf in the subsampled sediment cores, and the isotopically heavier trend of DSi flux with increasing time determined from the incubated bottom water samples may imply a selective utilization of light isotope in sediments. Together they are suggested to prove the applicable implications of silicon isotopes on reverse weathering. On the other hand, where silicon isotope signatures changed suddenly without sufficient evidence from other conventional parameters, an assumption is made that silicon isotopically signals might be too sensitive in low BSi content to work as indicators, such as 35 and 70 cmbsf.

Overall, investigations of early diagenesis can be facilitated by using Si isotopes, despite potential analytical errors overlying on the deduced isotope values are estimated to be magnified in low-BSi conditions.

TABLE OF CONTENT

Abstract	1
1 Introduction	3
1.1 SILICON CYCLE	3
1.1.1 Global silicon cycle.....	3
1.1.2 The marine biogeochemical silicon cycle	4
1.2 EARLY DIAGENESIS.....	5
1.2.1 Biogeochemical pathways of early diagenesis.....	5
1.2.2 Alkalinity changes during early diagenesis	6
1.2.3 Early diagenesis of BSi and reverse weathering	7
1.3 SILICON ISOTOPES	8
1.4 BIOGEOCHEMICAL SI CYCLE IN THE BALTIC PROPER	9
1.5 AIM	10
2 Materials and Method.....	11
2.1 STUDY SITE DESCRIPTION.....	11
2.2 SAMPLE COLLECTION.....	11
2.3 PORE WATER ANALYSIS.....	12
2.3.1 Total Alkalinity (Alk_T)	12
2.3.2 Porewater dissolved silicon (DSi).....	13
2.4 DSI FLUX ANALYSIS	14
2.5 SOLID PHASE ANALYSIS	15
2.5.1 Biogenic silica (BSi)	15
2.5.2 Reactive iron ($Fe_{reactive}$)	16
2.6 SILICON ISOTOPE ANALYSIS.....	18
2.6.1 Sample preparation	18
2.6.2 Silicon isotope analysis	19
2.6.3 Data reduction and analysis.....	20
3 Results.....	21
3.1 PORE WATER CHEMISTRY	21
3.1.1 DSi distribution	21
3.1.2 Alkalinity distribution.....	21
3.2 SOLID PHASE CHEMISTRY.....	22
3.2.1 Biogenic silica (BSi)	22
3.2.2 Reactive iron ($Fe_{reactive}$)	23
3.3 DSI FLUX	25
3.4 SILICON ISOTOPE DISTRIBUTION	26
4 Discussion	29
4.1 METHODOLOGICAL CONSIDERATIONS	29
4.2 PRELIMINARY QUANTIFICATION OF SILICA EARLY DIAGENESIS.....	30
4.2.1 Coupling of benthic oxygen uptake and silica release	30
4.2.2 Particular diffusion zones of DSi and Alk_T	31
4.2.3 Implications of $Fe_{reactive}$ on BSi solubility	33
4.2.4 Implications of DSi concentration and BSi content.....	34
4.2.5 Comparison with high resolution data	36
4.2.6 Isotope indications from DSi and BSi	37
4.2.7 Isotope indications from extracted non-biogenic silica.....	38
4.3 APPLICATION OF $\Delta^{30}Si$ ON SILICA DIAGENETIC ALTERATION.....	41
4.3.1 Possibility of reverse weathering.....	41
4.2.2 Estimation of isotope effect on silica early diagenesis	43
5 Conclusion	45
Acknowledgements.....	47
References	48
Appendix	54

1 Introduction

1.1 Silicon cycle

1.1.1 Global silicon cycle

Silicon (Si), at about 28%, is the second most abundant element in the Earth's crust after oxygen (Wollast and Mackenzie, 1983). Principally the Si cycle begins with the weathering processes of silicates. The weathering released Si is then mobilized into rivers, lakes, soils, terrestrial and freshwater organisms, aerosols, seawater, marine organisms, ends with burial in sediment and eventually becomes minerals back again via biomineralization with dissolved Si (DSi) being utilized (Fig.1), and reverse weathering that provides alternative key sink for remineralized DSi instead of returning to the ocean reservoir (Sutton et al., 2018).

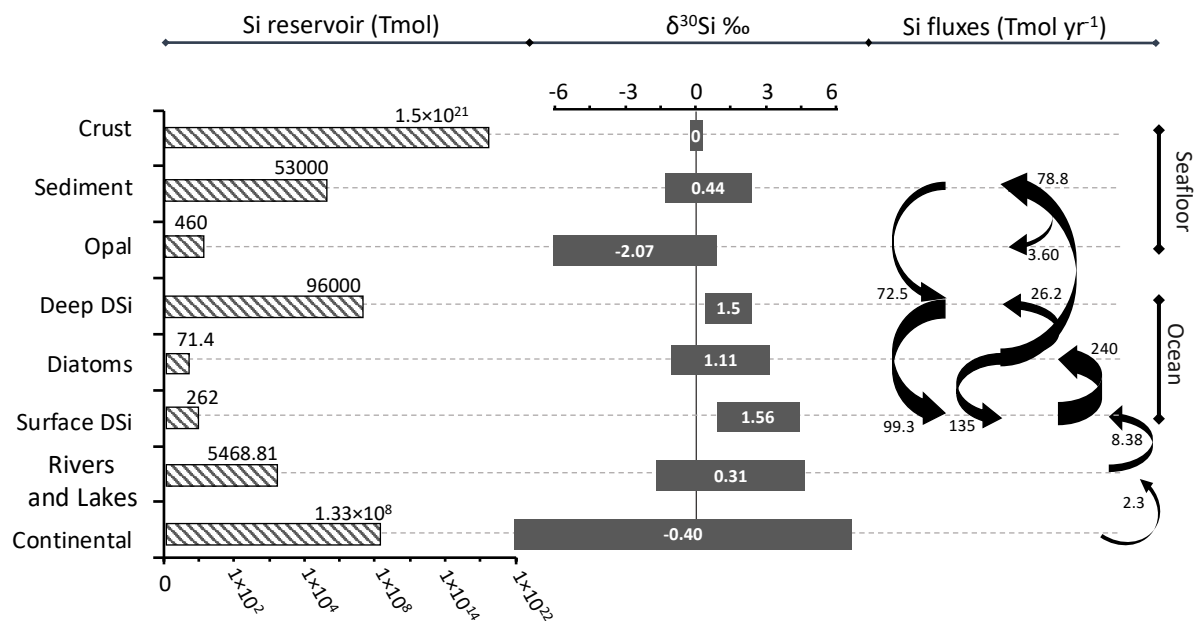
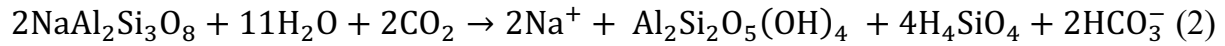
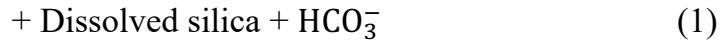


Fig.1 Schematic of the modern-day global Si cycle grouped by reservoir and their associated $\delta^{30}\text{Si}$ values (in ‰), modified from Sutton et al. (2018). The figure is divided into three graphs. The right panel indicates the magnitude of the fluxes (in 10^{12} mol yr⁻¹; Tmol yr⁻¹) between each reservoir with black bent arrows indicating the fluxes of DSi, the middle panel shows their associated $\delta^{30}\text{Si}$ values, and the left panel shows reservoir size (Tmol) (note the ununiform scaling for its abscissa axis).

There are two motivations for studying the Si cycle, silicate weathering and primary products utilization, with both processes determining the partitioning of carbon into the atmosphere (Frings et al., 2016). Firstly, the biogeochemical Si cycle is strongly tangled with the C cycle through the weathering of silicate minerals, with organic carbon being a key driver (Wedepohl, 1978; Cappellen, 2003; DeMaster, 2013). Weathering of silicate minerals contributes a net consumption of atmospheric CO₂ (Berner, 1990). Over geological time, atmospheric CO₂ concentrations are strongly controlled by weathering of silicates on the continents, with CO₂ transformed to carbonate alkalinity and eventually carbonate rocks (Eq.1) (Wallmann, 2001), such as the weathering of albite (Eq.2) (Berner and Berner, 2012). Secondly, in fact, Si is not only a dominant constituent of silicate rocks but also an essential nutrient fueling primary productions (e.g., diatoms and grass) (Van Cappellen, 2003) with diatom being of a key component

of the ocean biological pump (De La Rocha, 2006). Despite marine siliceous production ($240 \text{ Tmol Si yr}^{-1}$) presents the same level of size as the terrestrial consumption ($60\text{-}200 \text{ Tmol Si yr}^{-1}$), the oceanic reservoir, with a longer than one magnitude turnover time of Si (ca. $1\text{--}2 \times 10^4$ years), appears to combine a much larger storage capacity of Si (Conley, 2002). As a result, many investigations so far focus on marine Si cycle, with a few addressing continental cycle to reveal the fluxes of Si from land to sea (Frings et al., 2016).

Reactive silicates + H_2O + $\text{CO}_2 \rightarrow$ Dissolved cations + Clay minerals



1.1.2 The marine biogeochemical silicon cycle

In the ocean, DSi mostly occurs ($\sim 95\%$) as the non-ionic monosilicic acid (i.e., H_4SiO_4 or $\text{Si}(\text{OH})_4$, with the latter form of a better description of ionic structure), a weak acid that remains undissociated below pH 9 (Iler, 1979), with the rest occurring as the dissociated anion ($\text{SiO}(\text{OH})_3^-$) (Sarmiento and Gruber, 2006). It is the transfer of DSi from the marine hydrosphere to the biosphere promotes the biogeochemical cycle of Si (Treguer et al., 1995). Whilst biogenic silica (BSi), an amorphous form of silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) which also be termed opal or amorphous silica, is an important component of the marine biogenic matter commonly accumulated in coastal and abyssal sediments (Conley and Carey, 2015).

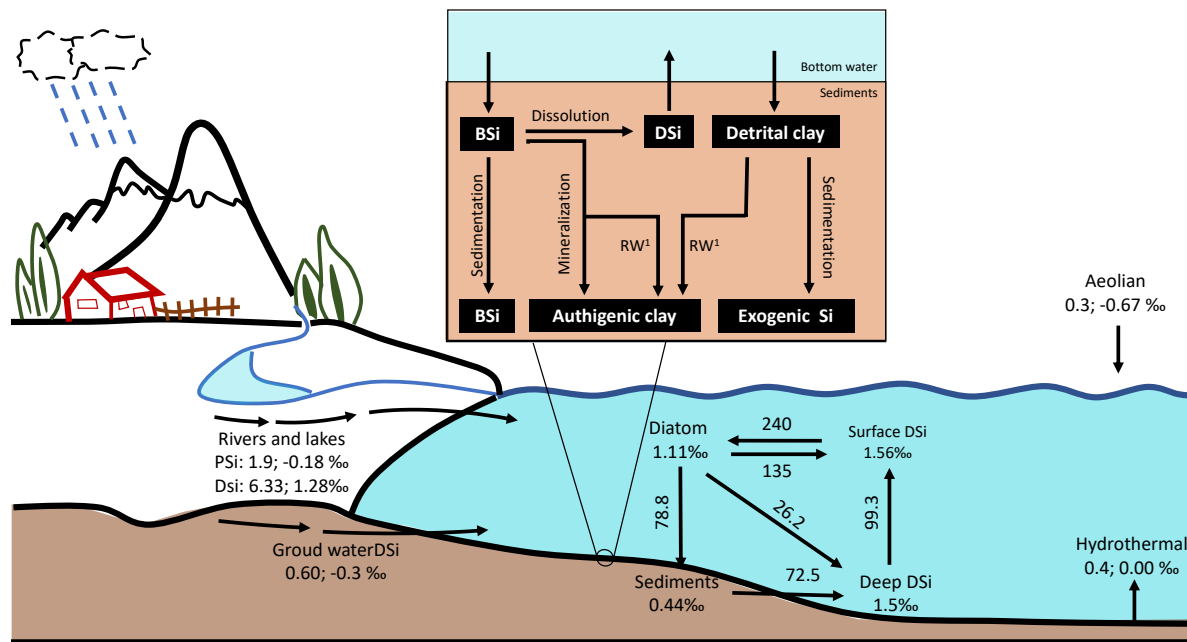


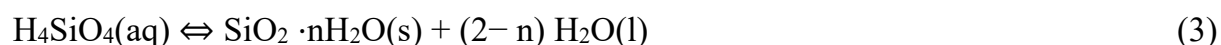
Fig.2 Schematic representation of the marine biogeochemical Si cycle coupled with exchanging rates (in Tmol Si yr^{-1}) and $\delta^{30}\text{Si}$ values (in ‰). The data used are cited from Frings et al. (2016) and Sutton et al. (2018). RW¹ is the abbreviation of reverse weathering.

Marine biogeochemical Si cycle is highly related to the fate of DSi and BSi, which can be divided into two aspects, DSi input and DSi uptake (Fig.2). First, in terms of DSi input, it can be further divided into the surface reservoir and the deep reservoir. The surface reservoir receives DSi inputs from the lithosphere via eolian contribution and chemical weathering of the continental crust in forms of DSi and reactive particulate Si.

The ocean's deep reservoir receives DSi input from the lithosphere through high- and low-temperature weathering of the oceanic crust and weathering of deposited siliceous minerals; Second, in terms of DSi uptake, the siliceous organisms such as diatoms, build up their skeletons by taking up DSi from seawater. Once DSi is incorporated into diatoms, it is primarily exported to deep water through sinking of phytoplankton particulate silicon (opal) or DSi-rich fecal pellets (Staresinic et al., 1983), with the dissolution of BSi initiating immediately after the death of the organisms (Holstein and Hensen, 2010). However, some portion of BSi escaping dissolution settles downward, ultimately reaching the ocean floor where they either remain forming a siliceous ooze, or dissolve returned to the photic zone by upwelling (Tréguer and De La Rocha, 2013). Accumulation of BSi in sediments depends on the rain rate of BSi, the accumulation of other particles, and the degree of preservation in sediments, with effective dissolution before final deposition potentially attributing to a negligible amount of BSi in sediments. (Schulz, 2006).

Siliceous phytoplankton (i.e., primary productivity) in the world ocean is a key member who acts as a prime biological pump on both silicon cycle and carbon cycle (Sarmiento and Gruber, 2006). Diatoms (unicellular autotrophic algae), a phytoplankton group that essentially dissolves Si to form their siliceous frustule (silica-secreting microplankton), are the world's largest contributors to biosilicification in marine systems and also are important contributors to global carbon fixation (Nelson et al., 1995; Jin. et al., 2006). Such a key group of organism first appears during the early Jurassic (ca. 185 Ma) (Baldauf, 2003) and accounts for around half (ca.40-75%) of the modern oceanic primary production globally (Ragueneau et al., 2000; Van Cappellen, 2003).

Owing to high photosynthetic capacity and low maintenance energy requirements, diatoms often prevail over other primary producers as long as nutrients are plenty. As a result, diatoms can dominate at the early stages of open ocean blooms, coastal seas and upwelling areas, where nutrient supplies are high (Van Cappellen, 2003). However, the production of diatoms is found to be limited by the availability of nutrients including major nutrients (i.e., N, P and Si) and micronutrients (e.g., Fe) (Sarmiento and Gruber, 2006). While, the availability of DSi has shown to be essential and could dramatically control the species composition and biomass (e.g., Egge and Aksnes, 1992; Van Cappellen, 2003). The overall reaction describing biomineralization process during the utilization of DSi for building opal by diatom is summarized by Van Cappellen (2003) as following equation:



1.2 Early diagenesis

1.2.1 Biogeochemical pathways of early diagenesis

Early diagenesis in marine sediments, referring to changes occurring during the early stage of burial where pore spaces of sediments are continually filled with seawater, are of special interesting in global biogeochemical cycles (Burdige, 2006). Almost all biogeochemical processes of early diagenesis are linked with the degradation of organic matter as electron donor. Meanwhile, it is characterized by a vertical sequence of mineralization processes (i.e., which are of both metabolic and energy-yielding redox reactions), with O_2 , NO_3^- , Mn(IV) , Fe(III) and SO_4^{2-} serving in a stepwise manner as the

electron acceptors (i.e., the oxidants) (Sørensen and Jeørgensen, 1987) (Table.1). Based on many previous researches, as demonstrated by Sarmiento and Gruber (2006), the remineralization of organic matter in sediments is started with aerobic respiration within the top of oxic sediments (5-10 cmbsf) where the supply of oxygen is sufficient. Once sediments suffer anoxic, it is the anaerobic remineralization that takes over the organic matter diagenesis, despite there is still labile organic carbon available. Even though the aerobic remineralization is more efficient than the anaerobic degradation.

Table.1 Biogeochemical pathways of remineralization reactions with the changes in alkalinity (ΔAlk). This table is adapted from Sarmiento and Gruber (2006) and Kuliński et al. (2017).

Mineralization	Free Energy Change (KJ mol ⁻¹ of CH ₂ O)	ΔAlk (mol mol ⁻¹ of 106 CO ₂)
(CH ₂ O) ₁₀₆ (NH ₃) ₁₆ (H ₃ PO ₄) + 138O ₂ → 106CO ₂ + 16H ⁺ + 16NO ₃ ⁻ + 122H ₂ O + H ₃ PO ₄	-476	-16
(CH ₂ O) ₁₀₆ (NH ₃) ₁₆ (H ₃ PO ₄) + 84.8H ⁺ + 84.8NO ₃ ⁻ → 106CO ₂ + 42.4N ₂ + 16NH ₃ + 148.4H ₂ O + H ₃ PO ₄	-452	+100.8
(CH ₂ O) ₁₀₆ (NH ₃) ₁₆ (H ₃ PO ₄) + 472H ⁺ + 236MnO ₂ → 106CO ₂ + 8N ₂ + 236Mn ²⁺ + 366H ₂ O + H ₃ PO ₄	-388	+472
(CH ₂ O) ₁₀₆ (NH ₃) ₁₆ (H ₃ PO ₄) + 848H ⁺ + 212Fe ₂ O ₃ → 106CO ₂ + 16NH ₃ + 424Fe ²⁺ + 530H ₂ O + H ₃ PO ₄	-187	+864
(CH ₂ O) ₁₀₆ (NH ₃) ₁₆ (H ₃ PO ₄) + 53SO ₄ ²⁻ → 106CO ₂ + 16NH ₃ + 53S ²⁻ + 106H ₂ O + H ₃ PO ₄	-82	+122
(CH ₂ O) ₁₀₆ (NH ₃) ₁₆ (H ₃ PO ₄) → 53CO ₂ + 53CH ₄ + 16NH ₃ + H ₃ PO ₄	-71	+16

Chemical concentration gradients, combined with dissolution/precipitation and adsorption /desorption of chemicals, occur within the pore water (which is of the trapped seawater in the void part of sediments) and throughout the interface with the overlying seawater (Sarmiento and Gruber, 2006). Mass flow can thus be influenced by the chemical potential gradients of a particulate solute from highly enriched sediment layers to low concentrated parts through the process of diffusion (Schulz, 2006). According to Fick's first law of diffusion (Eq.3), the diffusive flux (J_D) is directly proportional to concentration gradient ($\partial C / \partial x$) and approximated along one dimension in sediments.

$$J_D = -\phi \varepsilon_s \frac{(\partial C)}{(\partial Z)} \quad (4)$$

where ε_s refers to whole sediment diffusion coefficient (m² s⁻¹), which is temperature-dependent and substance-dependent; C refers to concentration (mmol m⁻³); and z refers to space coordinate (m).

1.2.2 Alkalinity changes during early diagenesis

Alkalinity (Alk), defined as the equivalent sum of the bases which are titratable with strong acid, is a conservative water property indicating the excess bases over acids (Stumm and Morgan, 1981; Sarmiento and Gruber, 2006). The measured value is primarily a function of carbonate, bicarbonate, and hydroxide content and may include contribution from borates, silicates, or other bases if these components are present (Eq. 5). However, mostly, total alkalinity can be reasonably set equal to the carbonate

alkalinity ($[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$), since other substances in pore water contribute negligibly to the titration of alkalinity (Schulz, 2006).

$$\text{Alk} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{B}(\text{OH})^4] + \text{minor bases} \quad (5)$$

The Alk distributions in the ocean are primarily modified by two important biological processes, the photosynthesis, and the reverse processes involving respiration and remineralization. The pore water Alk depends on various redox processes of early diagenesis mineralization, which can be closely linked to a variety of organic matter degradation pathways and secondary re-oxidation reactions. (Schulz and Zabel, 2006; Thomas et al., 2009; Krumins et al., 2013; Brenner et al., 2016; Kuliński et al., 2017) (Table.1). According to model-derived estimation from Krumins et al. (2013), the largest amount of benthic alkalinity generation (70–82%) is contributed by sulfate reduction, with ammonification, denitrification and iron reduction yields only 4.2–9.0%, 1.4–3.6% and 1.0–2.8% of it respectively. While carbonate mineral dissolution is the second largest contributor after sulfate reduction to in situ alkalinity generation. In addition, the alkalinity flux is also influenced by the availability of reactive iron ($\text{Fe}_{\text{reactive}}$) in the sediment, because the effect of iron reduction on sediment alkalinity especially depends on the fate of reduced species. While $\text{Fe}_{\text{reactive}}$ is defined as the fraction of readily reacted iron with respect to sulfide that is a product of dissimilatory sulfate reduction, and it can form various iron sulfide minerals with pyrite playing as the ultimately terminal-product (Canfield, 1989). It is noticed that in the Baltic Sea the Alk variation in pore water is remarkably decrease driven by oxic respiration and increase with the re-oxidation of reduced species like HS^- , with the burial of iron (II) minerals like pyrite (FeS_2) or vivianite ($\text{Fe}^{2+}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) also acting as important contributors. (Kuliński et al., 2017).

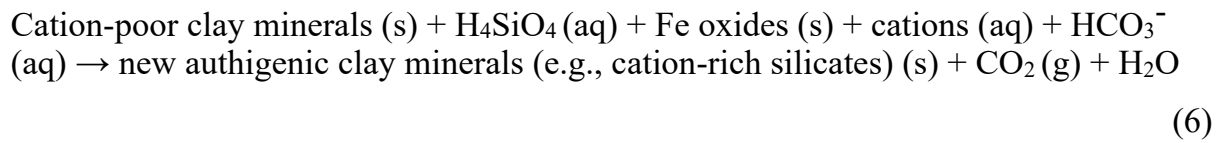
1.2.3 Early diagenesis of BSi and reverse weathering

During early diagenesis, there are various ways for BSi to participate within the geological cycle: i) some build-up in pore waters and diffuse out of the sediment into upward water in the form of DSi (Aller, 2014); ii) some transform into authigenic aluminosilicates ($\text{Al}_2\text{Si}_{2.4}\text{O}_{5.8}(\text{OH})_4$, which is analog to kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) except containing more silica component) through co-precipitation with the terrigenous-minerals-released Al (Van Cappellen and Qiu, 1997; Dixit et al., 2001); iii) and some portion of authigenic silicate minerals probably with other detrital clay minerals then undertaken reverse weathering through reaction with Al and Fe (oxyhydr)oxides and cations (mainly K and Mg) dissolved in the pore waters, leading to the formation of authigenic K- and Fe-rich aluminosilicate minerals (Michalopoulos and Aller, 1995, 2004; Michalopoulos et al., 2000) (Eq. 6). iv) at last, the rest preserved BSi eventually crystallizes primarily as chert (Burdige, 2006; Libes, 2011; Sutton et al., 2018).

Regarding the solubility of BSi, laboratory experiments and theoretical studies both agree that it depends on a wide range of parameters including the temperature, pH, pressure, degree of undersaturation, surface area of the silica per unit mass, the inclusion of trace metal contaminants in the silica crystal, and the presence or authigenic formation of other silica phases in the sediment which is tightly linked with aluminum (Al) (Sarmiento, 2006). As Dixit et al. (2001) recognizing, dissolved Al, which derives from the dissolution of detrital minerals at the water-sediment interface, may lead to a significant reverse impact on the solubility of biogenic silica in ways including the

diatom formation (i.e., primary uptake), early diagenesis (i.e., secondary uptake), and the formation of authigenic aluminosilicate phases in sediments (so called reverse weathering).

Aluminosilicates formed in marine sediment was first proposed by Mackenzie and Garrels (1966), are poorly crystalline Al–Si phases containing various amounts of K, Fe, Mg and Cl (Michalopoulos et al., 2000). Processes of aluminosilicates formation are named reverse weathering owing to their opposite effects of terrestrial weathering reactions. It has been found as a critical control on the biogeochemical cycle of marine cations (e.g., Al, Fe, Mg, K, Li, Na), and carbon cycle by consuming bicarbonate and producing CO₂ into seawater and eventually into atmosphere (Mackenzie and Garrels, 1966; Sillén, 1967; Michalopoulos and Aller, 2004; Sun et al., 2016). During this process, major ions are removed from pore water as well as bicarbonate and DSi (Libes, 2011; Church, 2016) (Eq. 6).



Therefore, during reverse weathering, a negative effect on pore water alkalinity, which are dominated by organic carbon degradation, and influences on both the distribution of pore water DSi and the distribution of iron oxides in particle sediments can be expectable.

1.3 Silicon isotopes

Silicon has three stable isotopes, ²⁸Si, ²⁹Si and ³⁰Si, with the most abundant stable isotope ²⁸Si existing atom %²⁸Si=92.22% and the other two isotopes existing much less abundance (%²⁹Si=4.68%; %³⁰Si=3.09%) (Coursey et al., 2011).

The Si isotope values are conventionally expressed in δ^xSi values (‰) relative to the standard, NBS 28, whose isotopic composition is ³⁰Si/²⁸Si = 0.033532 and ²⁹Si/²⁸Si = 0.0508204 (Coplen et al., 2002).

$$\delta^x\text{Si}(\text{‰}) = \left(\frac{\left(\frac{x\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{x\text{Si}}{^{28}\text{Si}} \right)_{\text{standard}}} - 1 \right) \times 1000 \quad (7)$$

where x = 29, 30.

Si isotopes follow mass-dependent fractionation, hence generally most studies use δ³⁰Si as a representative for Si isotope compositions. Additionally, isotope fractionation factor (enrichment), α, as an important parameter in isotope geochemistry, is defined as:

$$\alpha = R_A/R_B = \frac{(\delta_A + 1000)}{(\delta_B + 1000)} \quad (8)$$

where R_A and R_B are the isotope ratios of two phases, A and B.

The fractionation of isotopes between two phases is often reported as separation factor (Δ_{A/B}) or enrichment factor (ε_{A/B}) as well:

$$\Delta_{A/B} = \delta_A - \delta_B \approx \epsilon_{A/B} = (\alpha - 1) \times 1000 \quad (9)$$

Based on an overview of the Si isotopic composition of terrestrial and extraterrestrial materials which is summarized by Sutton et al. (2018), Fig.1 is referenced here to achieve a wide sight on the distribution and transformation of Si isotope. The extent of fractionation of Si isotopes between silicate and metal phases (i.e., the core) has been determined to decrease with temperature, with isotopically light Si preferentially partitions into the metal phase (Ziegler et al., 2010; Shahar et al., 2011; Schauble et al., 2007)). While a slight fractionation associated with melting and fractional crystallization has been found, with lighter silicon isotopes tending to partition into SiO₂-poor mafic minerals (Savage et al., 2012). In spite of all the above reactions with small extent fractionations, fractionations at lower temperatures where silicic acid (H₄SiO₄) is involved are much greater. These processes can be mainly subjected to the transformation processes of Si which are weathering of silicate rocks combining with the formation of secondary minerals and release of DSi, uptake of DSi by organisms for the biomineralization of BSi, and the remineralization of Si. For instance, weathering of silicate rocks is expected to produce isotopically light clays (with fractionation factor of $\Delta^{30}\text{Si}_{\text{kaolinite-quartz}} = -1.6\text{‰}$, at 25°C) and an isotopically heavy solution (Méheut et al., 2007).

As shown in Fig.2, in the ocean, diatoms have lower $\delta^{30}\text{Si}$ values relative to that in DSi because they prefer to utilize the lighter isotopes for silicification. The fractionation between DSi and BSi ($\Delta^{30}\text{Si}_{\text{BSi-DSi}}$) is estimated to be around -1.1‰ and is found to be independent of temperature and ambient pCO₂ but species-dependent (De la Rocha et al., 1997; Milligan et al., 2004; Sutton et al., 2013). On the other hand the isotope effect during BSi dissolution appears not associated with significant silicon isotope fractionation, which is further found to be independent of temperature, specific surface area and degree of undersaturation (Demarest et al., 2009; Wetzel et al., 2014; Egan et al., 2012). Therefore, isotope compositions of BSi are believed to be robust against dissolution and have been interpreted as variability in the utilised fraction of DSi in a number of studies (e.g., Reynolds et al., 2008; Swann et al., 2010; Fripiat et al., 2012). However, isotope compositions of the porewater DSi and precipitated solids are suggested to be affected by several factors, including selective dissolution of silicon sources of variable isotope composition, isotope fractionations during precipitation, and the mass balance between dissolution and precipitation (Tatzel et al., 2015). As Sutton et al. (2018) summarized, variations in Si isotope contents could well characterize changes of oceanic silicon cycling, despite the impacts of dissolution, diagenesis and reverse weathering on the stable isotope analysis of BSi still remain an important challenge to understand.

1.4 Biogeochemical Si cycle in the Baltic Proper

The Baltic Sea (Fig. 2) in Northern Europe is one of the largest estuarine systems in the world. It is the world's largest body of brackish water (373 000 km², 21000 km³), with a fourfold larger drainage area ($\sim 1.7 \times 10^6$ km²), and a human population of ca. 84 million living in its vicinity (Hannerz and Destouni, 2006). The Baltic Sea can be divided into a number of sub-basins separated by sills. Shallow sills between the North Sea and the Baltic Sea restrict the water exchange, leading to a long water residence time of more than 20 years (Papush et al., 2009). Eutrophication in the Baltic Sea with signs emerging in the 1950s has come up to be a relevant issue ever since (Conley et al., 2008).

With regard to the silica loads, the Baltic Sea is a non-homogeneous water body. DSi concentrations reach the highest in the northernmost basins and are lower in the southern-eastern and western regions. Despite the limited riverine nutrient loaded along the western border of Baltic Sea, the water flow transporting from Bothnian Sea to Kattegat which is rich in DSi with low DIP and DIN (Rahm and Danielsson, 2007) is found to be the main resource of the DSi in the Baltic Proper. In 1978, DSi in the Baltic Sea are claimed to be very high concentrated and will not become limiting for diatom growth (Fonselius, 1978). On the contrary, to date, it has been shown that the current DSi concentrations in Baltic Sea were almost three times lower than the historical concentrations at around 1900, leading to the serious worry about the widespread trend of DSi limitation which will further cause destruction of ecosystem (Conley et al., 2008).

Consistent to the global marine cycle of Si in section 1.1, silicon in the Baltic Sea originates from weathering of silicate minerals and is supplied to the sea by river fluxes, and to a minor extent by eolian transportations (Fig. 1). The modifications in terrestrial and aquatic environments will influence the DSi reservoirs in the sea and thereby affect the production of diatoms. Therefore, two reasons, dams on major rivers in the drainage area causing a 30%–40% decrease of riverine DSi loads (Humborg et al., 2002), and eutrophication effect on exhausting the DSi in water column by primary uptake followed by an enhanced accumulation of biogenic silica (BSi) in sediment (Conley et al., 2008), are considered to result in the long term declines of DSi in the Baltic Sea, which is rather significant during 1970-1990 and turn to level off during the last decade.

According to the surveys of Papush and Danielsson (2006), despite a high total primary production, the Baltic Proper has fairly low silica accumulation rates. This may be attributed to the impact of its high salinity, mild climate and anoxic conditions in deep water. Moreover, there are considerable temporal variations within single years that the highest nutrient concentrations usually occur during winter and the lowest during summer (Hagström et al., 2001).

1.5 Aim

The object of the project is to determine the concentration and silicon isotope compositions ($\delta^{30}\text{Si}$) of porewater and solid-phase components (DSi, BSi, non-biogenic silicates) and reactive Fe species in a sediment core from the Baltic Sea. The ultimate aim of this study is to investigate stable silicon isotopic implications on silica early diagenesis and on the reactions of authigenic silicates formation, especially reverse weathering.

Hypothesis: (i) There are significant Si isotopic fractionations during authigenic silicate formations, resulting in a heavier DSi flux into the overlying water. (ii) The extent of transformations of BSi into authigenic silicates in sediment are strongly coupled with pore water DSi, alkalinity, and BSi. (iii) Reactive iron can be used as a good indicator of new authigenic silicate formations to supply the interpretation of Si isotopes on reverse weathering. (iv) The authigenic silicate formations prevail below anoxic condition and can be reflected by the stable isotope variations between different phases (i.e., DSi, BSi, detrital silicates, authigenic silicates). To be brief, two scenarios have been assumed: (i) There are pervasive reverse weathering processes throughout the sediment. (ii) Reverse weathering processes are limited in some particular zones.

2 Materials and Method

2.1 Study site description

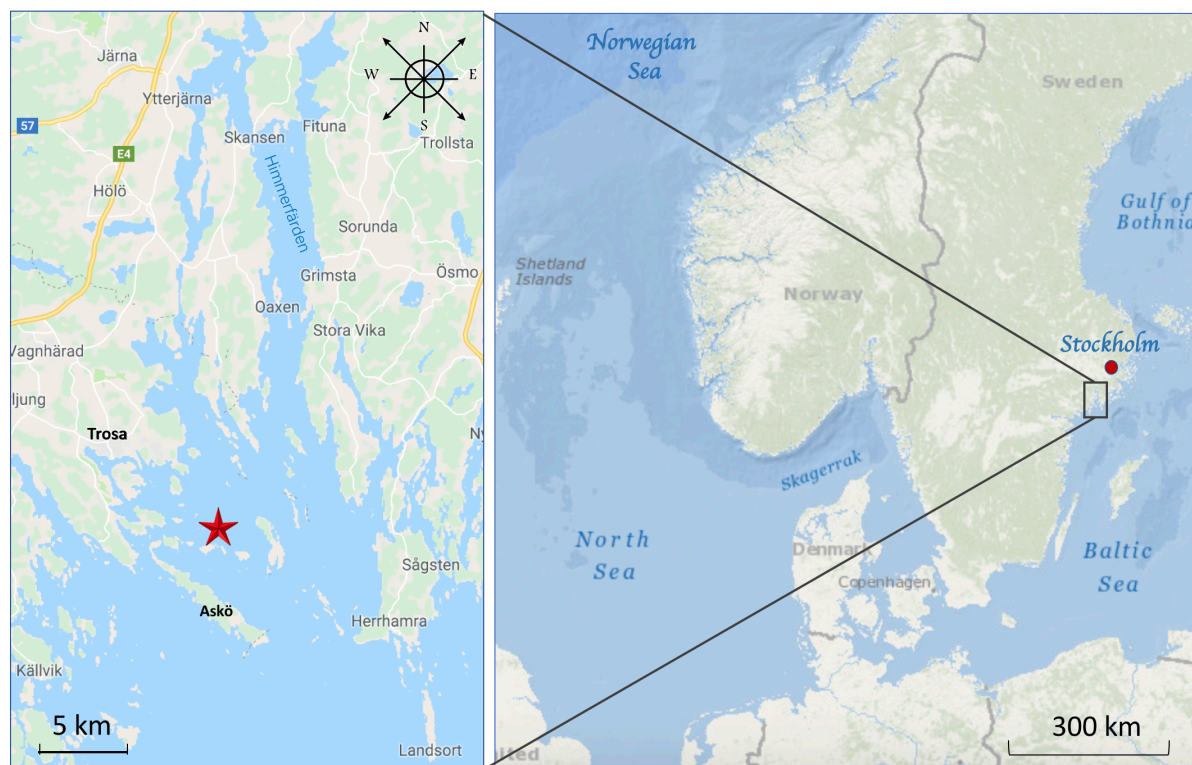


Fig.3 Map of the study area. Right: overview location of the study site (i.e., the base map is cited from NOAA). Left: map of the Trosa archipelago with the red star illustrating the site where sampling was conducted (i.e., the underlying map is from Google Map).

As illustrated in Fig. 3, this study site is located in the Trosa archipelago in the Fifång Deep, on the southwest of Himmerfjärden. Sedimentation areas in Himmerfjärden can be divided into accumulation and transport bottoms (Sawicka and Brüchert, 2017). About 21 % of the sediment surface in Himmerfjärden is classified as the accumulation bottom of particulate material and receives $3.3\text{--}9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Thang et al., 2013; Karlsson et al., 2010). Sediments dating for Himmerfjärden have been reported previously in Thang et al. (2013) using the activities of the radionuclides ($^{210}\text{Pb}_{\text{excess}}$ and ^{137}Cs). Comparing to the historical sediment record, Himmerfjärden sediments have been determined to accumulate at very high rates that are 1.5–3.5 fold higher than in the open Baltic Sea basins ($0.26\text{--}0.62 \text{ cm yr}^{-1}$) (Mattilav et al., 2006). It is suggested to range from $0.98 \pm 0.31 \text{ cm yr}^{-1}$ in the innermost part of the estuary to $0.77 \pm 0.31 \text{ cm yr}^{-1}$ in the outer part of the estuary. According to the closed geographic property, the later rate (0.77 cm yr^{-1}) was been employed in this study.

2.2 Sample collection

The study site is situated in the Trosa archipelago ($58^{\circ}51'37.22\text{N}$, $17^{\circ}39'68\text{E}$), as shown in Fig. 3. At this location, bottom-water and sediment samples were collected at a water depth of 25m with the research vessel R/V Limanda on November 20th, 2017. Sediments were taken using different coring techniques and instruments, including gravity corers (Rumohrlot corer) and multicores, in tape-sealed perforated acrylic tubes.

Two sediment cores were retrieved with small gravity corers of 80 and 70cm length, respectively. For the whole core sediment incubation, four cores were collected with a multicorer, while the bottom water was collected with a Niskin bottle and subsequently stored in a polyethylene water bottle. All of the cores were capped with rubber stoppers onboard.

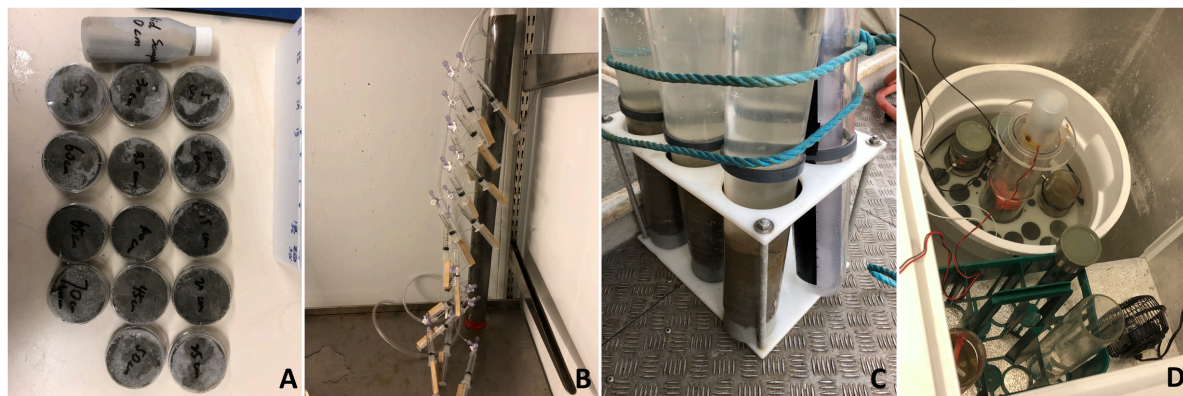


Fig.4 Samples collected from the field. A) Solid sediment samples; B) Pore water extraction with Rhizons and syringes; C) Multicores on board; D) Incubated multicores in lab.

Once on deck, those cores were directly transported to the marine laboratory on Askö and stored in a cold room at bottom-water temperature (3.4°C) for later subsampling (Fig.4). Whilst the group of multicores with undisturbed sediment surfaces and clear overlying water were done sub-coring on the shore in acrylic tubes (internal diameter 6.2 cm, area 30.19 cm²) retaining about 10 cm of the overlying water and kept at in situ bottom water temperature for subsequently whole core flux incubation. The sediment height in the tubes was 20 cm. Porewater samples were directly extracted from the first Rumohrlot core (80cm length) using Rhizons connected to 10-mL syringes, a kind of method designed by Elverfeldt et al. (2005), at a resolution of 5 cm depth. Two aliquots at each depth were prepared for the parallel analysis for alkalinity and silicic acid, respectively. While the second Rumohrlot core (70cm) was removed from the supporting frame and immediately sub-sampled by collecting approximate 40 cm³ wet sediment every 5cm slice.

2.3 Pore water analysis

2.3.1 Total Alkalinity (Alk_T)

The total alkalinity (referred as Alk) of pore water was measured potentiometrically using an automatic titration system (Metrohm Titrando 814, Metrohm Aquatrode Plus Pt1000, connected with a pc through the programme tiamo 2.4), which was calibrated with pH 4 and 7 standard solutions. The alkalinity samples are less sensitive to handle and store than the DIC samples, since the exchange of carbon dioxide will affect pH but not alkalinity. During the measurement, pore water samples were weighted and diluted to 30ml with Milli-Q water in cups and then titrated with 0.01N hydrochloric acid and backtitrated with 0.01N sodium hydroxide. The Gran equivalence point was determined according to Haraldsson et al. (1997):

$$FI = (V_0 + V_t) * [H^+] \quad (10)$$

where $[H^+] = (10^{-pH})/\alpha$

α = Activity of H^+

V_0 = initial volume of the sample

V_t = volume of acid titrant added

The total alkalinity is hence calculated by the equation:

$$Alk_{BT} = \frac{(V_{HCl} \times C_{HCl} - V_{NaOH} \times C_{NaOH}) \times 1000}{(V_{Sample} + V_{HCl} + V_{NaOH})} \quad (11)$$

in which V_{HCl} describes the volume of added hydrochloric acid, C_{HCl} represents the molality of the added hydrochloric acid, V_{NaOH} describes the volume of added sodium hydroxide, C_{NaOH} represents the molality of the added sodium hydroxide, V_{sample} is the pre-pipetted sample volume.

2.3.2 Porewater dissolved silicon (DSi)

For calibration, a fusion procedure was deployed to make a stock solution with certain Si concentration. Since silica is an acid oxide, alkali and high temperature are used here to break the Si-O-Si bonds so that a Si can be converted to silicic acid (i.e., $Si(OH)_4$). 42.86mg high purity quartz powder (>99.99%) was mixed with ca. 300mg sodium hydroxide (NaOH) in a silver (Ag) crucible and fused at 750°C for 10 min in a muffle furnace. After the heating, when the furnace temperature decreased to around 70-80 degrees, the Ag crucible was soaked into a 50ml teflon vial. The incomplete dissolution of fused Si-NaOH was avoided by leaving it overnight. This was followed by washing with MilliQ water into a 0.2M HCL solution in order to neutralize the NaOH. The final stock solution ($[Si]=20mgL^{-1}$; $[HCL] \approx 0.2M$) was stored in pre-cleaned HDPE bottles so that Si polymerization could be avoided. Every measurement, working standards, ranging from 0 to 100 μM , were prepared by diluting certain amount of the stock solution.

For dissolved silicate measurements, a colorimetric method, adopted from the molybdate-blue spectrophotometric method (Strickland and Parsons, 1972; Pettersson and Karlberg, 1999), was used on the spectrophotometer (Thermo Scientific, Evolution 260 BIO). The concentration of the stock solution was firstly cross checked by testing the other standards used for isotope analysis (IRMM-18). The accuracy of this test is insignificant, 0.11mg/L (i.e., accuracy = tested concentration - known concentration = 18.42-18.31mg/L; CV=0.006). Briefly, a suit of calibration curve was built up by running standards with uniform increasing concentrations through the spectrophotometer at 800nm to produce a reference for quantifying the variation in forms of absorbance (nm) for samples with unknown Si concentrations. After a conversion graph for concentration calculation was developed, all the samples were measured their absorbances which are able to be converted into concentrations. During the measurement, one hundred millilitres of 20% ammonium molybdate solution was mixed with 150 ml of 7.2N sulphur acid (H_2SO_4) to produce a reducing reagent ahead. When cuvettes were filled in with the reducing reagent (0.03mL) at the second step and with the porewater samples (1mL) at the third step, the formation of a yellow molybdosilicate acid complex took place in the pH range 0.8-2.5. Thereafter, in order to enhance the sensitivity of the method, 0.02ml of 1.75% ascorbic acid was added for reducing the silicomolybdate complex to a blue colored heteropolysilicic acid. Additionally, to avoid intervention of phosphate, the selective masking with 0.02ml of

10% oxalic acid was used before the addition of ascorbic acid, which could transform excessive molybdate to a non-reducible form and reduce the interference from phosphate by decomposing the phosphomolybdic acid.

2.4 DSi flux analysis

Whole cores incubation experiment was performed to determine the DSi flux. During the experiment, one of the four multicores was disturbed and failed to be monitored, hence there are only three intact cores left with undisturbed sediment surfaces and clear overlying water. These three cores were incubated in an incubation tank filled with bottom water from the same site (Fig. 4 D). The overlying water in the cores was stirred by small magnetic bars mounted in the core liners and driven by an external magnet at 20-30 rpm. The O₂ concentration in each core was measured by oxygen sensor spots attached to the inner wall of the cores and logged during the incubations. The cores were subsequently capped and incubated for periods ranging from 26.77 to 185.89 hrs. Each core was done subsampling of overlying water and measured its DSi concentration at a certain time point followed by exchanging of the overlying water with ambient water in the incubation tank. Such refilling could ensure that the chemical composition of the overlying water in each core is closely comparable to the in-situ condition and resembles each other. Hence it is noted that in this experiment samples from even a same core represent individual points rather than a continuous time series (i.e., n=10).

Sediment total oxygen uptake flux (J_{O₂}) were computed by linear regression of the O₂ concentration over time (Eq. 12). Fluxes of DSi (J_{DSi}) going out to the bottom water during the whole core sediment incubations were calculated according to Eq. 13.

$$J_{O_2} = ([O_2]_0 - [O_2]_{end}) / t * (V / A) \quad (12)$$

$$J_{DSi} = ([DSi]_0 - [DSi]_{end}) / t * (V / A) \quad (13)$$

where the unit of TOU and F_{Si} is μmol m⁻²d⁻¹. [DSi]₀ and [DSi]_{end} represent the start and end concentrations of DSi in μmol m⁻³, with Δ[DSi]=[DSi]₀-[DSi]_{end}. V is the headspace volume (m³), A is the surface area of the incubation core (m²), and t is the incubation time (days). Generally, DSi and Oxygen concentrations were employed to develop a linear regression of DSi/Oxygen versus time (day), with the slope retrieved representing statistical concentration gradients, fluxes (e.g., Fig.16 and Fig. 17).

2.5 Solid phase analysis

2.5.1 Biogenic silica (BSi)

This study utilized the wet-chemical method proposed by DeMaster (1981). Such wet chemical digestion techniques rely on the ability of weak bases to quantitatively dissolve all amorphous Si components of the sediments, while only a small fraction of mineral silicates dissolves. Dissolution experiments by DeMaster (1979) indicate that diatoms are quantitatively dissolved in 2 hr or less using an 85°C, 1% Na₂CO₃ leaching solution (pH = 11.2). Under the same leaching condition, the amount of extracted silica from clay minerals (e.g., illite, kaolinite or montmorillonite) increases linearly with time. Based on this, a sequential alkaline digestion was employed within strict time intervals to extract the silica extracted from biogenic phases and aluminosilicates (i.e., clay minerals) along typical time series, as shown in Fig.5.

Prior to the extraction procedure, all wet sediment samples were oven dried (105°C, 24h), ground and powdered using a Si-free mortar and pestle. Meanwhile, the difference between wet and dried mass was used to calculate the porosity. Dried sediment powders (ca. 50-200mg) were then leached using a time-course sodium carbonate (Na₂CO₃) extraction at 85 °C with sub-samples taken at 1, 2, 3, 5 and 21 hr. In order to strictly control the interval time of the water bath, dried sediments were divided for each depth

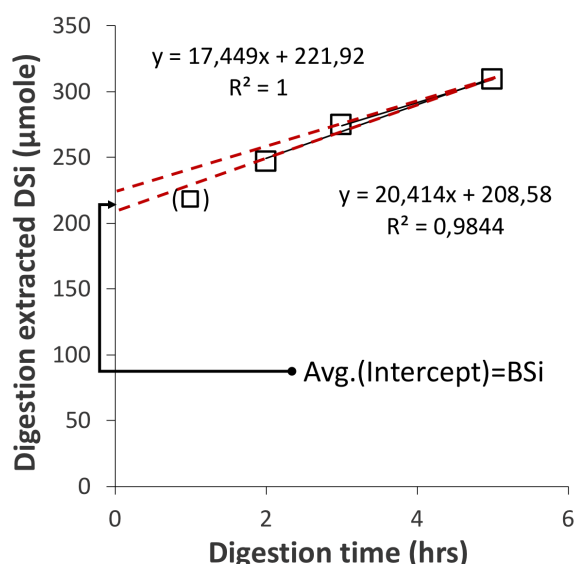


Fig.6 Time series of digestion-extracted silica for sample (e.g., 15cmbsf depth). The Avg. (Intercept) represents the mean of two intercepts calculated on three points regression (2,3,5 hrs) and two points regression (3,5 hrs), respectively.

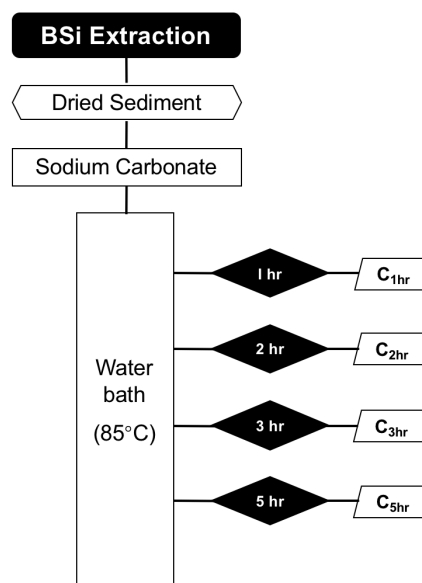


Fig.5 Sequential alkaline extraction flow chart.

into duplicates, whose two were placed into the hot water at the same time with the next group of duplicates from deeper 5cm depth loaded 10 minutes later, and so on. Each subsampling (1ml) was instantly neutralized by 0.01N hydrochloric acid into 3ml and further monitored its DSi concentration by using the molybdate-blue spectrophotometric method (Strickland and Parsons, 1972) following the same time sequence (10min per each depth duplicates).

As such analytical technique relies on the difference between the rapid dissolution of biogenic silica and slower release of silica from coexisting clay minerals, the biogenic-silica content of sediments could be evaluated by linear regression with

extrapolation to the intercept. An example of dissolution curve in this study is illustrated (Fig.6).

Based on the extrapolated BSi content, the BSi accumulation rates are further calculated (Eq. 14). Thereafter, the accumulation rate of BSi is able to be calculated as:

$$J_{BSi} = (C_{BSi}/100) \times 10000 \times \omega \times \rho \text{ (g SiO}_2 \text{ m}^{-2} \text{ year}^{-1}) \quad (14)$$

Where J_{BSi} is the BSi accumulation rate, C_{BSi} is the BSi content (g SO₂ percent dry weight, SO₂ wt. % dry weight), ω is the sedimentation rate (centimeter per year, referred from Thang et al. (2013)), and ρ is the density of dry bulk sediment (grams per cubic centimeter; retrieved from Sawicka and Brüchert (2017)).

Moreover, for calculating the BSi accumulation rate, the porosity profile is analyzed and evaluated in advance. As shown in Fig.7, the porosity measurement of this study is fairly coherent with the other two studies (Thang et al., 2013; Mannucci, 2015). Such consistency suggests that these sediments collected in the same site in spite of different years are capable of reflecting common physical and chemical characteristics over depth, especially porosity. Considering the limited volume of sediment used for porosity measurement in this study, the porosity gradient from Thang et al. (2013) is relied on as the most creditable data.

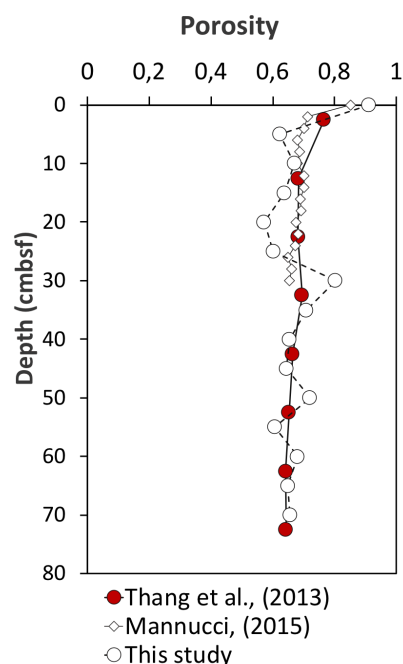


Fig.7 The comparison of porosity measurements of this study and other two researches.

2.5.2 Reactive iron (Fe_{reactive})

For the purpose of quantitatively identifying the different reactive iron phases, a sequential extraction procedure (Kostka and Luther, 1994; März et al., 2008) was applied to the solid samples. This procedure was constituted with the ascorbate extraction and sodium dithionite extraction steps, which lead to reduction of easily reducible (amorphous) iron (oxyhydr)oxides (Fe_{asc}), commonly referred to the ferrihydrite (Fe(OH)₃), and crystalline iron (oxyhydr)oxides (Fe_{dith}) such as goethite and magnetite, respectively. Thus, the most reactive Fe phases (Fe_{reactive}) can be referring to the sum of both extraction steps.

The extraction process was simplified to two steps: the ascorbic acid extraction (Canfield, 1988) and the sodium dithionite extraction (Ferdelman, 1988) (Fig. 8). At the ascorbate extraction step, 200–250 mg of freshly thawed sample, shaken (125rpm) over 20 h with 20 ml buffer solution I (including 5% sodium citrate and 5% sodium bicarbonate), to which 12 g ascorbic acid was slowly added for the purpose of carbon dioxide degassing (i.e., final pH 7.5). This was followed by a washing step with the same kind of buffer solution added to the residuum of the former step and shaken over 2 h. Whereas, during the next dithionite extraction step, residuum from the last washing

step was shaken (125rpm) over 4 h with 20 ml buffer solution II (including 7.047% sodium citrate and 2% acetic acid) to which 18.02 g sodium dithionite was added (i.e., final pH 4.8). After each step, the extraction solutions were centrifuged (2000rpm) for 15 mins, while the supernatants were analyzed using the ferrozine method (Stookey, 1970) after 1:10 dilution with MilliQ water.

For the statistical data analysis, each experiment containing triplicate aliquots (i.e., named as AI, BI, CI for the ascorbic acid extraction and AII, BII, CII for the sodium dithionite extraction). Furthermore, the limitations of the lab materials and lab condition have spawned an additionally exam, which could identify the dependence of the approach on anoxic environment by selectively using degassed or non-degassed buffer solution. The situations whether the buffer solution used in each step had been degassed with nitrogen were varied between triplicates and therefore illustrated in Fig.8 as well.

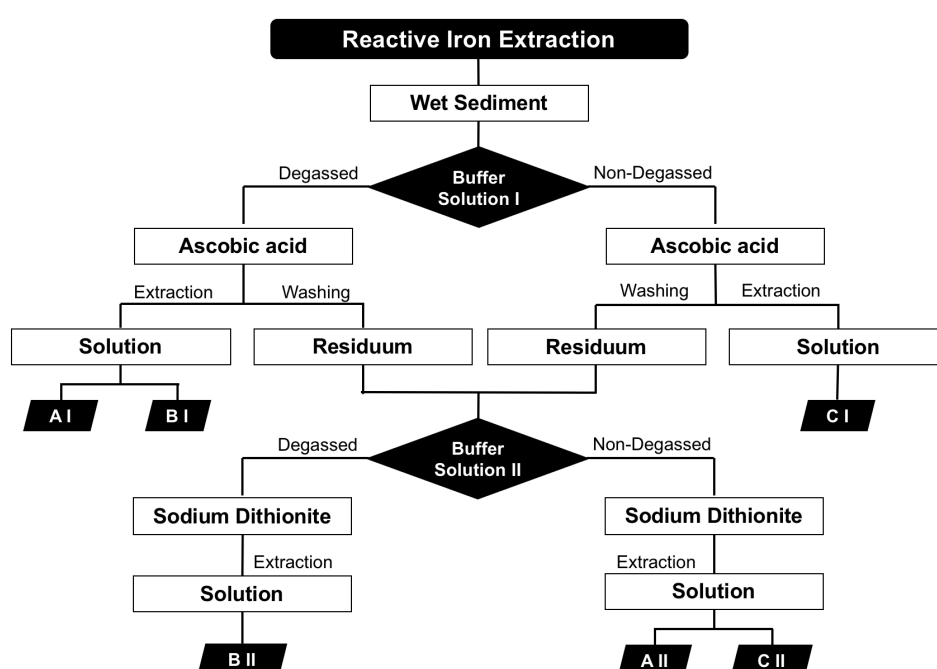


Fig.8 Sequential reactive iron extraction flow chart.

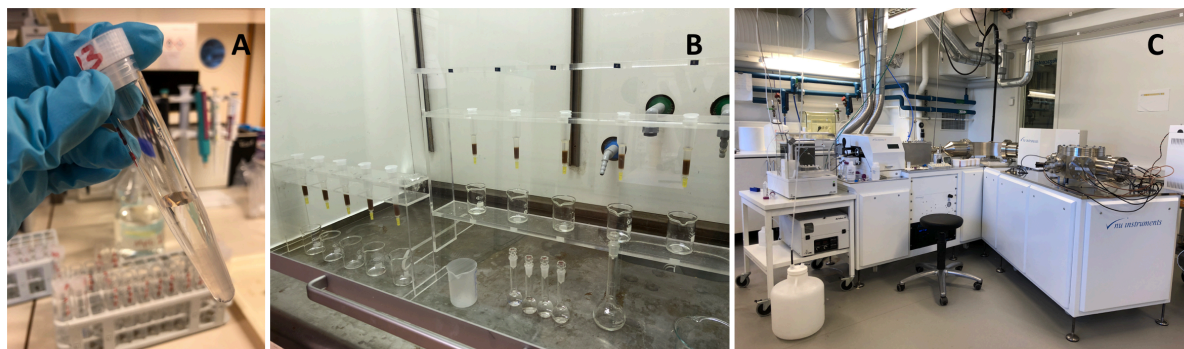


Fig.9 Photographs taken during silicon isotope analyzing, including the preparation step (A and B). A) co-precipitation reaction in one sample; B) cation exchange resin beds; C) the Nu plasma (II) MC-ICP-MS (at Vegacenter, the Swedish Museum of Natural History, Stockholm)

2.6 Silicon isotope analysis

2.6.1 Sample preparation

Isotope analysis was carried out on porewater samples, bottom water sample and samples from alkaline silica digestion by Na_2CO_3 (i.e., 72 samples in total). Prior to the analysis, a magnesium co-precipitation technique followed by ion-exchange chromatography (Reynolds et al., 2006; Sun et al., 2014) was utilized to sequentially separate, purify and pre-concentrate silicon in the analyte.

The magnesium co-precipitation technique (Reynolds et al., 2006) is based on brucite ($\text{Mg}(\text{OH})_2$) precipitation, accompanying with the absorptions of Si, from the porewater samples and sediment extracts at a pH of ~ 10 , while such high pH is attained by the addition of 2% by volume of 1M NaOH. Additionally, the precipitation is visible to the naked eyes (e.g., Fig.9 A). During the first round of co-precipitation, two hundred microliters of 1 M NaOH was added to 10 ml of the diluted samples. After, samples were shaken and left for two hours, centrifugation was performed at 4200 rpm for 5 mins. During the second round of co-precipitation, another 100 μl of 1 mol L^{-1} NaOH was added into the separated supernatant to precipitate more $\text{Mg}(\text{OH})_2$. After shaken and left for another two hours, the samples were centrifuged, followed by the removal of the supernatant. Specifically, for the Na_2CO_3 digested samples, extra addition of MgCl_2 is required to ensure sufficient Mg to achieve co-precipitation with respect to silicon. For samples having low concentrated DSi, especially the 1-hour Na_2CO_3 digested samples and bottom water sample, an extra third round of co-precipitation was carried out with both MgCl_2 and NaOH added one after another. All the precipitates were entirely dissolved in 4 M hydrochloric acid (HCl) for the next step. To eliminate the isotope fractionation during precipitation, at least 95% of Si should be removed from the sample. For such purpose, the efficiency of Si removals (i.e., recovery rate) have been selectively checked by testing [DSi] of supernatants using the molybdate method (Strickland and Parsons, 1968) (Appendix Table.1).

The purification of redissolved silicon was performed using a BioRad AG50W-X12 cation-exchange resin (Fig.9 B). Each resin bed filled with 1ml BioRad AG50W-X12 is loaded three times with HCl for precleaning and twice with Milli-Q water for conditioning. Two microliters of samples diluted from HCl dissolved precipitates was loaded on the cation ex-change column and eluted using 3 ml Milli-Q water. The Si has

no charge so that it can readily pass through the resin with Milli-Q water while other interfering elements (mainly Mg^{2+} , Na^+) were captured. This kind of resin system could be reused as long as each round starts with precleaning using HCl (i.e., detailed recovery information could be seen in Sun et al., 2011).

2.6.2 Silicon isotope analysis

The Si isotope analyses were carried out on the Nu plasma (II) MC-ICP-MS (at Vegacenter, the Swedish Museum of Natural History, Stockholm) (Fig. 9 C). The 1.5 ppm Si solutions were introduced into the plasma via an Apex HF Desolvator equipped with a PFA nebulizer using 100 $\mu\text{L}/\text{min}$ uptake rate. The sensitivity for element Si with m/z of 28 is around 2 to 2.5 V/ppm. samples and standards measured at 1.5 ppm Si ($53.57 \mu\text{mol L}^{-1}$ Si) in 0.12 M HCl.

The isotope compositions were measured using a standard-sample-standard bracketing technique. Briefly, analyses consisted of 2 blocks and 18 cycles per block. A 75 sec wash cycle between samples and standards, NBS-28 (a universally used zero-reference material for silicon isotopes and has a comparable Si isotope composition to that of Caltech Rose Quartz). Other standard materials such as the Big-Batch and diatomite with an isotopic composition different than NBS-28 have been employed as secondary reference materials. Each sample was measured 3 times with NBS 28 measured 4 times, which resulted in an error of 0.10‰ (2σ ; double of standard deviation, hereafter) for $\delta^{29}\text{Si}$ and 0.13‰ for $\delta^{30}\text{Si}$ (Eq.5; Appendix Table.1). The detailed measurement procedure has been documented in Sun et al. (2018). Additionally, good reproducibility of the measurements is confirmed by comparison with data measured by other labs. The external reproducibility shown for the other standards is further summarized in Table 2.

Table 2. Summary of measurements of Si standards by MC-ICP-MS employed in this study in comparison to other published data (Reynolds et al., 2007; Grasse et al., 2017).

Sample	$\delta^{29}\text{Si}$	2σ	$\delta^{30}\text{Si}$	2σ	n
Diatomite	0,64	0,10	1,29	0,13	22
Diatomite ¹	0,64	0,07	1,26	0,10	100
IRMM-018	-0,82	0,12	-1,56	0,17	5
IRMM-018 ¹	-0,85	0,01	-1,65	0,01	740
Aloha1000m	0,70	0,11	1,29	0,28	3
Aloha1000m ²	0,65	0,08	1,24	0,20	217
Big Batch	-5,41	0,10	-10,62	0,14	8
Big Batch ¹	-5,35	0,15	-10,48	0,27	198

¹ Reynolds et al., 2007

² Grasse et al., 2017

2.6.3 Data reduction and analysis

As shown in Fig.10, the wet alkaline digestion experiment was set up in closed containers without replenishing DSi and BSi. This means that substrates (BSi, detrital clay and authigenic clay) from solid sediment are continuously removed to increase the DSi concentration in the alkaline solution, but never undergoes any exchange with an outside system. According to the pattern observed by DeMaster (1979), the one hour digested DSi is totally attributed to be the dissolution of BSi. Therefore, the pattern of $\delta^{30}\text{Si}_{1\text{hr}}$ are able to represent the isotope signatures of BSi. Therefore, as the bath time going by, diversiform solid phase silicon, including BSi, detrital clay mineral and authigenic clay mineral, were extracted and continuing mixed. In another word, increasing amount of dissolved clay minerals were continually mixed with BSi-originated DSi as time goes on during digestion. In order to observe this phenomenon, two notations, NonBSi_A and NonBSi_B, are introduced as shown in Fig.10, with the removal of BSi-originated DSi component from the extracted solutions achieved by mixing model (Eq.20 and Eq.21).

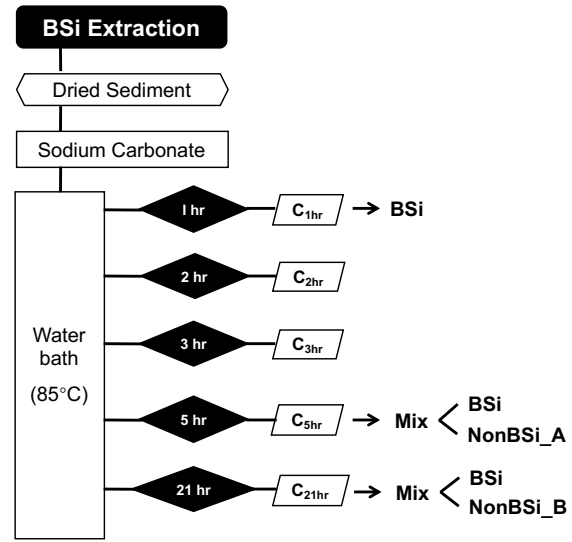


Fig.10 Wet alkaline digestion scheme.

$$\delta^{30}\text{Si}_{5\text{hr}} \times C_{5\text{hr}} = \delta^{30}\text{Si}_{\text{BSi}} \times C_{\text{BSi}} + \delta^{30}\text{Si}_{\text{NonBSi_A}} \times C_{\text{NonBSi_A}} \quad (15)$$

$$\delta^{30}\text{Si}_{21\text{hr}} \times C_{21\text{hr}} = \delta^{30}\text{Si}_{\text{BSi}} \times C_{\text{BSi}} + \delta^{30}\text{Si}_{\text{NonBSi_B}} \times C_{\text{NonBSi_B}} \quad (16)$$

where:

C_{BSi} has been calculated by extrapolation (Fig.6) and $\delta^{30}\text{Si}_{\text{BSi}}$ approximates $\delta^{30}\text{Si}_{1\text{hr}}$.

$\delta^{30}\text{Si}_x$: isotope ratio ‰, with the subscript 'x' denoting different components, including BSi, 5 hours extracted silicon, 21 hours extracted silicon, NonBSi_A and NonBSi_B.

C_x : concentration $\mu\text{mol/g}$, with x representing the same as above.

NonBSi_A: 5 hours extracted non-biogenic mineral.

NonBSi_B: 21 hours extracted non-biogenic mineral.

A caution should be taken that 5hrs-extracted DSi is a mixture of BSi-originated DSi and the DSi added over 4 hours (i.e., from 1hrs to 5hrs), while 21hrs-extracted DSi is a mixture of BSi-originated DSi, NonBSi_A-originated DSi and the DSi added over the next 16 hours (i.e., from 5hrs to 21hrs). Furthermore, NonBSi_A and NonBSi_B still both represent two mixtures rather than two categories of clay mineral. Their characteristics are derived from the total extracted clay mineral in different extraction time intervals. As the mass conservation, concentrations of extracted solution can reflect the combination of BSi concentrations and variable amounts of clay continually added:

$$C_{5hr} = C_{BSi} + C_{NonBSi_A} \quad (17)$$

$$C_{21hr} = C_{BSi} + C_{NonBSi_B} \quad (18)$$

3 Results

3.1 Pore water chemistry

3.1.1 DSi distribution

The pore water DSi concentrations vary with depth by more than an order of magnitude from 47.5 to 594 μM (Fig.11 A). Above 30 cmbsf, there is a maximum at 15 cmbsf (centimeter below the seafloor), albeit very weak. The strongest vertical gradients, however, is towards the sediment-water interface, and the 25 cm depth may represent a significant minimum in concentrations (see further discussion below). Below 25 cm depth, the concentration of DSi increases again remaining fairly stable between 30 and 60 cmbsf and approaching a high value (496 μM) at 40 cmbsf. Owing to the lack of a pore water sample at 65 cm depth, there might be a trend that continuous replenished DSi is reaching value up to the highest (593 μM) or might be a decline. In any cases, the pore water DSi concentration is likely to approaching an asymptotic value with depth.

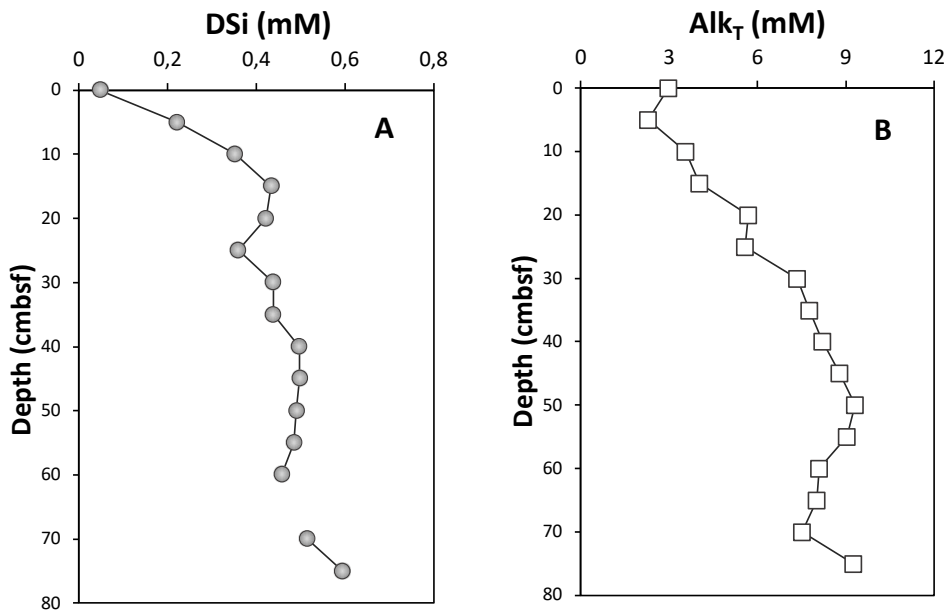


Fig.11 Pore water chemistry of this study, including concentration variation of pore water (0-75 cmbsf) on DSi ($R^2=0.98$) (A) and carbonate alkalinity ($R^2=0.86$) (B).

3.1.2 Alkalinity distribution

The pore water total alkalinity (Alk_T) concentrations vary with depth ranging from 2.30 to 9.30 mM (Fig.11 B). There is a slightly drop of Alk_T from sediment-water interface to 5cm depth. Thereafter, there is a linear increase of Alk_T of pore water to the subsurface maximum of 9.30 mM at 50 cmbsf, despite an invariable value over 20 to 25 cm depth. Below that depth, a decrease rather than an approach to an asymptotic value occurs. In the sample at 75 cmbsf, the value of Alk_T suddenly peaks to 9.25 mM.

3.2 Solid phase chemistry

3.2.1 Biogenic silica (BSi)

The results of BSi determination have been summarized in Table 3. In the alkaline digestion procedure, the DSi concentrations increased with digestion time and shifted with depth (Fig.12) (Appendix Fig.1 and Fig.2). Recalling the method by which BSi content is determined mathematically, it is an average of two intercepts of linear regression analysis on silicate concentrations versus time using three points (i.e., 2 hrs, 3 hrs, and 5 hrs) and two points (i.e., 3 hrs and 5 hrs), respectively (e.g., Fig.6). BSi contents, as shown in Fig.13 (A), show considerable variations with depth, ranging from 2.07 to 0.460 wt.% dry weight, with the lowest value occurring occasionally at 5 cmbsf and the highest value peaking at 45 cmbsf. The profiles feature a conspicuous plateau (ca. 1.41 wt.%) for BSi content at 10-30 cm depth. Below 45 cm depth, the BSi content gradually decreases to 0.518 wt.%. The BSi accumulation rate varies in a similar way to the BSi concentration, ranging between 46.5 and 171 g SiO₂ m⁻² yr⁻¹ (Fig. 13 B). The profile also shows the lowest accumulation rate at 5cm depth (59.8 g SiO₂ m⁻² yr⁻¹), below which a relative high rate (avg. 106 g SiO₂ m⁻²yr⁻¹) is reached that remains constant until 30cm depth. The highest rate occurs at 45cm depth (168 g SiO₂ m⁻² yr⁻¹).

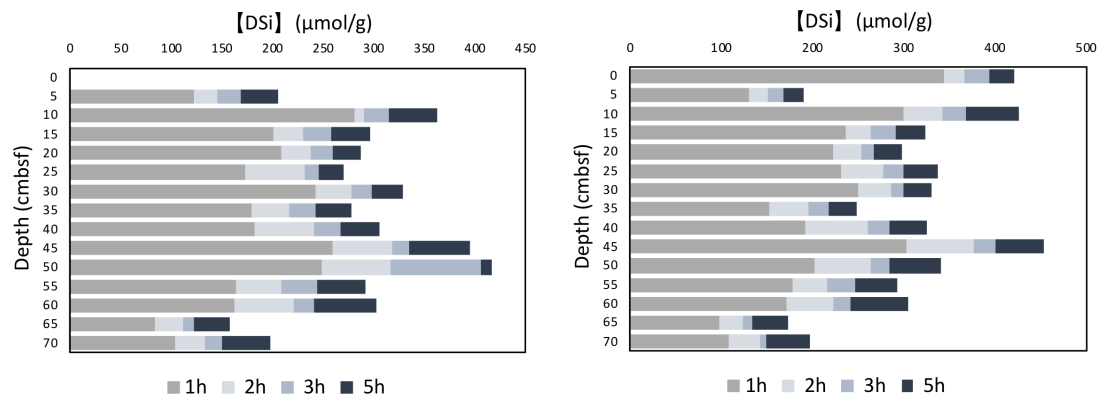


Fig.12 Concentration profiles of extractable silica as a function of extraction time and sediment depth, with each stack representing a time point.

Table 3. The results of BSi determination. Noted that concentration data of extractable silica are listed as a function of extraction time by sequential alkaline digestion (μM/g dry weight).

Depth (cm)	1hr (μM/g)	CV	2hr (μM/g)	CV	3hr (μM/g)	CV	5hr (μM/g)	CV	21hr (μM/g)	CV	BSi (SiO ₂ wt.% dry)	CV	J _{BSi} (g SiO ₂ m ⁻² year ⁻¹)
0	345	N/A	367	N/A	393	N/A	420	N/A	549	N/A	0.485	0.15	40.1
5	126	0.23	148	0.11	168	0.02	197	0.25	311	0.48	0.170	0.17	14.0
10	291	0.21	316*	0.51	342	0.49	395*	0.51	528	0.43	0.435	0.02	33.0
15	218*	0.51	246	0.43	274	0.37	309	0.28	453	0.12	0.410	0.20	28.4
20	215	0.19	245	0.20	264	0.09	292	0.11	414	0.02	0.416	0.09	30.5
25	202*	0.91	254*	0.58	273*	0.64	303*	0.70	429*	0.73	0.429	0.05	33.3
30	246	0.10	282	0.10	299	0.01	330	0.01	469	0.11	0.470	0.02	37.6
35	165*	0.51	206	0.31	230	0.34	263	0.34	397	0.40	0.321	0.18	26.5
40	187	0.14	250	0.24	275	0.19	316	0.21	464	0.22	0.407	0.09	36.5
45	281*	0.50	348*	0.53	368*	0.56	424	0.44	595	0.20	0.583	0.11	56.5
50	225*	0.64	291*	0.57	345*	1.11	378*	0.63	512*	0.66	0.557*	0.57	50.6
55	171	0.26	213	0.12	245	0.03	292	0.02	453	0.02	0.353	0.22	29.9
60	167	0.16	222	0.03	241	0.01	304	0.03	442	0.07	0.328	0.31	33.2
65	91	0.48	117	0.31	128	0.27	165	0.29	272	0.03	0.165	0.43	19.4
70	106	0.15	138	0.22	150	0.00	197	0.02	299	0.22	0.184*	0.59	16.6

CV: coefficient of variation, CV= σ/mean , while σ =(90% confidence interval)/2

*: CV>50%

J_{BSi}: BSi accumulation rate

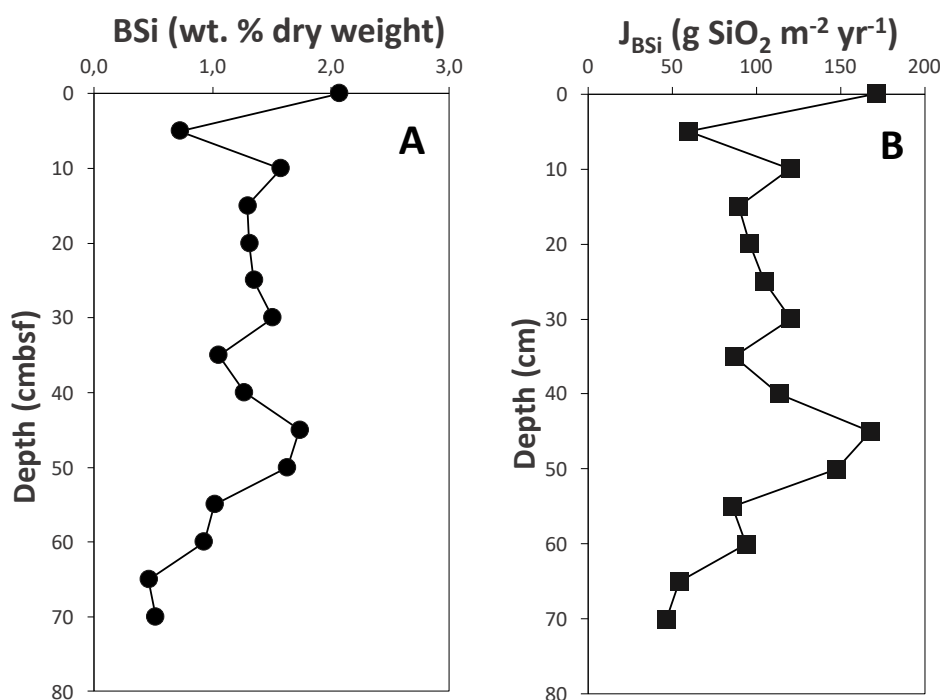


Fig.13 The distribution of BSi content as a function of depth. Left: BSi profile. Right: BSi accumulation rate distribution.

3.2.2 Reactive iron ($\text{Fe}_{\text{reactive}}$)

As mentioned in section 2.5.2, the dependence of the reactive iron extraction method on anoxic conditions was tested by comparing the amount of iron extracted under anoxic (i.e., using degassed buffer solution) or oxic conditions (using non-degassed buffer

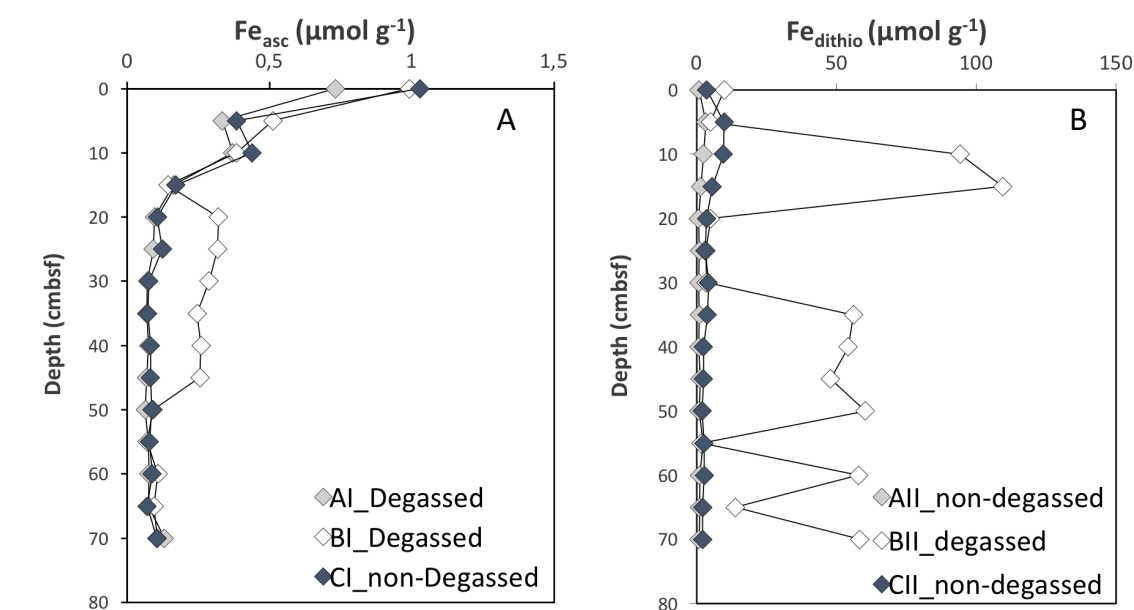


Fig.14 The triplicate measurements of reactive iron analysis. A) the ascorbic extracted iron distribution with depth. B) the dithionite extracted iron distribution. Note that the concentration unit is $\mu\text{mol g}^{-1}$ wet weight.

solution) (Fig.7). As shown in Fig.14 (A), the agreement between the triplicates (AI, BI and CI) of the ascorbic acid extraction procedure (Fe_{asc}) is very good. Despite a slightly higher value from 20 to 45cm depth for BI, these triplicates measurements all present an asymptotically decrease from a maximum (avg. $0.92 \mu\text{mol g}^{-1}$) to a minimum (avg. $0.080 \mu\text{mol g}^{-1}$). On the contrary with the other two groups (AII CII) whose buffer solution were both not degassed, the dithionite-extracted iron (Fe_{dithio}) with a degassed buffer solution named BII varied strongly, ranging from 1.74 to $109 \mu\text{mol g}^{-1}$ wet weight (Fig.14 B). Considering the compromising role of oxygen as an oxidant for reduced iron minerals, only the Fe_{dithio} concentrations of group B using a degassed buffer solution for iron extraction are considered reliable. Therefore, the total reactive iron content ($Fe_{reactive}$) is constituted by Fe_{asc} , which is the mean of three triplicates (AI, BI and CI) for Fe_{asc} ($2\sigma=0.24$), and Fe_{dithio} based exclusively on group BII (Fig.15 B).

Table 4. Results of reactive iron analysis. The concentration unit is $\mu\text{mol/g}$ wet weight.

Depth (cm)	Fe_{asc} ($\mu\text{mol/g}$)	CV (n=3)	Fe_{dithio} ($\mu\text{mol/g}$) ¹	CV (n=2)	Fe_{dithio} ($\mu\text{mol/g}$) ²	CV (n=1)	$Fe_{reactive}$ ($\mu\text{mol/g}$)	CV (n=3)
0	0,92	0,24	2,31	1,75	9,93	N/A	10,8	0,24
5	0,41	0,30	6,62	1,45	4,97	N/A	5,38	0,30
10	0,40	0,12	6,07	1,70	94,3	N/A	94,7	0,12
15	0,16	0,13	3,61	1,69	109	N/A	110	0,13
20	0,17	0,99	2,15	1,88	5,05	N/A	5,22	0,99
25	0,18	0,93	2,03	1,48	3,35	N/A	3,53	0,93
30	0,14	1,16	2,58	1,97	3,53	N/A	3,67	1,16
35	0,13	1,07	2,43	1,69	56,1	N/A	56,2	1,07
40	0,14	1,02	1,66	1,46	54,2	N/A	54,4	1,02
45	0,14	1,05	1,91	0,93	47,9	N/A	48,1	1,05
50	0,08	0,25	1,49	1,02	60,3	N/A	60,4	0,25
55	0,07	0,07	2,53	0,17	1,74	N/A	1,82	0,07
60	0,09	0,25	1,93	1,25	57,9	N/A	58,0	0,25
65	0,08	0,22	1,69	0,93	13,8	N/A	13,9	0,22
70	0,11	0,18	1,57	1,11	58,4	N/A	58,5	0,18

CV: coefficient of variation, $CV = \sigma/\text{mean}$, while $\sigma = (90\% \text{ confidence interval})/2$

¹: Dithionite extraction results derived from non-degassed duplicates.

²: Dithionite extraction results derived from degassed buffer solution.

$$Fe_{reactive} = Fe_{asc} + Fe_{dithio}$$

Based on the triplicate tests, $Fe_{reactive}$ is here defined as the sum of Fe_{asc} and Fe_{dithio} , with all of the data are summarized in Table 4 and Fig.13. As shown in Fig.15 (A), the trend of Fe_{asc} decreases significantly from the top of the sediment ($0.92 \mu\text{mol g}^{-1}$) to 15 cm depth ($0.16 \mu\text{mol g}^{-1}$), staying stable around $0.15 \mu\text{mol g}^{-1}$ from 15 to the bottom of the core. The profile of Fe_{dithio} shows low content over the upper 5 cm depth and switches several times between high and low values with increasing sediment depth (Fig. 15 B). At 10 cm depth it suddenly leaps by an order of magnitude from 4.97 to $94.3 \mu\text{mol g}^{-1}$, peaking to the maximum $109 \mu\text{mol g}^{-1}$ at 15cm depth. Thereafter, it remains low and jumps up again over the lower part (avg. $55.8 \mu\text{mol g}^{-1}$), except 55 cm depth ($1.74 \mu\text{mol g}^{-1}$) and 65 cm depth ($13.8 \mu\text{mol g}^{-1}$).

Since Fe_{dithio} exceeds Fe_{asc} by two orders of magnitude on average, the profile of $Fe_{reactive}$ is similar to the profile of Fe_{dithio} (Fig.15 C). It is divided into several zones, including two highly-concentrated zones over 10-15 cmbsf (avg. $102 \mu\text{mol g}^{-1}$) and 35-50 cmbsf (avg. $54.8 \mu\text{mol g}^{-1}$), and two depleted zones over 0-5 cmbsf (avg. $8.12 \mu\text{mol g}^{-1}$) and 20-30 cmbsf (avg. $4.14 \mu\text{mol g}^{-1}$). Bellow 50 cm, the profile fluctuates between the manually selected depth intervals (i.e., 5 cm).

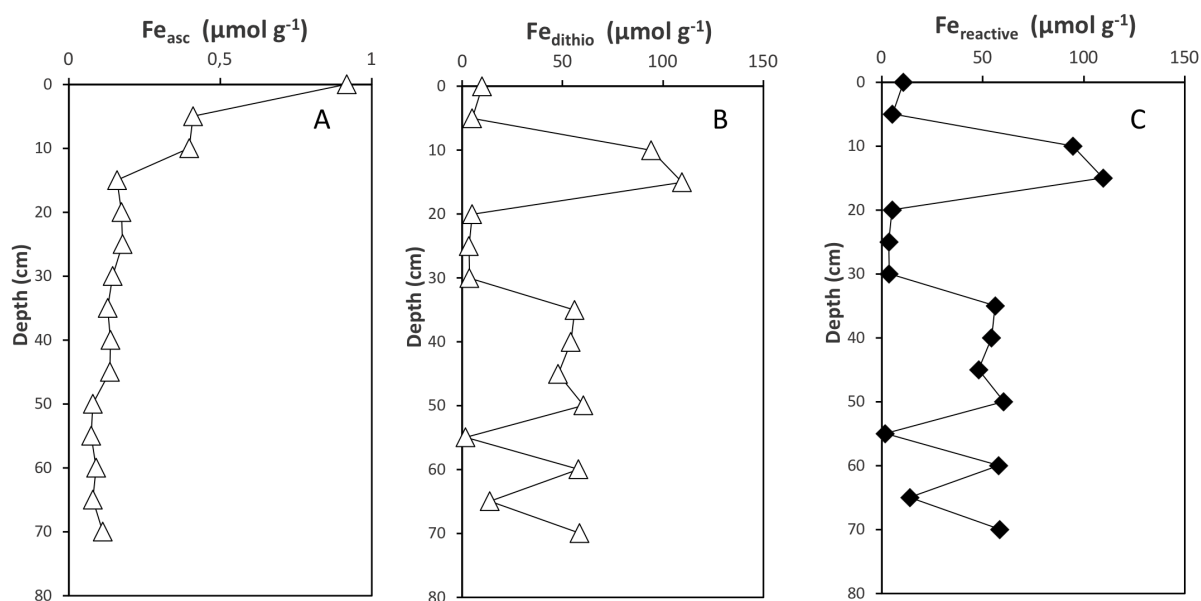


Fig.15 Results of reactive iron analysis. A) the ascorbic extracted iron (Fe_{asc}) distribution with depth. B) the dithionite extracted iron ($\text{Fe}_{\text{dithio}}$) distribution. C) total reactive iron ($\text{Fe}_{\text{reactive}}$), which is estimated as the sum of Fe_{asc} and $\text{Fe}_{\text{dithio}}$. Note that the concentration unit is $\mu\text{mol g}^{-1}$ wet weight.

3.3 DSi flux

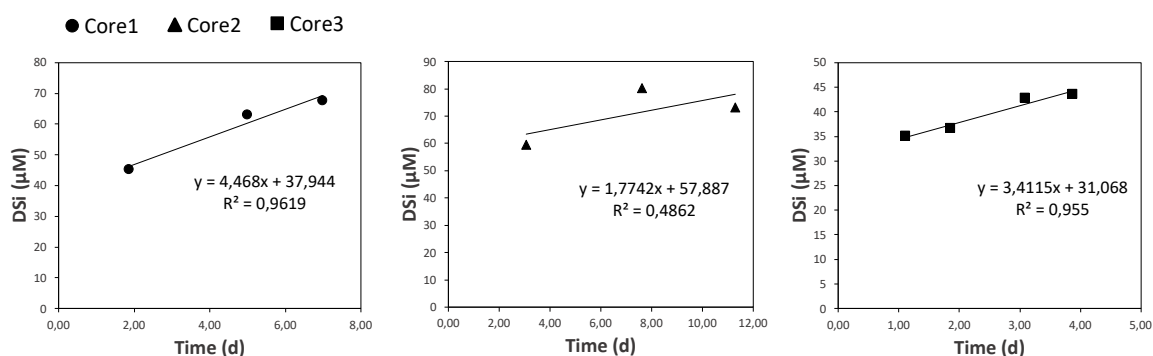


Fig.16 Benthic DSi profiles versus time in each core, respectively.

The DSi inventory in the water overlying the cores increased from 35.1 to 80.1 μM over time, as shown in Table 5. To deduce the DSi flux (J_{DSi}) the increase in the DSi inventory was taken a derivative with respect to time by linear regression, which yielded the gradient of DSi (dC_{DSi}/dt) that varied between 1.8 and 4.5 $\mu\text{M d}^{-1}$ (Fig.16). With $J_{\text{DSi}(\text{Core}_1)}$, $J_{\text{DSi}(\text{Core}_2)}$, and $J_{\text{DSi}(\text{Core}_3)}$ working as triplicates, $J_{\text{DSi}(\text{Core}_m)}$ (i.e., $m=1, 2$ or 3) can be inferred from the slope of linear regression of DSi versus time (day) that vary from 0.18 to 0.45 $\text{mmol m}^{-2} \text{d}^{-1}$ averaging at $0.32 \pm 0.14 \text{ mmol m}^{-2} \text{d}^{-1}$ (i.e., $n=3$).

In an alternative approach linear fitting regression have been further taken on the whole sample pool including the three cores (i.e., $n=10$) for greater statistically significance assuming the flux is of core-independent. This mean, the time-independent DSi flux was determined to be $0.43 \pm 0.19 \text{ mmol m}^{-2} \text{d}^{-1}$ ($R^2=0.74$; $n=10$) (Fig.17).

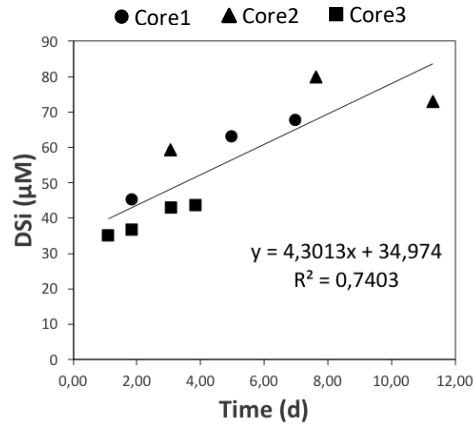


Fig.17 Benthic DSi profiles versus time.

Table 5. Summary of DSi fluxes and total oxygen uptake (TOU) during whole-core incubation.

Core ID	Time (d)	$\Delta[\text{O}_2]$ (μM)	[DSi] (μM)	TOU ($\text{mmol m}^{-2}\text{d}^{-1}$)	DSi flux ($\text{mmol m}^{-2}\text{d}^{-1}$)
				CI=9,97 ^b	2,10 ± 2,56
1	1,86	-171	45,3	4,56	0,45
1	5,00	-354	62,9		
1	7,00	-398	67,6		
2	3,05	-151	59,4	2,83	0,18
2	7,62	-321	80,1		
2	11,29	-381	73,1		
3	1,12	-160	35,1	10,73 ^a	0,34
3	3,09	-404	42,8		
3	1,85	-208	36,6		
3	3,87	-428	43,6		

^a the high TOU might be due to a visible organism living in the surface of the third sediment core.

^b CI: 90% confidence interval

3.4 Silicon isotope distribution

Silicon isotope compositions are reported in the $\delta^{30}\text{Si}$ notation as deviations of the measured $^{30}\text{Si}/^{28}\text{Si}$ from the international Si standard NBS28 in parts per thousand (‰) (Eq. 7) (Appendix Table.1). Error bars provided in the graphs (e.g., Fig.18 and Fig.19) correspond to the external reproducibility of the matrix standards ($2\sigma[^{29}\text{Si}] = 0.10$; $2\sigma[^{30}\text{Si}] = 0.13$) unless the uncertainties of the repeated sample measurements were higher.

For an overview of the isotope patterns within the sediment core, the profiles of $\delta^{30}\text{Si}$ of both porewater samples ($\delta^{30}\text{Si}_{\text{pw}}$) and extracted solid-phase samples ($\delta^{30}\text{Si}_{1\text{hr}}$, $\delta^{30}\text{Si}_{5\text{hr}}$ and $\delta^{30}\text{Si}_{21\text{hr}}$) are shown in Fig.18. The ranges in isotope composition in both phases are comparable, varying between 0.15 and 0.85 ‰ in porewater samples (Fig.18 A) and between 0.09 and 0.82 ‰ in the solid-phase samples (Fig.18 B).

As shown in Fig.18 (A), the pore waters have the lowest value around 0.15 ‰ in the deeper parts of the profile and maximum values of 0.85 ‰ at 10-cm depth. The profile shows an increase from the sediment-water interface downward with an isotope ratio of 0.45 ‰ in the bottom water to the maximum at 10 cmbsf, followed by varying values

between 0.52 and 0.75 ‰ over the 20 cm. Below 20 cm depth, the isotope value remains stable around 0.76 ‰, followed by a decrease to 0.59 ‰ at 50 cm depth and a notable drop to the minimum value of 0.15 ‰ at 60 cm depth. Due to a lack of porewater, no isotope information is available for the 65-70 cmbsf layer. At the bottom of the core the ^{30}Si composition increased again.

As shown in Fig. 18 (B), there are no significant differences between the extracted silicon isotope composition, averaging around 0.5 ‰, with $\delta^{30}\text{Si}_{1\text{hr}}$ averaging at 0.57 ‰, $\delta^{30}\text{Si}_{5\text{hr}}$ averaging at 0.53 ‰ and $\delta^{30}\text{Si}_{21\text{hr}}$ averaging at 0.38 ‰, respectively. In general, the three suites of data are intertwined along the sediment profile, with the trends of $\delta^{30}\text{Si}_{1\text{hr}}$ and $\delta^{30}\text{Si}_{5\text{hr}}$ most comparable ($p=0.589$) and the difference between $\delta^{30}\text{Si}_{1\text{hr}}$ and $\delta^{30}\text{Si}_{21\text{hr}}$ profiles greatest ($p=0.079$). At most of the depth intervals, the $\delta^{30}\text{Si}_{21\text{hr}}$ continually has the lightest value of these three groups, except 0 cmbsf (0.09 ‰) and 35 cmbsf where it shows the heaviest value (0.81 ‰).

The difference between NonBSi_A and NonBSi_B (as denoted in Fig.10 and illustrated in Fig.19) have been well distinguished on their isotope signatures according to Eq.20 and 21, with $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ ranging from -0.42 to 1.51 ‰ and $\delta^{30}\text{Si}_{\text{NonBSi_B}}$ ranging from -0.19 to 1.35 ‰ (Fig.19 A). The $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ fluctuated every 15-cm depth, with three significant maxima peaking at 1.51 ‰ (10 cmbsf), 1.49 ‰ (25 cmbsf) and 50 cm 1.20 ‰ (50 cmbsf) respectively. In contrasted to NonBSi_A, $\delta^{30}\text{Si}_{\text{NonBSi_B}}$ varied little with depth, on average 0.08 ‰, with the exception of samples in the top layer (0.79 ‰) and at 30-35 cm depth of the core where it reaches the maximum value of 1.14 ‰.

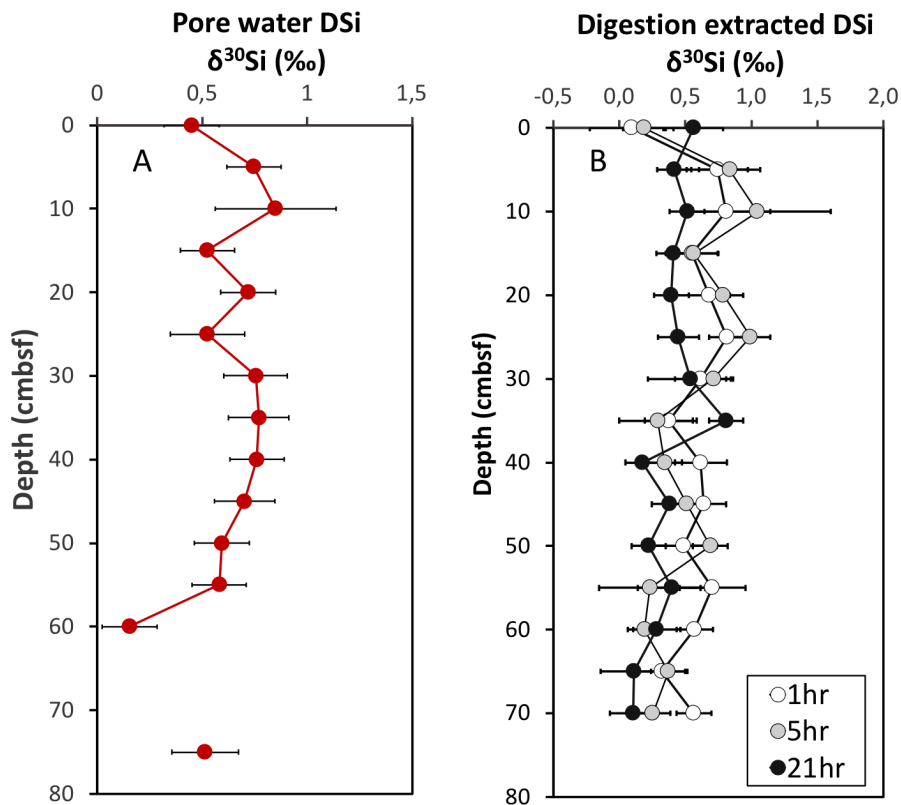


Fig.18 Isotope profiles of pore water samples (A), and DSi from solid phase sediment digestion (B).

Additionally, in terms of the DSi samples collected from the overlying water of the incubated cores, their Si isotope ratios range from 0.60 to 1.19 ‰ with an average of 0.83 ‰. The relationship between the overall isotope distribution and DSi is almost linear ($R^2=0.5102$), having a positive slope (53.9) (Fig.20 A). Whilst the linear relationship between the overall isotope distribution and O₂ uptake is inconspicuous ($R^2=0.1105$) (Fig.20 B).

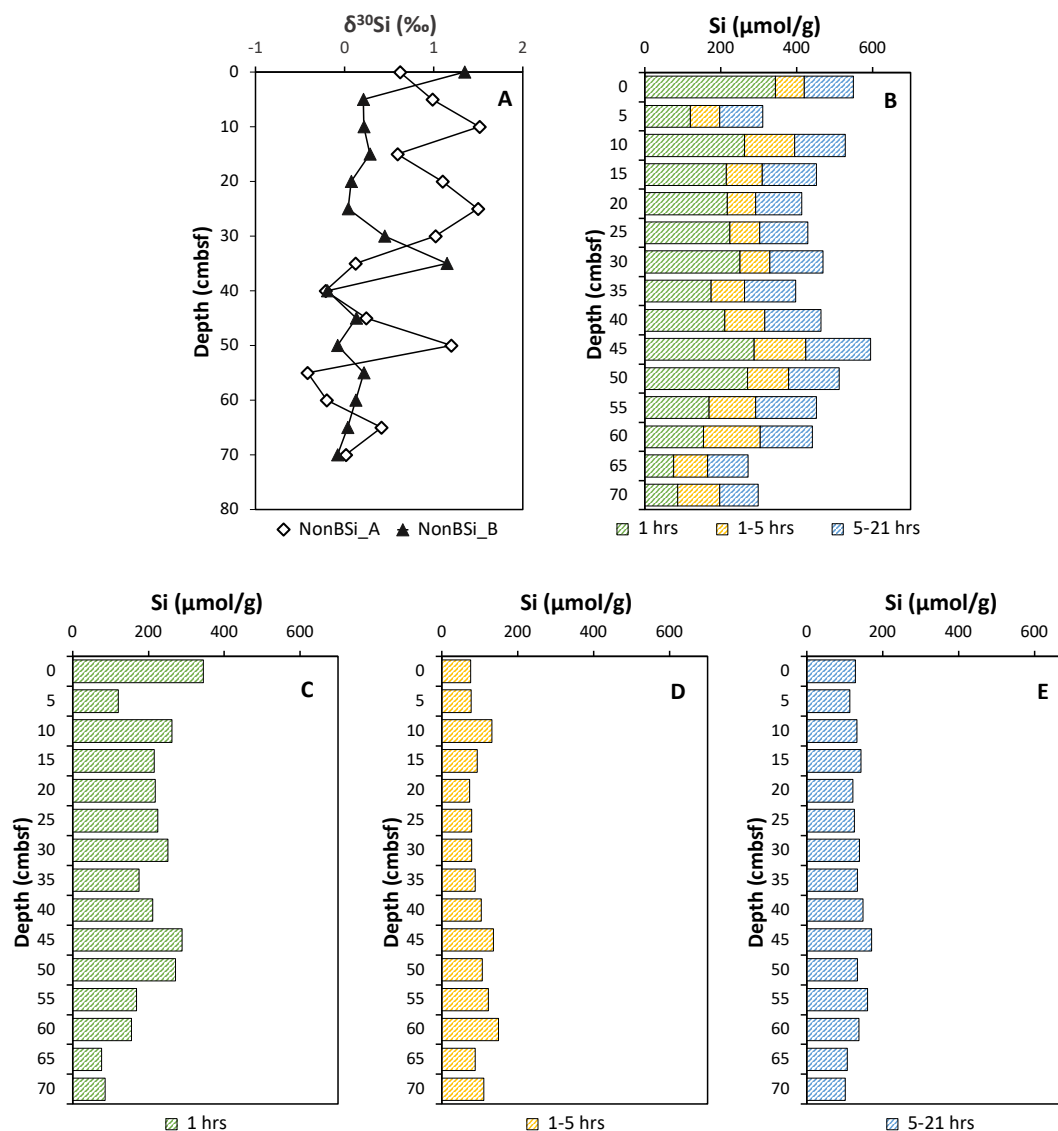


Fig.19 Isotope profiles of two components deduced from mixing model (A) and their concentration variations per depth (B) with C D and E present 1hrs, 1-5 hrs and 5-21 hrs extracted silicon, respectively.

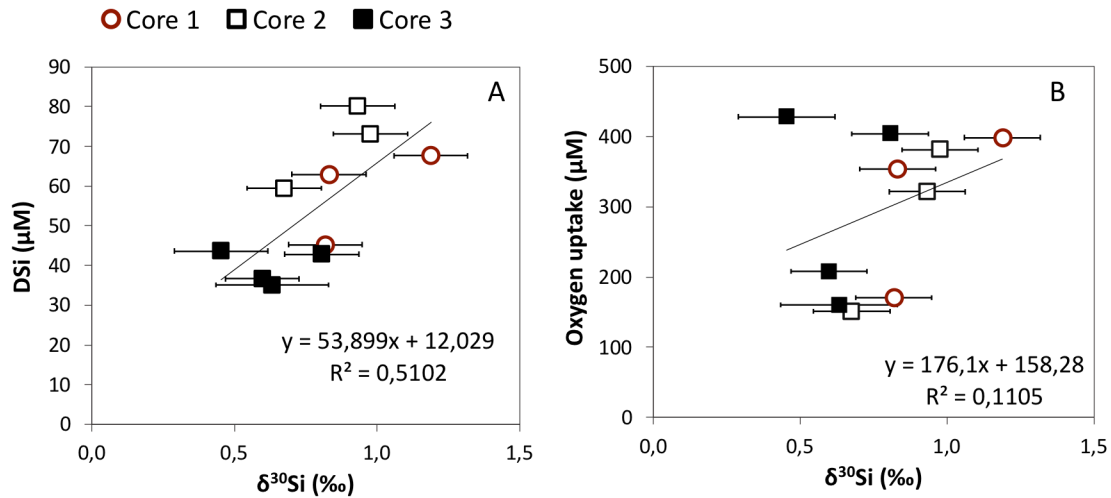


Fig.20 Isotope patterns on the DSi outflow and oxygen consumption from incubation experiment. A) Cross plot of DSi outflow versus $\delta^{30}\text{Si}$ composition. B) Cross plot of Oxygen uptake versus $\delta^{30}\text{Si}$ composition.

4 Discussion

4.1 Methodological considerations

In this study, sources of error on various data are various. In terms of directly measured data, including DSi, Alk_T , Fe_{asc} and $\text{Fe}_{\text{dithio}}$, their sources of error are commonly arisen from the preparation and analysis of the sample, with the error on $\text{Fe}_{\text{reactive}}$ is the sum of error on Fe_{asc} and error on $\text{Fe}_{\text{dithio}}$. However, since the contents of BSi were deduced from extrapolation by linear regression rather than measured directly, it is necessary to consider the effect of the mathematic calculation itself on overall accuracy and reproducibility. Because of this, the isotope compositions of BSi, and moreover, non-biogenic silicates which are deduced based on BSi content and BSi isotope composition (Eq.20 and Eq.21), are considered to have propagated errors that are the errors yielded by isotope measurement multiply the errors yielded by BSi measurement and mathematical derivation.

Moreover, low content of BSi can be a vital defect exaggerating errors generated by the deduction procedure of BSi. Original signal of $\delta^{30}\text{Si}_{\text{BSi}}$ in high BSi-content sediments is more likely to be preserved because of limited exchanging with ambient pore water and the relatively small fraction of authigenic silicate formations (Sutton et al., 2018). The BSi content within the sediment core of this study (0.17 - 0.58 wt.% dry weight), however, is too low to directly extract diatom particle for isotope analysis such as what Sun et al. (2011) did. The method applied in this study is doing isotope analysis on alkaline extracted Si solution, which is thus of an indirect measurement approach. The assumption used in this indirect approach is that the first 1hrs released DSi can be able to represent BSi. This assumption is based on what DeMaster (1981) suggested from experimental observations that are widely used by a number of studies (e.g., Pastuszak et al., 2008; Barão et al., 2015; Jakobsson et al., 2017). However, in this particular study, such low content of BSi may lead to an extra uncertainty of the feasible of this method.

Therefore, errors originated from the potential uncertainty of the method, which are further associated with $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{nonBSi}}$, cannot be ignored either.

Overall, in this study, using isotope data of BSi and non-BSi to interpret diagenetic alteration of silica introduces more uncertainty than using the concentration data themselves (i.e., $[\text{DSi}]$, $[\text{Alk}_T]$ and $[\text{Fe}_{\text{reactive}}]$) and using $\delta^{30}\text{Si}_{\text{pw}}$ that is directly analyzed in sediment-released pore water samples.

4.2 Preliminary quantification of silica early diagenesis

4.2.1 Coupling of benthic oxygen uptake and silica release

In this study, there are totally two outcomes of DSi flux from sediment upward into the sediment-water interface, including the whole-core DSi flux ($0.43 \text{ mmol m}^{-2} \text{ d}^{-1}$) observed by incubation (Fig.16) and the modeled DSi flux ($0.063 \text{ mmol m}^{-2} \text{ d}^{-1}$) calculated from the DSi profile which is going upward to the overlying bottom water (Fig.22). Comparing these two values, the latter is significant smaller (i.e., 85% less than the former). Such a difference might attribute to the simplification of the pure diffusion model which ignores the effects of negative advection, i.e. bioirrigation, and bioturbation, while boundary layer limited transport likely has a subordinate effect since there is no significant difference between DSi concentration in bottom water ($23.2 \mu\text{M}$) and the topmost sediment layer ($47.5 \mu\text{M}$). With both reasons together, it is expected that the seasonal in situ data is needed to be collected for producing more realistic constraint parameters.

Holstein and Hensen (2010) observed an inherent linkage of oxic respiration and BSi dissolution derived a simple empirical formulation relating the benthic Si flux to the oxygen flux. That model has been successfully applied by Seiter et al. (2010) on the southern Atlantic Ocean:

$$J_{\text{Si}} = 0.54 \times J_{\text{O}_2} \quad (19)$$

The application of oxygen fluxes as a proxy parameter to evaluate biogenic flux particles is based on the interrelation between the decay of organic carbon and the associated increase of the opal mineral surface area (Holstein and Hensen, 2010). However, such empirical correlation has not been validated globally. In the incubation experiments of this study, J_{Si} ($0.43 \text{ mmol m}^{-2} \text{ d}^{-1}$; $0.16 \text{ mol m}^{-2} \text{ y}^{-1}$) is around 0.21 times of J_{O_2} ($2.10 \text{ mmol m}^{-2} \text{ d}^{-1}$; $0.77 \text{ mol m}^{-2} \text{ y}^{-1}$), with a rate of J_{DSi} to J_{O_2} (0.2) around 61% lower than the empirical rate (0.54). It was suggested by Seiter et al. (2010) that some regional low rate might be attributed to the high riverine input of Al, which reduces the solubility of BSi. In this case, the rate is even lower than the lowest rate derived by Seiter et al. (2010) which is 0.31. Therefore, there must be another prominent sink of DSi suppressing DSi flux out of the sediments. This assumption is further consistent with a trend observed in this incubation experiment that DSi flux are prone to be isotopically heavy, which is inverse with the condition observed by Grasse et al. (2013) (i.e., benthic dissolution of BSi leads to a flux of isotopically light silicon from the sedimentary pore waters into the bottom water).

On the other hand, when plotting the isotope data with DSi as well as oxygen uptake, they have both shown a positive correlation ($R^2_{\text{DSi}}=0.51$; $R^2_{\text{oxygen}}=0.11$) (Fig.21). Such results are strongly related to the fact that theoretically, the produced DSi should be

isotopically heavier and heavier with the increasing DSi concentration in the water overlying the core, with the isotope composition of bottom water sample (0.45 ‰) serves as the lowest starting value. This may be explained that the dissolution of sedimentary BSi is accelerated with the decay of organic carbon. In order to better decipher the relationship between the flux factors, one more cross plot is performed on Fig.21 (C), where E_{SIO} is introduced (i.e., $E_{SIO} = \sqrt{(DSi) \cdot (O_2 \text{ uptake})}$ (μM)). Judging from the distribution of Fig.21 (B), there is one outlier, which was measured in core 3 far away from the trend line, which may be related to the interference by the visible organism (Table 5). With this outlier eliminated, as shown in Fig. 21 (D, E and F), the linear relationships between DSi and $\delta^{30}Si$ ($r^2=0.518$), between oxygen uptake and $\delta^{30}Si$ ($r^2=0.549$), and especially between E_{SIO} and $\delta^{30}Si$ ($r^2=0.710$) all strengthened, showing that the isotope distribution is more linearly correlated with the oxygen weighted DSi ($r^2=0.71$) than single DSi flows without oxygen weighting, with the slope positive (170.5).

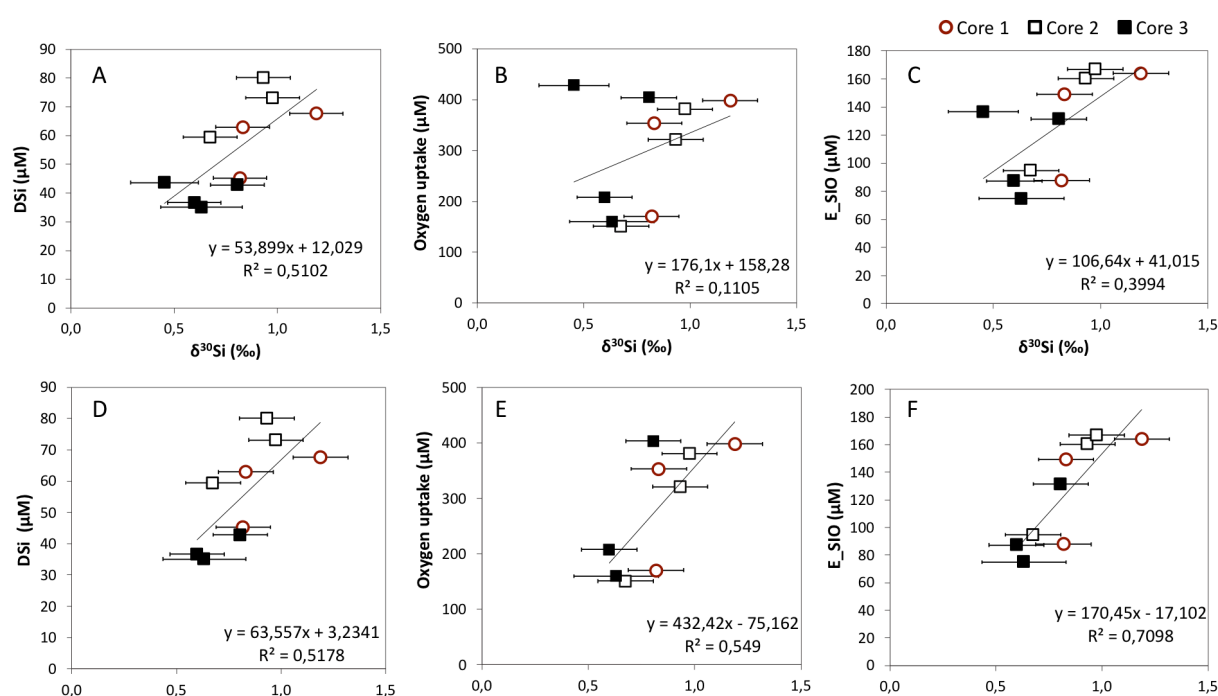


Fig.21 Isotope patterns on the DSi and oxygen uptake from incubation experiment. A) Cross plot of DSi versus $\delta^{30}Si$ composition. B) Cross plot of Oxygen uptake versus $\delta^{30}Si$ composition. C) Cross plot of E_{SIO} versus $\delta^{30}Si$ composition (i.e., where $E_{SIO} = \sqrt{(DSi) \cdot (O_2 \text{ uptake})}$ (μM)). While plot D, E and F is the correlated plots of A, B and C respectively, without one outlier.

4.2.2 Particular diffusion zones of DSi and Alk_T

As the correlated relationship between organic carbon degradation pathway and alkalinity generation along sediments elaborated in Table 1, alkalinity in pore water is strongly related to the organic carbon degradation, with the aerobic respiration reaction having negative effect on it and anaerobic mineralization reactions having positive effect. In general, alkalinity profiles in sediments appear to be increasing gradually with depth, strengthen with sulfate reduction (Schulz, 2006; and references therein). Hence two abnormal zones where alkalinity declines have been noted, including 20-30 cmbsf and 50-75 cmbsf respectively.

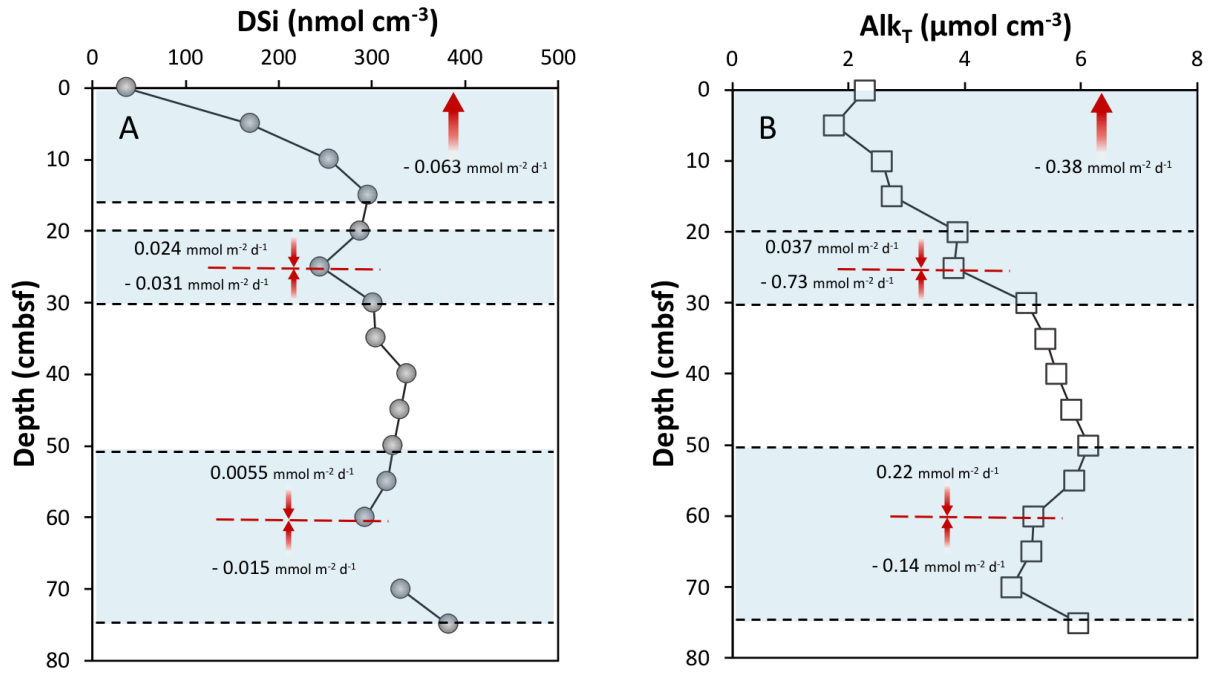


Fig.22 Molded Fickian diffusion fluxes of DSi (A) and alkalinity (B) coupled with corresponding measured concentrations. The DSi and alkalinity profiles have been normalized into per one cubic centimeter, while fluxes were calculated over particular zone illustrated by blue shallow.

Moreover, assuming under steady state condition, i.e. the concentration of porewater silica is not changing with time, diffusive flux of DSi and alkalinity (J_{DSi} and J_{Alk}) can be both modeled based on Fick's first law (Eq.4) (Schulz, 2006). Based on this, by calculating the linear diffusive flux between each depth interval, a mathematic model of first diffusion fluxes, J_{DSi} and J_{Alk} , were produced. In terms of alkalinity, Two assumptions have been taken on J_{Alk} , which are i) Alk_T is equal to carbonate alkalinity, ii) and pore water pH is 7.5, i.e. the dynamic range for pH commonly observed in marine waters and sediments ranging between 7.5 to 8.2 (DeMaster, 2013). Under these assumptions, a specific dissociation equilibrium proportion of different carbonate species is established (i.e., $\text{H}_2\text{CO}_3:\text{HCO}_3^-:\text{CO}_3^{2-}=0.65:0.935:0$). Therefore, bicarbonate (HCO_3^-) is the only substance concerned when doing modeling (Fig.22 B). In like manner, assuming a porewater temperature of 5°C, the DSi diffusion coefficient of the sediment ranges from $3.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ to $3.72 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. By calculating the linear diffusive effects over particular depth interval, a mathematic model of J_{DSi} along the sediment core was produced (Fig.22 A).

Changes of concentration profiles can reflect a variety of processes (i.e., consumption, production and diffusion transport) happening simultaneously in sediment (Schulz, 2006). These processes can be further interpreted by a change in the flux. As shown in Fig.22, a positive flux reflects a downward flux into the sediment section while the negative flux reflects an upward flux relative to the sediment, as illustrated with red arrows (Fig.22). By taking linear regression on the DSi concentration gradient over 0-15 cmbsf, the DSi flux of the sediment upward into the sediment-water interface are calculated to be $-0.063 \text{ mmol m}^{-2} \text{ d}^{-1}$ ($R^2=0.98$), with the alkalinity flux being $-0.38 \text{ mmol m}^{-2} \text{ d}^{-1}$ ($R^2=0.78$) according to the alkalinity concentration gradient over 1-20 cmbsf (Appendix, Fig.3). These concentration gradients in the sediment top-layer sections are suggested to support a steady accumulation condition of the studied area,

which is more stable comparing to transport sediment bottom. Therefore, it further validates a precondition of interpretations on solid phase constituents which are believed to accumulate continually and remain robust without turbulence.

4.2.3 Implications of $\text{Fe}_{\text{reactive}}$ on BSi solubility

BSi dissolution is found to be increased in the presence of high iron oxide concentrations (Mayer et al., 1991). There has been numerous experimental and field measurements consistently supported an association of BSi and $\text{Fe}_{\text{reactive}}$ during early diagenesis, the presence of even minor Fe can influence BSi dissolution owing to formations of mineral coatings and authigenic silicates (Rickert et al., 2002; Dixit and Van Cappellen, 2002; Michalopoulos et al., 2004). Therefore, it is valuable to relate the reactive iron shift to the effect of BSi solubility. According to März et al. (2008), $\text{Fe}_{\text{reactive}}$ is termed as the sum of ascorbate and dithionite-extracted Fe, which are amorphous Fe (oxyhydr)oxides (Fe_{asc}) and crystalline Fe (oxyhydr)oxides (Fe_{dith}), respectively. In this study, crystalline Fe (oxyhydr)oxides (Fe_{dith}) appear to be the main content of $\text{Fe}_{\text{reactive}}$. Since the quantity of Fe_{dith} is hundred times larger than the Fe_{asc} and the trend of $\text{Fe}_{\text{reactive}}$ is highly controlled by Fe_{dith} , it is necessary to put Fe_{asc} individually along with $\text{Fe}_{\text{reactive}}$, as shown in Fig.23 (A).

As shown in Fig.23, positive correlations between decreased $\text{Fe}_{\text{reactive}}$ contents and decreased BSi and probably DSi as well can be found in specific intervals. On one hand, when focusing on the 10-30 cmbsf interval, it is interesting to note that $\text{Fe}_{\text{reactive}}$ is extremely high at upper part of this zone (10-15 cmbsf), while almost depleted at lower part (20-30 cmbsf). From 0-15 cmbsf, the Fe_{asc} component is also progressively declining into a relative low content with respect to its initial value. Together, it might imply a rapid consumption of the iron in such depth, where the trend of DSi bends back at 25 cmbsf with the content of BSi also curving back slightly; On the other hand, below 30 cm depth, the drop of $\text{Fe}_{\text{reactive}}$ happened twice from 50 to 55 cmbsf and from 60 to 65 cmbsf, respectively. These points are somehow correlated to lower trends of BSi content at the same depth while DSi also declines from 50 to 55 cmbsf. These phenomena are supposed to be related to two hypothetic scenarios. i) First, it might be related to the Fe-coating effects leading to a significant decrease of alkaline extractable BSi, which also can inhibit BSi dissolution into pore water, resulting in a decline of porewater DSi at the same depth. This is suggested to be further verified by using the boiling HCl (hydrochloric acid) method to eliminate interference of such coating-effect (e.g., Ku and Walter, 2003). ii) Second, it might be implications of reverse weathering processes, which is stated by Michalopoulos and Aller (2004) with the capacity on promoting $\text{Fe}_{\text{reactive}}$ consumption, BSi dissolution, and DSi utilization.

However, when put insight into 35 to 50 cmbsf, the second-high concentration plateau of $\text{Fe}_{\text{reactive}}$ is neither correlated to the change of BSi nor correlated to the DSi concentration. This phenomenon is thereby supposed to be unrelated to the reverse weathering. Considering there might also be some portion of acid volatile sulfide (AVS) such as greigite Fe_3S_4 or pyrrhoite Fe_{1-x}S , extracted from the dithionite extraction due to low pH (i.e., 4.8) (März et al., 2008). An explanation hence arises that over this deeper depth interval (35-50 cmbsf), the stability of $\text{Fe}_{\text{reactive}}$ (avg. $50 \mu\text{mol g}^{-1}$) mainly depends on a dynamic balance that microbe-mediated iron reduction consuming iron (oxyhydr)oxides and sulfide produced during sulfate reduction reducing the stability of

iron (oxyhydr)oxides with AVS formed from sulfide and iron (oxyhydr)oxide and misdeemed for $\text{Fe}_{\text{reactive}}$ (Latour et al., 2018).

4.2.4 Implications of DSi concentration and BSi content

Generally, for a substance that is constantly released from sediment to pore water, the profile of a DSi concentration gradient is convex-shaped and eventually attains to an asymptotic value (Schulz, 2006). In this study, however, over 15-40 cmbsf interval,

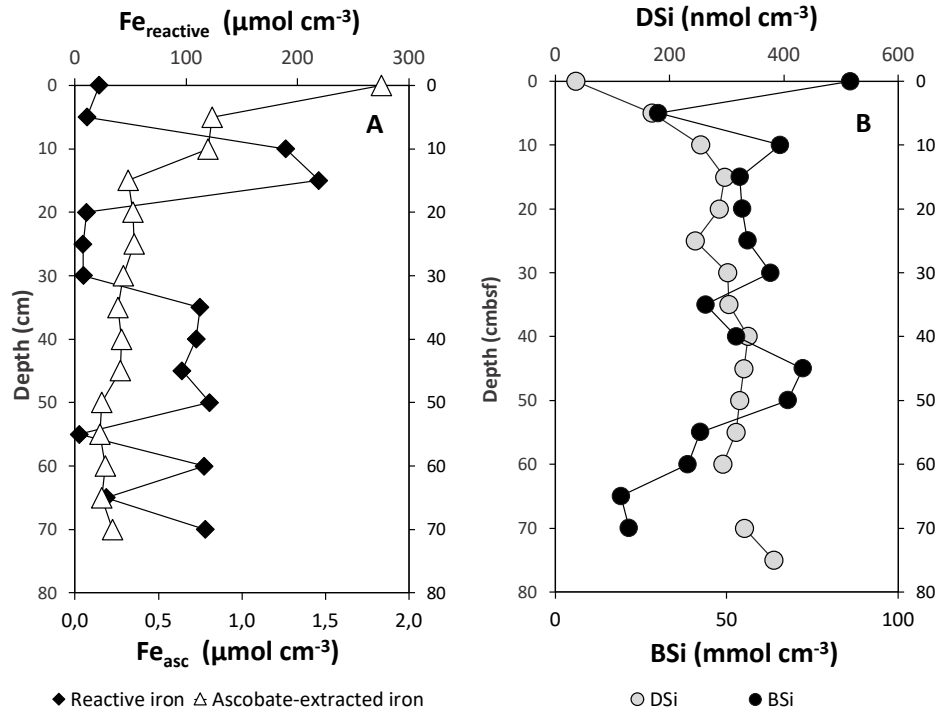


Fig.23 The distribution of reactive iron (A) and silica in forms of DSi and BSi (B) as a function of depth.

particularly in the 20-30 cmbsf layer, there are some distinct reactions taking place that result in an abnormal decrease in the DSi concentration, which cause fluxes in both the upward (i.e., $-0.031 \text{ mmol m}^{-2} \text{ d}^{-1}$, from 30 cmbsf to 25 cmbsf) and downward (i.e., $0.024 \text{ mmol m}^{-2} \text{ d}^{-1}$, from 20 cmbsf to 25 cmbsf) direction (Fig.22 A). This phenomenon is concurrent with a stagnant Alk_T profile with J_{Alk} closed to zero over 20 to 25 cmbsf (i.e., $0.037 \text{ mmol m}^{-2} \text{ d}^{-1}$) comparing to the upward flux from 30 to 20 cmbsf (i.e., $-0.74 \text{ mmol m}^{-2} \text{ d}^{-1}$) (Fig.22 B). Considering the early diagenesis pathways (Table 1), alkalinity profiles should be progressively increase in sediments. This excursion might reflect a consumption of Alk_T occurring at 25 cmbsf. Furthermore, this kind of suspicion is also in line with the steep declined $\text{Fe}_{\text{reactive}}$ profile over 20-30 cmbsf (Fig.23 A). Therefore, it is suspected that Si is consumed in this interval by a process that not only simultaneously neutralizes the alkalinity in the same interval but also links to a consumption of $\text{Fe}_{\text{reactive}}$ – in other words a process similar to reverse weathering. Such abnormal conditions occur again at deeper zone of the sediment (55-70 cmbsf), where almost the same situation is observed, i.e., a decrease of DSi coupled with a stagnant Alk_T and a drop of $\text{Fe}_{\text{reactive}}$ at 55 and 65 cmbsf.

To gain a better understanding of these hot spots (20-30 cmbsf and 55-70 cmbsf), BSi combined with DSi has been further interpreted, as solid phase sediment is an

indispensable aspect of early diagenesis. As shown in Fig.23 (B), plotting DSi and BSi profiles together, it is clearly that their trends differ along with depth. Such uncorrelation is reasonable because of the different conservation mechanism between dissolved constituent and solid particles (Dixit et al., 2001). When put insight into relative movement, it appears to be stable from 20 to 30 cmbsf. This phenomenon might be explained as a dynamic scenario with two combined processes where BSi is dissolved into DSi and porewater DSi is further removed by authigenic silicates formation. This explanation is in line with experiments carried out by Dixit et al. (2001) which shows that precipitation of authigenic silicates may prevent the pore waters from reaching equilibrium with DSi. To date, although the Si solubility of authigenic silicates is still poorly investigated, a 150 to 300 μM lower solubility of authigenic aluminosilicates compared to amorphous BSi (ca. $[\text{DSi}]=1\text{mM}$) is observed by Dixit et al. (2001) in a deep-sea sediment in the Southern Ocean. In this consideration, low concentration of DSi in porewater combined with relative high content of BSi in solid phase may imply a reverse weathering process over 20-30 cmbsf and 45-50 cmbsf in this study. Furthermore, an abnormal declined DSi concentration combined with a slightly increase of BSi content at 25 cmbsf appears to coincide with the demonstration that the solubility of biogenic silica is reduced with authigenic silicates formation due to their capability of forming coatings on BSi (Hurd, 1973; Michalopoulos and Aller, 2004).

On the other hand, BSi content has much faster decrease rate than that of DSi over 55-70 cmbsf, and it is likely that most of the DSi at 60cmbsf is supported by the upward flux from deeper part of sediment ($-0.015 \text{ mmol m}^{-2} \text{ s}^{-1}$) and downward flux from upper section ($0.0055 \text{ mmol m}^{-2} \text{ s}^{-1}$) rather than in situ BSi dissolution (Fig.22 B). Therefore, two assumptions are arisen here. i) First, the original BSi accumulation might be too low to stimulate the authigenic silicates formation (i.e., reverse weathering), while DSi is in equilibrium with BSi without any other utilization. However, this explanation can not be well supported owing to the low concentration of DSi in this sediment layer with respect to the solubility of BSi (i.e., 1mM; Dixit et al., 2001). ii) Second, more likely, a large fraction of BSi dissolved may produce plenty amount of DSi at such bottom section of sediment which is however transient and transformed into other poorly soluble phases rapidly. Nevertheless, this interpretation is very preliminary and requires further support of silicon isotope signatures.

Additionally, the significant low BSi content at 5 cmbsf could be real or just an outlier resulting from the subsampling of wet alkaline extraction of BSi. Given the solubility of BSi at such low pressure and temperature conditions (ca. 1 mM; Dixit et al., 2001; Loucaides et al., 2012), the low concentration of DSi in pore water near the sediment surface (0-10 cmbsf) could be a dominant factor that accelerates BSi dissolution. A contradiction with the low BSi content should also be noticed that although the value of DSi at such depth is higher than 0 cmbsf, it is lower than 10 cmbsf, which not matches with the low level of BSi. Therefore abundant authigenic silicates formations have a high opportunity there of working as a sink for DSi which ought to be remarkable high at 5 cmbsf, which is also coherent with the low content of $\text{Fe}_{\text{reactive}}$ there. This hypothesis also needs to be further investigated with other data, especially the measurements of Al/Si and Ge/Si ratios in solid phases of sediments (e.g., Ozkan et al., 2014; Hamade et al., 2003).

4.2.5 Comparison with high resolution data

Moreover, in order to compensate for the lack of high-resolution data, the 75cm depth below sea floor (cmbsf) profile of DSi and Alk_T are displayed side by side with data of sediment (0-12 cmbsf) in the same location analyzed by Waldheim (2018) (Fig.24). These two profiles of DSi (I_a and II_a) both show increasing trends with depth, with the high-resolution data (Waldheim, 2018) revealing detailed gradient changes in the upper layer and our study showing an overall shift in a longer sediment record. By comparison, the seasonal difference between samples of this study (Nov. 2017) and Waldheim (2018) (May 2018) has been noted here, showing that DSi is ranging from 123 to 890 μM in spring while DSi is lower in winter, ranging from 47 to 594 μM . Furthermore, the diffusion rate of DSi during spring is significantly higher than the rate during winter. Based on temperature records from the Himmerfjären eutrophication study (www.ecology.su.se), the temperature of the deep water 20-30m in May 2018 (5°C) was slightly lower than Nov. 2017 (7.5°C). Therefore, this temperature factor might not be a significant reason because high temperature should promote BSi dissolution that takes place in sediments, although low temperature is a benefit for high oxygen solubility so that more organic mass could be decomposed. Therefore, the bloom of diatom in the spring water column might play as the main motivation, leading to higher DSi from more abundant fecal pellets of diatoms and enhanced dissolution of sinking opal in this season.

In addition, the porewater profile of dissolved iron and total alkalinity could explain the biogeochemical zonation to some extent. Production of dissolved iron indicates an iron reduction zone starting at 3 cmbsf with high consumption occurring below such depth, revealing the existence of a reaction that transforms dissolved iron into solid phases by precipitation, possibly precipitation of iron with sulfide originating from the bacterial sulphate reduction. Considering the thicker suboxic zone due to deeper mixing layer of

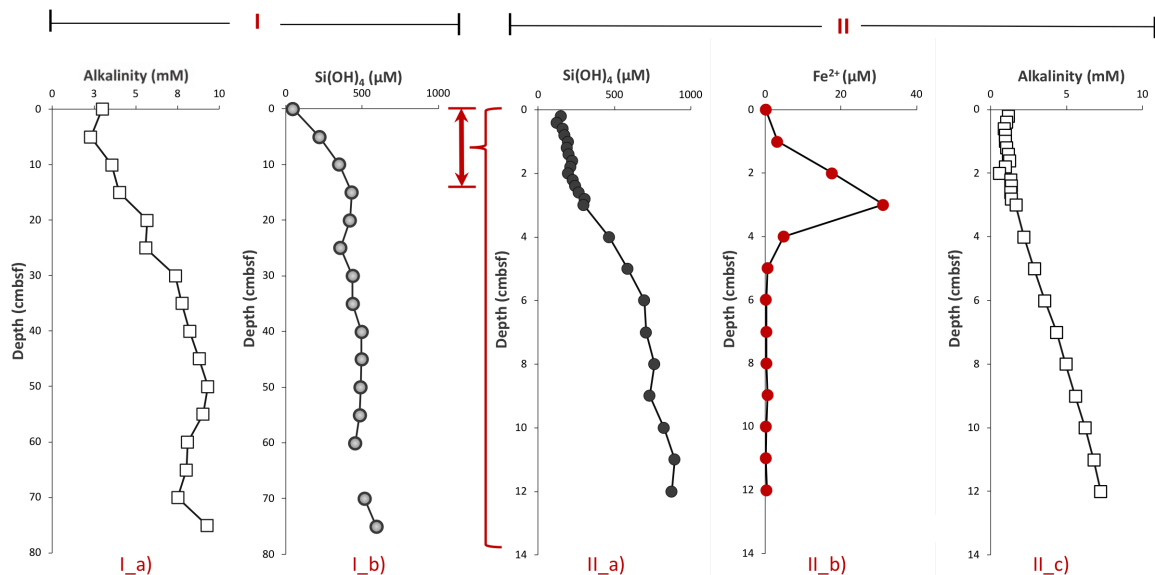


Fig.24 Comparison of pore water profiles between this study and Waldheim (2018). I) pore water profiles of this study, including concentration variation of pore water (0-75 cmbsf) on Alk_T (I_a) and DSi (I_b). II) pore water profiles quoted from Waldheim (2018), including concentration variation of pore water (0-12 cmbsf) on DSi (II_a), dissolved iron (II_b) and Alk_T (II_c).

water column in winter, the depth of the iron reduction zone might shift downward in this study. While in respect to the alkalinity variation measured by Waldheim (2018), it increases from 4 cmbsf below, which usually occurs overwhelmingly under anoxic conditions (Aller, 2014). This phenomenon is comparable of the Alk_T profile of this study as well, except the depth tends to be deeper, up to 10cmbsf.

4.2.6 Isotope indications from DSi and BSi

The Si isotope compositions of BSi and DSi in solid phase and pore water, respectively, have been determined to further investigate the diagenetic reaction of silica. As shown in Fig.25 (A), there is a covariance of $\delta^{30}Si_{BSi}$ and BSi content except the top layer (0-5 cmbsf) and 50-55 cmbsf. Hence, in general, the greater the contents of BSi the heavier their isotope values, which could be explained well by the increased utilization and accompanied decreased isotopic fractionation during diatom growth in water column (Milligan et al., 2004; Sutton et al., 2013). For the 0 cm depth sample, the lightest $\delta^{30}Si_{BSi}$ might imply a situation that an abundant proportion of BSi have not suffered from dissolution's fractionation, which might be due to the protection coating effect of aluminum (Al) released from detrital minerals (Presti and Michalopoulos, 2008). A caution should be seen here that significant high concentrated DSi released during 1 hrs water bath at this depth (Fig.19) might not be only attributed to BSi dissolution but also attributed to non-biogenic reactive silica from external sources.

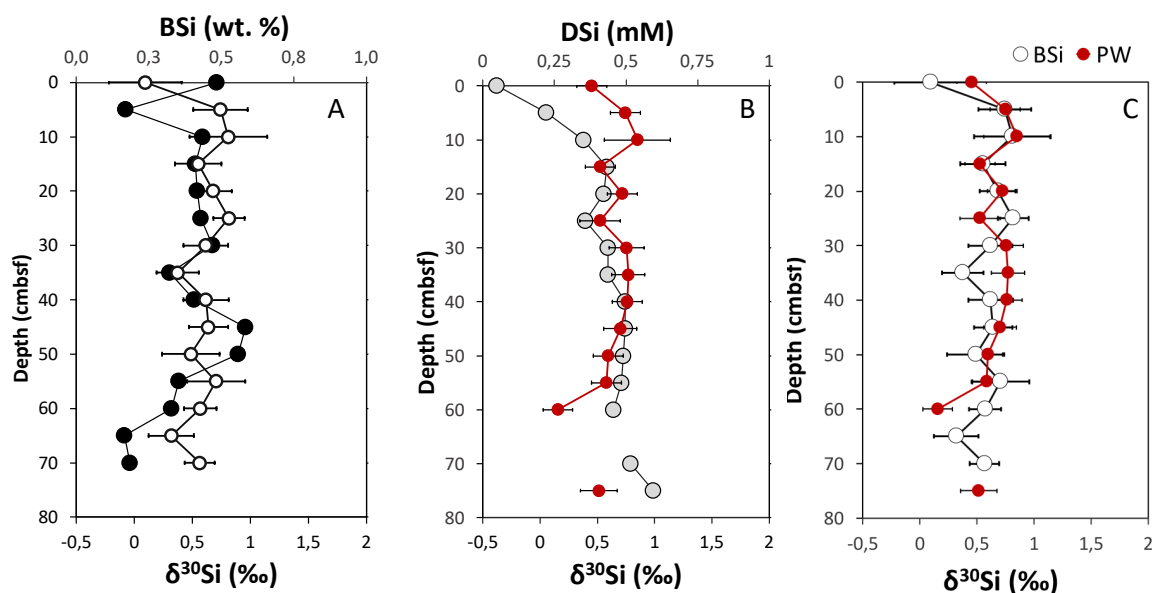


Fig.25 The distribution of silica in forms of DSi and BSi (A), Si isotope composition distribution of pore water (B), and Si isotope composition distribution of BSi and reduced non-biogenic silicates as a function of depth.

Unlike $\delta^{30}Si_{BSi}$, owing to the mobile property of DSi that cannot simply represent characteristics of one fixed depth, superimposed diffusion effects from upward and downward need to be put into consideration for calibrating interpretations as well. As shown in Fig.25 (B), there is a covariant of $\delta^{30}Si_{DSi}$ and DSi concentration ([DSi]) except for a 10 cm interval (10-20 cmbsf), with $\delta^{30}Si_{DSi}$ and [DSi] suddenly declining at 60 cmbsf. Isotope effect during BSi dissolution has been revealed to be insignificant, with only a slight enrichment of lighter isotopes in DSi been observed (Demarest et al., 2009; Egan et al., 2012; Wetzel et al., 2014). Hence, $\delta^{30}Si$ in DSi derived from BSi, must be

always similar to or even lighter than $\delta^{30}\text{Si}_{\text{BSi}}$. Comparing $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{DSi}}$ (Fig.25 C), at 0 cmbsf and 30-50 cmbsf, values of $\delta^{30}\text{Si}_{\text{DSi}}$ are heavier than values of $\delta^{30}\text{Si}_{\text{BSi}}$ values. Combined with the isotopic flux data having a tendency to become heavier (Fig.21), these differences might indicate that some of the BSi-originated lighter isotopes in DSi have been removed from lower layers where authigenic mineral precipitations (i.e., reverse weathering) are suggested to happen. This assumption could be supported by the hypothesis made by Tatzel et al., (2015) that precipitation of authigenic silicates is able to result in pore waters enriched in heavy silicon isotopes. Moreover, this assumption is further consistent with the collective observations (Ehlert et al., 2016) that the values of $\delta^{30}\text{Si}_{\text{DSi}}$ are of the same order or higher than the values of $\delta^{30}\text{Si}_{\text{BSi}}$ extracted from the same sediments at the Peruvian shelf, which was attributed to the authigenic alumino-silicate precipitation.

The silicon isotope fractionation in case of fixation of Si from DSi to many siliceous secondary minerals, which are often enriched in ^{28}Si , has been by far explored and suggested to be a kinetic isotope effect affected by non-equilibrium processes (Oelze et al., 2015; and references therein). Considering the kinetic isotope fractionation of Si during rapid precipitation, $\delta^{30}\text{Si}_{\text{DSi}}$ will be enriched with the heavy Si isotope. On the contrary, when such precipitation stops, the lighter Si isotope is retained in solution resulting in a lower $\delta^{30}\text{Si}_{\text{DSi}}$ composition. At 60 cmbsf, since the DSi is low mainly replenished by a downward flux from the upper layer plus an upward flux from the lower layer, and the $\delta^{30}\text{Si}_{\text{BSi}}$ is remarkable lower than $\delta^{30}\text{Si}_{\text{DSi}}$ at 65 cmbsf, it is reasonable to suspect that the $\delta^{30}\text{Si}_{\text{DSi}}$ at 60 cmbsf might indicate an exceptional stagnant precipitation, despite the $\delta^{30}\text{Si}_{\text{DSi}}$ at 65 cmbsf was absent.

4.2.7 Isotope indications from extracted non-biogenic silica

Considering the complexity of formations of authigenic clay (Fig.2), the time sequential extracted solid phase silica has also been taken isotopic analyzation. In addition to alterations of silica early diagenesis estimated from the relative shift of $\delta^{30}\text{Si}_{\text{BSi}}$ accompanied with $\delta^{30}\text{Si}_{\text{DSi}}$, Si isotope profiles in different phases influenced by various early diagenetic reactions between BSi and DSi, and between BSi and new authigenic silicate minerals are believed to play considerable important roles on determination of reverse weathering. Thereby isotope composition shifts of NonBSi_A and NonBSi_B were deduced and made for comparisons with BSi and DSi to meet the need of reflecting

an alteration of authigenic silicates formations, further leading to an extra hypothesized component, NonBSi_B-A (Fig.26).

As shown in Fig.27, there are different kinds of non-biogenic silicates with different isotope signatures, which could indirectly denote isotope fractionations varied along with the sediment depth. NonBSi_A represents an easily dissolvable fraction of NonBSi_B, while NonBSi_B-A represents a hardly dissolvable fraction of NonBSi_B. Isotope compositions in NonBSi_A are generally heavier than that in NonBSi_B-A in most depth. Since non-biogenic silicates is believed to release slowly with bath time, the difference of $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ and $\delta^{30}\text{Si}_{\text{NonBSi_B-A}}$ could serve as good evidence that there are at least two groups of non-biogenic silicate minerals derived from different diagenetic processes.

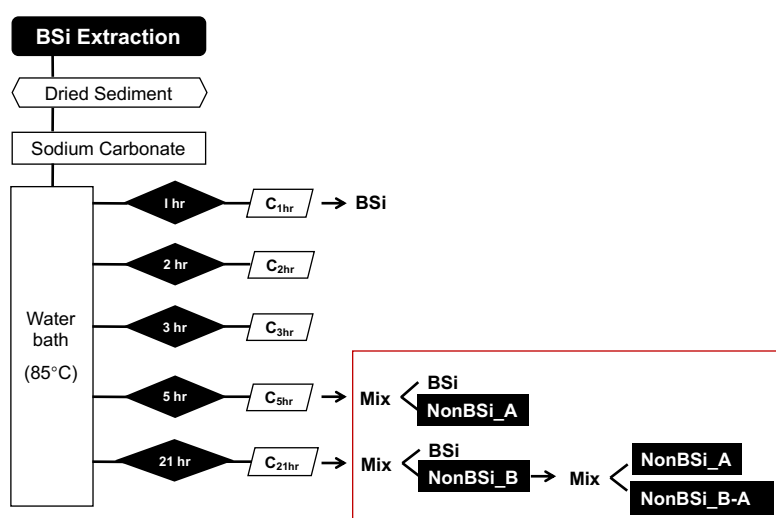


Fig.26 Schematic illustration of the relationships for extracted non-biogenic silicates, termed NonBSi_A, NonBSi_B and NonBSi_B-A, respectively.

Beside the upper most layer (0 cmbsf) where $\delta^{30}\text{Si}_{\text{NonBSi_B}}$ and $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ are both higher than $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{DSi}}$, changes of $\delta^{30}\text{Si}_{\text{NonBSi_B}}$ and $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ are generally centered on $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{DSi}}$ in most part of the sediment. At 0 cmbsf, there may exist other interference such as extractable detrital clay, leading to such irrelevant relationship. Except for the 0-cmbsf case, three different relationships have been noted.

Over 5 to 30 cmbsf as well as 50 cmbsf and 65 cmbsf, $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ is shown to be higher than $\delta^{30}\text{Si}_{\text{NonBSi_B-A}}$, which together are centered on $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{DSi}}$. The light isotope compositions in NonBSi_B-A with respect to $\delta^{30}\text{Si}_{\text{BSi}}$ may be corresponded to the isotope fractionation effect during reverse weathering. In terms of NonBSi_A, however, there are two alternative inferences arising here. i) The first inference is that NonBSi_A may be constituted of a fraction of detrital silicates which is reactive and isotopic heavier than BSi in this location, while NonBSi_B-A may represent authigenic silicates matrix whose isotope compositions are believed to be lighter than $\delta^{30}\text{Si}_{\text{BSi}}$ and BSi-dissolved $\delta^{30}\text{Si}_{\text{DSi}}$ (Tatzel et al., 2015; Ehlert et al., 2016). ii) The second inference is that NonBSi_A may be mainly made up of authigenic cation-poor silicates which are initially isotopically lighter than BSi but turn to be isotopically heavier phase, producing new authigenic silicates through reverse-weathering process that preferentially utilizes lighter isotopes. Hence, NonBSi_B-A may represent new authigenic silicate matrix.

Both assumptions could produce rather reasonable sequences of solubilities of the solid phases (i.e., in terms of the first assumption: BSi > reactive detrital silicates > authigenic silicates; in terms of the second assumption: BSi > authigenic cation-poor silicates > new authigenic silicates). However, neither two can be confirmed in this study and might be further argued with other new evidence by further researching.

At 35 cmbsf and 55-60 cmbsf, the $\delta^{30}\text{Si}_{\text{NonBSi_B}}$ is heavier than $\delta^{30}\text{Si}_{\text{NonBSi_A}}$, with $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ reaches its minimum at 55 cmbsf. i) An explanation of such abnormal point

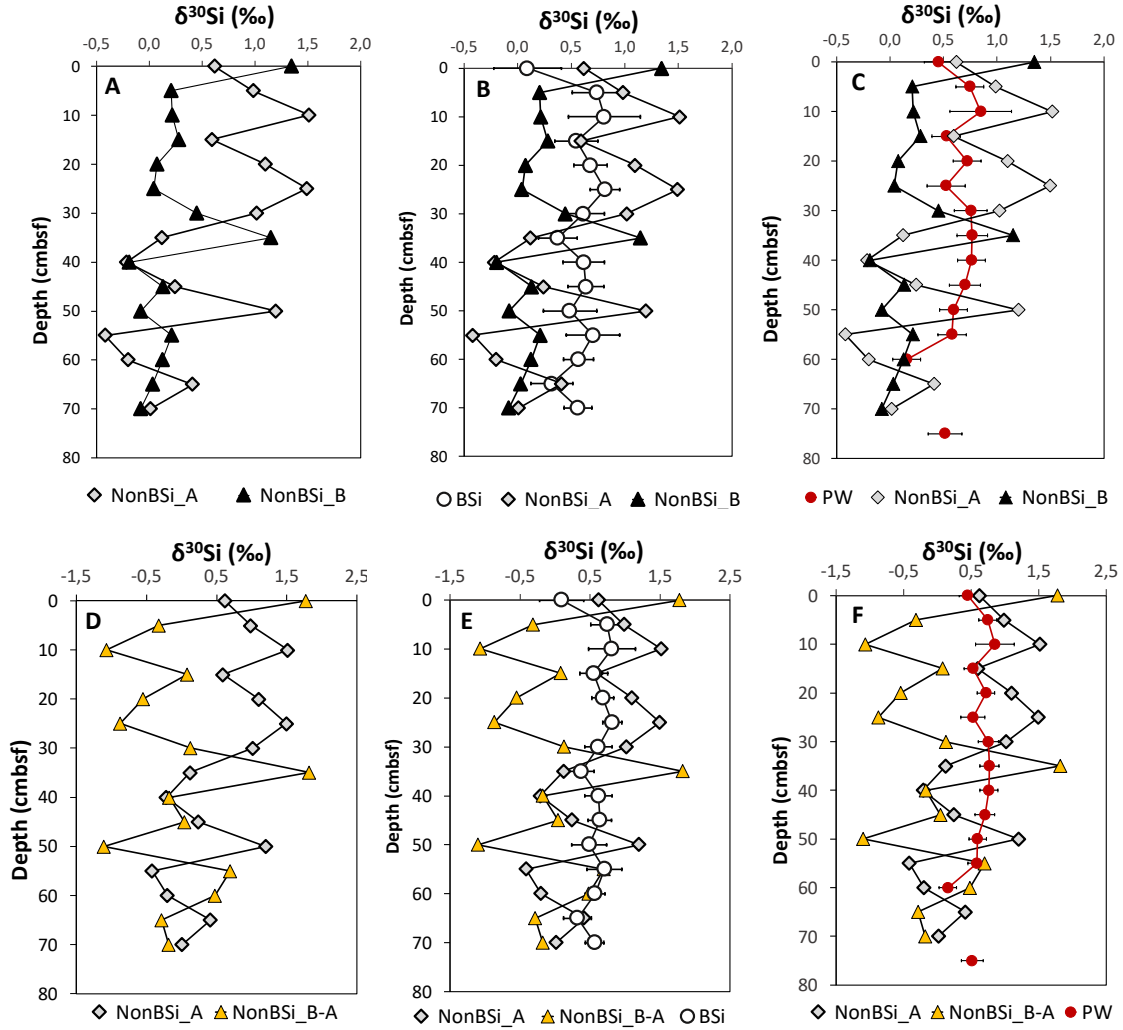


Fig.27 Si isotope composition distributions of reduced non-biogenic silicates as a function of depth (A and D) and the same profiles overlying with $\delta^{30}\text{Si}_{\text{BSi}}$ distribution (B and E) and with $\delta^{30}\text{Si}_{\text{DSi}}$ distribution (C and F).

for $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ may be that the sources of NonBSi_A-represented cation-poor authigenic silicates has changed with an endmember having much lighter isotope compositions, since detrital silicates with multiple sources which could change between riverine to eolian originated. Concurrently, there might be some further polymerization process happening after the secondary authigenic silicates formation, further promoting light Si isotopes moving out from the new authigenic clay (i.e., secondary authigenic clay plays a role as precursor here) which makes that fraction of minerals more stable and unextractable leaving the remaining minerals heavier. some other reactions with isotope fractionation effect carry out here leaving the new authigenic clay (NonBSi_B-

A) isotopically heavier. With this consideration, the degree of reaction over 55-60 cmbsf appearing not as great as it is at 35 cmbsf might be the reason behind the relative relationship discrepancy of $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{DSi}}$ between 35 cmbsf ($\delta^{30}\text{Si}_{\text{BSi}} > \delta^{30}\text{Si}_{\text{DSi}}$) and 55-60 cmbsf ($\delta^{30}\text{Si}_{\text{BSi}} < \delta^{30}\text{Si}_{\text{DSi}}$). ii) Another explanation is that the NonBSi_A-represented detrital silicates suddenly change into isotopically light form at this depth and NonBSi_B-A-represented authigenic silicates have further been isotopically fractionated during subsequent process, such as polymerization. iii) Most importantly, as there is no record by far implying the possible source changing of detrital silicates, the reliability of these abnormal points is questioned. This suspicion can be related to the relatively low BSi contents at these two concerned sections, comparing to that in the 10-30 cmbsf interval, that may play a key role resulting in analytical errors of uncertainty amplified. Comparing to the Alk_T profile, from 30 to 50 cmbsf, total alkalinity increases linearly with depth, implying a relative steady zone with regard to the total effect of alkalinity-production and consumption reactions. This contradiction further enhanced the suspicion that isotope signals at these particular zones might be inaccurate and unreliable.

Over 40-45 cm depth and 70 cm depth, the values of $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ and $\delta^{30}\text{Si}_{\text{NonBSi_B-A}}$ are comparable in size and lower than $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{DSi}}$, which might indicate the absent of reverse weathering. As a result, NonBSi_A and NonBSi_B can be hardly discriminated. Especially, at 45 cmbsf where $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ appears to be slightly higher than $\delta^{30}\text{Si}_{\text{NonBSi_B-A}}$, it might indicate a small extent of reverse weathering resulting in such minute difference, which might be further supported by the slightly shifting-back trend of $\text{Fe}_{\text{reactive}}$ at this depth. Considering a high BSi content at the same depth, some other limitations might affect inhibiting reverse weathering, such as aluminum (Al).

4.3 Application of $\delta^{30}\text{Si}$ on silica diagenetic alteration

4.3.1 Possibility of reverse weathering

At same depth, DSi released from wet alkaline extraction may be separated by different time duration and characterized by distinguishable isotope signals due to the alteration of silica early diagenesis alterations, especially reverse weathering. Reverse weathering processes are suggested to couple with the consumption of DSi, BSi, $\text{Fe}_{\text{reactive}}$ and Alk_T , and the formation of new authigenic silicates, involving isotopically enrichment of DSi, and isotopically disparity of non-biogenic silicates (Michalopoulos and Aller, 1995, 2004; Michalopoulos et al., 2000; Dixit et al., 2001; Sun et al., 2016; Sutton et al., 2018). Thus, combining all of relevant factors obtained in this study, three types Si early diagenesis with regards to reverse weathering are estimated to occur in this studied sediment (Fig.28).

Firstly, according to a distinguished relationship of isotope compositions (i.e., $\delta^{30}\text{Si}_{\text{NonBSi_A}} > \delta^{30}\text{Si}_{\text{BSi}} > \delta^{30}\text{Si}_{\text{NonBSi_B-A}}$), concurrence of authigenic cation-poor silicates and new authigenic silicates, or reactive detrital silicate and authigenic silicates are assumed to be extracted over 5-30 cmbsf, 50 cmbsf and 65 cmbsf. In these layers, $\delta^{30}\text{Si}_{\text{BSi}}$ and $\delta^{30}\text{Si}_{\text{DSi}}$ are overlapping together except 25 cmbsf. By combining with the high-resolution data (Waldheim, 2018), an anoxic condition from 10 cmbsf is estimated in this study, which is consistent with a suggestion (Presti and Michalopoulos, 2008) that anoxic condition may favor reverse weathering. Particularly, at 5 cmbsf, 20-30 cmbsf and 65 cmbsf, the depleted $\text{Fe}_{\text{reactive}}$, accompanied with decreased Alk_T and

extremely low content of BSi, could strengthen the assumed reverse weathering effect. Modifications of DSi reservoirs caused by dams in the drainage area and enhanced accumulation of BSi due to eutrophication effect have been observed during 1970-1990 (Humborg et al., 2002; Conley et al., 2008). This period is estimated corresponding to 20-30 cmbsf of the sediment core, according to 0.77cm yr^{-1} sediment accumulation rate. The initially great amount of BSi content over this depth interval may also provide a favorable environment for reverse weathering reactions.

On the contrary, at 15 cmbsf, the discrepancy between $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ and $\delta^{30}\text{Si}_{\text{NonBSi_B-A}}$ shrinks into remarkable small, indicating a low extent of transformation from authigenic cation-poor clay into new authigenic clay, or a negligible isotope effect between reactive detrital silicates and authigenic silicates. This assumption is coherent with the highest $\text{Fe}_{\text{reactive}}$ content at such depth as well as the stagnant alkalinity, which might attribute to a possibility that limitation of other cations leads to a slow reaction rate of reverse weathering in this sediment section. At 50 cmbsf, same assumption is correlated to a slightly reduced DSi which is supplied by a downward flux implying a consumption of the substance (Fig.22 A), while the relatively high $\text{Fe}_{\text{reactive}}$ is thought to be interfered by AVS. However, it is uncorrelated with the Alk_T profile, which implies a marked production of alkalinity. Such uncorrelation could be inferred from a pair of concurrent biomineralization redox reactions at this depth. In other words, the principle of such pronounced Alk_T content at this depth is of a net production output that the contribution of sulfate reduction to alkalinity here is higher than the loss of alkalinity owing to the consumption of reverse weathering.

Secondly, in addition to the first situation, according to another relationship of isotope compositions (i.e., $\delta^{30}\text{Si}_{\text{NonBSi_B-A}} > \delta^{30}\text{Si}_{\text{BSi}} > \delta^{30}\text{Si}_{\text{NonBSi_A}}$), a further reaction onto the new authigenic silicates are assumed to take place at 35 cmbsf and 55-60 cmbsf, with the sources of reactive detrital silicates or authigenic cation-poor silicates are supposed

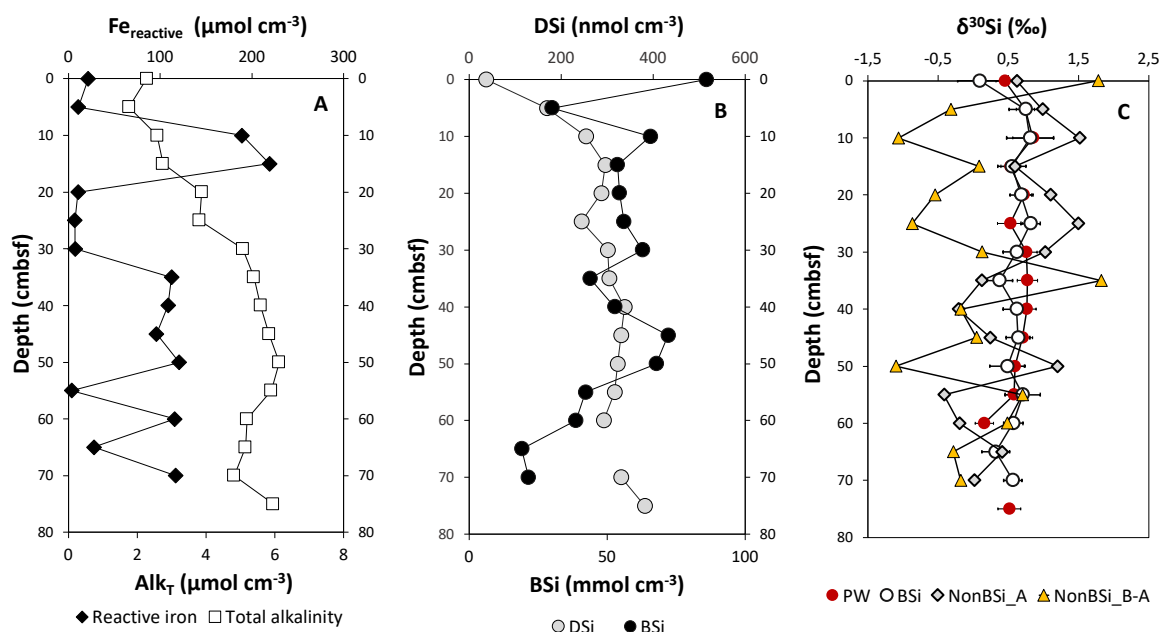


Fig.28 Distributions of relative constituents and Si isotope profiles in solid phase, pore water, including reactive iron and total alkalinity(A), DSi and BSi (B) and Si isotope compositions of pore water, BSi and extracted non-biogenic Si (C).

to change. Combining other profiles, in terms of 55-60 cmbsf, this assumption can be further supported by a declined Alk_T at 60 cmbsf, an extremely low $\text{Fe}_{\text{reactive}}$ at 55 cmbsf and a low content of BSi over 55-60 cmbsf. However, at 35 cmbsf, such assumption is only coherent with the low content of BSi at 35 cmbsf that might imply a high BSi utilization. According to the argument in section 4.1, large analytical errors of $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ and $\delta^{30}\text{Si}_{\text{NonBSi_B-A}}$ might be amplified resulting in a large deviation to true values. A new set of experiment is further needed for validating the reproducibility of the method developed in this study.

Thirdly, authigenic cation-poor silicates without new authigenic silicates are assumed to present over 40-45 cmbsf and 70 cmbsf according to different isotope signatures (i.e., $\delta^{30}\text{Si}_{\text{NonBSi_A}} \approx \delta^{30}\text{Si}_{\text{NonBSi_B-A}} < \delta^{30}\text{Si}_{\text{BSi}}$). In terms of the hypothesis above, over 40-45 cm depth, as the value of $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ and $\delta^{30}\text{Si}_{\text{NonBSi_B-A}}$ are comparable in size, there is no evidence of reverse weathering found, which is also corresponded to a linearly increased Alk_T over 35-45 cm depth interval (Fig.21 B), suggesting an extraordinary layer. Considering there are still large amount of $\text{Fe}_{\text{reactive}}$ remained over this depth interval, although such amount of $\text{Fe}_{\text{reactive}}$ is doubted to be AVS rather than iron (oxyhydr)oxide minerals, there might be another limiting factor instead of BSi and $\text{Fe}_{\text{reactive}}$ in this sediment section. Such a situation might due to a short supply of detrital Al deposited over such period, so that the prerequisite of reverse weathering reactions cannot be fulfilled, despite that BSi content over the same depth even peaks as maximum. Therefore, it is suggested that the Al/BSi ratio of solid phase sediment need to be checked in the future to eliminate the effect of detrital clay. At 70 cmbsf, the identical value of $\delta^{30}\text{Si}_{\text{NonBSi_A}}$ and $\delta^{30}\text{Si}_{\text{NonBSi_B-A}}$ might attribute to an assumption that BSi content is too low to stimulate reverse weathering. Even though, Considering the solubility of DSi with co-present of Al (600 μM) (Dixit et al., 2001; Rickert et al., 2002), DSi is undersaturated and BSi might be dissolved spontaneously at this depth. BSi might still be able to remain under metal-rich coating protects (Michalopoulos and Aller, 2004). However, this assumption cannot explain an increased $\delta^{30}\text{Si}_{\text{BSi}}$ and a low concentrated Alk_T measured at this depth. Maybe there is another limitation suppressing reverse weathering at this depth, either chemical or physical factors should be taken into consideration in further researches. Importantly, at this depth, the alkaline-extracted sample has an extremely low BSi, closed to the minimum. Hence, the isotope signal might be more sensitive with large errors inevitable.

In addition to the estimation that reverse weathering might carry out along the sediment core, as a corollary, a sequence of extractable silicates in this study might be preliminary estimated with respect to their dissolution capability. Some part of detrital clay is dissolvable and usable as BSi, and the solubility sequence from large to small are: BSi, authigenic cation-poor silicates / reactive detrital silicates, and new authigenic silicates / authigenic cation-poor silicates, based on two assumptions. Moreover, as shown in Fig.19, the amount of wet-alkaline extractable non-biogenic clay minerals is comparable with BSi content, implying a large alternative effect of reverse weathering transforming BSi into authigenic minerals.

4.2.2 Estimation of isotope effect on silica early diagenesis

Behaviors of Si isotope fractionation during BSi preservation and transformation, reconstitution and reprecipitation (i.e., reverse weathering) has shown a significant potential in revealing the early diagenetic reactions of Si. Research at Peruvian shelf

(Ehlert et al., 2016), where about 24% of the dissolving BSi is assumed to be reprecipitated as authigenic phases, estimated that Si isotope fractionation factor between authigenic precipitates and DSi is -2.0‰, leaving the pore waters enriched in the heavy Si isotopes. This estimation further confirmed previous experimental studies (Geilert et al., 2014; Oelze et al., 2014, 2015; Tatzel et al., 2015). However, caution should be seen in our study that silicon isotope fractionations between BSi and non-biogenic silicates is still not diagnostic yet. This is because that authigenic silicates may be formed from a number of sources, including other non-biogenic Si such as reactive detrital clay, and formed from diverse reactions including reverse weathering with cation-poor authigenic clay or new authigenic clay act as two produces. Hence, fractionation factors estimated by Ehlert et al. (2016) can not be compared in this study. To compensate for this defect, the isotope effect of Si isotope compositions between alterations of different silicon phases have been calculated here, attempting to achieve a rough overview of isotope changes during silica early diagenesis in this studied sediment, as shown in Fig.29 (Appendix Table 2).

Since it is difficult to compare all the silicate phases as shown in Fig.29 (A), especially with considerably mixed causes and ample potential transformations, three different components are separated below for better interpretation (Fig.29 B, C and D). Based on such anticipation, isotope effect (i.e., represented by isotope separation factor Δ (A/B); Eq.9; here after) between BSi and all other constituents are expected to get an overview on how the isotopic effect on Si varies along with depth (Fig.29 B). By the same principle, isotope separation factor between NonBSi_A and all other constituents are expected to reflect how isotopic discrimination looks like on the assumed formation of new authigenic clay (or the reactive detrital silicates) along with depth (Fig.29 C). Isotope separation factor between NonBSi_B-A and all other constituents are expected to reflect isotopic discriminations on the assumed formation of new authigenic silicates (or the authigenic silicates) along with depth (Fig.29 D).

Differences of isotope composition between BSi and porewater DSi appear subtle to see, in agreement with previous experiments that did not observe isotopic fractionation during BSi dissolution (Demarest et al., 2009; Wetzel et al., 2014; Egan et al., 2012; Ehlert et al., 2016). Apart from, four patterns could be seen among these isotope signal variations of BSi, NonBSi_A and NonBSi_B-A (Fig.29). i) Firstly, Δ are all negative, which occurs at 0 cmbsf; ii) Secondly, Δ (PW/NonBSi_A) and Δ (BSi/NonBSi_A) are negative, while Δ (PW/NonBSi_B-A), Δ (BSi/NonBSi_B-A) and Δ (NonBSi_A/NonBSi_B-A) are positive with each one smaller than the next. This pattern takes place at 5-30 cmbsf, 50 and 65 cmbsf; iii) Thirdly, Δ (PW/NonBSi_A) and Δ (BSi/NonBSi_A) are positive, while Δ (PW/NonBSi_B-A), Δ (BSi/NonBSi_B-A) and Δ (NonBSi_A/NonBSi_B-A) are negative with each one smaller than the next. This kind of pattern takes place at 35 cmbsf and 55-60 cmbsf; iv) Fourthly, Δ are all positive. That situations occur at 40-45 cmbsf and 70 cmbsf. These four patterns might be responsible to four stages of silica early diagenesis, which can be associated with the assumption in section 4.2.2. Reverse weathering reactions are more likely characterized by the second pattern. However, in terms of the fourth pattern argued by the author, these isotope values might be disturbed by large errors from not only measurement but also mathematical deduction.

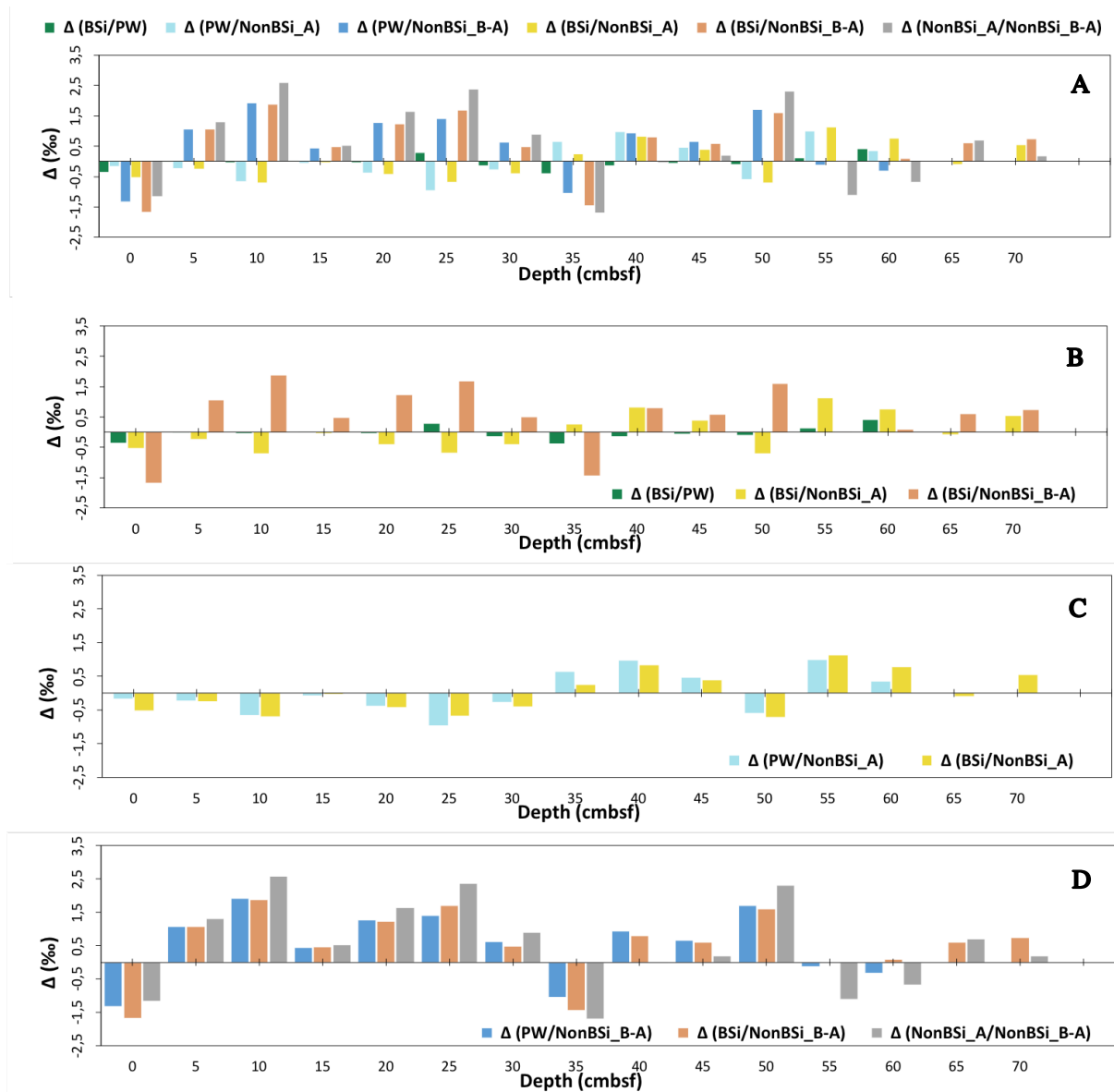


Fig.29 Distributions of silicon isotope effects as a function of depth.

5 Conclusion

This study documents the pore water solute constituents and solid-phase component, accompanied by their silicon isotope signatures, in Baltic Sea sediments. Several lines of evidence have suggested the occurrence and alteration of reverse weathering, through which isotope fractionations between different phases making them have various isotopic characteristics. It is emphasized that the incorporation of isotope data with conventional concentration data has considerable advantages of providing transformation informations during early diagenesis, especially with regard to reverse weathering.

An empirical rate of J_{DSi} to J_{O_2} (0.2) observed in this study is lower compared with what Holstein and Hensen (2010) observed. The amount of J_{DSi} going out to the overlying water estimated by incubation ($0.43 \text{ mmol m}^{-2} \text{ d}^{-1}$) is greater than that deducted from the DSi profile ($0.063 \text{ mmol m}^{-2} \text{ d}^{-1}$). These observations are suggested to be influenced by not only the comprehended early diagenetic and diffusion effects as well as boundary layer and advection effect. Hence, more constrain parameters are expected to unlock the principle behind sediment profiles composed of equilibrium and kinetic reactions. Moreover, DSi fluxes out of water-sediment interface tend to be enriched with heavy isotopes with incubation time increasing, indicating a potential utilization of DSi occurring in the sediment cores.

In the context of the biogeochemical remineralization pathway along sediments, reverse weathering process deduced in this studied sediment is indicated by isotope variations to be selectively promoted with depth correlated to the abundance of reactive silica (mostly BSi) and iron ($\text{Fe}_{\text{reactive}}$). Anoxic condition appears to favor the formation of authigenic silicates with expense of $\text{Fe}_{\text{reactive}}$ and BSi. Furthermore, some other cations such as aluminum, sodium, potassium, magnesium and germanium should also be taken into account as multi-proxies to reveal the threshold conditions of reverse weathering alteration in the future.

Two stages of silica early diagenesis processes are estimated to be concurrent, with both processes withdraw DSi from porewater and form authigenic cation-poor silicates and new authigenic silicates. Silicon isotope responses can be used here to indicate these transformations. However, it is impossible to separate and identify different types of minerals according to the information provided in this study. Only through a comprehensive study including mineralogical, chemical and isotopic analyses, the relationship between transformation of authigenic clays and their corresponding isotope signature could be deciphered. Therefore, detailed TEM (transmission electron microscope) examinations and SEM (scanning electron microscopy) observations with EDS elemental mapping of selected specimens of sediments is expected in the future for the identification task.

In response to Si early diagenesis along sediments, silicon isotope effects are suggested to have certain patterns which are expected to be further quantified and broadly used on the determination of different products of reverse weathering. For such purpose, except for the requirement of classification and determination of authigenic silicates isotope compositions, incubation experiments are suggested to be designed first in order to reduce uncertainty factors, whilst spatial and seasonal in situ data is crucial to confirm the correlated incubation results and produce more realistic local constraint parameters.

Acknowledgements

Special thanks to my supervisors Dr. Volker Brüchert and Dr. Xiaole Sun who are so supportive, patient and inspiring to me. What I learned from them are not only a drop of their academic knowledge but also their attitude towards researches. I also gratefully thank Sandra Gdaniec for teaching me alkalinity titration, Jonas Fredriksson for the whole-core incubation operation and subsampling, and Melanie Schmitt from the lab of Vegacenter for helping me achieve silicon isotope measurement. Gratefully acknowledge Klara Hajnal, Julia Steinbach, Mikaela Holm, Heike Siegmund, Carl-Magnus Mörtz, Rienk Smittenberg, Christophe Dupraz and so on, for their support and concern. I have benefited from their excellent laboratorial expertise and deep knowledge. I also would like to express my sincere gratitude to Elisabeth Däcker and Krister Junghahn for their kind logistical support. The Bolin Centre for Climate Research are acknowledged for their finance support on this study. Last but not least, I would like to gratefully thank all my family, especially my better half, mother-in-law, and father-in-law, who have been standing by me from the beginning.

References

- Aller, R. C. (2014). Sedimentary Diagenesis, Depositional Environments, and Benthic Fluxes. In *Treatise on Geochemistry: Second Edition*, 293-334.
- Andersson, P., Håkansson, B., Håkansson, J., Sahlsten, E., Havenhand, J., Thorndyke, M., & Dupont, S. (2008). Marine Acidification : On effects and monitoring of marine acidification in the seas surrounding Sweden (2008:92). SMHI (Sveriges meteorologiska och hydrologiska institut).
- Baldauf, S. L. (2003). The deep roots of eukaryotes. *Science*, 300(5626), 1703-1706.
- Berner, R. A. (1990). Atmospheric carbon dioxide levels over Phanerozoic time. *Science*, 249(4975), 1382-1386.
- Berner, E. K., & Berner, R. A. (2012). Global environment: water, air, and geochemical cycles. Princeton University Press.
- Brenner, H., Braeckman, U., Le Guitton, M., & Meysman, F. J. (2016). The impact of sedimentary alkalinity release on the water column CO₂ system in the North Sea. *Biogeosciences*, 13(3), 841-863.
- Brüchert, V., Nguyen, T. M., Deutschmann, A., Böttcher, M. E., & Ferdelman, T. G. (2010, May). Bacterial sulfate reduction and methanogenesis in brackish, oligotrophic northern Baltic Sea sediments. In *EGU General Assembly Conference Abstracts* (Vol. 12, p. 15252).
- Burdige, D. J. (2006). Geochemistry of marine sediments. Princeton University Press.
- Canfield, D. E. (1989). Reactive iron in marine sediments. *Geochimica et Cosmochimica Acta*, 53(3), 619-632.
- Canfield, D. E. (1988). Sulfate reduction and the diagenesis of iron in anoxic marine sediment. Ph. D. Dissertation, Yale University.
- Church, T. M. (2016). Marine chemistry in the coastal environment: principles, perspective and prospectus. *Aquatic geochemistry*, 22(4), 375-389.
- Conley, D. J. (2002). Terrestrial ecosystems and the global biogeochemical silica cycle. *Global Biogeochemical Cycles*, 16(4).
- Conley, D. J., Humborg, C., Smedberg, E., Rahm, L., Papush, L., Danielsson, Å., ... & Mörrth, C. M. (2008). Past, present and future state of the biogeochemical Si cycle in the Baltic Sea. *Journal of Marine Systems*, 73(3-4), 338-346.
- Conley, D. J., & Carey, J. C. (2015). Biogeochemistry: Silica cycling over geologic time. *Nature Geoscience*, 8(6), 431.
- Coradin, T., & Lopez, P. J. (2003). Biogenic silica patterning: simple chemistry or subtle biology?. *ChemBioChem*, 4(4), 251-259.
- Coursey, J. S., Schwab, D. J., Tsai, J. J. and Dragoset, R. A. (2011). Atomic Weights and Isotopic Compositions with Relative Atomic Masses [Online]. Gaithersburg, MD: U.S. National Institute of Standards and Technology Physical Measurement Laboratory. Available at: www.nist.gov/pml/data/comp.cfm 2011 (accessed September 1, 2018).
- Danielsson, Å. (2014). Influence of hypoxia on silicate concentrations in the Baltic Proper (Baltic Sea). *Boreal Environment Research*, 19(4), 267-280.
- Demarest, Mark S., Mark A. Brzezinski, and Charlotte P. Beucher. (2009). Fractionation of Silicon Isotopes during Biogenic Silica Dissolution. *Geochimica et Cosmochimica Acta* 73(19): 5572-83.
- DeMaster, D. J. (2013). The Diagenesis of Biogenic Silica: Chemical Transformations Occurring in the Water Column, Seabed, and Crust. In *Treatise on Geochemistry: Second Edition*, , 103-11.

- DeMaster, David J. (1981). The Supply and Accumulation of Silica in the Marine Environment. *Geochimica et Cosmochimica Acta* 45(10): 1715–32.
- DeMaster, D. J. (1979). Marine budgets of silica and Si . Yale Univ., New Haven, CT (USA).
- De La Rocha, C. L., Brzezinski, M. A., & DeNiro, M. J. (1998). Fractionation of silicon isotopes by marine diatoms during biogenic silica formation. *Oceanographic Literature Review*, 4(45), 631.
- Dixit, S., & Van Cappellen, P. (2002). Surface chemistry and reactivity of biogenic silica. *Geochimica et Cosmochimica Acta*, 66(14), 2559–2568.
- Dixit, Suvasis, Philippe Van Cappellen, and A. Johan Van Bennekom. (2001). Processes Controlling Solubility of Biogenic Silica and Pore Water Build-up of Silicic Acid in Marine Sediments. *Marine Chemistry* 73(3–4): 333–52.
- Egan, K. E., Rickaby, R. E., Leng, M. J., Hendry, K. R., Hermoso, M., Sloane, H. J., ... & Halliday, A. N. (2012). Diatom silicon isotopes as a proxy for silicic acid utilisation: a Southern Ocean core top calibration. *Geochimica et Cosmochimica Acta*, 96, 174–192.
- Egge, J. K., & Aksnes, D. L. (1992). Silicate as regulating nutrient in phytoplankton competition. *Marine ecology progress series*. Oldendorf, 83(2), 281–289.
- Ehlert, Claudia et al. (2016). Stable Silicon Isotope Signatures of Marine Pore Waters – Biogenic Opal Dissolution versus Authigenic Clay Mineral Formation. *Geochimica et Cosmochimica Acta* 191: 102–17.
- Ferdelman, T. G. (1988). The distribution of sulfur, iron, manganese, copper and uranium in a salt marsh sediment core as determined by a sequential extraction method (*Doctoral dissertation*, University of Delaware).
- Fonselius, S. (1978). On nutrients and their role as production limiting factors in the Baltic. *Acta Hydrochim. Hydrobiol.* 6, 329–339.
- Frings, P. J., Clymans, W., Fontorbe, G., Christina, L., & Conley, D. J. (2016). The continental Si cycle and its impact on the ocean Si isotope budget. *Chemical Geology*, 425, 12–36.
- Fripiat, F., Cavagna, A. J., Dehairs, F., Brauwere, A. D., André, L., & Cardinal, D. (2012). Processes controlling the Si-isotopic composition in the Southern Ocean and application for paleoceanography. *Biogeosciences*, 9(7), 2443–2457.
- Geilert, S., Vroon, P. Z., Roerdink, D. L., Van Cappellen, P., & van Bergen, M. J. (2014). Silicon isotope fractionation during abiotic silica precipitation at low temperatures: Inferences from flow-through experiments. *Geochimica et Cosmochimica Acta*, 142, 95–114.
- Grasse, P., Brzezinski, M. A., Cardinal, D., De Souza, G. F., Andersson, P., Closset, I., ... & François, R. (2017). GEOTRACES inter-calibration of the stable silicon isotope composition of dissolved silicic acid in seawater. *Journal of Analytical Atomic Spectrometry*, 32(3), 562–578.
- Grasse, P., Ehlert, C., & Frank, M. (2013). The influence of water mass mixing on the dissolved Si isotope composition in the Eastern Equatorial Pacific. *Earth and Planetary Science Letters*, 380, 60–71.
- Hagström, Å., Azam, F., Kuparinen, J., & Zweifel, U. L. (2001). Pelagic plankton growth and resource limitations in the Baltic Sea. In *A systems analysis of the Baltic Sea* (pp. 177–210). Springer, Berlin, Heidelberg.
- Hamade, T., Konhauser, K. O., Raiswell, R., Goldsmith, S., & Morris, R. C. (2003). Using Ge/Si ratios to decouple iron and silica fluxes in Precambrian banded iron formations. *Geology*, 31(1), 35–38.
- Hannerz, Fredrik, and Georgia Destouni. (2006). Spatial Characterization of the Baltic Sea Drainage Basin and Its Unmonitored Catchments. *Ambio* 35(5): 214–19.
- Haraldsson, Conny et al. (1997). Rapid, High-Precision Potentiometric Titration of Alkalinity in Ocean and Sediment Pore Waters. *Deep-Sea Research Part I: Oceanographic Research Papers*, 44(12),

2031-2044.

- Helcom, (2006). Development of tools for assessment of eutrophication in the Baltic Sea. BSEP No 104, 64 pp.
- Helgeson, H. C., & Mackenzie, F. T. (1970). Silicate-sea water equilibria in the ocean system. In *Deep Sea Research and Oceanographic Abstracts* (Vol. 17, No. 5, pp. 877-892). Elsevier.
- Holstein, J. M., & Hensen, C. (2010). Microbial mediation of benthic biogenic silica dissolution. *Geo-Marine Letters*, 30(5), 477-492.
- Humborg, C., Blomqvist, S., Avsan, E., Bergensund, Y., Smedberg, E., Brink, J., & Mörtz, C. M. (2002). Hydrological alterations with river damming in northern Sweden: Implications for weathering and river biogeochemistry. *Global Biogeochemical Cycles*, 16(3).
- Jakobsson, M., Pearce, C., Cronin, T. M., Backman, J., Anderson, L. G., Barrientos, N., ... & Mörtz, C. M. (2017). Post-glacial flooding of the Bering Land Bridge dated to 11 cal ka BP based on new geophysical and sediment records. *Climate of the Past*, 13(8), 991.
- Jin, X., Gruber, N., Dunne, J. P., Sarmiento, J. L., & Armstrong, R. A. (2006). Diagnosing the contribution of phytoplankton functional groups to the production and export of particulate organic carbon, CaCO₃, and opal from global nutrient and alkalinity distributions. *Global Biogeochemical Cycles*, 20(2).
- Johanna Waldheim. (2018). Exploring reverse weathering processes in Baltic Sea sediment pore waters. Stockholm University Bachelor Thesis.
- Karlsson, M., M. Malmaeus, M., Rydin, E., and Jonsson, P. (2010): Bottenundersökningar i Upplands, Stockholms, Södermanlands och Östergötlands skärgårdar: 2008–2009, Svenska Miljöinstitut, B1928, 102.
- Kostka, Joel E., and George W. Luther. (1994). Partitioning and Speciation of Solid Phase Iron in Saltmarsh Sediments. *Geochimica et Cosmochimica Acta* 58(7): 1701–10.
- Krumins, V., Gehlen, M., Arndt, S., Cappellen, P. V., & Regnier, P. (2013). Dissolved inorganic carbon and alkalinity fluxes from coastal marine sediments: model estimates for different shelf environments and sensitivity to global change. *Biogeosciences*, 10(1), 371-398.
- Ku, T. C.W., and L. M. Walter. (2003). Syndepositional Formation of Fe-Rich Clays in Tropical Shelf Sediments, San Blas Archipelago, Panama. *Chemical Geology*, 197(1-4), 197-213.
- Kuliński, K., Schneider, B., Szymczycha, B., & Stokowski, M. (2017). Structure and functioning of the acid–base system in the Baltic Sea. *Earth System Dynamics*, 8(4), 1107-1120.
- Latour, Pauline et al. (2018). Dynamic Interactions between Iron and Sulfur Cycles from Arctic Methane Seeps. *Biogeosciences Discussions*.
- Libes, S. (2011). Introduction to marine biogeochemistry. Academic Press.
- Mackenzie, F. T., & Garrels, R. M. (1966). Chemical mass balance between rivers and oceans. *American Journal of Science*, 264(7), 507-525.
- Mannucci (2015) Field report: Geochemistry of Fifång sediment; *Cand. course Geochemical Field Methods*. Instructor: Dr. Volker Brüchert
- Mattila, Jukka, Harri Kankaanpää, and Erkki Ilus. (2006). Estimation of Recent Sediment Accumulation Rates in the Baltic Sea Using Artificial Radionuclides ¹³⁷Cs and ^{239,240}Pu as Time Markers. *Boreal Environment Research*, 11(2), 95.
- Mayer, L. M., Jorgensen, J., & Schnitker, D. (1991). Enhancement of diatom frustule dissolution by iron oxides. *Marine Geology*, 99(1-2), 263-266.
- Méheut, M., Lazzeri, M., Balan, E. and Mauri, F. (2007). Equilibrium isotopic fractionation in the kaolinite, quartz, water system: Prediction from first-principles density-functional theory. *Geochimica et Cosmochimica Acta*, 71:3170 – 3181.

- Michalopoulos, P., Aller, R. C., & Reeder, R. J. (2000). Conversion of diatoms to clays during early diagenesis in tropical, continental shelf muds. *Geology*, 28(12), 1095-1098.
- Michalopoulos, P., & Aller, R. C. (2004). Early diagenesis of biogenic silica in the Amazon delta: alteration, authigenic clay formation, and storage. *Geochimica et Cosmochimica Acta*, 68(5), 1061-1085.
- Milligan, Allen J., Diana E. Varela, Mark a. Brzezinski, and François M. M. Morel. (2004). Dynamics of Silicon Metabolism and Silicon Isotopic Discrimination in a Marine Diatom as a Function of PCO₂. *Limnology and Oceanography* 49(2): 322–29.
- März, C., Hoffmann, J., Bleil, U., De Lange, G. J., & Kasten, S. (2008). Diagenetic changes of magnetic and geochemical signals by anaerobic methane oxidation in sediments of the Zambezi deep-sea fan (SW Indian Ocean). *Marine Geology*, 255(3), 118-130.
- Nelson D. M., Treguer P., Brzezinski M. A., Leynaert A. and Queguiner B. (1995) Production and dissolution of biogenic silica in the ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation. *Global Biogeochem. Cycles* 9, 359–372.
- Oelze, M., von Blanckenburg, F., Hoellen, D., Dietzel, M., & Bouchez, J. (2014). Si stable isotope fractionation during adsorption and the competition between kinetic and equilibrium isotope fractionation: Implications for weathering systems. *Chemical geology*, 380, 161-171.
- Oelze, M., von Blanckenburg, F., Bouchez, J., Hoellen, D., & Dietzel, M. (2015). The effect of Al on Si isotope fractionation investigated by silica precipitation experiments. *Chemical geology*, 397, 94-105.
- Ozkan, E. Y., Buyukisik, H. B., & Kontas, A. (2014). Biogeochemical behavior and distribution of biogenic silica in marine sediments from Izmir Bay, Aegean Sea (Turkey). *Marine Chemistry*, 164, 1-8.
- Papush, L., & Danielsson, Å. (2006). Silicon in the marine environment: dissolved silica trends in the Baltic Sea. *Estuarine, Coastal and Shelf Science*, 67(1-2), 53-66.
- Papush, L., Danielsson, Å., & Rahm, L. (2009). Dissolved silica budget for the Baltic Sea. *Journal of Sea Research*, 62(1), 31-41.
- Pastuszek, M., Conley, D. J., Humborg, C., Witek, Z., & Sitek, S. (2008). Silicon dynamics in the Oder estuary, Baltic Sea. *Journal of Marine Systems*, 3(73), 250-262.
- Presti, M., & Michalopoulos, P. (2008). Estimating the contribution of the authigenic mineral component to the long-term reactive silica accumulation on the western shelf of the Mississippi River Delta. *Continental Shelf Research*, 28(6), 823-838.
- Ragueneau, O., Tréguer, P., Leynaert, A., Anderson, R. F., Brzezinski, M. A., DeMaster, D. J., ... & Heinze, C. (2000). A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. *Global and Planetary Change*, 26(4), 317-365.
- Rahm, L., & Danielsson, Å. (2007). Spatial heterogeneity of nutrients in the Baltic Proper, Baltic Sea. *Estuarine, Coastal and Shelf Science*, 73(1-2), 268-278.
- Reynolds, B. C., Frank, M., & Halliday, A. N. (2008). Evidence for a major change in silicon cycling in the subarctic North Pacific at 2.73 Ma. *Paleoceanography and Paleoclimatology*, 23(4).
- Reynolds, B. C., Aggarwal, J., Andre, L., Baxter, D., Beucher, C., Brzezinski, M. A., ... & Opfergelt, S. (2007). An inter-laboratory comparison of Si isotope reference materials. *Journal of Analytical Atomic Spectrometry*, 22(5), 561-568.
- Rickert, D., Schlüter, M., & Wallmann, K. (2002). Dissolution kinetics of biogenic silica from the water column to the sediments. *Geochimica et Cosmochimica Acta*, 66(3), 439-455.
- Sarmiento, J L, and N Gruber. (2006). *Ocean Biogeochemical Dynamics*. Princeton University Press.
- Sawicka, Joanna E., and Volker Brüchert. (2017). *Annual Variability and Regulation of Methane and*

- Sulfate Fluxes in Baltic Sea Estuarine Sediments. *Biogeosciences* 14(2): 325–39.
- Savage, P. S., Georg, R. B., Williams, H. M., Turner, S., Halliday, A. N., & Chappell, B. W. (2012). The silicon isotope composition of granites. *Geochimica et Cosmochimica Acta*, 92, 184-202.
- Schulz, H. D. (2006). Quantification of early diagenesis: dissolved constituents in pore water and signals in the solid phase. In *Marine Geochemistry* (pp. 73-124). Springer, Berlin, Heidelberg.
- Schauble, E. A., Georg, R. B. and Halliday, A. N. (2007). Silicate metal fractionation of silicon isotopes at high pressure and temperature. *Eos Trans. AGU Fall Meet. Suppl.*, 88 (52): V42A-07.
- Schulz, H. D., & Zabel, M. (2006). *Marine geochemistry* (Vol. 2). Berlin: Springer.
- Schlitzer, R., Ocean Data View, odv.awi.de, (2018). (map)
- Seiter, K., Hensen, C., & Zabel, M. (2010). Coupling of benthic oxygen uptake and silica release: implications for estimating biogenic particle fluxes to the seafloor. *Geo-Marine Letters*, 30(5), 493-509.
- Shahar, A., Hillgren, V. J., Young, E. D., Fei, Y., Macris, C. A., & Deng, L. (2011). High-temperature Si isotope fractionation between iron metal and silicate. *Geochimica et Cosmochimica Acta*, 75(23), 7688-7697.
- Sillén, L. G. (1967). The ocean as a chemical system. *Science*, 156(3779), 1189-1197.
- Sørensen, J., & Jeørgensen, B. B. (1987). Early diagenesis in sediments from Danish coastal waters: microbial activity and Mn-Fe-S geochemistry. *Geochimica et Cosmochimica Acta*, 51(6), 1583-1590.
- Stookey, L. L. (1970). Ferrozine---a new spectrophotometric reagent for iron. *Analytical chemistry*, 42(7), 779-781.
- Sun, X., Andersson, P., Humborg, C., Gustafsson, B., Conley, D. J., Crill, P., & Mörtz, C. M. (2011). Climate dependent diatom production is preserved in biogenic Si isotope signatures. *Biogeosciences*, 8(11), 3491-3499.
- Sun, X., Andersson, P., Land, M., Humborg, C., & Mörtz, C. M. (2010). Stable silicon isotope analysis on nanomole quantities using MC-ICP-MS with a hexapole gas-collision cell. *Journal of Analytical Atomic Spectrometry*, 25(2), 156-162.
- Sun, X., Olofsson, M., Andersson, P. S., Fry, B., Legrand, C., Humborg, C., & Mörtz, C. M. (2014). Effects of growth and dissolution on the fractionation of silicon isotopes by estuarine diatoms. *Geochimica et Cosmochimica Acta*, 130, 156-166.
- Sun, X., Higgins, J., & Turchyn, A. V. (2016). Diffusive cation fluxes in deep-sea sediments and insight into the global geochemical cycles of calcium, magnesium, sodium and potassium. *Marine Geology*, 373, 64-77.
- Sun, X., Mörtz, C. M., Porcelli, D., Kutscher, L., Hirst, C., Murphy, M. J., ... & Andersson, P. S. (2018). Stable silicon isotopic compositions of the Lena River and its tributaries: Implications for silicon delivery to the Arctic Ocean. *Geochimica et Cosmochimica Acta*, 241, 120-133.
- Staresinic, N., Farrington, J., Gagosian, R. B., Clifford, C. H., & Hulburt, E. M. (1983). Downward transport of particulate matter in the Peru coastal upwelling: role of the anchoveta, *Engraulis ringens*. In *Coastal Upwelling Its Sediment Record* (pp. 225-240). Springer, Boston, MA.
- Strickland, J. D. H., & Parsons, T. R. (1972). A practical handbook of seawater analysis. *Bull. Fish. Res. Board Can.* 167.
- Stumm, W., & Morgan, J. J. (1981). *Aquatic Chemistry*, 780 pp.
- Sutton, J. N., André, L., Cardinal, D., Conley, D. J., De Souza, G. F., Dean, J., ... & Grasse, P. (2018). A review of the stable isotope bio-geochemistry of the global silicon cycle and its associated trace elements. *Frontiers in Earth Science*, 5, 112.

- Sutton, J. N., Varela, D. E., Brzezinski, M. A., & Beucher, C. P. (2013). Species-dependent silicon isotope fractionation by marine diatoms. *Geochimica et Cosmochimica Acta*, 104, 300-309.
- Swann, G. E., Leng, M. J., Juschus, O., Melles, M., Brigham-Grette, J., & Sloane, H. J. (2010). A combined oxygen and silicon diatom isotope record of Late Quaternary change in Lake El'gygytyn, North East Siberia. *Quaternary Science Reviews*, 29(5), 774-786.
- Tatzel, M., von Blanckenburg, F., Oelze, M., Schuessler, J. A., & Bohrmann, G. (2015). The silicon isotope record of early silica diagenesis. *Earth and Planetary Science Letters*, 428, 293-303.
- Thang, N. M., Brüchert, V., Formolo, M., Wegener, G., Ginters, L., Jørgensen, B. B., & Ferdelman, T. G. (2013). The impact of sediment and carbon fluxes on the biogeochemistry of methane and sulfur in littoral Baltic Sea sediments (Himmerfjärden, Sweden). *Estuaries and Coasts*, 36(1), 98-115.
- Thomas, H., Schiettecatte, L. S., Suykens, K. O. N. É., M Kone, Y. J., Shadwick, E. H., F Prowe, A. E., ... & Borges, A. V. (2008). Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments. *Biogeosciences Discussions*.
- Tréguer, P. J., & De La Rocha, C. L. (2013). The world ocean silica cycle. Annual review of marine science, 5, 477-501.
- Uścińowicz, S. (2014). The Baltic Sea continental shelf. Geological Society, London, Memoirs, 41(1), 69-89.
- Wallmann, K. (2001). Controls on the Cretaceous and Cenozoic evolution of seawater composition, atmospheric CO₂ and climate. *Geochimica et Cosmochimica Acta*, 65(18), 3005-3025.
- Wedepohl, K. H. 1978. Handbook of geochemistry. Berlin: Springer
- Wetzel, F., De Souza, G. F., & Reynolds, B. C. (2014). What controls silicon isotope fractionation during dissolution of diatom opal?. *Geochimica et Cosmochimica Acta*, 131, 128-137.
- White, W. M. (2015). Isotope geochemistry. John Wiley & Sons.
- Wollast, R., & Mackenzie, F. T. (1983). The global cycle of silica. *Silicon geochemistry and biogeochemistry*, 39-76.
- Van Cappellen, P. (2003). Biomineralization and global biogeochemical cycles. *Reviews in mineralogy and geochemistry*, 54(1), 357-381.
- Van Cappellen, P., & Qiu, L. (1997). Biogenic silica dissolution in sediments of the Southern Ocean. II. Kinetics. *Deep Sea Research Part II: Topical Studies in Oceanography*, 44(5), 1129-1149.
- Ziegler, K., Young, E. D., Schauble, E. A., & Wasson, J. T. (2010). Metal-silicate silicon isotope fractionation in enstatite meteorites and constraints on Earth's core formation. *Earth and Planetary Science Letters*, 295(3-4), 487-496.

Appendix

Table.1 Silicon isotope data in solid phase extracted samples, bottom water sample, pore water samples and whole core incubation overlying water samples.

Sample ID	Depth (cm)	Recovery rate (%)	$\delta^{29}\text{Si}$ (‰)	2 σ	$\delta^{30}\text{Si}$ (‰)	2 σ	$\delta^{30}\text{Si}/\delta^{29}\text{Si}$	2 σ	n
1h 0x	0		-0,03	0,10*	0,09	0,32	-3,29	16,23	3
1h 1	5	92,46	0,37	0,10*	0,74	0,23	2,03	0,85	3
1h 2x	10	92,88	0,39	0,16	0,81	0,34	2,05	1,17	4
1h 3	15		0,33	0,11	0,55	0,20	1,65	0,82	3
1h 4	20		0,36	0,10*	0,68	0,16	1,90	0,69	3
1h 5	25		0,38	0,10*	0,82	0,14	2,12	0,66	3
1h 6	30		0,29	0,10*	0,62	0,19	2,15	1,01	6
1h 7	35		0,16	0,10*	0,37	0,18	2,29	1,78	3
1h 8	40		0,28	0,10*	0,62	0,19	2,19	1,04	3
1h 9	45		0,36	0,15	0,64	0,17	1,78	0,86	3
1h 10	50		0,22	0,11	0,49	0,25	2,25	1,63	5
1h 11	55		0,23	0,10*	0,70	0,25	3,03	1,69	3
1h 12	60		0,24	0,10	0,57	0,14	2,36	1,15	4
1h 13	65		0,10	0,14	0,32	0,20	3,27	5,04	3
1h 14	70		0,19	0,10*	0,56	0,13*	2,92	1,66	3
5h 0	0		0,12	0,11	0,19	0,16	1,58	1,98	4
5h 1	5	96,10	0,34	0,14	0,84	0,23	2,43	1,20	3
5h 2x	10	95,88	0,52	0,26	1,04	0,55	2,01	1,46	5
5h 3	15		0,38	0,10*	0,56	0,18	1,49	0,62	3
5h 4	20		0,43	0,10*	0,79	0,15	1,82	0,55	3
5h 5	25		0,53	0,13	0,99	0,15	1,87	0,53	3
5h 6	30		0,40	0,10*	0,71	0,13*	1,80	0,56	3
5h 7x	35	96,59	0,14	0,11	0,29	0,29	2,05	2,58	3
5h 8	40		0,22	0,13	0,34	0,13*	1,52	1,08	3
5h 9	45		0,20	0,10*	0,51	0,13*	2,51	1,39	3
5h 10	50		0,36	0,10*	0,69	0,13*	1,91	0,64	3
5h 11x	55		0,15	0,13	0,23	0,38	1,56	2,93	3
5h 12	60		0,06	0,10*	0,19	0,13*	2,97	5,03	3
5h 13	65		0,16	0,10*	0,37	0,13*	2,25	1,58	3
5h 14	70	97,23	0,12	0,10*	0,25	0,13*	2,04	1,96	3
21h 0	0		0,27	0,16	0,56	0,22	2,06	1,49	3
21h 1	5	98,13	0,26	0,10*	0,41	0,13*	1,58	0,78	3
21h 2	10		0,27	0,10*	0,51	0,13*	1,92	0,87	3
21h 3	15		0,18	0,10*	0,41	0,13*	2,22	1,39	3
21h 4	20		0,19	0,10*	0,39	0,13*	2,05	1,26	3
21h 5	25		0,22	0,10*	0,45	0,15	2,07	1,20	3
21h 6x	30		0,27	0,20	0,54	0,33	2,02	1,93	3
21h 7	35		0,46	0,10*	0,81	0,13*	1,77	0,48	3
21h 8	40		0,11	0,10*	0,18	0,13*	1,59	1,86	3
21h 9	45		0,14	0,10*	0,38	0,13*	2,64	2,06	6
21h 10	50		0,10	0,11	0,22	0,13*	2,29	2,95	6
21h 11x	55		0,21	0,15	0,40	0,26	1,85	1,77	6
21h 12	60		0,14	0,10*	0,28	0,18	1,96	1,86	5
21h 13x	65		0,03	0,10	0,11	0,26	3,78	15,64	5
21h 14	70	98,12	0,02	0,14	0,11	0,18	4,42	25,93	6
BW	0	87,46	0,19	0,13	0,45	0,13*	2,43	1,88	6
PW2	5	96,59	0,39	0,10	0,75	0,13*	1,92	0,60	3
PW3x	10		0,41	0,22	0,85	0,29	2,05	1,29	6
PW4	15	98,77	0,28	0,10*	0,52	0,13*	1,88	0,82	3
PW5	20		0,32	0,11	0,72	0,13*	2,23	0,88	3
PW6	25		0,33	0,10*	0,52	0,18	1,61	0,74	3
PW7	30		0,35	0,10*	0,75	0,15	2,17	0,76	3
PW8	35		0,36	0,10*	0,77	0,14	2,16	0,73	3
PW9	40	98,84	0,30	0,10*	0,76	0,13*	2,53	0,94	6
PW10	45		0,34	0,10*	0,70	0,14	2,07	0,74	3
PW11	50		0,28	0,10*	0,59	0,13*	2,08	0,86	3
PW12	55	99,17	0,32	0,10*	0,58	0,13*	1,79	0,68	3
PW13	60		0,06	0,10*	0,15	0,13*	2,53	4,66	3
PW16	75	99,25	0,31	0,16	0,51	0,16	1,64	0,96	3
Inc. 1	N/A		0,25	0,10*	0,60	0,13*	2,41	1,10	2
Inc. 2	N/A	93,15	0,38	0,10*	0,82	0,13*	2,16	0,67	3
Inc. 3	N/A		0,29	0,10*	0,68	0,13*	2,34	0,93	3
Inc. 4	N/A		0,37	0,10*	0,63	0,20	1,69	0,70	4
Inc. 5	N/A		0,47	0,10*	0,83	0,13*	1,76	0,46	6
Inc. 6	N/A		0,25	0,10*	0,45	0,16	1,85	1,01	3
Inc. 7	N/A	97,56	0,54	0,10*	0,98	0,13*	1,81	0,41	3
Inc. 8	N/A		0,44	0,16	0,81	0,13*	1,83	0,71	3
Inc. 9	N/A	95,51	0,66	0,10*	1,19	0,13*	1,80	0,34	3
Inc. 10	N/A		0,48	0,10*	0,93	0,13*	1,94	0,49	3

x: potential matrix effect (i.e., 2 σ ($\delta^{30}\text{Si}$) > 0.25 ‰ despite repeated measurements)

*: external reproducibility

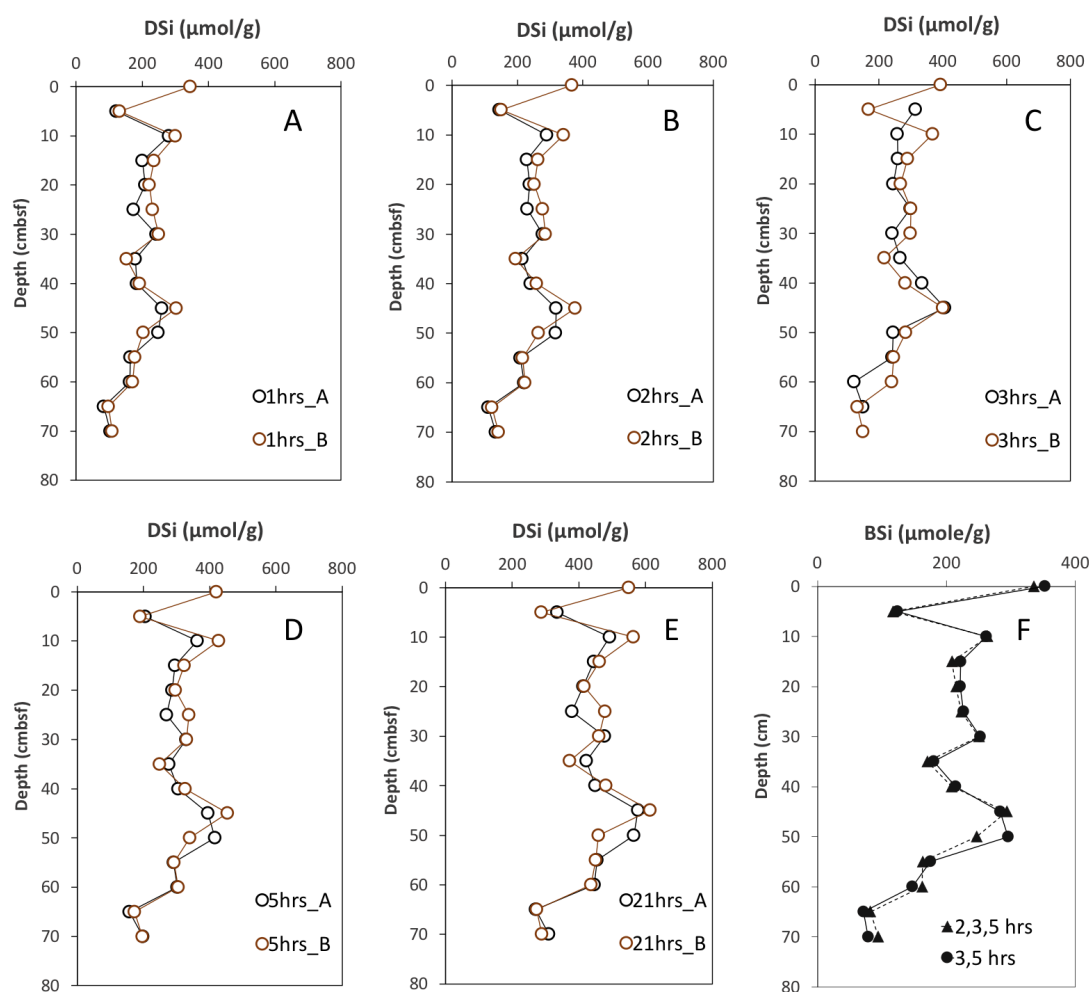


Fig.1 The duplicate concentration profiles of extractable Si by sequential alkaline digestion as a function of time and depth. From plot A to plot E, they are concentration data ($\mu\text{M/g}$ dry weight) changed with in prolonged water-bath time from 1 hrs to 21 hrs, individually. While plot F is the deduced BSi content by two ways of calculation, which are based on three-points extrapolation (2,3,5 hrs) and two-points extrapolation (3,5 hrs) respectively.

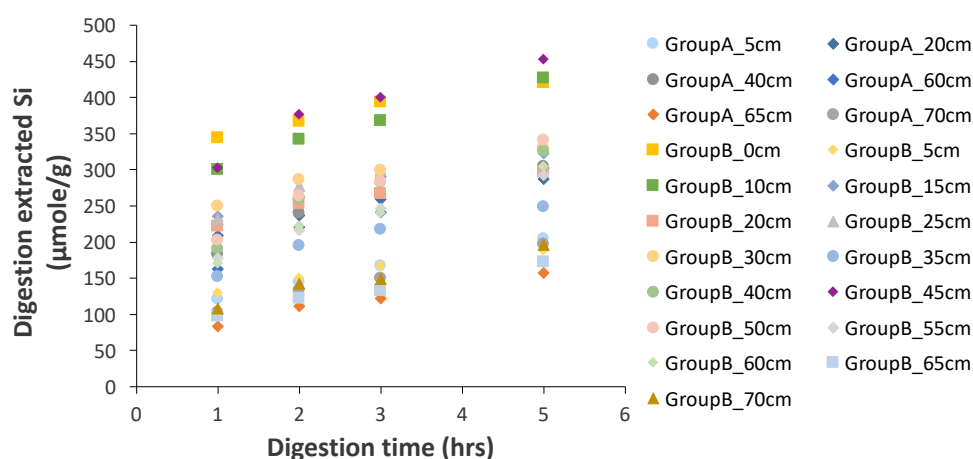


Fig.2 The concentration variation of silicon extracted versus time. Different shapes represent samples of different depth. The extrapolation of each suit of data to the intercept is employed as the BSi content.

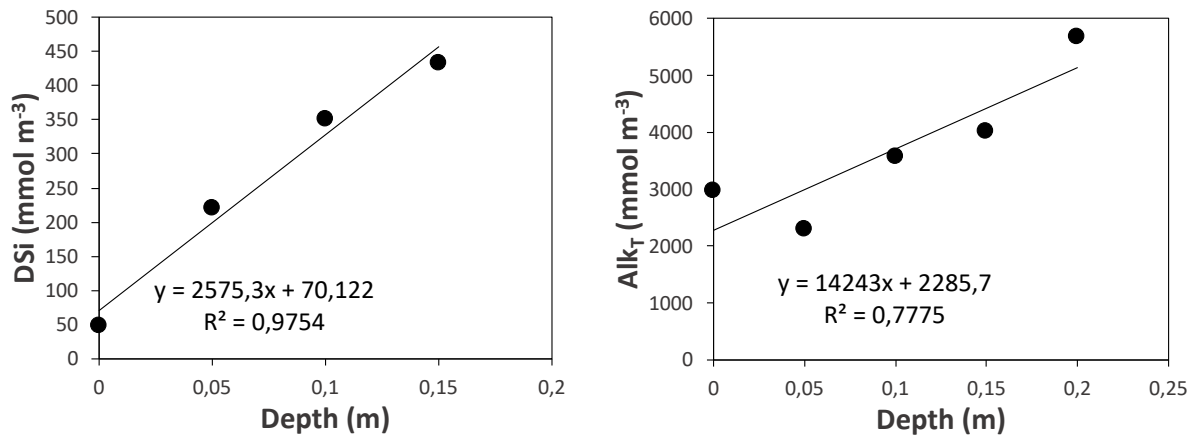


Fig.3 Linear regression of DSi (left) and Alk_T (right) over upper depth of sediment, 0-15 cmbsf and 0-20 cmbsf, respectively. The slopes denote their concentration gradients with respect to depth.

Table.2 Summary of the calculations of silicon isotope effect (separation factor Δ). PW is the abbreviation of pore water.

Depth (cm)	PW $\delta^{30}\text{Si}(\text{‰})$	BSi $\delta^{30}\text{Si}(\text{‰})$	NonBSi_A $\delta^{30}\text{Si}(\text{‰})$	NonBSi_B-A $\delta^{30}\text{Si}(\text{‰})$	BSi/PW $\Delta(\text{‰})$	N/NonBSi $\Delta(\text{‰})$	PW/NonBSi_B-A $\Delta(\text{‰})$	BSi/NonBSi_A $\Delta(\text{‰})$	BSi/NonBSi_B-A $\Delta(\text{‰})$	NonBSi_A/NonBSi_B-A $\Delta(\text{‰})$
0	0,45	0,09	0,62	1,78	-0,36	-0,17	-1,33	-0,53	-1,68	-1,16
5	0,75	0,74	0,98	-0,32	0,00	-0,24	1,06	-0,24	1,06	1,30
10	0,85	0,81	1,51	-1,07	-0,04	-0,66	1,92	-0,70	1,88	2,58
15	0,52	0,55	0,59	0,08	0,03	-0,07	0,45	-0,04	0,47	0,51
20	0,72	0,68	1,10	-0,55	-0,04	-0,38	1,27	-0,42	1,23	1,65
25	0,52	0,82	1,49	-0,87	0,29	-0,97	1,40	-0,68	1,69	2,37
30	0,75	0,62	1,02	0,13	-0,14	-0,26	0,63	-0,40	0,49	0,89
35	0,77	0,37	0,12	1,82	-0,39	0,65	-1,05	0,25	-1,45	-1,70
40	0,76	0,62	-0,21	-0,18	-0,14	0,98	0,94	0,83	0,79	-0,04
45	0,70	0,64	0,24	0,05	-0,06	0,46	0,66	0,40	0,59	0,20
50	0,59	0,49	1,20	-1,10	-0,11	-0,60	1,70	-0,71	1,59	2,30
55	0,58	0,70	-0,42	0,70	0,12	1,00	-0,12	1,12	0,01	-1,11
60	0,15	0,57	-0,20	0,48	0,41	0,36	-0,33	0,77	0,09	-0,68
65	N/A	0,32	0,41	-0,29	N/A	N/A	N/A	-0,09	0,60	0,70
70	N/A	0,56	0,01	-0,18	N/A	N/A	N/A	0,55	0,74	0,19
75	0,51	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A