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Changes in ocean geochemistry across the K-Pg boundary interval

TJÖRDIS STÖRLING

LITHOSPHERE AND BIOSPHERE SCIENCE | DEPARTMENT OF GEOLOGY | LUND UNIVERSITY 2024



Changes in ocean geochemistry across the K-Pg boundary interval

Tjördis Störling



DOCTORAL DISSERTATION

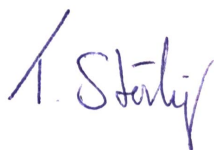
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University of Copenhagen

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Title: Changes in ocean geochemistry across the K- Pg boundary interval	
<p>Abstract</p> <p>The Cretaceous - Paleogene boundary (K-Pg, 66 Ma) was a time interval with dramatic changes in the Earth's climate and the ocean environment. It was characterized by severe disruptions of marine biogeochemical cycles due to a meteorite impact during a time of active volcanism. The extinction of calcifiers, among others, influenced biogeochemical cycles and changed the conditions for carbonate deposition in the global ocean. Our understanding of how these cycles and the ocean geochemistry have changed through this time is still limited. Questions remain about the extent of these changes and their relationship to the biotic recovery in the surface and deep ocean. This thesis aims to provide more insights into the changes in the ocean geochemistry across the K-Pg boundary and the Paleocene (66 – 56 Ma) to improve our knowledge. A goal is to investigate how the marine silicon (Si) cycle has been changed and recovered during this time. This is important due to its link to carbon drawdown and climatic changes via silicate weathering and the biological pump. Additionally, a goal is to gain a better understanding of how ecosystems reacted and recovered in the aftermath of the crisis.</p> <p>The Cerithium Limestone Member (Mb) was deposited in the earliest Paleocene in the aftermath of the crisis and provides an excellent opportunity to investigate the development of non-tropical carbonate depositional systems throughout this time interval. Paper I aims, therefore, to better constrain the genesis and paleoenvironmental conditions of the deposition of Cerithium Limestone Mb. For this study, a detailed analysis of the microfacies and microfossil content of the Cerithium Limestone in the Rødvig section of Stevns Klint succession in Denmark was made. Analysis of thin sections and SEM has revealed four different microfacies with varying amounts of bioclasts in two distinct stratigraphic parts. The lowermost part consists of a thin layer of a bryozoan-rich packstone, which is interpreted as reworked material from the crests of the underlying Maastrichtian mounds. In the upper part, the microfacies appear randomly distributed due to significant bioturbation. The Cerithium Limestone is interpreted as formed in a mainly low-energy, open-marine, outer ramp-like sedimentary environment. Cyanobacteria are likely producers of the micrite of the Cerithium Limestone, as indicated by the dominance of very fine crystals (1– 4 µm).</p> <p>Silicon plays a crucial role in global biogeochemical cycles as an essential nutrient for many marine organisms due to its link to the biological pump. Since the onset of the Phanerozoic, Si cycling has been strongly impacted by the biosilicification of sponges and radiolaria. The stable silicon isotope composition ($\delta^{30}\text{Si}$) of siliceous marine diatoms, radiolaria and sponges can be used as a proxy for past changes in dissolved Si (dSi) concentrations and Si cycling processes. Paper II discusses the changes in the marine Si cycle across the K-Pg boundary with the main focus on the early-mid Paleocene. The study presents the results of $\delta^{30}\text{Si}$ analyses of sponge spicules and radiolaria from sediment samples from DSDP Site 208 (Leg 21) in the Southwest Pacific and suggests that the deep Southwest Pacific was already dSi depleted at the base of the Paleogene (66 Ma).</p> <p>In recent years, the Si isotope fractionation during radiolaria biomineralization has been a topic of interest in the scientific community. In this context, the determination of order-specific and taxa-specific fractionation factors of radiolaria is crucial for the accurate interpretation of the $\delta^{30}\text{Si}$ record. Paper III investigates the $\delta^{30}\text{Si}$ signatures of radiolaria from the orders Nassellaria and Spumellaria. Our results show that it is crucial to consider changes in $\delta^{30}\text{Si}$ of individual taxa (especially from the same order) by the interpretation of the $\delta^{30}\text{Si}$ record in the past. We advise caution when interpreting $\delta^{30}\text{Si}$ signatures from the taxa <i>Spongodiscoidea</i> due to the potential influence by deeper dwelling species on their $\delta^{30}\text{Si}$ record.</p> <p>This thesis fills some of the existing knowledge gaps regarding the development of the Si cycle across the K-Pg boundary and in the early-mid Paleocene and provides new insight into the genesis and paleoenvironmental conditions of the deposition of Cerithium Limestone.</p>	
Key words: K-Pg boundary, Paleocene, ocean silicon cycle, stable silicon isotopes, sponge spicules, radiolaria, Cerithium Limestone	
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Changes in the ocean geochemistry across the K-Pg boundary interval

Tjördis Störling



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List of Papers

This thesis is based on the three papers listed below, referred to by their Roman numerals:

Paper I

Störling T., Demangel I., Lindskog A., Andersson J., Calner M., Conley J. D. and Richoz S. (2023) Insights into the K-Pg extinction aftermath: The Danish Cerithium Limestone. *Revision following initial review submitted to DGF.*

Paper II

Störling T., Doering K., Pickering R. A., Stamm F. M., Zhang Z., Cassarino L., Friberg L., Hendry K. R., Richoz S., Frank M. and Conley D. J. (2023) The Influence of the K-Pg Boundary Events on the Ocean Silicon Cycle. *Submitted to Paleoceanography and Paleoclimatology.*

Paper III

Störling T., Doering K., Zhang Z., Hendry K. R., Richoz S. and Conley D. J. (2024) Silicon isotope signatures of different radiolaria taxa in the early-mid Paleocene. *Manuscript.*

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1 Introduction

The ocean is home to various fascinating processes, including the biogeochemical cycles of elements. The knowledge of how these cycles have changed over geological time is still limited. By understanding how the biogeochemistry in the ocean has changed over time, scientists can provide more insights into how the ocean works and how it might change in the future. The Cretaceous - Paleogene boundary (K-Pg, 66 Ma) was a time interval with dramatic changes in the Earth's climate and ocean environment. To improve the knowledge of changes in the ocean during this time, this thesis investigated changes in the ocean biogeochemistry across the K-Pg boundary and during the Paleocene (66 – 56 Ma).

The K-Pg boundary is a period that was characterized by severe disruptions of marine biogeochemical cycles (Macleod et al., 1997; Schulte et al., 2010). A meteorite impact at 66 Ma (e.g., Alvarez et al., 1980) during a time of active massive Deccan volcanism (e.g., Chenet et al., 2009; Schoene et al., 2019) resulted in catastrophic changes in the Earth's climate and ecosystem interruptions (Schulte et al., 2010). The extinction of calcifiers led to a weakening of the biological pump (the sum of processes that transport carbon from the surface to the deep ocean) and to changes in marine biogeochemical cycles (D'Hondt, 2005; Henehan et al., 2019). As a result, conditions for carbonate deposition in the global ocean changed (e.g., Bown, 2005; Bralower et al., 2020). Carbon drawdown and climatic changes through geological time have been closely coupled to the global silicon (Si) cycle via silicate weathering and the biological pump. Silicon is the second most abundant element by mass in the continental crust, and the chemical weathering of silicate minerals, a process that consumes atmospheric CO₂ and releases solutes such as dissolved silica (dSi; Si(OH)₄), couples the silicon and carbon cycles (Treguer & De La Rocha, 2013). Mainly via rivers, dSi is then transported to the ocean. In the ocean, dSi is a key macronutrient required by marine organisms, such as sponges, radiolaria and diatoms. These silicifying organisms use dSi to build an opaline skeleton of biogenic silica (bSi; SiO₂). Silicifiers transfer the dSi to sediments by incorporating bSi, followed by burial in the sediment (Tribovillard, 2013). How the marine Si cycle responded to the significant environmental changes is still uncertain.

This PhD study aims to investigate the processes that influence the marine silicon cycle across the K-

Pg boundary and the sedimentary deposition in the Paleocene to enhance our understanding of changes in ocean geochemistry during this time interval. The dissertation thus comprises both biogeochemical and sedimentological approaches.

2 Scope of the Thesis

The aim of this thesis is to improve the knowledge of changes in ocean geochemistry across the K-Pg boundary interval at 66 Ma and during the Paleocene (66 – 56 Ma).

The objectives can be summarized as:

- Investigation of changes in the marine silicon cycle across the K-Pg boundary using stable silicon isotope composition of siliceous fossils (sponge spicules and radiolaria).
- Reconstruction of past dissolved silica (dSi) concentrations in the ocean using stable silicon isotope signatures of sponge spicules and radiolaria.
- Analysis of stable silicon isotope signatures of different radiolaria taxa from the early- and mid-Paleocene to improve the present knowledge on order-specific silica utilization.
- Detailed sedimentological description of the Cerithium Limestone Member (Denmark) deposited in the direct aftermath of the K-Pg boundary in the early Paleocene.

3 Background

3.1 The Cretaceous-Paleogene Boundary (K-Pg)

The K-Pg boundary interval refers to the transition period between the uppermost stage of the Cretaceous, the Maastrichtian (72.1- 66 Ma) and the lowest stage of the Paleogene, the Danian (66- 61.6).

The global climate of the Late Cretaceous to Danian was punctuated by massive upheavals in the geosphere and biosphere (Barnet et al., 2019). An impact from a large asteroid at ~66 Ma (e.g., Alvarez et al., 1980; Schulte et al., 2010; Hull et al., 2020) and active massive Deccan volcanism (Deccan Traps) (e.g., Chenet et al., 2009; Schoene et al., 2019) resulted in catastrophic changes of the Earth's climate and ecosystem disruptions (Schulte et al., 2010)(Fig. 1A). The Deccan Traps were located in today's western India and marked a period of extensive volcanic activity, starting in the Late Maastrichtian approximately 250,000 years before the K-Pg boundary (Schoene et al., 2019).

It is widely accepted that the impact of the asteroid in the Yucatan Peninsula in Mexico (~66 Ma) triggered several catastrophic events (Alvarez et al., 1980; Schulte et al., 2010; Morgan et al., 2016; Sepúlveda et al., 2019). Resulting in widespread wildfires, earthquakes, tsunamis, acid rain, global darkness, and global temperatures dropping (Alvarez et al., 1980; D'Hondt et al.; Schulte et al., 2010; Henehan et al., 2019). Evidence of the impact can be found in a clay layer at the K-Pg boundary, which is synchronous worldwide (Sepúlveda et al., 2019). This so-called "boundary clay," with an iridium anomaly at its base, gave rise to the hypothesis that an asteroid impact caused the mass extinction at the K-Pg boundary (Alvarez et al., 1980).

To date, the K-Pg boundary interval is well known as one of the largest five mass extinctions in the past 500 million years (Alvarez et al., 1980; Macleod et al.; Kring, 2007; Schulte et al., 2010; Renne et al., 2013; Vajda & Bercovici, 2014). The K-Pg extinction wiped out 60-75% of all life on Earth (Raup & Sepkoski, 1982) and ~75 % of marine species (e.g., Alvarez et al., 1980; Schulte et al., 2010). The likeliest cause for the K-Pg mass extinction was a selective food chain collapse due to a worldwide disruption of photosynthesis as atmospheric particulates reduced the sunlight after the impact (Brugger et al., 2017; Collins et al., 2017; Gulick et al., 2019).

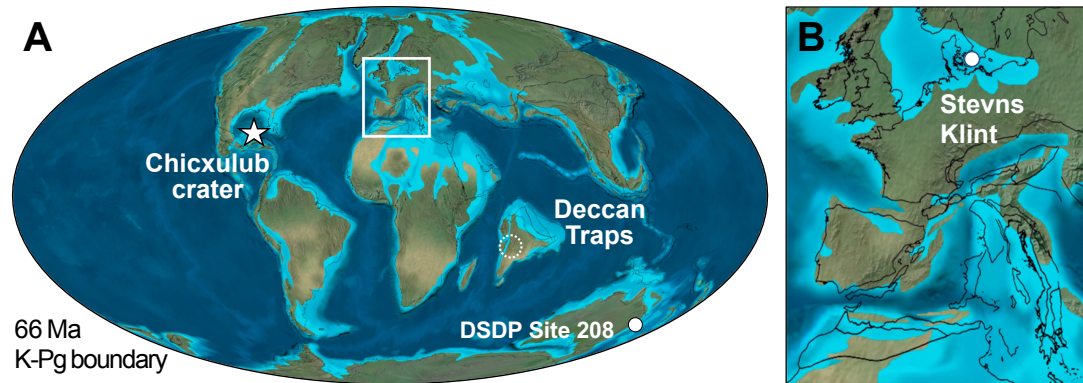


Figure 1: Palaeomap during the Cretaceous–Paleogene boundary interval (~66 Ma). (A) Global paleogeographic reconstruction with the Chicxulub impact site (white star), the Deccan traps (white, dashed line), our study site DSDP site 208 (white dot) and the area of interest (white box). (B) Map of the paleogeography of Europe with the study site (white dot) located at Stevns Klint. Green, light blue, and dark blue denotes emerged land, shallow seas, and open oceans, respectively. Modified from Sepúlveda et al. (2019) © Deep Time Map™ by Robert Blakey.

3.1.2 Ocean Changes Across the K-Pg Boundary

In the ocean, strongly enhanced global darkness, acidification, cooling and reduced primary productivity, which led to food chain collapse, are suggested to be important drivers of the mass extinction (e.g., Kring, 2007; Schulte et al., 2010; Henehan et al., 2019). Rapid ocean acidification, driven by the loss of plankton functional groups (Henehan et al., 2016), could have been the main factor for an ecological collapse in the ocean. Consequently, a dramatic drop in the diversity of marine microplankton groups occurred, especially in calcifiers living in the photic zone (e.g., Bown, 2005; Macleod et al., 2007; Bralower et al., 2020).

In particular, the biological pump was weakened as a consequence of marine extinctions (Birch et al., 2016). The biological pump is the sum of processes transporting organic carbon from the surface to the deep ocean. Inorganic carbon (e.g., atmospheric carbon dioxide (CO_2)) is fixed into organic matter via photosynthesis in the surface ocean and then exported to depth (De La Rocha & Passow, 2014). The biological pump in the ocean has the potential to be a large feedback to climate changes in the past and to future changes in climate as a response to anthropogenic warming (Archer & Jokulsdottir, 2014). However, the weakening of the biological pump resulted in a reduction and transformation of the carbon cycle (D'Hondt, 2005; Henehan et al., 2019), with alterations in the export, burial, and accumulation rates of organic carbon (D'Hondt, 2005; Alvarez et al., 2019; Sepúlveda et al., 2019). Therefore, the extinction of pelagic calcifiers not only transformed biogeochemical cycles but also changed the conditions for carbonate deposition in the global ocean. Afterward, a new ecologic equilibrium set off, with diatoms and dinoflagellates dominating over calcareous nannoplankton (Katz et al., 2004; Knoll & Follows, 2016). In the aftermath of the K–Pg mass

extinction event, oceanic productivity recovered rapidly in terms of biomass (Alegret et al., 2012). However, the specific effects on biogeochemical cycles and ecosystems are not yet fully understood. The marine Si cycle is coupled to the carbon cycle via silicate weathering and the biological pump. Consequently, transformations of the carbon cycle could have resulted in drastic changes in the marine silica cycle. Siliceous planktonic organisms, such as diatoms, silicoflagellates, radiolarians, and sponges, survived possibly better than their calcareous counterparts (Alvarez et al., 2019). It is still uncertain how marine silicifiers and the marine Si cycle responded to these major environmental changes (discussed further in Paper II).

3.2 The Paleocene

The Paleocene (66 – 56 Ma) is a geological time period between two remarkable events in Earth's history: The K-Pg mass extinction (66 Ma) and the Paleocene-Eocene Thermal Maximum (PETM)(~56Ma). Following the aftermath of the K-Pg boundary interval with extreme disruptions of marine biogeochemical cycles, the Paleocene provides insight into how these cycles were affected and recovered. Despite significant research on the extinction interval, the knowledge of the recovery processes during the earliest Paleocene remains limited. Complex changes in climatic, ecological and evolutionary processes characterize the beginning of the Paleocene. The global climate during the Paleocene was characterized by a greenhouse climate state reflected by global temperatures that were more than 5 °C warmer than today (Westerhold et al., 2020). This warming trend is corroborated by rising atmospheric CO_2 concentrations that increased from ~100 ppm at the beginning of the Paleocene to >1000 ppm at the end of the Paleocene (Barnet et al., 2019). Smaller temperature differences between the Earth's poles have led to the absence of ice in these

areas (Zachos et al. 2001). During the Paleocene, the continents continued to drift toward their present positions, but the Supercontinent Laurasia still existed, and North and South America remained separated. The Tasman Gateway and the Drake Passage were closed (Fig. 9B) (Zachos et al., 2001; Straume et al., 2020), resulting in a different circulation of water masses and formation of bottom waters than today (Thomas et al., 2014).

In the marine realm, ocean acidification, darkening and cooling significantly impacted primary producers (Hull et al. 2020), particularly calcifiers living in the photic zone (Olsson et al., 1999; Bown, 2005; MacLeod et al., 2007; Bralower et al., 2020). After the extinction of more than 90% of calcifiers (Bown, 2005), the oceans were repopulated in the immediate aftermath of the extinction event by atypical communities dominated by temporary species (e.g., Bown, 2005; Birch et al., 2016). The marine life of the Paleocene experienced then different stages, from low diversity and abundance, to recovery and diversification. It is assumed that the carbon cycle and the biological pump were fully recovered by ca. 64.2 Ma, ~1.8 Ma after the event (Birch et al., 2016). Diversification continued with species richness only reaching pre-extinction levels 10 Ma after the mass extinction (Alvarez et al., 2019).

Overall, an increasingly detailed record of the biotic, climatic and environmental development during this time was provided by previous paleontological and geochemical studies (e.g., Rasmussen et al., 2005; Alvarez et al., 2019; Westerhold et al., 2020). Additionally, the studies of sedimentology and carbonate microfacies have proved to be useful for understanding the complex interactions between geology, oceanography, and climate in the past. By analyzing the sedimentation patterns and the characteristics of microfacies in carbonates, insights into the physical and chemical processes that occurred in the earliest Paleocene can be gained.

3.3 Stevns Klint and the Cerithium Limestone Member

Stevns Klint, a 14.5 km long coastal cliff in south-eastern Denmark, has been of scientific interest for more than 250 years and is historically significant for the study of the K–Pg boundary (Fig. 1B). To highlight this importance, Stevns Klint was designated in 2014 as a UNESCO World Heritage Center.

The coastal cliffs along Stevns Klint have a succession that spans the upper Cretaceous to the lower Paleogene. These cliffs offer a comprehensive record of non-tropical carbonate depositional systems throughout this time interval. The Stevns Klint succession is well known for the iridium anomaly in a very thin but distinct clay bed known as the Fiskeler

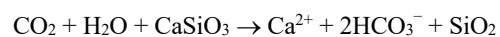
Member (Mb) (Alvarez et al. 1980). Just above the Fiskeler Mb, the Cerithium Limestone Mb is apparent (Surlyk et al. 2006). The Cerithium Limestone Mb was deposited in the earliest Paleocene in the aftermath of the crisis.

The Cerithium Limestone is named after the gastropod *Cerithium* (Forchhammer, 1825) and is preserved as a disjointed series of small depression fills, which are separated by truncated Maastrichtian mounds (Surlyk et al., 2006). The unit was deposited in a marine environment that ranged from mid-neritic (30–100 m) to a deeper milieu based on the high proportion of planktic foraminifera (e.g., Rasmussen et al., 2005; Surlyk et al., 2006). The Cerithium Limestone is beige-yellowish, has an average thickness of about 30–60 cm and is characterized by a dense network of *Thalassinoides* burrows and flint nodules in the upper part (Surlyk et al., 2006). The unit is described as fossil-rich, with gastropods, echinoids, and crinoids (Rosenkrantz, 1939), foraminifera (e.g., Schmitz et al., 1992; Hart et al., 2005; Rasmussen et al., 2005), bivalves (Heinberg, 1999), siliceous sponges (Bernecker & Weidlich, 2005), ammonites (Machalski & Heinberg, 2005) and (very) rare bryozoans (Heinberg, 2005).

Despite numerous studies, the genesis and depositional conditions of the Cerithium Limestone remain poorly understood. However, this unit provides an excellent opportunity to investigate the development of non-tropical carbonate depositional systems in the early Paleocene. Analyses of the Cerithium Limestone can gain a better understanding of how ecosystems reacted and recovered in the aftermath of the K–Pg boundary crisis. Paper I, with a detailed sedimentological description of the Cerithium Limestone Mb and analysis of microfacies and the microfossil content, provides new knowledge about the formation and paleoenvironmental conditions for the deposition of this limestone.

3.4 The Global Silicon Cycle

The global biogeochemical Si cycle can be divided into a continental and oceanic sub-cycle (Frings et al., 2016) and results from a complex interplay between physical, chemical and biological processes (Fig. 2). The cycling of Si is closely coupled to the climate system and plays an important role in long-term global climate regulation. The chemical weathering of silicate minerals, a process that consumes atmospheric CO₂ and releases solutes such as dSi, couples the silicon and carbon cycles (Treguer & De La Rocha, 2013). For example, during the silicate weathering of calcium-bearing-silicate minerals, the chemical pathway is as follows:



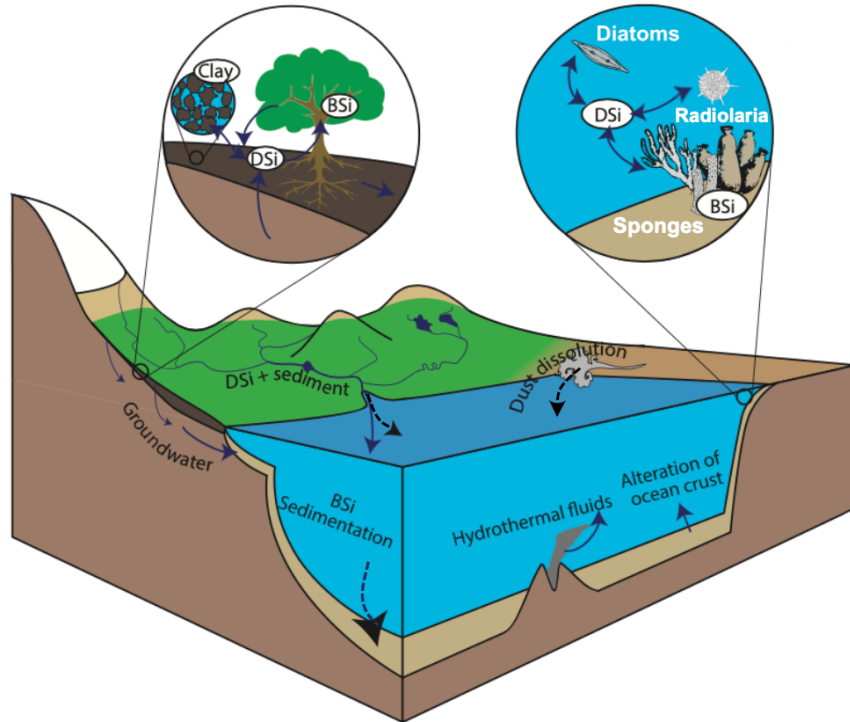
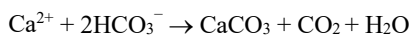


Fig. 2: Simplified schematic of the modern-day global Si cycle. Dashed lines indicate particulate fluxes whereas solid lines indicate solute fluxes or transformations. Modified from Frings et al. (2016).

Silicate (simplified as CaSiO_3) reacts with CO_2 and water (H_2O) to calcium (Ca^{2+}), bicarbonate (HCO_3^-) and silicon dioxide (SiO_2). As a result, silicate weathering provides a natural thermostat to buffer Earth's climate by removing CO_2 from the atmosphere (e.g., Walker et al., 1981; Worsley & Nance, 1989; Berner & Caldeira, 1997).

The formed dSi , Ca^{2+} and HCO_3^- will be transported to the oceans via the riverine system, where marine calcifying organisms use Ca^{2+} and HCO_3^- to build their shells and skeletons of calcium carbonate (CaCO_3), a process called carbonate biomineralization:



Silicon occurs in natural waters as dSi and is used as a nutrient by many plant and animal species. In the oceans, dSi is one of the key macronutrients required by marine organisms that take up dSi to build an opaline skeleton consisting of bSi . The major groups of silicifiers are diatoms (planktonic photosynthetic algae), radiolaria (planktonic protozoa) and sponges (benthic metazoan) (Tréguer & De La Rocha, 2013; Hendry et al., 2019). Different studies (e.g., Fontorbe et al., 2016; Conley et al., 2017; Fontorbe et al., 2017; Hendry et al., 2019) support the idea that ocean dSi concentrations have been coupled with the evolution of silicifiers, e.g., diatoms, sponges, and radiolarians, over geological timescales.

Phototrophic silicifiers, like diatoms, consume high amounts of dSi along with inorganic carbon and contribute to the burial of atmospheric CO_2 in the ocean (Tréguer & Pondaven, 2000). This transfer of dSi from the marine hydrosphere to the biosphere is responsible for initiating the marine biological cycle of Si and links the silicon cycle to the carbon cycle (Ikenoue et al., 2021). After the marine organisms die, shells and skeletons sink and are deposited on the ocean floor (Ruddiman, 2008).

3.4.1 The Marine Silicon Cycle

It is crucial to understand the marine Si cycle as it affects marine food webs, biogeochemical cycles, and the biological carbon pump (Tréguer et al., 2021). Silicon is an essential nutrient in the ocean and exists as dSi , which silicifiers incorporate to form their skeletons (Sarmiento, 2006; Tréguer et al., 2021).

Dissolved silica is transported to the ocean via six pathways (Fig. 2, 3): Rivers, aeolian input, dissolution of minerals, submarine groundwater, (sub-) polar glaciers, and hydrothermal activity. All pathways are ultimately driven during the weathering of the Earth's crust (Tréguer & De La Rocha, 2013; Frings et al., 2016). It is hypothesized that the modern marine Si cycle is approximately in a steady state with inputs = $14.8(\pm 2.6)$ Tmol Si yr^{-1} and outputs = $15.6(\pm 2.4)$ Tmol Si yr^{-1} (Tréguer et al., 2021). The vast majority of dSi is delivered to the ocean via the continental fluvial system. (Tréguer et

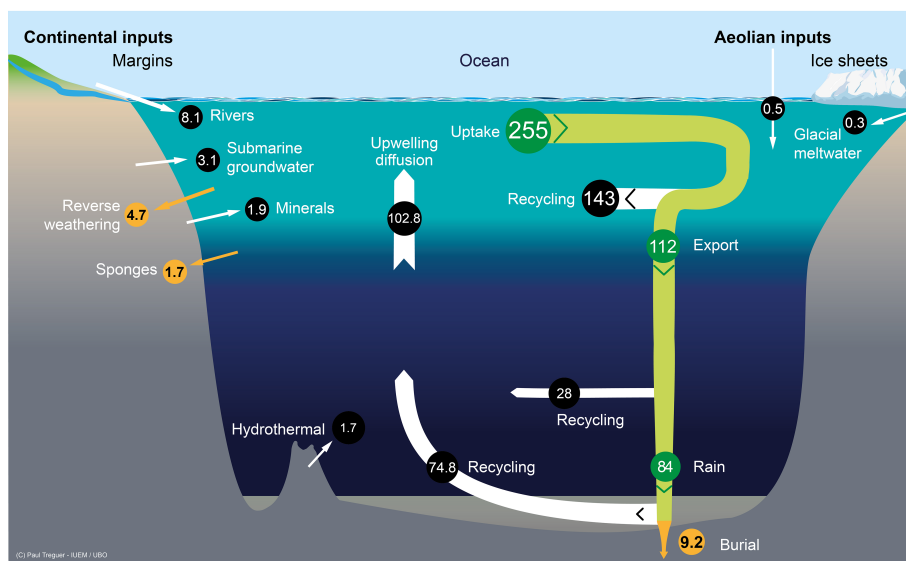


Fig. 3: Schematic view of the Si cycle in the modern ocean (input, output, and biological Si fluxes). White arrows represent fluxes of net sources of silicic acid (dSi) and/or of dissolvable amorphous silica (aSi) and of dSi recycled fluxes. Orange arrows indicate sink fluxes of Si. Green arrows correspond to biological fluxes. All fluxes are in teramoles of silicon per year (Tmol Si yr⁻¹) by Tréguer et al., (2021).

al., 2021; Frings et al., 2016). Rivers contribute 8.1 Tmol Si yr⁻¹ to the total Si budget of the ocean and are thus the main Si source (Tréguer et al., 2021). Other major dSi inputs are submarine groundwater (3.1 Tmol Si yr⁻¹), the dissolution of siliceous minerals (1.9 Tmol Si yr⁻¹), and hydrothermal fluids (1.9 Tmol Si yr⁻¹). The cycle of Si in the water column and burial into sediments is widely dominated by biological processes. Diatoms, radiolarians, and sponges are sinks of Si in the ocean by transferring dSi to sediments via incorporation of bSi followed by burial (Tribouillard, 2013). Deep seafloor deposition is the largest long-term sink of the marine Si cycle (9.2 Tmol Si yr⁻¹) (Tréguer et al., 2021).

In the modern ocean, the distribution of dSi is primarily driven by the general ocean circulation and dissolution of bSi (Sutton et al., 2018; Farmer et al., 2021). A significantly lower dSi concentration observed in near-surface waters than in deeper waters is a consequence of dSi utilization in surface waters by diatoms (De La Rocha et al., 1997; Egan et al., 2012). The dissolution of sinking bSi (i.e., by opal dissolution) causes an accumulation of dSi in older water masses (e.g., North Pacific Deep Water, NPDW), generating water masses with high dSi concentrations. In contrast, newly formed deep waters, such as North Atlantic Deep Water (NADW), have lower dSi concentrations (e.g., De Souza et al., 2014).

3.4.2 Silicon Isotopes

Silicon isotopes have been shown to have great potential to understand the Si cycle by

revealing past and present patterns of dSi concentration. Silicon has three stable isotopes, ²⁸Si, ²⁹Si and ³⁰Si, with relative abundances of approximately 92.23 %, 4.67 % and 3.10 % (De Bièvre & Taylor, 1993). The isotopic composition of different materials (e.g., rocks, plants, waters, etc.) can be compared by normalizing measured atomic ratios of ²⁹Si / ²⁸Si or ³⁰Si / ²⁸Si respectively to the international reference standard NIST RM-8549 (NBS-28) (Georg et al., 2006; Reynolds et al., 2007). Silicon isotopic compositions in samples are expressed as δ²⁹Si or δ³⁰Si and are calculated according to the equation below, where x denotes either ²⁹Si or ³⁰Si:

$$\delta^x\text{Si} = \left\{ \left(\frac{(^x\text{Si})_{\text{sample}}}{(^{28}\text{Si})_{\text{sample}}} \right) / \left(\frac{(^x\text{Si})_{\text{NBS28}}}{(^{28}\text{Si})_{\text{NBS28}}} \right) - 1 \right\} \times 1000$$

Variations or fractionation of the isotope compositions of different reservoirs occur in natural systems as a result of physical, chemical or biochemical reactions (Fig. 4). The strongest Si fractionations occur during biological processes (Opfergelt & Delmelle, 2012).

The biological uptake of dSi by siliceous organisms (sponges, radiolarians and diatoms) and the subsequent formation of bSi discriminates against the heavier Si isotopes (³⁰Si), resulting in a lighter isotopic composition compared to the surrounding seawater (e.g., De La Rocha et al., 1997; Hendry et al., 2019; Doering et al., 2021). This isotopic fractionation varies between different organisms (Frings et al., 2016). Cultured diatoms show a fractionation factor ranging between -2.10‰ to -0.50‰ (De La Rocha et

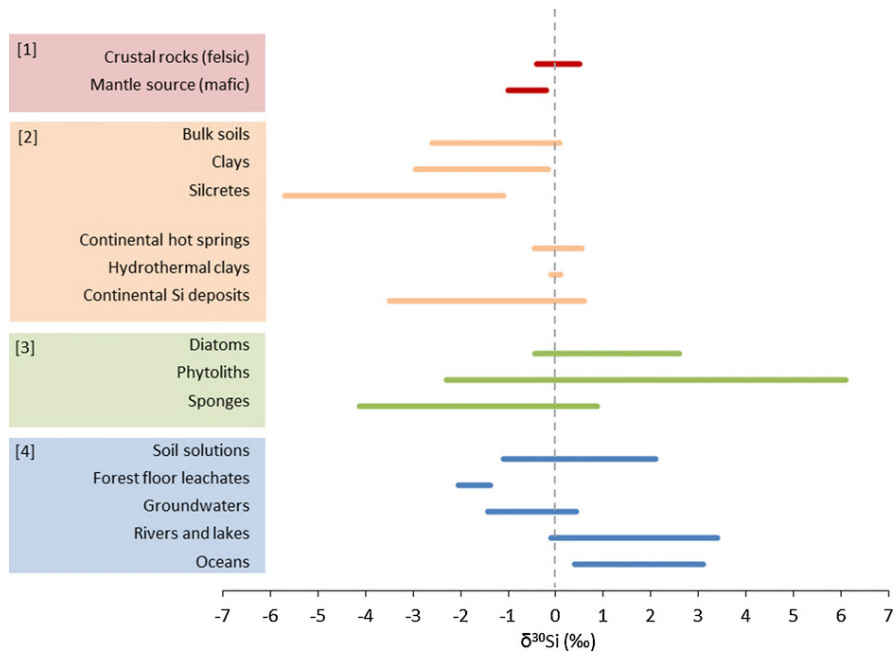


Fig. 4: Variation of $\delta^{30}\text{Si}$ in the different materials. [1] rock-forming processes, [2] water-rock interactions, [3] biological processes, [4] water reservoirs (Opfergelt & Delmelle 2012).

al., 1997; Sutton et al., 2018), sponges from -6.52‰ to -0.77‰ (Wille et al., 2010; Hendry & Robinson, 2012; Hendry et al., 2019) and radiolaria from -2.10‰ to $+0.20\text{‰}$ (Abelmann et al., 2015; Hendry et al., 2014; Doering et al., 2021). The Si isotope composition (denoted by $\delta^{30}\text{Si}$) of bSi consisting of amorphous silica (opal-A) is commonly believed to be unaffected by early diagenetic processes or dissolution (Egan et al., 2012; Hendry & Robinson; Wetzel et al., 2014; Panizzo et al., 2016). Siliceous microfossils from older sediments can be altered by diagenetic processes due to the transformation from opal-A to cristobalite and tridymite (opal-CT), which influence their original $\delta^{30}\text{Si}$ signatures (Tatzel et al., 2015). Therefore, when siliceous microfossils have undergone a diagenetic transformation, they are unreliable for interpreting the $\delta^{30}\text{Si}$ record of the past.

3.4.3 Radiolaria as Geochemical Archives

Radiolaria, a type of marine zooplankton (Fig. 5A), are globally distributed in the oceans from the surface to deep waters of more than 4000m water depth (Suzuki & Not, 2015). Polycystine radiolaria (i.e., the orders of Spumellaria and Nassellaria) produce their opaline skeletons by the biological uptake of dSi from the surrounding water (Anderson, 1983). This uptake is associated with the fractionation of Si isotopes between radiolaria ($\delta^{30}\text{Si}_{\text{rad}}$) and seawater ($\delta^{30}\text{Si}_{\text{dSi}}$) as $\epsilon \sim \Delta^{30}\text{Si}_{\text{rad-dSi}} = \delta^{30}\text{Si}_{\text{rad}} - \delta^{30}\text{Si}_{\text{dSi}}$, where ϵ is the fractionation factor. The two orders, Spumellaria and Nassellaria, are the most abundant Polycystine radiolarians and most important for the silica cycle (Ikenoue et al., 2021).

Recently, $\delta^{30}\text{Si}$ signatures of radiolaria have been investigated as a potential proxy for surface-to-intermediate water conditions and paleo-Si cycle dynamics (Hendry & Robinson, 2012; Abelmann et al., 2015; Fontorbe et al., 2016, 2017; Doering et al., 2021). However, difficulties in culturing radiolaria, potential habitat and biomineralization differences between taxa, and an overall scarcity of $\delta^{30}\text{Si}$ data available for different radiolaria make it challenging to establish a reliable calibration with subsurface dSi concentrations. The scarcity of $\delta^{30}\text{Si}$ data from different radiolaria orders and taxa impedes the establishment of a reliable fractionation factor for radiolaria. However, the determination of order-specific and taxa-specific fractionation factors of radiolaria is crucial for the accurate interpretation of the $\delta^{30}\text{Si}$ radiolaria record. To date, only a few studies on $\delta^{30}\text{Si}$ of radiolaria records are available (Egan et al., 2012; Hendry et al., 2014; Abelmann et al., 2015; Fontorbe et al., 2016; 2017; Doering et al., 2021) and existing estimates of the Si fractionation in radiolaria are solely based on the comparison of radiolaria $\delta^{30}\text{Si}$ ($\delta^{30}\text{Si}_{\text{rad}}$) of surface sediments and seawater $\delta^{30}\text{Si}$ ($\delta^{30}\text{Si}_{\text{dSi}}$) (Abelmann et al., 2015; Doering et al., 2021). If a variable fractionation factor in different radiolaria taxa, families, or orders exists, it should be possible to detect in the $\delta^{30}\text{Si}$ signatures of the different taxa. This will be investigated in Paper III.

3.4.4 Sponge Spicules as Geochemical Archives

Marine sponges (Porifera) can be considered as geochemical archives for the present and past oceanic

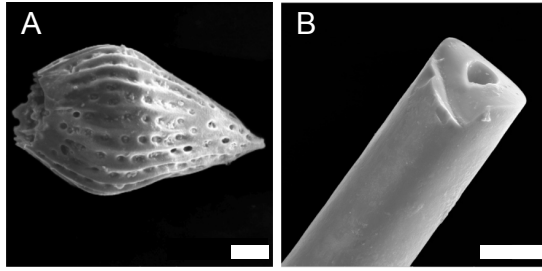


Fig. 5: Scanning Electron Microscope images of siliceous microfossils. A: Radiolaria (order Nassellaria) and B: Sponge spicule. Scale bars in white represent 20 μm .

Si cycle (Cassarino et al., 2018) since they have been present in the oceans since the Precambrian (Love et al., 2009; Antcliffe et al., 2014). Sponges have a worldwide distribution, they are sessile and seafloor-dwelling. Siliceous sponges (Demosponges, Hexactinellids) take up dSi from bottom waters to form skeletal elements called spicules (Fig. 5B). The $\delta^{30}\text{Si}$ signature of siliceous sponge spicules can be used to infer dSi concentrations at the seafloor and as a proxy for bottom water dSi concentrations (e.g., De La Rocha, 2003; Wille et al., 2010; Hendry et al., 2010, 2019; Cassarino et al., 2018). Of particular promise is the relationship between increasing isotopic fractionation of Si in sponge spicules ($\Delta^{30}\text{Si}$, ‰) with increasing dSi seawater concentrations (μM) (Fig. 6), which is apparently not driven by temperature, pH, salinity, or the concentration of other nutrients (Wille et al., 2010; Hendry & Robinson 2012; Hendry et al., 2019). The uptake of dSi is regulated by availability, and growth experiments in laboratory-cultured sponges have shown that there is an exponential relationship between uptake and dSi concentration (e.g., Maldonado et al., 2011). This relationship between ambient dSi concentrations and the magnitude of sponge spicule Si isotope fractionation ($\Delta^{30}\text{Si}_{\text{sponge-dSi}}$, which is approximated as the difference between sponge $\delta^{30}\text{Si}$ and dSi $\delta^{30}\text{Si}$) has made the quantitative reconstructions of past dSi

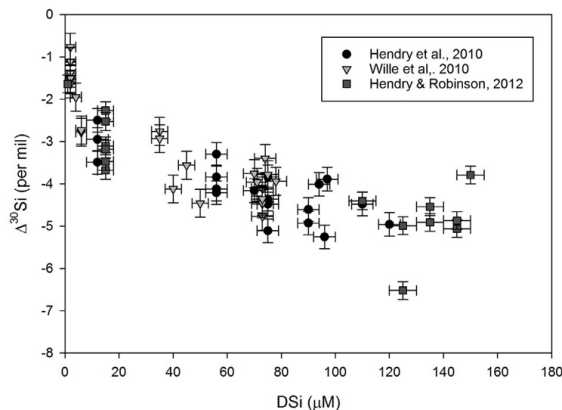


Fig. 6: Sponge calibration data from Hendry et al. (2010), Wille et al. (2010) and Hendry & Robinson (2012) of apparent Si isotopic fractionation $\delta^{30}\text{Si}$ (‰) against dissolved Si concentration (DSi) in μM by Hendry & Robinson (2012).

concentrations (Box 1) possible (Wille et al., 2010; Hendry & Robinson, 2012; Hendry et al., 2019). The previously oldest reconstruction of bottom water dSi concentrations based on published $\delta^{30}\text{Si}$ data dates back to 60 Ma (Fontorbe et al., 2017). Only three existing studies have reconstructed the marine Si cycle during the Paleogene, combining diatoms and sponges (Egan et al., 2013) and radiolaria and sponges (Fontorbe et al., 2016, 2017).

Box 1: Calculation of past dSi in bottom waters

Based on new data compilations by Hendry et al. (2019), the Si isotope fractionation factor $\Delta^{30}\text{Si}$ (‰) of sponges is given by:

$$\Delta^{30}\text{Si}_{\text{sponge-dSi}} = -4.6 + 27.6/(7.4 + \text{dSi})$$

Further, the dSi concentration (in μM) of the source water can be estimated based on $\Delta^{30}\text{Si}_{\text{sponge-dSi}} = \delta^{30}\text{Si}_{\text{sponge}} - \delta^{30}\text{Si}_{\text{dSi}}$ as follows:

$$\text{dSi} = (27.6/(\delta^{30}\text{Si}_{\text{sponge}} - \delta^{30}\text{Si}_{\text{dSi}} + 4.6)) - 7.4$$

3.4.5 Past Marine Silicon Cycle

To study the marine Si cycle in the past, stable Si isotope measurements of siliceous sponges spicules and polycystine radiolaria (Spumellaria, Nassellaria) have been demonstrated to be highly useful tools for the reconstruction of dSi concentrations (e.g., De La Rocha, 2003; Egan et al., 2012; Hendry et al., 2014; Fontorbe et al., 2016; 2017). A decrease in bottom water dSi concentration should be visible in an increase of the $\delta^{30}\text{Si}$ signatures of sponge spicules, whereas a decrease in dSi concentration in subsurface-to-intermediate waters will be seen in an increase of radiolarian $\delta^{30}\text{Si}$ signatures. It is counterintuitive to imagine higher dSi concentrations in the surface layer than in the deep layer of the ocean, then the dissolution of sinking bSi (i.e., by opal dissolution) causes an accumulation of dSi in bottom water masses (Garcia et al., 2013; De Souza et al., 2014). The modern oceanic distribution of dSi is controlled by the general ocean circulation and dissolution of bSi (De Souza et al., 2014).

In the Late Cretaceous and Paleocene, the position of landmasses was significantly different, which resulted in a different circulation of water masses and formation of bottom waters (Thomas et al., 2014). For example, the Tasman Gateway and the Drake Passage were shallow (Fig. 9B) and did not allow an exchange of deep water masses (Straume et al., 2020). The reconstruction of bottom water dSi concentration from sponge spicules provides insights into changes in ocean circulation patterns and nutrient concentrations of the deep ocean in the past.

It has been suggested that the evolution of biogenic silicification and the subsequent deposition of bSi on the seafloor has significantly influenced the global cycle of Si and, therefore, the marine Si cycle. Major macro-evolutionary events in the history of silicifiers have been linked to several significant declines in global marine dSi levels over geological time (Siever, 1991; Conley et al., 2017)(Fig. 7).

A significant decline in marine dSi to modern low levels is hypothesized to have occurred between the end of the Cretaceous and the early Cenozoic, attributed to the evolutionary expansion of diatoms (Maliva et al., 1989; Siever, 1991). According to this theory, the diversification of diatoms set off in the Late Cretaceous and occurred especially during the Cenozoic (Knoll & Follows, 2016). Previous studies presented roughly constant reconstructed surface water dSi concentrations dating back to 60 Ma in the Atlantic (Fontorbe et al., 2016) and 34 Ma in the Southern Ocean (Egan et al., 2013). These Si isotope findings suggest that any diatom-driven drawdown of silica must have occurred prior to this time. Data from Fontorbe et al. (2016, 2017) correspond to the hypothesis from Conley et al. (2017), in which the diatom radiation occurred much earlier than previously hypothesized (Fig. 7).

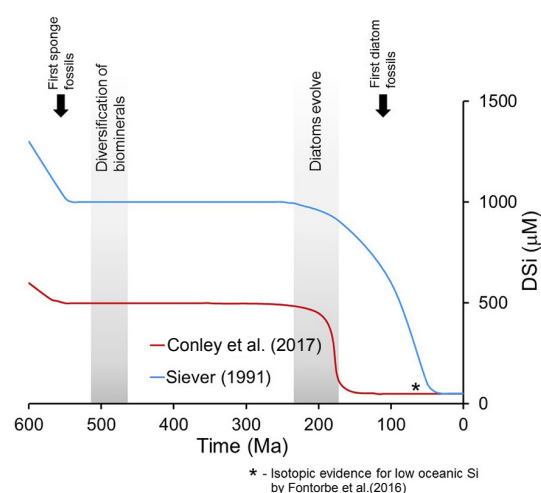


Fig. 7: The evolution of the oceanic Si cycle through geologic time. Envisioned by Siever (1991) (blue line) together with narrative for reductions in dSi primarily through biosilicification (red line) by Conley et al. (2017). Modified after Conley et al. (2017).

4 Study sites

4.1 Stevns Klint- Rødvig, Denmark

Stevns Klint is a 14.5 km long coastal cliff in eastern Denmark rising up to 20 m above present day sea level (Fig. 8A). This location shows the transition from the white chalks of the Maastrichtian (ca. 72–66 Ma) to the bryozoan-rich mounds of the lower Danian (66–61.6 Ma) (e.g., Surlyk, 1997; Hart et al., 2005; Surlyk et al., 2006). The sampling location called the Rødvig section throughout this thesis is in the southern area of Stevns Klint, immediately east of Rødvig at Korsnæb (55.25403, 12.39624) (Fig. 8B).

The Rødvig section is part of the Chalk Group of the upper Maastrichtian and lower Danian. The lower Danian limestones are subdivided into two formations, the Rødvig Formation with the Fiskeler Member (Mb) and the Cerithium Limestone Mb and the Stevns Klint Formation represented by the Korsnæb Mb. The basal Danian Fiskeler Mb, with the famous iridium anomaly at its base (Alvarez et al. 1980), is a stratified clay-marl layer of up to 5–10 cm thickness lying just above the K–Pg boundary (e.g., Surlyk et al., 2006). This unit passes gradually or, in some places, abruptly upwards into the lower Danian Cerithium Limestone (Surlyk et al. 2006). The Cerithium Limestone Mb is a beige-yellowish, partly cemented unit with an average thickness of about 30–60 cm and is characterized by a dense network of *Thalassinoides* burrows and flint nodules in the upper part (Surlyk et al., 2006).

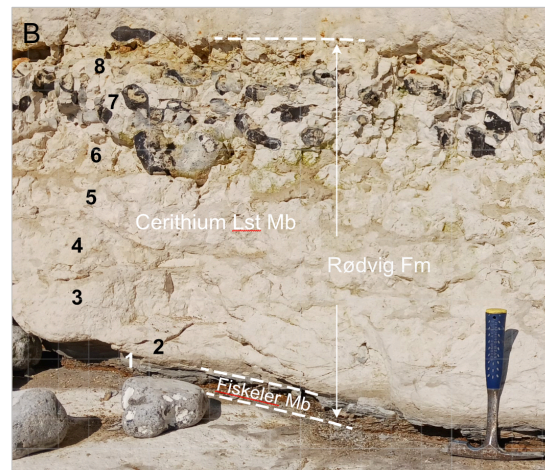


Fig. 8: A: Map of Denmark with the position of the studied section at Stevns Klint (blue star). B: Outcrop photograph of the studied Rødvig section with numbers indicating the sample levels. The Rødvig Formation includes the lowermost Danian Fiskeler Mb, recording the iridium anomaly, and the overlying Cerithium Limestone Mb studied in detail herein. The hammer is 30 cm.

4.2 DSDP Site 208- Leg 21 (Southwest Pacific)

This thesis aims to expand the knowledge of changes in the marine Si cycle across the K-Pg boundary. To achieve this goal, preserved sponge spicules and radiolaria were searched for in more than 240 samples from 26 sediment cores and outcrops that cover the K-Pg boundary interval (see supplements paper II). This search succeeded only in sediments from the Deep Sea Drilling Project (DSDP) Leg 21 Site 208 in the Southwestern Pacific.

Site 208 from DSDP Leg 21 is located on the Lord Howe Rise (-26.11020, 161.22120) in a water depth of 1545 m in the Southwest Pacific Ocean (Fig. 9A) (Shipboard Scientific Party, 1973). The Lord Howe Rise, a fragment of continental crust, was separated from eastern Australia during the Cretaceous break-up of the Eastern Gondwana margin and by the Tasman Sea opening from 85 to 52 Ma (Gaina et al., 1998). It reached its current position once seafloor spreading ended around 52 Ma ago. Paleogeographic reconstructions indicate that DSDP Site 208 had a paleolatitude of approximately 44°S from 70 to 60 Ma (van Hinsbergen et al., 2015).

The recovered sediments (34 core section, 83% recovery) of Leg 21 cover an age range from the Upper Cretaceous to the upper Cenozoic, but sediments after the K-Pg event between 65.5 and 64 Ma were not recovered. The cored sequence can be divided into two lithological units (Shipboard Scientific Party, 1973): Unit 1 is composed of a 488-m-thick sequence of calcareous ooze ranging from the upper Pleistocene to the upper Oligocene. Unit 2 is a 106-m-thick sequence of siliceous fossil-bearing nannofossil chalk to nannofossil-bearing radiolarite or diatomite extending from the lower-middle Eocene to the Upper

Cretaceous. The age model of Site 208 was established by Kuroda et al. (2021) based on biostratigraphic calcareous nannofossils data, magnetostratigraphic and chemostratigraphic data.

Deep and intermediate water formation already took place in the South Pacific (South Pacific Deep Water, SPDW), the North Pacific (NPDW), and the Southern Ocean (AAIW/AABW; Thomas et al., 2014) between ~70 and ~40 Ma, including an already established convection in the North and South Pacific (Fig. 9B). Furthermore, the South Pacific was the primary source of intermediate and deep water formation during the early Paleogene (Thomas et al., 2003; Huber & Caballero, 2011; Sijp et al., 2011) and model simulations (Ladant et al., 2020) show that deep waters (> 1500 m) formed in the western part of the South Pacific basin might have flown northwestward along the Australian coast (Fig. 9B).

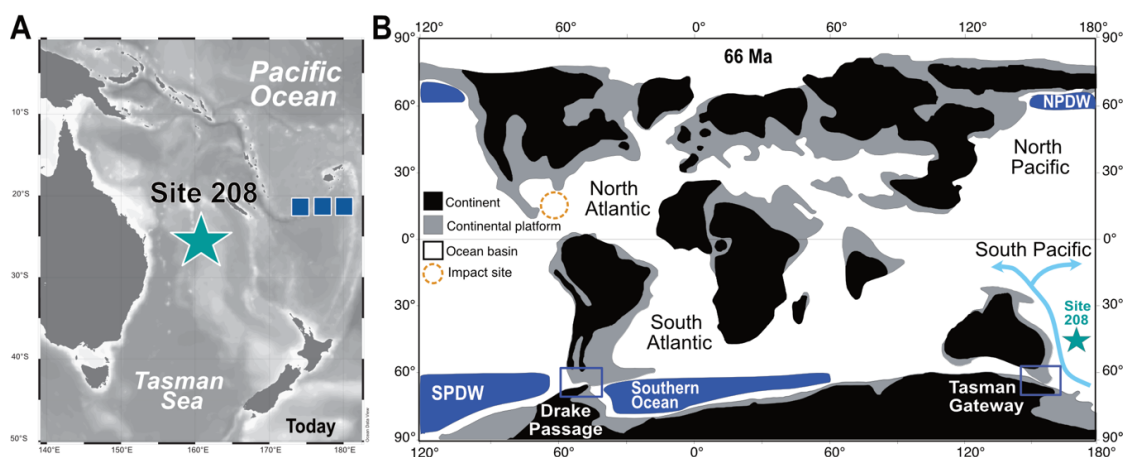


Fig. 9:A: Map from Ocean Data View shows DSDP Site 208 (26°06.612'S, 161°13.272'E) highlighted by a green star and water stations by blue squares. B: Paleogeographic reconstruction for the K-Pg boundary interval (66 Ma) and location of our study Site 208 (denoted by a green star). The meteorite impact site is marked by a yellow dashed circle. Regions of the deep-water formation are schematically highlighted in blue. NPDW = North Pacific Deep Water; SPDW = South Pacific Deep Water. Schematic deep water paleo-ocean circulation close to Australia is highlighted in pale blue arrows. The map was adapted from Bralower et al. (2020) and regions of deep water formation from Barnet et al. (2019).

5 Methods

The three different studies presented in this thesis required different sample preparation techniques and were analyzed by a variety of analytical methods briefly described below.

5.1 Cerithium Limestone Analysis

5.1.1 Sample Collection

The material analyzed in this project was collected from an outcrop located close to Rødvig, Denmark. Albeit being a UNESCO-protected area, official permission from Geomuseum Faxe allowed us to collect samples from the outcrop. Two sampling profiles across the Cerithium Limestone Member were analyzed. The initial profile is a 60 cm block that encompasses the vertical extent of the limestone. Samples were initially chosen for analysis based on distinct characteristics of the limestone, such as borrows, color changes, or textural patterns. Following the observation of diverse microfacies in different thin sections, seven samples were later collected in stratigraphic order from a 60 cm vertical profile, with number 2 at the base until number 8 at the top of the section (Fig. 8B). These samples were prepared for further analyses of the microfacies variation and for quantitative analyses of bioclast content in the stratigraphic succession.

5.1.2 Thin Sections Preparation

In order to obtain insights into microfacies and the fossil content, samples were carefully selected for thin section preparation and then cut into approximately 1 cm thick rectangles with the dimension of a glass slide (about 28x48mm). Subsequently, the samples were embedded in epoxy and a vacuum chamber was used to ensure the compactness of the brittle and soft Cerithium Limestone samples. After drying, the samples were cut into two halves of 0.5 cm thickness. Each slab was glued with epoxy resin on a pre-grounded and signed glass slide. Samples were then manually grounded and polished with a 1200-grit diamond plate.

5.1.3 Optical Microscopy

Thin sections were examined in detail using an Olympus BX50 petrographic microscope equipped with a digital camera (Olympus SC50) at the Department of Geology, Lund University. Lithologies were classified according to the Dunham classification (Dunham, 1962) and the modified scheme of Embry & Klovan (1971). Analyses of the microfacies (e.g., composition, fabrics, and textures) were described according to Wilson (1975) and Flügel (2010).

5.1.4 Scanning Electron Microscope Imaging and Elemental Mapping

Scanning Electron Microscope (SEM) analyses were conducted to image and investigate the microstructures found within the Cerithium Limestone unit at the micro- and nanometer scale. For this purpose, the samples were cut into small squares, polished, and sputter-coated with platinum-palladium. Samples were imaged to investigate microstructures and if these can be related to sediment-influencing/producing organisms and diagenetic processes. For this purpose, a Tescan Mira3 High-Resolution Schottky field emission-scanning electron microscope equipped with an Oxford energy dispersive X-ray spectroscopy (EDS) at the Department of Geology, Lund University was used. Furthermore, elemental distributions were analyzed to determine the chemical composition of the main components using EDS.

5.2 Silicon Isotope Method

For a precise analysis of Si isotope ratios, it is essential to thoroughly remove any sedimentary remnants, such as clay minerals, from the samples. Following this, the samples are further purified using cation chromatography to guarantee a reliable analysis of Si isotope ratios.

5.2.1 Sediment Sample Preparation

A combination of chemical cleaning and handpicking of siliceous microfossils was used to obtain samples that were as pure as possible and free of contaminating sources. The sediment samples for silicon isotope analyses were prepared according to the protocols of Hendry et al. (2010) and Hendry & Robinson (2012). In brief, the sediments were chemically cleaned to remove carbonates and organic matter using 10 % hydrochloric acid (HCl) and 33% hydrogen peroxide (H₂O₂). The pre-cleaned samples were subsequently wet-sieved and the > 25 µm fraction was dried overnight. Biogenic siliceous material (sponge spicules and radiolaria) was handpicked from this fraction using a stereomicroscope.

The fraction < 25 µm was saved and further proceeded for diatom analyses. For the separation of diatoms from the marine sediments, well-established cleaning procedures (Shemesh et al., 1988; Morley et al., 2004; Minoletti et al., 2009) were followed. Clay separation, followed by different microfiltration steps with a 5 µm and 12 µm filter was used to clean diatoms from any contaminants. This step was repeated until no more clay was detected by SEM analyses. Diatoms were then extracted and diluted with Milli-Q® water.

5.2.2 Structural and Elemental Characterization of bSi

For the interpretation of the silicon isotope record, it is crucial that biogenic opal is not influenced by diagenetic transformation and is free from contamination. To be sure that the samples have not undergone a diagenetic structural change from amorphous silica (opal-A) to the higher crystallographic silica phase of cristobalite and tridymite (opal-CT), the silica phase of the sponge spicules and radiolaria was analyzed with X-ray diffraction (XRD). XRD patterns of handpicked siliceous material were acquired with a STOE Multipurpose Diffractometer System Stadi MP at the Centre for Analysis and Synthesis (CAS), Lund University. Following the data collection, the background was removed, and the data were analyzed using the HighScore Plus™ Software from Malvern Panalytical.

SEM imaging and elemental mapping, using energy dispersive X-ray spectrometry (EDS), were performed to confirm that the siliceous microfossils were free of contaminating sources of Si (e.g., clay coatings, authigenic Al-Si phases). EDS was used to analyze the chemical characteristics of the siliceous microfossils. Sponge spicules, radiolarian and bulk diatom samples were analyzed using a Tescan Mira 3 High-Resolution Schottky field emission SEM equipped with an Oxford EDS at the Department of Geology, Lund University (Fig. 5).

5.2.3 Silicon Isotope Analysis

Prior to Si isotope composition analyses siliceous microfossil samples were dissolved and purified according to Hendry & Robinson (2012). After several cleaning steps, sponge spicules were dissolved by heating to 100°C in 0.4M sodium hydroxide (NaOH) and radiolaria in 0.2M NaOH. Diatom samples were dissolved via wet alkaline digestion (Ragueneau et al., 2005) with 0.1M NaOH. The final sample solutions were acidified to a pH of ~2 with 0.16M HCl or 1M HCl.

Seawater samples of three Stations (41, 42 and 43) of GEOTRACES cruise GP21 in 2022 (Achterberg et

al., 2022) were analyzed for a comparison with our biogenic silica data (Fig. 9A). Sample preparation and δ³⁰Si measurements of the seawater samples from Stations 41, 42 and 43 were conducted at GEOMAR in Kiel, Germany. For the analysis of δ³⁰Si, the seawater Si was pre-concentrated and separated from the major matrix elements using the two-step magnesium-induced co-precipitation method called MAGIC (Reynolds et al., 2006, after Karl & Tien, 1992). For this, the pH of the samples was raised with 1M NaOH to precipitate Mg(OH)₂ together with dSi from seawater. The precipitate was isolated by centrifugation and dissolved in 10M HCl.

All sample solutions were purified before silicon analysis by using cation-exchange chromatography following published protocols (Georg et al., 2006). Prior to the analyses, Si solutions were doped with matching magnesium concentrations to correct for isotope mass bias effects (Cardinal et al., 2003). Silicon isotope ratios of the purified sponge and mixed radiolaria Si solutions were then analyzed on a Thermo Finnigan (Neptune) Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS, Thermo Fisher Scientific) (Box 2) located at the Bristol Isotope Group facilities, University of Bristol, UK. Replicates, seawater samples and different radiolaria samples were analyzed on the ThermoFisher (Neptune Plus) MC-ICP-MS at the GEOMAR in Kiel, Germany. During the measurements, all sample analyses were repeated three times and followed standard-sample bracketing methods (Albarède et al., 2004).

The silicon isotope compositions (²⁸Si, ²⁹Si and ³⁰Si) of samples were normalized to the standard reference material NBS-28 (NIST SRM 8546) and reported in δ-notation in per mil (‰):

$$\delta^{30}\text{Si} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where R_{sample} is the ³⁰Si/²⁸Si ratio of the sample and R_{standard} is the ³⁰Si/²⁸Si ratio of the NBS-28 standard. The long-term reproducibility was determined based on the reference standard Diatomite and LMG08 and agreed with published values (Reynolds et al., 2007; Hendry et al., 2011). For seawater samples, the standards ALOHA₁₀₀₀ and PacificDeep were measured and were in good agreement with values obtained in the GEOTRACES intercalibration study of Grasse et al. (2017) and with deep water values from Grasse et al. (2020).

Box 2: MC-ICP-MS

The MC-ICP-MS is based on the principle of the physical separation of isotopes in an ion beam by the combination of an energy filter (electrostatic analyzer) and a magnet, working as a mass filter. The ions will be deflected by the magnet according to their mass to charge ratio, resulting in an individual path for each isotope according to their mass. The beams are collected in different cups, where an electrical signal is detected, and allows the determination of the relative isotopic abundance. This mass spectrometer is widely used in Earth sciences, as it provides precise isotope ratio measurements for a variety of isotopic systems.

6 Summary of Papers

The thesis is comprised of three papers, which are summarized and discussed below. Author contributions are detailed in Table 1.

Paper I

Störling T., Demangel I., Lindskog A., Andersson J., Calner M., Conley D. J. and Richoz S. (2023) Insights into the K-Pg extinction aftermath: The Danish Cerithium Limestone. Revision submitted to DGF.

The Cerithium Limestone Member (Mb) was deposited in the earliest Paleocene in the aftermath of the mass extinction and provides an excellent opportunity to investigate the development of non-tropical carbonate depositional systems throughout this time interval. Paper I aims, therefore, to better constrain the genesis and paleoenvironmental conditions of the deposition of the Cerithium Limestone Mb. For this study, a detailed analysis of the microfacies and microfossil content of the Cerithium Limestone in the Rødvig section of Stevns Klint succession in Denmark was provided. It was demonstrated in our study that the Cerithium Limestone Mb contains more variability than expected from its overall homogeneous appearance at the macroscopic scale. Based on thin sections and SEM analyses, it was shown that the heavily bioturbated member consists of four principal microfacies: A mudstone, a wackestone, and two types of packstones. Our study suggests that the Cerithium Limestone is composed of two stratigraphically distinct parts. The lowermost part consists of a thin layer of a bryozoan-rich packstone, which is interpreted as reworked material from the crests of the underlying Maastrichtian mounds. The second, thicker part is an

intensely burrowed limestone mainly consisting of a wackestone with predominantly foraminifera, a mudstone with some foraminifera, and a foraminifera-bivalve-dominated packstone microfacies. A random systematic distribution of these microfacies suggests a high degree of bioturbation, as visible by a variety of burrows. The varying microfossil content and random distribution of the different microfacies may be explained by strong bioturbation caused by burrowers and/or changes in bottom current velocities over time. Our SEM observations also revealed that the Cerithium Limestone is composed of dispersed micrite, mainly consisting of very fine calcite crystals of 1–4 μm in size. These small calcite crystals might have originated from cyanobacterial activity.

Paper II

*Störling T., Doering K., Pickering R. A., Stamm F. M., Zhang Z., Cassarino L., Friberg L., Hendry K. R., Richoz S., Frank M. and Conley D. J. (2023) The Influence of the K-Pg Boundary Events on the Ocean Silicon Cycle. Submitted to *Paleoceanography and Paleoclimatology*.*

Paper II expands our knowledge of changes in the marine Si cycle across the Cretaceous - Paleogene boundary (K-Pg, 66 Ma), which was marked by severe disruptions of marine biogeochemical cycles. The stable silicon isotope composition of marine radiolaria and sponge spicules can be used as a proxy for past changes in dSi concentrations and Si cycling processes. Paper II presents the results of $\delta^{30}\text{Si}$ analyses of sponge spicules and radiolaria from sediment samples from DSDP Site 208 (Leg 21) in the Southwest Pacific, from the late Cretaceous to the mid-Paleocene (70 to 57 Ma). To the best of our knowledge, our study is the first to employ this approach in the Southwest Pacific during this timeframe. Sponge spicules were extracted and their $\delta^{30}\text{Si}$ signatures were measured to expand the reconstruction of bottom waters. Based on the $\delta^{30}\text{Si}$ of sponge spicules from the Paleocene, it was demonstrated that the deep Southwest Pacific waters were dSi depleted already at the base of the Paleogene (66 Ma). However, it is not possible to interpret from

our record if there was a drawdown of dSi in bottom waters across the K-Pg boundary in this ocean region due to a lack of non-diagenetically altered sponge spicules from this time interval. Additionally, the $\delta^{30}\text{Si}$ signatures of radiolarians were analyzed to reconstruct the paleo-dSi of subsurface waters at this location. Higher dSi concentrations in subsurface water at 70 Ma and 65.6 Ma with a possible drop in dSi approximately 3 Ma after the K-Pg boundary were reconstructed.

Paper III

Störling T., Doering K., Zhang Z., Richoz S. and Conley D. J. (2024) Silicon isotope signatures of different radiolaria taxa in the early-mid Paleocene. Manuscript.

Following the work presented in Paper II, Paper III explores the $\delta^{30}\text{Si}$ signatures of different radiolaria taxa from the Paleocene in the Southwest Pacific. To improve our interpretation of radiolarian $\delta^{30}\text{Si}$ records and the understanding of Si isotope fractionation during radiolaria biomineralization, radiolarians from DSDP Site 208 spanning 64 to 60 Ma were analyzed. Isotope signals from radiolaria provide insights into subsurface-to-intermediate water conditions. The scarcity of $\delta^{30}\text{Si}$ data from different radiolaria orders and taxa impedes the establishment of a reliable fractionation factor for radiolaria. In Paper III, it was investigated if potential differences in order-specific and taxa-specific fraction factors of radiolaria would influence the reconstruction of dSi in the past. An analysis of the $\delta^{30}\text{Si}$ signatures was conducted, differentiating between the orders of Spumellaria (two families: *Actinommioidea* and *Spongodiscoidea*) and Nassellaria (mixed species samples and genus *Buryella*). Additionally, $\delta^{30}\text{Si}$ of diatoms from the same sediment horizons were analyzed for comparison. Only little differences between *Actinommioidea* (Spumellaria), the genus *Buryella* (Nassellaria), and mixed Nassellaria assemblages are present. Only radiolarians from the family *Spongodiscoidea* show significantly more negative $\delta^{30}\text{Si}$ signatures, possibly due to deeper habitat depths of certain taxa.

7 Discussion

7.1 The Genesis of the Cerithium Limestone Mb

Despite significant research on the extinction interval of the K-Pg boundary, knowledge of the recovery processes during the earliest Paleocene remains limited. The studies of sedimentology and carbonate microfacies have proved to be useful for understanding the complex interactions between paleobiology, geology, oceanography, and climate in the past. These studies can help to improve the knowledge about the type of sediment that was deposited and the conditions that led to the formation of specific microfacies. The Cerithium Limestone Mb was studied in the past before, but a detailed description of the genesis of the limestone was still missing. Over the years, different (mis-)interpretations regarding the Cerithium Limestone occurred, leading to the assumption that the Fiskeler Mb and the overlying Cerithium Limestone Mb belonged to the Cretaceous (Forchhammer, 1825). Another assumption was the existence of a gradual faunal transition from the Cretaceous into the Danian (Nielsen, 1917). Later, it was shown that the mixing of fossils from the uppermost Cretaceous chalk and the early Danian Cerithium Limestone during sampling led to this confusion (Rosenkrantz, 1924).

At Rødvig, the Cerithium Limestone appears homogeneous at the macroscopic scale (Fig. 8B). This was also our initial impression during field studies. The unit was reported as very uniform by Hansen (1990), which is typical for a fine micrite. Our thin sections and SEM analyses in Paper I revealed more details and variability in this member. Four different microfacies with varying amounts of bioclasts in two stratigraphically distinct parts were identified. The lowermost part consists of a thin layer of a bryozoan-rich packstone, which is interpreted as reworked material from the crests of the underlying Maastrichtian mounds. In the upper part, the microfacies (mudstone, wackestone and foraminifera-bivalve-dominated packstone) appeared randomly distributed due to heavy bioturbation, which may have erased any stratigraphic structure. It is plausible that seasonal and relatively strong winds or storm events resulted in periodic alternation of bottom currents (Bjerager & Surlyk, 2007), and facilitated the transportation of fossils, which accumulated in previously formed burrows.

The fact that all microfacies are dominated by fine calcite crystals in the micron size range $< 4 \mu\text{m}$ and

rare or absent microbioclast debris suggested a microbial origin of the Cerithium Limestone, such as cyanobacteria (Flügel 2010). Global post-impact 'whittings' caused by cyanobacterial blooms may have contributed to the formation of the pale grey marly chalk of the Fiskeler Mb, directly underlying the Cerithium Limestone (Bralower et al. 2020). Whiting events are the episodic precipitation of fine-grained suspended calcium carbonates in the water column and are likely a major source of carbonate mud. In certain locations, these global whiting events might have persisted for thousands of years after the K-Pg event (Bralower et al. 2020) and continued until the deposition of the Cerithium Limestone. This theory is supported by the observation of low-Mg calcite with microcrystals in a 1 - 4 μm size range presented in all four microfacies, which are typical of cyanobacterial whiting (Bralower et al. 2020). Cyanobacterial blooms in whittings require CaCO_3 supersaturation in seawater (Jones et al., 2019). The abrupt extinction of calcifiers (Bown, 2005) possibly resulted in supersaturated surface waters (Bralower et al. 2020). When the Maastrichtian mounds were exposed to water with a lower pH following the K-Pg crisis, carbonate minerals might have been dissolved and released back CO_2 into the ocean or at least, the early carbonatic cementation has slowed down. Another factor could have been that the reworking of the sediments potentially released trapped nutrients like phosphorus and nitrogen, which might have triggered phytoplankton blooms. The dominance of cyanobacteria in the Cerithium Limestone might indicate that the marine ecology still did not recover until the end of its deposition. Some noncalcareous phytoplankton, such as cyanobacteria, are able to thrive in unfavorable growing conditions, such as more acidic waters or cold temperatures (Bardeen et al., 2017). They have the potential to perform photosynthesis even in worst-case scenario environmental changes, such as the aftermath of the K-Pg crisis (Perez et al., 2013).

It was interpreted that the Cerithium Limestone was deposited in an open marine, outer-ramp-like setting in a dominantly low-energy environment. The different identified microfacies types are typical for open marine, mid-outer carbonate ramps/shelves (Flügel, 2010). A deposition of the Cerithium Limestone in a deeper open marine outer ramp setting was also suggested by the finding of shark teeth belonging to species dwelling in deeper waters (Adolfsson & Ward, 2015). The term 'ramp-like' was chosen due to the huge seas during this time, which were topographically complex and did not form a homogenous or simple slope across the seascape. A mainly low-energy condition in a calm marine area was implied by the deposition and accumulation of carbonate mud clouds from the water surface.

Paper I provided new insights into the genesis and paleoenvironmental conditions during the deposition of the Cerithium Limestone Mb in Stevns Klint. A detailed analysis of the microfacies and microfossil

content of the Cerithium Limestone increased the knowledge of the sea-floor environment in the earliest aftermath of the K-Pg event. Further interpretation requires additional thin sections and SEM analyses. It would be interesting to obtain more samples from this unit along the cliff from different sampling localities for comparison with our results. Additionally, analyses of organic biomarkers such as steranes and hopanes would be of interest to test our theory of cyanobacteria as possible producers of the Cerithium Limestone. Overall, a better understanding of the sedimentation patterns and the characteristics of microfacies in carbonates can help gain knowledge of the physical and chemical processes that occurred during a specific time, like the earliest Paleocene.

7.2 Constraining the Si Cycle in the Past

As stated in the background section, changes in the marine Si cycle through geological time have been studied in the past. The oldest reconstruction of the marine Si cycle based on published data dates back to 60 Ma in the Atlantic Ocean (Fontorbe et al., 2016) and to 50 Ma in the Equatorial Pacific (Fontorbe et al., 2017). Reconstructions of the marine Si cycle during the Paleogene have been carried out by three studies before, combining diatoms and sponge spicules (Egan et al., 2013) and radiolaria and sponge spicules (Fontorbe et al., 2016, 2017). Low dSi concentrations (< 20 μM) in bottom waters of the North Atlantic from 60 to 34 Ma were indicated by Fontorbe et al. (2016). Reconstructions of bottom water dSi concentrations for the Equatorial Pacific ranged between ~0 to ~20–30 μM from ~50 to 37 Ma and between ~10–20 to 50–70 μM from 37 to ~23 Ma (Fontorbe et al., 2017). These changes in reconstructed dSi concentrations in the equatorial Pacific were attributed to changes in global ocean circulation at 37 Ma with the opening of the Tasman Gateway and Drake Passage (Fontorbe et al., 2017). Egan et al. (2013) associated a doubling in dSi concentrations (from 10–50 μM to 50–100 μM) in deep waters with the final establishment of deep-water exchange through the Tasman Gateway and Drake Passage.

In the modern ocean, the dSi distribution is widely controlled by the oceanic overturning circulation and dissolution of bSi (Sutton et al., 2018; Farmer et al., 2021). In the past, the positions of landmasses differed greatly from those in the modern world (Fig. 1A), resulting in different ocean circulation patterns. Neodymium isotopes (denoted by ϵ_{Nd}), together with palaeogeographical reconstructions, show separated overturning circulations in the Pacific and Atlantic Basins during the Paleocene (Martin & Scher, 2004; Thomas et al., 2014). Briefly, ϵ_{Nd} signatures from various materials (e.g., foraminifera, fish teeth) in sediment can be used to track temporal changes in water mass mixing and circulation over geological

time scales (Frank, 2002, and references therein). Between ~70 and ~40 Ma, separated circulation patterns in the North and South Pacific took place as indicated by different ϵ_{Nd} signatures (Thomas et al., 2014). Deep and intermediate water formations were already established in the South Pacific (South Pacific Deep Water, SPDW), the North Pacific (NPDW), and the Southern Ocean (AAIW/AABW; Thomas et al., 2014). Overall, paper II has demonstrated that $\delta^{30}\text{Si}$ signatures of siliceous microfossils can complement more established proxies, such as ϵ_{Nd} , for ocean circulation reconstructions, as previously shown by Fontorbe et al. (2017). Paper II suggested that the $\delta^{30}\text{Si}$ signals of sponge spicules in the Southwest Pacific were influenced by water masses from SPDW during the early Paleogene.

Paper II showed that reconstructed dSi concentrations in bottom waters (of sponge spicules $\delta^{30}\text{Si}$) of the Southwestern Pacific were already low at 66 Ma (Fig. 10). Reconstructed dSi concentrations in subsurface waters (of radiolarian $\delta^{30}\text{Si}$) at 70 Ma, 65.5, and 64 Ma show higher dSi concentrations in the past with a drop in dSi approximately 3 Ma after the K-Pg boundary. It is possible that a reorganization towards enhanced diatom growth was only reached by 63 Ma. An increase in surface dSi utilization and recirculation of water masses to subsurface depth could clearly lower the subsurface dSi concentration similar to today. An observed smaller difference in dSi values between subsurface and bottom waters during the Paleocene, might have been caused by changes in oceanic currents and stratification patterns or a reduced primary productivity at the time. Modern water masses in the Southwestern Pacific have dSi concentrations of about 80 to 90 μM at 1500 m water depth (Garcia et al., 2019). These data are generally higher than our reconstructed dSi concentrations of 6 to 76 μM . This difference likely reflects a different oceanic configuration in the early Cenozoic compared to today. Since the South Pacific was the main source of intermediate and deep water formation during the early Paleogene (Thomas et al., 2003; Huber & Caballero, 2011; Sijp et al., 2011), lower dSi concentrations may have resulted from a lower dSi supply during this time, perhaps due to enhanced

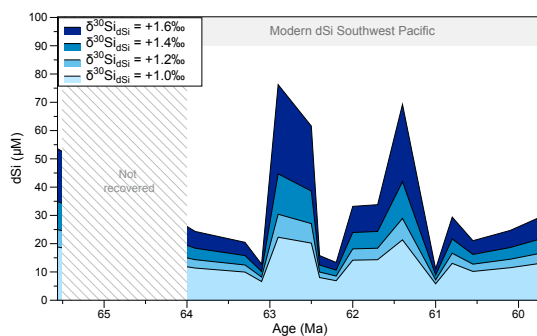


Figure 10: Reconstructed bottom water dSi concentrations of sponge spicule $\delta^{30}\text{Si}_{\text{dSi}}$ signatures. Reconstructed dSi concentrations calculated according to different $\delta^{30}\text{Si}_{\text{dSi}}$ values. (very light blue = +1.0‰, light blue = +1.2‰, blue = +1.4‰, dark blue = +1.6‰).

stratification in the Southern Ocean prior to the opening of the Tasmanian Gateway and the Drake Passage (Egan et al., 2013).

The work presented in Paper II extended our knowledge of changes in the marine Si cycle and the evolution of dSi concentrations in the ocean over the geologic timescale, in particular before and after the extinction event of the K-Pg boundary. It would be interesting to gain more $\delta^{30}\text{Si}$ data from sponge spicules and radiolaria from sediment cores of different oceans during this time span to compare the data with ours. Additionally, a $\delta^{30}\text{Si}$ record of the late Maastrichtian would be a good complement to our results. For a better understanding of our $\delta^{30}\text{Si}$ signatures and reconstructed dSi values, it would be beneficial to have more information about the paleoenvironment during this time interval. In particular, it would be interesting to get more details about the influx of dSi to the ocean and the ocean circulation during this time, as it would allow us to assess how these factors influenced our $\delta^{30}\text{Si}$ record across the K-Pg boundary interval and during the Paleocene.

7.3 Marine Radiolarian $\delta^{30}\text{Si}$ Signature Interpretation

Radiolaria are closely involved in the biogeochemical cycles of silica, carbon and strontium sulfate, carrying important amounts of these elements to the deep ocean (Biard, 2022). They are found from polar to tropical regions, in the sunlit layers of the ocean, down to the deep and cold bathypelagic (Suzuki & Oba, 2015). The fossil record of radiolaria stretches back to the early Cambrian and the $\delta^{30}\text{Si}$ signatures of the fossilized skeleton of radiolaria are a potential proxy to investigate different aspects of the marine silica cycle, such as biomineralization processes and ocean circulation (Abelmann et al., 2015; Fontorbe et al., 2016; 2017; Doering et al., 2021; Bôle et al., 2022).

In recent years, $\delta^{30}\text{Si}$ signatures of marine radiolaria have been investigated as a potential proxy for surface-to-intermediate water conditions (Abelmann et al., 2015; Fontorbe et al., 2016, 2017; Doering et al., 2021). An overall scarcity of $\delta^{30}\text{Si}$ data available for different radiolaria makes it challenging to establish a reliable calibration with subsurface dSi concentrations. However, little is known about Si isotope fractionation in radiolaria taxa or families. To investigate potential differences on order level, the $\delta^{30}\text{Si}$ signatures of radiolaria from Nassellaria and Spumellaria were analyzed in Paper III.

In Paper III, the first taxa-specific $\delta^{30}\text{Si}$ analyses of radiolarian samples from the Southwest Pacific during the Paleocene are presented. The new $\delta^{30}\text{Si}$ data from different radiolaria samples reveal values ranging from -0.6‰ to +1.2‰ during the Paleocene (Fig. 11).

This range in $\delta^{30}\text{Si}$ is consistent with previously published paleo-data of -1.1‰ to +1.7‰ (Abelmann et al., 2015; Fontorbe et al., 2016, 2017).

Paper III shows that radiolaria from the family *Actinommidae* (order Spumellaria), the genus *Buryella* (order Nassellaria), and mixed Nassellaria assemblages have the same mean values and have similar $\delta^{30}\text{Si}$ signatures during the Paleocene. Recent $\delta^{30}\text{Si}$ data of different radiolaria taxa (*Dictyocoryne*, *Stylochlamydidium* and *A. murrayana*) along the Peruvian coast range from +0.6‰ to +1.8‰ (Doering et al., 2021) and show on average a difference of up to 0.9‰ in the $\delta^{30}\text{Si}$ signals between Nassellaria (*A. murrayana*) and Spumellaria (*Dictyocoryne sp.*, *Stylochlamydidium sp.*). In our study, Spumellaria and Nassellaria samples do not show an order-specific difference in their $\delta^{30}\text{Si}$ signatures. Only certain *Spongodiscoidea* (order Spumellaria) samples present more negative values and show significantly different $\delta^{30}\text{Si}$ signatures than the other analyzed samples.

Abelmann et al. (2015) observed more negative $\delta^{30}\text{Si}$ signatures in diverse radiolaria assemblage that included deeper-dwelling radiolarians (for example, *Spongopyle osculosa*- family *Spongodiscoidea*, *Spongogurus pylomaticus*, and *Cromyechinus antarctica*) with habitat depths generally deeper than 400 m. This led to the assumption that the presence of deeper-dwelling radiolarians shifts the $\delta^{30}\text{Si}$ signal to lower values. A possible explanation for the observed negative $\delta^{30}\text{Si}$ values in our study is a higher abundance of deep dwelling radiolaria taxa from the family *Spongodiscoidea* with more negative $\delta^{30}\text{Si}$ signatures due to a deeper habitat depth and lower $\delta^{30}\text{Si}_{\text{dSi}}$. In the modern ocean, the $\delta^{30}\text{Si}_{\text{dSi}}$ depth profiles from different stations (Cardinal et al., 2005; Wille et al., 2010) near our study Site 208 show a decreasing trend with depth. Here $\delta^{30}\text{Si}_{\text{dSi}}$ values range from +2.0‰ in surface waters to +1.1‰ in water depths down to 1500 m. Water masses with lower $\delta^{30}\text{Si}_{\text{dSi}}$

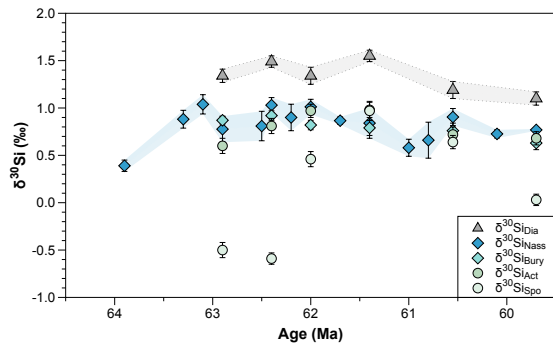


Fig. 11: Silicon isotope composition ($\delta^{30}\text{Si}$ in ‰) of radiolarians and diatoms from the Paleocene. Radiolarian samples from the order Nassellaria include mixed Nassellaria samples ($\delta^{30}\text{Si}_{\text{Nass}}$, blue diamonds) from Störing et al. (in review) and samples from the genus *Buryella* ($\delta^{30}\text{Si}_{\text{Bury}}$, light blue diamonds). Radiolarian samples from the order Spumellaria are from the families *Actinommidae* ($\delta^{30}\text{Si}_{\text{Actio}}$, green circles) and *Spongodiscoidea* ($\delta^{30}\text{Si}_{\text{Spo}}$, light green circles). Diatoms are marked by grey triangles. Vertical error bars denote 2 s.d. uncertainties of the measurements.

signatures would result in lower $\delta^{30}\text{Si}$ values of certain *Spongodiscoidea* taxa in deeper water depths.

Alternatively, the difference $\delta^{30}\text{Si}$ signatures of our radiolaria samples might be explained by a species-specific Si isotope fractionation during dSi uptake, as has been observed in diatom cultures (Sutton et al., 2013). Currently, there is no experimental evidence of what causes the difference in $\delta^{30}\text{Si}$ signatures between radiolaria species. Another factor might be the different skeletal structures of radiolaria from the orders Spumellaria and Nassellaria (Suzuki & Not, 2015). However, our $\delta^{30}\text{Si}$ signatures from samples of both orders, e.g., *Actinommoidea* (Spumellaria) and *Buryella* (Nassellaria), show similar $\delta^{30}\text{Si}$ values. Moreover, our samples from the same order Spumellaria (*Actinommoidea* and *Spongodiscoidea*) have significant differences in their $\delta^{30}\text{Si}$ signatures. Therefore, it is suggested that habitat depth and available dSi had more influence on the *Spongodiscoidea* $\delta^{30}\text{Si}$ signatures of our samples than the skeleton structure.

Paper III shows that the $\delta^{30}\text{Si}$ signatures of individual radiolaria taxa (as likely seen in our *Spongodiscoidea* samples) can have a significant influence on $\delta^{30}\text{Si}$ records of mixed radiolaria samples, especially if the radiolarian assemblage is changing. This agrees with the study from Doering et al. (2021). Our study further demonstrates the importance of considering the composition of the radiolarian assemblages in the interpretation of mixed radiolarian $\delta^{30}\text{Si}$ signatures and strongly recommends avoiding mixed radiolaria samples with radiolaria from the family *Spongodiscoidea*.

By comparing radiolarian $\delta^{30}\text{Si}$ signatures from the Paleocene with published studies, a distinct difference is noticeable: In our study, Spumellaria and Nassellaria samples do not show an order-specific difference in their $\delta^{30}\text{Si}$ signatures. Doering et al. (2021) suggested not to mix different orders (Nassellaria and Spumellaria) and other studies used mainly Spumellaria (Hendry et al., 2014; Abelman et al., 2015) and/or nearly single taxa samples (> 90% *Actinomma antarctica*; Abelman et al., 2015).

Our work in Paper III revealed that changes in $\delta^{30}\text{Si}$ of individual taxa (especially from the same order) must be taken into account by the interpretation of the $\delta^{30}\text{Si}$ record in the past. This knowledge can help by the interpretation of future $\delta^{30}\text{Si}$ records of the Paleocene. It would be interesting to see if similar $\delta^{30}\text{Si}$ signatures of the same families and genera are visible in other radiolaria in different ocean basins during this time. Overall, our study sheds light on the challenges associated with determining Si isotope fractionation in radiolaria and emphasizes the need for further research in this area.

7.4 Future Research Perspectives

The outcome of this thesis has improved our understanding of changes in ocean biogeochemistry across the K-Pg boundary and the Paleocene and highlighted some constraints. The silicon isotopic composition of siliceous microfossils (radiolaria, sponge spicules and diatoms) has proven to be a good way to get insights into the evolution of Si cycling over a range of timescales. However, the topic needs further investigation and the number of Si records of sponge spicules and radiolaria from different ocean basins during various timescales needs to be increased. For example, new sponge spicules and radiolarian $\delta^{30}\text{Si}$ records from the Southwest Pacific Ocean spanning the mid-end Campanian to the Paleocene could provide information on the effects of ocean spreading and drifting of Australia on the distribution of dSi concentrations in the Pacific and the ocean circulation.

The difficulty of carrying out culture experiments for radiolaria has resulted in a significant gap in our understanding of Si isotope fractionation in radiolaria and their ability to incorporate dSi into their tests. More $\delta^{30}\text{Si}$ data of different radiolaria combined with modern seawater dSi concentration would be helpful in investigating the uptake mechanisms in various radiolaria taxa, families, and orders. It would be of interest to see if certain species are adapted to specific dSi ranges and habitat depths and if we could use these species for a reliable reconstruction of dSi in the past.

Determining the marine Si cycle in the past is built on data, which for sponge spicules and radiolaria are sparse. An interpretation, if there was a drawdown of dSi concentration in bottom waters across the K-Pg boundary in the Southwest Pacific, was not possible due to a lack of sponge spicules and radiolaria, which limited the $\delta^{30}\text{Si}$ data that could be measured from this time interval. Obtaining biogenic silica samples from the K-Pg boundary interval has been challenging due to a lack of available core material and preservation issues. Siliceous microfossils from older sediments can be altered by diagenetic processes, influencing their original $\delta^{30}\text{Si}$ signatures (Tatzel et al., 2015). Future studies that use $\delta^{30}\text{Si}$ signatures of sponge spicules and radiolaria as proxies for reconstructing Si cycling in deep time need to carefully consider the potential influence of early diagenesis and post-depositional dissolution and alteration (Hendry & Robinson, 2012). Additionally, IODP orders have shown that many cores are already depleted in material from the K-Pg boundary interval. Unfortunately, oversampling is an important and widespread problem for many IODP cores, especially in the K-Pg interval. New sediment cores covering this interval would be useful for further studies of the Si cycle in the past. Filling the knowledge gaps is also essential for the interpretation of changes in the biogeochemical cycles of Si and carbon and their ecological and biogeochemical impacts on the future ocean.

8 Conclusions

- The Cerithium Limestone can be divided into two stratigraphically distinct parts: (1) A lowermost part consisting of a thin layer of a bryozoan-rich packstone, which is interpreted as reworked material from the crests of the underlying Maastrichtian mounds. (2) A second, overlying thicker part, which is an intense burrowed limestone mainly consisting of a wackestone with predominantly foraminifera, a mudstone with few foraminifera, and a foraminifera-bivalve-dominated packstone microfacies.
- A random distribution of the microfacies in the upper part of the Cerithium Limestone suggests a high degree of bioturbation, as visible by a variety of burrows. A possible former stratigraphic structure was erased due to bioturbation.
- Reconstructed subsurface water dSi of $\delta^{30}\text{Si}$ from radiolarians in the Southwestern Pacific, indicating a higher dSi concentration in subsurface waters in the past and a drop in dSi approximately 3 Ma after the K-Pg boundary. Based on the $\delta^{30}\text{Si}$ of sponge spicules from the Paleocene, dSi concentrations in bottom waters in the Southwestern Pacific were already low at the very base of the Paleogene (66 Ma). It is not entirely conclusive whether there was a drawdown of dSi concentrations in bottom waters across the K-Pg boundary in this ocean region.
- A smaller difference in dSi concentrations of reconstructed subsurface and bottom waters during the Paleocene was caused by changes in oceanic currents and stratification patterns or a reduced primary productivity at the time.
- Radiolaria from the family *Actinommioidea* (order Spumellaria), the genus *Buryella*, and mixed Nassellaria assemblages (order Nassellaria) show the same mean values and have similar $\delta^{30}\text{Si}$ signatures during the Paleocene. Only radiolaria from the family *Spongodiscoidea* differ significantly by showing lighter $\delta^{30}\text{Si}$ signatures.

These negative values were probably caused by an increase in deep dwelling radiolaria taxa from the same family with lighter $\delta^{30}\text{Si}$ signatures due to a deeper habitat depth and lower $\delta^{30}\text{Si}_{\text{dSi}}$ in the deep ocean.

This thesis fills some of the existing knowledge gaps regarding the development of the Si cycle across the K-Pg boundary and in the early-mid Paleocene and provides new insight into the genesis and paleoenvironmental conditions of the deposition of Cerithium Limestone. It has been shown that the Southwest Pacific had low dSi concentrations in bottom waters from 66 to 60 Ma without large changes in dSi levels during this time. Analyses of microfacies in thin sections have shown that the paleoenvironment during the deposition of Cerithium Limestone was still affected by the environmental changes following the mass extinction. Radiolaria $\delta^{30}\text{Si}$ signatures throughout the Paleocene have demonstrated that it is crucial to consider changes in $\delta^{30}\text{Si}$ of individual radiolaria taxa (especially from the same order) for the interpretation of the $\delta^{30}\text{Si}$ record.

Overall, the study of ocean geochemistry is incredibly important for our understanding of marine life and climate change in the past and in the future. Geochemical signatures in ocean sediments act as records of past climate conditions and offer insights into Earth's history. They can help to predict the future impact of climate and how marine life will change. Understanding the cycles of elements in the ocean is crucial for predicting the health and productivity of marine ecosystems. These cycles are directly linked to biodiversity, ocean food webs, and therefore, also to fisheries.

A better understanding of our oceans will hopefully increase awareness, leading to sustainable treatment of our environment and responsible decisions for a healthier planet.

Authors Contribution

Table 1: Author's contributions to papers included in this thesis.* Responsible for the Instrument lab.

	Paper I	Paper II	Paper III
Study design	S. Richoz T. Störling I. Demangel	D. Conley T. Störling K. Doering	T. Störling K. Doering
Data collection			
Field sampling/ Samples requested	S. Richoz T. Störling	T. Störling Z. Zhang	T. Störling
Sample preparation	T. Störling A. Lindskog I. Demangel J. Andersson	T. Störling Z. Zhang F. M. Stamm	T. Störling K. Doering
XRD analysis	-	T. Störling R. A. Pickering	T. Störling
SEM imaging and elemental mapping (EDS)	T. Störling I. Demangel	T. Störling	T. Störling
MC-ICP-MS	-	L. Friberg L. Cassarino K. Doering T. Störling Z. Zhang *K. Hendry *M. Frank	K. Doering T. Störling Z. Zhang
Writing of Original Manuscript Draft	T. Störling	T. Störling	T. Störling
Preparation of Figures	T. Störling I. Demangel J. Andersson	T. Störling K. Doering	T. Störling
Review of Manuscript	All author's	All author's	All author's

Populärvetenskaplig sammanfattning

Havet är en fascinerande plats med många olika processer som pågår. Forskarna försöker fortfarande förstå hur vissa av dessa processer har uppkommit och förändrats miljontals årtillbaka i tiden. En av de största förändringarna inträffade för cirka 66 miljoner år sedan när en stor meteorit träffade jorden, vilket orsakade dramatiska förändringar för livet och klimatet. Meteoriten tillsammans med ovanligt hög vulkanism dödade dinosaurierna och många andra djur och växter. Denna här händelsen var så stor att den till och med påverkade havet och många elements kretslopp, det vi kallar geokemiska cykler. Genom att förstå hur olika näringscykler i havet har förändrats över tid hoppas forskarna kunna lära sig mer om hur havet fungerar och hur det kan förändras i framtiden. Målet med denna avhandling är att öka kunskapen om hur de geokemiska cyklerna i havet påverkades av förändringarna för 66 miljoner år sedan och hur cyklerna återhämtade sig efteråt. Stenar och fossiler från tiden direkt efter meteoritnedslaget, kallad Paleocen, har också studerats för att förstå vad som hände under denna tid.

Ett viktigt element för livet i havet är kisel (Si). Många olika typer av organismer behöver kisel för att växa och leva, inklusive kiselalger (mycket små fotosyntetiska organismer som lever vid havsytan), svampdjur och radiolarier (små organismer som lever nära havsytan). Dessa organismer tar upp upplöst kisel-dioxid (dSi) i form av isotoper (atomer med olika massa) från havet för att bygga upp sina skelett och de tenderar att införliva fler av de lättare isotoperna, vilket lämnar kvarvarande dSi i havsvattnet anrikat i tyngre isotoper. Denna process kallas isotopfraktionering. Isotopfraktionering är ett nyckelverktyg för forskare att studera kislets marina kretslopp och vilken roll kiselhaltiga organismer har i kislets globala biogeokemiska cykel. Därför är sammansättningen av kiselisotoper i skelett från radiolarier och skelettbitar (spikler) från svampdjur ett användbart verktyg för att rekonstruera havets kiselcykel miljontals år tillbaka i tiden. Denna avhandling undersöker hur mycket kisel som fanns i havet tidigare och hur det förändrades efter att meteoriten träffade jorden. För vår studie användes de spikler, som utgör det mikroskopiska skelettet av svampdjur, för att rekonstruera halterna av upplöst kisel i havets bottenvatten. Sammansättningen av kiselisotoper i radiolarier som lever nära havsytan användes för att uppskatta dSi-nivån i det nära-ytvattnet långt tillbaka i tiden. En rekonstruktion av

det nära-ytvattnet och av bottenvattnet påvisar en viss skillnad i deras dSi-nivåer efter meteoritnedslag, antingen på grund av förändringar i havsströmmar eller på grund av minskad bioproduktivitet hos djur vid havsytan vid den tiden. Beräknade dSi-koncentrationer i bottenvatten i sydvästra Stilla havet var redan låga för 66 miljoner år sedan, kanske på grund av en annan havscirkulation under denna tid eller på en hög produktion av kiselalger redan.

Radiolarier är små organismer (zooplankton) som lever i havet på djup från nära ytan till djupare vatten. Olika familjer och släkten av radiolarier tar sannolikt upp kiselisotoper och fraktionerar på olika sätt och i olika grad, vilket kan påverka tolkningen i det geologiska arkivet. Som ett exempel har olika släkten av radiolarier olika skelett. Vissa radiolarier har en bollform (Spumellaria), medan andra har en iskonform (Nassellaria). Denna avhandling undersökte skillnaderna mellan två grupper av radiolarier Spumellaria och Nassellaria. Resultaten visar att vissa typer av radiolarier kan användas för att förstå förändringar i havet och att blandade radiolarier från en mängd grupper kan användas för tolkning, men radiolarier från familjen *Spongodiscoidea* bör undvikas. Studien påvisar att förändringar i kiselisotoper hos specifika radiolarier måste beaktas vid tolkning av kisel i det geologiska arkivet.

Genom att titta på stenar och fossiler kan man få ny kunskap om hur klimatet var, vilken typ av sediment som avsattes och hur havsförhållandena var vid tiden. I denna avhandling studerades en typ av sten som kallas cerithiumkalksten, som bildades under det tidigaste Paleocen. Det visades att cerithiumkalksten kan delas upp i två olika delar. Den nedersta delen är möjligen bildad av omarbetat material av det underliggande kalksten. Den övre delen med tre olika sammansättningar av spår-fossil med en slumpmässig fördelning från de många organismer som var aktiva i sedimenten innan det blev en sten. Kalkstenen har många mycket små kristaller som främst kan ha bildats av små organismer som kallas cyanobakterier. Cerithiumkalkstenen avsattes troligen i en djup, öppen del av havet, med en mestadels lugn och tyst miljö.

Sammanfattningsvis bidrar denna avhandling till att utöka den befintliga kunskapen om hur geokemin i havet förändrades för cirka 66 miljoner år sedan. Att förstå havet i geologisk tid, är som att lägga ett gigantiskt pussel. Denna avhandling är en bit av det pusslet.

En bättre förståelse för våra hav i samhället kommer förhoppningsvis att leda till en mer ansvarsfull och hållbar behandling av vår miljö.



Popular summary

The ocean is a fascinating place with many different processes happening all the time. Scientists are still trying to understand how some of these processes have changed over millions of years. One of the biggest changes happened about 66 million years ago when a large meteorite hit the Earth and caused dramatic changes in climate and the environment. A larger number of active volcanoes than normal and the meteorite killed the dinosaurs and many other animals and plants. This event was so important that it even affected the ocean and the way how elements moved around in it, which we call geochemical cycles. By understanding how different nutrient cycles in the ocean have changed over time, scientists hope to learn more about how the ocean works and how it might change in the future. This thesis aims to increase knowledge of how geochemical cycles in the ocean were affected by the catastrophe 66 million years ago and how they recovered afterward. Rocks and fossils from the time directly after the meteorite impact called the Paleocene, have also been studied to understand what was happening during this period.

One important element for life in the ocean is silicon (Si). Many different types of organisms need silicon to grow and live, including diatoms (very tiny photosynthetic organisms living in the ocean surface), sponges, and radiolarians (tiny organisms living in the ocean near the surface). These organisms take up dissolved silica (dSi) in the form of isotopes (atom species of a chemical element) from the ocean to build their skeletons and they tend to incorporate more of the lighter isotopes, leaving the remaining dSi in the seawater enriched in the heavier isotopes. This process is called isotopic fractionation. Isotopic fractionation is a key tool for scientists to study how silicon moves through the marine environment and understand the role of siliceous organisms in the global biogeochemical cycle of silicon. Therefore, the composition of silicon isotopes in the skeletons of radiolaria and skeleton pieces (spicules) of sponges is a powerful tool to reconstruct different aspects of the ocean silicon cycle deep in time. This thesis investigates how much silicon was in the ocean in the past and how it changed after the meteorite hit the Earth. For our study, the tiny, needle-like structures called spicules that make up the skeleton of sponges were used to reconstruct the levels of dissolved silicon in the bottom water of the ocean. The composition of silicon isotopes in radiolaria living near the ocean surface was used to estimate the dSi level of the sub-surface water in the past. Reconstructed sub-surface and bottom waters show a smaller difference in their

dSi levels after the meteorite impact, either due to changes in oceanic currents or reduced productivity of diatoms in the surface waters at the time. Calculated dSi concentrations in bottom waters in the Southwestern Pacific were already low at 66 million years ago, maybe due to a different ocean circulation during this time or to a high production of diatoms.

Radiolaria are tiny organisms (zooplankton) found in oceans from near the surface to deeper water depths. Different families and groups of radiolaria probably incorporate isotopes in different ways, which might affect the interpretation of silica isotope records. As an example, groups of radiolaria have different skeletons. Some radiolarians have a ball form shape (Spumellaria), whereas others have an ice cone shape (Nassellaria). This thesis explored the differences between two groups of radiolaria- Spumellaria and Nassellaria. The results show that some types of radiolaria can be used to understand changes in the ocean and that mixed radiolaria from different groups can be used for interpretation, but radiolaria from the family *Spongodiscoidea* should be avoided. It was found that changes in silicon isotopes of specific radiolaria must be considered when interpreting silica isotope records.

By looking at rocks and fossils, new knowledge can be gained as examples of what the climate was in the past, what kind of sediments were deposited, and how the ocean conditions were at a specific time. In this thesis, a type of rock called the Cerithium Limestone, which formed in the earliest Paleocene, was studied. It was shown that the Cerithium Limestone can be divided into two different parts. The lowermost part is possibly formed from reworked material of the underlying rock. The upper part has three different compositions with a random distribution due to the many organisms that were active in the sediments before it became a rock. The limestone has many very small crystals, which may have primarily been formed by tiny organisms called cyanobacteria. The Cerithium Limestone was likely deposited in a deep, open part of the ocean, and the environment was mostly calm and quiet.

In summary, this thesis contributes to expanding the existing knowledge of how the geochemistry in the ocean changed around 66 million years ago. The ocean from the past is like a giant complex puzzle with many different pieces that need to fit together to create the whole picture. This thesis helped to uncover more pieces of this puzzle.

A better understanding of our oceans in society will hopefully lead to a more responsible and sustainable treatment of our environment.



Allgemeine Zusammenfassung

Der Ozean ist ein faszinierender Ort mit vielen verschiedenen Prozessen, die ständig ablaufen. Die Wissenschaftler versuchen immer noch zu verstehen, wie sich einige dieser Prozesse im Laufe der Jahrmillionen verändert haben. Eine der größten Veränderungen fand vor etwa 66 Millionen Jahren statt, als ein großer Meteorit die Erde traf und dramatische Veränderungen des Klimas und der Umwelt verursachte. Eine größere Anzahl aktiver Vulkane als normal und der Meteorit töteten die Dinosaurier und viele andere Tiere und Pflanzen. Dieses Ereignis war so groß, dass es sogar den Ozean und die Art und Weise, wie sich Elemente darin bewegen, was wir geochemische Kreisläufe nennen, beeinflusst hat. Indem sie versuchen zu verstehen, wie sich die verschiedenen biogeochemischen Kreisläufe im Ozean im Laufe der Zeit verändert haben, erhoffen sich Wissenschaftler mehr darüber zu erfahren, wie der Ozean funktioniert und wie er sich in Zukunft verändern könnte. Ziel dieser Arbeit ist es, das Wissen darüber zu erweitern, wie die geochemischen Kreisläufe im Ozean durch die Veränderungen vor 66 Millionen Jahren beeinflusst wurden und wie sie sich danach erholten. Gesteine und Fossilien aus der Zeit unmittelbar nach dem Meteoriteneinschlag, dem Paläozän, wurden ebenfalls untersucht, um zu verstehen, was in dieser Zeit geschah.

Ein wichtiges Element für das Leben im Ozean ist Silizium (Si). Viele verschiedene Arten von Organismen brauchen Silizium, um zu wachsen und zu leben, darunter Kieselalgen (sehr winzige photosynthetische Organismen, die an der Meeresoberfläche leben), Schwämme und Radiolarien (winzige Organismen, die im Meer nahe der Oberfläche leben). Diese Organismen nehmen gelöstes Silizium (dSi) in Form von Isotopen (Atomsorten eines chemischen Elements) aus dem Meer auf, um ihr Skelett aufzubauen, und sie neigen dazu, mehr der leichteren Isotope aufzunehmen, so dass das verbleibende dSi im Meerwasser mit den schwereren Isotopen angereichert ist. Dieser Prozess wird als Isotopenfraktionierung bezeichnet. Die Isotopenfraktionierung ist ein wichtiges Instrument für Wissenschaftler, um zu untersuchen, wie sich Silizium durch die Meeresumwelt bewegt, und um die Rolle der siliziumhaltigen Organismen im globalen biogeochemischen Kreislauf des Siliziums zu verstehen. Daher ist die Zusammensetzung der Siliziumisotope in den Skeletten von Radiolarien und Skeletteilen (Schwammnadeln) von Schwämmen ein

leistungsfähiges Instrument, um verschiedene Aspekte des Siliziumkreislaufs im Ozean in der Vergangenheit zu rekonstruieren. In dieser Arbeit wird untersucht, wie viel Silizium sich in der Vergangenheit im Ozean befand und wie es sich nach dem Meteoriteneinschlag verändert hat. Für unsere Studie wurden die winzigen, nadelartigen Strukturen, die sogenannten Schwammnadeln die das Skelett von Schwämmen bilden, verwendet, um den Gehalt an gelöstem Silizium im Bodenwasser des Ozeans zu rekonstruieren. Die Zusammensetzung von Siliziumisotopen in Radiolarien, die nahe der Meeresoberfläche leben, wurde verwendet, um den dSi-Gehalt des Wassers nahe der Oberfläche in der Vergangenheit zu rekonstruieren. Die rekonstruierten dSi-Konzentrationen im nahen Oberflächen- und Bodenwasser unterscheiden sich nach dem Meteoriteneinschlag weniger stark, was entweder auf Veränderungen der Meeresströmungen oder auf eine geringere Produktivität der Kieselalgen im Oberflächenwasser zurückzuführen ist. Die berechneten dSi-Konzentrationen im Bodenwasser des südwestlichen Pazifiks waren bereits vor 66 Millionen Jahren niedrig, was möglicherweise auf eine andere Ozeanzirkulation zu dieser Zeit oder auf eine hohe Kieselalgenproduktion zurückzuführen ist.

Radiolarien sind winzige Organismen (Zooplankton), die in den Ozeanen von der Oberfläche bis in größere Wassertiefen vorkommen. Verschiedene Familien und Gruppen von Radiolarien nehmen Isotope wahrscheinlich auf unterschiedliche Weise auf, was sich auf die Interpretation von Siliziumisotopenaufzeichnungen auswirken könnte. Ein Beispiel: Radiolariengruppen haben unterschiedliche Skelette. Einige Radiolarien haben die Form einer Kugel (Spumellaria), während andere die Form einer Eiswaffel haben (Nassellaria). In dieser Arbeit wurden die Unterschiede zwischen zwei Gruppen von Radiolarien - Spumellaria und Nassellaria - untersucht. Die Ergebnisse zeigen, dass einige Arten von Radiolarien sowie gemischte Gruppen zur Interpretation herangezogen werden können, wobei Radiolarien aus der Familie der Spongodiscoidea vermieden werden sollten. Es wurde festgestellt, dass Veränderungen in den Siliziumisotopen bestimmter Radiolarien bei der Interpretation von Siliziumisotopenaufzeichnungen in der Vergangenheit berücksichtigt werden müssen.

Durch die Untersuchung von Gesteinen und Fossilien können neue Erkenntnisse darüber gewonnen werden, wie das Klima in der Vergangenheit war, welche Art von Sedimenten abgelagert wurden und wie die Meeresbedingungen zu einem bestimmten Zeitpunkt waren. In dieser Arbeit wurde eine Gesteinsart namens Cerithium-Kalkstein untersucht, die sich im frühesten Paläozän bildete. Es konnte gezeigt werden, dass der Cerithium-Kalkstein in zwei verschiedene Teile unterteilt werden kann. Der unterste Teil ist möglicherweise aus umgearbeiteten Material des darunter liegenden Gesteins entstanden. Der obere Teil weist drei verschiedene

Zusammensetzungen mit einer zufälligen Verteilung auf, was auf die vielen Organismen zurückzuführen ist, die in den Sedimenten aktiv waren, bevor er zu einem Gestein wurde. Der Kalkstein enthält viele sehr kleine Kristalle, die hauptsächlich von winzigen Organismen, den so genannten Cyanobakterien, gebildet worden sein dürften. Der Cerithium-Kalkstein wurde wahrscheinlich in einem tiefen, offenen Teil des Ozeans abgelagert, und die Umgebung war meist ruhig und still.

Zusammenfassend lässt sich sagen, dass diese Arbeit dazu beiträgt, das vorhandene Wissen darüber zu erweitern, wie sich die Geochemie des Ozeans vor etwa 66 Millionen Jahren verändert hat. Der Ozean aus der Vergangenheit ist wie ein riesiges komplexes Puzzle mit vielen verschiedenen Teilen, die zusammenpassen müssen, um das gesamte Bild zu erstellen. Diese Arbeit hat dazu beigetragen, weitere Teile dieses Puzzles aufzudecken.

Ein besseres Verständnis unserer Ozeane in der Gesellschaft wird hoffentlich zu einem verantwortungsvolleren und nachhaltigeren Umgang mit unserer Umwelt führen.

