

ALKOR-Berichte

***Sedimentary fluxes of trace metals, radioisotopes and greenhouse  
gases in the southwestern Baltic Sea***

Cruise No. AL543

23.08.2020 – 28.08.2020

Kiel – Kiel

SEDIRACE



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## **1 Cruise Summary**

### **1.1 Summary**

R/V Alkor Cruise AL543 was planned as a six-day cruise with a program of water column and sediment sampling in Kiel Bight and the western Baltic Sea. Due to restrictions related to the Covid-19 pandemic, the original plan had to be changed and the cruise was realized as six one-day cruises with sampling in Kiel Bight exclusively. The first day was dedicated to water column and sediment sampling for radionuclide analyses at Boknis Eck and Mittelgrund in Eckernförde Bay. On the remaining five days, water column, bottom water, sediment and pore water samples were collected at eleven stations covering different types of seafloor environment (grain size, redox conditions) in western Kiel Bight. The data and samples obtained on cruise AL543 will be used to investigate (i) the sedimentary cycling of bio-essential metals (e.g., nickel, zinc, and their isotopes) as a function of variable redox conditions, (ii) the impact of submarine groundwater discharge and diffusive benthic fluxes on the distribution of radium and radon as well as greenhouse gases (methane and nitrous oxide) in the water column, and (iii) to characterize and quantify the impact of coastal erosion on sedimentary iron, phosphorus and rare earth element cycling in Kiel Bight.

### **1.2 Zusammenfassung**

FS Alkor-Reise AL543 sollte ursprünglich als Mehrtagesfahrt mit Wassersäulen- und Sedimentbeprobungen in der Kieler Bucht und der westlichen Ostsee durchgeführt werden. Aufgrund von Einschränkungen der zulässigen Anzahl an Fahrteilnehmern in Zusammenhang mit der Covid-19-Pandemie musste dieser Plan geändert und die Forschungsarbeiten in der Kieler Bucht stattdessen im Rahmen von sechs Tagesfahrten realisiert werden. Auf der ersten Tagesfahrt wurden in Boknis Eck und Mittelgrund in der Eckernförder Bucht Wassersäulen- und Sedimentbeprobungen für die Bestimmung von Radionuklidkonzentrationen durchgeführt. An den verbleibenden Tagen wurden Wassersäulen-, Bodenwasser, Sediment- und Porenwasserproben an elf Stationen innerhalb der westlichen Kieler Bucht gesammelt. Die Stationen sind durch unterschiedliche Redoxbedingungen und Korngrößenverteilungen im Sediment gekennzeichnet. Die während der Forschungsreise AL543 gewonnenen Daten und Proben sollen zur Bearbeitung der folgenden wissenschaftlichen Fragestellungen genutzt werden: (i) wie verhalten sich bioessentielle Spurenmetalle (z.B. Nickel und Zink) und deren Isotope bei der Frühdiagenese im Sediment unter unterschiedlichen Redoxbedingungen, (ii) wie beeinflussen submarine Grundwasserfreisetzung und diffusive benthische Stoffflüsse die Verteilung von Radium, Radon und Treibhausgasen (Methan und Lachgas) in der Wassersäule und (iii) welchen Einfluss hat die Küstenerosion auf die biogeochemischen Stoffkreisläufe von Eisen, Phosphor und Seltenen Erdelementen in der westlichen Kieler Bucht.

## 2 Participants

Principle Investigators	Institution
Scholz, Florian, PD Dr.	GEOMAR
Scholten, Jan, Dr.	CAU Kiel
Bange, Hermann, Prof. Dr.	GEOMAR

Scientific party	Discipline	Institution
<b>23.08.2020</b>		
Scholten, Jan, Dr.	Radionuclides/chief scientists	CAU Kiel
Liebetau, Volker, Dr.	Radionuclides	GEOMAR
Gross, Kathy	Radionuclides	CAU Kiel
Schelke, Dennis	Radionuclides	CAU Kiel
Kock, Annette, Dr.	Trace gases	GEOMAR
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Scholz, Florian, PD Dr.	Sediment geochemistry/chief scientists	GEOMAR
Surberg, Regina	Sediment geochemistry	GEOMAR
Retschko, Anna-Kathrin	Sediment geochemistry	GEOMAR
Schnohr, Melanie	Sediment geochemistry	GEOMAR
Fleischmann, Sarah	Sediment geochemistry	ETH Zürich
Qelaj, Kastriot	CTD, trace gases	GEOMAR
Vosteen, Paul	Sediment geochemistry	GEOMAR
Bodenbinder, Andrea	Sediment geochemistry	GEOMAR
Bardhan, Pratirupa, Dr.	CTD, trace gases	GEOMAR
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Surberg, Regina	Geochemistry	GEOMAR
Retschko, Anna-Kathrin	Geochemistry	GEOMAR
Schnohr, Melanie	Geochemistry	GEOMAR
Fleischmann, Sarah	Geochemistry	ETH Zürich
Qelaj, Kastriot	CTD, trace gases	GEOMAR
Vosteen, Paul	Sediment geochemistry	GEOMAR
Bodenbinder, Andrea	Sediment geochemistry	GEOMAR
Bardhan, Pratirupa, Dr.	CTD, trace gases	GEOMAR
Türk, Matthias	Benthic Trace Profiler	GEOMAR
Pläß, Anna	Benthic Trace Profiler	GEOMAR
Xu, Antao	Rare earth elements, Nd/Hf isotopes	GEOMAR
<b>26.08.2020</b>		
Scholz, Florian, PD Dr.	Geochemistry/chief scientists	GEOMAR
Surberg, Regina	Geochemistry	GEOMAR
Retschko, Anna-Kathrin	Geochemistry	GEOMAR
Schnohr, Melanie	Geochemistry	GEOMAR
Fleischmann, Sarah	Geochemistry	ETH Zürich
Qelaj, Kastriot	CTD, trace gases	GEOMAR
Vosteen, Paul	Sediment geochemistry	GEOMAR
Bodenbinder, Andrea	Sediment geochemistry	GEOMAR
Pläß, Anna	Benthic Trace Profiler	GEOMAR
Xu, Antao	Rare earth elements, Nd/Hf isotopes	GEOMAR

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Scholz, Florian, PD Dr.	Geochemistry/chief scientists	GEOMAR
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Retschko, Anna-Kathrin	Geochemistry	GEOMAR
Schnohr, Melanie	Geochemistry	GEOMAR
Fleischmann, Sarah	Geochemistry	ETH Zürich
Qelaj, Kastriot	CTD, trace gases	GEOMAR
Vosteen, Paul	Sediment geochemistry	GEOMAR
Bodenbinder, Andrea	Sediment geochemistry	GEOMAR
Pläß, Anna	Benthic Trace Profiler	GEOMAR
Xu, Antao	Rare earth elements, Nd/Hf isotopes	GEOMAR
Hathrone, Edmund, Dr.	Rare earth elements, Nd/Hf isotopes	GEOMAR

**28.08.2020**

Scholz, Florian, PD Dr.	Geochemistry/chief scientists	GEOMAR
Surberg, Regina	Geochemistry	GEOMAR
Retschko, Anna-Kathrin	Geochemistry	GEOMAR
Schnohr, Melanie	Geochemistry	GEOMAR
Fleischmann, Sarah	Geochemistry	ETH Zürich
Qelaj, Kastriot	CTD, trace gases	GEOMAR
Pläß, Anna	Benthic Trace Profiler	GEOMAR

**3 Research Programme****3.1 Description of the Work Area**

Kiel Bight is a semi-enclosed basin in the western Baltic Sea surrounded by the coasts of Schleswig-Holstein and the Danish islands of Lolland, Langeland, Ærø, and Als. The complex seafloor morphology of Kiel Bight (Fig. 3.1) was formed by the Scandinavian Ice Sheet during the last Glacial (Seibold et al., 1971). Seafloor highs, which today represent shoals of less than 10 m water depth represent end moraines whereas the surrounding basins represent outwash plains. Local depressions up to 39 m deep represent sub-glacial or ice-marginal channels.

The predominant sediment source of Kiel Bight is erosion at coastal cliffs and abrasion at submarine moraines whereas riverine and atmospheric sediment supply is negligible (Healy and Wefer, 1980; Healy and Werner, 1987). Coastal cliffs surrounding Kiel Bight consist of basal till delivered by the Scandinavian ice sheet. The till is characterized by a wide, unsorted grain size spectrum ranging from boulder and rock debris of variable mineral composition (feldspar, quartz, micas) and provenance in Scandinavia to fine-grained material consisting of calcium carbonate, clay minerals and iron (oxyhydr)oxides (Seibold et al., 1971). Coastal Cliffs in Kiel Bight retreat by decimeters to meters each year, mainly during storm events. Coarse grained sediment particles are retained near-shore on beaches and shallow platforms whereas the fine-grained fraction is transported over longer distances and accumulates in the low-energy reaches of deeper basins together with marine biogenic material (Seibold et al., 1971; Orsi et al., 1996).

Due to sluggish circulation in summer through fall and trapping of organic material, the deepest areas of Kiel Bight are characterized by highly reducing conditions in the surface sediment and lower water column (Lennartz et al., 2014; Dale et al., 2014). Quantitative consumption of nitrate and nitrite by denitrification occasionally results in the release of hydrogen sulfide from the sediments into the bottom waters. Such anoxic and sulfidic events are typically terminated in late fall by wind-induced vertical mixing and lateral advection of well-oxygenated water from the belt sea (Lennartz et al., 2014).

Submarine groundwater discharge has been observed at the southern end of Mittelgrund, a submarine moraine located at the outlet of Eckernförde Bay (Bussmann and Suess, 1998; Schlüter et al., 2004). The groundwater derives from several interconnected sandy aquifers of Miocene to late Pleistocene age, which are capped by late glacial clays (Jensen et al., 2002). According to these authors, submarine groundwater discharge occurs where the clayey seal is thinned and the Holocene mud coverage is weak enough to be penetrated by artesian groundwater. Moreover, free gas produced by methanogenesis in the organic-rich Holocene mud is uplifted by the local ascent of groundwater forming the characteristic intrapockmark structures at Mittelgrund (Hoffmann et al., 2020).

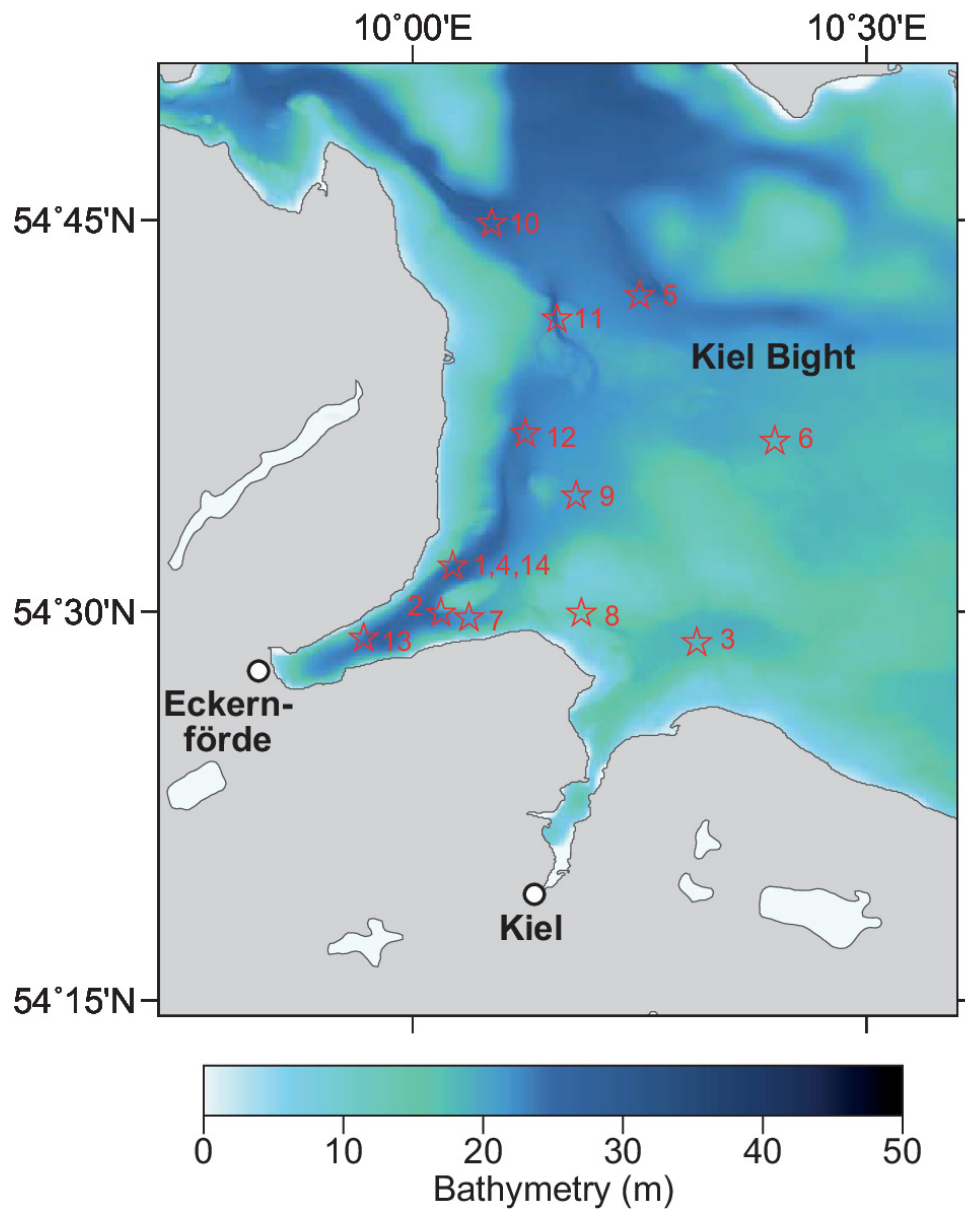
### **3.2 Aims of the Cruise**

Coastal sediments represent an important source or sink of macronutrients, bio-essential metals and greenhouse gases in the ocean. In the coming decades, source and sink fluxes will be altered by global environmental change and the associated trends of ocean deoxygenation and acidification as well as sea-level change and an anticipated increase in coastal erosion. Due to the broad range of sedimentary redox conditions in close vicinity and well-characterized seasonal cycles of temperature, salinity and oxygen, Kiel Bight is an ideal location to investigate those trends under well-defined boundary conditions. Moreover, erosion at coastal cliffs and submarine groundwater discharge represent additional sources of nutrients, trace metals and/or greenhouse gases to the water column in Kiel Bight. The aims of cruise AL543 were the following:

1. Investigate the impact of variable redox conditions on the sedimentary release or fixation of bio-essential metals (e.g., nickel, zinc, and their isotopes) as well as radium and radon (tracers for submarine groundwater discharge and sedimentary efflux in general).
2. Investigate the impact of diffusive sedimentary fluxes versus ground water discharge on the distribution of greenhouse gases (methane and nitrous oxide) in the water column.
3. Characterize and quantify the impact of coastal erosion on sedimentary iron, phosphorus and rare earth element (REE) cycling in Kiel Bight.

To realize these goals, we identified 12 target sites in Kiel Bight (Fig. 3.1) where an extensive program of water column and sediment sampling was realized. These sites cover different water depth and thus sediment types (mud, sandy mud, muddy sand) and differing bottom water redox

conditions (fully oxic to anoxic and sulfidic). Very shallow sites with sandy or lag sediment were avoided because no pore waters can be recovered in such environments. Moreover, we took samples off major cliffs in Stohl (Station 8) and Schönhagen (Station 12) as well as at the submarine groundwater discharge site southwest of Mittelgrund. Finally, the sampling sites are equally distributed throughout western Kiel Bight to gain an overview about the distribution of greenhouse gas fluxes and concentrations in the water column.



**Fig. 3.1** Bathymetric map showing sampling locations during AL543.

### 3.3 Agenda of the Cruise

Originally, it was planned to realize AL543 as a multiday cruise where relatively shallow sampling stations in Kiel Bight are combined with deeper stations within the Baltic Proper. Due to the Covid-19 pandemic and the related restriction of the number of overnight participants aboard R/V Alkor during multi-day cruises (6 instead of 12), the principle investigators (PIs) were forced to modify this plan. According to the hygiene concept for research cruises aboard R/V Alkor, up to 12 scientists can participate in one-day cruises. Therefore, the distant stations within the Baltic Proper were cancelled so that all sampling stations could be reached within the framework of one-day-cruises departing and arriving at the home dock of R/V Alkor in Kiel.

The first day of the cruise (23.08.2020) was used by the radionuclide group lead by PI Jan Scholten to conduct research at Boknis Eck (Stations 1, 4 and 14) and the submarine groundwater discharge site southwest of Mittelgrund (Station 2). On the following days (24.08.2020 – 28.08.2020), the other groups lead by PI Florian Scholz conducted research at Stations 3 to 14. Due to the time-consuming sample processing and laboratory work, five scientists of the sediment geochemistry group stayed on-board overnight. A variable number of additional scientists embarked in the morning and disembarked in the late afternoon. Due to the mixed character of the cruise involving both overnight and day-only participants, all scientists taking part in the cruise from 24.08.2020 to 28.08.2020 were tested for Covid-19.

## 4 Narrative of the Cruise

The Covid-19 test for cruise participants took place on August 21<sup>st</sup> 2020 at 8:00 a.m. local time. At the same time, our scientific equipment was transferred to the ship and loaded by the ship's crew at the GEOMAR east shore docks. Upon availability of the negative Covid-19 test results in the morning of August 22<sup>nd</sup> a subset of the scientific party installed sampling and laboratory equipment aboard R/V Alkor.

On August 23<sup>rd</sup> R/V Alkor left Kiel harbor at 8 a.m. towards Boknis Eck, Eckernförde Bay. Here, a CTD was deployed for full water-column methane, nitrous oxide and nutrient sampling. Three Rumohr lots (RML) recovered sediments for pore water sampling for radon and radium analyses and for incubation experiments in the home lab. For the determination of radium and radon in the water column, two diving pumps were attached to the CTD and water was pumped from different water depths on-board the ship and for each water depth about 60-100 l of seawater was collected in barrels. Thereafter, the ship moved to the location Mittelgrund, which is characterized by submarine groundwater discharge. Here, the same sampling was performed as at Boknis Eck, i.e. CTD water columns sampling, recovering of three sediments cores and CTD pump for large volume water sampling for radium and radon measurements. Due to limited time, only deep-water radon concentrations could be measured. R/V Alkor arrived at Kiel harbor at 9 p.m.



On August 24<sup>th</sup> R/V Alkor departed at 8 a.m. The station work at Station 3 at the outlet of Kiel Fjord began at 9 a.m. with a CTD followed by a minicorer (MIC). We then headed to Station 4 off Boknis Eck at the outlet of Eckernförde Bay. Between 10:45 and noon, we deployed 2 CTDs as part of the monitoring program, which has been conducted by marine scientists in Kiel at this site since the nineteen fifties. After another MIC deployment, the ship steamed back to Kiel, where we arrived at about 4 p.m. in the afternoon. Subsampling of sediment cores and on-board chemical analyses continued until 8 p.m.

On August 25<sup>th</sup> R/V Alkor departed at 7:30 a.m. and steamed to Station 5 in the northern reaches of Kiel Bight, where we arrived at 10 a.m. We deployed one CTD for nutrient, oxygen and trace gas analyses and another one for large volume samples for the analyses of rare earth element concentrations and neodymium isotope ratios. After the water column program was completed, a multicore was taken and the ship steamed to Station 6 in central Kiel Bight, where again two CTDs were deployed. We then deployed the Benthic Trace Profiler (BTP), a trace metal-clean bottom water sampler, which was recently developed at the Technology and Logistics Centre of GEOMAR. After recovery of the BTP and another MIC deployment the ship steamed back to Kiel, where we arrived in the afternoon. Subsampling of sediment cores and on-board chemical analyses continued until the early evening.

On August 26<sup>th</sup> moderate gale and seas prevailed. Since calm winds and seas are required for a successful deployment of the BTP, we decided to sample sheltered stations close to land on that day. R/V Alkor departed at 7:30 am and we conducted research at Stations 7 (south of Mittelgrund: CTD, MIC), 8 (Channel off Stohl: 2 CTDs, MIC, BTP) and 9 (CTD, MIC). The ship returned to port in the afternoon and subsampling of sediment cores and on-board chemical analyses continued until 10 p.m.

On August 27<sup>th</sup>, R/V Alkor departed at 6:30 a.m. to reach our most distant station (Station 8) at the outlet of Flensburg Fjord at 9:15 a.m. We deployed a CTD and MIC and steamed southward along the coast to Station 10, where also CTD and MIC were deployed. Station 11 was reached around noon and the station work continued with 2 CTDs, a BTP and a MIC. The ship returned to port in the afternoon and subsampling of sediment cores and on-board chemical analyses continued until 9 p.m.

On August 28<sup>th</sup>, R/V Alkor left at 7:30 p.m. and steamed to Station 12 in Eckernförde Bay, where we deployed a CTD and a MIC between 9:30 and 10:00 a.m. We then steamed back to Station 1 (4, 13), where the CTD and BTP were deployed. The ship then returned to port and subsampling of sediment cores and on-board chemical analyses continued until 3 p.m. Following the completion of the scientific work, the labs were uninstalled and cleaned and the equipment was stowed in the hangar on deck. All scientists left the ship in the evening of August 28<sup>th</sup>.

The cruise ended with the unloading of our equipment and samples on Monday August 31<sup>st</sup> 8 a.m. at the east shore docks of GEOMAR.

## **5 Preliminary Results**

### **5.1 Water column measurements**

#### **5.1.1 Methodology**

(Hermann Bange, Annette Kock, Kastriot Qelaj, Pratirupa Bardhan)

Water column samples were collected using a HydroBIOS MWS 12 rosette water sampler equipped with a CTD, fluorescence, pH and oxygen sensor. In total, 21 CTD profiles were recorded during the cruise.

Samples for dissolved oxygen were collected first from the CTD/Rossette to avoid degassing of O<sub>2</sub>. Samples were collected in 100 ml bottles. To each sample, 1 ml each of manganese (II) chloride and sodium iodate solutions were added and then titrated by the Winkler method. The measurements were carried out onboard within a few hours of sample collection.

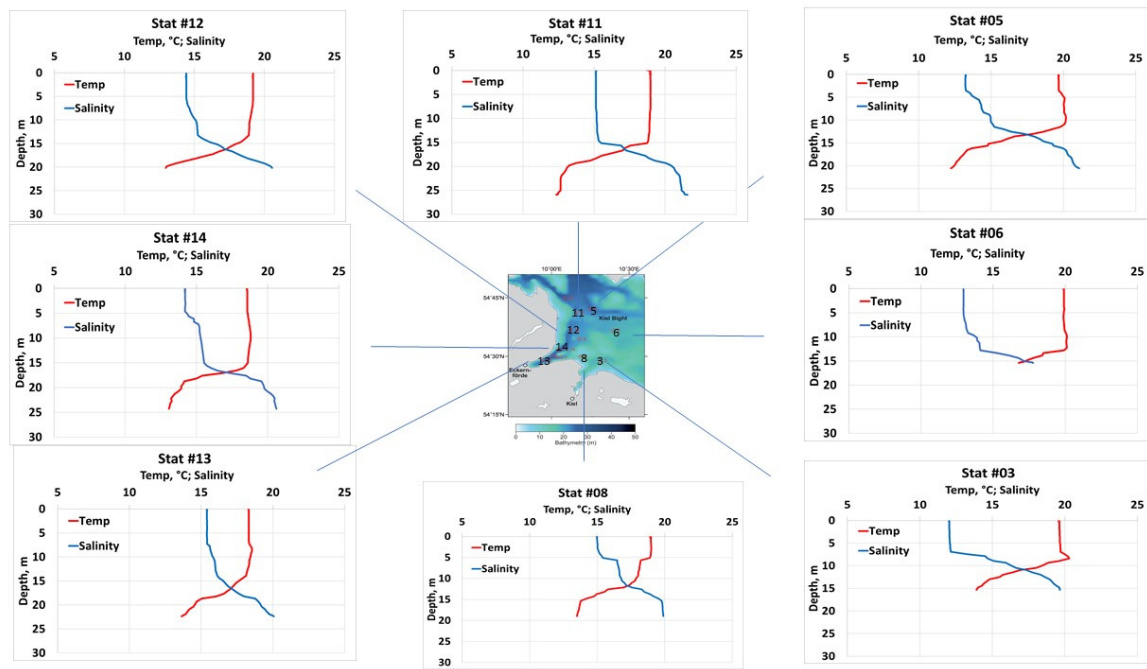
The samples for dissolved nutrients (nitrate, nitrite, silicate and phosphate) were collected in polypropylene bottles and filtered through 0.2 µPSE-filters. They were frozen and subsequently analyzed in the shore laboratory using a Quattro Seal Autoanalyser.

Samples for trace gases (methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O)) were collected in triplicates in 20 ml amber glass vials. Samples were taken after collecting dissolved oxygen avoiding air bubbles. The bottles were then crimped and stored at room temperature, poisoned with 50 µL dissolved mercuric chloride (HgCl<sub>2</sub>, 2 g/100 ml) to prevent biological activity and transported back to the laboratory for later analysis.

Samples for dissolved N<sub>2</sub>O isotopomers were collected in 160 ml glass serum bottles. Gastight sampling was followed, similar to trace gases. A headspace of 10 ml was created and each sample was poisoned with saturated HgCl<sub>2</sub>. Bottles were crimped and stored upside down at room temperature in dark conditions. Samples for dissolved nitrate (<sup>15</sup>NO<sub>3</sub><sup>-</sup>) isotopes were collected in 50 ml plastic bottles and frozen until analysis.

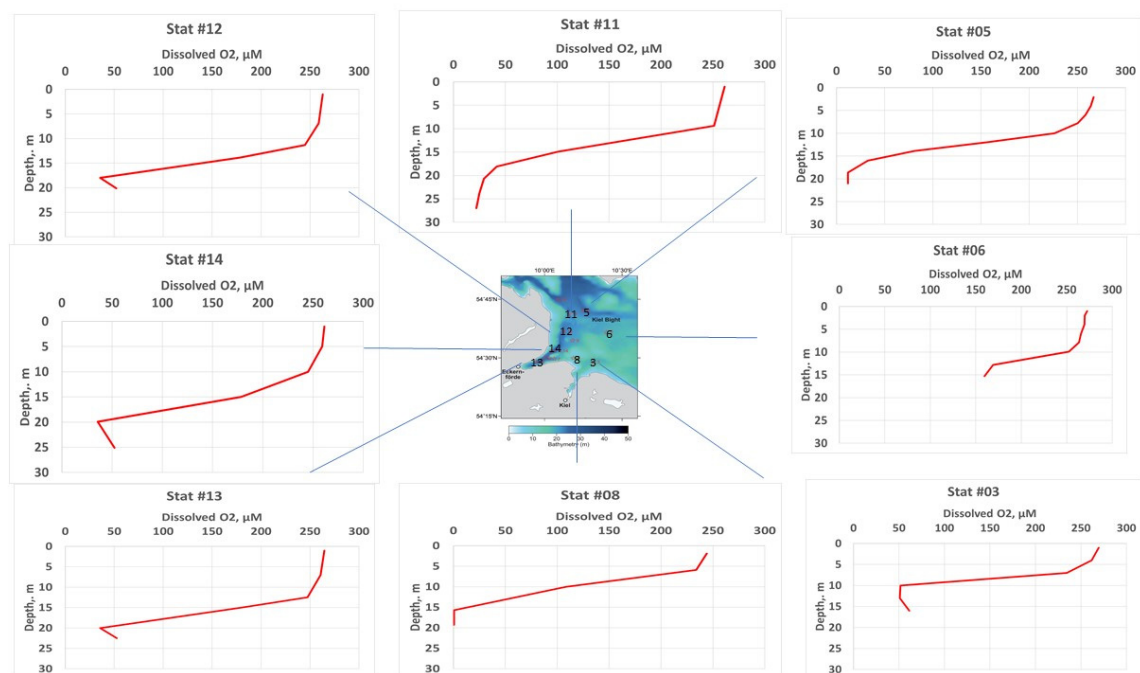
#### **5.1.2 Preliminary Results**

Surface (0 - 1 m) water temperatures and salinities ranged from 18.3 to 19.9 °C and from 12.0 to 15.4, respectively. Bottom (> 20m) water temperatures and salinities ranged from 12.2 to 14.6 °C and from 19.1 to 21, respectively. The water temperature and salinity profiles usually showed pronounced pycnoclines indicating a strong stratification with mixing depth up to 15 m (Fig. 5.1).



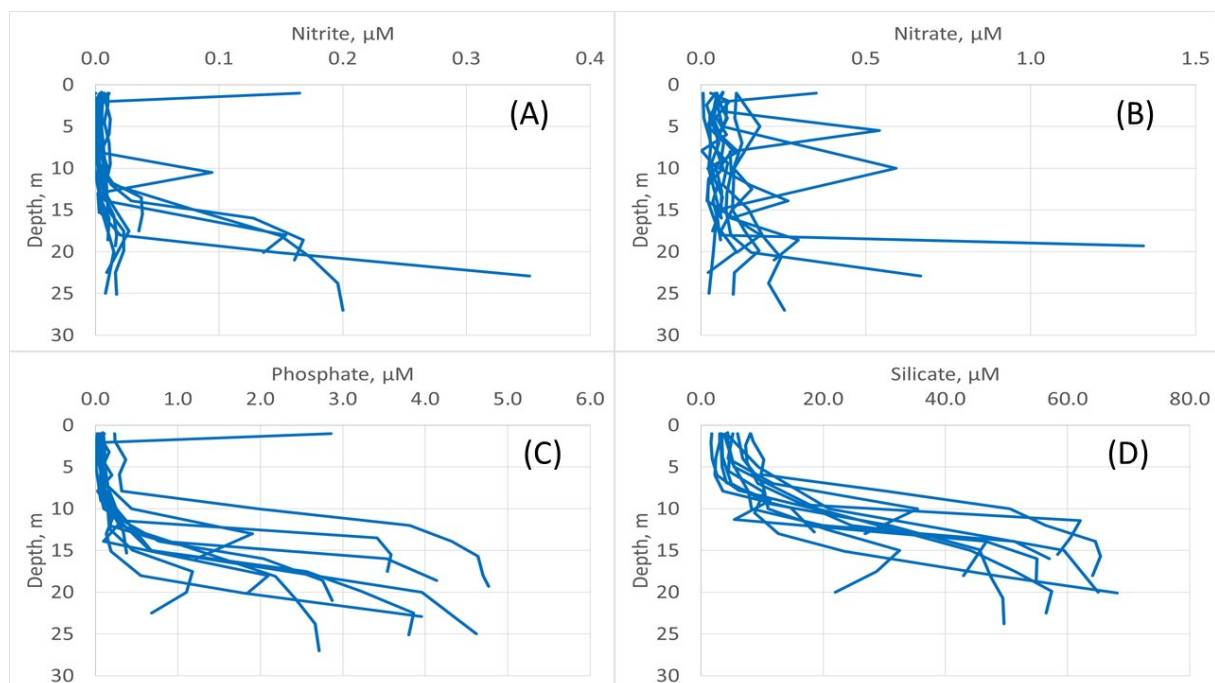
**Fig. 5.1** Temperature and salinity profiles at selected stations.

Surface (0 - 2 m) concentrations of dissolved oxygen were in the range of 240 to 270  $\mu\text{M}$ . Pronounced decreasing  $\text{O}_2$  concentration gradients were associated with the pycnocline (Fig. 5.1 and 5.2). The  $\text{O}_2$  concentrations below the pycnocline (> 10-15 m) were usually <50  $\mu\text{M}$  (except for station 3, where  $\text{O}_2$  was already decreased to 50  $\mu\text{M}$  at a water depth of 10 m). Hypoxic conditions ( $\text{O}_2 < 20\mu\text{M}$ ) were observed in the bottom layer of stations 4, 5, 7 and 8. Station 8 was anoxic ( $\text{O}_2 < \text{detection limit of } 2 \mu\text{M}$ ) at depths >16 m.



**Fig. 5.2** Dissolved oxygen ( $\text{O}_2$ ) profiles at selected stations.

In general, the concentrations of dissolved nitrite, phosphate and silicate were depleted in the mixed layer (0-15 m) and showed increasing concentrations below the pycnocline (>10-15 m) (Fig. 5.3 A, C and D). Enhanced concentrations (>0.1  $\mu\text{M}$ ) of nitrite were measured in the bottom layer (>16 m) of stations 5 and 10-12. Dissolved nitrite concentrations showed significant (negative) linear correlations with  $\text{O}_2$  concentrations at stations 4, 9, 11, 12 and 14. Dissolved phosphate concentrations started to increase at  $\text{O}_2$  concentrations of >100  $\mu\text{M}$ . Dissolved phosphate concentrations showed an increasing trend with dissolved nitrite and were significantly correlated with dissolved nitrite concentrations at stations 5, 7 and 9-13. Silicate concentrations showed a negative linear trend with  $\text{O}_2$  concentrations. The concentrations of dissolved nitrate were very low (<1.5  $\mu\text{M}$ ) throughout the water column and were in general more variable compared to the other nutrient concentrations (Fig. 5B).



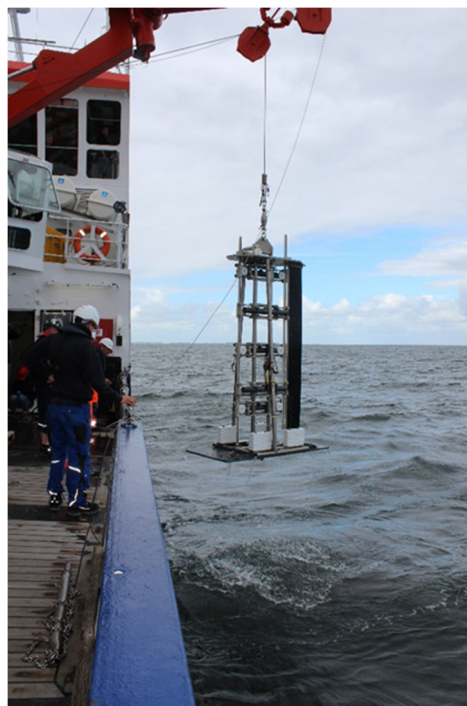
**Fig. 5.3** Dissolved nitrite (A), nitrate (B), phosphate (C) and silicate (D) profiles (all stations).

Overall, the biogeochemical setting in the water column reflected a typical summer period with strong stratification, depleted nutrient concentrations in the mixed layer and depleted  $\text{O}_2$  concentrations (i.e. hypoxic/anoxic conditions) in the bottom layer (i.e. below the pycnocline) which, in turn, were associated with enhanced nutrient concentrations in the bottom layer.

## 5.2 Bottom water sampling

(Florian Scholz, Anna Plaß, Matthias Türk)

To resolve chemical profiles of both dissolved and particulate species close to the seafloor, a novel trace metal-clean bottom water sampler was deployed at four stations. The “Benthic Trace Profiler” (BTP) (Fig. 5.4) consists of a freely rotating titanium frame (approx. 3.5 m height) to which five modified trace metal-clean Go-Flo water sampling bottles (General Oceanics) are attached. The distance of the Go-Flo bottles from the seafloor can be adjusted according to the scientific needs of the operator (60 cm, 87.5 cm, 125 cm, 202.5 cm and 260 cm during AL543). The five bottles are opened and closed simultaneously via a programmable electric engine that is connected to a gear transmission. Prior to deployment, the bottles are closed to avoid contamination with ship-derived emissions during immersion or sampling of re-suspended sediments upon positioning at the seafloor. To avoid implosion of the closed, air-filled bottles during lowering of the device to the seafloor, the bottles are filled with deionized water prior to deployment. Once the Benthic Trace Profiler reaches the seafloor, a bottom contact sensor is triggered and the bottles are opened after a programmable time period (e.g., 5 minutes) that is necessary to allow re-suspended sediments to drift away with bottom currents. The bottles remain opened for another programmable time period so that the buoyant deionized water can be replaced by the denser bottom-near seawater. After the bottles have been closed, the device is heaved on deck and the bottles can be easily detached from the titanium frame and transferred to a clean lab on the vessel. There, an argon or nitrogen gas line is attached to pressurize the bottles and collect the dissolved and particulate trace metal fraction under oxygen-free and uncontaminated conditions.



**Fig. 5.4** Recovery of the Benthic Trace Profiler at Station 12 off Schönhagener Cliff.

A total number of 19 water samples and 19 particulate matter samples on filters were collected during the cruise. The water samples were subdivided into aliquots for nutrient, major element and trace metal/isotope analyses. Hydrogen sulfide concentrations were determined on-board during the cruise. At station 4, H<sub>2</sub>S concentrations decreased from 5 µM in the bottom water overlying the minicore to 3.86 µM (60 cm), 3.60 µM (125 cm), 0.7 µM (202.5 cm) and 0 µM (260 cm) in the Go-Flo bottles of the BTP. At station 8, H<sub>2</sub>S concentrations decreased from 50 µM in the bottom water overlying the minicore to 40 µM in the BTP bottles to 30 µM in the lowermost Niskin bottle of the CTD. These were the first successful deployments of the BTP where H<sub>2</sub>S gradients within the lowermost water column could be resolved. The subsamples will be used to investigate how trace metals behave in the particle-rich water layer overlying the sediment.

### 5.3 Sediment geochemistry

(Florian Scholz, Andrea Bodenbinder, Sarah Fleischmann, Anna-Kathrin Retschko, Mark Schmidt, Melanie Schnohr, Regina Surberg, Paul Vosteen)

#### 5.3.1 Methodology

Sediment cores were retrieved with a minicorer (MIC). This sampling device is similar to a multicorer inasmuch as undisturbed surface sediments and the overlying bottom water are retrieved, but with fewer liners and a smaller head weight. Between 15 and 30 cm of surface sediments were recovered during each deployment. Upon recovery on deck one liner for pore water recovery and another liner for hydrocarbon sampling were selected and transferred to the sediment laboratory.

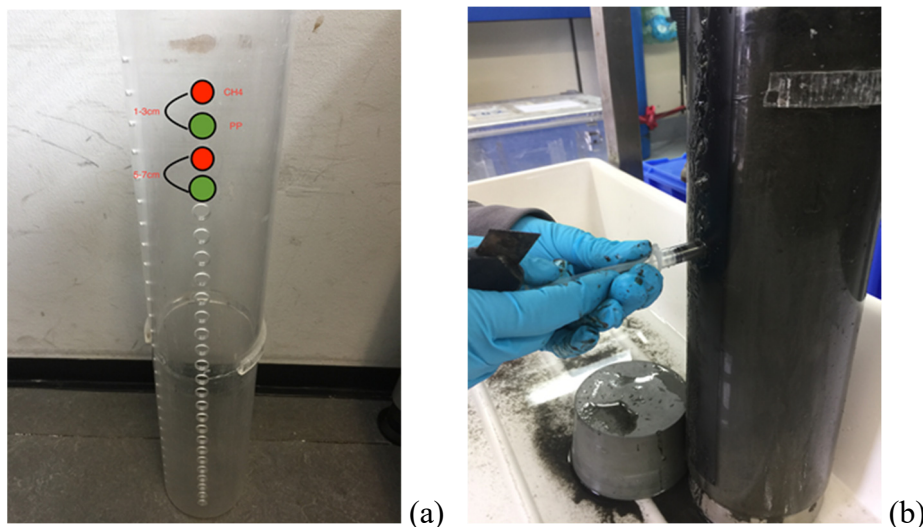
The bottom water overlying the sediment in the MUC liners was siphoned with a plastic tube and filtered for subsequent analyses. To prevent oxidation of reduced substances, sediment cores were subsampled in a glove bag under argon atmosphere at a resolution increasing from 1 cm at the surface to 4 cm at greater depth. A defined volume of sediment was sampled into pre-weighed plastic cups for the determination of water content and porosity. Pore water was separated from the solid phase by centrifuging sediment samples for 15 minutes at 4000 rpm. The supernatant pore water samples were filtered (0.2 µm cellulose-acetate filters) under argon atmosphere in a second glove bag. Sediment samples in centrifuge tubes were kept for shore-based analyses of the solid phase.

Pore water analyses of the following parameters were carried out onboard: ferrous iron (Fe<sup>2+</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>), silicate (H<sub>4</sub>SiO<sub>4</sub>), total alkalinity (TA) and hydrogen sulfide (H<sub>2</sub>S). Concentrations of NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, H<sub>4</sub>SiO<sub>4</sub> and H<sub>2</sub>S were determined by standard photometric methods (Grasshoff et al., 2002) using a HITACHI Model U-2900 UV-VIS Spectrophotometer. For the analysis of dissolved Fe<sup>2+</sup> concentrations after Stookey (1970), subsamples of 1 ml were taken within the glove bag and immediately stabilized with ascorbic acid. Samples for TA were analyzed by titration of 0.25 - 1 ml pore water according to Ivanenkov

and Lyakhin (1978). Titration was ended when a stable pink colour appeared. During titration, the sample was degassed by continuously bubbling nitrogen to remove any generated CO<sub>2</sub> and H<sub>2</sub>S. The results were calibrated relative to IAPSO seawater solution.

In addition to the on-board analyses, subsamples were taken for shore-based analyses of major cations and anions (sulfate, chloride, bromide, iodide) as well as trace metals and trace metal isotopes. Subsamples for metal analyses were acidified with concentrated nitric acid (sub-boiled distilled).

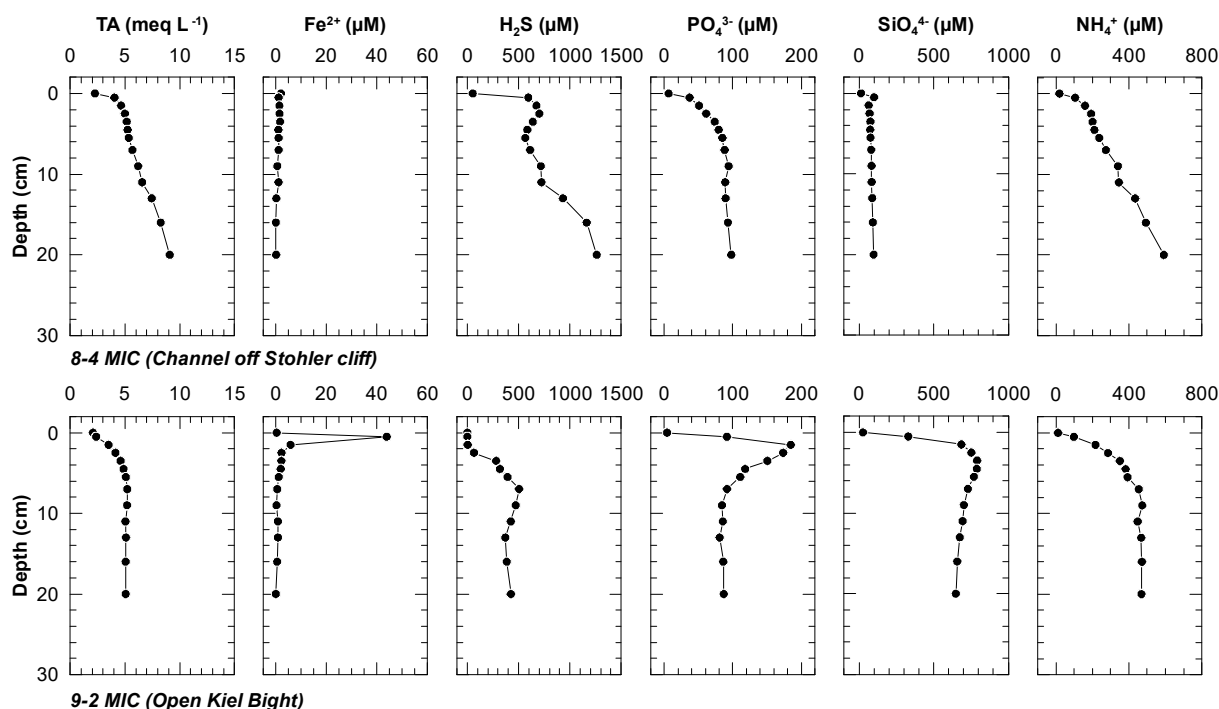
For the analysis of hydrocarbon gases, a separate sediment core was sampled by pushing plastic syringes (open inlet; 3 ml volume) into pre-drilled plastic liners (Fig. 5.x a, b). Subsamples for determining sediment porosity on the same core were stored in pre-weight plastic cups closed with plastic cap. Headspace vials were filled with 3 ml sediment, 1.2 g NaCl, and 9 ml of saturated NaCl-solution, then crimped with silicone rubber and aluminum cap for subsequent onshore gas chromatography (Sommer et al., 2009).



**Fig. 5.5** (a) Pre-drilled plastic liner, drill-holes are sealed with tape during coring operation. Alternating sampling sections for headspace gas (red) and porosity (green) analyses; (b) 3 ml plastic syringes are pushed through the drilled holes into the wet sediment.

### 5.3.2 Preliminary Results

Eleven MICs were processed for pore water geochemical data yielding a total number of 147 bottom water and pore water samples, which were analyzed on-board and subsampled for shore-based analyses. Examples for pore water profiles that were generated during the cruise are shown in Fig. 5.6.



**Fig. 5.6** Pore water profiles of total alkalinity (TA), dissolved ferrous iron (Fe<sup>2+</sup>), hydrogen sulfide (H<sub>2</sub>S), phosphate (PO<sub>4</sub><sup>3-</sup>), silica (SiO<sub>4</sub><sup>4-</sup>) and ammonia (NH<sub>4</sub><sup>+</sup>).

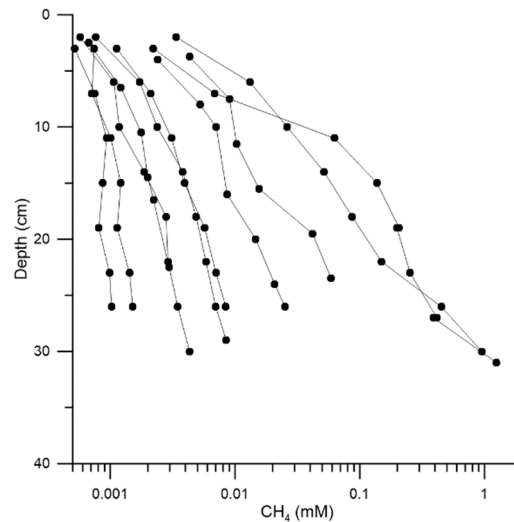
Alkalinity (i.e. bicarbonate), phosphate and ammonia are released during the decomposition of organic material. The steepness of the gradients and absolute concentration within the sediment core are, thus, indicative for the intensity of organic carbon degradation at the respective site. Dissolved ferrous Fe is generated by reductive dissolution of Fe (oxyhydr)oxide minerals and hydrogen sulfide is the product of bacterial sulfate reduction.

All of the sediment cores recovered during AL543 are characterized by anoxic and iron-reducing to sulfidic conditions in the surface sediment. At Station 9-2, which is located in the central area of Kiel Bight, a pronounced peak of Fe<sup>2+</sup> is observed in the uppermost 2 cm of the sediment. The steep gradient across the sediment-water interface indicates that ferrous Fe is released into the bottom water. By contrast, at stations that are located closer to shore, hydrogen sulfide is present in the surface sediment so that Fe accumulation in the pore water and sedimentary Fe release are prevented by the precipitation of Fe sulfide minerals.

The most reducing conditions and highest H<sub>2</sub>S concentrations in the surface sediment and bottom water were observed within deep basins and channels, presumably because the deep-water in these environments has the longest residence. Overall, we observed a complex pattern of benthic redox conditions, which is controlled by interlinked factors such as water depth, distance from shore, deep-water restriction and sediment composition (mud versus sand). Due to the variety of benthic redox conditions encountered during AL543, the samples obtained are well-suited for our ongoing research on how nickel and zinc isotopes respond to changing and variable redox conditions in the surface sediment and bottom water.



Highest porewater methane concentrations were determined at stations MIC4 and MIC13 located near Boknis Eck and in the inner Eckernförde Bay, respectively (Fig. 5.7). Measured maximum methane concentrations (1 and 1.2 mM) are still below solubility limit of 1.38 mM of methane in seawater at bottom water conditions (i.e.,  $T=15.4^{\circ}\text{C}$ ,  $S=21$ ) exposed to atmospheric pressure.



**Fig. 5.7** Porewater methane concentrations given in millimole per liter (mM).

## 5.4 Radionuclides

(Jan Scholten, Volker Liebtrau)

### 5.4.1 Methodology

For the analyses of radon ( $^{222}\text{Rn}$ ,  $t_{1/2} = 3.8$  d) and radium ( $^{226}\text{Ra}$ ;  $t_{1/2} = 1600$  y) in sediment pore waters, rhizons were pushed in pre-drilled holes of the sediment core plastic liners. Sample resolution varied between 2 and 5 cm. Plastic syringes were connected to the rhizons and between 8 -12 ml of pore water was extracted. About 1.5 ml of the pore water was filled in plastic vials for later major cation analyses. The remaining sample was filled in 20ml scintillation vials and subsequently was covered with 10 ml of scintillator. Measurements of  $^{222}\text{Rn}$  and  $^{226}\text{Ra}$  (after 4 weeks) were performed in the home lab.

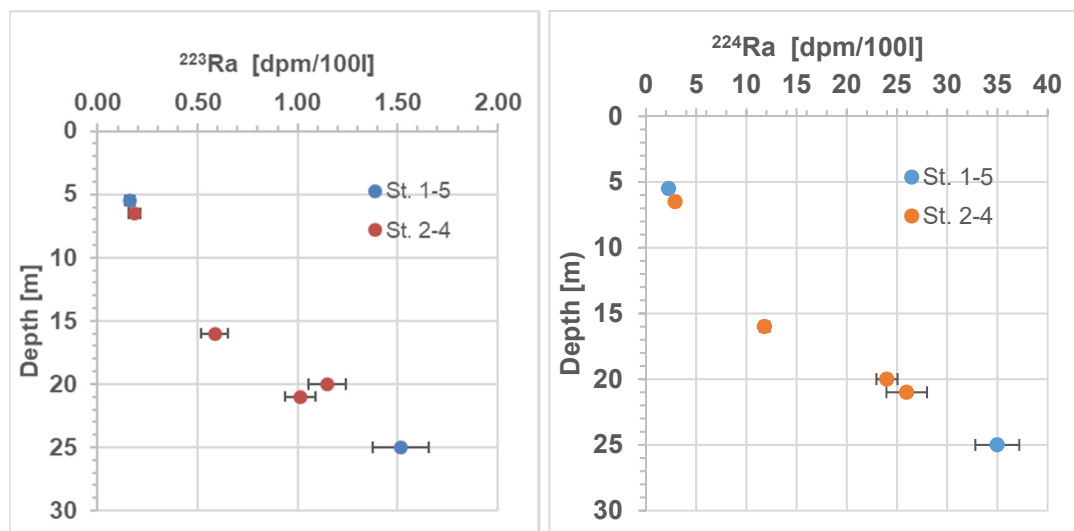
For the determination of the four radium isotopes ( $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ ), the seawater collected in the barrels were filtered over manganese coated acrylic fibers (flow rate  $\sim 1$ l/min) to quantitatively remove radium from seawater. These manganese fibers were measured in the home lab for radium isotopes.

For the determination of  $^{222}\text{Rn}$  in seawater two mobile radon-in-air monitors (RAD-7, DurrIDGE) were combined with two gas extraction modules ((MiniModule®, Membrana GmbH) (Schmidt et al., 2008). The water pumped from the diving pumps was connected to the modules in which  $^{222}\text{Rn}$  diffuses from the water phase to a closed air loop, which is connected via a desiccant to the RAD-7. In order to reduce uncertainties of  $^{222}\text{Rn}$  measurements the two RAD 7 instruments were run in parallel with a 20 min counting cycle. Counting time for station St. 1-5 (25 m) was

approx. one hour. For station St.2-4 (21 m) counting had to be stopped after 30 min due to a lack of ship time.

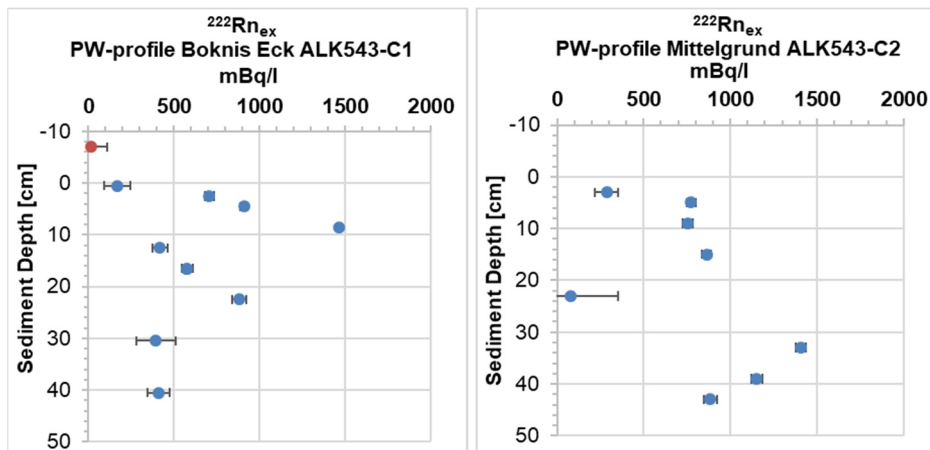
#### 5.4.2 Preliminary Results

The water column distribution of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  at the stations St.1-5 (Boknis Eck) and St. 2-4 (Mittelgrund) shows an increase of the concentrations of both isotopes with increasing water depth (Fig. 5.8). While it is well known that at Mittelgrund high radium is caused by submarine groundwater discharge (Schlüter et al., 2004) such a discharge has not been observed yet at Boknis Eck. The deep waters at Boknis Eck were characterized by a lack of oxygen during the sampling campaign. Therefore, one hypothesis is that high deep-water radium at Boknis Eck is caused by an increase of radium porewater supply caused by low oxygen in sediments and deep waters. From the sediment incubation experiment we expect to obtain information to what extent the diffusive radium supply from sediments can balance the radium water-column inventory.



**Fig. 5.8** Water-column distribution of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  at Boknis Eck (St. 1-5) and Mittelgrund (St. 2-4).

The two  $^{222}\text{Rn}_{\text{ex}}$  (i.e.,  $^{222}\text{Rn}$  corrected for supported  $^{226}\text{Ra}$ ) sediment pore water profiles obtained from Boknis Eck and Mittelgrund show a comparable range of  $^{222}\text{Rn}_{\text{ex}}$  concentrations (Fig. 5.9). Both profiles are characterized by a gradient between ~10 cm sediment depth and the sediment/water interface indicating the release of  $^{222}\text{Rn}$  to the water column.



**Fig. 5.9** Sediment pore water  $^{222}\text{Rn}_{\text{ex}}$  profiles from Boknis Eck and Mittelgrund. The concentration measured in the supernatant of the sediment core at Boknis Eck is indicated in red.

### 5.5 Rare Earth Elements and radiogenic Nd/Hf isotopes (Antao Xu, Ed Hathorne, Martin Frank)

Dissolved Rare Earth Elements (REEs) and Hf (hafnium) in seawater are introduced via riverine detrital and dissolved inputs and via partial dissolution of the coastal rocks. The advection of the coastal REEs and Nd/Hf isotope signals with water masses and their mixing in the open ocean are applied as tracers for the present and past ocean circulation given that the open ocean residence time is on the order of several 100 years resulting in a quasi-conservative behaviour. It is, however, unclear to what extent interaction with glacial deposits such as those forming the cliffs of the Baltic affect the concentrations and distribution patterns of the REEs and the Nd/Hf isotope signatures.

For this purpose 20 liter samples were collected from intermediate water depths (7 m) at 5 stations, and selected depths closer to the seafloor at 2 stations, at variable distance from the shore. At each depth, a 20 liter aliquot was taken unfiltered to monitor the immediate effect of particle exchange and a 20 liter aliquot was filtered directly from the Niskin bottles through an Acropak filter (0.45 – 0.2  $\mu\text{m}$ ) into 20 l collapsible containers. The samples were subsequently taken to the GEOMAR laboratory where they either will be directly measured for dissolved REEs or will be further processed (co-precipitation of the REEs and Hf, ion chromatographic separation of Nd/Hf) for Nd/Hf isotope analysis via MC-ICPMS.

## 6 Station List

Date	Time UTC	Station	Gear	Longitude deg E	Latitude deg N	Longitude dec deg	Latitude dec deg	Water depth m
23.08.2020	7:46	1-1	CTD	10°02.643	54°31.751	10.044	54.529	28
	08:20	1-2	RML	10°02.566	54°31.775	10.043	54.530	28
	08:29	1-3	RML	10°02.577	54°31.776	10.043	54.530	28
	08:41	1-4	RML	10°02.575	54°31.789	10.043	54.530	28
	09:03	1-5	CTD/Pump	10°02.668	54°31.742	10.044	54.529	28
	11:28	2-1	CTD	10°01.854	54°29.935	10.031	54.499	24
	12:01	2-2	RML	10°01.778	54°29.896	10.030	54.498	25
	12:03	2-3	RML	10°01.777	54°29.874	10.030	54.498	25
	12:37	2-4	CTD/Pump	10°01.709	54°29.836	10.028	54.497	24
	24.08.2020	07:04	3-1	CTD	10°18.782'	54°28.313'	10.313	54.472
07:17		3-2	MIC	10°18.789'	54°28.784'	10.313	54.480	18
08:43		4-1	CTD	10°02.652'	54°31.747'	10.044	54.529	28
09:58		4-2	CTD	10°02.551'	54°31.769'	10.043	54.529	28
11:35		4-3	MIC	10°02.497'	54°31.741'	10.042	54.529	28
25.08.2020	08:01	5-1	CTD	10°14.944'	54°42.106'	10.249	54.702	24
	08:43	5-2	CTD	10°14.963'	54°42.108'	10.249	54.702	24
	08:46	5-3	MIC	10°14.977'	54°42.104'	10.250	54.702	24
	09:56	6-1	CTD	10°23.957'	54°36.513'	10.399	54.609	19
	10:27	6-2	CTD	10°23.946'	54°36.516'	10.399	54.609	19
	10:58	6-3	BTP	10°23.938'	54°36.515'	10.399	54.609	19
	11:27	6-4	MIC	10°23.930'	54°36.512'	10.399	54.609	19
26.08.2020	07:00	7-1	CTD	10°03.780'	54°29.731'	10.063	54.496	22
	07:10	7-2	MIC	10°03.737'	54°29.755'	10.062	54.496	22
	07:19	7-3	MIC	10°03.747'	54°29.750'	10.062	54.496	22
	08:03	8-1	CTD	10°11.103'	54°29.927'	10.185	54.499	23
	08:38	8-2	CTD	10°11.145'	54°29.931'	10.186	54.499	23
	09:00	8-3	BTP	10°11.154'	54°29.942'	10.186	54.499	23
	09:49	8-4	MIC	10°11.174'	54°29.952'	10.186	54.499	23
	10:43	9-1	CTD	10°10.804'	54°34.442'	10.180	54.574	20
	11:25	9-2	MIC	10°10.794'	54°34.429'	10.180	54.574	20
	27.08.2020	07:18	10-1	CTD	10°05.316'	54°44.859'	10.089	54.748
07:30		10-2	MIC	10°05.232'	54°44.855'	10.087	54.748	26
08:15		11-1	CTD	10°09.480'	54°41.211'	10.158	54.687	30
08:53		11-2	MIC	10°09.515'	54°41.209'	10.159	54.687	30
09:42		12-1	CTD	10°07.462'	54°36.781'	10.124	54.613	24
10:16		12-2	CTD	10°07.498'	54°36.789'	10.125	54.613	24
10:46		12-3	BTP	10°07.499'	54°36.822'	10.125	54.614	24
11:26		12-4	MIC	10°07.473'	54°36.826'	10.125	54.614	24
28.08.2020	11:33	12-5	MIC	10°07.434'	54°36.822'	10.124	54.614	24
	07:33	13-1	CTD	09°56.794'	54°28.960'	9.947	54.483	26
	07:42	13-2	MIC	09°56.787'	54°28.969'	9.946	54.483	26
	08:22	14-1	CTD	10°02.545'	54°31.754'	10.042	54.529	28
	08:44	14-2	BTP	10°02.541'	54°31.760'	10.042	54.529	28

## 7 Data and Sample Storage Availability

Chief scientist F. Scholz and the Data Management Team at GEOMAR are responsible for data archiving. The station list and all metadata has been entered into the Ocean Science Information System (OSIS), a central information and data sharing utility maintained by the GEOMAR Data Management Team. The view of all information in OSIS is open to the public: <https://portal.geomar.de/metadata/leg/show/354248>. All scientific data that were collected during the cruise will be submitted to PANGAEA. After a protection period of three years after the end of the cruise, these data will be freely available to the scientific community. All data that will be generated onshore after the cruise will be published at PANGAEA upon publication

in scientific journals. Water and sediments samples will be stored in the sample archive of the Research Unit of Marine Geosystems at GEOMAR.

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