Geochemistry on the Baltic Sea

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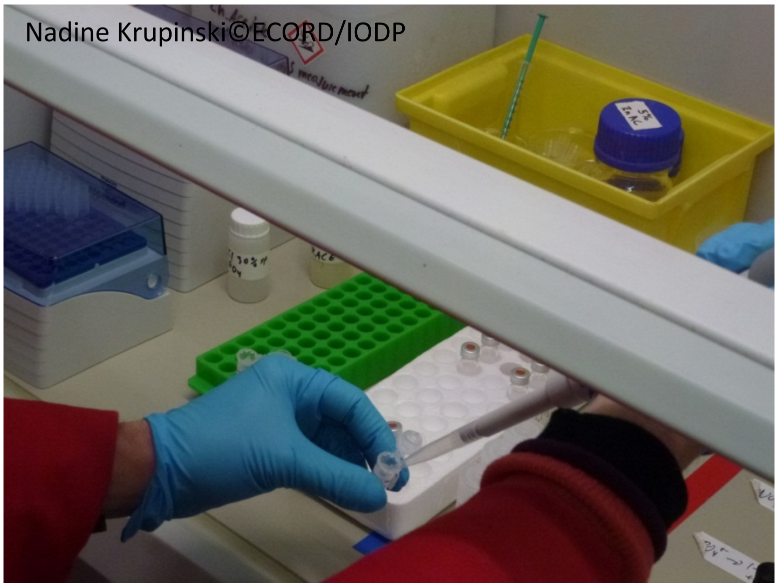
The Baltic Sea Expedition encompasses a wide range of exciting scientific questions. How has the expansion and contraction of glaciers shaped life in the Baltic Sea? What microbes persist in the deep subsurface and how do they survive? How has the presence of bottom water oxygen changed in the Baltic Sea through time?

Despite the wide range of expertise and tools required to tackle these and other important questions, they are all connected in the illustration of a big picture of the Baltic Sea environmental history, with each discipline heavily relying on the others for background information. One discipline strongly linking each of these is geochemistry.

Geochemistry is the determining of chemical characteristics related to the water column, sediments, and sedimentary pore waters, each important to the goals of this expedition. Sediments are collected and stored for later subsampling and chemical description onshore, but many characteristics related to the pore water chemistry are time sensitive and inform decisions made during drilling, and thus must be measured onboard. The job of a geochemist is to make these essential measurements, all while keeping in mind the big picture scientific questions to inform our decisions and interpretations.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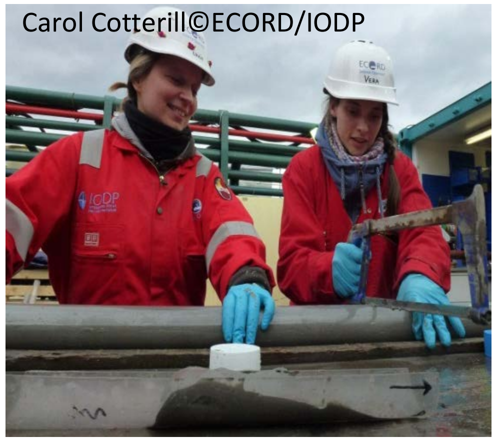
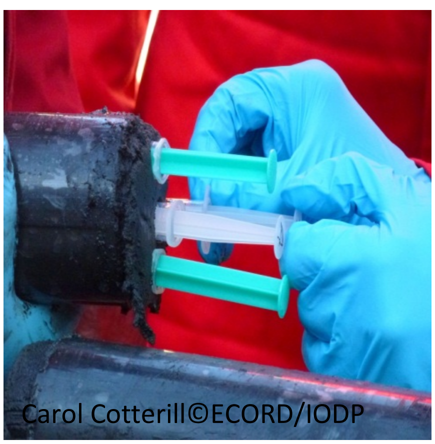
Now we start our tour of the job of a geochemist on board the Baltic Sea Expedition. As part of the expedition there are 6 geochemists on board: Luzie, Patrizia, Caroline, Jeanine, Thorsten, and myself. The sediments are stored away on the ship and analyzed following the expedition, so our job is to characterise the sedimentary pore fluids here on the ship. Together we make the shipboard analyses of pore water pH and alkalinity and concentrations of hydrogen sulfide, methane, and ammonium. Just like the rest of operations on the ship, we work 24/7 with both a night and dayshift. This is essential, as the job starts as soon as the cores are brought up to the surface…



Core on deck! After sediments are brought up from the seafloor, Luzie and Vera (core curator) start dividing it into sections..

Patrizia and Holger (core curator) collecting fresh sediments for methane analysis.



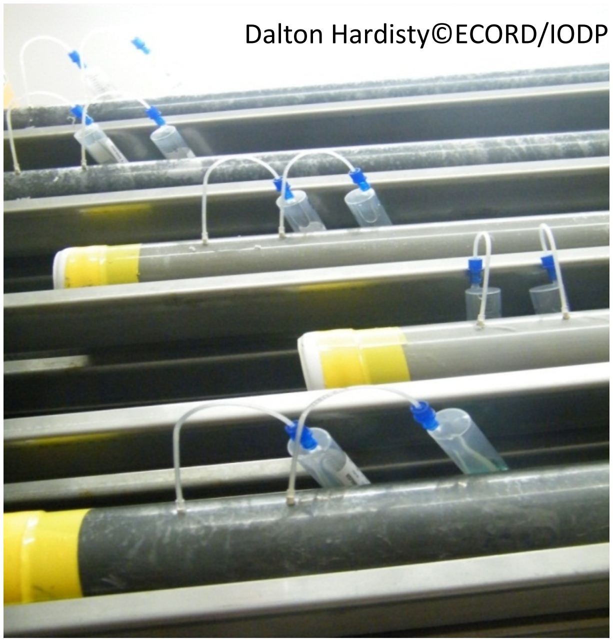
Syringes collecting fresh sediment for methane and other analyses.

Patrizia storing away the sediment she collected in the photo above. Nice work!

After the sediment is brought up and unloaded on the drill floor, the cores are quickly capped, limiting the exchange of the sediments with the ambient environment at the surface, which varies widely from the sedimentary environment. This, and proper storage of the sediments, is essential for ensuring the sediments have changed as little as possible prior to later geochemical analysis both off and on the ship.

Pore water extraction

Syringes are used to pull pore water from the sediments. If it seems simple so far, that's because it is. We will use this pore water for required shipboard analyses and store the remaining water properly for a whole new suite of chemical analyses once we are off the ship. Again, great care is made that pore waters are not exposed to the atmosphere, ensuring the quality of the analyses to come.



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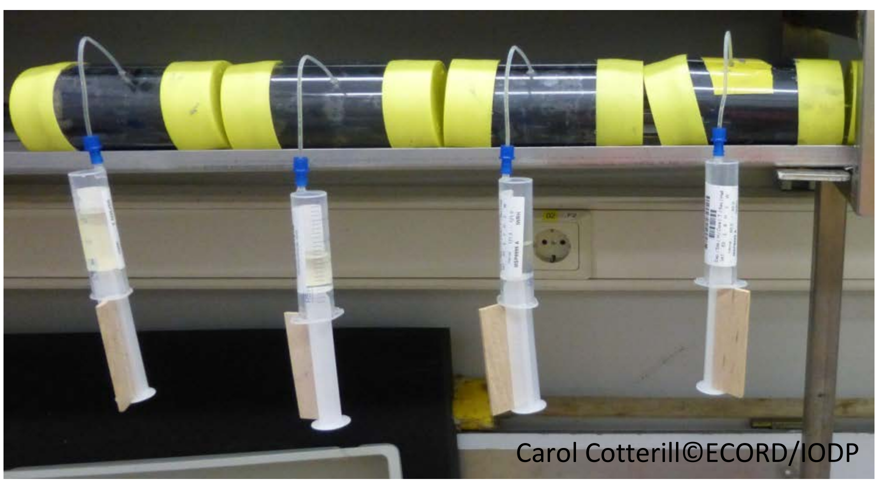
Syringes sucking away pore water from fresh cores on the rack in the curation container. We need all the pore water we can get to make sure all the scientists can do their anticipated research. The amount of pore water we extract from each core can vary widely based on the sediment type.



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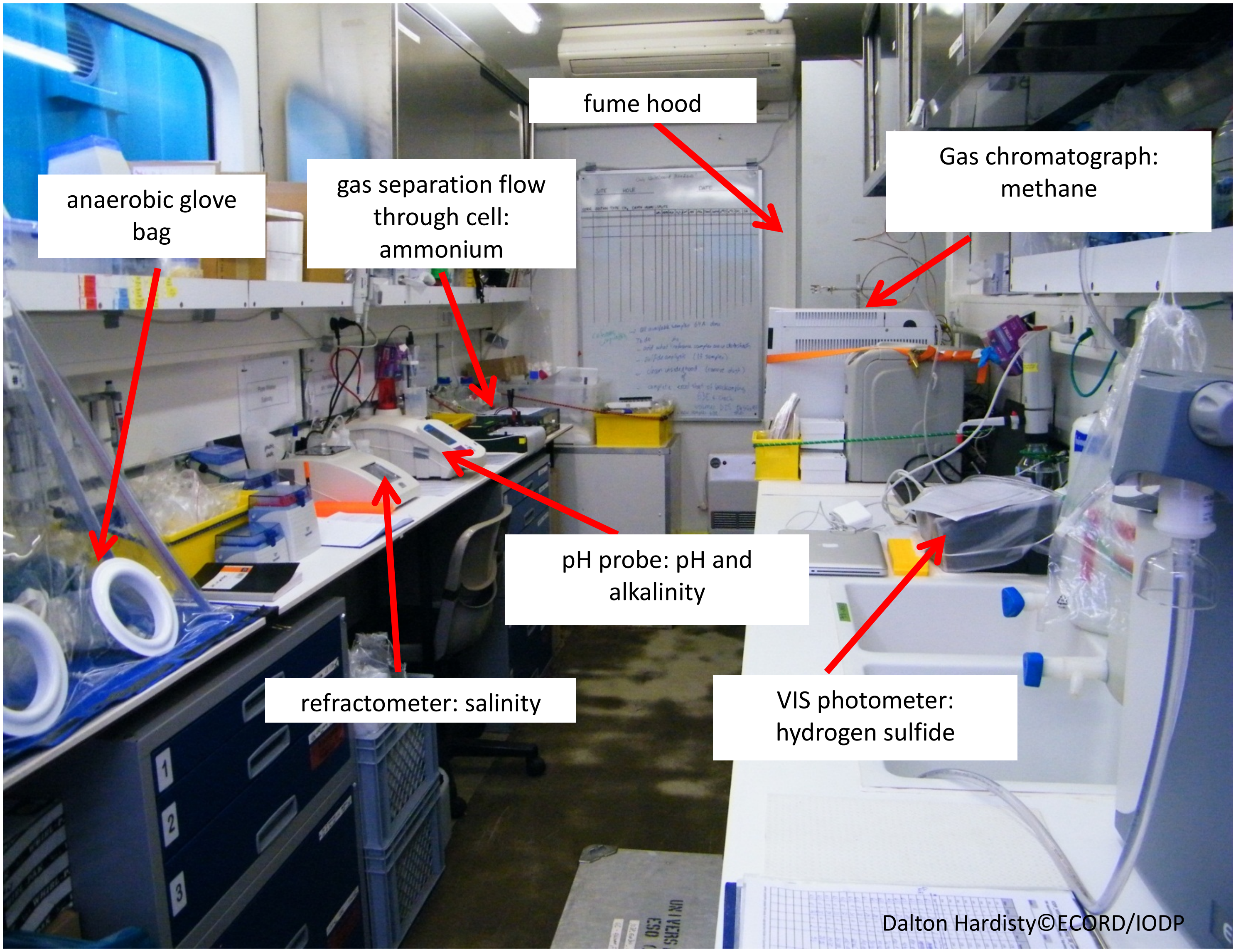
First cores of the expedition. I approve.

We have a mobile geochemistry lab on the ship. It's nice and cozy. Once the pore water is extracted, it is brought here. Below is the lab with the instruments for all the necessary shipboard analyses.



The main culprit that can alter pore fluids and sediments from their original state is oxygen. Therefore, addition of chemicals that fix the compounds of interest prior to their exposure to the atmosphere, preventing outgassing and oxidation, must be done in a nitrogen filled glove bag. After this step, care is no longer necessary to prevent exposure of oxygen to the pore waters. Now we can relax!

Hard at work. Preparing the porewater in the glove bag is the first step once they enter the geochemistry lab.

Caroline working away in the glove bag. I hope you're taking notes. She's a pro!

Though our atmosphere and most of the ocean have abundant oxygen, microbes quickly consume oxygen during respiration in the upper portions of the sediment. Once oxygen is consumed, microbes that breathe other compounds to harvest energy take over. These processes combined contribute to the decay of organic matter from marine life deposited in the sediments. Understanding these changes in metabolisms with depth is essential information for characterising the microbial communities as well as understanding how the sediments change after deposition in a process called diagenesis. This information allows geochemists to infer what the originally deposited sediments were like, and what that means concerning the water column of the Baltic Sea in the past. Subsampling under oxygen free conditions similar to that of the sediments is therefore an essential step in preserving the chemistry beneath the seafloor and unlocking these key questions.

Salinity

An important part of reconstructing the past environment of the Baltic Sea is fingerprinting transitions from fresh to marine waters. Low sea level and ice dams during past glacial intervals have caused the Baltic Sea to be cut-off from the ocean and be characteristic of a freshwater setting rather than the sea it is today. Paleontologists can detect these periods using foram abundances (a marine organism) and sedimentologists infer these intervals from changes in sediment type such as the presence or absence of clays and till typical of glacially-derived sediments. Geochemists compliment this information by measuring the specific salinity of the pore waters. Marine water has a characteristically higher salinity than fresh water, and this salinity is captured in the pore fluids during the time of deposition.

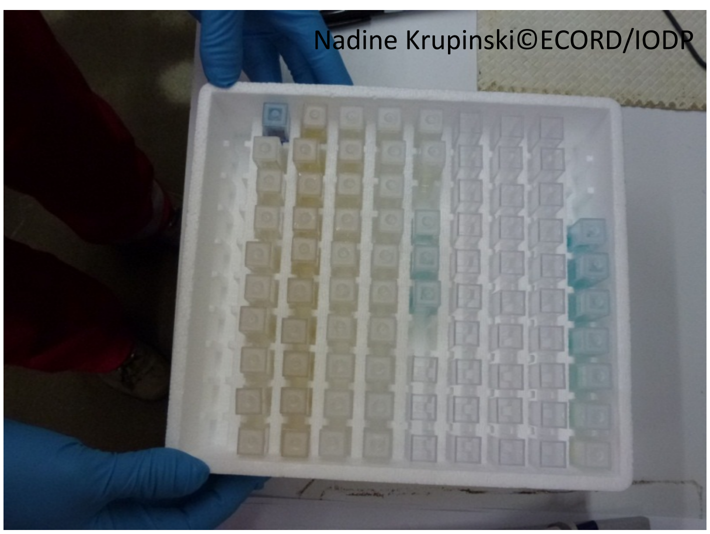
A taste test might do the job just as well,
but good luck publishing that data!

Today the Baltic Sea is a brackish water body, meaning the salinity is influenced by both seawater and freshwater input.

Hydrogen sulfide

An important measurement taken directly onboard the ship is the concentration of hydrogen sulfide gas. Maybe you've been wading in a lake or seashore and reached down and pulled up some mud, only to get a whiff of a stench similar to rotten eggs. That's sulfide! During a process known as sulfate reduction, microbes breathe the chemical ion sulfate, extracting energy to stay alive and in the process producing sulfide gas. This process only happens in the sediments once all of the oxygen has been consumed, as much more energy can be gained breathing oxygen. We measure the amount of sulfide in the pore waters as an indicator that sulfate reduction is occurring, informing geochemists about the types of minerals that might be forming (for example, pyrite, or 'fools gold', is a mineral formed when sulfide reacts with iron in sediments) and informing microbiologist about the types of microbes living at these depths.

That is rank! I'm getting a whiff of sulfidic muds fresh from the seafloor. Living the dream.



Thorsten has prepped the pore waters for sulfide analysis. A color complex is used to aide in sulfide detection via a VIS photometer. The blue ones probably have sulfide. The yellow ones: not so much.

Sulfide is particularly interesting in the Baltic Sea because known water column oxygen deficiencies in the past and today allow sulfide to form directly in the water column and seep from the sediments into the water column. As you might guess, fish and other organisms requiring oxygen are forced out of these locations. Not good for fish and not good for those who eat the fish, including us.

pH and alkalinity

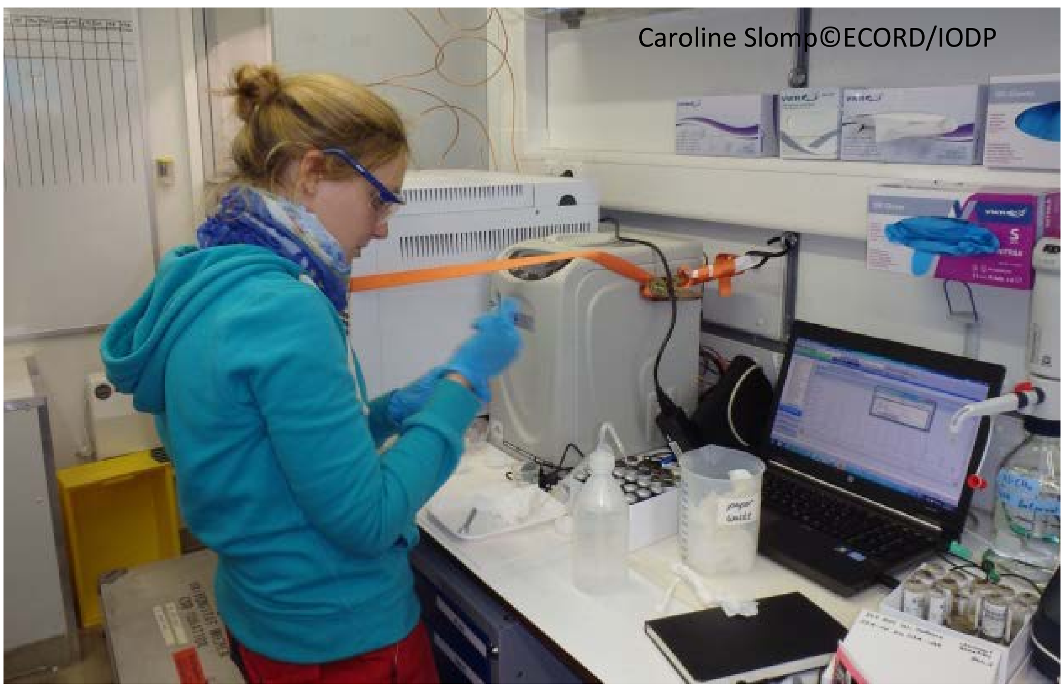
Another important time sensitive measurement is pH. Fresh versus marine waters can have variable pH, but pore water pH can also vary depending on the host sediments and as the process of organic matter decay progresses.

Alkalinity is a term used to describe the ability of the pore fluids to buffer against the additions of acids. Similar to taking a Tums to relieve acid reflux when you have heartburn or adding solutions to control the pH of your pool, there are compounds added to pore fluids during the decay of organic matter that buffer against other acidic compounds, like sulfide, added during the same process.

Preparing to measure pH and alkalinity. Basically, I'm just an over-educated pool boy.

<u>Methane</u>

After the sulfate in the sediments is used up, microbes called methanogens harvest energy by breathing carbon dioxide in a process called methanogenesis. Carbon dioxide is available in the sediments because it is a byproduct of the degredation of organic matter during the previous intervals of sulfate reduction and oxygen consumption. Again, like with sulfide, we use the presence of methane to determine if and where methanogenesis is occurring. Microbiologists are very interested in knowing the depth intervals at which sulfide production ceases and methane production starts, making the measurement of methane and sulfide onboard the ship important for guiding their sample collection.



Remember Patrizia from before collecting sediment on the drill floor for methane analyses? Well now she’s finishing the job, measuring the methane concentrations via gas chromatography. Fancy!

Ammonium

As organic matter is degraded during oxic respiration, sulfate reduction, and methanogenesis, ammonium is released into the pore fluids. Ammonium is a N-containing compound, an element essential to life and therefore abundant in organic matter. An abundance of ammonium might tell us about nearby sources of organic matter or if organic matter concentrations were once much higher at a location prior to long-term degradation. This analysis is time-sensitive, meaning the measurement must be made onboard the ship in order to ensure we are measuring the original concentration.

Thorsten is making a calibration curve in preparation for the ammonium measurements. It takes a steady hand. In the Wild West he would've been a gun slinger, but today he is a geochemist. Clint Eastwood would be lucky to play such a role.

Jeanine is injecting pore water into the flow through cell for ammonium measurement. Don't hurt yourself with that syringe, Jeanine!

Alright, you are now an expert geochemist. So, time to go play in the mud!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