FS METEOR
Cruise M200
22.03.2024 – 09.04.2024
Rostock – Rostock

MnION
Elemental coupling of manganese cycling
across redoxclines of the Baltic Sea

3rd Weekly Report
01.04. – 07.04.2024

After successful research activities at Gotland Deep and Farö Deep, we made it to Landsort Deep this week.
A central component of the research activities is identifying the distribution and influence of manganese (Mn) oxide minerals that are formed within the stratified water column in the Baltic Sea. Mn oxides are reactive minerals that play an important role in the cycling of numerous elements, including the degradation of carbon, adsorption of trace metals, and oxidation of nutrients and metals. Historically, Mn oxidation to form Mn oxides has been attributed to the activity of Mn(II)-oxidizing bacteria that require oxygen to survive. These bacteria are heterotrophs, which couple the oxidation of organic carbon to the reduction of oxygen. The oxidation of Mn(II) to form Mn oxide minerals is a side reaction during aerobic metabolism, and the reason for the process remains unknown. In the Baltic Sea, however, Mn oxides have been found to predominate in waters lower in the oxycline where oxygen (O_2) levels are declining. Our research aims to better understand the distribution of Mn oxides and the mechanisms responsible for their formation (and dissolution).
This past week, we continued to measure Mn oxide concentrations within the water column along the oxycline. We found that like Gotland and Farö, the concentration of Mn oxides is highest at the base of the chemocline, where O_2 levels are low (see Figure 1). This peak in Mn oxide concentration coincides with a small turbidity peak. Just below this peak, Mn oxides are undetectable, and a larger turbidity peak is observed. Our prediction is that hydrogen sulfide diffusing up in the water column reacts with Mn oxides at this depth leading to the reduction (loss) of Mn oxides and likely formation of elemental sulfur (S).
To understand this distribution, we also conducted Mn(II) oxidation experiments along the chemocline using the radiotracer ^{54}Mn(II). We also collected samples for mineralogical characterization using X-ray absorption spectroscopy (XAS). These analyses will be conducted back in the USA over the course of the next 6 months.
To help identify mechanisms of Mn oxide formation within these O_2 depleted waters, we also conducted incubation experiments of waters within gas tight bags collected off the CTD. We added ^{15}N-labeled nitrate and nitrite along with Mn(II) to test the potential coupling of these elemental cycles. Analysis is ongoing, but our initial timepoints from Gotland and Farö indicate that addition of nitrate and nitrite stimulate Mn(II) oxidation and Mn oxide formation within these waters. Samples were collected from these incubations to conduct isotopic and microbial analysis to identify the reactions responsible for this potential coupling.

Figure 1: Mn oxide samples from Landsort Deep. Picture illustrates the particles collected on filters spanning the depth range from 3m to 85m. The brown color is indicative of Mn oxides. The peak of Mn oxide concentration is observed at 80m at the base of the chemocline.

The hydrogen sulfide that interacts with manganese oxides at the chemocline derives principally from the microbial mediated reduction of sulfate to hydrogen sulfide in the anoxic regions of the deeper Baltic basins and sediments. A potential, and perhaps underestimated source of hydrogen sulfide, is the hydrolysis of sulfur containing biomolecules, such as proteins and S-linked sugars. Such a process has been shown to be important in wastewater treatment systems and biofilms. As the middle Baltic deep basins trap large amounts of sinking biological detritus, such a hydrolysis may play a role in the total dissolved sulfide efflux. We are testing this hypothesis by comparing total sulfide production and efflux using microsensor methods (Figure 2), and the measurement of sulfate reduction through radiochemical experiments.

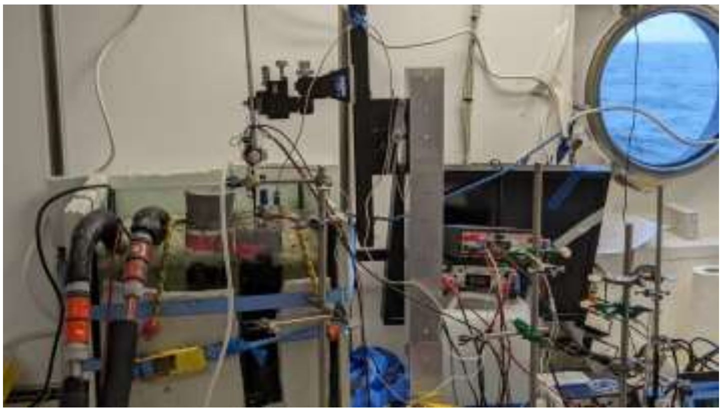

Figure 2: Microsensor set-up for measuring hydrogen sulfide, pH and dissolved oxygen at micrometer resolution in the surface sediments.

Hydrogen sulfide is toxic for many life forms, including us, but is an excellent source of energy for a wide range of bacteria. They have the ability to transform the sulfide into a wide range of compounds of intermediate oxidation states, such as elemental sulfur and thiosulfate, and eventually back to sulfate. The Gotland, Farö and Landsort Deeps are natural reactors for study of the reaction between upward diffusing hydrogen sulfide and the manganese oxides, and the production of these intermediate oxidation state compounds. We have been taking discrete samples of the sulfide and sulfur intermediate oxidation states to analyze in our home laboratories.

Nature has also provided us with an extra, exceptionally exciting experiment during this cruise. Due to last winter's storms, a stream of saline, oxygen-rich North Sea water has been flowing along the bottom of the Baltic, and is just now intruding upon the sufidic bottom waters of the Gotland Deep. This inflow event provides us with an excellent chance to examine how the hydrogen sulfide and manganese oxides interact with the oxygen-bearing inflow waters. Characterizing the physical, chemical and biological aspects of this inflow event has dominated the focus of our research in the last days of the expedition (Figure 3).

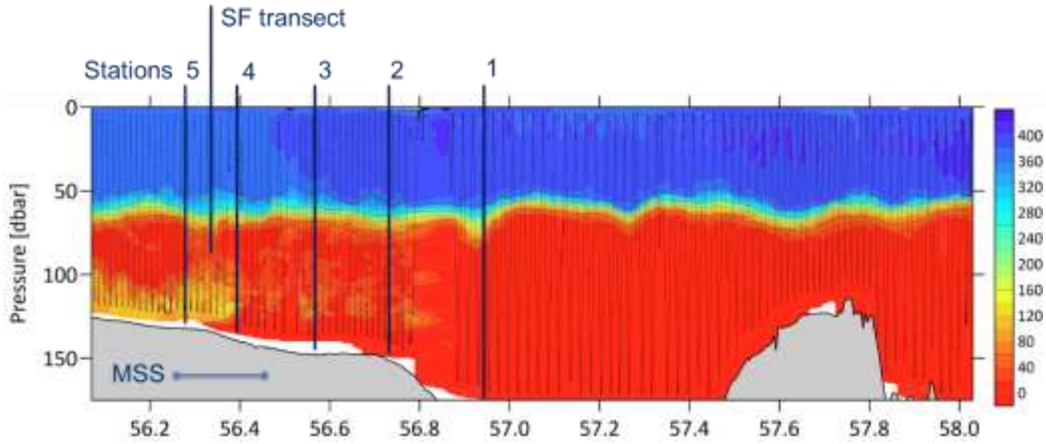

Figure 3: Scanfish tow profile showing dissolved oxygen concentrations through the Gotland Basin. The stations are placed to intercept the main saline inflow and “whiffs” of oxygen preceding the front.

Our research activities were successful finished on Sunday afternoon. The remaining two days will be needed for the travel to Rostock. We will use this time to dismount our equipment and pack it back into the containers, process the last samples and clean up the laboratories. The weather continues to be kind to us, so that we will be able to complete this work as well. The expedition is slowly coming to an end and we are looking forward to our journey home.

Best regards on behalf of all participants,

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