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Accumulation mechanisms of trace metals into Arctic sea ice

（北極海における海氷への微量金属蓄積メカニズムの解明）

By Evans La Kenya Elizabeth

In the last 20 years the Arctic Ocean has experienced over 32% loss of summer sea ice. This loss can influence the cycling of biogeochemical materials, affecting seawater's biology and chemistry. Sea ice is important for the supply of biogeochemical materials (trace metals, nutrients, dissolved organic matter, suspended particulate matter, etc.) to the surface waters of the polar oceans, but its role in the supply of trace metals is not clear. In this study we focus on trace metals iron (Fe), manganese (Mn), and cadmium (Cd). Iron and Mn are essential micro-nutrients necessary for phytoplankton growth whereas Cd creates adverse effects. These three metals were chosen as they exhibit both similar and different geochemical behaviors (i.e. REDOX potential, supply source, biochemistry, etc.) in seawater. These behaviors may influence how they are accumulated and retained into sea ice and ultimately released to the surface seawater. To fully understand the health of the polar ocean it is important to understand the geochemical role of sea ice in the supply of trace metals.

Chapter 2 describes the methods used in this thesis. Iron, Mn and Cd in the dissolved (D, <0.2 μm), and labile particulate (LP, Total Dissolvable - Dissolved) size fractions were observed in sea ice and seawater collected from the Arctic Ocean. Trace metal concentrations, especially in the dissolved fraction, in the Arctic are low, which prevents reliable direct analytical analysis. To avoid unreliable analysis and analytical interferences due to sea salts, the solid-phase extraction NOBIAS Chelate PA-1 resin (Hitachi High-Technologies Corporation) method was used. The NOBIAS resin is composed of a hydrophilic polymer holding both ethylenediaminetriacetic acid and iminodiacetic acid. These two functional groups allowed the NOBIAS resin to form up to five coordinate bonds with trace metals, out competing binding with natural ligands. After pre-concentration, all samples were analyzed on a Graphite Furnace Atomic Absorption Spectrometer (GFAAS). The analysis of trace metals requires clean

conditions as contamination can affect the sample value. To avoid this problem, the pre-concentration of samples was performed in a class 100 clean room on a manual system. The NOBIAS resin and all components of the manual system were acid cleaned before use. All reagents used for pre-concentration were of pure or ultra-pure chemical grade. During pre-concentrations, all solutions (0.05 M HAcO-NH_4AcO buffer, Milli-Q water, 1 M HNO_3, and sample) were loaded onto the NOBIAS resin column. After loading, the resin column was removed, and back hand eluted with an acid cleaned hand syringe with 1 M HNO_3 into acid cleaned sample tubes.

To ensure that the pre-concentration materials and method clean, contamination tests, on Milli-Q water, were performed to ensure that the process was trace metal clean. The Milli-Q water procedural blanks values were below the detection limit (DL) for all elements analyzed (0.3 nM for Fe, 0.06 nM for Mn and 0.0002 nM for Cd). To test the recovery of the NOBIAS resin, known concentrations of metals were spiked in Milli-Q water. The Milli-Q water recover test yielded good recovery for all metals (102.1 ± 5.6% Fe, 100.3 ± 1.8% Mn, and 106.3 ± 5.1% Cd). To test the recovery of metals in seawater, NASS-6 reference seawater from the National Council of Canada was pre-concentrated and yielded comparable values to the certified values (9.5 ± 1.3 nM Fe, 11.2 ± 1.4 nM Mn and 0.3 ± 0.1 nM Cd). The clean Milli-Q water procedural blanks and good trace metal recovery (Milli-Q water and NASS-6 seawater reference samples) by the NOBIAS resin indicated that, the acid cleaned in-line manual manifold and pre-concentration method, was trustable and reliable for the determination of low trace metal concentrations in Arctic sea ice and seawater.

After creating a trace metal clean procedure for the NOBIAS pre-concentration procedure, field samples were ready for analysis. In chapter 3 we were interested to understand the form of trace metal that was retained in drifting ice, in comparison to the surround surface waters, collected from a shelf area. Drifting sea ice and seawater samples were collected from the Chukchi Sea and analyzed for the dissolved and labile particulate fractions of Fe, Mn and Cd. To understand the geochemical behavior of trace metals, seawater concentrations were observed.

Chukchi seawater showed high percentages for DMn (71.5%) and DCd (66.3%) with a high percentage of LPFe (94.1%). In seawater, DCd was the only metal to correlate with phosphate ($R^2 = 0.78$) indicating an internal biogeochemical cycling source. The size fractions of Fe and Mn in Chukchi seawater were controlled through different external sources. High concentrations of LPFe an LPMn in the Barrow Canyon site correlated with low N** values indicating a supply from the sediments (shelf or river). In contrast, DFe and DMn were high in the Pont Lay sites. These values correlated with low salinity and high temperature values indicating an external supply by the Alaskan Coastal Current.

Trace metal concentrations in Chukchi drifting ice were heterogeneous. Drifting ice showed high percentages for the LP fraction (99.2% Fe, 63.6% Mn and 71.2% Cd). When the concentrations of dissolved and labile particulate Fe, Mn and Cd in drifting ice were compared to the trace metal concentrations in seawater, the labile particulate concentrations were higher in drifting ice. This data indicated that, regardless of the trace metal geochemical behavior in Chukchi seawater, Chukchi drifting ice was observed to have a preference to accumulate or retain the labile particulate trace metal fraction.

In chapter 3 we were able to observe the form of trace metal that was retained in sea ice but the mechanisms behind trace metal accumulation were not observed. Therefore, the goal of chapter 4 was to examine the possible trace metal accumulation processes utilized by Arctic sea ice by comparing the concentrations of trace metals to the observed ice structures within floe ice. The structure of sea ice reflects the process of ice formation, which may aid in the determination of accumulation processes. An Arctic sea ice core was examined. During the coring process, the outer layers of the sea ice will be contaminated. To avoid this contamination to the trace metal sample, the core sample was shaved (planed) in a -20°C cold tub located in a class 100 clean room with acid clean ceramic knives. Two layers, each 1 cm thick, of the outer ice were planed off. The inner, cleaned, core was then analyzed for trace metals. Contamination tests for the planing procedure were performed on Milli-Q ice. The chips from each layer, and the inner, cleaned, core were collected and analyzed. The results showed that after planing 2 cm of the outer ice layers, Fe, Mn and Cd were below the detection limit.

Therefore, the planing procedure was used to prepare the floe ice core sample.

To determine the sea ice structure, photographic analysis for the percentage of pore area and $\delta^{18}O$ analysis was used. After planing, the core sample was photographed and then separated based on the visually observed ice structure. The photographs were transformed to black and white, with a filter overlaid, to represent the outline of the micropores (porosity %). This Porosity % was use to aid in the determination of the ice structure. Each ice section was then melted at room temperature and analyzed for trace metals, salinity, nutrients and $\delta^{18}O$. For trace metals, the dissolved and labile partiulate fractions of Fe, Mn and Cd were pre-concentrated with the NOBIAS resin. Results showed that salinity and nutrients were low, indicating brine drainage and multi-year ice. For $\delta^{18}O$, the 0 - 24 cm core section was sourced by a mixture of snow and seawater, with the 24 - 103 cm sections sourced from seawater. Based on the results of the picture, Porosity % and $\delta^{18}O$ analysis the sea ice structure was determined as snow (0 - 24 cm), granular (24 - 75 cm), mixed (granular + columnar, 75 - 91 cm) and columnar ice (91 - 103 cm).

The results of the trace metal analysis showed high trace metal concentrations in snow ice, indicating a meteoric snow source. High concentrations of LPFe in granular ice indicated possible particulate trace metal scavenging by frazil ice. Concentrations of LPMn and LPCd were low compared to DMn and DCd in granular and snow ice. It is possible that reduction of LPFe and LPM after particle entrainment released DMn and DCd, indicating a chemical transformation process. Low dissolved and labile particulate trace metal concentrations in mixed and columnar ice indicated a release due to brine drainage.

Based on the results from the trace metal analysis, the possible mechanisms for trace metal accumulation into Arctic floe ice include the following. High concentrations in snow ice indicated that snow ice formation, through the mixing of meteoric snow and seawater, can add atmospheric trace metals. High and heterogeneous concentrations of LPFe (and LPMn, oxides) in granular ice indicate particle entrainment by frazil ice scavenging. Once the oxides accumulates into sea ice, it can undergo reduction to release DFe, DMn and (adsorbed) DCd in granular ice. This chemical transformation

process within sea ice can increase the bioavailability of trace metals. Low trace metal concentrations observed in mixed and columnar ice show that these structures are unable to retain metals following brine drainage. The differences observed in trace metals within sea ice structure show that sea ice formation, chemical reduction, and brine release were the possible processes behind trace metal accumulation and release in this Arctic sea ice.

The two different sea ice forms, degraded drifting and floe ice, used for the observation of trace metals in this study expressed different trends in the concentrations of D and LP trace metals. These trends indicate that the accumulation and retention of trace metals into Arctic sea ice may be influenced by the form of sea ice. The concentrations of dissolved metals were comparable in drifting ice ad floe ice. The concentrations of labile partiulate metals were higher in floe ice than for drifting ice. This maybe due to the characteristics of the ice form. For example, drifting ice is oxidic and highly mobile due to seawater interactions. In contrast, floe ice is stable with suboxic conditions due to protection from seawater waves. This influences the interactions with trace metals and sea ice. Brine drainage acts on both ice types to release trace metals. The accumulation of trace metals can occur through particle scavenging in floe ice, or wave filtration in drifting ice. Both ice types will retain high concentrations of LPFe, but floe ice can undergo reduction, increasing the dissolved concentrations over time. Snow ice that forms on floe ice will also increase the overall concentrations of trace metals.

Based on the results of this thesis, we were able to conclude the following accumulation and release processes available to Arctic sea ice. During initial sea ice formation in rough conditions, the suspension freezing of suspended particles from the water column accumulates labile partiulate metals (oxides). As sea ice thickens, forming a granular ice structure, the release of brine decreases the oxygen concentrations and initiates oxide reduction. Restriction of seawater waves limits the addition of oxygen to the ice floe. This can increase the concentrations of dissolved metals over time. The mixed and columnar ice structures that form, creating an ice floe, will not retain trace metals as they are released during brine drainage. The formation of snow ice, above the

ice floe, accumulates atmospheric trace metals. Over time these trace metals can be reduced through photochemical reduction, increasing the dissolved concentrations over time. Therefore, the stable floe ice can a be long-term local storage and/or source of dissolved and labile particulate metals.

When the floe ice deforms, constant wave action (and/or brine drainage) can flush out the dissolved metals from the ice and add labile partiulate metals that are available in the surface waters. This creates an oxic environment, eliminating oxide reduction that can increase the concentrations of dissolved metals. The retention of labile particulate metals and the high mobility of the drifting ice can allow it to be a long-range transporter of labile partiulate metals (Fig. 1). Therefore, sea ice form, processes of sea ice formation, chemical transformation and brine release, are important for the accumulation, retention and release of trace metals from sea ice.

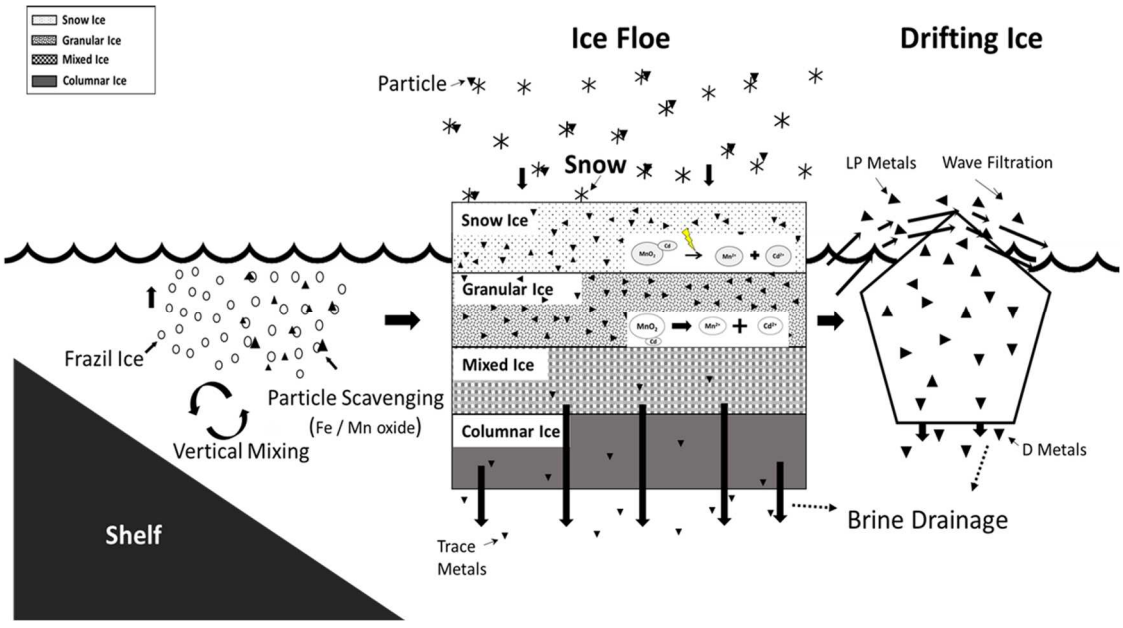

Figure 1. Schematic of trace metal accumulation, chemical transformation and release processes in drift ice from the shelf area and interior floe ice from the basin area. Sea ice structure of interior floe ice are represented in the schematic.