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学 位 論 文 題 名

Accumulation mechanisms of trace metals into Arctic sea ice

(北極海における海水への微量金属蓄積メカニズムの解明)

In the last 20 years the Arctic Ocean has experienced over 32% loss of summer sea ice. This loss can influence the biogeochemical cycling of trace metals, affecting seawater's biology and chemistry. Sea ice is important for the health of the polar oceans yet its role in the biogeochemical cycling of trace metals is not clear. To understand the geochemical behavior of trace metals and their accumulation into sea ice, dissolved (D, $<0.2 \mu\text{m}$), and labile particulate (LP, Total Dissolvable - Dissolved) Fe, Mn, and Cd were examined in sea ice and seawater collected from the Chukchi Sea, Arctic Ocean. Samples were pre-concentrated utilizing the solid-phase extraction NOBIAS Chelate PA-1 resin (Hitachi High-Technologies Corporation) and analyzed on a Graphite Furnace Atomic Absorption Spectrometer. 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 a biogeochemical cycling source. Chukchi seawater concentrations of Fe and Mn may have been controlled through external sources. Sediments (shelf or river) supplied LPFe and LPMn. DFe and DMn were supplied by the Alaskan Coastal Current. Trace metal concentrations in Chukchi drift ice were heterogeneous. Drift ice showed high percentages for the LP fraction (99.2% Fe, 63.6% Mn and 71.2% Cd). This data indicated that, regardless of the trace metal behavior in Chukchi seawater, Chukchi drift ice was observed to have a preference to accumulate or retain the LP trace metal fraction.

To examine possible trace metal accumulation processes utilized by Arctic sea ice, the association between trace metal concentrations and ice structure were observed in 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. Using photographic analysis for the percentage of pore area and $\delta^{18}\text{O}$ analysis, sea ice structure in the core sample showed snow, granular, mixed (granular + columnar) and columnar ice. Salinity and nutrients were low, indicating brine drainage and multi-year ice. High trace metal concentrations in snow ice indicated meteoric snow as a 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 ice. It is possible that reduction of LPFe and LPM after particle entrainment released DMn and DCd, indicating a

chemical transformation processes. Low dissolved and labile particulate trace metal concentrations in mixed and columnar ice indicated a release due to brine drainage.

The accumulation and retention of trace metals into Arctic sea ice may be influenced by the type of sea ice. Drift sea ice can be a long-range transporter of LP metals. Floe ice can provide both D and LP metals to the local area. Therefore, sea ice type, processes of sea ice formation, chemical transformation and brine release, are important for the accumulation, retention and release of trace metals from sea ice.

The overall results obtained through this study clearly document the accumulation mechanisms of trace metals into Arctic sea ice, which are important for understanding biogeochemistry and biological production in the Arctic Ocean.

In addition to the excellent academic knowledge in the research, her academic records throughout the Ph.D course are excellent. Based on these evidences, the committee reached to a conclusion that Evans La Kenya Elizabeth deserves to become a Doctor of Environmental Science.