More than just "brown layers": Manganese enrichments in Quaternary Arctic Ocean sediments

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Brown manganese-rich layers are well-known and widespread features in Quaternary deposits in the central Arctic Ocean, but despite their use as stratigraphic marker horizons, the processes leading to their formation are debated. Both glacial-interglacial climatic variations (e.g., increased river runoff, decreased bottom water ventilation) and early diagenetic processes have been suggested to explain the sedimentary Mn distributions. In an attempt to solve this conundrum, we applied inorganic geochemical analyses to pore waters and sediments of two sediment cores from the western Arctic Ocean (Mendeleev Ridge, RV Polarstern Expedition ARK-XXIII/3) that showed marked brown to gray-yellowish colour variations (März et al., 2011). Our results show that most brown layers are associated with detrital (ice-rafted) and biogenic carbonate enrichments, as indicated by peaks in Ca/Al, Mg/Al, Sr/Al and Sr/Mg ratios. In addition, all Mn-rich layers are also enriched in Fe (oxyhydr)oxides, and in the trace metals Co, Cu, Mo and Ni that were most probably scavenged by Mn/Fe (oxyhydr)oxides. Independent from the geochemical patterns, distinct bioturbation patterns (specifically well-defined brown burrows into the underlying sediments) suggest these metal enrichments formed close to the sediment–water interface. We thus infer that these metal- and carbonate-rich layers indeed formed under warmer (interglacial/interstadial) climate conditions with an intensified continental hydrological cycle and only seasonal sea ice cover. Under these conditions, trace metals were delivered to the Arctic Ocean by rivers, sea ice and coastal erosion, while under enhanced seasonal productivity more reactive organic matter was exported to the sea floor. The coeval deposition of organic matter, Mn/Fe (oxyhydr)oxides and trace metals triggered an intense diagenetic Mn and Fe cycling at the sediment-water interface. In combination, these climate-induced primary and secondary processes resulted in the enrichments of Mn/Fe (oxyhydr)oxides and trace metals, and the degradation of labile organic matter. With the onset of cooler (glacial/stadial) conditions, the reduction of river runoff and the lower sea level strongly decreased the input of land-derived metals, and a solid sea ice cover terminated the production and export of fresh organic matter. Under these conditions, grayish-yellowish sediments with lower metal contents were deposited. Oxygen depletion of the Arctic bottom waters under these cooler conditions is not supported by our data, and did not cause the sedimentary Mn distribution. While the original composition and texture of the brown layers resulted from specific climatic conditions and the corresponding diagenetic processes, pore water data show that diagenetic redistribution of Mn and also Mo is still affecting the organic-poor deeper sediments. Under stable diagenetic conditions, purely authigenic Mn-rich brown layers may form, while others may be partly or completely dissolved. The degree of diagenetic Mn redistribution largely depends on the depositional environment, especially the Mn and reactive organic matter availability. In summary, brown layers in Arctic sediments contain valuable paleoenvironmental information, but they are definitely affected by diagenetic overprint.