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Diagenetic regimes in Arctic Ocean sediments: Implications for sediment geochemistry and core correlation

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Abstract

Dark brown sediment layers are a potential stratigraphic tool in Quaternary Arctic Ocean sediments. They are rich in Mn, Fe, and trace metals scavenged from the water column and were most likely deposited during interglacial intervals. In this study, we combine sediment and pore water data from sediment cores taken in different parts of the Arctic Ocean to investigate the influence of early diagenetic processes on sediment geochemistry. In most studied cores, Mn, Co, and Mo are released into the pore waters from Mn oxide dissolution in deeper (>1.5 m) sediment layers. The relationship between sedimentary Mn, Co, and Mo contents in excess of the lithogenic background (element$_{xs}$) shows that Co_{xs}/Mo_{xs} values are a diagnostic tool to distinguish between layers with diagenetic metal addition from the pore waters ($Co_{xs}/Mo_{xs} < 1$), layers affected by Mn oxide dissolution and metal release ($Co_{xs}/Mo_{xs} > 10$), and unaffected layers (Co_{xs}/Mo_{xs} from 1 to 10). Steady-state calculations based on current pore water profiles reveal that in the studied cores, the diagenetic addition of these metals from the pore water pool alone is not sufficient to produce the sedimentary metal enrichments. However, it seems evident that dissolution of Mn oxides in the Mn reduction zone can permanently alter the primary geochemical signature of the dark brown layers. Therefore, pore water data and Co_{xs}/Mo_{xs} values should be considered before core correlation when this correlation is solely based on Mn contents and dark sediment color. In contrast to the mostly non-lithogenic origin of Mn in the dark brown layers, sedimentary Fe consists of a large lithogenic (80%) and a small non-lithogenic fraction (20%). Our pore water data show that diagenetic Fe remobilization is not currently occurring in the sediment. The dominant Fe sources are coastal erosion and river input. Budget calculations show that Fe seems to be trapped in the modern Arctic Ocean and accumulates in shelf and basin sediments.

The Fe isotopic signal $\delta^{56}Fe$ of the solid phase is positive (~0.2–0.3‰) in samples defined as the lithogenic background without significant Fe enrichments. With increasing non-lithogenic Fe contents in the sediment, $\delta^{56}Fe$ becomes more negative, which indicates a shelf-to-basin export of an isotopically lighter Fe fraction. We assume that the same transport process is true for Mn.

Keywords: Arctic Ocean; Sediment; Pore water; Diagenesis; Manganese; Iron isotopes; Budget

1. INTRODUCTION

The Arctic Ocean plays an important role for the global climate because it impacts deep water formation in the

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North Atlantic and therefore the global overturning circulation (Aagaard and Swift, 1985). As the Arctic Ocean is very sensitive to climate change, research into the impacts of current global warming, sea ice melting and sea level rise has been intensified over the last decades (e.g., Lambeck et al., 2002; Anisimov et al., 2007). Sedimentary records are valuable archives of different climate conditions in the past, and the response of the Arctic Ocean to these conditions. Extraction of this information can provide unique insights into the past, and possibly future effects of changing environmental conditions in this highly sensitive environment. An important requirement for such studies is the establishment of an accurate age model for the sediments, which is an omnipresent problem in the Arctic environment (Alexanderson et al., 2014). The use of several conventional dating techniques in the Arctic (e.g., ^{14}C dating, δ^{18}O stratigraphy) is hindered by low organic matter contents in the basin sediments, poor preservation of calcareous tests, and problematic correlations of Arctic to lower latitude oxygen isotope records due to the changing fresh water contribution from Arctic rivers (Backman et al., 2004; Spielhagen et al., 2004). An alternative potential stratigraphic tool for core correlation in Quaternary Arctic sediments are widespread, cyclically occurring dark brown Mn-rich sediment layers. They seem to have formed during interglacial intervals by enhanced Mn input (Jakobsson et al., 2000; März et al., 2011; Meinhardt et al., 2014; recent review by Löwemark et al., 2014). In oxic waters Mn particles in the form of (oxyhydr)oxides are often associated with Fe (oxyhydr)oxides. During settling to the sea floor, these Mn- and Fe-rich particulates scavenge trace metals from the water column, creating parallel sedimentary enrichments in, e.g., Co, Mo, and Ni (Goldberg, 1954; März et al., 2011, 2012; Meinhardt et al., 2014). The dark brown layers may be used for core correlation if they were deposited synchronously across the whole Arctic Ocean during interglacials (Löwemark et al., 2012, 2014). However, this stratigraphic use of the brown layers is only justified when significant diagenetic modification can be excluded. Dissolution and re-precipitation of Mn or Fe (oxyhydr)oxides and other sediment components after deposition have the potential to completely erase primary Mn layers, and form new Mn layers at the redox boundary in the sediment (e.g., Li et al., 1969; Burdige, 1993; Macdonald and Gobeil, 2012). These processes may disrupt the climatically forced sequence of Mn enrichments, and therefore prevent their use for stratigraphic purposes (Sundby et al., 2015).

In addition to these marked Mn enrichments, another prominent feature of Arctic Ocean sediments is the enrichment of Fe relative to average shale in different sediment layers. In sediment cores from the Mendeleev Ridge, many dark brown Mn-rich layers have elevated Fe contents as well, although the variations in Fe contents are less pronounced (März et al., 2011, 2012; Meinhardt et al., 2014). Particularly in Mendeleev Ridge surface sediments, Fe contents in excess of the lithogenic background (Fe_{xs}) are on the same order of magnitude (by weight) as Mn_{xs} contents (Meinhardt et al., 2014). However, despite significant progress in our understanding of Arctic Mn-, Fe-, and trace metal-rich layers, a more systematic investigation of these particular geochemical features is still missing. In this study, we combine solid phase and pore water data of sediment cores from different parts of the Arctic Ocean to determine which elements are currently influenced by dissolution/reprecipitation processes, and to what extent the location and composition of dark brown layers is modified by diagenesis. By analyzing Fe isotope ratios in selected sediment layers we will further extend our discussion of potential sources for the Fe enrichments in Arctic Ocean sediments. We also evaluate whether diagenetic processes influence the sedimentary Fe and Mn records in the same way.

2. MATERIALS AND METHODS

During R/V *Polarstern* expeditions ARK-XXIII/3 in 2008 and ARK-XXVI/3 in 2011 (Jokat, 2009; Schauer, 2012), five gravity corer (GC) and eight multicorer (MUC) cores were collected (Fig. 1, Table 1). Shortly after core recovery, the GC cores were cut into 1 m segments. Pore water sampling was performed immediately with rhizons (polymer filter with 0.1 μm pore size, Rhizosphere; Seeberg-Elverfeldt et al., 2005) at 4 °C. Every 20 cm, holes were drilled into the liners of the GC cores. The rhizons were placed into the holes and syringes were attached. Pore water sampling of the MUC cores was performed in the same way on pre-drilled holes of the MUC tube (1–5 cm intervals). Variable amounts of pore water were retrieved (5–10 ml) and stored at 4 °C in polypropylene tubes. For later analyses of dissolved metals the pore water was acidified with distilled HNO_3 to a pH of <2. Pore water for nutrient analyses was preserved by addition of $HgCl_2$. Sediment samples were taken with a plastic spatula at a resolution of 1–5 cm and stored in plastic bags at 4 °C. Sediments from all MUC cores and one GC core (248-6) were taken on board. For later on-shore sampling of GC cores 206-3, 220-7, and 237-3, plastic U-channels were used. After freeze-drying at the University of Oldenburg, the samples were finely ground (<0.125 mm) in an agate ball mill for further analyses.

Analysis of pore water ammonia was performed on board with the untreated pore water via photometry using a microtiter plate reader (Spectra Tecan; modified protocol based on Benesch and Mangelsdorf, 1972). Nitrate was analyzed on shore with a microtiter plate reader as well (Multiskan Go, Thermo Scientific; Schnetger and Lehners, 2014). Dissolved Mn (Mn_{diss}) and S (calculated as SO_4^{2-}) were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo-Fisher iCAP 6000). Dissolved Co, Fe, and Mo (Co_{diss}, Fe_{diss}, Mo_{diss}) were analyzed in medium resolution (4500) by ICP-mass spectrometry (Element 2, Thermo-Finnigan) with Lu and Y as internal standards. Sediment analyses of Al, Co, Fe, Mn, Mo, and Ni were performed by wavelength-dispersive X-ray fluorescence (XRF, Philips PW 2400) on fused borate glass beads (detailed method in data repository of Eckert et al., 2013). For ICP-OES analyses, accuracy and precision were determined with the standard NASS-5 ($n = 7$) and Mn-spiked Atlantic Sea Water