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Nature of Fe-precipitates in sediments from the Mendeleev Ridge, Arctic Ocean

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Sedimentary environments in the Arctic Ocean are only partially understood because of difficulties with collecting quality sediment cores and developing a reliable chronostratigraphy. This study is aimed to provide insights in the geochemistry of Quaternary Arctic Ocean sediments in relation to the history of Arctic riverine discharge. We analyzed samples from a sediment core collected on the 2005 Healy-Oden Trans-Arctic Expedition (HOTRAX) from the Mendeleev Ridge off the eastern Eurasian margin. As common for the Arctic Ocean, this core features cyclically occurring brown layers (mostly 10YR 4/3 in the Munsell notation) that represent interglacial/interstadial periods including the Holocene. The brown colour is believed to result primarily from the presence of Mn oxides. Our X-ray diffraction, Mõssbauer and diffuse reflectance UV-Vis spectroscopy (DRS), voltammetric and thermomagnetic analyses of brown sediments reveal extremely poorly crystalline, probably low-molecular oligomeric Fe(III) oxidic species. Transformation of these species to more common ferrihydrite or thermodynamically stable FeOOH is effectively prevented either by organic ligands chemisorbed on their surface or by fine clayey matrix disabling crystal growth. The organic ligands covering oligomeric hydrolyzed Fe(III) nanoparticles would indicate their riverine origin, while nanocomposite of Fe oxides with clay minerals will be more indicative of in-situ oxidative hydrolysis of Fe(2+) in clay suspension. We also suggest that these Fe(III) species play an important role in sediment color as their voltammetric signal is more than an order of magnitude higher than that of Mn(III,IV) oxides. Comparison of DRS and voltammetric properties of these ferric accumulations with visually similar, brownish (10YR 5/4) deglacial sediments from the Alaskan margin reveals their different nature and hence also genesis, with the lat-

ter being characterized by nanoparticulate ferric oxides (FeOOH), possibly formed at the mixing zone of marine and fresh (deglacial) water.