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

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In Quaternary deposits of the Arctic Ocean, brown Mn-rich layers are well-known, widespread, but also debated features. Both glacial-interglacial climatic variations (in river runoff, bottom water ventilation etc.) and early diagenetic processes might explain the sedimentary Mn distributions. We applied inorganic geochemical analyses to pore waters and sediments of two sediment cores from the western Arctic Mendeleev Ridge (RV Polarstern Expedition ARK-XXIII/3) [1]. Our results show that most brown layers are associated with detrital (ice-rafted) and biogenic carbonate enrichments. In addition, all Mn-rich layers are enriched in Fe (oxyhydr)oxides, and in Co, Cu, Mo and Ni that were most probably scavenged by Mn/Fe (oxyhydr)oxides. Distinct bioturbation patterns (i.e., brown burrows into the underlying sediments) suggest these metal enrichments formed close to the sediment–water interface.

We infer that the metal-rich layers formed under warmer (interglacial/interstadial) conditions with an intensified continental hydrological cycle and only seasonal sea ice cover. Metals were delivered to the ocean by rivers/sea ice/coastal erosion [2], while seasonal productivity increased the reactive organic matter export to the sea floor. The coeval deposition of organic matter and Mn/Fe (oxyhydr)oxides triggered an intense diagenetic Mn and Fe cycling at the sediment-water interface. These climate-induced primary and secondary processes resulted in the enrichments of Mn/Fe (oxyhydr)oxides, scavenging of trace metals, and the degradation of labile organic matter. With the onset of glacial/stadial conditions, the riverine/erosive delivery of metals strongly decreased, a solid sea ice cover terminated the production and export of fresh organic matter, and gray-yellowish sediments with lower metal contents were deposited. Our data do not support glacial/stadial bottom water oxygen depletion that might have affected the Mn distribution.

Despite the climatic control on the composition of the brown layers, pore water data show that diagenetic redistribution of Mn and Mo is still affecting the deeper sediments. The degree of Mn remobilisation (potentially causing complete dissolution of existing, and formation of new Mn layers) largely depends on the availability and reactivity of Mn (oxyhydr)oxides and organic matter.

[1] C. März, A. Stratmann, J. Matthiessen, A.-K. Meinhardt, S. Eckert, B. Schnetger, C. Vogt, R. Stein, H.-J. Brumsack (2011) *Geochim. Cosmochim. Acta* **75**, 7668-7687.
[2] R.W. Macdonald and C. Gobeil (in press) *Aquat. Geochem.*

SIMS sputter pit volume estimation in SHRIMP zircon analysis using an $^{18}O_2^-$ primary beam

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Abstract

A novel method of estimating the volume of sputtered material was discovered while performing SHRIMP (Sensitive High-Resolution Ion MicroProbe) zircon U/Pb geochronology using an $^{18}O_2^-$ primary beam. During analysis, the ratio of Th and U oxide isotopologues was found to be equal for each individual spot. Assuming that the $U^{16}O/U^{18}O$ (or $Th^{16}O/Th^{18}O$) ratio was equal to the $^{16}O/^{18}O$ ratio of the sputtered material, multiplying this by the total ^{18}O primary beam fluence (true beam current times analytical time) yields total sputtered oxygen. Dividing by the density of oxygen in the zircon crystal lattice (about 63 atoms per nm^3) yields an analytical volume.

Comparison with pit volumes from AFM (Atomic Force Microscopy) shows that this isotopic volume estimation agrees with AFM pit measurements to within 10%. This relationship holds for primary beam impact energies from 5 to 15 kV.

This agreement in volume between isotopic and AFM measurements suggests that oxygen migration in the sputtering process is limited. As oxygen activity is crucial to governing the Pb/U vs UO/U calibration that makes accurate SIMS U/Pb geochronology possible, further investigations are planned into minerals such as baddeleyite, which calibrate poorly.

As the SHRIMP duoplasmatron consumes only \$50-\$100 of $^{18}O_2$ per day, this method appears to be cost-competitive with paying for analytical time on a second instrument for analytical volume determination. However, it requires that the sample and the primary beam are the only sources of oxygen in the sputtering process.