Benthic fluxes of iron and manganese under various redox conditions

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Fluxes of dissolved forms of iron and manganese across the sediment-water interface were studied *in situ* in the Gulf of Finland and the Vistula Lagoon (Baltic Sea), and in the Golubaya Bay (Black Sea) from 2001 to 2005. Fluxes were measured using chamber incubations (Jch), and sediment cores were collected to assess the porewater and solid phase metal distribution at different depths to calculate diffusive flux (Jpw). Measured and calculated benthic fluxes of manganese and iron were directed out of sediment for all sites and were found to vary between 70–4450 and 5–1000 µmole m^{-2} day^{-1} for manganese and iron, respectively. Benthic fluxes of manganese were found to correlate with manganese concentration in the porewater of the top sediment layer positively. The manganese fluxes were not influenced by redox conditions in the near-bottom water. On a large timescale manganese fluxes depend on redox conditions in bottom water, because a change of redox conditions would lead to a change of dissolved manganese content of the porewater. However, on a timescale of a single chamber incubation manganese fluxes did not depend on oxygen concentration (redox conditions), because for dissolved manganese the rate of oxidation is much lower than the rate of release from sediment. Diffusive flux of manganese constitutes 25–70% of the measured flux determined with the chamber incubation (on average Jch/Jpw=3). This indicates that another processes such as bacterial dissolution or bio-irrigation also play an important role in manganese benthic flux formation. Our results showed the importance of bottom water redox conditions for benthic iron fluxes. We measured no fluxes at oxic conditions, intermediate fluxes at anoxic conditions and high fluxes at suboxic conditions. Oxidation of released dissolved iron occurred very rapidly under oxic conditions right after its release from the sediment. Under suboxic and anoxic conditions in the bottom water, the iron flux was dependent both on its concentration in porewater of the surface sediment and on the content of iron in the solid phase of sediment. The chamber measured and diffusive fluxes of total iron differed much more than for manganese, 0.01<Jch/Jpw<50. Thus, bio-irrigation, sediment resuspension and chemical processes at the interface are much more important for iron fluxes than for manganese fluxes.

Peformance characteristics of an enhanced Daly ion counting system for TIMS

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We have developed matched and close-coupled pulse amplification electronics for the ion-counting Daly detector used on Phoenix and IsoProbe-T thermal ionization mass spectrometers. These developments have largely eliminated post pulse ringing and permit the use of very low discrimination thresholds resulting in a new ion-counting Daly detector system which is linear (within ~0.05%) from zero to 3.5e6cps (~50-60mV) using a single deadtime correction.

The large dynamic range of the new Daly provides a significant overlap with the range of the Faraday detectors. This provides an exciting opportunity to obtain high precision measurements of minor isotopes such as ^{234}U and ^{230}Th using a combination of Faraday and ion-counting Daly. It also extends the range of large ratios that can be measured by peak jumping on the Daly alone, eliminating the requirement for a Daly/Faraday gain calibration. The large dynamic range also provides the ability to resolve small differences in deadtime (<0.1ns) to allow accurate and precise measurements of Pb isotopes by peak jumping i.e. for high resolution geochronological applications.

A further benefit of the large dynamic range is the ability to measure 20-30mV ion signals with zero noise. This will be of real benefit for the measurement of sub-ng levels of e.g. Nd by peak jumping. It could also offer an alternative to the use of $1e^{12}\Omega$ gain resistors on Faraday detectors since noise, linearity and signal decay times are significantly better than can be attained using these resistors.

Examples of different applications will be presented with indications of the level of precision that can be attained using different analytical combinations.