In situ Pb-isotope analysis by LA-MC-ICP-MS: Applications to geochemistry, geochronology, palaeoceanography and archaeology

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Variations in Pb-isotope ratios provide an unparalleled tool for isotope tracing and dating studies in the Earth Sciences and many other disciplines. Recent development of LA-MC-ICP-MS techniques allows rapid and accurate in situ laser ablation analysis of Pb-isotope ratios in a wide range of sample matrices, including silicate, titanate and phosphate minerals, silicate glasses, ferromanganese oxides and metals. In materials with sufficiently high Pb concentration (~>10 ppm) individual 30-60s Pb-isotope analyses can be made at a level of precision that approaches conventional (non double-spike) TIMS analysis, but requires just nanograms of matrix material and picogram to femtogram quantities of Pb.

In-situ Pb-isotope measurements, made using a CETAC 266 nm Nd-YAG laser in conjunction with an AXIOM multi-collector ICP-MS, have been successfully applied to a number of problems in the Earth and Archaeological Sciences. Rapid in situ single grain Pb-Pb dating of rutile, monazite, apatite and sphene provide detailed and precise (± 0.2%) geochronological and thermo-chronological constraints on the evolution of ancient crustal rocks. High-resolution (~10-50 ka/analysis) Pb-isotope records of oceanic ferro-manganese nodules reveal changing Pacific deepwater Pb sources over the last 14 Ma, and combined Pb-isotope and LREE analyses (using a multistatic measurement technique) provide a detailed record of the relation between ocean bioproductivity and deep water circulation. Depth profile analyses of nodule surfaces provide Pb-isotope data at a spatial resolution of $\leq 5\mu m$ (~2.5 ka/analysis), and allow clear distinction of anthropogenic and the most recent glacial and interglacial Pb sources. Analysis of Pb-isotope ratios in feldspar, glass shards and groundmass from silicic pyroclastic rocks in Yemen and Ethiopia allow correlation of volcanic units across the Red Sea and to ash horizons in ODP leg 115 sediment cores ~2600 km from the eruption site. Analysis of metals provides rapid tracing of metal sources in archaeological material with minimal sample destruction.

Natural enrichment of organic halogens during peat formation

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There is an ongoing discussion on the natural formation and the fate of organic chlorine compounds in the environment. Recent studies on the formation of stable chlorinated organic compounds in weathering plant material (Myneni, 2002) provides interesting data about initial processes of the formation of organochlorines in the environment but also poses many questions. So, it remains unclear whether humification of plant material is the predominant process for the enrichment of organochlorines in nature.

Previously we have shown that peatlands are a major sink of organic chlorine (Keppler and Biester, 2002).

We now demonstrate that humification of plant material in peatlands is a major process to transform inorganic halides - originated from sea salt aerosols - into organically bound halides.

Two ombrotrophic peat bogs from remote pristine sites in the Magellanic Moorlands, Chile (53° S) were studied for the relationship between humification of plant material and the natural chlorination and storage of organic chlorine in wetlands. Concentrations of organic chlorine in peat were found to reach up to 0.2 % (d.w.). Based on our measurements and results from Canadian and continental European peat bogs (Silk et al., 1997; Müller et al., 1996), we estimate that between 300 and 1,100 million tonnes of organically bound chlorine have been stored in Earth's peatlands since the last glacial period.

Moreover, concentrations of total organic chlorine (TOX) in environmental samples are often used to indicate pollution from anthropogenic sources. The observation that concentrations of naturally formed organochlorines in peatlands can exceed current threshold values of TOX to a large extent implicates that the use of this parameter requires critical discussion.

References

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