Lead isotope analysis: Removal of ^{204}Hg isobaric interference from ^{204}Pb for U/Pb dating using an (MS/MS capable) ICP-QQQ-MS

GLENN WOODS[1 A] AND JEAN-PIERRE LENER[2]

[1]Agilent Technologies (UK) Ltd. 5500 Lakeside, Cheadle Royal Business Park, Stockport, SK8 3GR United Kingdom

[2]7 Agilent Technologies, Avenue des Tropiques, ZA Courtaboeuf 2, BP 12, 91941 Les Ulis, FRANCE

Lead is an element whose isotopic pattern naturally varies more than any other element in the periodic table. The various stable isotopes are derived from uranium and thorium decay (238U – 206Pb, 235U – 207Pb; 232Th – 208Pb) with the only non-radiogenic isotope being the 204Pb isotope. Lead is an important element for providence testing (e.g. tracing the origin of an atrefact, food product, pollution event etc.) and its isotope analysis has been used in applications as far afield as pollution tracer studies for TEL (tetraethyl lead fuel additive), ore, olive oil & wine origin testing and forensic analysis of bullets.

One of the most important and difficult analyses for lead isotopes is for dating of minerals and Pb containing artefacts. For successful dating, all of the stable isotopes of Pb are required however there is an isobaric overlap from 204Hg on the 204Pb isotope. If any Hg is present in the sample, reagents or as a contaminant in the Ar gas, this would significantly bias the data whether solution or laser analysis is employed.

Removal of the Hg-based isobaric overlap can be achieved by addition of ammonia to a collision-reaction cell (CRC) equipped instrument. Mercury ions undergo rapid charge-transfer reaction in the presence of ammonia (the Hg+ ion is neutralised to Hg0 and the charge is passed to the ammonia molecule).

This could lead to the successful removal of Hg isobaric interference from Pb – however the potential issue of new molecular interferences created within the cell remain unless the reaction can be sufficiently controlled by ion pre-selection. This paper demonstrates the benefit of a MS/MS capable ICP-MS for the effective interference-free analysis of lead isotopes.

Increasing spatial resolution of lipid biomarker analysis by LDI FT-ICRMS

L. WÖRMER[1]*, M. ELVERT[1], J. FUCHSER[2], J.S. LIPP[1] AND K.-U. HINRICHS[1]

[1]MARUM and Department of Geosciences, University of Bremen, 28359 Bremen, Germany

[2]Bruker Daltonik GmbH, 28359 Bremen, Germany

Planktonic archaea and other marine microorganisms are known to adapt their membrane lipids to temperature – a phenomenon exploited in a number of molecular proxies for the reconstruction of past sea surface temperature (SST) from dated sediment cores. One widely applied proxy is the TEX_{86} index [1], which is based on the number of rings in the structure of the archaeal lipid GDGT. Given typical sample sizes and analysis by LC-APCI-MS, such SST records can resolve decadal to millennial variations, dependent on the geological setting examined. Our goal was to combine the temperature proxy potential of lipids in the sedimentological record with the high spatial resolution of laser desorption ionization (LDI) coupled to FT-ICRMS. Micrometer-scale resolution of LDI may produce estimates on sub-decadal to sub-annual scales and potentially provide crucial, previously hidden insights on the heartbeat of past climates.

We demonstrate that LDI FT-ICRMS efficiently ionizes GDGTs and that the high resolving power of FT-ICRMS is crucial for their unequivocal identification. We also observe a strong correlation between TEX_{86}-based SST analysis by LC-APCI-MS and ring distributions obtained by LDI FT-ICRMS, which proves the utility of the proposed method for correctly quantifying the different GDGT species.

We analyzed a several-cm long sediment core segment of Mediterranean Sapropel S1 with a spatial resolution of 200 μm, which corresponds to a temporal resolution of about 6 yrs. The observed GDGT distributions are consistent with short-term rhythmic variations of SST with relatively high amplitudes of several °C. Further validation of these trends is ongoing. These first results demonstrate the capacity to obtain a continuous, high resolution profile of GDGTs directly on an intact sediment core, thus setting the stage for lipid-based paleotemperature estimations with unprecedented temporal resolution and suggesting an enormous potential of this approach for future biomarker applications.

[1] Schouten *et al*. (2002), *EPSL* **204**, 265-274.

www.minersoc.org
DOI:10.1180/minmag.2013.077.5.23