

4.63.51**Deconvolving the Pb isotope signal of marine sediments**W. ABOUCHAMI¹, S.J.G. GALER¹ AND M. ZABEL²¹Max-Planck Institut fuer Chemie, Postfach 3060, 55020 Mainz, Germany (wafa@mpch-mainz.mpg.de)²University Bremen, FB5 Geosciences; Postfach 330440, 28334 Bremen, Germany

Past seawater radiogenic isotopic compositions (Nd, Pb, Hf, Os) have been inferred using the record of Fe-Mn crusts. The question as to whether these faithfully record past seawater compositions can be addressed by extracting the authigenic component of marine sediments using sequential leaching methods. Such a method has been successfully applied using Nd isotopes in oxide coatings of sediments from the Cape Basin [1]. Recently, Abouchami and Zabel (2003) [2] demonstrated that the Pb isotope record of bulk marine sediments from the Equatorial Atlantic matches remarkably well the climate fluctuations of the past 200 ka, with alternating glacial, unradiogenic Pb and interglacial, radiogenic Pb signatures.

Sequential leaching on Holocene and Last Glacial Maximum (LGM) samples from these sediments cores have been performed. Pb isotopes were measured on the different fractions using the Pb triple spike technique by TIMS and by MC-ICPMS (Nu Plasma). First results indicate significant differences in isotopic compositions between the Holocene and the LGM fractions. The isotopic signatures found in the Eastern and Western Atlantic, at a given time, suggest that the input sources to the two basins have remained distinct. These results bear some implications on the oceanic cycling of Pb, the geographic distribution and temporal trends of Pb isotopic compositions observed in the oceans, as well as the ocean circulation pattern across the Equatorial Atlantic.

References

- [1] Rutberg R.L. et al., 2000 *Nature* **405**, 935-938
 [2] Abouchami W. and Zabel M., 2003 *Earth Planet. Sci. Lett.* **213**, 221-234

4.63.52**Links between mercury and methane emissions: Mercury in lake sediments on modern to Holocene time scales**

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We evaluate depth profiles of mercury and find that methanogenesis is a significant control. New methods were used to examine the mercury biogeochemistry of two immediately adjacent lakes in Kejimikujik National Park, Nova Scotia, Canada. Several lines of evidence illustrate that mercury remobilization occurs in the sediments: (1) Acoustic sub bottom profiling was used to determine the total volume and mass of lake sediments and mercury contained in them, and how it has varied through time since the inception of the lake after deglaciation some 13,000 years ago. The rate of accumulation in sediment traps over 1 year is higher than that in the sediments over 20 years, which in turn is higher than that in the sediments over 200 years and so on up to 13,000 years. Simply by mass balance, the excess that is missing from the older sediments must be recycled upwards back into the lake. (2) Porewater concentrations of mercury have a decreasing upward gradient. Upward diffusion from low to high concentration must therefore occur. (3) A porewater spiking experiment empirically shows that the direction of aqueous mercury diffusion is upwards and that diffusion occurs for the natural gradients observed. (4) The presence and distribution of methane gas bubbles in the sediments was imaged acoustically demonstrating that old organic matter in the lakes is decaying by methanogenesis. Upward moving bubbles provide an advection pathway for dissolved gaseous mercury (DGM) to ascend to the SWI. (5) Thermodynamic modelling of the stability of mercury species for the Eh and pH conditions observed in this study show that at relatively shallow depths, DGM becomes the stable species. DGM strongly partitions into methane bubbles therefore facilitating upward advection..

This model does not make all lake sediments poor archives of mercury deposition. The role of sulphide traps in low Eh zones and oxide traps in high Eh zones needs further evaluation. Preservation of paleo-mercury deposition may be best in sediments that rapidly develop a reduced zone rich in sulphides (stable for meta-cinnabar). Good candidates may be the sediments in estuarine fiords due to their high sedimentation rates (and therefore excellent temporal resolution), low Eh, and high sulphur.

Evaluating, the impact of paleo-climatic conditions on mercury in lakes would provide further insights into this model. An important parameter for mercury fluxes may be the rate of decay of organic matter and how it has varied through time. Mercury fluxes to the lake when it began life at the end of the last glaciation 13,000 years ago (a dynamic climatic period) are also unknown.