APPLICATION NOTE 30071

# Geochemical Applications using High Resolution ICP-MS

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## Introduction

The examination of ancient and recent geochemical processes is of increasing interest as it allows us to track both the historical record and man's recent influence on the environment. In all cases, scientific excellence can only be obtained from the highest quality data. There is, therefore, a high demand in the geological community for highly sophisticated instrumentation. In many laboratories this has led to the use of for a tremendous variety of geochemical studies.

This application report showcases some of these applications from individual scientists in their particular areas. The contributions range from Pb-isotope analyses at ultra-trace concentrations to linking trace metal contents of near-shore waters to biological cycles, determining colloidal associations of an enormous range of elements and the investigation of metamorphic rock evolution by trace element analysis and high precision REE patterns.

# Tracing Pollution History in Peat Bogs by their Pb Isotope Signatures

Michael Krachler, William Shotyk, Institute of Environmental Geochemistry, University of Heidelberg, Germany.

**Figure 1. Peat core sampling.**

Rain-fed peat bogs can act as important archives of atmospheric trace element deposition. Age-dated peat profiles represent a powerful tool for the reconstruction of atmospheric fluxes and predominant sources of Pb and other trace metals. The peat cores obtained (Figure 1) are split, digested and analyzed with the Thermo Scientific™ Element™ 2 High Resolution ICP-MS for their total lead concentration and $^{206}$Pb/$^{207}$Pb ratio.

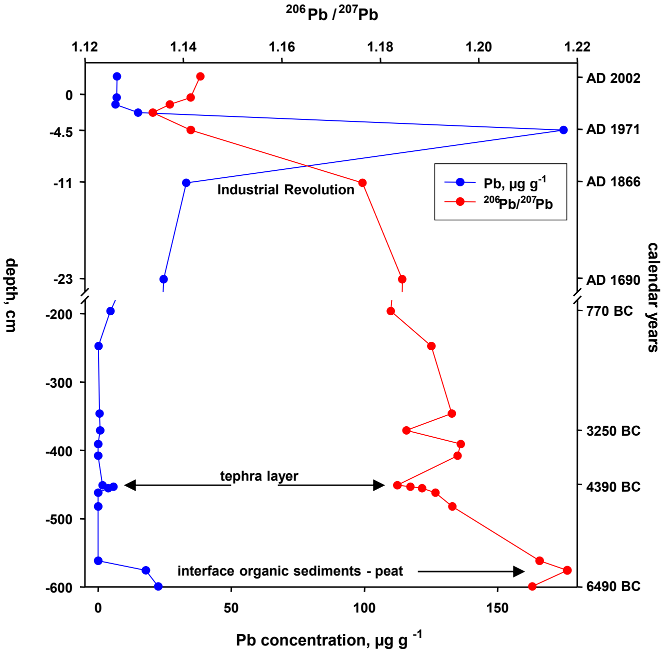

**Figure 2. Depth profiles of Pb isotope ratios and Pb concentrations in peat bog.** The right scale shows calibrated ages for this core.

Results from a core from the Black Forest, Germany, are shown in Figure 2. The preliminary data set presented here from the ongoing research demonstrates the potential of the analytical protocol developed.

In pre-anthropogenic times, background Pb concentrations and a geogenic $^{206}$Pb/$^{207}$Pb ratio are found. Coal consumption during the Industrial Revolution and later use of leaded gasoline causes tremendous amounts of Pb to be released. Accordingly, the lowest $^{206}$Pb/$^{207}$Pb values indicate the maximum impact of leaded gasoline, while the ban on leaded gasoline shows up as a slight increase for the relatively recent samples.

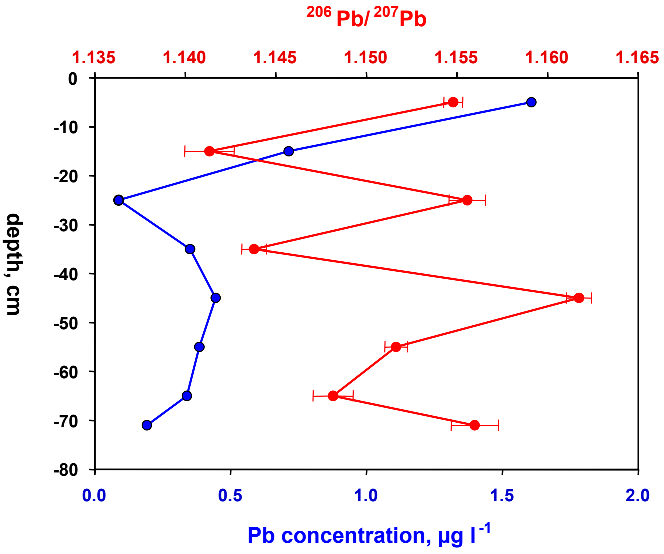

**Figure 3. Depth profiles of Pb isotope ratios and Pb concentrations in snow samples.**

The most recent isotopic data clearly show that there is still significant anthropogenic Pb contamination. This is confirmed in snow samples from 2002 with $^{206}$Pb/$^{207}$Pb ratios of 1.14 - 1.16 (Figure 3). The surface layer of the snow profile contains the highest Pb concentration (1.6 µg l$^{-1}$), while the lowest Pb concentrations is 0.088 µg l$^{-1}$. Even for these small Pb concentrations the $^{206}$Pb/$^{207}$Pb ratio could be analyzed with a precision of 0.12% and this suggests that the scatter of the isotopic data is caused by short term variations in the Pb input in the area considered.

## Reference

M. Krachler, G. Le Roux, B. Kober, W. Shotyk, 2004, Optimising accuracy and precision of lead isotope measurement ($^{206}$Pb, $^{207}$Pb, $^{208}$Pb) in acid digests of peat with ICP-SMS using individual mass discrimination correction. J. Anal. At. Spectrom., 19, 354-361

## High Resolution ICP-MS Analysis of Seawater from the Wadden Sea

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**Figure 4. Stationary sampling station in the German Wadden Sea.**

Tidal flats, in their role as the transition between terrestrial and marine environments, are important potential sources of trace metals and nutrients to the ocean. At the ICBM, an interdisciplinary Research Group was established in 2001 to study the fundamental biogeochemical processes of the Wadden Sea of N.W. Germany. The major goal of the project is to balance the input/output budget of dissolved and particulate compounds between the tidal flats and the open North Sea beyond the Wadden Sea. Therefore, it is important to determine the individual element sources and the biogeochemical transformations influencing the geochemical budget.

Tidal and seasonal variations are seen in salinity and temperature, but also in geochemical parameters such as alkalinity, DOC, nutrients, and concentrations of redox-sensitive trace metals. For instance, Mn exhibits distinct tidal and seasonal variations with maximum concentrations during low tide in summer due to the contribution of extremely Mn-rich porewaters (Figure 5), which drain out of the tidal flat sediments during low tide. A similar but less pronounced behaviour is observed for V, while Mo and U behave conservatively and follow salinity.

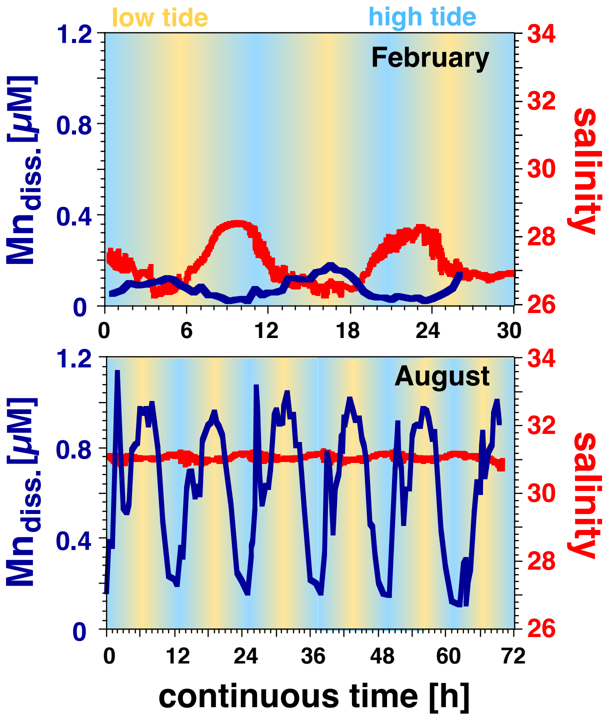

**Figure 5. Time series showing tidal and seasonal variability of dissolved Mn and salinity in Wadden Sea water.**

During the summer, Mo changes its behaviour and shows a strong coupling to the Mn-cycle. Particles are also enriched in Mn and Mo due to microbial and/or photochemical Mn-oxidation accompanied by scavenging of Mo. During the winter, when microbial activity is low, the freshwater input from small coastal tributaries becomes more significant as evidenced by balance calculations and 'gelbstoff' fluorescence. This freshwater is extremely rich in dissolved organic matter as well as in dissolved and particulate metals. Therefore, the freshwater contribution, although of small volume, cannot be neglected when performing elemental mass-balance calculations in the Wadden Sea environment.

For balancing the input/output budgets, several parameters are now recorded by a newly installed monitoring station (Figure 4) in the major tidal outlet of Spiekeroog Island.

Figure 6. Sampling site for natural fresh water in a Swedish forest.

## FFF Sector-Field ICP-MS: Determination of the Elemental Composition of Colloids in Natural Water

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Colloids have been proven to be a significant binding phase for trace metals in natural fresh water (Figure 6), seawater and groundwater. Since binding to colloids will have an impact on transport, bioavailability and toxicity of heavy metals in natural water, it is important to determine their colloidal fraction.

Field-Flow Fractionation (FFF) is a size fractionation method for colloids and macromolecules (Figure 7), using their selective ability to diffuse against a liquid flow.

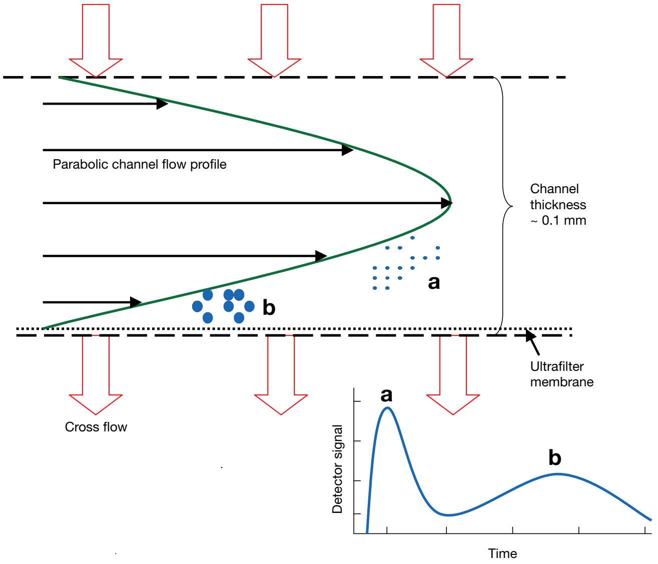

Figure 7. Field-Flow Fractionation Principle.

Retention time is therefore proportional to hydrodynamic diameter. Online coupling of FFF to the Element 2 HR-ICP-MS is a powerful technique that has provided us with new knowledge about the colloidal distribution of over fifty elements, among these toxic heavy metals such as As, Pb and Cd (Figure 8). Two main colloidal carriers have been identified in the size range 1–50 nm, small (1–5 nm) - organic carbon based colloids (humic material) and slightly larger (3–25 nm) iron rich colloids.

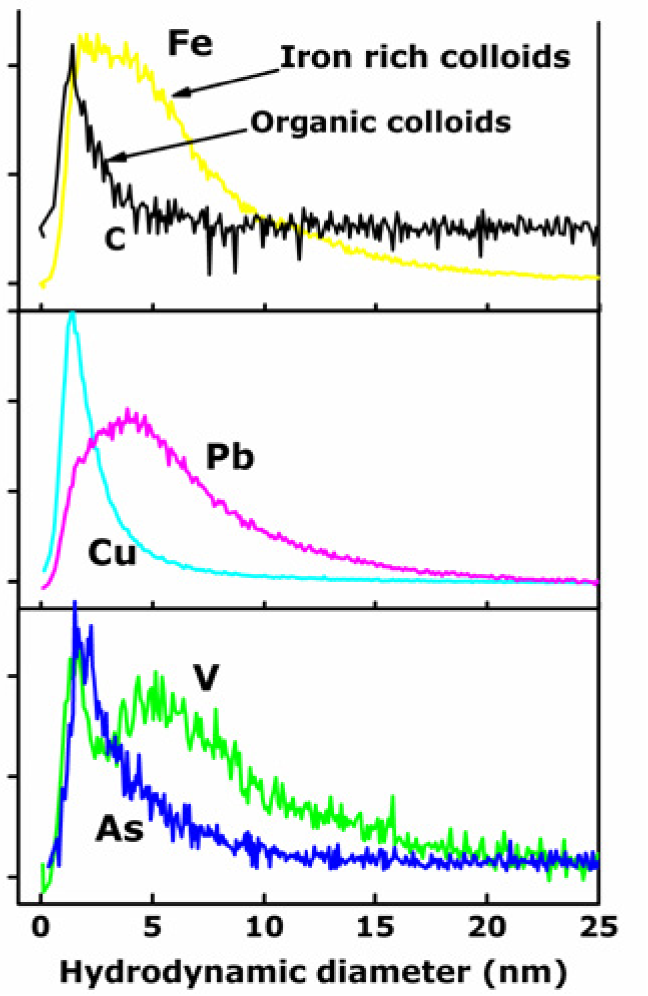

Figure 8. Elemental concentrations vs. hydrodynamic diameter of colloids.

These are found to carry over 50% of the total dissolved fraction of many elements. Most metals are associated with both phases, while Cu and Ni are exclusively bound to humic materials. In contrast, Pb, P, V and Ti are mostly associated with the iron oxyhydroxide colloids.

These different affinities will have an impact on the way that elements are transported from rivers into the sea, since colloidal iron is settled in estuaries more than humic materials.

## REE Analysis of Metamorphic Rocks using HR-ICP-MS

Heike Anders, Universität Bremen, Geowissenschaften, Germany.

The Rare Earth Element (REE) measurements shown here form part of a multi-element program developed with the Element 2 HR-ICP-MS at the University of Bremen. We use a microwave digestion with a $HNO_3$-HCl-HF-mixture to obtain complete sample dissolution, which is essential for accurate analytical results. After fuming off the acids, the samples are brought up into dilute $HNO_3$ for analysis.

Seventeen elements are measured in low resolution mode, nine in medium resolution and ten in high resolution.

For the REE, particularly in geological applications, the high mass resolution capabilities of the Element 2 HR-ICP-MS are essential as it resolves oxides formed by the light REE on heavier REE masses (Figure 9). Since the concentration of the light REE can be much higher than the heavy REE, the results of the latter would otherwise be inaccurate in low resolution.

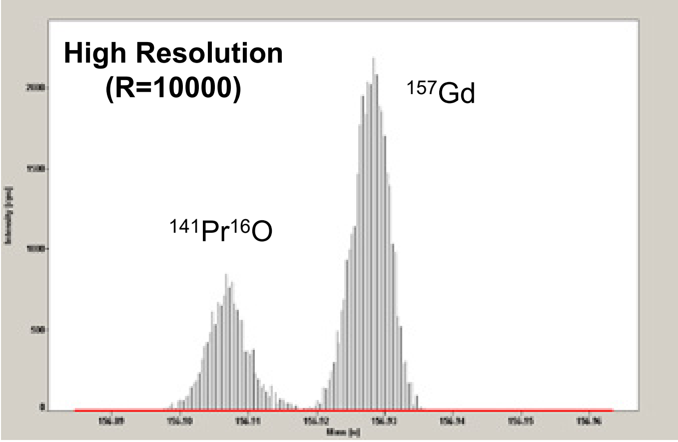

Figure 9. $^{141}Pr^{16}O$ separated from $^{157}Gd$ in high resolution.

The reference material BCR2 is analyzed for quality control periodically during the analysis series, since it resembles the composition of our basaltic samples. La, Ce, Pr, Nd are measured in low resolution mode, all other rare earth elements are measured in high resolution mode. The resulting REE plot (Figure 10) shows chrondrite normalized REE data for BCR2, collected from seven different digestions and measurements. Although the data cover different resolutions and detector modes, the REE pattern is smooth, indicating accurate results.

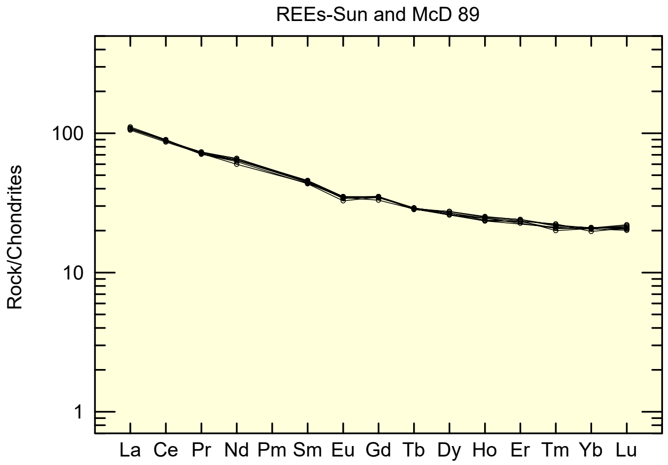

**Figure 10. Normalized Rare Earth Element distribution (chondritic composition, Sun & McDonough, 1989).**

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