

On the Trail of the Earth's History with EDXRF

By Katharina Wien, Prof. Dr. Horst D. Schulz, Martin Kölling I, Dirk Wissmann²

Sedimentary accumulations on the seabed provide information about the earth's most recent geological past, the Quaternary period. The properties of these sediments were affected by a variety of factors. Climatic and oceanographic conditions at the time played an important role in their formation. After formation of the sediment, however, the material is further affected by diagenetic modifications (biogeochemical processes), or by shift and transport processes. Stratigraphy, or subsurface geology, is concerned with describing the sequence of sediment layers, and provides a timescale for dating geological events. Element stratigraphy is one approach to the geochemical characterization of sediment sequences. The concentration of different elements, and the variations in their concentration, permit conclusions to be drawn both as to their origins and to the processes that lead to the enriched or depleted element levels.

For the first time, much of the geochemical investigation of the sediments was carried out while still on board during an expedition with the research ship METEOR in the waters off the South African coast. The data collected was used to generate an element stratigraphy soon after the samples were removed from the sea bed by the sediment corer. The analytical technique used was energy-dispersive X-ray fluorescence analysis with polarization excitement (EDPXRF). The simple and rapid sample preparation, and the high-performance of the SPECTRO XEPOS instrument used, allowed analysis for the elements Si, Ti, Al, Fe, Mn, Mg, Ca, K, Sr, Ba, Rb, Zn, S, Cl and Br to be carried out on more than 200 individual samples from one sediment core within 24 hours of taking the sample. The element profile could be interpreted immediately, and used for short-term decisions intended to optimize sample extraction, even as the expedition proceeded.

EXPERIMENTAL PART

Extracting and preparing the samples

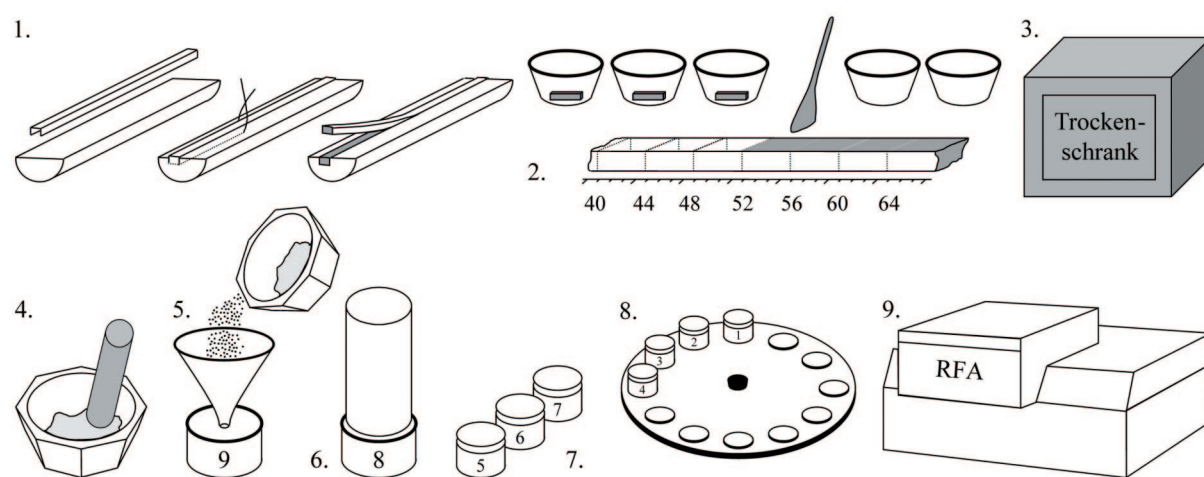
After removing a sample from the seabed with the sediment corer it is first cut into segments 1 m long, and these are then sliced in half lengthways. Samples are then taken for the XRF analysis using the cable channel method. A cable channel, 1 m long, is pressed lengthwise into a core segment, and a strand of sediment cut out with a plastic wire. This 1 m strand is divided into a continuous sequence of single samples every 4 cm, so that 25 individual samples are provided by each segment. This procedure is carried out on all the segments. The samples are dried in glass dishes for 60 min at 200°C, after which they are crushed in a mortar sufficiently finely for analysis and homogenized. At least 4 g of the powder is then placed into a cuvette, sealed by a polypropylene film on the side where the analysis will be carried out.

The powder in the cuvette is compressed with a stamp to remove air enclosures. Finally, twelve samples are placed in a sample tray and subjected to



Figure 1: Schematic illustration of sample preparation for XRF analysis

1. Extracting a sample from the 1 m core segment with a cable duct; 2. Transfer of the 4 cm individual samples to glass dishes; 3. Drying the samples; 4. Crushing and homogenization; 5. Filling the cuvettes with sample powder; 6. Compressing the powder; 7. Final preparation of the cuvettes; 8. Placing the cuvettes on the sample tray; 9. XRF analysis



XRF analysis. The sample preparation routine is illustrated schematically in Figure 1.

Instrumentation

The XRF analysis was carried out with the SPECTRO XEPOS, a compact EDXRF spectrometer. The excitation system was using a 50 W-Pd end-window tube together with three different optimizations through polarization and secondary targets. The measuring parameters applied are quoted below.

A high-resolution silicon drift chamber detector was used as the detection system. When analyzing for the elements Mg, Al and Si the sample chamber was rinsed with He. A 50 l bottle of He was sufficient for up to 1000 measurements. Typical spectra are illustrated in Figures 2 and 3.

The spectra were evaluated using the supplied "Turboquant" program for the analysis of loose powders.

Reliability of the instrument was not found to be impaired, even under rough conditions with wind force 8 and waves 3 to 4 m high.

Analytical results

The quality of the XRF analyses can be illustrated by

Instrument configuration and measuring parameters

Instrument	SPECTRO XEPOS
X-ray tube	50 W Pd end-window X-ray tube 25 kV, 1 mA
Excitation system	HOPG Target Mo secondary target Al ₂ O ₃ polarization target
Detection system	Si drift chamber
Gas rinse	He
Measuring time	100 s

* Continued on page 16

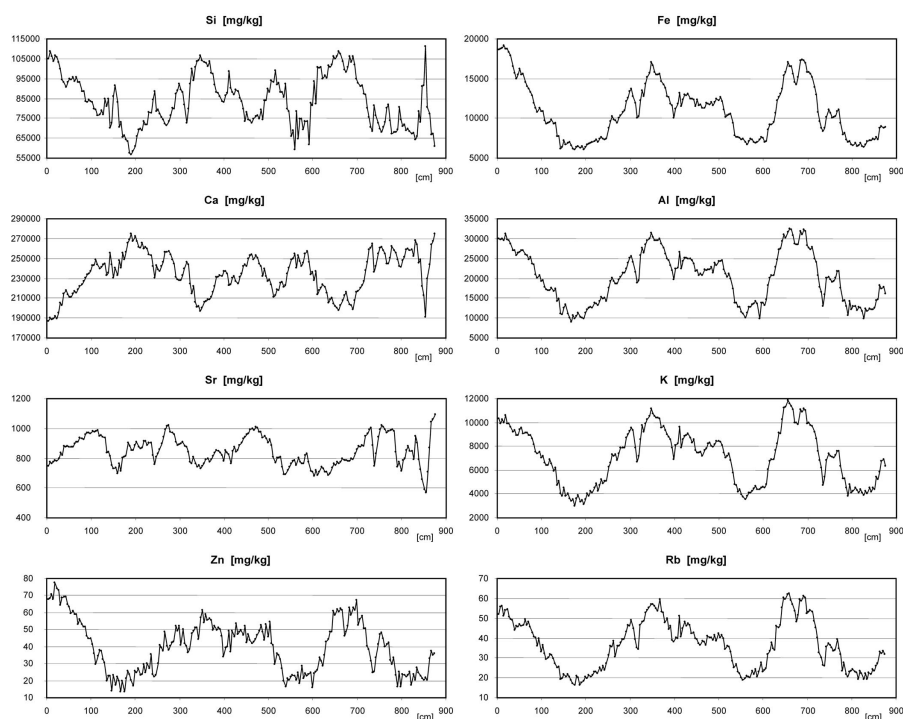


Figure 4: Analytical data from sediment core GeoB 8301-6

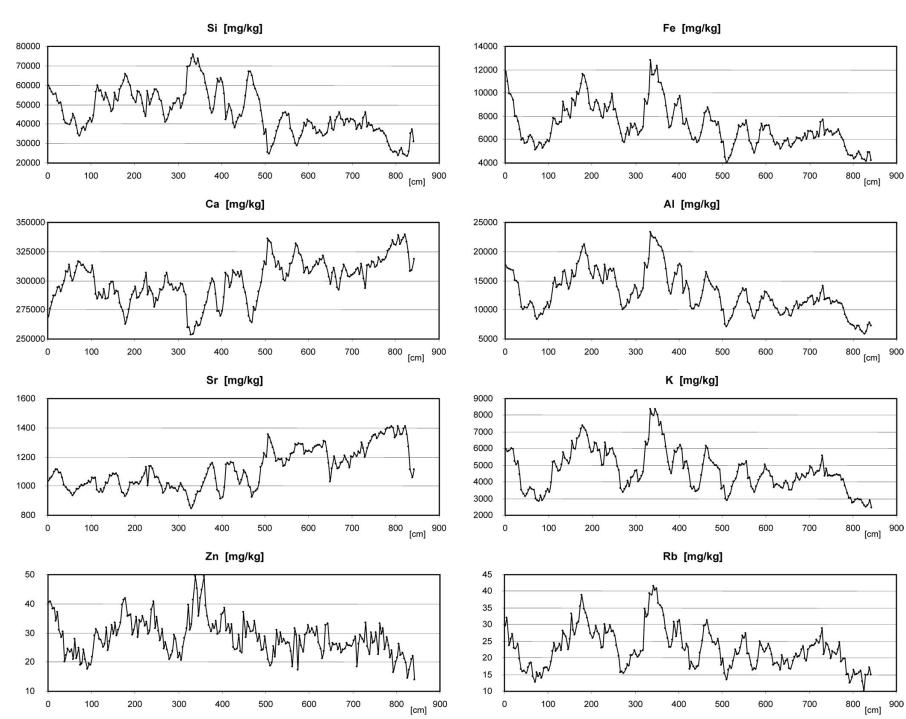


Figure 5: Analytical data from sediment core GeoB 8307-6

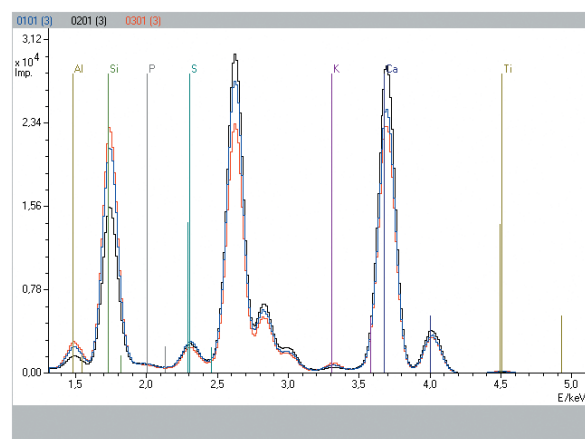


Figure 3: Typical spectra from various samples using HOPG crystal excitation

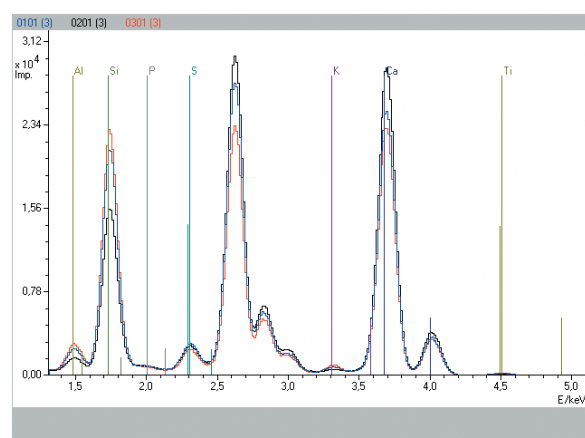


Figure 2: Typical spectra from various samples using Mo target excitation

standard measurements and by the values measured for two sediment corers that were investigated (Figures 4 and 5). The elements Fe, Al, Si, Ca, K, S, Sr, Br and Rb have the smallest relative standard deviation. Their curves, correspondingly, are found to be smooth. Less stable, but nevertheless meaningful, are the graphs for the elements Zn, Mg, Ti, Mn, Ba and Cl. Noise is noticed in particular when an element is only present in low but constant concentrations in the sediment, such as in the case of Mn.

Discussion

The distribution of the various elements in a sediment core provides information about climatic and environmental conditions and their changes in the geological past. This can be explained briefly, taking core GeoB 8301-6 as an example. The core contains sediments from the last 250,000 years, a period over which cold and warm periods have alternated several times. The concentration profiles of the various elements allow conclusions as to the origin of the deposits to be drawn. The correlation of the curves for Si, Fe, Al, K, Zn and Rb can easily be seen. These elements are of terrestrial origin, which means that they originate from the rocks of the neighboring African continent, and were carried into the ocean by rivers or by wind. The curve for Ca, in contrast, is inverted. Ca is a marine element, originating primarily from the shells of a variety of marine organisms, some of which, such as stromboid conches or foraminifera, are found in the water above. Part of the explanation for the inverted form of the curves is that if a large quantity of weathered continental material flows into the sea, the Ca is diluted, weakening the marine signal. On the other hand, a high multiplication of the marine organisms can enrich the Ca content, thus suppressing the terrestrial signal. If Si is compared closely with the other terrigenous elements it can be seen that the curves deviate from each other to some extent. Si also has a marine signature superimposed upon it, probably originating from diatomic organisms. A Si peak at a depth of 8.5 m is particularly clear, presumably indicating a full layer of diatoms. The elements mentioned here therefore reflect the conditions applying during the warm and cold periods and during the transition phases.

Summary

Energy-dispersive X-ray fluorescence analysis embodied in a compact, high-resolution analytical system makes it possible to carry out geochemical investigations of marine sediments immediately on

board a research ship. The preparation and analysis of approximately 200 samples from a sediment core can be carried out within 24 hours, and the concentrations of 15 elements recorded quasi simultaneously. The SPECTRO XEPOS analytical system used has now proven itself, over a total of 11 weeks on three research trips, to be reliable and suited to work at sea. It has, for instance, been used under rough conditions such as wind force 8 and in seas with a 3 to 4 m swell.

The on-board evaluation of the geochemical analyses makes it possible to optimize strategies for measuring and extracting samples from the seabed, and to extend them in order to be able to obtain the most precise possible information about the area under investigation.

Thanks

We wish to thank Karsten Enneking, Silvana Hessler, Luzie Schnieders and Rainer Zahn most sincerely for their support in the laboratory work on the research ship METEOR during trip M 57-1. We must also thank Ralph Schneider from the University of Bremen who, as expedition leader, saw to it that this part of the trip was organized and executed to perfection. This research project was supported by the Deutsche Forschungsgemeinschaft (German Research Community) operating through the Forschungszentrums Ozeanränder (RCOM - Research Center Ocean Margins) at the University of Bremen.

Author Details

Katharina Wien¹, Prof. Dr. Horst D. Schulz¹,
Martin Kölling¹, Dirk Wissmann²
¹ University of Bremen, FB 5 Geowissenschaften
(Geological Sciences), Bremen
² SPECTRO Analytical
Instruments GmbH & Co. KG, Kleve, Germany

Tel: + 49 2821 8 92-2102

Fax: + 49 2821 8 92-2202

info@spectro.com, www.spectro.com