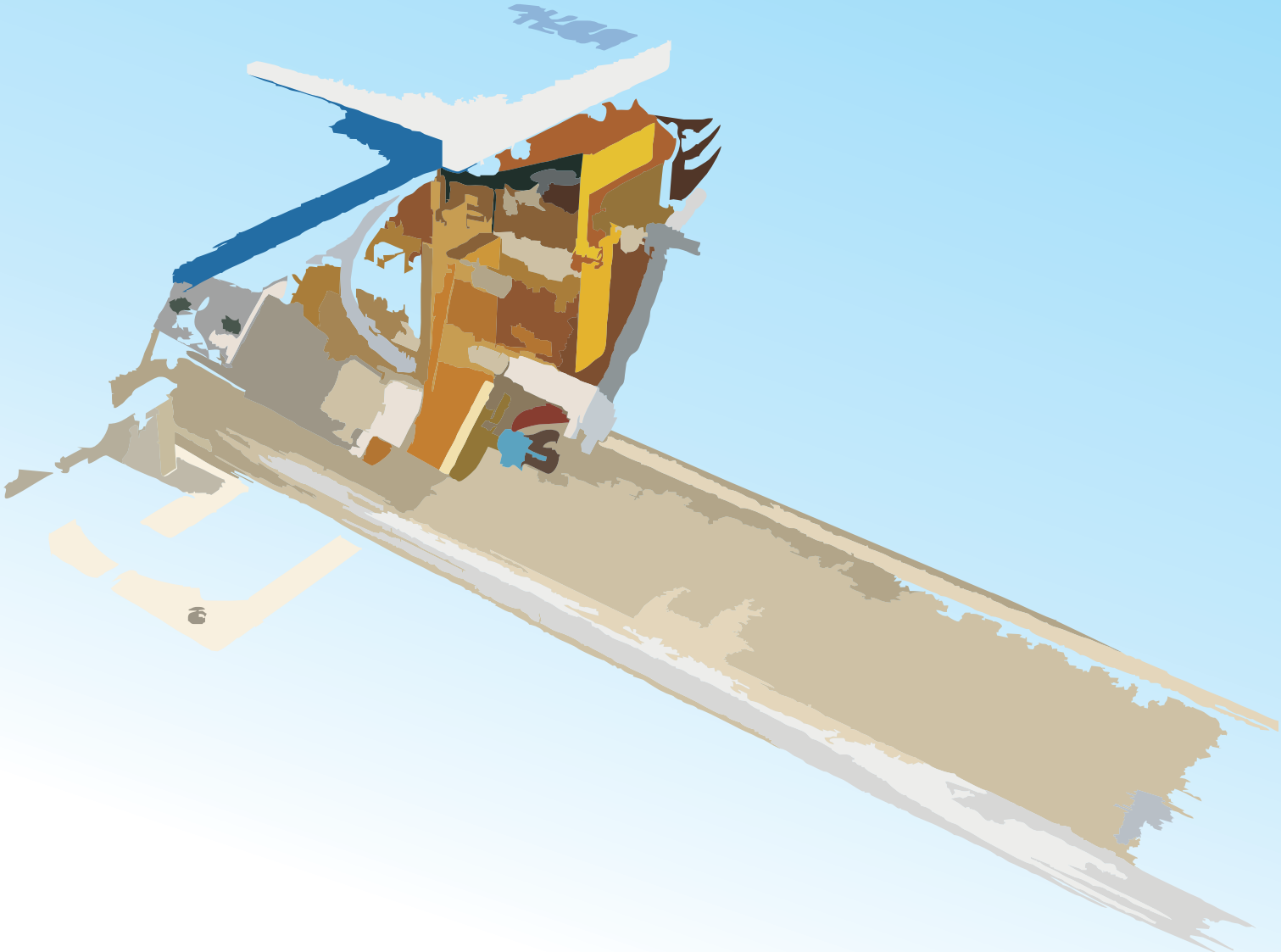
XRF core scanning workshop

8 - 10 September 2010

Royal NIOZ, Texel - The Netherlands

Program



We thank our sponsors

Welcome on Texel at the 2010 XRF workshop!

We are glad there is such a large interest for this first workshop on XRF core scanning. Evidently, with a growing number of XRF core scanning labs and users, also the interest in sharing and exchanging knowledge and experience increases.

The aim is to share experience and have a relaxed forum of discussion on:

- Application and calibration of XRF data in geosciences
- Technical aspects and processing of XRF data
- Future developments of XRF core scanning

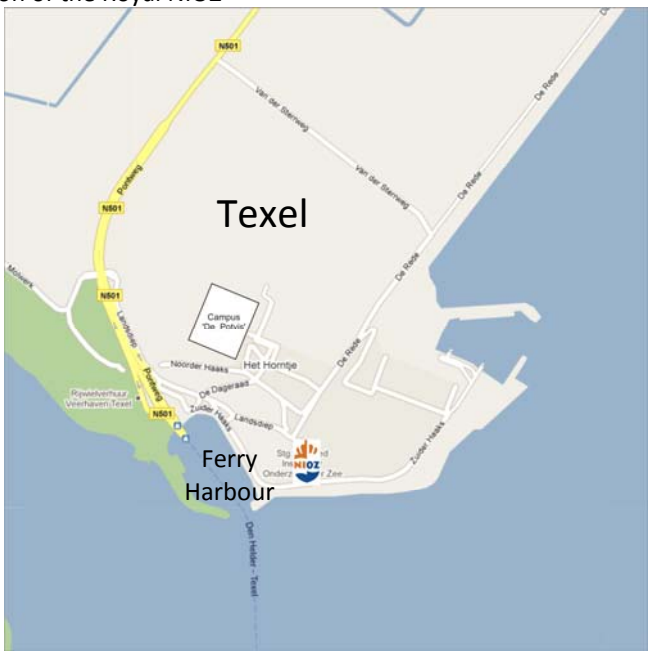
As such we tried to blend talks, posters and open discussions to provide and exchange information and address both general and individual questions of technicians and users of this method.

We like to thank the Royal NIOZ for hosting this workshop and offering us the opportunity to visit the research vessel *Pelagia* which just had its half-life overhaul. We thank all our sponsors that financed this workshop and took care of the social program for the evenings.

We hope you all enjoy the workshop,

Rik Tjallingii
Yvonne Hamann
Dieter Garbe-Schönberg
Isabelle Billy

Location of the Royal NIOZ



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PROGRAM XRF WORKSHOP 2010

Wednesday 08.09.2010

Application of XRF data

09:00 Coffee & registration

09:30 Opening & welcome

10:00 XRF Core Scanning for unlocking fine-scale paleoceanography: Detailed insights from more than 12 years of experience at the University of Bremen
Ursula Röhl, Thomas Westerhold, Vera Lukies, Heike Pfletschinger (MARUM, Bremen, Germany)

11:00 ***Break***

11:30 Comparing data by XRF-scan and data from individual samples by ICPAES/XRF of the same sediment intervals
Gert de Lange (UU, Utrecht, NL)

Lunch

13:30 Sedimentary geochemistry of the Chilean fjords: Spatial variability and potential to reconstruct Holocene climate and environmental change
Sebastien Bertrand (AWI, Bremerhaven, Germany)

14:15 Variability in the oxygen minimum zone of the Northeastern Pacific over the past 70 kyr inferred from high-resolution XRF measurements: Comparing XRF scanners
Olivier Cartapanis (CEREGE, Aix en Provence, France)

15:00 ***Break***

15:30 Physical parameters and XRF core scanning
Rik Tjallingii (Royal NIOZ, Texel, The Netherlands)

16:00 Semi-automatic log-ratio calibration of XRF core-scanner data
Gert Jan Weltje (TU Delft, Delft, The Netherlands)

17:00 Poster discussions

18:00 **AVAATECH Ice Breaker**

Thursday 09.09.2010

Processing of XRF data

09:00 The Avaatech XRF core scanner
Bob Koster (AVAATECH/NIOZ, Texel, The Netherlands)

09:30 Overview of X-rays detectors. Advantages and disadvantages
Vincente Osorio (Canberra N.V, Antwerp, Belgium)

10:15 ***Break***

10:45 Advantages of DSP-based instrumentation
Vincente Osorio (Canberra N.V, Antwerp, Belgium)

11:30 NAxil: New Spectrum Analysis Features
Piet van Espen (University of Antwerp/MIT, Antwerp/Boston, Belgium/USA)

Lunch

13:30 Discussion on WinAxil operations and data processing problems
Ursula Röhl, Thomas Westerhold, Vera Lukies, Heike Pfletschinger (MARUM, Bremen, Germany)
Piet van Espen (University of Antwerp/ MIT, Antwerp/Boston, Belgium/USA)
Vincente Osorio (Canberra N.V, Antwerp, Belgium)
Sjerry van der Gaast (AVAATECH, Texel, The Netherlands)

15:00 ***Break***

15:30 Open discussion on calibration of X-ray Fluorescence data
Piet van Espen (University of Antwerp/MIT, Antwerp/Boston, Belgium/USA)
Gert Jan Weltje (TU Delft, Delft, The Netherlands)
Sjerry van der Gaast (AVAATECH, Texel, The Netherlands)

17:00 Visit to the renovated research vessel Pelagia in NIOZ Harbor

18:00 Canberra Dinner

Friday 10.09.2010

Complementary Tools & Technical Aspects

09:00 Laser Ablation-ICP-MS: Extending XRF scanner data to trace elements
Dieter Garbe-Schönberg (CAU Kiel, Kiel, Germany)

09:30 River runoff reconstructions from novel spectral luminescence scanning of massive coral skeletons
Craig Grove (Royal NIOZ, Texel, The Netherlands)

10:00 Combining Magnetic Susceptibility and XRF measurements: A tool for paleo-environmental reconstructions
Cecile Blanchet (IFM-GeoMar, Kiel, Germany)

10:30 ***Break***

11:00 Technical hour with Avaatech
Aad Vaars, Bob Koster, Sjerry van der Gaast (AVAATECH, Texel, The Netherlands)

12:00 ***Lunch***

- NIOZ Colloquium -

13:15 El Nino, Climate and Societies
Gerald Haug (ETH Zürich, Zürich, Switzerland)

14:00 ***Break***

14:30 Summary and closing of the 2010 XRF workshop

Participants

Aad Vaars
Sjerry van der Gaast
Bob Koster

Danny Meert
Vincente Osorio
Piet van Espen

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Yvonne Hamann	ETH Zürich, Switzerland

ABSTRACTS ORAL PRESENTATIONS Wednesday 08-09-2010

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Sebastien Bertand	AWI Bremerhaven, Germany /WHOI, USA / Gent University, Belgium
Olivier Cartapanis	CEREGE Université d' Aix en Provence, France
Rik Tjallingii	Royal NIOZ, The Netherlands
Gert Jan Weltje	Technical University Delft, The Netherlands

A comparison between traditional analytical techniques, XRF-core-scanning, and LA-ICP-MS for detecting paleoceanographically relevant signals in core sediments

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Traditional techniques to analyse core sediments in a relevant resolution for paleoclimate studies is not only time-consuming but also costly. XRF core scanning seems to be a competitive technique that might at least in part replace such effort, provided that reliable and reproducable data can be obtained. In our recent studies we have used the XRF-core scanner to compare cores within a region to assess the completeness of recovered sediments and the comparability of recovered intervals between cores, so as to make the best possible choice for advanced high-resolution studies. Excellent correlation was found between XRF-scans within one region but these results appeared to be different from published data, mostly coincident with our own ICP-AES data, but also in some intervals clearly different. Thus in this case XRFscan data are 'reproducable' within even a region, but for some intervals inconsistent with 'real' data for as yet unknown reasons. It is important to know the backgrounds for such deviation so as to advance the capabilities for XRF-scanning. A similar comparison was made for another region where XRFscan data could be compared with data done on discrete samples by XRF and ICPAES. Using Br as a tracer for marine organic matter worked very well for samples from cores taken in extremely different environments, the NW Indian Ocean and an eastern Mediterranean brine basin.

We also made a comparison between XRFscan, discrete-sample ICPAES and Laser Ablation-ICPMS on resin-embedded core-intervals and found the latter technique superior not only in the number of detectable, paleoceanographically relevant trace elements but also in the acquired resolution and consistent concentration levels.

Several examples will be shown to illustrate the points made above.

Sedimentary geochemistry of the chilean fjords: Spatial variability and potential to reconstruct Holocene climate and environmental change

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Reconstructing the nature, timing and amplitude of past climate and environmental changes at various locations across the globe is of primordial importance to constrain the physics of the climate system and to understand how the environment adapts to a rapidly changing climate. The mid- and high-latitudes of the Southern Hemisphere, however, remain relatively understudied. At these latitudes, the sediments deposited in the Chilean fjords are particularly promising because of their high accumulation rates and because of their potential to record changes in river discharge, which is linked to precipitation and glacier melting in the Andes. Here, we investigate the sedimentary geochemistry of the Chilean fjords to assess (1) the parameters that control sediment geochemistry in the fjords, and (2) their potential to reconstruct Holocene precipitation and glacier variability in the southern Andes.

Our results are based on a geochemical, mineralogical and sedimentological analysis of a series of surface sediment samples from the fjords of Northern Chilean Patagonia (44-47°S). Our data demonstrate that, under the cold climate conditions of Patagonia, chemical weathering is weak and inorganic geochemistry of the fjord sediments is primarily controlled by hydrodynamic mineralogical sorting. The distribution of Fe, Ti and Zr is linked to their association with heavy and/or coarse minerals. Our data also provide evidence that Al is independent of hydrodynamic processes. Its concentration reflects the proportion of lithogenic particles, which supports the common practice of normalizing other lithophile elements by Al in view of assessing changes in the composition of the lithogenic fraction. The elemental ratios Fe/Al, Ti/Al and Zr/Al are therefore well suited for estimating changes in the energy of terrestrial sediment supply into the fjords through time. Zr/Al and Ti/Al are particularly sensitive in proximal environments, while Fe/Al is most useful in outer fjord and continental margin basins. In the most proximal environments, however, Fe/Al is inversely related to hydrodynamic conditions. Caution should therefore be exercised when interpreting Fe/Al data in terms of past river discharge.

Application of these proxies to two sediment cores will be presented:

(1) Sediment core JPC14 was collected in a proximal glacio-marine environment. It is located a few kilometers off the current ice front of Gualas glacier, which is one of the northernmost outlet glaciers of the Northern Patagonian Ice Field. Variations in Zr/Al in core JPC14 (15 m long, 46°S) faithfully reflect changes in sediment grain-size. Since the biogenic and organic content of the sediment is negligible, Al concentrations do not vary downcore and Zr concentrations can be directly interpreted as changes in hydrodynamic conditions associated with advances/retreat of Gualas glacier.

(2) Sediment core PC29A (2m long) is from Quitralco fjord (45°S). It was collected in front of a river that drains a non-glaciated region. It is therefore particularly sensitive to changes in precipitation. At this inner fjord site, increases in Fe/Al and Ti/Al mark a significant decrease in sediment grain-size, which is interpreted as a decrease in the energy of river discharge. This interpretation is supported by synchronous changes in SST, which were likely caused by a reorganization of the zonal systems, i.e., the Southern **Westerlies** and the Antarctic Circumpolar Current.

Variability in the oxygen minimum zone in the North-eastern Pacific over the past 70 kyr inferred from high-resolution XRF measurements

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This contribution focuses on analytical consideration using XRF core scanners for paleoceanography and paleoclimatology reconstruction. We first compare measurements of major elements performed with 2 different-types of core scanners (CORTEX & ITRAX) on the same marine sediment core from the Western Pacific Warm Pool, highlighting the importance of sediment surface condition for optimizing XRF measurements. Then, we apply XRF technique to a well-dated core MD02-2508 (606m water depth) retrieved off Baja California at the northern limit of the present Oxygen Minimum Zone (OMZ) in the northeastern Pacific. Marine sediment cores from OMZ are characterized by striking change in major component proportion (organic, terrigenous and carbonates fractions) and redox sensitive trace element concentrations on millennial timescales. This variability is related to Greenland air temperature during the last glacial period: Dansgaard-Oeschger (DO) and Heinrich (H) events. This study aims at evaluating how high-resolution XRF measurements contribute to better understanding low and high latitude climate linkage. We performed high-resolution elemental analyses (5 mm to 500 µm corresponding to decadal time resolution) of Ca, Sr, Ti, Fe, Mn, Cl and Br using the ITRAX core scanner. This approach is combined with redox sensitive trace element and major element analysis by ICP-MS (10 to 20 cm corresponding roughly to 500 years resolution) and CNS analyzer (Total Organic Carbon (TOC) and carbonates).

MD02-2508 core is characterized by nearly equivalent proportion for the three major components of the sediment: terrigenous fraction corresponds to 30-50% of the sediment, carbonates ranges between 15% and 40%, and TOC ranges between 4% and 15% (corresponding roughly to 10 to 40% of organic matter). Since Br XRF intensity is well correlated to TOC (R^2=0.85), and Br/Cl ratio correlates with Br counts (Cl is indicator of pore water content), the Br record of core MD02-2508 is linked to TOC rather than pore water content. The intensity ratio of Compton (incoherent) and Rayleigh (coherent) scatter (Inc/Coh) obtained by XRF measurements shows similar variability to Br counts with higher values in organic-rich laminated layers. This ratio represents variations of relative proportion of light to heavy elements, thus semi quantitative indicator of organic matter. Calcium counts are linearly correlated to biogenic CaCO3 whereas terrigenous matter can be traced by Ti. High resolution Br variability in core MD02-2508 is similar to the oxygen isotopic composition in Greenland ice core over the last 70 kyr, attesting the tight relationship between high and mid latitude climate on millennial timescale. Moreover, high Fe/Ti ratio based on XRF measurements is consistent with increase in trace element concentrations (ex. Cd, Mo, U, As) during Holocene and DO warm events whereas carbonates (Ca and Sr) and terrigenous matter (Ti) are high during the last glacial maximum (LGM) and H events. An excellent agreement between Fe/Ti (XRF) and the trace elements suggests that millennial scale variability of redox properties is captured by the high-resolution measurements.

Physical parameters and XRF core scanning

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XRF core scanning allows non-destructive, fast and near-continuous analyses of the sediment compositions that can be explained by paleoceanographic and paleoclimatic changes. Element compositions acquired by XRF core scanners are expressed as element intensities reflect its chemical concentration, but are biased by physical parameters (e.g. grain-size, density, water content) and matrix absorption and enhancement effects. XRF core scanning of a split core surface and equivalent discrete dry powder samples reveals that especially lighter elements, such as Al and Si, are susceptible physical properties.

XRF core scanning data only measures a distinct amount of elements are measured depending of the settings (e.g. 10, 30 or 50 kV) which represent only a part of the total composition. As all compositional data sets, the measured element intensities are affected by dilution effects that can potentially result from elements that are not present in the analyzed elemental spectrum.

Ratios and log-ratios are a very simple and effective way to minimize the effects of physical properties and closed-sum dilution effects. The additional advantage of log-ratios over ratios is the fact that these are symmetrical and therefore better suited for the application of goodness-of fit statistics.

Semi-automatic log-ratio calibration of XRF core-scanner data

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On-line analysis of split sediment cores by XRF core scanners allows non-destructive extraction of near-continuous records of element intensities from sediment cores with a minimum of analytical effort. A disadvantage of XRF core scanning relative to conventional geochemical analysis is the problematic conversion of core-scanner output to element concentrations. The main reason for this long-standing problem is the poorly constrained measurement geometry, attributable to inhomogeneity of the specimens (e.g. variable water content and grain-size distribution), irregularities of the split core surface, and in some setups, spatial variations in thickness of an adhesive pore-water film which forms directly below a protective foil covering the core surface.

We developed a log-ratio calibration equation (LRCE) for XRF core scanners based on elementary XRF spectrometry theory and empirical evidence. In addition, estimation of quantitative bulk chemistry by means of the LRCE is fully consistent with the statistical theory of compositional data analysis. The LRCE provides accurate and precise predictions of sediment composition (element concentrations) from XRF core-scanner output with a limited number of parameters, namely $2(D-1)$, where D equals the number of chemical elements to be estimated. The model can accommodate the inherent non-linearity of the relation between (relative) intensities and concentrations, which is apparent from the fact that it provides unbiased estimates.

The relative error (precision) of predicted element concentrations obtained with the LRCE is in the same range as conventional destructive XRF analyses of complex mixtures of elements. Stochastic simulations indicate that this level of precision can be attained with ~40 randomly selected calibration specimens. An algorithm for automatic selection of calibration samples provides results of the same quality with less than half the number of calibration samples, which reduces analytical costs and damage to the core. If automatic sample selection is combined with multivariate filtering algorithms, a significant reduction of the uncertainty associated with the estimated bulk chemistry may be achieved. Current work is aimed at:

1) improving the error model, in order to develop XRF core scanning into a statistically rigorous semi-automatic measurement technology;
2) modifying the LRCE for inter-laboratory and inter-instrument calibration.

Log-ratios of element intensities, which are related to log-ratios of element abundances by a simple linear transformation, provide the only easily interpretable signals of changes in chemical composition. Consistent use of log-ratios of element intensities or concentrations will minimize the risk of drawing erroneous conclusions from geochemical proxies. In practice, calibration is only needed in cases where quantitative estimates of bulk chemistry are required. XRF-core scanning in fully non-destructive mode (without calibration) is sufficient for most studies in which use is made of geochemical proxies for the purpose of correlation and qualitative palaeoclimate reconstructions.

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Laser Ablation-ICP-MS: Extending XRF scanner data to trace elements

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In situ major and minor element compositional data for sediment cores as obtained from a XRF core scanner gives the general picture on the depositional environment and variation of sedimentation styles over time. A lot of additional information, however, can be extracted from the distribution of trace elements in the sediment core allowing more detailed insights into paleo-primary production (Ba, Cd etc.), origin of the sedimented material and minerals (Cr, Ni, REE, Th, U/Pb, Zr/Hf etc.), redox conditions during deposition and diagenesis (Fe, Mn, Mo, U, Re etc.), individual phases of carbonate cementation, past SST and salinity during growth of biogenic carbonate (Sr/Ca, Mg/Ca, Ba/Ca, $\delta^{11}B$), and so on. For this, small sections of bulk sediment, individual biogenic tests, single mineral grains etc. can be analysed by modern *in situ* micro-analytical techniques like electron micro probe (EMP), proton induced x-ray emission (PIXE), synchroton radiation-µXRF (SR-µXRF), secondary ion mass spectrometry (SIMS), and laser ablation ICP-mass spectrometry (LA-ICP-MS).

Shortly after the introduction of the first commercial ICP-MS instrument in 1983, the first paper reporting the use of a solid-state laser for the direct microanalysis of solid samples was published by Gray (1985). Since those days, LA-ICP-MS has been continuously improved providing fast and accurate multi-element analyses with detection limits in the (sub-) ppb range, 100µm to sub-µm spatial resolution, and significant reduction of interferences from elemental fractionation and overlap of polyatomic ions. Today, LA-ICP-MS has become a standard tool in geochemistry.

In LA-ICP-MS, a pulsed laser beam is focused onto the surface of a solid sample contained in an air-tight ablation cell. The very high energy in the focal spot of the beam vaporizes the sample generating a particulate aerosol that is transported by a carrier gas into the hot plasma of the ICP, and ionized. Ions are extracted from the ICP into the mass spectrometer and analysed according to their mass-to-charge ratio. In most configurations, the sample is positioned on a motorized x,y,z-stage and can be observed by means of a microscope or video camera.

This short presentation introduces into fundamentals and basic operation principles of both parts the ICP-mass spectrometer and the laser ablation unit for the generation of particle aerosols, discusses some strengths and current weaknesses of the technique, and illustrates the wide field of applications in geochemistry with a few examples from own work in Kiel.

River runoff reconstructions from novel spectral luminescence scanning of massive coral skeletons

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Inshore massive corals often display bright luminescent lines that have been linked to river flood plumes into coastal catchments and hence have the potential to provide a long-term record of hinterland precipitation. Coral luminescence is thought to result from the incorporation of soil-derived humic acids transported to the reef during major flood events. Corals far from terrestrial sources generally only exhibit dull relatively broad luminescence bands, which are attributed to seasonal changes in coral density. We therefore tested the hypothesis that spectral ratios rather than conventional luminescence intensity provides a quantitative proxy record of river runoff without the confounding effects of seasonal density changes. For this purpose we have developed a new, rapid spectral luminescence scanning (SLS) technique that splits emission intensities into Red, Green and Blue domains (RGB) for entire cores with an unprecedented linear resolution of 71.4µm. Since humic acids have longer emission wavelength than the coral aragonite, normalisation of spectral emissions should yield a sensitive optical humic acid/aragonite ratio for humic acid runoff, i.e. G/B ratio. Indeed G/B-ratios rather than intensities are well correlated with Ba/Ca, a geochemical coral proxy for sediment runoff, and with rainfall data, as exemplified for coral records from Madagascar. Coral cores also display recent declining trends in luminescence intensity, which are also reported in corals elsewhere. Such trends appear to be associated with a modern decline in skeletal densities. By contrast, G/B spectral ratios not only mark the impact of individual cyclones but also imply that humic acid runoff increased in Madagascar over the past few decades while coral skeletal densities decreased. Consequently, the SLS technique deconvolves the long-term interplay between humic acid incorporation and coral density that have confounded earlier attempts to use luminescence intensities as a proxy for river runoff.

Combining Magnetic Susceptibility and XRF measurements: A tool for paleo-environmental reconstructions

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Magnetic susceptibility (MS) is widely used to monitor sedimentological changes along freshly-cored sediments. Indeed, it is often one of the first parameters measured after core recovery, especially when using the Geotek™ core logger as a shipboard equipment. Down core profiles of MS are for instance used to obtain regional correlations of sedimentary sequences. However, if changes in MS are driven by variations in terrigenous content and origin in many sedimentary settings, it has also been shown that diagenetic processes can largely overprint the magnetic signal.

MS and XRF measurements are both rapid and non-destructive logging methods, which provide information about down core mineralogical and elemental changes. Combining these two types of measurements could help deciphering sedimentologic features related to sediment origin and diagenetic processes.

After giving a physical definition of MS, I will review the influences of various minerals on the MS and the different types of magnetic behaviour. Then, the influences of grain-size variations and diagenetic processes, which lead to formation of authigenic phases, on MS will be examined. Finally, by showing a few examples, I will demonstrate the utility of combining XRF and MS measurements in order to reconstruct past sedimentary dynamics and paleo-environmental changes.

El Nino, Climate and Societies

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A unifying theme in paleoclimate research is well summarized by a piece of advice that I once heard the late Sir Nicolas Shackleton give to an audience of paleoceanographers: "Whatever you do, do it in high resolution." The underlying message, I believe, is that much 'noise' in geologic records is actually composed of meaningful environmental signals. A central goal is to use new approaches and techniques that do justice to the complexity of geologic records, in order to allow previously hidden signals to emerge.

On the millennial to subdecadal timescale, climate archives with an appropriate memory are anoxic marine basins and lakes. In the anoxic Cariaco Basin off northern Venezuela, millimeter to micrometer-scale geochemical data in the laminated sediments of the Cariaco Basin have been interpreted to reflect variations in the hydrological cycle and the mean annual position of the Intertropical Convergence Zone (ITCZ) over tropical South America during the past millennia. These data with decadal to (sub)annual resolution show that the Terminal Collapse of the Classic Maya civilization occurred during an extended dry period from 700 to 900 AD. Data of comparable quality and resolution have been extracted from sediments of lake Huguang Maar in coastal southeast China. The record indicates a stronger winter monsoon prior to the Bølling Allerød warming, during the Younger Dryas, and during the middle and late Holocene, when cave stalagmite oxygen isotope data indicate a weaker summer monsoon. A remarkable similarity in the records of ITCZ migration in east Asia and the Americas from 700 to 900 AD raises the possibility that the coincident declines of the Tang Dynasty in China and the Classic Maya in Central America were catalyzed by the same ITCZ migrations. Comparison of our records with the Chinese dynastic history suggests that drought played a role in the terminations of Dynasties during the past 4000 years.

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Paleohydrological and limnological signatures in small karst lakes based on XRF analyses: La Parra Lake (Cuenca, Spain)

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We analyze the hydrological and geochemical response of La Parra karst lake (Iberian Range, NE Spain) to anthropogenic and climate forcing for the last 4000 years. We use a multidisciplinary approach to study at watershed and lake scales, the modern and past depositional processes and to evaluate their interactions with various environmental controls (climate and human impact) at different time scales. To achieve these goals, we need a better understanding of depositional processes in karst lake systems, particularly sedimentological, geochemical and limnological as depositional processes, carbonate formation, clastic input, meromixis evolution, and paleohydrology.

La Parra Lake is a circular sinkhole, of 17.5m depth and 111-116m diameter, located in a karst region of the Iberian Ranges, central-eastern Spain (UTM30596745, 4426442). The doline in which the lake developed in a dolomite formation that overlaying impermeable Middle-Upper-Cenomanian green clay-marls. The climate is Mediterranean and the hydrology is controlled by groundwater sources with very limited surface runoff. The lake level fluctuates significantly in response to changing aquifer fluxes and agricultural extraction wells around the area.

In May 2010, two sediment cores (up to 6.93m (A) and 5,24m (B)) long were recovered from La Parra Lake from the deepest part of the lake (17.5m) using a UWITEC corer installed in a UWITEC platform raft. Four short cores were also retrieved to preserve the topmost sediment (water-sediment interface). The sections were split longitudinally and imaged using a digital photographic camera. XRF (X-Ray Fluorescence) analyses were performed using the Avaatech core scanner located at the Department of Marine Geosciences of the University of Barcelona (UB). Both cores were measured in two runs at 10kV (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Rh, Ag) and second at 30kV (Ni, Cu, Zn, Ga, Ge, As, Br, Rb, Sr, Y, Zr, Pb) with a 5mm sampling resolution.

XRF analyses have provided high resolution reconstructions of past global and climate changes in karst lakes like Laguna Taravilla (Moreno et al., 2008) and Laguna Estanya (Morellón et al., 2008). At Lake La Parra, we use XRF core scanning to study:

1) ***Clastic input***. Increased human impact in the watersheds during the last millennia and short term flooding events can be identified using a number of geochemical indicators. Carbonate deposition in these karst lakes includes exogenic (clastic) and endogenic (authigenic) minerals and the identification of these mineral phases is not always a simple task. We are trying to use some geochemical ratios to distinguish between lacustrine and exogenic carbonates on a karst area. For example, the Ca/Sr since Sr is usually higher in lacustrine carbonates formed under relatively higher chemical concentration (magnesium-rich calcite and aragonite). However the presence of dolomite in the watersheds may pose a problem to this approach. Evolution of REDOX stages at the bottom of the lake, with fluctuating periods of water stratification, anoxia and reducing conditions and holomixis and oxic conditions. Commonly we focused on Fe/Mn ratio, but we also investigate other relations, like Fe/S or Fe/Ti.

2) ***Organic productivity***. In some cases, the amount of organic matter in the sediments could be a proxy for organic productivity. The incoherence/coherence radiation index provided by some XRF core scanners (Moreno et al., 2007; Sáez et al., 2009) is a valuable indicator. Phosphorous values are usually low and it is not clear the relationship between detrital P and organic productivity. On the other hand, the signal of biogenic and detrital silica is difficult to differentiate. We are using Si/Ti ratio, assuming Ti comes from external contributions only.

XRF analyses provide high-resolution data series, but they have to be integrated with sedimentological, compositional and mineralogical data to better define the involved lake processes and thus provide the basis for the reconstruction of climate change and anthropogenic impact on lake systems.

References

Moreno et al., "A 14kyr record of the tropical Andes: The Lago Chungará sequence (18°S, northern Chilean Altiplano)," *Quaternary International* 161, no. 1 (2, 2007): 4-21.

Moreno et al., "Flood response to rainfall variability during the last 2000 years inferred from the Taravilla Lake record (Central Iberian Range, Spain)," *Journal of Paleolimnology* 40, no. 3 (4, 2008): 943-961.

Morellón et al., "Holocene palaeohydrology and climate variability in northeastern Spain: The sedimentary record of Lake Estanya (Pre-Pyrenean range)," *Quaternary International* 181, no. 1 (2008): 15–31.

Sáez et al., "Glacial to Holocene climate changes in the SE Pacific. The Raraku Lake sedimentary record (Easter Island, 27°S)," *Quaternary Science Reviews* 28, no. 25-26 (12, 2009): 2743-2759.

Richter et al., "The Avaatech XRF Core Scanner: technical description and applications to NE Atlantic sediments," *Geological Society, London, Special Publications* 267, no. 1 (1, 2006): 39-50.

A multi-proxy approach to assess oceanographic variability in the Southern Gulf of Cadiz during the last glacial cycle

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A multi-proxy approach, based on a combination of Avaatech X-ray core scanner-data (Fe/Al, K/Al, and Ca/Fe), grain-size distribution (mean grain size, sorting, skewness, and kurtosis), stable isotope data ($\delta^{18}O$ and $\delta^{13}C$) and lipid biomarkers (the archaeal glycerol dialkyl glycerol tetraether index (TEX_{86}), $U^{K'}_{37}$ and the **branched** and **isoprenoid** tetraethers (**BIT**)) was applied to reconstruct environmental changes in the Gulf of Cadiz over the past 150 ky. We used undisturbed sediments (MD08-3227) from the Pen Duick Escarpment area, offshore Morocco, collected with the French R/V *Marion Dufresne* during the 2008 MiCROSYSTEMS cruise.

A strong correlation between hematite sourced Fe/Al and grain-size related Ti/Al and Zr/Al values suggests a common forcing by the influx of Saharan dust particles. The mean grain size data are also in a good agreement with these ratios as shown by a record-to-record correlation. The K/Al ratio, possibly revealing fluvial dynamics, was tested against the molecular BIT-index, a proxy for soil organic matter input in the ocean. The anticorrelation between these parameters is weak, but present. This weak correlation is not unexpected, as the mechanism behind K/Al is more related to the continental humidity while the BIT-index rather is a proxy for the total volume of fluvial input. However, Fe/Al and K/Al also correlate strongly. Possibly the anti-correlation between the BIT and K/Al proxy is thus solely caused by a correlation between the BIT and Fe/Al proxy.

The results obtained are in good agreement with earlier published studies describing the north-west African upwelling and trade winds-system (e.g. Lezine and Casanova, 1991).

The sea surface temperature (SST) records based on TEX_{86} and $U^{K'}_{37}$ indices show a good correlation with only a minor offset in absolute SST. This offset became more pronounced during colder periods, i.e. MIS2, MIS4, MIS5b and MIS5d. Furthermore, the $U^{K'}_{37}$-based signal shows distinct drops in MIS3 that are not seen in the TEX_{86} record. Changing water properties can be the cause of this offset, affecting the effective niche of these species. The trends observed can for instance be caused by upwelling. We will therefore try to reconstruct the intensity of upwelling using XRF-data. As siliceous organisms are upwelling indicators, the presence of biogenic silica (opal) could give an indication when more extensive upwelling occurred. In absence of opal and without differences in grainsizes, the sedimentary Si and Al content will covary downcore. In case grainsizes differ downcore Si and Al will not covary, but Si/Al and other grain-size related Ti/Al and Zr/Al will still covary. The offset observed between Si/Al and these other proxies can thus possibly be interpreted as the presence of opal in the sediments.

Until this is groundtruthed, for instance by direct measurements of the opal content, other explanations regarding this offset should be considered. Affecting the sedimentary composition could be changing sources of terrigenous material, affecting aeolian and/or fluvial input, next to fluctuations in Si-saturation of the prevailing ocean waters. Downcore differences in XRF core scanner sensitivity could be accounted for the offset as well.

References

Lezine, A. M. and Casanova, J. (1991) 'Correlated oceanic and continental records demonstrate past climate and hydrology of North-Africa (0-140 ka)', *Geology,* 19(4), 307-310.

Data analysis and reduction in XRF

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The capacity for generating very large quantities of high resolution data is an outstanding strength of the XRF technique. The sheer volume of data generated does however pose its own challenges; how to identify the most relevant variables for a particular study, and what is the best way to represent both the variance that is unique to particular elements or elemental ratios, and the variance which is held in common with other groups of elements.

Ratios between elemental counts can provide a way of correcting some "disruptions" in the elemental composition of sedimentary sequences caused by - for example - the dilution of particular elements by a separately varying sedimentary component. Usually this approach is limited to analysing the ratios of elemental pairs, such as Calcium/Strontium. Would ratios of groups of elements provide additional useful information? What would be an objective procedure for identifying potentially relevant simple or complex ratios? What are the strengths and weaknesses of factor analyses, cluster analyses, factor rotations, and the use of covariation matrices? What are the most useful graphical representations of multivariate datasets over time/depth?

Given the number of multivariate techniques potentially at researchers' disposal, it would be useful to identify and focus development efforts on those methods most likely to highlight environmentally significant signals and this could also help to facilitate inter-laboratory collaboration.

Sedimentological study of cold-water coral mounds on Pen Duick Escarpment (Gulf of Cadiz): XRF results

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Cold-water corals are widely distributed along the Northeast Atlantic margin where they occur as patches and may even form reefs or mound structures. Within the Gulf of Cadiz mud volcanoes, submarine ridges and steep fault escarpments occur, which favour the settlement of scleractinians and facilitate the build up of coral mounds. One of these sites is the Pen Duick Escarpment, situated in the El Arraiche mud volcano field, 35 km offshore the city of Larache. Pen Duick Escarpment is a 6 km long, SSE-NNW oriented, 80 to 125 m high wall with a southwest-facing slope of 8 to 12°. Up to now, 15 coral mounds are indentified on top of the escarpment with an average estimated elevation of 15 m. Although cold-water corals are a common feature on the adjacent cliffs, mud volcanoes and seafloor, no actual living coral has been observed.

This study is based upon three on-mound gravity cores (Alpha, Beta and Gamma mound) acquired by R/V Marion Dufresne in 2008 (MD169). The major chemical element composition of each core was analysed using an AVAATECH X-ray Fluorescence (XRF) core scanner (Royal NIOZ). Although the results are promising, the interpretation is not straightforward since different processes, such as diagenetic interactions, terrigenous input and oceanic processes intervene with each other. Hence, a multidisciplinary approach, combining XRF with other techniques (CT-scanning, U/Th dating, stable isotopes, grain-size analysis) is necessary to disentangle the various signals recorded in these cores and obtain a holistic view on mound build-up.

ITCZ-monsoonal climate variability during the last 80'000 years (Cariaco Basin, Northern Arabian Sea)

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The anoxic Cariaco Basin on the northern shelf of Venezuela is a sensitive recorder of large and abrupt shifts in the hydrologic cycle of the tropical Atlantic. Sediments from the oxygen minimum zone off Pakistan in the Northern Arabian Sea represent archives of the low-latitude monsoonal climate variability.

Major element chemistry and color data have been measured on sediments from these two settings which cover the last 80'000 years with a centennial to annual resolution. Individual Dansgaard-Oeschger events can be well correlated between the two archives. An age model was set up by correlation to the δ18O record of NGRIP.

These data suggest a direct connection between the position of the ITCZ over northern South America, the strength of trade winds, and the temperature gradient to the high northern latitudes, ENSO, and monsoonal climate in Asia. The mechanisms behind these decadal-scale ITCZ-monsoon swings can be further explored at major climate events such as the Younger Dryas and the Dansgaard-Oeschger events. Recently published marine, lacustrine and ice core records are interpreted in concert with our new data from the Cariaco Basin and the Arabian Sea. They indicate major reorganizations of the atmosphere/ocean system in the entire Northern Hemisphere at these warming and cooling events. The warmings seem to occur in abrupt steps of a few years, the coolings more transitional within centuries, however, decadal scale steps are superimposed.

Creative scanning techniques as demanded by a wide variety of sample types used in multi-disciplinary research projects

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At Scripps Institution of Oceanography (SIO), there has been great interest in using the XRF for a wide variety of applications. As such, creativity has been employed to make for highly successful scans, but questions still remain. Here questions and successes are both highlighted. Regarding questions:

1) When looking at laminations, in an attempt to interpret monsoonal cycles, that are neither perfectly horizontal nor homogeneous, what is the best way to scan different cores from the same depth intervals?
2) Is it possible to fill porous samples, such as corals, with an epoxy and then back out the epoxy signal? And what is the best way to UV image corals?
3) What is the best way to scan an irregular, hard surface; mainly rocks?
4) What is the best way to monitor XRF stability over time and do changes in XRF stability overtime effect the ability to make reproducible data sets over longer periods of time?
5) Is it possible to scan plastic of different origins and see chemical differences between them?

In regards to a few of our successes:

1) Using modeling clay for filling gaps between core samples;
2) Finding variations in terrestrial inputs as a result of changes in climate cycles;
3) Using barium ratio profiles as a proxy for variations on export productivity at the K-Pg boundary;
4) Seeing great reproducibility between high resolution scans of the same core section and also seeing added peaks as the resolution is increased;
5) Using lightness data to see annual growth bands in tree cores.

As our students and scientists here at SIO move towards multi-disciplinary research interests, such as biogeochemistry, we are able to use the XRF in creative ways to scan a wide variety of samples to produce data that allows us to make connections between the disciplines and to tell a more fully developed story about the material being investigated.

XRD derived Geochemical Data from Cretaceous Oceanic Anoxic Event 1a

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Marls deposited during the Cretaceous Oceanic Anoxic Event 1a (OAE 1a) yield important information about the climatic conditions during Barremian/Aptian times. By investigating a 67 m long limestone core from the Bedoulian type locality at La Bédoule, Southern France, we want to retrieve data about the onset of anoxia and the boundary conditions (e.g. atmospheric CO_2 content, SST) during OAE 1a. Methods used are stable oxygen and carbon isotope analysis and XRF core scanning.

At the onset of OAE 1a, data indicates a negative double trough followed by a steep positive shift in $\delta^{13}C$. The duration of the negative carbon isotope excursion suggests that the event was induced by volcanic CO_2 emissions, rather than a methane release event. XRF core scanning data will allow us to trace elemental content changes during this event and reconstruct past climatic conditions, especially the input of terrestrial material/nutrients and the productivity, which are caused by a higher atmospheric CO_2. XRF data will also allow us to determine cyclicities, and based on time series analysis, to reconstruct the influence of orbital parameters on the elemental composition preserved in the limestone.

Investigating sediment core datasets through advanced visualization technology

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Technological innovations, such as the X-ray fluorescence (XRF) corescanner, have enabled geoscientists to generate increasingly large and complex datasets. Thus, it has become essential to develop efficient tools for combining and visualising these datasets. *CoreWall** was developed in the USA to address the specific needs of scientists generating high-resolution records from sediment, ice and rock cores. The *Corelyzer* software, which belongs to the larger suite of *CoreWall* tools, is well suited to displaying and annotating data outputs from the XRF corescanner.

Corelyzer integrates high-resolution core imagery with numerical core logging data, lithology diagrams, smear slides, thin sections and user-generated freeform or structured annotations. Using standard computer interfaces, users can pan through metres of high-resolution core imagery and data, annotating along the length of the core itself, and the integrated zoom function of high-resolution core images allows detailed investigation of the core under even illumination. In summary, *CoreWall* provides a powerful tool for combining core images and other data. Here, I will demonstrate the utility and easy-use of this software using an integrated data suite including micro-XRF, optical images, x-radiographs, magnetic susceptibility and colour reflectance generated from a marine sediment core taken from the Agadir Basin.

*CoreWall was developed through collaboration between the US National Lacustrine Core Repository at the University of Minnesota, the Electronic Visualisation Laboratory, University of Illinois-Chicago, and the Integratedl Ocean Drilling Program (IODP) and is funded by the US National Science Foundation. It can be downloaded, free-of-charge, from www.corewall.org.
More information on the software and its applications can also be found on the website.

Hunting for Heinrich Events

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Occasional large breakouts of icebergs from the Laurentide Ice Sheet into the North Atlantic during the last glacial (between approximately 11-70 kyr BP) are known as Heinrich events (Broecker et al., 1992), and are marked in the geological record by the presence or Ice Rafted Debris (IRD) which consists of dropstones, often greater than 125 microns in diameter, released from melting icebergs. The lithology of the dropstones can indicate the provenance of the material entrained in the icebergs.

Heinrich events have been shown to be detectable in marine sediment records analysed at high resolution by XRF (eg. Hodell et al. 2008), a study which also showed that Heinrich-like events could be identified in earlier glacial episodes, back to about 640 ka BP. However, a detailed spatial tracking of the distribution of IRD layers and the identification of related Heinrich (like) events in older geological deposits remains a key objective of future research. In order to facilitate such studies, it would be helpful to develop a procedure to swiftly identify Heinrich-like events in marine cores from a variety of settings.

We have looked at a suite of ratios using factor analysis to attempt to identify the key ratios signalling Heinrich-like events. Using lithological counts to ground-truth the analysis, we have sought to identify element pairs with ratios that strongly respond to the presence of IRD, so that these pairs can be systematically investigated in other cores for which no lithological counts have been made.

Key questions are: is factor analysis the best way to identify the relevant variables? Is the factor that shows the Heinrich events strongly likely to be a climate-related dimension, and thus strongly "contaminated" by the local or global Milankovitch-driven climate cyclicity? Is there an optimal way of using factor analysis to home in on the best element pairs, or should another technique be used?

Sedimentary signature of the 2007 Aysén earthquake and tsunami in Aysén fjord (Chilean Patagonia): Interpretation of the XRF data

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On 21 April 2007, the M_w 6.2 Aysén earthquake caused several subaerial mass movements (landslides, rockfalls) along the slopes of Aysén fjord, the three most voluminous of which triggered several tsunamis. These mass movements and the subsequent tsunamis caused an event-deposit, which accumulated on the fjord floor. Although this type of event deposits and the processes that form them have already been described by several authors, the relations between the characteristics of these deposits, the processes that occurred on each slope, and the earthquake intensity remains unstudied. Historical records are often incomplete and –depending on the region– only range back a few hundred years in time. Therefore examples of event-deposits linked to well-documented original processes are scarce.

In December 2009, we collected 22 short gravity cores from the floor of Aysén fjord, in order to gain a better insight into the sedimentological characteristics of the event deposits caused by the 2007 landslide-induced tsunamis. The cores were subjected to a multiproxy analysis, aimed at fingerprinting this deposit with the highest detail. Sedimentological characterisation of the event-deposit is achieved by combining X-ray tomography-scanning, high-resolution (1-5 mm) grain-size analyses, XRF-scanning (2 mm) and magnetic-susceptibility measurements (3.5 mm) of the sediment cores.

The event deposit is characterized by strong variability –on centimetre- to metre-scale– of its sedimentological characteristics, composition and thickness, depending on the location. The internal structure varies between parallel laminations, fine cross-bedding, ripples and homogeneous, with grain sizes ranging from fine clay to gravel. Different phases in the deposition can be correlated between most of the cores, thereby allowing us to gain an insight into the evolution of the deposit. Comparing this complex sedimentary imprint with eye-witness reports, field observations, records of seismic shaking and macro-intensities allows us to better understand the processes forming these deposits.

The advantage of combining CT-scans with XRF-scans is that they can both be used to determine the source area of the sediments. CT-scans not only show alternations between heavy and light minerals, but also reveal structures in the sediment. These structures were used to determine flow direction during deposition and therefore show the direction of different source areas relative to each other. On the other hand, XRF-measurements show changes in chemical composition, thereby providing an indication of differences in mineralogy and petrology of the source areas. It has thus been possible to attribute observed changes in flow direction to differences in density and chemical composition of the mineral fraction. However, interpretation of the XRF-data is complicated due to the variable influence of variations in grain size, water content and organic-matter content on XRF elemental counts. In two cores, a decrease in counts by more than 90 % for Al and Si, about 80 % for K and Ca, 70 % for Ti and around 50 % for Fe has been observed. There is no influence on the heavier elements, indicating that lighter elements are considerably more susceptible to these changes. Synchronous increases in Cl counts indicate that variability in light elemental counts is probably related to variations in interstitial water content, which seem partly controlled by changes in grain-size. Magnetic susceptibility and the organic-matter content of the sediment, however, do not show significant variability. Bulk sediment density and water content still have to be measured. A better

understanding of the causes of light elemental counts variability is needed before interpreting our results in terms of sedimentological processes.

Notes