Geochemical variations detected with continuous XRF measurements on ANDRILL AND-1B core: Preliminary results

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Summary Antarctica and especially its ice sheets play a major role in both the global ocean current system and climate. The ANDRILL (Antarctic Geological Drilling) MIS deep drilling project (McMurdo Sound, NE Ross Ice Shelf, drilled core AND-1B during austral summer 2006/2007) is located in a flexural moat basin filled with glaciomarine, terrigenous, volcanic, and biogenic sediments (Horgan et al., 2005). This basin contains a well-preserved outstanding record of paleoclimate history. During the drilling phase, some major and minor chemical elements were measured directly using a non-destructive X-Ray Fluorescence Core Scanner (XRF-CS) method. For the first time, sediments beneath an ice shelf were drilled, which provides a unique opportunity to investigate the variability of the Ross Ice Shelf. The sediment core covers a time period much longer than any Antarctic ice core record. The high-resolution data set of non-destructive XRF-core scans makes it possible to estimate climate changes on small time scales. Due to the early stage of the project phase, this report will focus mainly on data preparation and correction and provides a first rough interpretation of the measured data.

Introduction

Extreme polar climate changes have an important influence on global climate. The ice sheets are important for the Antarctic cold and salty bottom water which drives the thermohaline circulation of the global Conveyer Belt (Barker, 1995). High-resolution studies of proximal glacio-marine sediments could be an important instrument for the recognition of rapid paleoclimatic changes in the Antarctic environment. High-resolution geochemical data from an XRF Core Scanner are typically used as indicators to detect different lithologies and provenances in marine sediments (Peterson et al., 2000; Roehl and Abrams, 2000). They provide information on short-term variations on a centennial to millennial scale whenever time resolution permits. Chemical elements are reliable proxies for these changes. In this study Si and Sn, for example, can be used as indicators for biogenic primary production and thus help to distinguish between different sedimentation conditions. Other elements (e.g. Fe, Ca and K) point at the presence of terrigenous ice-transported or diagenetically influenced material, respectively. XRF Core Scanners are commonly used to detect the above-mentioned and other chemical elements in wet sediment cores (Jansen et al., 1998; Peterson et al., 2000; Roehl and Abrams, 2000). The AVAATECH XRF Core Scanner used in this study is a transportable seagoing system that provides fast and non-destructive measurements for high-resolution element transitions. For the first time such elemental concentrations were measured on a 1284.87 m long drill core (99 % recovery) from the Antarctic margin directly with an XRF Scanner during the drilling field campaign in a RAC tent in McMurdo Station.

Methods

XRF core scanner

Continuous and accurate measurements are a prerequisite in order to get paleoclimate information from chemical proxies (Roehl and Abrams, 2000). During the drilling phase approximately 30 elements were measured in the range from Al (atomic no. 13) to Ba (atomic no. 56). Depending on the lithology and time restrictions some elements like Ni, Cu, Zn, Ga, Br, Rb, Y, Ru, Au, Pb and Bi were measured with optimized instrument settings only on some core intervals.

On-ice measurements spots were set to resolutions between 0.5 and 10 cm down-core. Most of the time, measurements were done with 10 cm spacing, but depending on occurring lithologies and core conditions the spacing was decreased, resulting in an average interspacing of 6 cm. The measuring spot size was 1x1 cm and set to 0.5x1 cm in specific core sections where higher resolution was needed. The XRF detector system is energy dispersive and the energy levels were set to 10 and 50 kV, and in some intervals also to 30 kV. The measuring time was set to 30 s live time for 10 and 30 kV energy levels and 40 s for 50 kV. To achieve high-resolution spectra, a copper filter was placed in the X-ray beam for the 50 kV setting. For the occasional 30 kV measurements a thick Pd filter was used. No filter was used for the energy setting with 10 kV. The non-destructive measurements were carried out directly at the split core surface of the archive halves which were covered by a 4 μm SPEXCerti Prep Ultralene® film. The core surface was slightly smoothed in case of soft sediment cores, and in case of hard rock cores a smooth roller was used to squeeze out air bubbles and water under the film. Element intensities were measured in total counts (cnts).

Several corrections of the data were done for the element profiles in the ANDRILL AND-1B core. All data points measured on cracks and rough surfaces due to saw marks or porosity of cores and clasts were removed. In the core section 297.46 to 444.55 mbsf the data for some elements (Ba, Sn, Ag and Zr) showed an offset possibly due to a loss in excitation of the X-ray tube and had to be shifted. The offset value was detected and shifting was done by repeated measurements in particular sections (core intervals 386.55 – 438.55 and 410.55 – 418.55) using linear regression or mean value shift, respectively.

Sampling

Additional individual samples were taken to calibrate the relative element intensity counts received from the XRF Core Scanner. These samples were freeze-dried, cracked, cleaned from small stones (> 2 mm), ground to an analytical powder and measured as a separate sample with the same XRF Core Scanner in the home laboratory. These measurements were then compared to the measurements on the wet core. This was done to estimate the effect of absorption by the occurring water film between the core surface and the covering SPEXCerti Prep Ultralene® film. To quantify the relative measurements of the XRF Core Scanner the individual samples will be measured by means of ICP-MS and conventional XRF.

Image collection and visual color reflectance

A 3CCD High Speed Color Line Scan Camera CV-L105 integrated in the XRF Core Scanner system was used for color scanning. The core was scanned in meter sections and the images were saved in different image formats. Profiles of the RGB (red-green-blue) channels and the CIE-lab L* (lightness), a* (redness) and b* (yellowness) values were produced by averaging pixels perpendicular to the core in a rectangle along the central core axis, and the resulting values were saved as ASCII files. The rectangle was adjusted for each core individually to avoid measuring points of the liner or missing core parts. In addition, quantitative measurements of diffuse spectral color reflectance integrated in an area with a spot size of 1 cm diameter were carried out with a hand held CM-2002 spectrophotometer (Minolta Camera Co., Osaka, Japan). The system was used with the same settings as described in Balsam et al. (1998). The spacing of measurements was mostly set to 2 cm, but increased to 1 cm in case of high variable lithologies and decreased to 5 cm in cores with homogenous colors. A clear plastic wrap covered the split core surface to avoid contamination. The calibration was done according to Minolta CM-2002 user's manual (Minolta Camera Co.Minolta Camera Co., 1991). Each data set contains the depth in core-run (which has to be converted to depth in core), CIE-lab L*a*b*, Munsell (Hue, Value, Chroma), the readings from each channel between 400 nm and 700 nm with 10 nm resolution (30 values), and CIE 1931 norm color values XYZ. Measurements were carried out only down to 984.87 mbsf because of instrument malfunction. The data were saved to ASCII files individually for each core-run and down to 200 mbsf; they are processed and depth correlated already.

Results & Discussion

Adsorption of X-ray fluorescence by air and SPEXCerti Prep Ultralene® film

A first quality check of the data set was carried out by using argon (Ar) as an indicator for air between the helium flushed prism and the core surface. Standard materials JB1, JBG1, JR1 and SARM4 (NIST, National Institute of Standards and Technology) were measured 10 times each setting with increasing air distances between the measuring unit and the sample in the XRF Scanner. A threshold of 300 Ar counts was determined by plotting the element counts against the Ar counts. Data points related to the lighter elements Al, Si, S, P, K, Ca and Ti had a decrease in total counts above this threshold corresponding to an air distance greater than 1.6 mm. Heavier elements did not show this effect according to their higher X-ray fluorescence energy.

The 4 μm SPEXCerti Prep Ultralene® film that covered the core surface as well as the windows of the helium flushed prism caused a drop in the element intensities due to absorption. Elements such as Al, Si and Cl had a reduced film transmission of 88 %, 92 % and 98 %, respectively (Tjallingii et al., 2007). These transmission reductions have to be considered thrice, because the X-ray fluorescence from the core had to penetrate three layers of film, one directly on the core and two on the prism.

Source stability

A loss of X-ray tube exitation during first run measurements between 297.46 to 444.55 mbsf was detected by a drop in total counts of the element rhodium (Rh), which represents the material of the X-ray anode. The drop of total counts of Rh could be quantified to 20 %. Stable measurements, however, are highly important for high-resolution element profiles down core.

An effect of this energy loss could also be detected in the elements Ba, Sn, Ag and Zr. To correct these data, parts of specific core sections were measured again. The largest differences between the first and the repeated measurements were found in elemental counts from Sn and Ag (Sn peak is on the flank of the Ag peak) which both could have been generated

by the Ag containing beam collimator of the detector. Zr showed only slight variations between the two measurements. Sn and also Ag count values were about 40 % or rather 8 % higher over the whole interval in the second measurement. Ba on average increased by about 13 %.

The initial element values were shifted using correction values derived from both the initial and the repeated measurements. Linear regression was used for all elements except Sn, for which the mean offset value was calculated.

Visual corrections

All high-resolution core images were checked carefully using Corelyzer 0.8.4 software (University of Illinois, Chicago's Electronic Visualization Laboratory) for measurements on cracks and clasts. Such measurement points were removed from the data set. Clasts measurements will be used for element composition estimations in collaboration with scientist working on petrographic clast analyses. Furthermore, measurement points on rough surface (e.g. due to saw marks) were excluded.

### Pebbles within the sediment matrix of discrete samples

Dried individual samples from the first 200 m were cleaned of small pebbles (> 2 mm). The removed stones were weighed for each sample. The stones reached a maximum of up to 60 % of the dry sample weight in a few extreme samples. No stones at all were found mostly in lithologies indicative for high diatom bioproductivity in the past. Since we tried to avoid clast rich sediments for most of the samples, the median pebble weight is about 7 % of the dry sample weight.

Wet core continuous versus discrete dry powder measurements

The comparison between wet core measurements and dry powder measurements shows variations between 10 % for the elements with a higher atomic number and up to factor 10 higher for the lighter elements like Si and Al. Absorption of X-ray fluorescence by water was described in the study of Tjallingii et al. (2007). They measured wet sediment cores on the split core surface and separate dried powder samples of the same core to determine the transmission related to physical properties. They estimated the water content by using the measured Cl intensities.

The discrepancies between wet core measurements and dry sample measurements are demonstrated on a selected core section with counts of the elements Si, Fe and Cl (Fig. 1). The intensities of the element Si show the largest difference between dry and wet samples with increased values in the dry samples. Values for Fe show only a slight increase. In contrast, decreased values were measured for all dry powder samples for the element Cl. The higher intensities in the wet core are related to artificially elevated salty porewater content. Cohesive and adhesive properties of the interstitial water form this thin water layer below the Ultralene® film and cause higher element intensities of salt ions in the wet core. Other elements besides major elements of sea salt showed a decrease in values. In these cases the water and the containing ions might absorb their X-ray fluorescence.
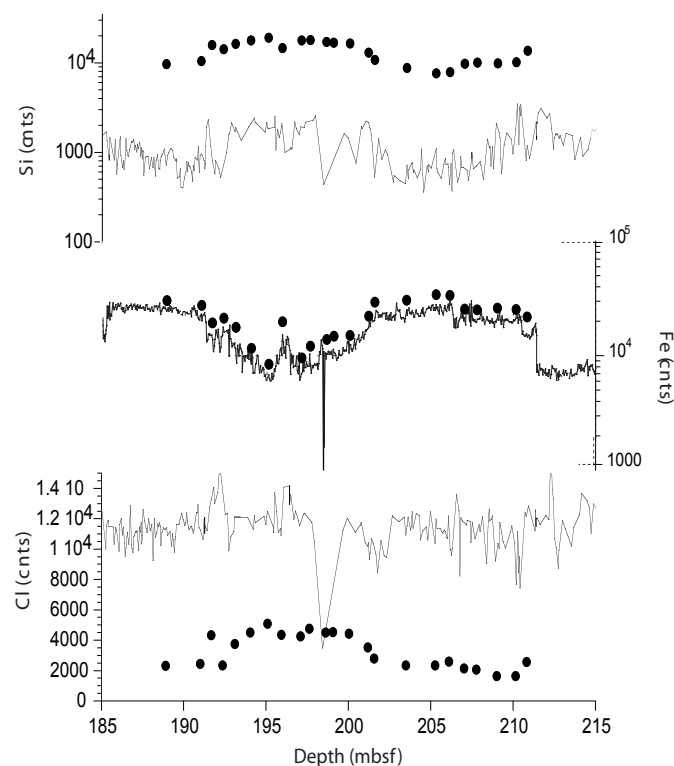

Figure 1. Comparison between wet core measurements (line) and discrete dry powder samples (dots) for the elements Si, Fe and Cl. Intensities of dry powder are much higher for Si and slightly increased for Fe. The measured counts for Cl are decreased in most dry samples.

Preliminary data interpretation

Within the data set a rhythmic pattern in element concentration was detected which corresponds to the changes in the lithologies. These are reflected in the chemical data as well as in the CIE-lab b* values of the spectrophotometer measurements. For better visualization of this pattern the measured values of the elements Si and Fe and the b* color data were smoothed two times by a 5-point moving average and displayed for the upper 200 m of core (that was corrected up to now) (Fig. 2). Maxima of Si in the lower part of this series correspond to minima in Fe and maxima in b* and are clearly related to sediments rich in
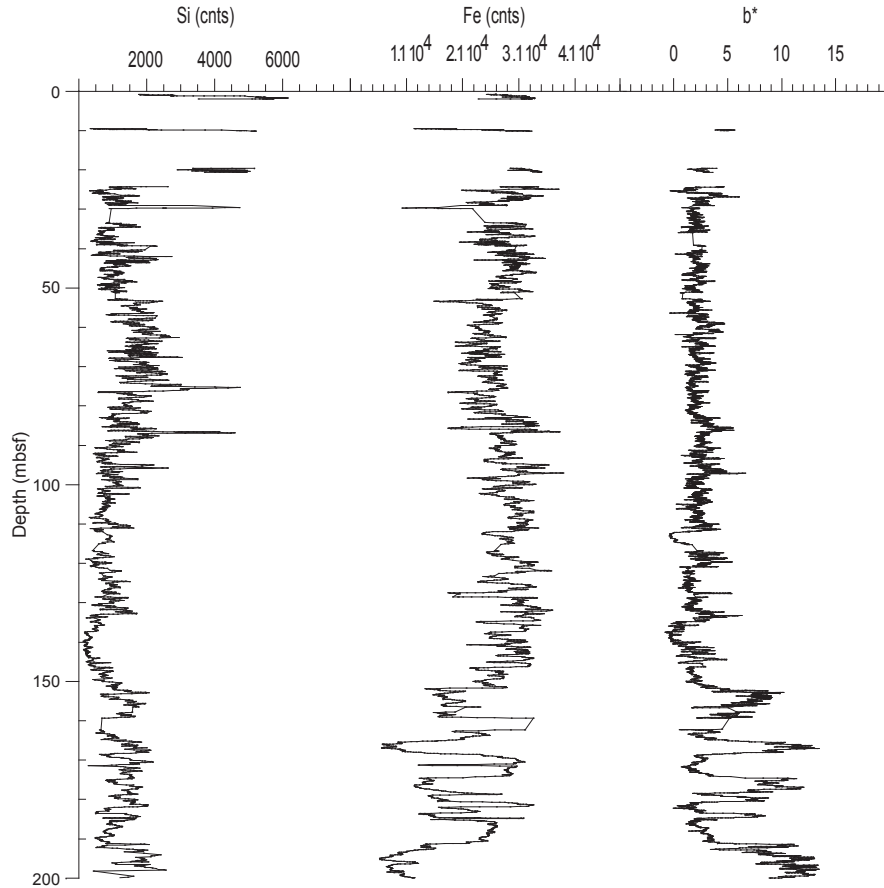
Figure 2. Down-core profiles of the chemical elements Si and Fe and the CIE-lab b* color values (yellowness) from the spectrophotometer measurements. Only the upper core section with corrected data is available in this stage of work and shown here. The curves are smoothed two times by a 5-point moving average.

diatoms (diatomites) which were deposited during open water conditions without an ice shelf being present in this area as it is today. In diamictites, deposited under stronger ice shelf or ice sheet influence, Si and b* mainly have minima values and Fe has maxima. In some parts of the diamictites, the Si values are also high and we have to search for a better geochemical indicator for this lithology.

The high-resolution geochemical data set of the ANDRILL AND-1B core provides an outstanding opportunity to obtain information about rapid paleoclimatic changes in the Antarctic realm. To ensure the quality of the on-ice collected data, diverse correction will be carried out for all core sections and the individual samples need to be analyzed by using ICP-MS and XRF analyzers for calibration of the XRF Core Scanner measurements.

Summary

This study presents preliminary high-resolution geochemical data from the ANDRILL AND-1B core. The data were corrected for factors like air path and interstitial water which influenced specific X-ray fluorescence and the detected element intensities. First results and interpretations demonstrate great opportunities incorporated in this high-resolution data set. To improve this study, the data from the XRF Core Scanner measurements have to be calibrated and additional measurements such as biogenic opal and CNS will have to be taken.

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