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Fast application of X-ray fluorescence spectrometry aboard ship: how good is the new portable Spectro Xepos analyser?

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Abstract A technique for onsite application of X-ray fluorescence (XRF) spectrometry to samples from sediment cores aboard a research vessel was developed and tested. The method is sufficiently simple, precise, and fast to be used routinely for high-resolution analyses of depth profiles as well as surface samples. Analyses were performed with the compact high-performance energy-dispersive polarisation X-ray fluorescence (EDPXRF) analyser Spectro Xepos. Contents of the elements Si, Ti, Al, Fe, Mn, Mg, Ca, K, Sr, Ba, Rb, Cu, Ni, Zn, P, S, Cl and Br were simultaneously determined on 200–225 samples of each core within 24 h of recovery. This study presents a description of the employed shipboard preparation and analysis technique, along with some example data. We show land-based datasets that support our decisions to use powder samples and to reduce the original measuring time for onboard analyses. We demonstrate how well the results from shipboard measurements for the various elements compare with the land-based findings. The onboard geochemical data enabled us to establish an element stratigraphy already during the cruise. Correlation of iron, calcium and silicon enrichment trends with an older reference core provided an age model for the newly retrieved cores. The Spectro Xepos instrument performed without any analytical and technical difficulties which could have been caused by rougher weather conditions or continuous movement and vibration of the research vessel. By now, this XRF technique has been applied during three RV Meteor cruises to approximately 5,000 Late Quaternary

sediment samples from altogether 23 gravity cores, 25 multicorer cores and two box cores from the eastern South Atlantic off South Africa/Namibia and the eastern Atlantic off NW Africa.

Introduction

X-ray fluorescence (XRF) spectrometry is a common tool for highly accurate and reproducible non-destructive element analyses. In land-based analytical laboratories, it is used routinely for investigation of a wide variety of materials such as minerals, rocks, slags, ceramics, metals, alloys, food, pharmaceuticals and fuels. Advantages include easy sample preparation and instrument operation, which make the technique also convenient for application onboard a research vessel. Thus, XRF analyses of marine sediment cores can provide data on the elemental composition of sediments which complement downcore colour scans or logs of sediment physico-chemical properties.

Previous studies have already described shipboard application of XRF for various purposes on different research vessels, using different instruments. However, analyses were mostly limited to a few samples only. Onboard research vessels, XRF has been applied for assessment of metal contamination in marine sediments. For example, measurements were performed on RV Ecos on 30 wet bulk samples from San Diego Bay using a Spectrace 9000 portable XRF spectrometer. These shipboard analyses allow quick onsite decisions for mapping strategies and detailed assessments of contaminated areas (Stallard et al. 1995). However, the use of wet sediment samples has the disadvantage that enhanced matrix and particle size effects can reduce the quality of the analyses.

XRF analyses for bulk composition of sediments and rocks have also been carried out for several years on the

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RV Joides Resolution using a fully automated ARL 8420 wavelength-dispersive spectrograph (Kastens et al. 1987; Detrick et al. 1988). Major and trace element contents were routinely determined on fused disks and pressed pellets respectively (e.g. Kastens et al. 1987; Detrick et al. 1988; Pettigrew et al. 1999; Barker et al. 1999; Dick et al. 1999; Coffin et al. 2000; Christie et al. 2001). For example, Barker et al. (1999) analysed trace elements (Nb, Zr, Y, Sr, Rb, Zn, Cu, Ni, Cr, V and Ba) on pressed pellets of 54 sediment samples during ODP (Ocean Drilling Program) Leg 178. The actual measurements were performed aboard ship. During ODP Leg 183, by contrast, Coffin et al. (2000) analysed 91 rock samples and, during ODP Leg 187, Christie et al. (2001) analysed 44 representative samples of major lithologic units. In both cases, major elements were determined from fused glass disks, trace elements from pressed powder pellets. On RV Sonne, sediment samples have been routinely analysed with the wavelength-dispersive XRF spectrometer Philips PW 1410 (Herzig and Plüger 1988; Plüger et al. 1988). This instrument is permanently installed on board.

Two major problems arise from the preparation of pressed pellets. Sample preparation as such is rather time-consuming, needing roughly 5–10 min for a single sample. In addition, onboard the ship it is difficult to accurately correct sample weight for the effect of analytical additives such as wax. Even more complicated and time-consuming is the shipboard preparation of fused disks.

In view of these limitations, the XRF scanner Cortex (Corescanner Texel) was developed for non-destructive analysis on wet split-core sections. Like other logging facilities, it can be used directly onboard the ship in its own container. Indeed, to date the Cortex is the only core scanner to have been applied onboard the ship. The instrument performs measurements of high resolution (maximum 1 mm), and produces reliable counts for K to Sr (Jansen et al. 1998). Together with other core scanners and, for that matter, other scanning tools such as colour spectrophotometry, however, the Cortex shares the disadvantage of assessing elemental levels only in relative (counts per second) rather than absolute terms.

At the Geosciences Department of Bremen University there are two XRF core scanners, one similar to the Cortex in that it provides element intensities from K through Sr (Röhl and Abrams 2000). The other is a more sophisticated core scanner which measures from Al to Ba (<http://www.avaatech.com/index.htm>). The two XRF core scanners at Bremen University have been used solely under stationary conditions onland.

An expedition with RV Meteor to the eastern South Atlantic was carried out during January/February 2003, focused on the reconstruction of the Late Quaternary climate history of the southern Benguela system, and the influence of the Agulhas warm water entrainment into the South Atlantic (Schneider and Cruise participants 2003). During cruise M 57-1, investigations of sediment cores from the shelf and continental slope off South

Africa were performed with the portable energy-dispersive polarisation X-ray fluorescence (EDPXRF) analyser Spectro Xepos (Spectro Analytical Instruments, Kleve, Germany) for the first time on a large scale. One advantage of this system is that it produces absolute measures of elemental levels.

Most XRF data presented in this study form a key component of a much larger dataset gathered during RV Meteor cruise M 57-1, one aim being to test and improve the new Spectro Xepos shipboard technique, the ultimate goal being to establish palaeoclimate links in the southern Benguela system. Thus, in order for the elemental information to be meaningfully interpreted, it is necessary to evaluate the quality of these measurements performed in a non-stationary laboratory, as well as their consistency with more conventional measurements under stationary conditions onland. Within this context, the aims of the present study are:

1. To present a detailed description of sample preparation and XRF analysis technique for the EDPXRF Spectro Xepos instrument
2. To determine and compare the accuracy and reproducibility of shipboard and land-based measurements
3. To compare XRF analyses carried out onland with corresponding inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements on the same material, and
4. To compare shipboard with land-based measurements of absolute levels for some elements.

In addition, we assessed the suitability of the shipboard core data for integration in an age model from a reference core.

Study site

During RV Meteor cruise M 57-1 from Cape Town to Walvis Bay in January/February 2003, five gravity cores were recovered from the eastern South Atlantic off South Africa for onboard XRF geochemical analyses (Table 1; Fig. 1). Four of these coring sites (GeoB 8301, GeoB 8307, GeoB 8310, GeoB 8315) are located in the southern Cape Basin, one (GeoB 8331) further to the north in the Holocene mud belt (Schneider and Cruise participants 2003). Also presented in this study are XRF analyses of three multicorer cores (MUCs) taken during RV Meteor cruises M 57-1 (sites GeoB 8301 and GeoB 8303; Schneider and Cruise participants 2003) and M 58-1 (site GeoB 8501; Schulz and Cruise participants 2003). MUC GeoB 8303 is located in the southern Cape Basin, MUC GeoB 8501-1 in the eastern Atlantic off Mauritania (location not shown in Fig. 1).

Prior to cruise M 57-1, two archived gravity cores were analysed by means of the Spectro Xepos, these serving as reference cores. Gravity core GeoB 3718-9 was obtained during RV Meteor cruise M 34-2 in January/February 1996 from the continental slope off Namibia, south of Walvis Bay (Schulz and Cruise par-

Table 1 Cruise and core number, geographic position, water depth, gear type and recovery of all cores referred to in this study, along with available data. *MUC* multicorer, *GC* gravity corer, *GPC* giant piston corer

Cruise	Core no.	Latitude	Longitude	Water depth (m)	Gear type	Recovery (cm)	Available data
M 57-1	GeoB 8301-5	34°46.48' S	17°41.92' E	1941	MUC	22	XRF; shipboard
M 57-1	GeoB 8301-6	34°46.00' S	17°41.54' E	1952	GC	879	XRF; shipboard
M 57-1	GeoB 8303-5	34°15.67' S	16°47.09' E	3447	MUC	21	XRF; shipboard
M 57-1	GeoB 8307-6	33°50.43' S	16°31.99' E	2667	GC	843	XRF; shipboard
M 57-1	GeoB 8310-2	32°54.57' S	16°22.92' E	1993	GC	833	XRF; shipboard
M 57-1	GeoB 8315-6	32°53.30' S	15°41.70' E	2995	GC	851	XRF; shipboard
M 57-1	GeoB 8331-4	29°08.12' S	16°42.99' E	97	GC	887	XRF; shipboard
M 58-1	GeoB 8501-1	18°30.26' N	18°45.51' W	2995	MUC	32	XRF; shipboard
M 34-2	GeoB 3718-9	24°53.60' S	13°09.80' E	1312	GC	1371	ICP-AES ^a XRF; land-based
M 23-1	GeoB 2004-3	30°52.10' S	14°20.50' E	2572	GC	966	XRF; land-based
NAUSICAA-IMAGES II	MD 962085	29°42' S	12°56' E	3001	GPC	3540	colour reflectance ^b $\delta^{18}\text{O}$ age (planktonic) ^c

^aExtracted from Heuer (2003)^bExtracted from Bertrand and Cruise participants (1997)^cExtracted from Chen et al. (2002)

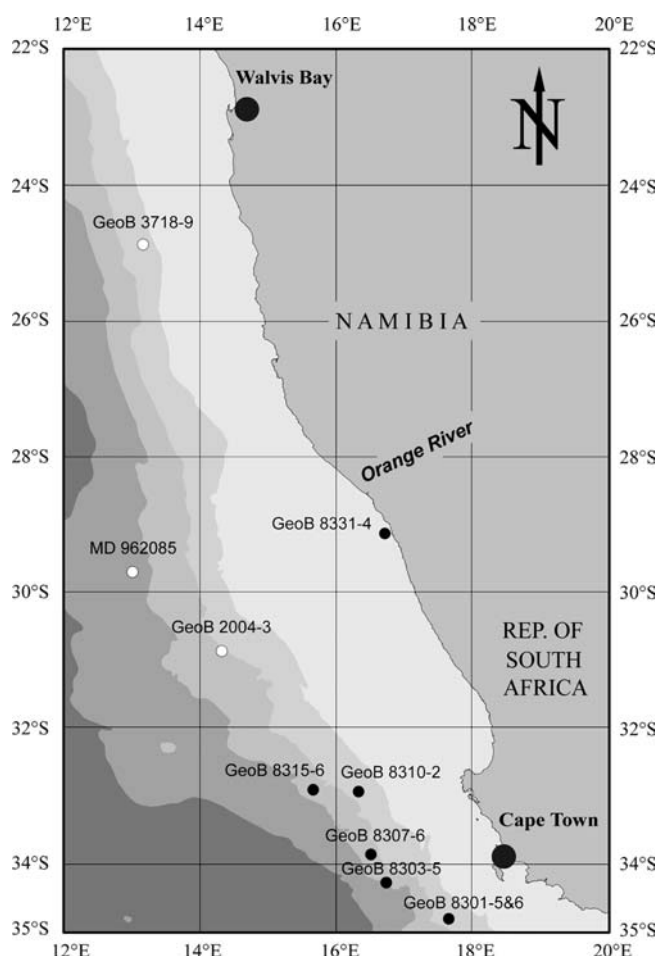


Fig. 1 Bathymetric map of the eastern South Atlantic showing locations of all cores referred to in this study. *Closed circles* indicate selected core positions during RV Meteor cruise M 57-1 (present study); the *open circles* indicate the positions of reference cores GeoB 3718-9 (RV Meteor cruise M 34-2), MD 962085 (RV Marion Dufresne cruise NAUSICAA-IMAGES II) and GeoB 2004-3 (RV Meteor cruise M 23-1). Source: GEBCO

participants 1996), GeoB 2004-3 during RV Meteor cruise M 23-1 in February 1993 in the northern part of the southern Cape Basin (Spieß and Cruise participants 1993; Fig. 1). Data on a third reference core, the giant piston core MD 962085, were used to fit an age model to core GeoB 2004-3. MD 962085 is located northwestwards of our study area on the lower slope of the eastern South Atlantic, and was taken aboard RV Marion Dufresne during the NAUSICAA-IMAGES II cruise in October/November 1996 (Bertrand and Cruise participants 1997; Table 1; Fig. 1).

Materials and methods

Land-based laboratory work

Prior to cruise M 57-1, an appropriate XRF preparation and analysis technique was developed in the land-based laboratory. Besides analyses with the certified standard reference material MAG-1 (e.g. Govindaraju 1994), the laboratory work involved analysis of the two archived reference cores GeoB 3718-9 and GeoB 2004-3.

A set of 77 ICP-AES analyses of core GeoB 3718-9 from Heuer (2003) was used to control the quality of the land-based Spectro Xepos XRF analyses. Unfortunately, it was not possible to use aliquots of the original ICP-AES samples, because the amount of leftover material was too small. For this reason, GeoB 3718-9 was resampled at the same depths. This material was powdered, homogenised and, in each case, 4 g was weighed accurately (two decimal places) and analysed using the XRF method Turboquant (Schramm and Heckel 1998) which is generally used at a specified measuring time of 300 s per target and sample.

In addition, MAG-1 standard material was used to develop an XRF measuring technique better suited for onboard application. Three main aspects were assessed: (1) the suitability of using powdered material lightly compressed by hand, thereby saving in time and equipment needed for the more traditional usage of

pressed pellets; (2) the suitability of estimating sample mass indirectly in terms of volume, thereby avoiding the problems associated with the deployment of a balance under non-stationary conditions aboard ship; and (3) the suitability of reducing measuring time from 300 to 100 s per target and sample, thereby increasing sample throughput.

In the shore-based laboratory, element profiles were established for core GeoB 2004-3 using the reduced 100-s measuring option. In order to use this core for age-fitting purposes during cruise M 57-1, it was dated by correlation with the giant piston core MD 962085 which has an age model based on Foraminifera oxygen isotope records (Chen et al. 2002). Thus, colour reflectance data (700 nm) for MD 962085 (Bertrand and Cruise participants 1997) were correlated with XRF Ca data for GeoB 2004-3. The main argument for using core GeoB 2004-3 as reference was that it allowed easily fitting age models to other study cores by means of a complete XRF element suite, in addition to the colour reflectance data of the dated reference core MD 962085.

Shipboard sample preparation

After recovery, 1-m sections were cut from each 8–9 m gravity core, capped immediately, and divided lengthways by sawing through the core liner and sediment. Subsamples were obtained from each split-core section by using the U-channel sampling technique (Figs. 2, 3). A plastic U-shaped channel (“conduit”) with a cross section of 1.5×2 cm and 1 m in length was pressed into the interior part of the split-core section, this being the region least affected by the coring operation. This strip

of sediment was subsequently separated from the core section by means of a plastic wire. These U-channel samples allowed continuous subsampling at a length resolution of 4 cm. In this way, 200–225 discrete samples were taken from each gravity core. In the present case, a U-channel was preferred to sampling with syringes. Thus, although element contents were integrated over 4 cm, no information was lost as may occur when inserting syringes at discrete depths. MUCs were sampled at a resolution of 2 cm (GeoB 8301-5, GeoB 8303-5) or of 1 cm for the top 10 cm, and a resolution of 2 cm below this depth (GeoB 8501-1).

The sediment samples were transferred into crystallising dishes and subsequently dried in a laboratory oven at 200°C for 60 min. This procedure eliminates abundant pore water typical for muddy continental shelf sediments, which otherwise would have a negative impact on the quality of the analyses. After removing the samples from the oven and cooling to room temperature, the material was ground and homogenised manually by means of an agate or ceramic pestle and mortar. The powder was then poured into previously prepared sample cups.

Each sample cup consists of a top and a bottom ring, 4- μ m prolene foil serving for the sides and the bottom. Spectro Analytical Instruments suggests a sample amount of 2–4 g dry sediment for XRF analysis. Since it is inconvenient to use highly accurate balances onboard the ship, sample dimensions had been predetermined in the land-based laboratory so that each cup, when filled to the brim with loose material, contained the desired mass for analysis. Note that this assumes a constant density for sediments in the study area. After filling, the material was compressed by means of a pestle so as to

Fig. 2 Schematic illustration of sample preparation for shipboard XRF analyses. 1 U-channel sampling; 2 subsample transfer into crystallising dishes; 3 drying; 4 grinding; 5 transfer of sediment powder into sample cup; 6 compacting the powder; 7 capping the sample cups; 8 arrangement of sample cups on a 12-position rotating tray; 9 XRF analysis

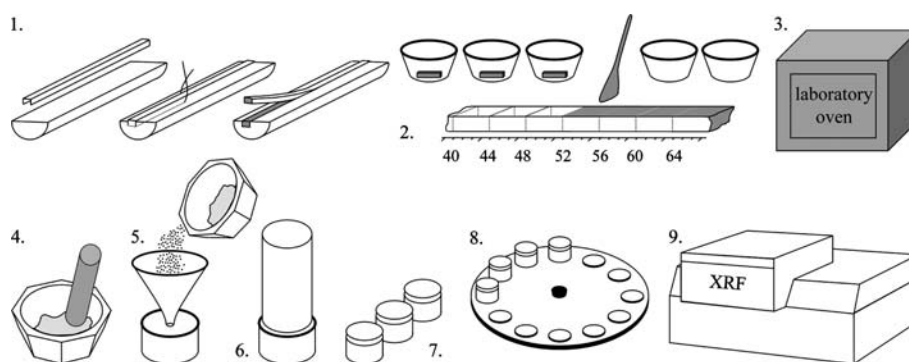


Fig. 3 Photographs showing various steps of XRF sample preparation. *Left* cutting a sediment strip from the split-core section using the U-channel and plastic wire; *centre* removing the sediment-filled U-channel; *right* subsampling at a depth resolution of 4 cm



obtain a flat and even surface and to eliminate air in interstices. After capping, the cups were arranged on a 12-position rotating tray, which was then inserted into the measuring chamber of the Spectro Xepos analyser.

Shipboard XRF analyses

The compact benchtop EDPXRF analysis system Spectro Xepos used for the analyses is shown in Fig. 4. Its small size (31×60×69 cm) and weight (\approx 45 kg) allow easy use and transport outside a traditional land-based laboratory. Onboard the ship, the instrument was immediately set up in standby mode to allow for adjustment. For one, thermic stabilisation is critical for the detector. The XRF was allowed to stabilise 2 h before being used for simultaneous measurements of elements from Mg (atomic number 12) through to U (atomic number 92). Elements important for this study are Si, Ti, Al, Fe, Mn, Mg, Ca, K, Sr, Ba, Rb, Cu, Ni, Zn, P, S, Cl and Br. All XRF datasets presented in this study are available on the Pangaia database www.pangaia.de/PangaVista?query=@Ref 25739.

Spectro Xepos uses a Pd-target end window tube at a maximum power of 50 W and a maximum voltage of 50 kV. The excitation radiation is optimised for three groups of elements, each with a specific target for modification in excitation energy and excitation energy distribution. The principle of this optimised excitation is already well known (Heckel et al. 1992). Targets, associated voltage values, and measured elements are listed in Table 2. Excitation conditions are not influenced by measuring time. The fluorescent radiation is measured with a Si(Li) semiconductor detector (RÖNTEC-Xflash) which is operated at a temperature of -10°C (optimum temperature: -5 to -15°C). Cooling is accomplished

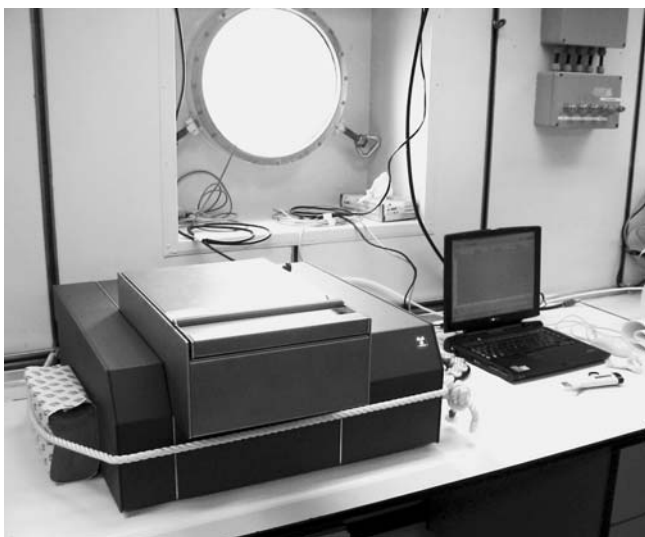


Fig. 4 Shipboard application of the XRF analyser Spectro Xepos

Table 2 Excitation conditions used for the Spectro Xepos

Target	Voltage (kV)	Elements
Mo secondary target	45	Cr–Y, Hf–U
Al ₂ O ₃ polarisation target	49.5	Zr–Ce
HOPG crystal	25	Mg–V

thermoelectrically by integration of a Peltier element into the detector module (Spectro Xepos 2000).

The sample chamber is flushed with helium to avoid loss of energy caused by scattering in air. This improves the sensitivity for light elements such as Mg, Al and Si. A 50-l helium gas bottle (200 bar) is sufficient for approximately 1,000 analyses performed with the 100-s measuring time option.

The instrument was operated by means of the software Spectro X-Lab Pro, Version 2.4, using the so-called Turboquant method. This is a fundamental parameters method for fluorescence and scattering, and allows preliminary screening of samples (Schramm and Heckel 1998). The method is generally used at a specified measuring time of 300 s per target and sample.

Readjustment of the multi-channel analyser (MCA) calibration of the XRF instrument was done weekly with a specially prepared glass disk. The calibration curves convert the MCA channel scale to a kiloelectronvolt (keV) scale and thus, shift the peaks to the desired positions. Accuracy and reproducibility of the XRF instrument were assessed by daily analyses of the standard reference material MAG-1 (e.g. Govindaraju 1994). For this purpose, pressed pellets of the standard (4 g MAG-1 standard powder + 0.9 g Hoechst Wax) had been prepared in the land-based laboratory prior to the cruise. The standard pellets had been accurately weighed onland, thereby avoiding the problem of not being able to accurately correct for wax mass during difficult shipboard operations. To exclude errors due to sample preparation, however, reproducibility and accuracy were determined by repeated measurement of one and the same pellet whereas the remaining pressed pellets served as backups.

Results

Accuracy, reproducibility and detection limits (MAG-1 standard reference material)

A comparison of analyses performed on a single pressed pellet of certified standard reference material MAG-1 allowed to assess the analytical quality of the Spectro Xepos instrument for the original 300-s method as well as for the time-reduced 100-s method, both onland and aboard. Note that this pressed pellet had been prepared from the MAG-1 powder sample which had been analysed earlier with the 300-s measuring time option in the land-based laboratory.

Pressed pellet

Table 3 shows 300-s and 100-s accuracy and reproducibility data for both land-based and shipboard XRF analyses of a single pressed pellet of MAG-1 standard reference material (cf. the standard deviation is an inverse measure of reproducibility). For the 300-s measuring time option under land-based laboratory conditions, reproducibility values are $< 5\%$ for all listed elements except Ba, Cu, Ni, P and Cl, and $\leq 1\%$ for Si and Al. Thus, reproducibility is generally good. Accuracy is sometimes excellent ($100 \pm 8\%$ for Sr, Ba, Rb, Cu, Ni, Zn) but mostly biased towards overestimating element contents, except for Sr and Rb, which tend to be underestimated. Because reproducibility is generally good, this bias is consistent.

Reduction of the measuring time to 100 s in the land-based laboratory leads to a decrease of accuracy and reproducibility, especially for Mn, Mg, Ba, Cu and Rb. Reproducibility values are $> 5\%$ for Ti, Ba, Cu, Ni, P and Cl, $\leq 5\%$ for Mn, Mg, Ca, Sr, Rb, Zn, S and Br, and $\leq 1\%$ for Si, Al, Fe and K. Accuracy remains similar to the 300-s measurements, showing excellent values ($100 \pm 8\%$) for Ti, Sr, Ba, Rb, Cu, Ni and Zn but usually overestimating element contents, except for Sr. A comparison of these land-based data justifies our choice of the 100-s measuring time for the shipboard analyses.

Shipboard 300-s measurements of the same pressed pellet of MAG-1 standard reference material even exceed the quality of land-based 300-s measurements in terms of reproducibility. Values are $< 5\%$ except for Cu and Cl, and $\leq 1\%$ for Si, Al, Fe, Ca, K, Sr, S and Br. Accuracy decreases slightly by 1–2% for most elements but it is excellent ($100 \pm 8\%$) for Sr, Ba, Rb, Cu, Ni and Zn. Again, there is a bias towards overestimating element contents, except for Sr.

Although reproducibility of shipboard 100-s measurements decreases in comparison to both land-based and shipboard 300-s measurements, values are still $\leq 1\%$ for Si, Al and Fe, and $< 5\%$ for the other elements, except Ti, Ba, Cu, Ni, P and Cl. Accuracy is excellent ($100 \pm 8\%$) for Sr, Ba, Rb, Cu, Ni and Zn, but mostly element contents are overestimated, except for Sr. A comparison of the land-based 300-s and shipboard 100-s measurements of the MAG-1 pressed pellet shows a decrease of both accuracy and reproducibility for Mn and Mg. Standard deviations of Ba and P increase from 6.7 to 14.3 and 5.0 to 7.7% respectively. Overestimation of element contents is highest for P (131–150% relative accuracy) and Mg (130–141% relative accuracy) with all four methods. On the other hand, the accuracy of shipboard 100-s measurements of Ca, K and Sr exceeds that of land-based 300-s measurements. For most other elements, shipboard 100-s data show either better reproducibility but lower accuracy than land-based 300-s data (Si, Al, Fe) or vice versa (Ti, Ba, Cu, Ni, Zn, P).

Powder sample

Land-based 300-s measurements of a single powder sample of MAG-1 standard reference material are shown in Table 4. Reproducibility values are $< 5\%$ for all listed elements except Ba and Cu, and $\leq 1\%$ for Si, Ti, Al, Fe, Ca, K, Sr, S and Br. Among the major elements, only Mg and Mn show values of 2.0%, P of 2.4%. Accuracy exceeds that of the pressed pellet for the major elements, with excellent values for Si, Ti, Fe, Mn and Ca, and also for the trace element Ni. For the trace elements Sr, Ba, Rb, Cu and Zn, however, accuracy is lower in the powder sample than in the pressed pellet. Except for P, Mg and Si, there is a bias to underestimate element contents. This bias is most significant for Sr, Ba and Rb which are underestimated by 15–19%. P shows the lowest accuracy, being overestimated by 30%. A comparison of land-based 300-s measurements of both the MAG-1 pressed pellet and the powder sample justifies our choice to use powder samples aboard.

The detection limit is defined as the element content corresponding to a signal three times the standard deviation. For measurements of both the powdered and pelleted MAG-1 standard reference material with the four methods, detection limits are well below (factor > 10) certified levels for Si, Al, Fe, Mg, Ca, K, Sr, Rb, Zn, S and Br. Only for those elements with detection limits closer to certified levels, especially Ba, Ni and P, did instrument performance improve substantially with increasing measuring time.

Comparison of land-based XRF and ICP-AES analyses

This is a comparison of two distinctly different methods, the XRF method being applied to the original solid phase samples, whereas the sediment samples used for ICP-AES analysis were fully digested. Results from linear regression analysis and statistical parameters are presented in Figs. 5 and 6 and Table 5. Element contents from ICP-AES analyses were set at 100%, and the relative accuracy represents the deviation of the XRF data from this reference level. Minimum and maximum values in relative accuracy represent the scattering of the data but note that, in the present case, this scatter can be attributed partly to resampling for XRF analyses and thus, to the inherent inhomogeneity of marine sediments. Outlier data are probably caused by the presence of, amongst others, larger shells or mineral grains. Outlier data for Al, Fe, Mg and K derive from sample 7, for Ti from samples 7, 15 and 63, and for Ni, Cu and Zn from samples 7 to 9.

Coefficients of determination are highest (≥ 0.7) for Ca, Sr, K, Al, Fe, Ni and S, and lowest (< 0.7) for Ti, Mn, Mg, Cu and Zn. Ba shows a seemingly good correlation but this results largely from the wide range of Ba content (320–6,015 mg/kg) in core GeoB 3718–9.

Table 3 Compilation of land-based and shipboard data, both for the original 300-s and the time-reduced 100-s measuring times, for a pressed pellet of MAG-1 standard reference material. *SD* standard deviation, *n* number of replicate analyses

Element	Si	Ti	Al	Fe	Mn	Mg	Ca	K	Sr	Ba	Rb	Cu	Ni	Zn	P	S	Cl	Br
Certified (mg/kg)	235600 ± 4500	4496 ± 420	86800 ± 1600	47560 ± 1600	759 ± 70	18090 ± 600	9790 ± 600	29470 ± 710	150 ± 15	480 ± 41	150 ± 6	30 ± 3	53 ± 8	130 ± 6	698 ± 92			
Land-based, 300-s; <i>n</i> = 91																		
Measured mean (mg/kg)	285700	4950	105300	53430	887	23510	10810	32450	139.6	508	146.6	31.8	55.2	137.1	1045	3556	17950	226.2
SD (mg/kg)	2800	225	1000	600	31	520	250	620	2.3	34	2.3	2.7	2.9	3.4	52	47	2840	3.7
Relative SD (%)	1.0	4.6	0.9	1.1	3.5	2.2	2.3	1.9	1.7	6.7	1.6	8.4	5.2	2.5	5.0	1.3	15.8	1.6
Relative accuracy (%)	121	110	121	112	117	130	110	110	93	106	98	106	104	105	150			
Detection limit (mg/kg)	8400	675	3000	1800	93	1560	750	1860	6.9	102	6.9	8.1	8.7	10.2	156	141	8520	11.1
Land-based, 100-s; <i>n</i> = 99																		
Measured mean (mg/kg)	289004	4814	105827	54056	907	24880	10825	32493	140.3	515	148.0	32.2	52.4	135.5	935	3472	13724	221.9
SD (mg/kg)	2319	266	694	422	37	709	148	309	2.4	60	2.6	3.4	5.3	4.3	64	48	1567	4.1
Relative SD (%)	0.8	5.5	0.7	0.8	4.0	2.9	1.4	1.0	1.7	11.7	1.8	10.6	10.1	3.2	6.9	1.4	11.4	1.8
Relative accuracy (%)	123	107	122	114	120	138	111	110	94	107	99	107	99	104	134			
Detection limit (mg/kg)	6957	798	2082	1266	111	2127	444	927	7.2	180	7.8	10.2	15.9	12.9	192	144	4701	12.3
Shipboard, 300-s; <i>n</i> = 97																		
Measured mean (mg/kg)	286600	5124	105800	53960	899	24490	11020	32950	140.5	507	147.7	31.3	55.9	135.6	970	3458	14040	225.1
SD (mg/kg)	1700	119	600	160	23	550	90	270	1.4	24	1.8	2.9	2.5	2.5	26	29	890	2.2
Relative SD (%)	0.6	2.3	0.5	0.3	2.5	2.2	0.8	0.8	1.0	4.8	1.1	9.3	4.4	1.9	2.7	0.8	6.3	1.0
Relative accuracy (%)	122	114	122	113	118	135	113	112	94	106	99	104	106	105	139			
Detection limit (mg/kg)	5100	357	1800	480	69	1650	270	810	4.2	72	5.4	8.7	7.5	7.5	78	87	2670	6.6
Shipboard, 100-s; <i>n</i> = 80																		
Measured mean (mg/kg)	288800	4872	106400	53810	893	25580	10780	32370	139.6	491	146.9	29.5	53.3	134.7	915	3387	11830	220.6
SD (mg/kg)	1700	254	700	520	34	650	200	440	2.3	70	3.0	4.2	5.2	4.3	71	53	940	4.1
Relative SD (%)	0.6	5.2	0.7	1.0	3.8	2.5	1.8	1.4	1.6	14.3	2.1	14.2	9.7	3.2	7.7	1.6	8.0	1.9
Relative accuracy (%)	123	108	123	113	118	141	110	110	93	102	98	99	101	104	131			
Detection limit (mg/kg)	5100	762	2100	1560	102	1950	600	1320	6.9	210	9	12.6	15.6	12.9	213	159	2820	12.3

Table 4 Compilation of land-based data, both for the original 300-s and the time-reduced 100-s measuring times, for a powder sample of MAG-1 standard reference material. *SD* standard deviation, *n* number of replicate analyses

Element	Si	Ti	Al	Fe	Mn	Mg	Ca	K	Sr	Ba	Rb	Cu	Ni	Zn	P	S	Cl	Br
Certified (mg/kg)	235600 ± 45004496	45004496 ± 42086800	42086800 ± 160047560	160047560 ± 4200759	4200759 ± 7018090	7018090 ± 6009790	6009790 ± 71029470	71029470 ± 1410150	1410150 ± 15480	15480 ± 41150	41150 ± 630	630 ± 353	353 ± 8130	8130 ± 6698	6698 ± 92	92	92	92
Land-based, 300-s; <i>n</i> = 21																		
Measured mean (mg/kg)	236262	4236	82296	45425	747	19564	9320	27510	122.0	391	127.7	26.8	45.5	117.1	908	3275	19839	196.1
SD (mg/kg)	953	43	411	120	15	390	92	194	1	34	1.4	2.0	1.7	2.2	22	34	292	1.9
Relative SD (%)	0.4	1.0	0.5	0.3	2.0	2.0	1.0	0.7	0.9	8.7	1.1	7.5	3.7	1.9	2.4	1.0	1.5	1.0
Relative accuracy (%)	100	94	95	96	98	108	95	93	81	81	85	89	86	90	130			
Detection limit (mg/kg)	2859	129	1233	360	45	1170	276	582	3	102	4.2	6	5.1	6.6	66	102	876	5.7

Thus, a reduced Ba dataset (Fig. 6), comprising only those data points with lower element contents ($< 1,000$ mg/kg), shows a much poorer correlation. The mean relative accuracy of the XRF values is $\pm 100\%$ for Ti, Mn, Mg, Ca, Cu and Zn but much lower (68%) for Ba.

Comparison of shipboard and land-based XRF analyses

To assess the performance of the Spectro Xepos instrument aboard ship, 40 powder samples from three MUCs (GeoB 8301-5, GeoB 8303-5, GeoB 8501-1) were analysed with the 300-s and the time-reduced 100-s methods, both aboard and subsequently onland. For the post-cruise analyses, the samples were accurately weighed in order to estimate whether the quality of shipboard measurements had been impaired by the volume-based weighing procedure.

For both the shipboard and land-based datasets, the relationships between the 100-s and 300-s methods show regression lines all running through the origin. Correlations are excellent ($R^2 \geq 0.99$) for Si, Al, Fe, Mn, Ca, K, Sr, S, Cl and Br, good for Ti, Mg, Rb and Zn ($R^2 = 0.9$ to 0.99), whereas Cu, Ni, P and especially Ba show a higher scatter of data ($R^2 < 0.9$; Figs. 7, 8, 9).

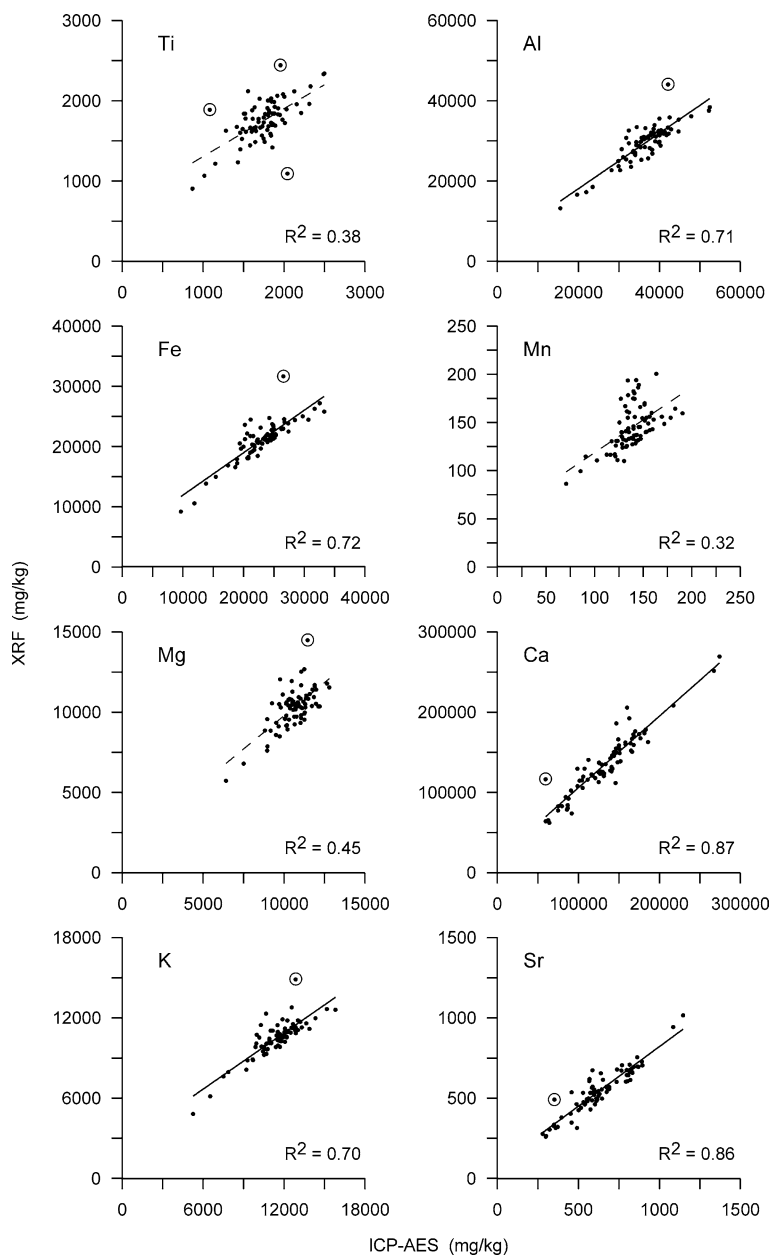
If shipboard and land-based measurements were to correspond perfectly, then a sample measured both aboard (triangles in Figs. 7, 8, 9) and onland (crosses in Figs. 7, 8, 9) would plot essentially as a single data point. A good correspondence exists between shipboard 100-s and land-based 300-s measurements, with an average deviation of $\leq 5\%$ for Si, Al, Fe, Ca, K, Sr and Br. For Rb, Zn, S and Cl, the average deviation is $\leq 10\%$, whereas it is $> 10\%$ for Ti, Mn, Mg, Ba, Cu, Ni and P. The seemingly low scatter in the Mn plot in Fig. 7 results largely from the wide range of Mn content from approximately 0.1 to 4.0 g/kg. The onboard procedure of estimating sample weight relatively crudely in terms of sample volume generally has only a minor effect on data accuracy.

Instrument performance at sea

After 2 h of stabilisation in the standby mode, necessary to adjust instrument parameters, the Spectro Xepos showed no irregularities in functioning which could have been caused by transport. At a measuring time of 100 s per target and sample, a complete analysis of one sample with all three targets takes 5 min, and a 12-position rotating tray is analysed within 80 min, rather than 200 min at the original measuring time of 300 s. Geochemical information on several elements (18 in the present case) is available immediately after analysis.

Spectro Xepos is generally capable of detecting all elements from Mg through U from powdered material in cups. For many elements (e.g. V, Cr, Co, As, Y, Zr, Mo, Ag, Cd, Sn, Pb, U) in the samples analysed, however, the

Fig. 5 Results from linear regression analysis for the elements Ti, Al, Fe, Mn, Mg, Ca, K and Sr, with ICP-AES data as independent and XRF data as dependent variables (core GeoB 3718-9). Part of the scatter has been caused by resampling for XRF analyses, rather than using the original ICP-AES samples, and thus results from the inherent inhomogeneity of marine sediments. Outlier data caused by extreme inhomogeneity are encircled



detection limits of the instrument were above or close to naturally occurring levels at the study site. This is a core-specific result and not due to shipboard effects. The “missing” elements would not have been reliably detected onland either.

Occasionally, single shipboard XRF analyses deviated from the general trend in the cores, for instance, for the elements Si, Ca, Al, Fe, K, Mg and S. Subsequent re-analyses of these samples often confirmed that the initial values were not erroneous. Presumably, the deviation from the general trend was caused by the inherent inhomogeneity of the sediments at the study site. However, 0.5% of the measurements performed during the three cruises M 57-1 (Schneider and Cruise participants 2003), M 58-1 (Schulz and Cruise participants 2003) and

M 58-2a & b (Bleil and Cruise participants 2004) was found to be erroneous, the value being 0.6% for cruise M 57-1 on its own. It is as yet not known whether this could have been due at least partly to unfavourable weather conditions. Dates of XRF analyses performed during cruise M 57-1 and prevailing weather conditions are listed in Table 6. The instrument certainly remained operational during heavy weather conditions, even at wind speed 8–9 B (19–22.5 m/s) and swells of 3–4 m.

The shipboard data show typical XRF trends, commonly observed in continental margin sediments. Example spectra are presented in Figs. 10 and 11 for the Mo-target and HOPG-crystal excitation for two samples collected at 9 and 193 cm core length in GeoB 8301-6. Note that both figures show an expanded energy scale.

Fig. 6 Results from linear regression analysis for the elements Ba, Cu, Ni, Zn and S, with ICP-AES data as independent and XRF data as dependent variables (core GeoB 3718-9). Part of the *scatter* has been caused by resampling for XRF analyses, rather than using the original ICP-AES samples, and thus results from the inherent inhomogeneity of marine sediments. Outlier data caused by extreme inhomogeneity are *encircled*

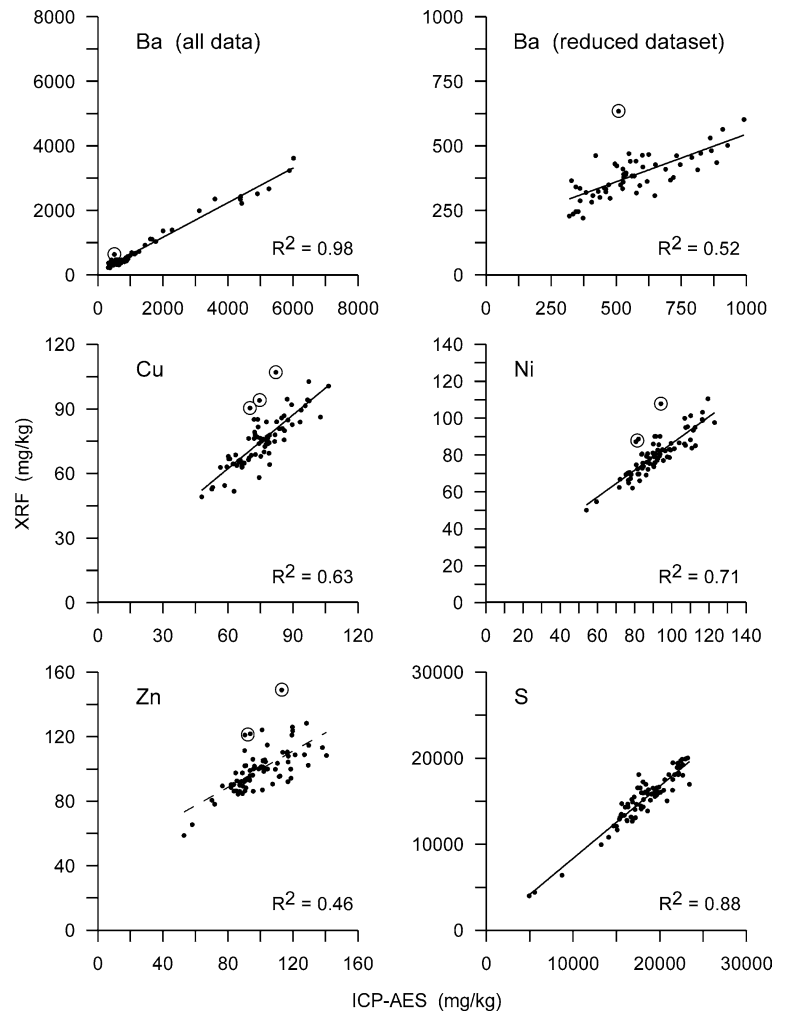


Table 5 Comparison of ICP-AES and land-based XRF analyses (powder samples; accurate sample weight; 300-s measuring time) of gravity core GeoB 3718-9

Element	ICP-AES; element content (mg/kg) ^a	XRF; relative accuracy (%)		
		Range	Mean	Min–max (outlier data in brackets) ^b
Ti	870–2,498	101	76 (53)–136 (174)	0.40
Al	15,500–52,500	81	69–100 (104)	0.74
Fe	9,670–33,290	92	78–117 (119)	0.74
Mn	71–191	105	84–144	0.33
Mg	6,410–12,800	97	85–123 (126)	0.48
Ca	59,430–274,330	103	77–131 (196)	0.87
K	5,260–15,810	92	80–115 (116)	0.71
Sr	279–1146	88	64–117 (140)	0.86
Ba	320–6,015	68	47–111 (125)	0.98
Cu	48–106	100	78–118 (130)	0.66
Ni	54–123	88	75–99 (115)	0.73
Zn	53–141	101	77–123 (134)	0.46
S	4,940–23,413	84	72–103	0.89

^aICP-AES analyses of core GeoB 3718-9 extracted from Heuer (2003)

^bOutlier data have been encircled in Figs. 5 and 6

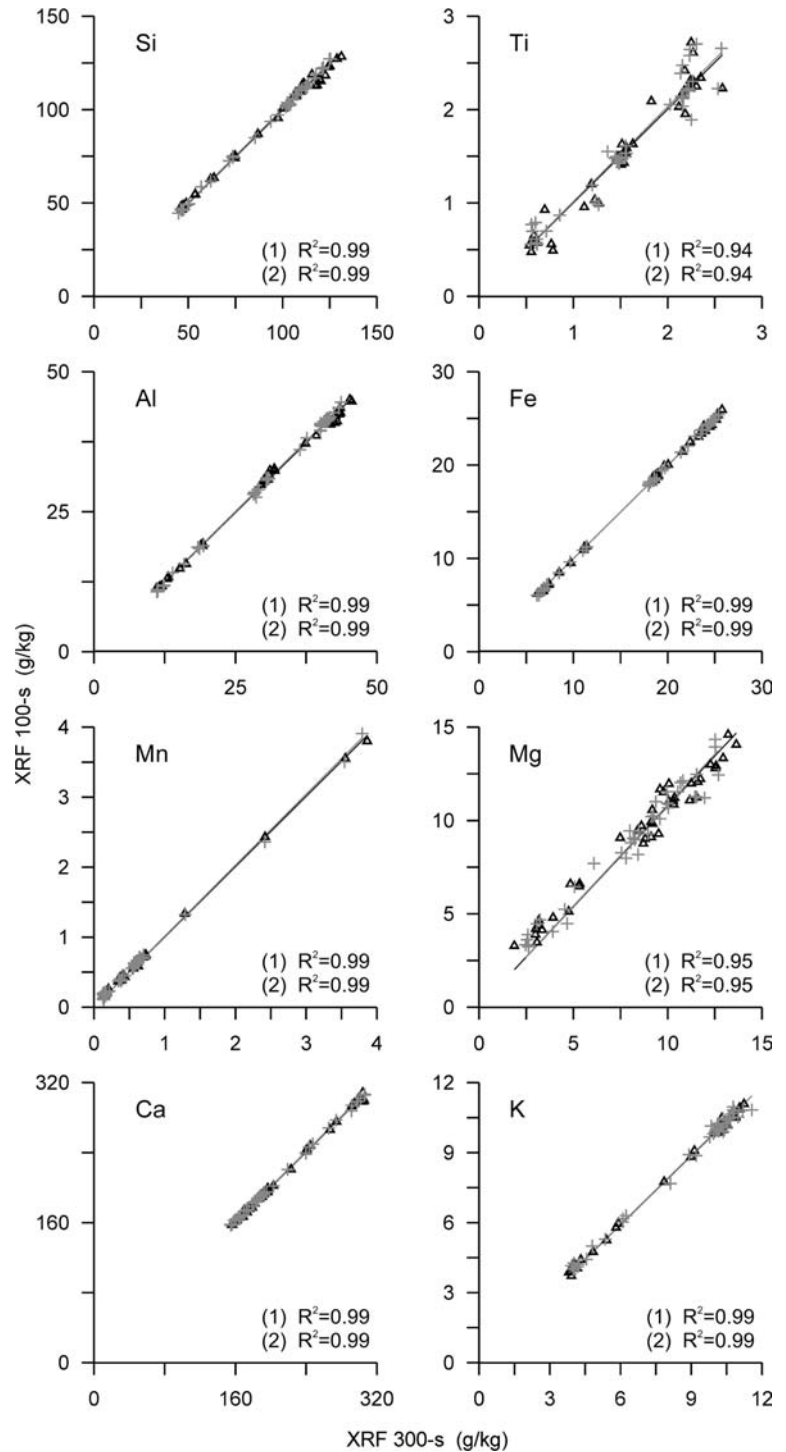
There is an excellent differentiation in the measured intensities of common elements such as Fe, Br and Sr (Fig. 10), and also Al, Si, S, Cl, K and Ca (Fig. 11). In particular, note the good sensitivity for the Al and Si peaks, a potential problem when using benchtop XRF equipment.

Downcore data

Shipboard downcore elemental variations are illustrated on the basis of selected datasets for four cores collected in the southern Cape Basin during RV Meteor cruise M 57-1 (Schneider and Cruise participants 2003), combined

Fig. 7 Results from linear regression analysis of shipboard (1) and land-based (2) XRF measurements on three MUCs (cores GeoB 8301-5, GeoB 8303-5, GeoB 8501-1) for the elements Si, Ti, Al, Fe, Mn, Mg, Ca and K, with 300-s data as independent and 100-s data as dependent variables.

Triangles denote shipboard, crosses denote land-based analyses. In each of these plots there are two regression lines, one for shipboard, one for land-based analyses

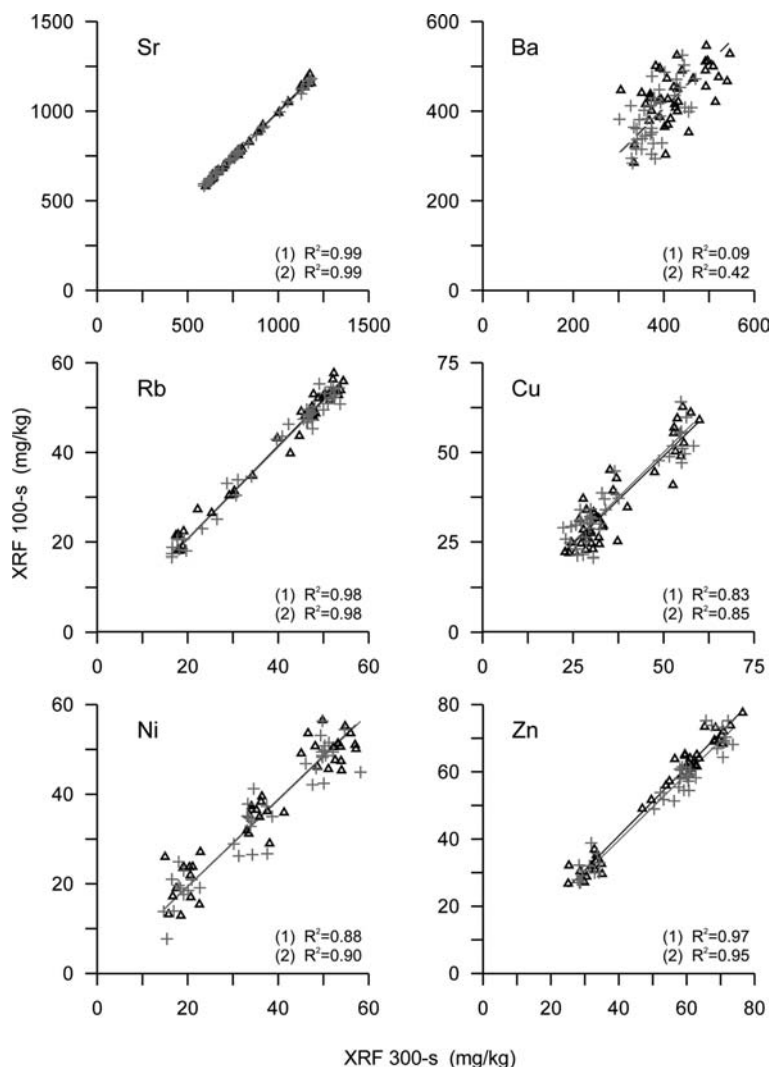


with the age data for one reference core collected earlier during RV Meteor cruise M 23-1 (Spieß and Cruise participants 1993) and analysed onland. Figure 12 a-c shows good correlation of the Fe, Si and Ca profiles between the dated reference core GeoB 2004-3 and the gravity cores GeoB 8315-6, GeoB 8307-6, GeoB 8310-2 and GeoB 8301-6. Core GeoB 2004-3 allows age-depth correlation back to 300 ka. Cores GeoB 8310-2 and GeoB 8301-6 are younger than 300 ka, whereas cores

GeoB 8315-6 and GeoB 8307-6 exceed this age. An age of approximately 190 ka is the oldest identified in all five gravity cores in the present study.

A more complete dataset for core GeoB 8301-6 (Fig. 13) indicates that the elements showing lowest relative standard deviations are Si, Al, Fe, Ca, K, Sr, Rb, Zn, S, Cl and Br, evident in the rather smooth appearance of specific peaks in the graph (cf. relatively low standard deviations in Tables 3, 4). More “noisy”

Fig. 8 Results from linear regression analysis of shipboard (1) and land-based (2) XRF measurements on three MUCs (cores GeoB 8301-5, GeoB 8303-5, GeoB 8501-1) for the elements Sr, Ba, Rb, Cu, Ni and Zn, with 300-s data as independent and 100-s data as dependent variables. *Triangles* denote shipboard, *crosses* denote land-based analyses. In each of these plots there are two regression lines, one for shipboard, one for land-based analyses



are the profiles for Ti, Mg, Cu, and especially Mn, Ba, Ni and P, reflecting the higher standard deviations (cf. Tables 3, 4).

Discussion and conclusions

Shipboard measurements carried out by means of Spectro Xepos were integrated downcore at a resolution of 4 cm, using dry material which had been ground and compressed conveniently by hand. Together with instrument-specific timesaving steps, this enabled us to prepare and analyse more than 200 samples for various elements within 24 h only. By now, the XRF technique has been applied during three RV Meteor cruises to approximately 5000 Late Quaternary sediment samples from altogether 23 gravity cores, 25 multicorer cores and two box cores from the eastern South Atlantic off South Africa/Namibia and the eastern Atlantic off NW Africa.

The findings of the present study convincingly demonstrate a generally excellent agreement between land-based and shipboard datasets. Reproducibility of XRF

analyses is good for elements which commonly occur at high levels in marine sediments, such as Si, Al, Fe, Ca, K and Sr. Elements occurring at lower levels, such as Ba and Cu, however, show standard deviations exceeding 5% for both shipboard and land-based analyses. Thus, Spectro Xepos XRF analysis of marine sediments evidently yields the best results for major elements. The quality of the XRF data is only marginally affected by the problem of not being able to determine highly accurate sample weights aboard ship, as long as the amount of sample material is sufficient to fill at least half the sample cup.

Analyses of a pressed pellet of the MAG-1 standard show good accuracy for the minor elements, but major element contents are generally biased towards overestimation. This bias cannot be explained by the duration of the measurement (300 or 100 s measuring time) or by the running of the instrument under stationary or non-stationary conditions. Analyses of a MAG-1 powder sample are in the range of or close to certified values for major elements whereas trace elements tend to be underestimated. Land-based laboratory work with

Fig. 9 Results from linear regression analysis of shipboard (1) and land-based (2) XRF measurements on three MUCs (cores GeoB 8301-5, GeoB 8303-5, GeoB 8501-1) for the elements P, S, Cl and Br, with 300-s data as independent and 100-s data as dependent variables. *Triangles* denote shipboard, *crosses* denote land-based analyses. In each of these plots there are two regression lines, one for shipboard, one for land-based analyses

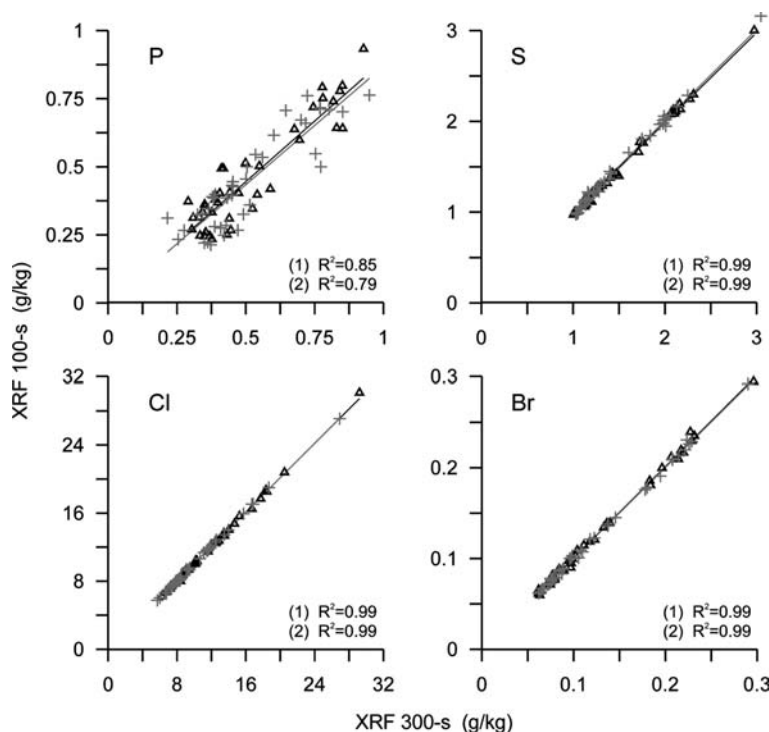


Table 6 Dates of XRF analyses during RV Meteor cruise M 57-1, dominating wind speed and swell during day of analysis, number of samples and erroneous measurements

Core no.	Date of XRF analysis	Wind speed		Swell (m)	Number of samples	Erroneous measurements
		(B)	(m/s)			
GeoB 8301-5	21.01.2003	1-3	1.0-4.5	3	11	0
GeoB 8301-6	22.01.2003	3-6	4.5-12.5	2-2.5	219	1
	23.01.2003	7-9	15.5-22.5	3		
GeoB 8303-5	22.01.2003	3-6	4.5-12.5	2-2.5	12	0
	24.01.2003	6-8	12.5-19.0	2.5-3		
GeoB 8307-6	26.01.2003	4-5	6.5-9.5	1.5-2	211	2
	27.01.2003	5-6	9.5-12.5	2		
GeoB 8310-2	28.01.2003	6	12.5	1.5-2.5	208	0
	29.01.2003	5-7	9.5-15.5	2.5		
GeoB 8315-6	31.01.2003	5	9.5	2.5-3	212	1
	01.02.2003	3-5	4.5-9.5	1.5-2		
GeoB 8331-4	02.02.2003	5	9.5	2.5-3	220	3
	03.02.2003	4-5	6.5-9.5	1.5		
	04.02.2003	3-5	4.5-9.5	1-1.5		

corresponding powder samples and pressed pellets, both of other standard reference materials (Asso, Nod-P1, PACS-1) and sediments from core GeoB 3718-9, showed element contents in pressed pellets to be almost always higher than those in the powder samples (Wien et al. unpublished data). Especially for analysis of major elements, therefore, powder samples are to be preferred whereas analytical quality for minor elements increases by the usage of pressed pellets. Our focus of interest being the major elements as well as a much faster and easier sample preparation is the main argument for using powder samples for shipboard XRF analyses. It should

be borne in mind that the absolute values for element contents are based on an internal calibration provided by the Turboquant method. The resulting bias towards overestimating or underestimating element contents can be easily reduced by subsequent external calibration with element-specific factors.

One reason for the better quality (higher reproducibility) of shipboard 300-s vs. land-based 300-s measurements of the MAG-1 pressed pellet may be linked to the essentially continuous operation of the Spectro Xepos during the cruise aboard the RV Meteor. Shipboard analyses were performed every day and, if necessary,

Fig. 10 View of the ≈ 6 –15 keV region in spectra of two different samples from GeoB 8301-6 (9 cm core length, *bold line*; 193-cm core length, *shaded line*), using the Mo-target excitation (0–25 keV)

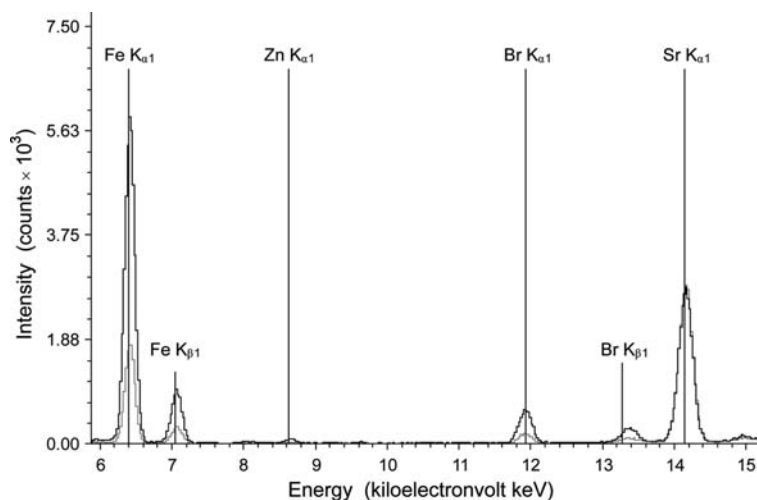
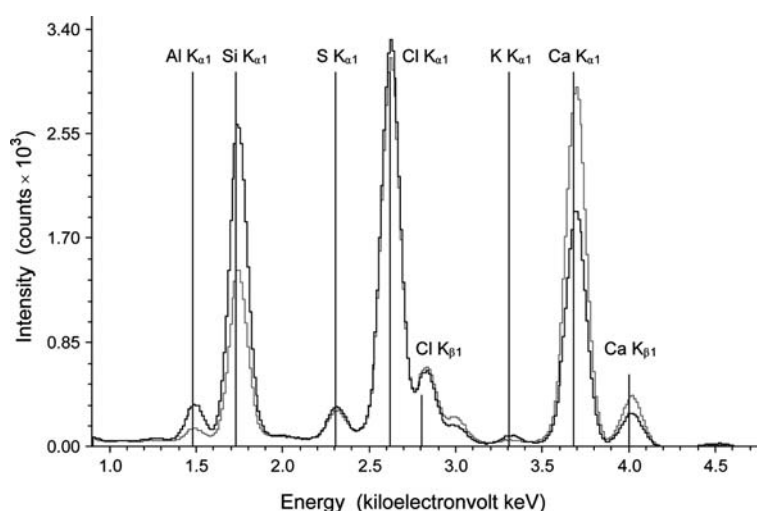


Fig. 11 View of the ≈ 1 –4.5 keV region in spectra of two different samples from GeoB 8301-6 (9-cm core length, *bold line*; 193-cm core length, *shaded line*), using the HOPG-crystal excitation (0–12.5 keV)



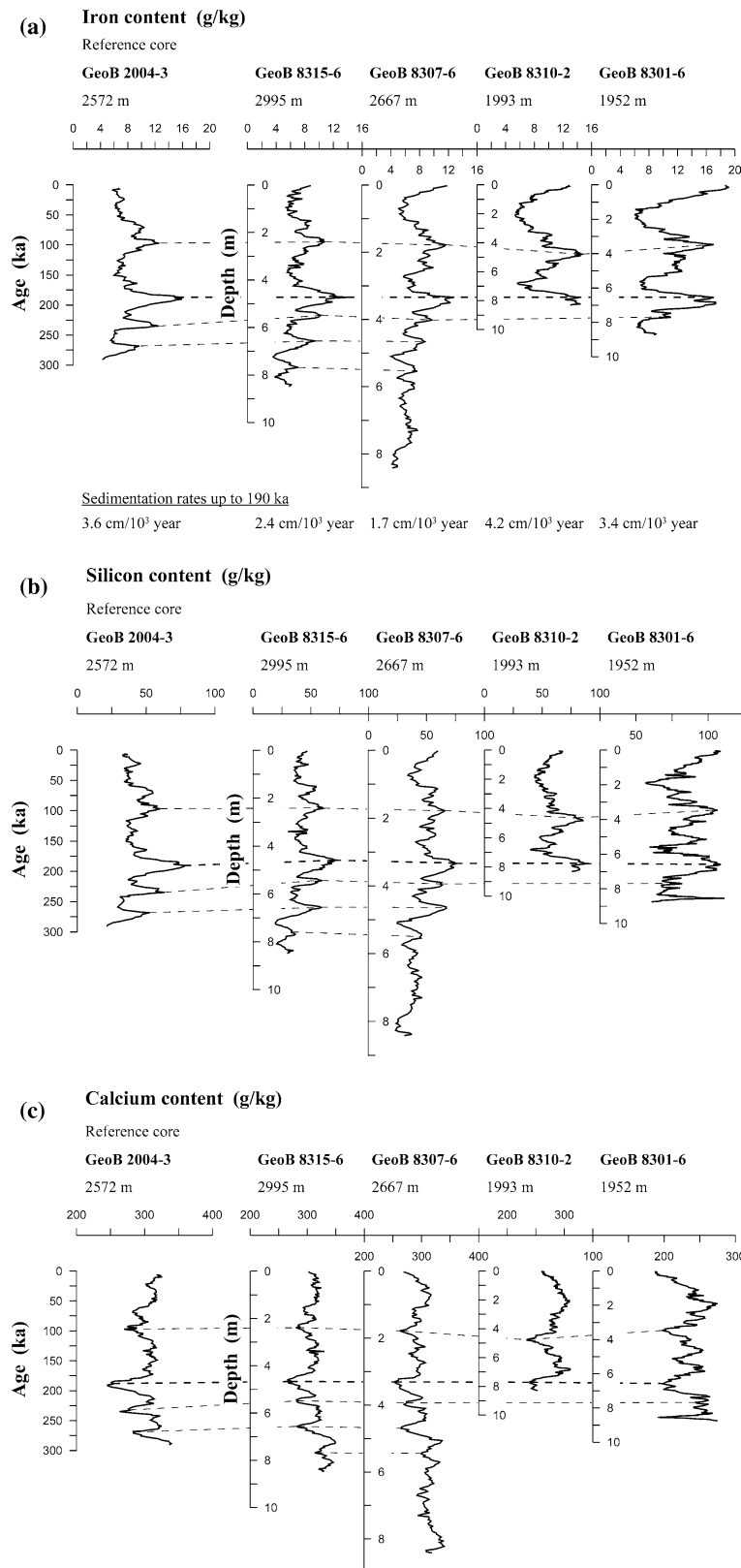
even overnight during the 3-week M 57-1 cruise (Schneider and Cruise participants 2003). The land-based analyses, on the other side, comprise a time span of 8 months during which the instrument was not operated that often. The high data quality resulting from a tight work schedule is also indicated by the comparison of shipboard 300-s measurements of the MAG-1 pressed pellet with the land-based 300-s measurements of the MAG-1 powder sample. The MAG-1 powder sample was analysed 21 times during a time span of only 8 days, before being processed into the pressed pellet. Reproducibility values are similar for both datasets.

The time-reduced 100-s measuring method is highly suitable for shipboard work because the duration of analysis of 100 samples is reduced from approximately 28 to 11 h. Thus, the method represents a substantial financial saving in terms of manpower and ship costs. Evidently, the high-quality data obtained by onboard 100-s measurements can be used meaningfully for comparisons of elemental profiles between cores. Since data from 300 and 100-s measurements correspond so well,

we have now adopted the 100-s measuring time and the use of powder samples for routine work in our land-based laboratory at Bremen University. Only for more difficult analyses of Ba do we improve analytical quality by using the original 300-s measuring time option. Moreover, for long-term documentation of instrument accuracy and reproducibility, both during shipboard operations and in the land-based laboratory, it is more convenient to use standard reference material in form of pressed pellets rather than powder.

Onboard application of the Spectro Xepos instrument was not limited by stormy weather conditions. During RV Meteor cruise M 57-1, wind speeds exceeded 6 B (12.5 m/s) during 7 days, and swells were ≥ 2 m during 14 days and ≥ 3 m during 6 days. Erroneous values may have been caused by stronger than usual movement of the ship at the time of analysis. However, we did not observe an obvious link between outlier data and stormier weather conditions and, besides, outlier data have been observed to a similar extent in the land-based analyses as well.

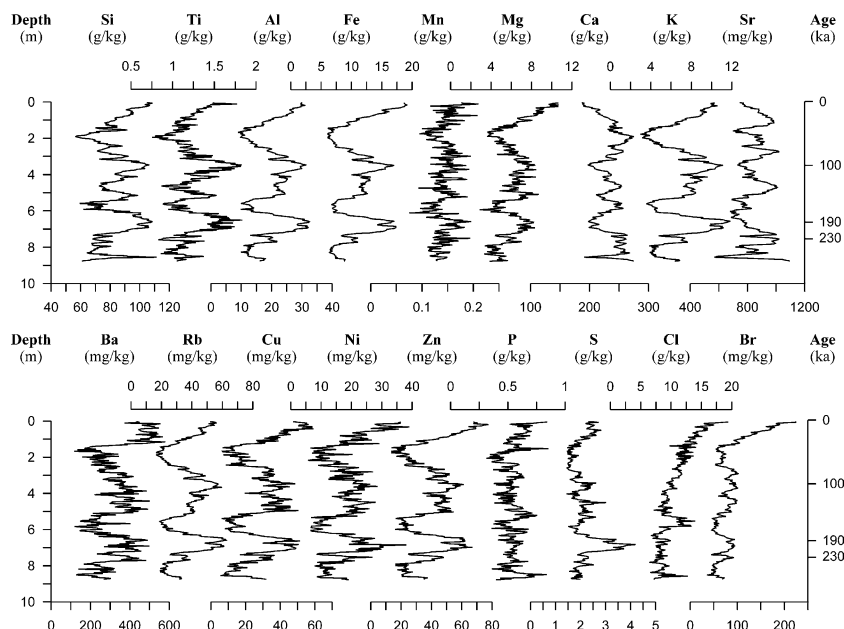
Fig. 12 Correlation of **a** Fe, **b** Si and **c** Ca profiles between the four study cores analysed onboard with the 100-s method and the reference core GeoB 2004-3 analysed onland with the 100-s method. Peaks which are well correlated are indicated by *dashed lines*. The *bold dashed line* marks the oldest age (190 ka) identified in all five cores in the present study. Depth-integrated sedimentation rates in **a** were estimated up to 190 ka



There are several aspects which argue in favour of the Spectro Xepos analyser aboard a research vessel. The XRF technique can provide fast and reliable data on the

elemental composition of sediment cores. It is possible, for instance, to gain immediate information on the distribution of terrigenous versus marine material in con-

Fig. 13 Downcore variations in 18 elements detected by shipboard 100-s measurements of gravity core GeoB 8301-6. Age model based on correlation with reference cores MD 962085 (Bertrand and Cruise participants 1997; Chen et al. 2002) and GeoB 2004-3



tinental shelf or margin sediments. These data can be qualitatively and quantitatively linked with terrigenous input, water mass chemistry, atmospheric circulation or ocean currents, and thus are highly important in studies of palaeoclimate, palaeoenvironment and palaeoceanography. For example, onboard XRF measurements were performed during Meteor cruise M 58-1 for the first time on highly disrupted sediment cores retrieved from the continental slope off NW Africa (Schulz and Cruise participants 2003). These sediments are strongly influenced by transport processes such as slides, debris flows and turbidity currents, one core from an intra-channel site comprising approximately 45% turbidite material. Downcore elemental profiles provided valuable stratigraphic information and thus, reliable age models for emplacement times of debris flows and turbidites, as has already been confirmed by subsequent radiocarbon dating (Wien et al., unpublished data). Thus, XRF data help tremendously to support scientific discussion on processes governing changes in sediment composition, related either to climate or to local sedimentation processes, or both, and this already during the cruise. Since geochemical data are available within 24 h after recovering a sediment core, it is possible for scientists to react quickly to new results by intensifying investigations in the study area before the end of the cruise. Thus, the geochemical data obtained by XRF analysis can guide onsite decisions for mapping and more detailed sampling and, moreover, form a key element of post-cruise studies and perspectives.

The most important advantage of the Spectro Xepos analyser over other well-established logging or scanning tools (e.g. multi-sensor core logger, colour spectrophotometry, XRF core scanner) is its capability to measure absolute element contents in sediments. These data allow interpretation both of absolute element values in a

core and their downcore variations and thus, can be directly correlated with environmental processes on a quantitative basis. By contrast, various XRF core scanners provide data on element intensities which basically only mirror downcore variations. In order to use these data on a quantitative basis, they have to be calibrated for each region or suite of cores with reference material analysed with other techniques such as ICP-AES, ICP-MS or AAS.

Elemental composition of the sediment is not affected by alteration due to atmospheric oxygen as, for example, is sediment colour, nor is information lost due to post-depositional reduction diagenesis, as is often observed for magnetic parameters. Moreover, sediment colour and physical properties are composite signals, with sediment colour, for example, depending on a variety of parameters such as mineral composition, species assemblage, organic matter content, bulk density, and also roughness of the scanned sediment surface. Although element content is not entirely unaffected either, interferences are less manifold and transport paths and processes are better known.

Another key advantage of the Spectro Xepos is its small size which allows operation even if shipboard laboratory facilities are limited. Even on smaller vessels, onboard measurements performed immediately after core recovery avoid potential elemental changes, for instance, carbonate dissolution or translocation of Mn, which may be caused during transport and subsequent long-term storage in a core tank.

In the present study, we have shown that shipboard Spectro Xepos XRF analyses can approach the quality of measurements performed under stationary conditions onland. Our future goal is directed towards a considerable simplification of the sample preparation technique for onboard XRF analysis.

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