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Testing the analytical performance of handheld XRF using marine sediments of IODP Expedition 355

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Original Article

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Abstract

Obtaining geochemical profiles using X-ray fluorescent (XRF) techniques has become a standard procedure in many sediment core studies. The resulting datasets are not only important tools for palaeoclimatic and palaeoceanographic reconstructions, but also for stratigraphic correlation. The International Ocean Discovery Program (IODP) has therefore recently introduced shipboard application of a handheld XRF device, making geochemical data directly available to the science party. In all XRF scanning techniques, the physical properties of wet core halves cause substantial analytical deviations. In order to obtain estimates of element concentrations (e.g. for quantitative analyses of fluxes or mass-balance calculations), a calibration of the scanning data is required. We test whether results from the handheld XRF analysis on discrete samples are suitable for calibrating scanning data. Log-ratios with Ca as a common denominator were calculated. The comparison between the handheld device and conventional measurements show that the latter provide high-quality data describing Al, Si, K, Ca, Ti, Mn, Fe, Zn, Rb and Sr content (R^2 compared with conventional measurements: ln(Al/Ca)=0.99, ln(Si/Ca)=0.98, ln(K/Ca)=0.99, ln(Ti/Ca)=0.99, ln(Mn/Ca)=0.99, ln(Fe/Ca)=0.99, ln(Zn/Ca)=0.99 and ln(Sr/Ca)=0.99). Our results imply that discrete measurements using the shipboard handheld analyser are suitable for the calibration of XRF scanning data. Our test was performed on down-core sediments from IODP Expedition 355 that display a wide variety of lithologies of both terrestrial and marine origin. The implication is that our findings are valid on a general scale and that shipboard handheld XRF analysis on discrete samples should be used for calibrating XRF scanning data.

1. Introduction

X-ray fluorescence (XRF) analysis is one of the most useful tools available for palaeoenvironmental research and it has become standard procedure to obtain such sediment geochemical data, along with grain size and mineralogy (Croudace & Rothwell, 2015). Applications include core characterization and recognition of sedimentological events such as ash layers, turbidites, ice-rafted debris and eolian dust. These data are also effective for provenance studies, facies interpretation, diagenetic studies and stratigraphic correlations. Croudace & Rothwell (2015) offer a good overview of the wide range of environmental processes documented using XRF analysis. Various XRF techniques are available, in all of which the sample is subject to high-energy (ionizing) X-rays capable of ejecting inner-shell electrons from atoms. The empty shells are filled using an outer-shell electron which sheds a significant part of its energy and produces fluorescent X-rays characteristic of each element (Schramm, 2012). The number of fluorescent X-rays produced at each energy (kV) is counted by a detector connected to a multichannel analyser. In sediment core studies, XRF scanning data are often used for palaeoclimatic and palaeoceanographic interpretations. However, raw scanner counts and even ratios are susceptible to data artefacts caused by the highly variable sample conditions that wet natural sediment cores present from core surface imperfections, the presence of organic material, water pooling, as well as variations in grain size and water content (Tjallingii *et al.* 2007; Hennekam & De Lange, 2012; Wilhelms-Dick *et al.* 2012; Weltje *et al.* 2015). It is therefore necessary to normalize, calibrate and/or validate the data in order to quantify the chemical composition, essential in studies dealing with the quantitative analyses of fluxes or mass-balance calculations (e.g. Weltje *et al.* 2015; Grant *et al.* 2017). In order to do this it is necessary to obtain a quantitative geochemical dataset using conventional XRF methods, generally conducted by wavelength dispersive (WD-) XRF, energy dispersive (ED-) XRF or inductively coupled plasma (ICP) measurements on homogenized, dry, ground samples (Weltje & Tjallingii, 2008; Weltje *et al.* 2015).

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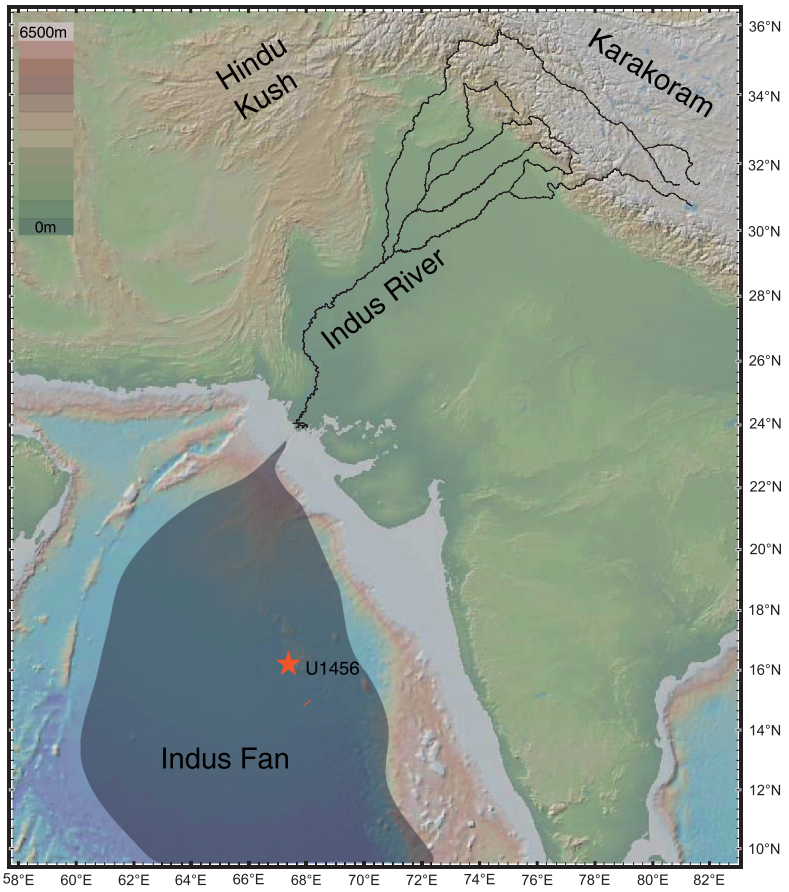

Fig. 1. Bathymetric map of the Arabian Sea and surrounding landmasses from GeoMapApp (Ryan *et al.* 2009). The red stars indicate expedition 355 Site U1456 and the grey shading the approximate extent of the fan (Kolla & Coumes, 1987). After Pandey *et al.* (2016).

In this study, we investigate whether it is possible to use a Olympus Delta Premium handheld analyser, which is now available shipboard on the International Ocean Discovery Program (IODP) RV *JOIDES Resolution*, to obtain elemental concentrations for the calibration, normalization or validation of slabbed core scanning data. For comparison, we use the ED-XRF PANayltical device, which has been used for this purpose in several studies (e.g. Häggi *et al.* 2016; Hahn *et al.* 2016; Voigt *et al.* 2017; Zhang *et al.* 2017). The handheld scanner has the advantage of being small in size and therefore transportable shipboard; however, it is disadvantaged in that both the detector and the source are lower performing than those installed in a conventional XRF device (e.g. the ED-XRF PANayltical device) or a (Avaatech) XRF scanner. We use Avaatech XRF scanning data from IODP Expedition 355 as a case study because the retrieved sediments span a variety of lithologies that allow for a broad applicability of the results (Pandey *et al.* 2016). Our study will lead to a better understanding of the Expedition 355 geochemical data, but also to a more generally applicable notion of the reliability of discrete XRF measurements performed by the handheld analyser shipboard.

2. Materials and methods

2.a. Materials

Sediments were obtained from the Laxmi Basin in the eastern Arabian Sea (16°37.28′ N, 68° 50.33′ E) during IODP Expedition 355 (see Pandey *et al.* 2016 for details). The site is situated in *c.* 3600 m of water depth, *c.* 500 km west of the Indian coast and 800 km south of the modern mouth of the Indus River (Fig. 1). Sediments of both marine and redeposited terrestrial origin of early Miocene age were recovered from this location. The studied lithologies range from nannofossil ooze to interbedded clays, silts and sands interpreted as turbidites deposited in a sheet lobe setting with an Indus River origin. Semi-indurated to indurated claystones, sandstones and chalk can also be found in a massive Miocene mass-transport deposit. An approximate sampling resolution of 1 m was selected to best represent the diversity of lithologies.

2.b. Methods

2.b.1. Conventional XRF

The sample aliquots (*c.* 3 g) were air dried and ground with a mortar and pestle. Single-element concentrations were determined on dispersed sediment powder (< 63 μm) samples by energy-dispersive polarization (EDF-) XRF spectroscopy using a PANalytical ϵpsilon3-XL instrument at the University of Bremen. The instrument is equipped with a rhodium tube, several filters and a SSD5 detector. A calibration based on 24 diverse certified and in-house standard reference materials (e.g. GBW07309, GBW07316, MAG-1; Govindaraju, 1994) was used to quantify elemental counts. Data quality was continuously checked using three reference materials of diverse Ca content. The accuracy of analysis (1%) and the standard deviation (2%) were tested using an internal standard (MAG-1 marine sediment standard) (Govin *et al.* 2012).

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Table 1. Correlation coefficients (R^2) of raw XRF scanning data and results from the handheld analyser compared with quantitative results from conventional XRF analysis for an array of commonly used elemental log-ratios. NA – not applicable

	Avaatech XRF raw data	Handheld device
ln(Al/Ca)	0.88	0.99
ln(Si/Ca)	0.94	0.98
ln(K/Ca)	0.86	0.99
ln(Ti/Ca)	0.80	0.99
ln(Mn/Ca)	0.77	0.99
ln(Fe/Ca)	0.94	0.99
ln(Zn/Ca)	0.73	0.99
ln(Rb/Ca)	0.93	NA
ln(Sr/Ca)	0.78	0.99

2.b.2. Handheld XRF analyser

Dry samples of weight 4–8 g were ground, homogenized, compacted and covered with a thin film (4 μm) of Spectrolene plastic. Measurements were made using the Olympus Delta Premium handheld analyser, a portable ED-XRF equipped with a rhodium anode x-ray tube. Two measurements were made, one at 40 keV emitted for 30 s and the other at 10 keV for 60 s. The manufacturer of the handheld analyser specifies that accuracy is within 20% of the certified values.

2.b.3. Avaatech scanner

Archived halves of IODP Site U1456 and U1457 cores were scanned wet at the IODP Gulf Coast Repository at 2 cm intervals using a third-generation Avaatech XRF core scanner (Kulhanek *et al.* 2018; Lyle *et al.* 2018). Core sections were covered with 4-mm-thick Ultralene film and scanned at 10 kV with a 0.8 mA current and no filter, with a 15 s live time, in order to measure Al, Si, K, Ca, Ti, Mn and Fe contents. They were then scanned at 30 kV,

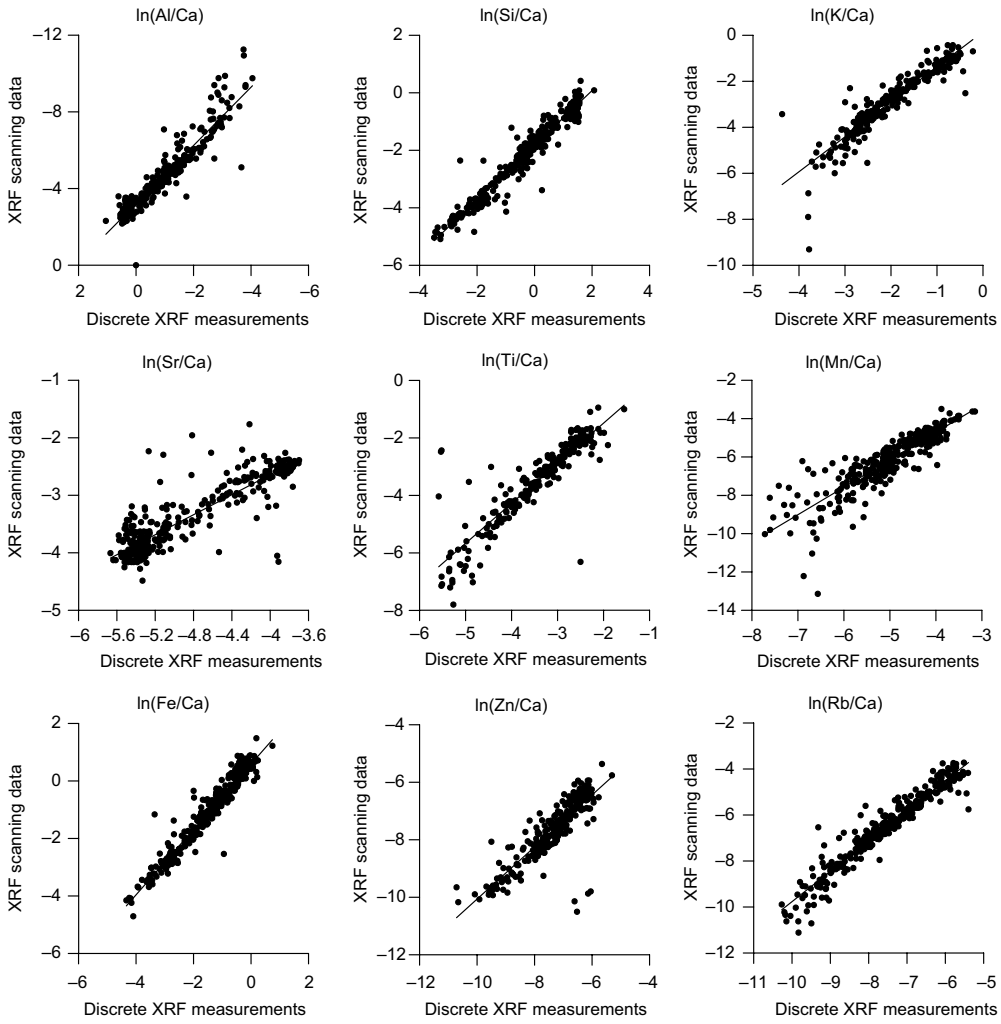

Fig. 2. Cross-plots for an array of commonly used elemental ratios: log-ratios calculated (a) from onshore XRF scanner data v. conventional XRF and (b) from the handheld scanner v. conventional XRF.

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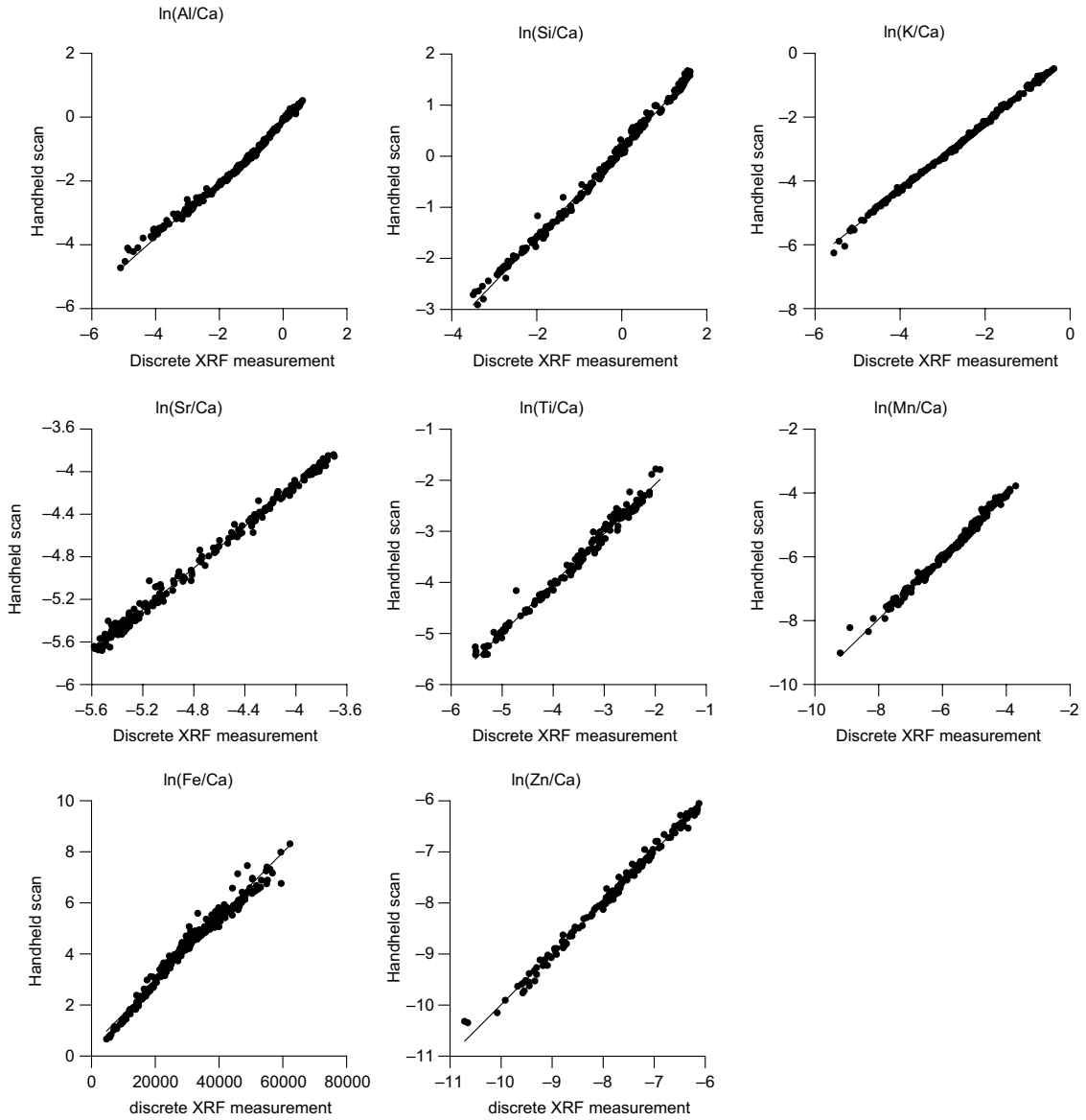

Fig. 2. (*Continued*)

1.0 mA current, 20 s live time with a Pd filter and data are reported for Br, Rb, Sr and Zr. Other raw peak elemental data were collected and reported but were not processed.

3. Results

In order to assess the performance of the shipboard handheld analyser and the onshore XRF scanner, the results are cross-plotted with the reference concentrations derived from the conventional XRF measurements (Fig. 2a, b). Since linearity only applies to log-ratios of concentrations and intensities (Weltje & Tjallingii, 2008), the goodness of fit of the handheld analysis and scanning data is illustrated and quantified in terms of log-ratios. Ca is chosen as the common denominator, as often done in marine studies. Correlation coefficients R^2 are used as indicators of the goodness of fit (Table 1). We report highly significant correlations (R^2: ln(Al/Ca)=0.99, ln(Si/Ca)=0.98, ln(K/Ca)=0.99, ln(Sr/Ca)=0.99, ln(Ti/Ca)=0.99, ln(Mn/Ca)=0.99, ln(Fe/Ca)=0.99 and ln(Zn/Ca)=0.99; Fig. 2b) between measurements made using the handheld device and the conventional XRF. The R^2 values between measurements made using the onshore XRF scanner and the conventional XRF are lower (R^2: ln(Al/Ca)=0.88, ln(Si/Ca)=0.94, ln(K/Ca)=0.86, ln(Sr/Ca)=0.78, ln(Ti/Ca)=0.80, ln(Mn/Ca)=0.77, ln(Fe/Ca)=0.94 and ln(Zn/Ca)=0.73; Fig. 2a). R^2 measures of predicted and measured concentration can be quite high in the presence of significant bias and scatter (cf. Weltje *et al.* 2015). The bias and scatter in the relationship between the XRF scanning and handheld analyser data compared with the conventional measurements (Fig. 2a, b respectively) can be observed in the cross-plots.

4. Discussion

Correlation coefficients of raw XRF scanning data with conventional measurements on discrete samples remain mostly below R^2=0.9, and considerable scatter and bias can be observed in the cross-plots (Fig. 2a). This is due to the differences in the physical properties (e.g. grain size, water content, porosity) of the wet core half and the ground, dry samples. We also compare XRF scanning

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data with conventional measurements on a 5 cc sample taken from the same depth interval; it is therefore possible that offsets are caused by actual differences in the measured material. Despite some scatter and bias observed in the cross-plots (Fig. 2b), the significant correlation between the discrete measurements made by the handheld analyser and the conventional XRF measurements suggest that the new shipboard instrument may be used to calibrate onshore XRF scanning data and obtain a better representation of the actual sediment composition. In general, this is not necessary if the research interest lies in the downcore changes of a specific proxy. Moreover, it is a vital step in studies where fluxes or mass balances are analysed (Weltje *et al.* 2015).

5. Conclusion

This study gives an idea of the data quality of XRF measurements of dried homogenized samples using the shipboard handheld analyser. We suggest that when conventional XRF measurements are not available, these measurements can be used for calibrating XRF scanning results in order to improve the data quality of these high-resolution datasets obtained onshore.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1017/S0016756819000189.

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