Compositional data analysis of Holocene sediments from the West Bengal Sundarbans, India: geochemical proxies for grain-size variability in a delta environment

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ABSTRACT

This paper is part of a special issue of Applied Geochemistry focusing on reliable applications of compositional multivariate statistical methods. This study outlines the application of compositional data analysis (CoDa) to calibration of geochemical data from a set of Holocene sedimentary cores from the Ganges-Brahmaputra (G-B) delta. Over the last two decades, understanding near-continuous records of sedimentary sequences has required the use of core-scanning X-ray fluorescence (XRF) spectrometry, for both terrestrial and marine sedimentary sequences. Initial XRF data are generally unusable in 'raw-format', requiring data processing in order to remove instrument bias, as well as informed sequence interpretation. The applicability of these conventional calibration equations to core-scanning XRF data are further limited by the constraints posed by unknown measurement geometry and specimen homogeneity, as well as matrix effects. Log-ratio based calibration schemes have been developed and applied to clastic sedimentary sequences focusing mainly on energy dispersive-XRF (ED-XRF) core-scanning. This study has applied high resolution core-scanning XRF to Holocene sedimentary sequences from the tidal-dominated Indian Sundarbans, (Ganges-Brahmaputra delta plain). The Log-Ratio Calibration Equation (LRCE) was applied to a sub-set of core-scan and conventional ED-XRF data to quantify elemental composition. This provides a robust calibration scheme using reduced major axis regression of log-ratio transformed geochemical data. The application of these techniques to Holocene sedimentary data offers an improved methodological framework for unravelling Holocene sedimentation patterns.

1. GEOCHEMISTRY OF HOLOCENE SEDIMENTARY ENVIRONMENTS

The composition and physical properties of sediments and sedimentary rocks are for the most part controlled by chemical processes taking place during weathering, transport, and burial (diagenesis) (Bjørlykke, 2010). Thus, understanding the physical properties of sediments and sedimentary rocks requires an understanding of the chemical processes underlying sedimentary deposition. The formation of clastic sediments is a result of the erosion and weathering of source parent rocks. The dissolved fraction of this clastic sediment flows into seas or lakes, with subsequent precipitation as biological or chemical sediments. During transport, grains continue to undergo weathering and abrasion, with resultant sediments potentially undergoing repeated cycles of deposition and erosion prior to final deposition. In order to establish the origin of these sediments, and to gain an understanding of the processes that have operated prior to their deposition, there is a need to analyse their geochemistry. For Holocene sediments (i.e., those deposited within the last 11.7 ka), environmental geochemistry offers a series of approaches to analyse sediment geochemistry. For example, the identification of minerals in soils and sediments usually involves high powered electron microscopy to image crystal forms, and diffraction and vibrational spectroscopy to determine crystallographic structures (Ryan, 2014). Understanding the elemental composition of sediment usually involves the analysis of elemental absorbance, emission, fluorescence or mass (Ryan, 2014). These approaches to elemental analysis fall into two groups: destructive and non-destructive. The former involve the dissolution of minerals into an aqueous solution, whilst the latter are characterised by the analysis of mineral powders (Ryan, 2014). These non-destructive approaches include X-ray fluorescence (XRF) which this study will examine for the purposes of the chemometric calibration of element geochemistry from the Sundarbans, West Bengal, India. This paper provides a background to XRF, XRF core-scanning and calibration through compositional data analysis (CoDa), with a focus on the sediments of the Sundarbans, to demonstrate the usefulness of the techniques. Through the application of CoDa, a number of calibration coefficients can be derived for key proxy geochemical indicators and used to study sedimentary provenance and depositional processes. The objective of the study is to investigate how the application of LRCE & PLS to Holocene sediments of a Delta environment can improve interpretation of geochemical indicators of grain-size variability.

2. BACKGROUND TO THE INDIAN SUNDARBANS

The Sundarbans is one of the largest coastal wetland sites in the world (~ 1 million hectares) covering the western delta of the Ganges and Brahmaputra (G-B) rivers (Fig. 1). The Sundarbans is a complex network of tidal creeks and deltaic islands with most sediment arriving indirectly from the G-B river systems (which drain the Himalayas). The Indian Sundarbans comprises just over 400,000 hectares in the western sector of the G-B delta, and is cross-cut by a number of approximately north-south estuarine channels (Fig. 2). Overall, the G-B delta is generally divided into two sub-systems of fluvially and non-fluvially dominated depositional environments (Fig. 1) (Rogers et al., 2013). The eastern sector of G-B delta comprises the fluvially dominated system, whilst the older abandoned part of the delta, in the west, comprises the non-fluvially dominated environment that is no longer directly linked to the G-B river sources (Fig. 1). This western part of the delta (which underlies the present day Indian Sundarbans) was fluvially abandoned prior to c. 5000 cal yr BP, as the Ganges River migrated eastward towards its present position (Goodbred and Kuehl, 2000). Shoreline progradation in the eastern delta complex following the joining of the Ganges and Brahmaputra rivers in the Meghna Estuary is considered to be fluvially-dominated (Allison, 1998a).

The western extent of the G-B delta is now thought to be undergoing net delta front erosion (Allison, 1998b; Allison et al., 2003), likely reflecting an eroding environment in areas distal to areas of contemporary fluvial-deltaic deposition (Allison (1998b). As the Ganges river shifted from its former western discharge channel (i.e., Hoogly River) to its current position in the east, a series of palaeo-distributary channels were left abandoned (Allison, 1998b). These channels reflect an almost exclusively tidal-driven geomorphology, with sediments and discharge from the main G-B rivers no longer entering the western delta front (Allison, 1998b; Bhattacharyya et al., 2013).

In order to fully explore the processes of sedimentation and the potential sources of variance in sediment composition during the late-Holocene (post Ganges shift), high resolution data analysis is required. Such analysis has never been performed on sedimentary cores from the Sundarbans, and this study represents the first attempt at characterising the sedimentary facies using high-resolution core-scan XRF and establishing variation in sediment deposition.

3. INTRODUCTION TO XRF CORE-SCANNING

The application of X-ray fluorescence (XRF) to geological materials is well established, and recognised as a conventional technique for deriving elemental composition (Ramsey et al., 1995; Jenkins, 1999; De Vries and Vrebos, 2002; Weltje and Tjallingii, 2008). The underlying principle of XRF analysis is that excitation of electrons by incident X-radiation (X-rays) leads to the ejection of electrons from the inner ring of an atomic shell. This ejection results in a vacancy, which is filled by cascading electrons from the outer shells, which, in turn, leads to the emission of energy (Weltje and Tjallingii, 2008). The emitted energy and wavelength spectra are atomically indicative of particular elements, allowing relative abundances of elemental compositions to be derived (Weltje and Tjallingii, 2008).

In the 1990s, the development of a non-destructive core logging technique which applies XRF for the determination of major-element concentrations in split sediment cores was first utilised by the Royal Netherlands Institute for Sea Research (NIOZ) (Jansen et al., 1998). The most advantageous surface for XRF sample determination is homogeneous, dry, and smooth (Jansen et al., 1998). Using split-cores surfaces provides comparable geochemical data to powder samples (Jensen et al., 1998). This is due to the response depths that vary between elements. However, it has been found problematic that larger particles tend to attenuate the fluorescent radiation of elements more than fine particles (Jansen et al., 1998). The 'ideal' homogeneity of a sample occurs when the majority of the material can pass through a 70-mm sieve (Potts, 1987; Jansen et al., 1998), with 'ideal' results derived from silts and clays, rather than from sands (which require careful interpretation of results) (Jansen et al., 1998). The key advantages of XRF core-scanning over conventional geochemical analysis of discrete specimens is that element intensities are obtained directly at the surface of a split sediment core (allowing for the extraction of near-continuous records of element intensities), and the spatial resolution of ED-XRF core-scanning is much higher than conventional discrete sampling destructive methods (Weltje and Tjallingii, 2008). However, one of the main drawbacks of the approach has been the conversion of element intensities measured by ED-XRF core-scanners to element concentrations (Weltje and Tjallingii, 2008). Thus, the results obtained by ED-XRF core-scanning are generally presented in the form of count rates (counts per unit time per unit area), or as ratios of counts, count rates, or intensities of elements (Richter et al., 2006; Rothwell et al., 2006; Thomson et al., 2006; Weltje and Tjallingii, 2008). Within regular calibration schemes, measurement geometry and specimen homogeneity is very poorly constrained due to the inhomogeneity of samples and the irregular surface of a split-core (Weltje and Tjallingii, 2008; Weltje et al., 2015). In addition, in some instances, spatial variations in the thickness of an adhesive pore-water film which forms directly below a protective polyester film covering the split core surface should be considered a further constraining factor on measurement geometry values in the calibration equation (Weltje and Tjallingii, 2008). Due to these poorly constrained and uncontrollable variations in the experimental setup, the measurement geometry becomes an ‘unknown’ in the calibration equation and renders its solution intractable within reasonable limits of uncertainty (Weltje and Tjallingii, 2008). As a result of this uncontrollable variable in the calibration equation, the experimental setup of quantitative XRF core-scanning must incorporate control specimens of known intensities (Weltje and Tjallingii, 2008). However, such calibration approaches often possess inherent intractability which can make the exercise inappropriate for fully quantifying core-scan ED-XRF intensities. As a result, calibration requires an alternative approach within the scope of CoDa in the form of the Log-Ratio Calibration Equation (LRCE): a univariate log-ratio calibration (ULC) approach that combines conventional calibration approaches in ratio form (Weltje et al., 2015).

The primary justification for the application of the LRCE and calibration in thist study is outlined by Bloemsma (2015) in terms of deriving meaningful data. As discussed by Bloemsma (2015) calibration can be considered going from a not very meaningful data set illustrated as 'X' to a meaningful data set 'Y', shown in the Venn diagram Fig. 1a, with a parametric model used to capture this overlap. With calibration, X\Y may be interpreted as noise and Y\X indicates the unpredictable variability in Y which may be interpreted as a shortcoming of X (Bloemsma, 2015). Since the main goal of such a multivariate calibration exercise, in the case of this study that of calibrating geochemistry and using calibrated geochemistry to examine grain-size variability, this is understood through the prediction of Y from X and Y\X has a different significance than X\Y, since calibration is an asymmetric exercise (Bloemsma, 2015). Also when both X and Y are meaningful measures (i.e., quantitatively & compositionally meaningful, and this is illustrated with the LRCE), then it may be possible to parameterise the overlap between X and Y in order to gain more insight into their relationship (Bloemsma, 2015). Thus in the case of Fig. 1a, the unique information (i.e., X\Y and Y\X) is of potential value as both data sets are quantitatively & compositionally meaningful, which is not the case with XRF intensity data (Weltje and Tjallingii, 2008; Bloemsma, 2015).

4. METHODOLOGY

4.1. Quantification of core-scan derived XRF through the LRCE

The LRCE works by using the relationship between elements derived from core-scan and conventional ED-XRF. Core-scan ED-XRF cannot be calibrated in standard equations due to unknown coefficients of such models, as it is not possible to correct for grain-size, water content etc., on a split core log without altering the sample. In principle, calibration of conventional ED-XRF faces the problems of being a closed dataset (i.e., appropriate data for compositional data analysis), but still representative of relative quantities of elements in a sample. However, although core-scan ED-XRF is semi-quantitative (i.e., data are in form of counts per second) there are also relative abundances of elements (i.e., core-scan ED-XRF counts are relative to the sum-total of counts that are present between each element). If a series of points is measured using core-scan ED-XRF and subsequently sub-sampled and processed with conventional ED-XRF, then there are two datasets for the same sample: conventional ED-XRF and core-scan ED-XRF.

The two datasets that are modelled in the LRCE are the core-scan ED-XRF counts (i.e., intensity data) for which the concentration is unknown, and the concentration values (e.g., %, ppm, etc.) dataset from the same set of samples as the intensity data, that form the reference dataset in the calibration procedure. The way in which the LRCE works is that the empirical model coefficients α and β are the log-ratio equivalents of the matrix effect and detection efficiency (this is true in the case of single-element XRF spectrometry), respectively (Weltje and Tjallingii, 2008). The LRCE uses a number of independent models for the binary sub-compositions of a given set of elements to the spectrum of relative XRF intensity data by using major axis regression based on singular value decomposition (SVD) (Weltje and Tjallingii, 2008).

The LRCE can be considered a form of additive log-ratio transformation (alr) (Aitchison, 1982; 1986), whereby the transformation is performed on every linear combination of the sub-compositions examined (Weltje and Tjallingii, 2008). The key principle however is that the calibration functions in log-ratio space and that these are linear. After which, inverse log-ratio transformation and closure, the same data can be expressed in relative intensities against concentrations in binary composition (Weltje and Tjallingii, 2008). Predictions of the most optimum log-ratio denominator are allowed for in this approach which reduces any non-linearity introduced by matrix effects (Weltje and Tjallingii, 2008). Although the calibration process is carried out in log-ratio space it is possible to inverse-transform the results using the inverse-alr function, giving compositional data as output (Weltje and Tjallingii, 2008; Bloemsma, 2010). The LRCE derives multiple element composition estimates from XRF core-scanner output by fitting a series of mutually independent models for binary sub-compositions of elements to the spectrum of (relative) intensities (Weltje and Tjallingii, 2008). The variables are only considered in the form of dimensionless log-ratios, which implies that normalisation prior to analysis is not relevant, and this is consistent with the key tenets of the CoDa approach (Weltje and Tjallingii, 2008). With this in mind, the model is unconstrained from the unit-sum and non-negativity problems imposed by a closed dataset (Weltje and Tallingii, 2008). A full derivation of the LRCE is given in Weltje and Tjallingii (2008) and Weltje et al. (2015).

In this study the prediction of the ED-XRF core-scan sub-composition was carried out according to the following scheme:

- The core-scan intensity ED-XRF data and the percentage (%) concentration PXRF data are examined for the α and β model parameters through major axis regression by SVD (Press et al., 1994).
- Binary sub-compositions between intensity ED-XRF (core-scan) and % concentration PXRF are plotted (i.e., the optimum log-ratio denominator that gives

the best linear fit is derived and a series of alr-transformations are used employing this optimum log-ratio denominator, to derive a linear relationship between % concentration data and intensity data).

- The best fit model for intensity ED-XRF – the ED-XRF data from both the % concentration and predicted concentration are permuted and calculated for each log-ratio pair of linear distances, which derives the best fit for the intensity ED-XRF sub-composition (Weltje and Tjallingii, 2008). This is empirically quantified by taking the median of the squared discrepancies between the predicted and the % concentration geochemical composition with discrepancies calculated through the use of a 'leave-one-out-cross-validation' (LOOCV) (Bloemsma et al., 2012).
- The Aitchison distance between predicted and reference composition is used as the determinant for the optimal denominator element in the sub-composition (i.e., the residual variance between measurements in both the regression and predicted models) (Bloemsma et al., 2012).
- The goodness-of-fit of the optimum log-ratio denominator is derived from the residual variance and the total variance (Weltje and Tjallingii, 2008).
- The relative abundance of each element in the sub-composition from the predicted weights is determined through an inverse alr-transformation, with data expressed in a conventional (closed) form (Weltje and Tjallingii, 2008).

Data from core-scan derived ED-XRF are now calculated based on the relative abundances of the sub-composition. However, to perform any further statistical analysis of the data, they are required to be subjected to further log-ratio transformation (e.g., alr-, centred log-ratio (clr), or isometric log-ratio (ilr) transformation). As the LRCE is founded on the CoDa principles, the use of a common log-ratio denominator is unrestricted and functions as a normalisation approach (Weltje and Tjallingii, 2008). The use of a common log-ratio denominator in the calibration model is generally independent of any environmental or sedimentological considerations (i.e., the log-ratio denominator is independent of any physical reasoning for use in the calibration model) (Weltje and Tjallingii, 2008).

4.3 Joint geochemical and grain-size modelling

Grain-size and geochemical composition of clastic sediments have been found to be highly correlated as a result of the processes that control the generation of sediment from crystalline rocks (Bloemsma et al., 2012). The composition of modern sediments and their grain-size variation is due to four key factors: (i) contributions of mineralogically and texturally distinct grains from a number of divergent sources (ii) rock fragments being mechanically weathered into a finer composition, (iii) labile grains being more susceptible to chemical weathering and (iv) transport associated sorting of compositionally distinct grains (Whitmore et al., 2004).

Bloemsma et al. (2012) have expanded on this relationship between geochemical and modal grain-size variation, as geochemical variation is generally considered to reflect the pervading environmental conditions of sediment genesis. In terms of relating grain-size variation to bulk geochemical composition, it may be postulated in terms of the chemical weathering of crystalline rocks, in which the release of unstable elements as solutes takes place, whereas elements such as Al remain in the solid phase (Nesbitt and Young, 1984; Bloemsma et al., 2012).

The development of the PLS modelling approach for joint geochemical and grain-size relationships is premised on whether in a series of sediment samples derived from a source area that, over time the extent of chemical weathering was static, then the bulk geochemical variation may be attributed to; selective entrainment, transport, and deposition (Bloemsma et al., 2012). In a sedimentological context, such a one-to-one relationship between grain-size and geochemistry is rare with geochemical variability being a function of: chemical weathering; hydraulic/aerodynamic sorting; mixing; and diagenesis (Bloemsma et al., 2012). In these regards, the variability between grain-size and geochemistry is considered as being what is shared and what is unshared, in which case if the former is removed from the data and the residuals calculated, then unknown trends such as provenance may be distinguished as a result (Bloemsma et al., 2012).

The Partial Least Squares (PLS) modelling approach was developed by Bloemsma et al. (2012) and has two key assumptions: (1) that there is a monotonic relationship between grain-size and geochemical composition, and; (2) grain-size distributions and geochemical compositions are both compositional in nature, necessitating the use of models in log-ratio space (Bloemsma et al., 2012).

Effectively, geochemical data are considered to contain two parts, with one part that is correlated with grain-size, and a second part which varies independently from grain-size (Bloemsma et al., 2012). The model is carried out by finding a basis for which maximizes the geochemical variance explained by the grain-size (Bloemsma et al., 2012). If then, the mean is subtracted from these geochemical and grain-size data matrices, the values of the residuals are provided (Bloemsma et al., 2012). If there is significantly high correlation found in the projection of both datasets onto the basis vectors, then these are considered to be the ‘shared signals’ (Bloemsma et al., 2012). The residual signal are then calculated by subtraction of the shared signals from the raw data, giving the variability unique to each dataset (Bloemsma et al., 2012). The number of uncorrelated (i.e., orthogonal) components is a hyperparameter that may vary between zero and N-1, with N being the minimum number of variables (e.g., grain-size bins or chemical elements) (Bloemsma et al., 2012). The implementation of the PLS modelling approach follows on from the work of Bloemsma et al. (2012) in which:

- clr-transformation of both the geochemical and grain-size data.
- Detection of replicate samples using the depth attribute.
- Derive the basis Q in $\mathbb{R}^D$ that can maximise the geochemical variance explained by the grain size through the Partial Least Squares (PLS) (Wold et al., 1982).
- Fit a model onto data matrices X^* (where X = L grain size classes) and Y^* (where Y = D variables).
- Subtract the mean from the X^* and Y^* to derive $X_c{}^*$ and $Y_c{}^*$ through the SIMPLS algorithm (de Jong, 1993) and calculate the PLS matrix decomposition.
- Orthogonalise the bases (i.e., the loadings) through SVD with the score matrices recalculated.
- Test the significance of correlation between geochemistry and grain-size distribution scores on the k-th basis vector using the Kendall and Stuart (1973) test.
- Derive *r* for any order of k, where *r* is the Pearson’s correlation coefficient between the k-th column and the previously orthogonalised bases.
- With a confidence level of α and $p = 1- \alpha$, the first k of shared signals is removed if for the k the Kendall and Stuart (1973) criterion is established.

- The model is applied to all grain-size and geochemical data as the transpose of the bases are orthonormal, thus the scores of all observed grain-size distributions and geochemical compositions may then be derived by the matrix product.
- Reduced-rank approximation is used to derive the shared signal in both the grain-size distributions (GSDs) and geochemistry datasets.
- The residuals are calculated and subtracted from the common variability for both the GSDs and geochemistry input data.
- The mean is added such that the residual signals centre around the mean of their corresponding raw data matrix as result (Bloemsma et al., 2012).

Thus, through this algorithm implementation it may be possible to derive the grain-size dependent and independent geochemical components from the dataset. It is not the objective of this study to outline the PLS modelling approach and the reader is referred to Bloemsma (2010), Bloemsma et al. (2012), and Bloemsma (2015) publications for a more exhaustive discussion. However, it is only through utilising the calibrated geochemical data presented here that proxy information for environmental change may be derived, in this case for grain-size variability and the depositional environment for the Dhanchi Island site. Grain-size data was gathered from the Dhanchi Island core samples prior to PXRF analysis, following the methodology of Flood et al. (2015).

4.3. Data acquisition: Grain-size analysis

GSDs were analysed following Flood et al. (2015) using a MalvernMastersizer 2000 instrument. Data were aggregated into quarter phi intervals (φ scale) over the range of 0.02 – 2000 μm, following collection of measurements from the instrument. The centred log-ratio transformation (clr-transformation) was implemented on all grain-size classes with any zero-valued bins of quarter phi intervals removed (i.e., where entire column vectors consisted of 0 row values). Classes of the grain-size distribution containing a zero in any of the observations (i.e., columns where only some of the row values are > 0), were amalgamated and the arithmetic mean calculated (cf. Bloemsma et al., 2012). This process was carried out on the 62.50 μm to 2000 μm fraction (i.e., 4.00 φ to –1.00 φ) for the Dhanchi Island GSD data.

4.3. Data acquisition: ITRAX™ core-scanning

Coring was carried out at Dhanchi, Bonnie Camp, and Sajnekhali in November 2011 (sites shown in Fig. 2). Three cores (one from each site) were extracted using a motor driven percussion coring device. These cores were analysed using the ITRAX™ core-scanner (Cox Analytical Systems, Mölndal, Sweden) housed at the School of Geography, University College Dublin. This is a non-destructive analytical approach which provides ED-XRF elemental profiles along with optical imagery and micro-density (X-radiography) information (Croudace et al., 2006). The geochemical data were acquired through an ED-XRF spectrometer consisting of a molybdenum cathode (Croudace et al., 2006). The voltage and current of the X-ray source was the 3kW Mo tube set to 30 kV and 50 mA respectively, with a measurement step-size of 300 μm and exposure time of 16 seconds. The latter setting was employed for expedience, to provide high-resolution scanning of all the cores (c. 25 m of material length). The element data (table of elements shown in Table 1) were processed using fitting procedures in the Q-Spec spectral analysis package in order to extract the individual elemental intensities from the spectra output (Croudace et al., 2006). Operation of the software involved selecting elements to be extracted from the XRF spectra, with any spurious or unnecessary elemental choices or incorrect fitting parameters adjusted post hoc through a batch-controlled post-processing of the spectra (Croudace et al., 2006). Invalid readings were noted and not employed in any post-hoc processing (i.e., invalid readings were not used in the LRCE). The scan-lengths from each of the cores were 666 cm for Dhanchi-2 (hole-depth of 728 cm), 923.2 cm for Bonnie Camp (hole-depth of 1022 cm), and 639.4 cm for Sajnekhali Island (hole-depth of 791 cm). The total number of readings from each core were Dhanchi-2 with n = 22,129 valid readings from a total output of 22,201 readings (72 invalid readings), Bonnie Camp with n = 30,517 valid readings from a total output of 30,773 readings (256 invalid readings), and Sajnekhali with n = 23,822 valid readings from a total output of 24,201 (379 invalid readings).

The LRCE was applied to the global discrete sampling dataset collected (n=568) with the model then unfolded onto the elemental data from the high-resolution ITRAX™ ED-XRF (n=76,468). The alpha (α) and beta (β) slope and intercept regression parameters derived from the LRCE were used to predict the relative concentration of a sub-composition of elements (see 5 Results of this study), for this higher resolution dataset.

4.4. Data acquisition for calibration: portable X-ray fluorescence spectrometry of reference samples

Data acquisition using ED-XRF was undertaken using a Bruker S1 TURBO SD portable X-ray fluorescence (PXRF) spectrometer (Bruker Corporation, Massachusetts, USA) consisting of a 10 mm X-Flash® SDD Peltier-cooled detector with a 4-watt (W) X-ray tube consisting of an Ag target and a maximum voltage of 40kV. Analysis was carried out on discrete samples collected from the Dhanchi-2, Bonnie Camp and Sajnekhali Island cores. In order to ascertain major and trace element composition, the elemental suite was generated using two analytical settings for each sample analysed. Major elements were acquired using a vacuum-pumped, low-energy and high current setting of 15kV and 55μA instrument setting with no filter. The vacuum-pump was used to remove air from between the sampling window and the detector and allowed for improved analysis of the material, in particular increased sensitivity to light major elements, below and including iron (Fe). The other analytical setting was used for trace element analysis and acquired without a vacuum-pump and employed a yellow filter (Ti and Al), high-energy instrument setting of 40kV and 19.60μA. With these instrument settings, elemental data are acquired for heavier elements with little sensitivity for those elements below calcium (Ca). The filter used consists of a 0.001" Ti and 0.012" Al and is already present in the instrument. Using the portable XRF, high and low energy data were acquired for each sample. Unknown samples from the Sundarbans were each measured for 16 seconds, with a set of 22 international geochemical reference standards (shown in Table 1) measured for 120 seconds, this was carried out so as to develop a robust calibration line for the PXRF instrument specific calibration. Since the Bruker software is proprietary, a full disclosure and discussion of the calibration routine is not possible in this study (cf. Rowe et al., 2012).

The calibration models used in this research depend on the estimation of error of the covariance matrices, where the magnitude of the uncertainty in the measured variables is accounted for (Bloemsma 2015; Weltje et al., 2015). With this in mind, due to lack of *a priori* knowledge concerning these uncertainties, replicated analysis is required in order to estimate these uncertainties (Bloemsma 2015). Repeated measurements were carried out on a total of 9 samples (3 per core) with 30 additional measurements on each of these samples (n = 270 repeated measurements in total) using the portable ED-XRF.

4.5. Data acquisition – portable ED-XRF spectra calibration

The raw spectra obtained from the Bruker S1 TURBO SD portable ED-XRF require a calibration to convert the data into quantitative weight percentages. The calibration for the portable ED-XRF unit is matrix-specific, so a calibration for major and trace elements of sediments and soils was developed using a suite of 22 reference materials. The calibration of the ED-XRF spectra was carried out using the Bruker AXS calibration software S1CalProcess Version 2.2.32 with the reference concentrations for the low and high energy calibrations produced for each element being evaluated against the concentration of the element as derived from the slope and baseline corrected peak heights. Linear regression analysis of the elemental concentrations quoted by the manufacturers for the international geochemical reference standards are examined along with elemental composition derived from the Bruker AXS S1CalProcess.

5. RESULTS

The results presented in this section reflect the data processing and outline how the LRCE was applied to the integrated core-scan ED-XRF data along with the discrete samples analyzed using conventional ED-XRF and grain-size analysis. The LRCE model depends on comparability of the intensity measured elemental composition (i.e., data from the core-scan ITRAX™ data) along with the % elemental composition (i.e., conventional XRF data) a sub-composition of the elements were examined for these modelling purposes.

The LRCE model was applied to all of the integrated core-scan samples from the cores. These input data consisted of the total sample population from the three cores (Dhanchi, n = 163; Bonnie Camp, n = 228; Sajnekhali, n = 176; with a total sample population, n = 567) with fifteen outliers removed. These outliers were removed as they deviated substantially from the general spread of data points and would bias the prediction of the model. Fig. 3 shows the cross plot of results from the closed, inverse transformed sub-composition of elements with calcium (Ca), iron (Fe), and potassium (K) depicted in the top row (a-c) and rubidium (Rb), titanium (Ti), and zirconium (Zr) shown in the bottom row (d-f). The conventional weighted (reference) ED-XRF composition is on the x-axis with the integrated ITRAX™ derived intensity (predicted) ED-XRF on the y-axis.

The lack of a full suite of elemental output is due to the fact that the majority of these elements correspond to the lower energy, and thus atomically lighter, end of the spectrum with poorer excitation efficiency and detection. Data derived from these lighter elements are more difficult to calibrate as there tend to be more peak-overlaps. Finally, as the penetration depth of ED-XRF for the light elements (e.g., Si, Al etc.,) tends to be ~ hundreds of μm, there is a risk of not actually measuring sediment (i.e., with core scan derived ED-XRF, it is possible to measure water pooled under the Mylar® polyester film). The efficacy of the LRCE is illustrated in Fig. 3, where data appears to be well spread along the model, with calcium, iron and titanium representing the best spread of data points. There appears to be some bias in the potassium modelled output where a number of sample points deviate from the model. This bias may be attributed to the measurement of potassium in ED-XRF (both core-scan and conventionally derived ED-XRF), where potassium appears close to calcium and in some cases there may be some peak overlap if the count time is low (Bloemsma 2015). However, given that the potassium is spread along the x-axis of the known weighted elemental composition, such an artefact of analysis may be attributed to the conventional ED-XRF. Rubidium data points appear to be spread across the regression and derive a reduced correlation. There is also a clustering of the data points from the regression model applied to zirconium.

The calibration coefficients, α and β, for the LRCE model are shown in Table 2 and Table 3, respectively. These coefficients can be considered to reflect the matrix effect (i.e., scattering, absorption and enhancement effects introduced during measurement, caused by the presence of other elements) and detection efficiency (i.e., sensitivity of the ED-XRF data after pre-processing) in a single-element from ED-XRF derived output (Weltje and Tjallingii, 2008). The LRCE removes the specimen effects, which relate to the deviations of measurement from ideal conditions, however not all of these effects are fully removed (Weltje and Tjallingii, 2008). The α and β regression parameters reflect physical parameters such as grain-size, core-surface elevation, and water content (Weltje and Tjallingii, 2008), and are the main criteria used in the LRCE for calculating the best model fit for each of the elements (i.e., what is the 'best' log-ratio denominator for each of the elements in the dataset) (Weltje and Tjallingii, 2008).

In Table 4 and Table 5 the residual variances of the regression and prediction of the dataset used in the LRCE are shown. The residual variance refers to noise as it does not correlate with the compositional variations in a specimen (Bloemsma, 2010). This variance is quantified by taking a clr-transformation of a set of measurements from the same core-locations (i.e., replicate measurements) with the Euclidean distance between the observations measured in order to calculate error estimation (Bloemsma, 2010). Thus, the residual variance effectively quantifies the level of relative ‘noise’ that may be derived from the regression and prediction. The residual variance for both the regression and prediction reveal that calcium accounts for the most consistent variance.

The α and β parameters from the log-ratio transformed dataset shown in Fig. 4 (a-e) with Ca found to be the best fitting denominator for Fe, K, Rb, Ti, and Zr. The R^2 values of goodness-of-fit in the LRCE denominator are shown in Table 6. The non-linearity found in the original back-transformed data (Fig. 3, Rb and Zr) along with bias (Fig. 3, K) is now removed. Ca is found to be the optimal denominator using the Aitchison distance between the predicted and reference composition. Table 4 shows the median variances and Table 5 depicts the 95% confidence limits corresponding to these residual variances. The non-linearity introduced by the matrix effects has been greatly reduced with log-ratio intensities now distributed linearly with the log-ratio relative concentration (cf. Weltje and Tjallingii, 2008). As a consequence, the elemental concentration can now be derived from any of the intensity observations based on the linear model (black line intersecting the point clouds in Fig. 4) (cf. Weltje and Tjallingii, 2008).

Using the residual variance of the prediction and the regression (Table 4 and Table 5), the sub-composition closure of the high-resolution dataset from the ITRAX™ ED-XRF has been estimated from the lower resolution calibration dataset. As a result, it is now possible, through the calibrated intensity derived ED-XRF with the weighted ED-XRF, to interpolate the high resolution intensity ED-XRF.

Shown in Fig. 5a is the PLS model output for the Dhanchi Island core with the PLS-coefficients of c. 0.3 for grain-size depicted by negative values corresponding to the coarse-clay to coarse-silt size fractions. Positive PLS coefficients of c. +0.3 are indicated by coarse-silt to sand sized. The PLS-scores for grain-size indicate positive score fluctuations appear to correspond to coarser sediment coefficients with negative scores found to correspond to that of finer sediment coefficients. The PLS-coefficients for geochemistry (Fig. 5b) show positive values for zirconium and calcium, with the highest negative values found for iron, potassium, rubidium, and titanium. Calcium and zirconium indicate the highest PLS coefficients at c. 0.4 and 0.3 respectively. In contrast, iron, potassium, rubidium and titanium are negatively correlated with PLS-coefficient values of between -0.3 and -0.4. The PLS-scores show a decline in grain-size with a concomitant decline in PLS-scores for geochemistry (calcium and zirconium) (Fig. 5c & d). Furthermore there is an apparent trend found in the PLS-scores for grain-size, firstly a trend consisting of a form of oscillation taking place from c. 787 cm to 491 cm that is superseded by a second trend of PLS-score decline. These trends in light of the PLS-scores may be interpreted as a form of grain-size variability, in which oscillations in grain-size appear to correlate with oscillation in zirconium, while a decline in zirconium is reflected in a decline in grain-size. When the PLS-data are considered along with the PC1-scores and PC1-coefficients for residual geochemistry (Fig. 5e & f), it is evident that throughout the Dhanchi Island core there is a consistent decline of calcium taking place. This can be discerned through the PC1-coefficients for residual geochemistry which depict positive values driven most strongly by calcium at c. 0.7 with negative values being concomitantly driven by zirconium at just over -0.6. Furthermore, negative PC1-coefficient values may be discerned for the rubidium and titanium compositions, with potassium and iron represented by positive coefficient values.

6. DISCUSSION

6.1 Reconstructing Late Holocene environmental change from sediments in the West Bengal Sundarbans, India

The objective of the study is to investigate how the application of LRCE & PLS to Holocene sediments of a Delta environment can improve interpretation of geochemical indicators of grain-size variability. The geochemistry derived from the application of the LRCE to Holocene sediments in the present study illustrates the efficacy of these subset of elements as useful indicators of environmental change. The LRCE shows that, in the case of the Sundarbans, K, Rb, Fe, Ti, Zr, and Ca can be calibrated, with Ca found to be the best-fit denominator. The utility of these elements for interpreting environmental change within the Sundarbans can be explored by examining the Dhanchi Island core and how these calibrated data may be employed in order to interpret the depositional environment through grain-size variability. However, in order to understand the data generated in this study, there is a requirement to place into the context the key aspects of deltaic environments and how these aid in the interpretation of facies variability derived through the LRCE & PLS models for the case study of the Dhanchi Island core. The role of this discussion is to outline a potential set of circumstances that may characterise a depositional model for this particular site in the Sundarbans.

6.2 Contextualising deltaic environments: implications for understanding the Sundarbans

In order to develop any interpretation of facies variability through geochemistry and grain-size analysis, illustrated in this study, an exposition is required on generalised ‘boundary conditions’ in deltaic environments. This is not an exhaustive discussion on every aspect of deltaic environments, but rather the principal aspects of these boundary conditions for understanding the Sundarbans and the results from the Dhanchi Island core.

Through high sediment availability with variability in ocean hydrodynamics and localised coastal progradation, river deltas develop as coastal features characterised as 'protuberances' (cf. Elliott, 1986; Wright, 1978; Hanebuth et al. 2012). Attempts to classify deltas into a ternary diagram representing endmembers of fluvial, tidal, and wave dominances have failed to capture the variability represented by the fact that many deltas do not fall into a singular regime classification (Hanebuth et al., 2012). There is a rather dynamic relationship in terms of laterally graded intensity between sediment discharge along defined channels counterbalanced with the influence of tides, waves and longshore currents (Hanebuth et al., 2012). In these regards, the differentiation of external forces in this manner leads to more diverse organisation of deltaic environments that are more locally segmented and temporally complex (Hanebuth et al., 2012). With this, the focus of deltaic research should consider the individual segments of a delta as opposed to the entire delta which transitions through different classification schemes (Ta et al., 2005; Yoshida et al., 2007; Hanebuth et al., 2012). This study attempts to apply this approach to considering the Sundarbans in this manner of localised variability in terms of sedimentary deposition as opposed to applying a generalised model over the entirety of the Ganges-Brahmaputra delta. Modern Holocene delta development has been demonstrated to have commenced between 9 and 7.5 cal ka BP associated with the deceleration of sea-level rise approximately 1 ka prior to the mid-Holocene sea level maximum (Stanley and Warne, 1994). It has been proposed however, that during this initial stage of delta growth deposits are, with the exception of the sedimentary facies succession filling central fluvial valley, not of a deltaic character but have formed under a strong tidal influence, comprised mainly of tidal flats, mangrove swamps and salt marshes (e.g., Tanabe et al., 2006) (Hanebuth et al., 2012). Although this proposition stands in contrast to the generally held concept of supply-dominated, progradational environments, the observation does hold some potential insight into the conditions that characterise the late Holocene (< c. 4,000 cal yr BP) environment of the Sundarbans.

In order to better understand geochemical and grain-size variability, and the implications that these have for teasing-out aspects of environmental change in the Sundarbans, some general aspects of sediment supply need to be considered. As discussed by Gao and Collins (2014) it has been found that the occurrence of coastal-shelf deposits are indicative of the provenance of sediment supply. In their argument, it is put forward that if the supply of sediment is 'small', then the seabed may consist only of bedrock, relict sediment or reworked materials (Gao and Collins, 2014). This condition is known as being "sediment starved" (Gao and Collins, 2014, pp. 270). If there is an abundant supply of sediment, then thick Holocene deposits with a large areal coverage may occur (Gao and Collins, 2014). Sediment supply is principally provided by rivers, derived from catchment erosion with the amount of available sediment dependent on the catchment characteristics (Milliman and Syvitski, 1992; Syvitski et al., 2003; Gao and Collins, 2014). Sediment supply, in terms of rivers at least, is dependent upon geographical variability at the global scale (Milliman and Farnsworth, 2011). An example of this can be seen in monsoon-controlled southeastern Asia, where the warm climate favours physical and chemical weathering and, therefore, generates a high sediment yield with intense rainfall that results in high river discharges (Liu et al., 2000; Gao and Collins, 2014). Thus, as a result of these conditions, southeastern Asia in these regards has the highest terrestrial denudation rates in the world with the majority of sediment input into oceans derived from this region (Milliman and Farnsworth, 2011; Gao and Collins, 2014). In terms of erosion at the coastal zone, more than half of all coastlines are undergoing erosion with sediments deposited in areas adjacent to the shoreline & littoral zone with the transport offshore of the remaining sediments (Bird, 1984; Gao and Collins, 2014). Combining these general aspects of sediment supply to understanding deltaic environments may be best considered when looking at grain-size variability.

Grain-size compositions examined with an experimental microdelta by Endo et al. (1996) have found that these compositions are strongly controlled by the textural composition of source sand, analogous to a real-world river system. These results indicate that textural composition of a depositional system is primarily determined by the textural composition of sediment input (Swift et al., 1971; Liu et al., 2000). With this the observed grain-size variability are a result of the transport and deposition processes of sediment delivery to a system, with subsequent reworking of sediments already deposited (Liu et al., 2000). Thus, the nature and amount of sediment input can therefore determine the textural characteristics of a depositional system in receipt of these sediments (Liu et al., 2000). Therefore, the textural characteristics of a marine depositional system, its sources, and processes by which delivery of sediments takes place and is deposited, may be understood as being highly connected (Liu et al., 2000). An example of this connected nature of sediments in depositional environments may be seen with the distributional patterns of individual grain-sizes on a wave-dominated shoreface by Liu and Zarillo (1990). It was found that both influence of source and the influence of hydrodynamics that have reworked and redistributed sediments during transport were discerned (Liu and Zarillo, 1990). Such unique grain-size distributions therefore highlight the different responses to processes of hydrodynamics on the shoreface and how these may be utilised in order to examine how sediments respond to hydrodynamic processes (Liu and Zarillo, 1989). It is therefore now possible to fully consider the data from the Dhanchi Island core and what may be gleaned from the geochemical and grain size variability found and how these fit into the present understanding of deltaic environments.

6.3 Use of Sundarbans elemental log-ratios as environmental proxies

The calcium variability in the Dhanchi Island sediments may therefore be understood as declining from a depth of approximately 500 cm to the core surface. This decline in calcium with the subsequent increase in zirconium, titanium, potassium, and rubidium composition may be interpreted as terrestrial sediment flux with diminished marine deposition. This calcium signal is pervasive in the four log-ratio pairs and does not appear to lend to the interpretation of grain size variability per se in the depositional characteristics of the Dhanchi Island site. It may be discernible that terrestrial sediment flux appears to be uncorrelated with calcium, thus, sediment provenance for the fine and coarse sediment appears to be independent of a marine or a tidally driven source.

In this context, the Dhanchi Island sediments exhibit a predisposition to terrigenous sediments, in agreement with Rogers et al. (2013) that geographical distance is not necessarily a limiting factor on sedimentation taking place (assuming the predominance of terrigenous sediment in the Dhanchi Island sediments). One of the key trends in all of these log-ratio pairs with calcium as the denominator, is that there appears to be a nonstationarity signal present, in which although the variability between log-ratio values appears to indicate some form of oscillation throughout the sequence, in each log-ratio pair however the overall behaviour as noted is an increase in the numerator value at the expense of the calcium denominator (Fig. 6). Non-stationary signals, in the case of these log-ratio pairs, implies that the depositional processes taking place are drifting in time, in particular the increase in zirconium relative to calcium may be derived from the aggradation of the island surface.

Grain size variation delivered by rivers has also been found to become finer in the seaward direction and this is more pronounced in an aggradational environment (Dalrymple and Choi, 2007). However, given that this part of the Sundarbans is an ‘abandoned’ deltaic-estuarine site, it may be classed as being part of the ‘middle estuary’ which occupies effectively the same environmental location within an estuary as active delta-plain distributary channels within a delta (Dalrymple and Choi, 2007). In terms of a deltaic system such an abandoned set of distributary channels are thought of as estuarine due to the fact that they do not carry as much river discharge and also experience reworking by tidal currents (Dalrymple, 2006; Dalrymple and Choi, 2007). These areas experience net landward transportation of sediment from the seaward margin, which is contrast to that of active delta channels that experience a reverse (Dalrymple and Choi, 2007). It has also been noted that in terms of evidence for river action in the physical structures present, there tends to be almost no evidence for seasonality in fluvial discharge (Dalrymple and Choi, 2007). Along with this, there tends to be a case in abandoned channels of such delta plain estuaries that sediments from somewhat older distributary-mouth-bar deposits experience reworking within these systems (Dalrymple and Choi, 2007). The overarching presence of silt and clay would suggest a muddy depositional environment.

As identified by Goodbred and Saito (2011) such environments are generally made of what are termed ‘sand-mud alterations’ consisting of flaser, lenticular and wavy laminations or bedding. Furthermore, such tidal flat environments are composed of bidirectional sedimentary structures such as sand-layer stacking, cross-laminations, mud-drapes, and potentially, double mud-drapes (Goodbred and Saito, 2011). These depositional features are usually indicative of tidal depositional constraints on a sedimentary system (Goodbred and Saito, 2011). In this regard, although such sedimentary structures are difficult to discern from a discrete number of grain size samples, it is possible to elucidate such a depositional environment, potentially through high-resolution core-scanning as shown in Fig. 6. However, without having a robust chronology, it is still difficult to discern such tidal sedimentary structures. In a study of grain size characteristics of tidal-bore deposition in the Qiantang Estuary by Fan et al. (2014), GSDs are found to be composed of a principal coarse and secondary fine component. The modal size, sorting, and proportions found in these coarse and fine components are ascribed to different depositional processes on the tidal flats (Fan et al., 2014). Sandy laminae were found to be well sorted compared to those of muddy laminae, reflecting disparate depositional stages of waning flow and slack tides (Fan et al., 2014).

The dominant, upward-fining in GSDs as shown in Fig. 5 & 6 may be attributed to what Dalrymple et al. (1992) refer to as ‘lateral shifting of channel bedforms’. Such lateral shifting leads to this trend in grain size as currents tend to be higher at greater depths and weaker when over bar crests (Dalrymple et al., 1992). These fining-up sequences comprising muddy tidal flats may actually cap subtidal sand ridges (Wells, 1995). A similar model of facies succession has been proposed by Goodbred and Saito (2011), where the migration of tidal channels and creeks across tidal flats, contribute to this fining up facies succession. The clay fraction elucidated from the first and second principal components may represent the mud-drapes and fluid-muds which may be attributed to slack water or poor water flows (cf. Wells, 1995).

Sediment that may have terrigenous origins may also be indicative of a fining-up, when considered with the Ca decline throughout the sequence. The element profile of Ca in sedimentary depositional environments is generally considered to reflect the predominant abundance of biogenic carbonates ($CaCO_3$) in marine sediments (Arz et al., 1998; Tjallingii, 2007; Tjallingii et al., 2010). There is known to be poor preservation of of $CaCO_3$ in the Sundarbans especially in the progradational lower delta plain sequence relative to the marsh and mangrove deposits of other deltaic systems around the world (see Allison et al., 2003). In the case of the Sundarbans however, the presence of Ca may be interpreted as indicative of the solubility of Ca in water. Since Ca has a low ionic potential it is unable to break the bonds in the water molecule and remains in solution as a hydrated cation (Bjørlykke, 2010). The result of this is that the Ca ion is surrounded by water molecules with the negative dipole towards the Ca cation (Bjørlykke, 2010). As water molecules have a strong dipole this causes them to be attracted to cations with the resulting cation, in this case, Ca becoming hydrated (Bjørlykke, 2010). This small cation is therefore less likely to be adsorbed to clay minerals that are negatively charged (Bjørlykke, 2010). Finally, Al has been known to replace Ca as the dominant exchangeable cation where the acidity of soil increases, thus, high Al concentrations are usually correlated with reduced

Ca concentrations (Salminen et al., 2005). In this regard, Ca may be interpreted as a proxy for marine flux in the Sundarbans sedimentary environment; given the ionic potential and physical properties outlined.

There appears to be greater agreement found between sediment provenance proposed by Rogers et al. (2013) and sediment depositional model outlined here in terms of distal sediment transport from fluvial sources, reflected in the log-ratio pairs discussed. The non-stationary signals found in elemental log-ratio pairs may be attributed to tidal processes in the manner described by Dalrymple and Choi (2007). However, what is further elucidated through the joint geochemical and grain-size analysis approach is tha the Sundarbans, through the Dhanchi Island example presented in this study reflects a locally segmented & temporally complex system that does not fall into a singular regime classification given the complex relationship that is exhibited by tidal variability (Hanebuth et al., 2012). Furthermore, although sediments may undergo reworking, what has been found is a predominantly terrestrial source for sediments present in the Sundarbans; this does not fit closely with the implication that the Sundarbans are ‘sediment starved’ as outlined by Gao and Collins (2014). Rather, geographically (Milliman and Farnsworth, 2011) and climatically (Liu et al., 2000; Gao and Collins, 2014) variable processes operate in producing a complex depositional environment. Sedimentary facies variability in the form of tidal processes can only be inferred in this study by the diminished calcium variability found. These tidal processes do not appear to operate in isolation and may be coupled to some form of monsoonal variability in the manner proposed by Liu et al. (2000) for Asia and by Rogers et al. (2013) more specifically applied to the Sundarbans.

The utility of these calibrated geochemical proxies from the Sundarbans is illustrated in Fig. 6 from the Dhanchi Island core. Through plotting the log-ratio pairs there appears to be some oscillating trend throughout the core, in particular with log-transformed Zr and Rb (see Fig. 5). There is a steady decline in Zr nearer to the top of the core (from a depth of 450 cm to the core surface). This indicates a decline in zirconium, and potentially an increase in rubidium. It is only through CoDa however that such a trend can be illustrated in the first place as ratios by themselves possess the undesirable property of asymmetry, meaning that conclusions based on evaluation of the ratio of two elements (e.g., A/B), cannot be directly translated into equivalent statements about B/A (Weltje, 2012; Weltje et al., 2015). Taking this approach further, the Rb and K log-transformed data shown in Fig. 5, appear to reflect the trend found in rubidium and zirconium; with an oscillating trend throughout the core. However, there does not appear to be any discernible increase or decrease in rubidium up core, with the log-ratio data remaining somewhat unvarying.

The overarching trend would suggest a strong relationship between zirconium and coarse grained sediment, as these sites are considered to reflect upward fining sequences (e.g., Allison et al., 2003; Flood et al., 2015). In particular the trend consists of coarse/very coarse-silt and sand with a concomitant relationship between coarse clay and medium/coarse-silt for rubidium. Furthermore, the variability of rubidium with potassium would suggest an unvarying relationship between the fine-grained sediments. This might indicate that fine-grained provenance is tied to rubidium and potassium, with coarse grained sediment provenance strongly linked to zirconium. Ca geochemistry (shown in Fig. 5) may be linked to some external environmental control, such as sea-level or tidal inundation as calcium is generally only present in liquid form in the marine environment. Ca appears to correlate negatively with Zr, Ti, K, and Rb in the Dhanchi Island core. This decline in calcium with concomitant increases in Zr, Ti, K, and Rb (Fig. 5) may be interpreted as reflecting terrestrial derived sediment flux with diminished marine or carbonate deposition (or at least a marine source of variability). Terrestrial sediment flux therefore appears to be uncorrelated with Ca, implying that sediment provenance is independent of a marine or tidally driven source.

7. CONCLUSION

Through CoDa it has been possible to calibrate core-scan derived XRF data, and produce useful elemental proxies for analysing a clastic sedimentary environment. When using the LRCE calibration model coefficients to examine such clastic sedimentary environments in the Indian Sundarbans quantified data outputs are possible, and combined with grain-size data a broader understanding of the depositional environment is possible. The lack of a full elemental suite, attributed to a poorer linear fit between weighted concentration and intensity data, does not detract from the approach to XRF core-scan calibration. The elements that have been calibrated through the LRCE in this study may be used to demonstrate provenance (e.g., Zr, Rb, Ti, etc.) and processes of sedimentation (e.g., Ca) in this area of the G-B delta. Ca has been found to be the optimum log-ratio denominator, and when examined in a log-ratio framework, it may be used to distinguish between marine-terrestrial sediment fluxes in a high-resolution XRF dataset. Future research should focus on building a more constrained calibration model for the G-B delta, with more sedimentary cores from different facies sequences and employing other geochemical analyses tools (e.g., ICP-OES/MS). The LRCE & PLS approaches applied in this study for calibration of sediments represent a robust application of the principles of CoDa, and it is recommended that future studies in the G-B delta and other delta environments should seek to refine core-scanning XRF and grain-size analysis in light of the approaches outlined in this study.

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Fig. 3 Results of the calibration of the ED-XRF data, with the reference bulk composition (x-axis) and predicted bulk chemistry (y-axis) of discrete samples from the Dhanchi-2, Bonnie Camp, and Sajnekhali Island cores. Calcium (Ca) is shown in (a), iron (Fe) is shown in (b), potassium is shown in (c), rubidium is shown in (d), titanium is shown in (e), and zirconium (Zr) is shown in (f)

Fig. 4 Linear fit between log-ratio measured intensities and log-ratio of the reference bulk chemistry with Ca as the optimum log-ratio denominator from the discrete samples of the Dhanchi-2, Bonnie Camp, and Sajnekhali Island cores. Fit of iron and calcium shown in (a), fit of potassium and calcium shown in (b), fit of rubidium and calcium shown in (c), fit of titanium and calcium shown in (d), and fit of zirconium and calcium shown in (e)

Fig. 5 Partial least squares (PLS) model of grain-size and calibrated geochemistry for the Dhanchi Island core

Fig. 6 log-ratio elemental logs from the Dhanchi Island core