Chapter 2
Twenty Years of XRF Core Scanning Marine Sediments: What Do Geochemical Proxies Tell Us?

R. Guy Rothwell and Ian W. Croudace

Abstract XRF core scanners, with their rapid and non-destructive analytical capability, have now been used for two decades in the analysis of marine sediments. Initially they were used to record variations in fundamental parameters such as calcium carbonate stratigraphy and terrigenous sediment delivery, using major element integrals, such as Ca and Fe, to provide detailed insights into oceanographic and climatic processes. In recent years, proxy selection has progressed to routine normalisation and presentation as log-ratios to include 60 elements or ratios to document a wide range of environmental and process changes. We review the development and application of XRF core scanning of marine sediments and discuss the basis of particular proxies, their uses and limitations to assist users in their selection. To date, there has been no systematic overview of elemental proxies and their application in the analysis of marine sediment records.

Keywords XRF core scanning · AVAATECH core scanner · ITRAX core scanner · X-ray fluorescence · Geochemical proxies · Environmental analysis · Marine sediments

Introduction

In a little over 20 years, XRF core scanners have developed from a single prototype instrument to commercially available high-resolution instruments routinely used in palaeoenvironmental research worldwide. Initially, use was restricted to marine sediments and the number of publications small, but use and resulting publications rapidly increased in the first decade of the twenty-first century with increasing application to lake cores and terrestrial records (Rothwell and Croudace, this volume).

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Modern core scanners can analyse sediments at sub-millimetric intervals (termed micro-XRF or μXRF), allowing insights at decadal, annual and even sub-annual scales.

Marine and lake sediments can provide detailed palaeoenvironmental archives accessible through element proxy data. These data commonly reflect past climate. On continents, precipitation, temperature and vegetation are the primary controls on chemical weathering and physical erosion. On geologic timescales, a measure of this is preserved in the chemistry and mineralogy of sediments transported by rivers and wind to the deep sea or lake. In the oceans, proxy elements can also provide valuable data on productivity, water movements and diagenesis.

Micro-XRF instruments have become increasingly powerful tools for studying high-resolution chemical variability linked to environmental change. High-resolution studies on continuous sedimentary archives are crucial for understanding climate change on seasonal to millennial scales. Ca, Fe, Sr, K and Ti, commonly occurring elements in marine sediments, are extensively used as tracers in environmental reconstructions (e.g. Gebhardt et al. 2008; Rooij van et al. 2007; Vidal et al. 2002; Grützner et al. 2003; Arz et al. 2001b, 2003; Kuhlmann et al. 2004b; Romero et al. 2008; Calvert and Pederson 2007; and others). In this paper we review the development and application of micro-XRF studies of marine sediments, discuss methods for robust data analysis and provide a catalogue of element integrals and ratios that have been used as proxies, discussing their origin, application and limitations. Finally we review proxy relationship to magnetic susceptibility, which together with spectrophotometry, may clearly correlate with element abundances.

This paper shows what proxies have been used by researchers investigating the marine record, it demonstrates what has been done and what can be done, with the aim of guiding core scanner users in proxy selection and potential. To date, there has been no systematic overview of element proxies and their application to marine sediments.

History of XRF Core Scanning of Marine Sediments

Early Non-chemical Methods of Determining Climate Changes

A major focus of marine geology since the 19th Century has been determination of environmental and process records from cored sediments. Initially temporal changes in microfossil distributions were used to record climate changes. Pioneering work includes Schott (1935) working on cores collected by the German *Meteor* expedition to the South Atlantic of 1925–1927; Cushman and Henbest (1940) using cores from a North Atlantic W-E transect by the American cable ship *Lord Kelvin*; Phleger (1947) using Tyrrhenian Sea cores collected by the Swedish vessel

Skagerak using the newly-developed piston corer (Kullenberg 1947); and Phleger et al. (1953) using cores collected by the *Albatross* during the Swedish deep-sea expedition of 1947–1948. Collectively, these works led to the founding of palaeoceanography as a distinct discipline within the earth sciences.

Discovery of X-ray Fluorescence

The discovery of X-ray fluorescence (XRF) revolutionised the capability to efficiently extract detailed environmental records from the marine realm. The ability of materials to fluoresce when excited by incident X-rays, emitting secondary radiation of characteristic wavelength depending on atomic number, was recognised within two decades of the discovery of X-rays by Röntgen in 1895. This phenomenon, the basis of XRF analysis (XRFA), arises as electrons are ejected from inner atomic shells through X-ray excitation. The resulting vacancies are filled by electrons moving from the outer electron shells with the energy difference emitted as electromagnetic radiation, the wavelength of which is characteristic for each element (see Jenkins and De Vries 1970, for further discussion).

The potential of X-ray excitation, and secondary fluorescence, to determine material composition was quickly realised when Henry Moseley demonstrated a systematic mathematical relationship between fluorescent X-ray wavelength and atomic number of metals used as targets in X-ray tubes (Moseley 1913/1914). Initially electrons were used as the excitation source, but these were highly inefficient in creating X-rays, with almost 99% of the energy lost as heat. However, Hadding analysed mineral samples in 1922 using this technique. A much more efficient method is to use an X-ray source with a metal target to induce fluorescence. This technique was first used by Coster and Nishina in 1925, with Glocker and Schreiber performing the first quantitative analysis of materials using XRF in 1928.

It took another 20 years for detector technology to make XRF a practical method for routine geochemical analysis, with the first commercially-available X-ray spectrometers appearing in the 1950s. In 1970, the advent of the high resolution solid-state lithium-drifted silicon detector, Si(Li) (e.g. Jenkins 1988), set the basis for what is the most widely used technology today, the Silicon Drift Detector (Gatti and Rehak 1984). There are two main XRFA variants, wavelength dispersive (WD-XRF) and energy dispersive (ED-XRF). The former provides the highest analytical resolution in terms of elemental separation. In WD-XRF elemental determination is commonly made by scanning through the wavelength range—in practice an angular goniometer moves to a particular elemental position as determined by the Bragg Law $n\lambda = 2d.\mathrm{Sin}\theta$. In practice, analysis of materials is destructive and is normally carried out in a vacuum on a homogenized disc-like sub-sample. The WD-XRF instruments are often sequential scanning devices although simulatneous spectrometers also exist. The demanding design of a WD-XRF does not lend itself to the scanning of sediment cores but they are excellent instruments for quantitative analysis of sub-samples from cores. The advent of compact solid-state devices

(diodes) allowed the development of energy dispersive detectors that collect an energy spectrum simultaneously. The Silicon Drift Detector is the latest variant of EDS devices and their development has made a significant technical contribution to core scanners and other XRF instruments. Their very good energy resolution and count-rate tolerance and the fact that they do not need LN2 cooling makes them the detector of choice in micro-XRF analysis.

Early Geochemical Studies of Marine Sediments

Geochemical analysis of marine sediments from the 1930s onward established the value of geochemical data in studying ocean properties and processes (e.g. Correns 1937; Bramlette and Bradley 1940; Arrhenius 1952; Goldberg 1954; Goldberg and Arrhenius 1958). Initially textural and mineralogical variations were used to document environmental processes and changes. For example, Radczewski (1939) used the presence of iron-coated *wüstenquartz* in cores collected by the *Meteor* in the Cape Verde Basin to demonstrate aeolian deposition in the deep sea. Rex and Goldberg (1958) showed variations of wind-blown quartz with depth in North Pacific sediments related to climate change. From this, recognition of elemental proxies for larger grain-size, such as Si/Al, Ti/Al and Zr/Al was a short step as Si, Ti and Zr typically reside in larger mineral grains (see Calvert and Pedersen 2007). Elemental proxies for palaeoproductivity were also recognised early with Goldberg and Arrhenius (1958) interpreting enhanced barium in Pacific sediments as reflecting enhanced surface productivity (see Dymond and Collier 1996; Klump et al. 2000) for further information on Ba as productivity proxy). Element analysis thus joined micropalaeontology as a major palaeoceanographic research tool.

The Development of XRF Core Scanners

By the 1970s laboratory-based X-ray fluorescence analysis was an established routine technique for analysing marine sediments, which were long recognised as holding long-term archives of past environmental change. Prior to 1988, XRF analysis required taking of discrete samples, which are ground to fine powders and pressed into pellets or fused with a borate flux to produce glass beads that can be analysed to calculate element abundances. This process, though still used to produce data of excellent quality, is destructive to the core and takes significant preparation and analysis time, and limits the practical resolution that can be achieved.

Standard analytical methods for discrete sample analysis are thus discontinuous, time consuming, and expensive. Relatively fast non-destructive core logging methods yield continuous data at much finer scales (down to sub-millimetre) than are practical for individual sampling methods and their application to XRF measurements proved a remarkable boon to the environmental sciences.

The first non-destructive XRF scanner that could produce continuous element records from split sediment cores was CORTEX (CORe scanner TEXel) developed

by the Netherlands Institute for Sea Research (NIOZ), Texel, The Netherlands, in 1988. This instrument was the forerunner of the modern commercially-available AVAATECH XRF core scanner, and because of its head start it has been responsible for producing about two-thirds of all peer-reviewed publications citing XRF core scanning as a method. CORTEX is described by Jansen et al. (1992, 1998).

Although, semi-quantitative in that elemental variations are measured as 'counts' per second, absolute concentrations can be obtained following calibration using relatively few conventional WD-XRF analyses of discrete samples (see for example, papers by Hunt et al., this volume).

A major advantage of the CORTEX instrument was that it could be containerised for sea-going, allowing acquisition of proxy records within a few hours of coring. First results from the Angola Basin (Jansen et al. 1990, 1996, 1998) showed CORTEX produced reliable semi-quantitative data for the elements K to Sr. The continuous downcore XRF records could be related to carbonate stratigraphy, the $\delta^{18}O$ record, and identify redox transitions and variations in terrigenous input (Jansen et al. 1998).

The value of the new instrument in palaeoceanography was quickly recognised. An updated CORTEX instrument was installed at the University of Bremen in 1997 (Röhl and Abrams 2000) with the capacity to measure a broad suite of elements from K ($Z=19$) to Sr ($Z=38$). A second-generation scanner, now produced by AVAATECH Analytical X-Ray Technology of Alkmaar, The Netherlands (normally referred to as the AVAATECH scanner), was delivered to Bremen and NIOZ in 2002. The AVAATECH core scanner has been improved and modified, enabling higher measurement speed, better detection limits, increased number of detectable elements and higher spatial resolution. Prior to 2005 the scanner was used almost exclusively for research on marine cores, and cores from the pre-Quaternary geological record, such as those collected by the Ocean Drilling Program (ODP). Technical details for both CORTEX and AVAATECH scanners are provided by Richter et al. (2006).

A parallel development was the Eagle II and III BKA XRF core scanners, built by Röntgenanalytik Messtechnik GmbH, Germany (Haschke et al. 2002; Hascke 2006). These instruments, developed from the Eagle µprobe, had several innovations including use of capillary optics to focus the incident X-ray beam allowing very high spatial resolution, down to 30 µm spot size and 10 µm step size. Further, analysis within an environmentally-controlled chamber, reduced the need to protect cores from drying during analysis, thus removing potential data artefacts caused by protective film applied during AVAATECH analysis to prevent core dessication. In a seminal paper, Haug et al. (2003) used the Eagle II scanner to show that intense droughts, inferred from using Ti as a proxy for rainfall and run-off (Fig. 2.1) in cores from the Cariaco Basin, offshore Venezuela, may have contributed to Classic Mayan civilisation collapse in the ninth Century A.D. Titanium, a common component in Fe-Ti oxides and other minerals in rocks such as gneisses or schists, is supplied to the oceans by wind and river transport. Recent work, however, suggests rainfall reductions in Central America may have been modest, but enough to cause critical water shortages (Medina-Elizalde and Rohling 2012).

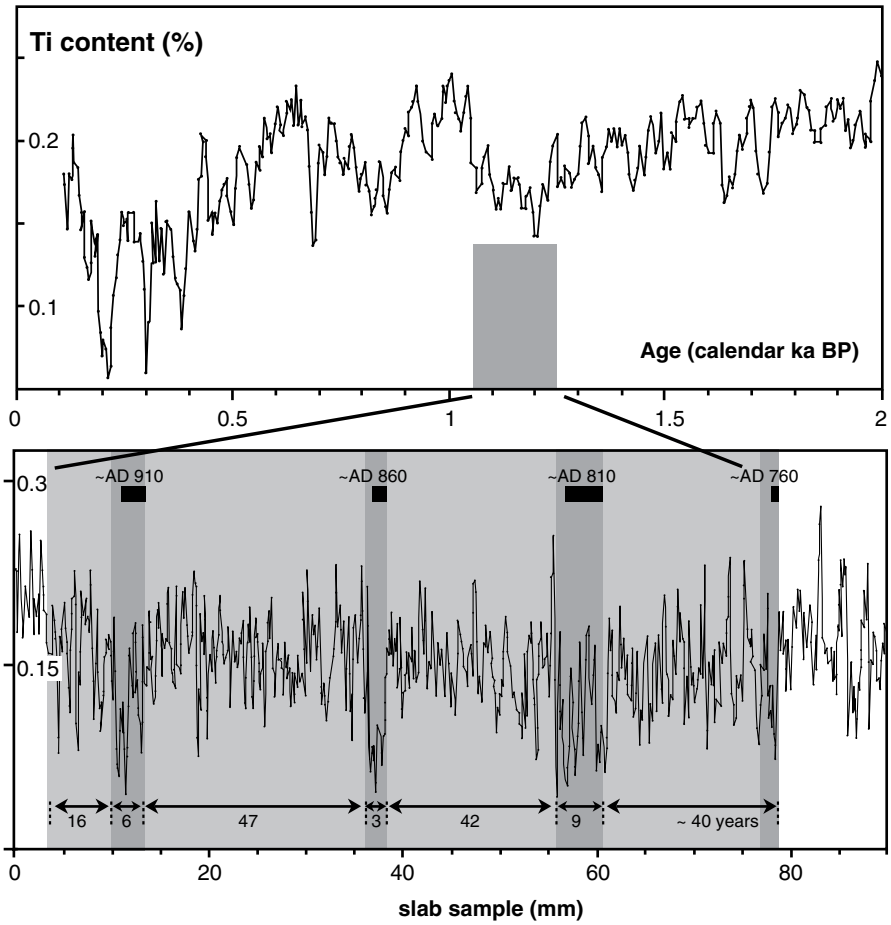

Fig. 2.1 Ti content in two cores from the Cariaco Basin, offshore Venezuela, measured at different spatial resolution. Ti is used here as a proxy for terrigenous sediment delivery from surrounding watersheds and reflects rainfall changes. Episodes of low Ti (dated thick black bars) correlate with times of Mayan city abandonment dated from the archaeological record. (Reproduced with permission from Haschke 2006, and adapted from Haug et al. 2003, Figs. 2.2 and 2.3)

Another instrument, the ITRAX μXRF core scanner, was developed and funded by the Southampton Oceanography Centre (now National Oceanography Centre, UK) as a joint collaborative venture with Cox Analytical Systems, Gothenburg, Sweden. The first ITRAX instrument was delivered to SOC in 2003. Unique features of the ITRAX are its combination of a rectangular capilliary x-ray wave-guide and a digital micro-radiographic system, allowing acquisition of continuous digital x-radiographs as well as μXRF records. The radiographic image produced has a high dynamic range of 2^{16} grey-level values and a minimum pixel size of 20 μm (see Francus et al., this volume). The ITRAX is described by Croudace et al. (2006) and has become, with the AVAATECH scanner, the two most widely used in palaeoenvironmetal research.

XRF measurements usually show a significantly higher signal-to-noise ratio and more consistent core-to-core agreement than any other physical property measurement such as density, colour reflectance and magnetic susceptibility, thus providing comprehensive archives for time-series analysis of relatively complete sections (e.g. Pälike et al. 2001; Röhl et al. 2003; Jaccard et al. 2005; Tjallingii et al. 2007; and others).

Review of Marine Science Applications

The past two decades have seen a wide variety of marine science applications for XRF core scanners but most fall into the following areas:

- core description and characterisation
- studies of climatically-driven cyclicities that are reflected, for instance, in $CaCO_3$ or Fe fluctuations over time
- sedimentological applications, where features or events such as ash layers, turbidites, ice-rafted debris, aeolian dust flux, or earliest stages of marine influences can be recognised through their exotic compositions or localised or organised character
- studies of sediment provenance based on chemical differences in source areas
- cluster analysis and facies interpretation of sedimentary environments
- diagenetic studies
- core correlation and orbitally-tuning high-resolution core log records
- environmental impact studies and environmental forensics.

Core Description and Characterisation

XRF core scanning has been used, like many other techniques, as a core characterisation tool, allowing lithological units and textural/mineralogical variations to be identified and described. Arguably XRF core scanning provides the most detailed analytical results in the quickest possible time, particularly for identifying sediment layers worthy of more detailed investigation or dating.

Rothwell et al. (2006), for example, used a range of element integrals and ratios to characterise interbedded turbidites and pelagites from the Balearic Abyssal Plain, Western Mediterranean Sea. Compton scattering, which relates inversely to mass absorption coefficient and mean atomic number, decreased in silt and sand layers due to size/density-related mineral fractionation. Grading due to mineral variation could also be seen in this parameter, even when not visually obvious. Discrete pteropod layers were characterised by sharp decreases in Compton scattering, possibly due to current winnowing, as mean atomic number falls with looser sediment packing. As Al was then at the limit of ITRAX detection and counts low, Rothwell et al. (2006) considered other detrital elements for normalisation. Rb was preferred to Ti, as ratioed Rb showed better relation to grading and Compton scattering values in the sediments studied.

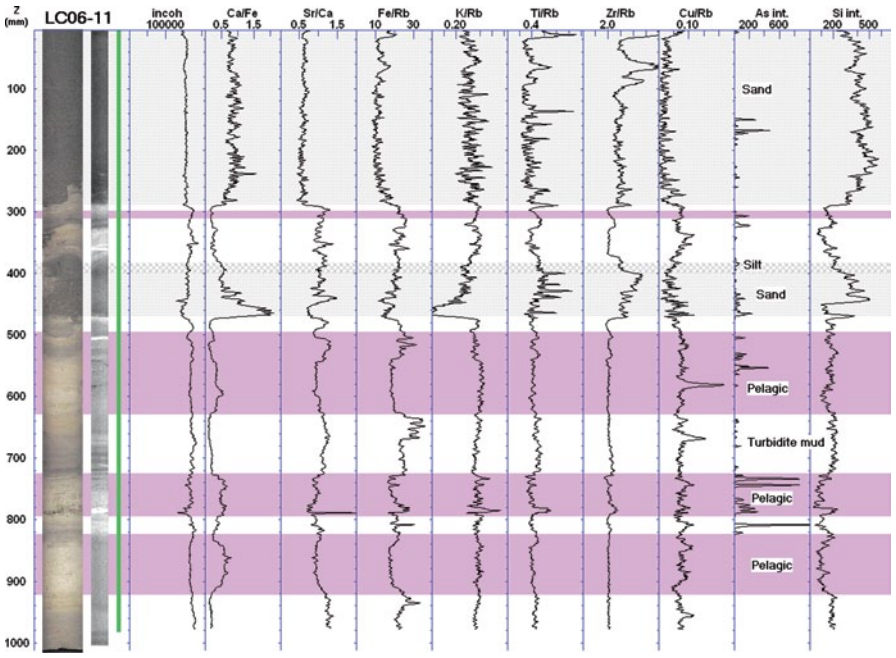

Fig. 2.2 ITRAX-acquired XRF element profiles through interbedded turbidites (white or ornamented) and pelagites (mauve) from the Balearic Abyssal Plain, western Mediterranean Sea. Boundaries between turbidite and pelagic muds are difficult to distinguish visually but are clearly seen in the Ca/Fe profile, with Ca/Fe showing more variability in pelagic muds due to scattered foraminifers. Turbidites have more uniform profiles due to removal of foraminifers through gravitative settling. The Si profile shows the upper sand (between 0 and 300 mm) is massive and ungraded, while the sand between 400 and 480 mm is normally graded (from Rothwell et al. 2006). The image was generated using ItraxPlot™ (see Croudace and Rothwell, this volume)

Element ratios found useful as proxies by Rothwell et al. (2006) are:

- Ca/Fe (biogenic carbonate:detrital clay ratio, useful for turbidite/pelagite discrimination (Fig. 2.2), sediment grading, assessing textural character, and source distality-proximality relationships)
- Sr/Ca (indicating high-Sr aragonite requiring a shallow-water source)
- Fe/Rb (commonly showed grain-size-related fractionation effects within turbidites and elevated Fe in oxic, or formerly oxic, parts of turbidites)
- K/Rb (commonly enhanced in turbidite muds compared to silts, sands and pelagic mud, reflecting presence of K, like Rb, in clays)
- Zr/Rb and Ti/Rb (commonly enhanced in turbidite bases, possibly having value as provenance indicators)
- Cu/Rb (showing diagenetic mobilisation of Cu)
- As (indicating presence of pyrite).

Rothwell et al. (2006) demonstrate that XRF core scanning provides a quick efficient way of distinguishing pelagic from turbidite muds that may look visually

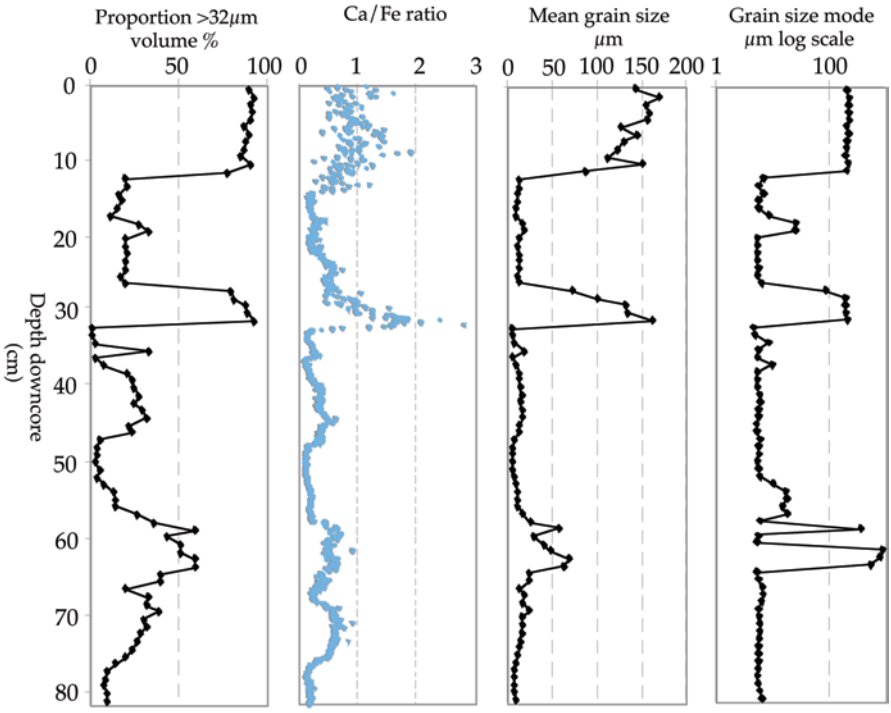

Fig. 2.3 Grain-size profiles and Ca/Fe profile through core interval shown in Fig. 2.2. Note Ca/Fe provides a good proxy for textural variation, with a close correspondence to mean grain-size and proportion of grains > 32 μm suggesting Ca relates to presence of foraminifers (From Rothwell et al. 2006)

similar; can identify early arrivals of turbidite beds; and provide reliable indicators for grain-size variation and grading (Fig. 2.3).

Further examples of XRF core scanners used for core characterisation are shown in Table 2.1.

Core characterisation is a prerequisite for further core analysis and determining environmental history. Bed characterisation may reveal different sedimentary environments and facies changes downcore. For example, Wolters et al. (2010) used XRF core-scanning to document a ~1500 year record of early Holocene vegetation changes and mire development in a North Sea landscape now 33 m below sea-level (Fig. 2.4). Combined application of botanical and geochemical methods rapidly determined key horizons indicative of marine conditions and different environments showed specific element signatures—basal glacio-fluviatile sandy mud by high Si and relatively high Al, K and Ti, and peat development by increased S and decrease in Si, Al, K and Ti (Fig. 2.4). Mn and Fe peaks suggested fluctuating ground water levels in the early stages of mire development, which were not apparent in the vegetation record. Fluctuation of Ca and S suggested an oscillating coastline. The authors conclude that transgressive contacts are most precisely located by XRF core

Table 2.1 Examples of studies where XRF core scanners have been used primarily to characterise marine sediment cores

Reference(s)	Area	Notes
Bergh et al. (2003), Kaars van der and Bergh van der (2004)	Teluk Banten embayment, NW Java	Characterised the 1883 Krakatau tsunamiite, Ca record quickly defined the tsunamiite—a thin sandy layer of reworked bioclasts, pellets and volcanic ash
Franke et al. (2004)	SW Atlantic	Established combined palaeomagnetic and sedimentological dataset, including carbonate, opal and terrigenous content, grain-size distribution and clay mineral composition
Nørgaard-Pedersen et al. (2006)	Loch Etive, W Scotland	Core scanner Ca and Fe profiles quantified by discrete sample XRF spectrometry
Bergh et al. (2007)	Ba Lat prodelta (Red River Vietnam)	Downcore Ca and Fe measured, with relatively low Fe in sandy shelf deposits
Lebreiro et al. (2009)	Portuguese continental margin	Characterised element composition of deep-sea and land-derived sediments. K/Ca, Ti/Ca and Fe/Ca and magnetic susceptibility followed similar trends with prominent peaks matching Heinrich events
Ren et al. (2009)	Ameralik Fjord, SW Greenland	Measured Fe, Ti, K, Si, Ca and Br. Fe, Ti, K and Si common elements in hinterland bedrock, and intensities used as indicators of terrestrial influence, including melt-water discharge. Ca and Br interpreted as reflecting biogenic production
Land et al. (2010)	Carbonate mounds, SW Rockall Trough margin	Ca/Fe and magnetic susceptibility suggested regional control on sediment accumulation, rather than local, site-specific control
Pirlet et al. (2010)	Magellan carbonate mounds, Porcupine Seabight, NE Atlantic	Fe, Ca and Sr effective in distinguishing lithological boundaries

scanning (through increase of K, Ti, Si), as visual interpretation of the lithostratigraphy can be uncertain and pollen analysis is mainly based on airborne particles.

Studies of Climatically-Driven Cycles in Sediment Deposition that are Reflected in Element (e.g. Ca or Fe) Fluctuations Over Time

A major application of XRF scanning of marine cores has been to determine climatically-driven changes in sediment composition, largely relating to glacial-intergla-

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