Europe's Lost Frontiers

General Editor
Vincent Gaffney

Volume 1

Context and Methodology

edited by

Vincent Gaffney and Simon Fitch

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Cover: Eleanor Ramsey

Landing by Ava Grauls (Duncan of Jordanstone College of Art & Design).
Oil and watercolour on Japanese shōji (障子) paper. 413 x 244cm

Landing is about location, ownership, shifting land and shifting borders. The painting was conceived after talking to academics about the space between Britain and Europe, and asking the question: 'How do you paint a forgotten landscape?' Landing was made to travel and interact with different environments and can be folded up and packed away into four boxes.
Ava Grauls 11/08/2021

Dedicated to our Families
For putting up with Doggerland for longer than any families since the Mesolithic

November 2021

Europe's Lost Frontiers

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Chapter 10

Applying chemostratigraphic techniques to shallow bore holes: Lessons and case studies from Europe's lost Frontiers

Alexander Finlay, Richard Bates, Mohammed Bensharada and Sarah Davies

Introduction

The range of applications of analytical geochemistry in the geosciences extends from hydrocarbon studies to forensic investigations with samples from billion year old material formed deep within the earth to material from contemporary environments (Poulton *et al.* 2010). Within archaeological and palaeoenvironmental research, elementary geochemistry can also provide an excellent analytical tool for the investigator. There are numerous examples of these techniques being applied, from the provenance and identification of manufacture of anthropogenic material (e.g. Finlay *et al.* 2012) through to palaeoenvironmental studies e.g. Croudacre and Rothwell (2015). This chapter will demonstrate how geochemical and chemostratigraphic techniques have been applied within the *Europe's Lost Frontiers* project. A review of commonly utilised analytical techniques in archaeological and paleoenvironmental studies is first presented, followed by details on the methods of data collection, quality control and interpretation. Key cores are used as case studies to demonstrate particular aspects of the method.

Case study 1 demonstrates how geochemical analysis can be utilised to characterise a core into a series of chemostratigraphic zones (chemo zones), assign these to geochemical facies (chemo facies) reflecting their depositional environment and then validate these chemo facies by integrating them with other ecological datasets.

Case study 2 demonstrates how a comparison of chemo zones and facies from multiple cores within a study area can be used to produce a regional chemostratigraphic correlation, and so aid palaeolandscape reconstruction.

Case study 3 demonstrates the integration of chemostratigraphy with other methods such as seismic interpretation through the production of chemical modelled density profiles to link to the seismic data. This in turn is utilised for a greater understanding of the spatial coverage of the chemo zones and interpreted facies.

The chapter concludes with an overview of other applications of geochemical analysis that may be applied to future studies using unconsolidated sediment cores and palaeoenvironmental reconstruction.

Elemental analysis

Quantitative methods

The range of geochemical analysis techniques available for sediment quantitative elemental data include inductively coupled plasma-optical emission spectrometer (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF Figure 10.1 e.g. Jarvis and Jarvis 1992; Ratcliffe *et al* 2012). ICP-MS and ICP-OES are laboratory based elemental tools requiring significant sample preparation including microwave, flux fusion or acid digest processes in order to place the sample into a solution prior to analysis (Olesik 1991). The ICP-MS detects the mass of the ions hitting its detector and provides a mass spectrum for the sample, with the intensity of each mass peak in the spectrum being directly proportional to the concentration of an element of the same mass within the sample. The mass is quantified by comparing the intensities of the mass spectrum to known calibration standards (Tyler and Jobin Yvon 1995). The ICP-OES differs in that it measures the effect of the ions on the sample on the plasma itself. When the sample solution is introduced to the plasma the elements contained within loose electrons and give off radiation with wavelengths characteristic to the element itself. The optical spectrometer detects this radiated energy, and through comparison with the intensities of known calibration standards the elemental abundance can be quantified within the sample (Jarvis and Jarvis 1992; Olesik 1991; Tyler and Jobin Yvon 1995). The combined use of both ICP-MS and ICP-OES enable the quantification of major elements (greater than one weight percent of the sample) and trace elements (typically down to parts per billion level; Jarvis and Jarvis 1992).

X-ray fluorescence (XRF) is the emission of characteristic 'secondary' (or fluorescent) X-rays from a material that has been excited by being bombarded with high-energy X-rays. Analytical tools vary from laboratory-based techniques that can produce analysis similar to ICP instruments to highly portable handheld tools that can be used in the field. Dependant on lithology it provides data for ten major and approximately twenty trace elements, importantly including both chlorine

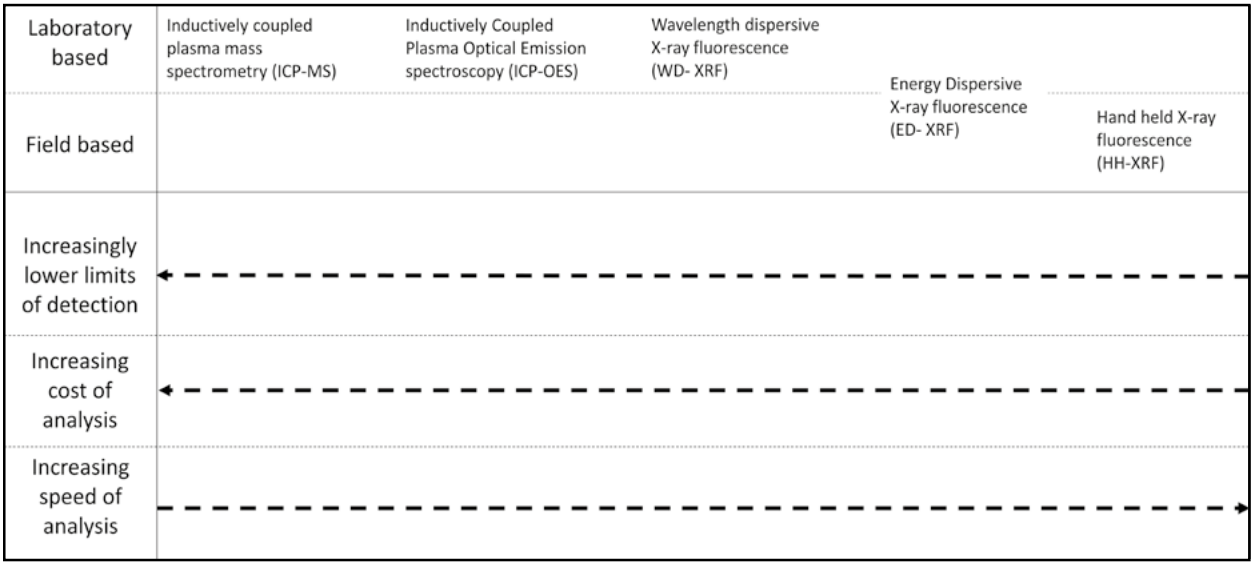

Figure 10.1 A summary of the benefits of typical analytical tools utilised in chemostratigraphic studies and their acronyms.

and sulphur making it the ideal tool for analysing saline samples. Handheld X-Ray Fluorescence is capable of providing rapid elemental data (Hennekam and de Lange 2012; Schmidt *et al.* 2018). The tool is non-destructive and capable of high spatial resolution analysis thus making it ideal for use in core scanning (Schmidt *et al.* 2018). However, it does not have the same limits of detection that more powerful x-ray tools possess.

Qualitative methods – Scanning/Micro XRF

An ITrax X-Ray Fluorescence core scanner (Cox Analytical Systems), based at Aberystwyth University, was used in *Europe's Lost Frontiers* project. The ITrax is a laboratory XRF scanner capable of very high resolution, continuous environmental core scanning at a relatively rapid automated rate (Croudacre and Rothewell 2015). While the data it collects is quantitative there are currently no standard reference materials for the technique and thus results are more appropriate to analysis of relative changes in elemental abundance rather than absolute elemental values reported by techniques such as ICP-MS. In *Europe's Lost Frontiers*, the ITRAX provided data at a resolution of 0.5mm thus allowing for chemical fingerprints of very short-lived climatic, depositional, and environmental changes. An additional benefit of the ITrax is its ability to record the incoherent (Compton) and coherent (Rayleigh) scattering caused by the XRF interaction with the core, enabling key information such as core density to be calculated (e.g. Fortin *et al.* 2013; Gaffney *et al.* 2020). Calculation of core density enables a comparison to be made of the geochemistry with other regional remote sensing techniques such as seismic analysis.

Data acquisition, quality control, data processing

A single data quality control and interpretation method was developed and utilised for all cores in the *Europe's Lost Frontiers* project in order to ensure that, as much as possible, data from different cores collected at different times was comparable.

The cores were initially split lengthwise, and the exposed surface scraped to ensure a smooth and flat surface. The scanner was typically set for a resolution of 0.5mm along core-interval and a dwell time of 15 seconds with the x-ray tube at 30kV and 50mA. For the individual core sections, the scanning line was adjusted to avoid sampling holes. All reported data was smoothed using a ± 4mm moving average filter applied to the data in order to remove any 'nugget' effect caused by clasts of a specific elemental composition leading to an overestimate of those elements compared to that of the core (e.g. Croudace and Rothwell 2015; Gaffney *et al.* 2020).

To test the validity of the recorded data, distance to sample surface, total counts and Argon (as the Ar signal is derived from the excitation of argon in air between the sample and X-ray source, rather than the sample) was plotted by core depth (below surface) and compared to the ITrax chemical data. A fall in total counts that coincides with a peak in Ar, suggest that any changes in chemical data at these depths may be caused by physical damage or irregularities in the core surface rather than elemental variations in the core (Croudace and Rothwell 2015). If these conditions were met, then the elemental data from these depths was not utilized in this study. Furthermore, any data that were outside two standard deviations of the mean depth to sample

Element	Symbol	Common mineralogical control	Common interpretations
Aluminium	**Al**	Clays	Depositional energy/Grain size
Bromine	**Br**	Organic material	Productivity/Salinity/marine influence
Calcium	**Ca**	Calcite	Evaporite or marine signal
Iron	**Fe**	Heavy and/or clay minerals	Detrital input
Potassium	**K**	Clay minerals	Detrital input and depositional energy
Magnesium	**Mg**	Dolomite	Dolomitisation
Sodium	**Na**	Halite	Salinity
Phosphorus	**P**	Apatite and phosphates	Heavy minerals or Nutrient enrichment
Sulphur	**S**	Organic material/Gypsum	Productivity/Salinity/marine influence/palaeosoils
Silica	**Si**	Quartz	Depositional energy/Grain size
Strontium	**Sr**	Aragonite	Shell material/marine signal
Thorium	**Th**	Heavy minerals	Depositional energy/Grain size. Link with gamma ray logs
Titanium	**Ti**	Heavy and/or clay minerals	Detrital input
Uranium	**U**	Heavy minerals or anoxia	Depositional energy/Grain size. Organic content. Link with gamma ray logs
Zirconium	**Zr**	Heavy minerals	Depositional energy/Grain size

Table 10.1 Elements commonly utilised for archaeological and paleoenvironmental research (summarised from Davies *et al.* 2015 and Chemostrat multiclient report NE118).

surface, thus indicating an irregular surface, were also treated with caution.

Three methods are proposed to ensure confidence in using ITrax derived identification of mineralogical or deposition drivers for variations in elemental chemistry. Where possible, additional quantitative mineralogical analysis (e.g. X-ray Diffractions/Raman minerology or SEM-EDS techniques) on a subset of samples can be made for comparison of the sediment chemistry with the minerology. If additional data is not available, a comparison with observed changes in the core from more traditional methods such as colour, shell fragments and grain size can be made. Finally, the data can be analysed using statistical methods such as principal component analysis (PCA).

Principal Component Analysis (PCA) is a mature statistical technique that is widely used for identifying patterns in data of multiple dimensions. PCA finds a set of orthogonal dimensions, which account for the variance in a specific dataset, by reducing the dimensionality of a complex system of correlations into a smaller number of dimensions. The first principal component accounts for as much data variance as possible and each subsequent principal component accounts for remaining data variance (Michoux 2020). For example, in a hypothetical interbedded sand/mud section that transitions from marine to fluvial control, PCA1 would likely be controlled by a variation in elements associated with the sand (e.g. Si and Zr) and clay fractions (e.g. Al, Rb and K), whereas PC2 may be marked by the variation between these detrital minerals and elements associated with marine settings (Ca and Sr).

An in-depth review of possible controls in elemental data are reported by Rothwell and Croudace (2015) for marine sediments and Davies *et al.* (2015) for fluvial sediments. Table 10.1 lists the common drivers of elemental variation within sedimentary units. However, it is stressed that sediments are complex mixtures of natural materials and so this may not always be true.

Case study 1 – Chemostratigraphic zonation, chemostratigraphic facies and integration with sedimentological and ecological data to establish the depositional environment of Core ELF19

Introduction

Case study 1 comprises a comparison of elemental data to microfossil analysis and observed variations in minerology within core ELF19. This was collected off the East Anglian coast in the *Europe's Lost Frontiers* study area (Figure 10.2) and measures ~4.3 meters long. Microfossil analysis shows that it contains three depositional settings:

- 0.18-1.34m depth – estuarine mudflats latterly with some algae; initially an eroded peat, with onset of tidal access
- 1.46-4.01m depth – river or lake with some cool/deep water, latterly with hint of low salinity as tidal access approaches with sea-level rise
- 4.27-4.29m depth – till

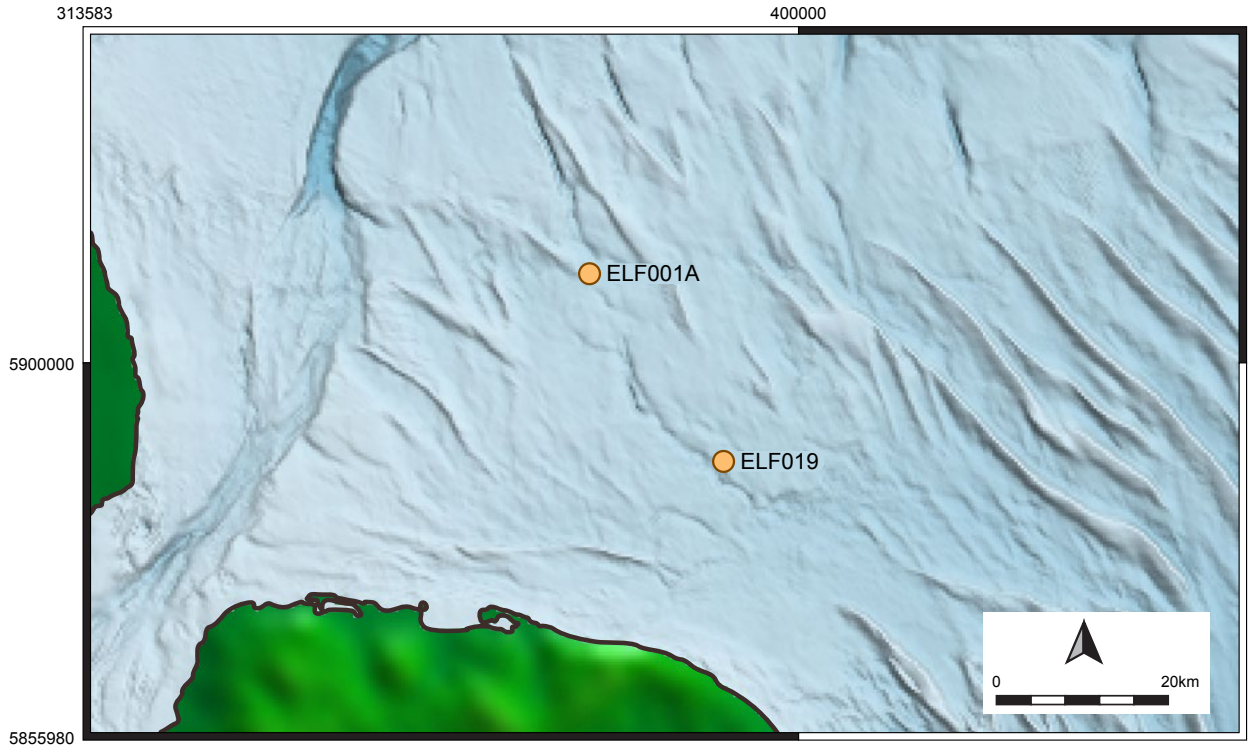

Figure 10.2 Location map of cores referred to in this paper. Bathymetric data is derived from the EMODnet Bathymetry portal - http://www.emodnet-bathymetry.eu. Topographic data derived from the NOAA ETOPO1 dataset, courtesy of the NCEI - https://www.ngdc.noaa.gov/mgg/global/

The top ~3m of core underwent elemental analysis and the data produced was used for chemostratigraphic interpretation. Chemostratigraphy (chemical stratigraphy) is the application of whole rock or sediment geochemistry to understand the depositional history, correlation and palaeoenvironment of a core. It involves building a chemostratigraphic zonation (chemo zone) of the analysed material, assigning each zone facies information based on its chemistry (chemo facies) and where there is the need, correlating similar chemo zones between different cores and/or outcrops and so producing a chemostratigraphic correlation (Ellwood *et al.* 2008).

The chemo zones produced in ELF19 were driven by variations in detrital grain size, carbonate, clay, organic material and salinity. These variations enabled the core to be subdivided into six chemo zones, each ascribed a chemo facies description. These chemo facies were then compared to available sedimentological and biostratigraphic information to produce a set of integrated core facies.

Elemental data and controls

Core ELF19 was scanned from a depth of ~18.5cm to ~296cm at a 0.05cm resolution. Reported data underwent the quality control methods outlined above, and eleven elements passed the test (Table 10.1). These elements were subject to PCA analysis (Figures 10.3a and 10.3b) to establish the dominant mineralogical controls on elemental variation (Table 10.2).

Chemostratigraphic zones

To establish a chemostratigraphic zonation, the dominant element from each principal component cluster in Table 10.2 were ratioed and plotted for each reported depth down the length of the core. Using ratios to compare elemental data is preferred as this removes any dilution effect caused by variations in other elements analysed at that depth (Weltje *et al.* 2015 and references inter alia). These elemental ratios likely reflect down core variations in:

- Si/Rb: quartz/clay – changes in detrital grain size
- Ca/Rb: carbonate/quartz – marine/fine terrestrial sediment
- S/Rb: organic material/clay
- Br/Ti: salinity (De Boer *et al.* 2014)

Visual comparison of the results of the analysis enabled the core to be split into five chemo zones (numbered top down; Figure 10.4; Table 10.3).

Chemo facies

It is possible to assign likely chemo facies to the above chemo zones based on their observed chemistry and

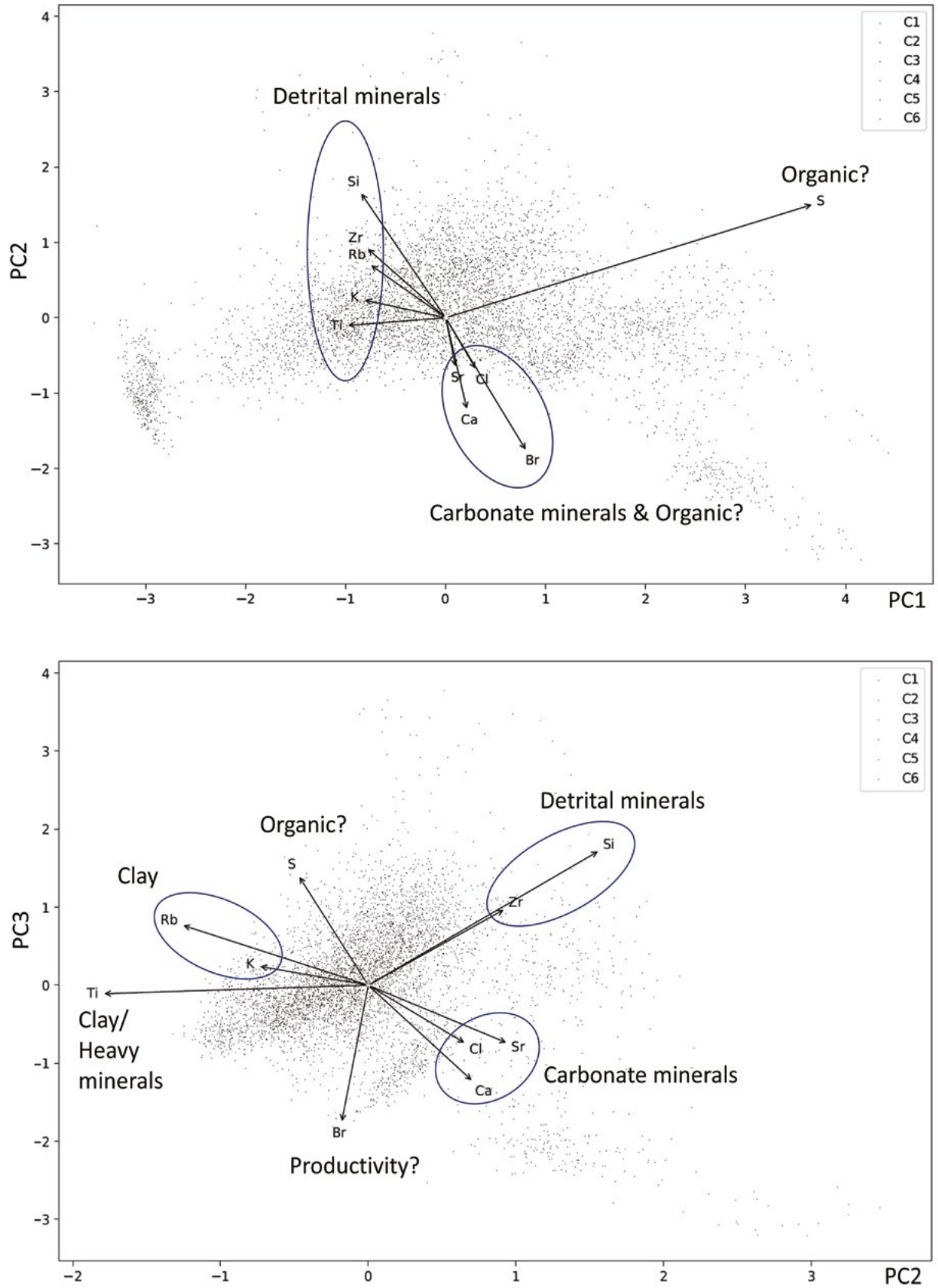

Figure 10.3 PCA of elemental data for core ELF19 showing the likely mineralogical and material drivers for variation in elemental compositions. a - component 1 and 2, b - component 2 and 3.

Element	Symbol	PC1 and 2 control cluster	PC2 and 3 control cluster	Likely mineralogical control
Silicon	Si	Detrital minerals	Detrital minerals	Quartz
Zirconium	Zr			Detrital Zircon
Rubidium	Rb		Clay minerals	
Potassium	K			
Titanium	Ti		Heavy Minerals/Clay minerals/Oxides?	
Sulphur	S	Organic material		
Bromine	Br	Carbonate minerals and salinity	Salinity?	Organic material/Salinity?
Calcium	Ca		Carbonate minerals	Carbonate minerals (Calcite)
Strontium	Sr			Carbonate (Aragonite)
Chlorine	Cl			Uncertain - Sea water chemistry?

Table 10.2 Likely elemental affinities for core ELF19.

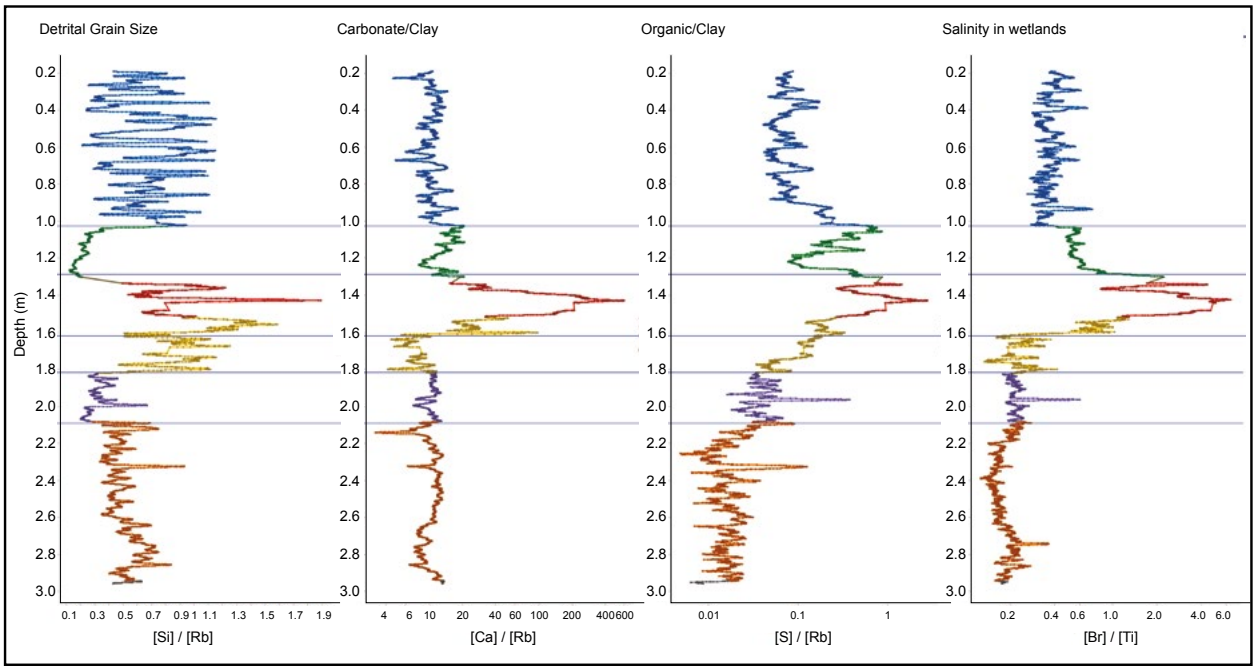

Figure 10.4 Chemostratigraphic zonation of core ELF19. Si/Rb likely reflects variations in grain size with higher values being more Sand (Quartz) rich and higher Rb being more Clay rich. Ca/Rb likely reflects variations in carbonate (Ca) compared to clay material. S/Rb likely reflects variations in organic material (S) to clay. Br/Ti is a proxy for salinity in wetlands (see text for references).

the hypothesised mineralogical controls on chemical data (Table 10.2):

- Chemo zone C1: interbedded sandy/silt and silty/clay horizons (Si/Rb variations) likely of a more saline depositional setting (moderate Br/Ti values) and some shell/carbonate material (Ca/Br); the finer horizons are more organic rich (Si/Rb troughs correlate with S/Rb peaks) and more saline (Si/Rb troughs correlate with Br/Ti peaks)
- Chemo zone C2: massive clay rich unit (very low Si/Rb values) with decreasing downhole organic (S/Rb) content; a higher level of salinity (Br/

Chemo Zone	Depth	Si/Rb (~Quartz/Clay)	Ca/Rb (~Carbonate/Clay)	S/Rb (~Organic material/ Clay)	Br/Ti (~Salinity; (De Boer *et al.* 2014)
C1		Highly variable, ranging from vales of ~1.1 to ~ 0.01 over ~10cm of stratigraphy	Variable, ranging from ~10 to ~5. Variations occur over a similar scale to Si/ Rb and troughs in Ca/ Rb correlate with Si/ Rb peaks	Moderate (~0.06) with three peaks at ~0.36, 0.6 and 0.7m depth.	Moderate to low
Boundary		Sharp fall	Sharp rise	Sharp rise	Sharp rise
C2		Constantly very low (~0.025)	Moderate to low (~17 at top dropping to ~8 at base of zone)	High at top of unit (0.8) dropping to moderate in centre (~0.08), rising to high again at base (0.5)	Moderate
Boundary		Sharp increase	Sharp increase	Sharp increase	-
C3		Rising to a very high peak in the centre of zone (~1.9)	Rising to a very high peak in the centre of zone (up to ~575)	Rising to a very high peak in the centre of zone (~2.8)	Rising to a very high peak in the centre of zone (~6.4)
Boundary		Trough	Decrease	Decrease	Decrease
C4*		Variable but decreasing from high (~1.6) at top of the zone to moderate at base (~0.8)	Moderate at top of zone (~23) dropping to low at base of zone (~1.7)	Moderate at top of zone (~0.19) dropping to low at base of zone (~0.08)	Moderate at top of zone (~0.8) dropping to low at base of zone (~0.25)
Boundary		Drop	-	Plateauing	Plateauing
C5		Very low/low (0.3)	Low (10.5)	Low (0.04)	Low (0.2)
Boundary		Increase	-	Decrease	Decrease
C6		Moderate (0.5) with a gradual down hole rise.	Low (10.5)	Low (~0.01)	Low (0.2) to very low (0.2) down hole
* Based on the variations in data over the unit it may be possible to split zone C4 into two sub zones.					

Table 10.3 Chemical definition of Chemo Zones and boundaries for core ELF19.

Ti) than zone C1 some shell/carbonate material (Ca/Br)

- Chemo zone C3: the coarsest unit in the core (Si/ Rb) that also contains a large carbonate content (Ca/Rb), organic material (S/Rb) and salinities (Br/Ti)
- Chemo zone C4: a coarse unit (Si/Rb) with low carbonate content (Ca/Rb), decreasing organic material (S/Rb) and low salinity (Ti/Rb)
- Chemo zone C5: a clay rich unit (Si/Rb) with low carbonate content (Ca/Rb), moderate to low organic content (S/Rb) and low salinity (Br/Ti)
- Chemo zone C6: a silty unit (Ca/Rb) with low carbonate content (Ca/Rb), low to very low organic content (S/Rb) and low to very low salinity (Br/Ti)

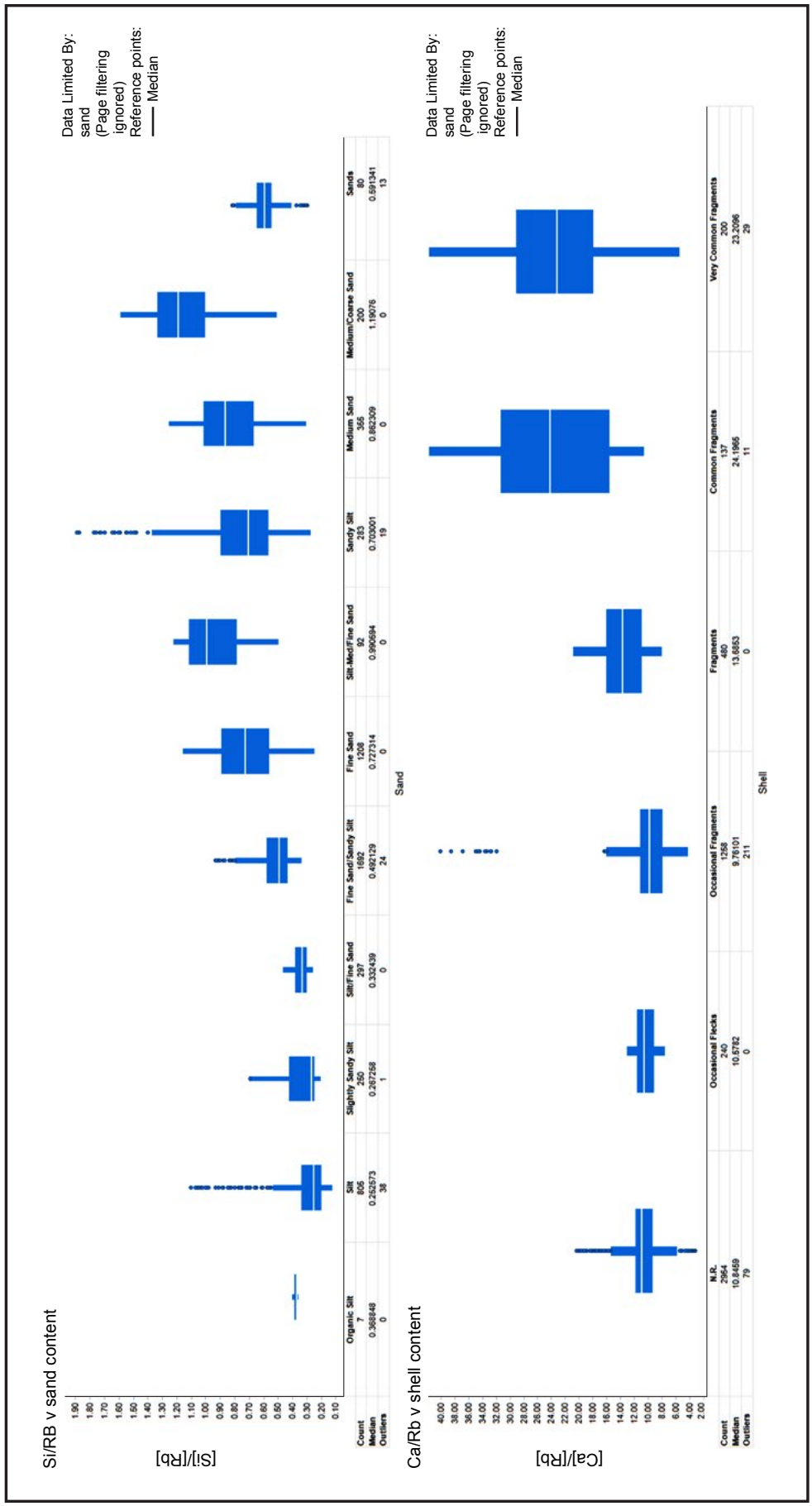

Figure 10.5 Boxplots showing the correlation of observed mineralogy and chemistry within core ELF19.

Integration of chemo zones with sedimentological and ecological data

Without any other data the chemo zones presented in section 3.3 are only hypothesised. However, the results can be compared to other geotechnical information such as grain size, shell content and biostratigraphy. A reasonable comparison is achieved between the Si/Rb values and observed sand content as is the comparison of Ca/Rb values with shell contents (Figure 10.5).

When ecological facies, derived from the biostratigraphic data, are compared to chemistry (Figure 10.6) there is also a good coincidence between the ecological boundaries and the chemo zone boundaries. Chemo zones C1 and C2 have Br/Ti values of ~0.4 and S/Rb values of ~0.1 whereas chemo zones C4, C5 and C6 have lower Br/Ti values of ~0.2 and S/Rb values of ~0.05 demonstrating a drop in salinity and organic content down core. Consequently, C1 and C2 are both interpreted as representing estuarine mudflats, whereas, C4-C6 are interpreted as river or lake sediments. Unit C3, shows greater complexity. Based on initial chemistry it is expected this would be a coarse marine bed. The ecological facies data also suggests that this is a course unit, however the lack of marine fossils suggest it is deposited in a freshwater setting.

Conclusions

The chemostratigraphic zonation of ELF19 based on an interpretation of the chemical, grain size and ecological analysis is summarised in Table 10.4 below.

Case study 2 – Chemostratigraphic correlation of chemo zones within Holeocene shallow cores.

Introduction

Case study 2 seeks to demonstrate how chemostratigraphic zonations can be used to produce a chemostratigraphic correlation for multiple cores across a palaeolandscape for further understanding of palaeotopography, geography and depositional setting.

Chemostratigraphic correlation is a stratigraphic technique that is commonly used in both the petroleum and minerals industries to correlate core and drill cuttings. This can be undertaken at a variety of different scales from regional scale (Ratcliffe *et al.* 2012), quarry or oil field scale (e.g. Pearce *et al.* 2010) through to field outcrop scale (Ellwood *et al.* 2008). Generally, the more localised the study area the more detailed a correlation is possible.

Chemostratigraphic correlation involves the characterisation, correlation or differentiation of sedimentary rock successions based on stratigraphic variations in the elemental geochemical data. This geochemical data is influenced by changes in the mineralogical and organic content of the rock, and in particular by changes in clay mineralogy and the heavy mineral content. Mineral and organic changes are often a manifestation of changes in palaeoclimate, palaeoenvironment, sediment provenance and both weathering or diagenesis. The dependence of chemostratigraphy techniques on minerals means that it can be used on any lithology, including those that are barren of biostratigraphy. For example, mapping the concentrations of elements such as Zr, Nb and Ti can display changes in heavy mineral abundance, which can provide insight into sediment dispersal patterns and changes in provenance. Mapping elements such as U and Mo reflect the presence and abundance of organic matter that, together with biostratigraphic information, enable the reconstruction of depositional environments.

Chemostratigraphic correlation

At the time of writing, work within *Europe's Lost Frontiers* had not progressed to the point that project data could demonstrate the use of chemostratigraphy to correlate unconsolidated cores, therefore a case study has been produced from data collected from cores sourced from Orkney (Figure 10.7). Three approximately 2 to 3m cores (Core A, B and C), spaced over approximately 300m, were collected from the same sub-basin and underwent geochemical analysis and data interpretation to identify three key elemental ratios:

- Sr/Br – shell material (aragonite)/organic content

Chemo Zone	Top depth (m)	Ecological facies	Integrated interpretation
C1	0.19	Estuarine mudflats	Interbedded estuarine sandy silts and silty clays
C2	1.03	Estuarine mudflats	Estuarine clay
C3	1.33	Freshwater channel in a fluvial system	Coarse sediment of an uncertain marine/fluvial system
C4	1.52	River or lake	Freshwater sands
C5	1.82	River or lake	Freshwater clays with some organic content
C6	2.08	River or lake	Freshwater silts

Table 10.4 Integrated chemical and ecological results for core ELF19.

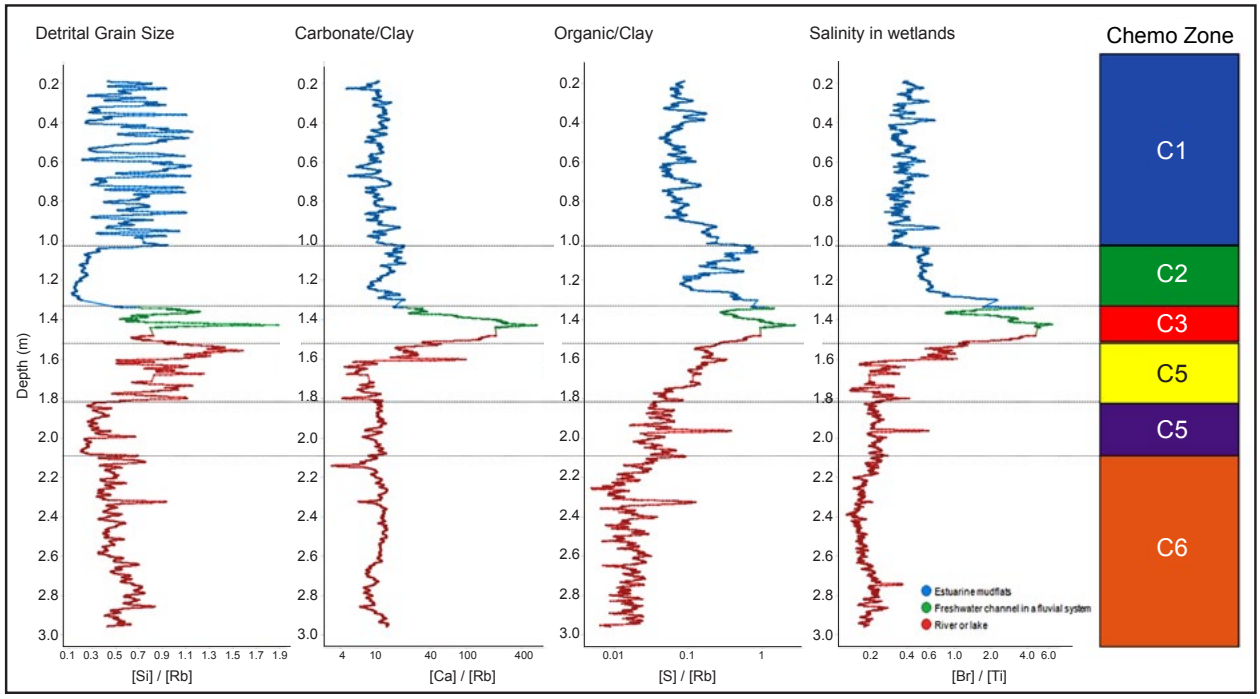

Figure 10.6 This figure demonstrates an excellent match in the chemostratigraphic zonation of core ELF19 and ecological biostratigraphic data.

- Sr/Rb – shell material (aragonite)/clay
- Si/Br – sand (quartz)/organic content

These key ratios were used to establish a chemostratigraphic zonation comprising four chemo zones (C1-C4), furthermore, chemo zone C2 was split into four sub zones (C2-1 to C2-4) in core B and C. Not all zones were present in all cores and so a composite core has been produced to illustrate the full chemostratigraphic zonation (Figure 10.8).

As in case study 1, chemo facies information was produced for each chemo zone. Core B had undergone biostratigraphic analysis and cores A and B had undergone sedimentological analysis and therefore it was possible to 'ground truth' the chemo zonation with other data to produce confident facies descriptions for each chemo zone (Table 10.5).

Chemostratigraphic zonation, correlation and palaeolandscape interpretation

The presence and absence of the chemo zones in each core enables the chemo zones and subzones to be correlated across the cores (Figure 10.9 and 10.10).

To the authors knowledge, this represents the first attempt to correlate shallow Holocene cores using chemostratigraphy. Based on this chemostratigraphy, the following depositional history is hypothesised for the study area (further work is currently ongoing to confirm this):

- Chemo zone C1 is found across all three cores, suggesting the carbonate sands blanket the study area
- Chemo zone C2 is only found in cores B and C and thickens from core B to core C; this suggests that this silty unit with differing levels of organic material was either infilling existing topography that deepens towards core C or it has been differentially eroded from the surface – the fact that all subzones within unit C2 thicken towards core C suggest the former is the more likely
- Chemo zone C3 is not found in core B and is underlain by peat in zone C4 – this suggests that core C may have been a sub-aerial peat when the possibly lacustrine C4 sediment was being deposited around it; the lacustrine C3 sediment is also much thicker in core C than A suggesting greater accommodation space formed by palaeotopography
- The peat zone C4 has not been penetrated in core C; in core A it is found below the thin lacustrine C2 unit and so may be present at depth

Due to the high resolution of the scanning XRF, the chemostratigraphic zonation is able to record the exact point at which major palaeoenvironmental changes occurred and the chemostratigraphic correlation map these boundaries spatially (Figure 10.9 and 10.10). Furthermore, the highly precise placement of these palaeoenvironmental changes means that future point sampling (e.g. geochronology, SedaDNA and biostratigraphy) can be carried out at the exact

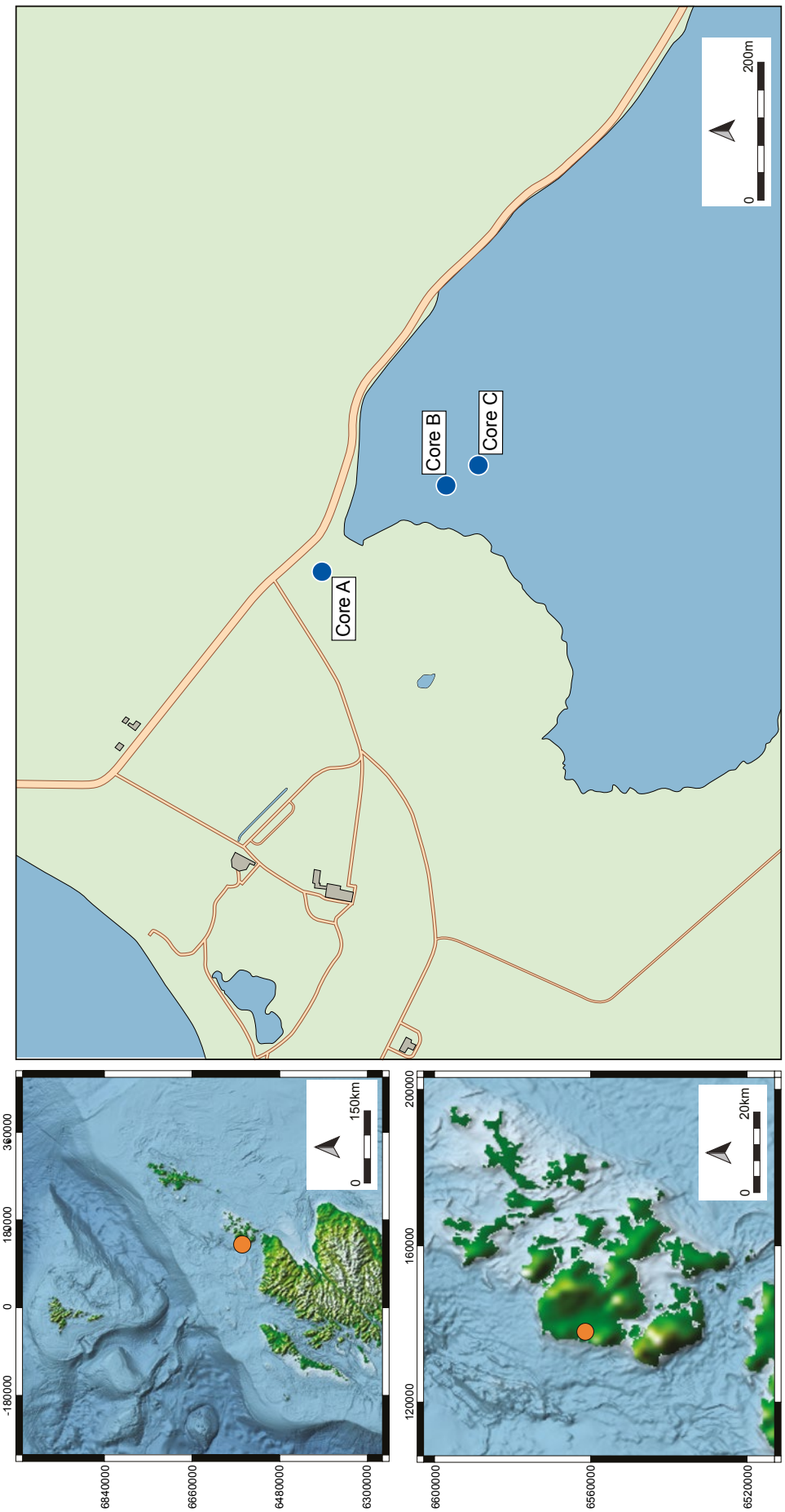

Figure 10.7 Orkney core locations

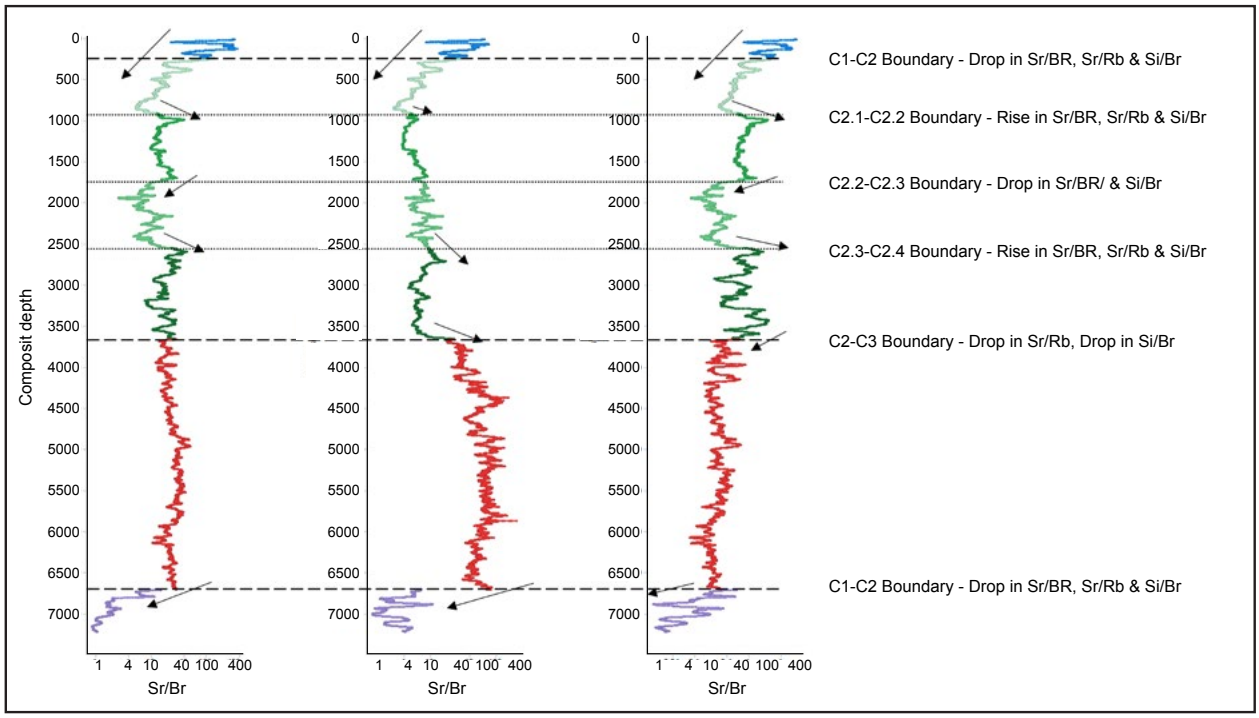

Figure 10.8 The elemental variations utilised to define the chemostratigraphic zonation in the study area. Sr/Br likely reflects variations in shell material (Sr - aragonite) and organic material (Br). Sr/Rb likely reflects variations in shell material (Sr - aragonite) and Clay (Rb). Si/Br likely reflects variations in sand (Si - Quartz) and organic material (Br).

Chemo Zone	Chemical interpretation	Sedimentology	Environmental interpretation	Integrated facies
C1	Shelly sand	Sand, Sand and Mud, Sand and Weed	Freshwater	Shell rich sand
C2	Silt with some shell material. Sub zones C2.1 and C2.3 marked by more organic rich material, where as subzone C2.2 and 2.4 are more shelly and sandy.	Mud	Brackish/ Freshwater	Fresh to brackish silt with some organic rich beds
C3	Carbonate rich	-	Freshwater	Freshwater carbonate rich sediment – Lacustrine?
C4	Low levels of all elements - organic rich sediment?	Peat	-	Peat

Table 10.5 Chemical, sedimentological and environmental interpretation of chemo zones and integrated facies identification.

point these changes take place, removing the need to interpolate between data.

Case study 3 integrating chemostratigraphy with seismic studies

Introduction

This case study seeks to demonstrate how, in addition to producing chemostratigraphic zonations and correlations from elemental data, incoherent (Compton) and coherent (Rayleigh) scattering caused by the XRF interaction with the core and recorded by the ITrax scanning XRF can be used to calculate a relative density profile for the analysed core. The variations in density can be utilized to link geochemistry to seismic geophysical data and by so doing enable interpretation of palaeo-depositional/environmental scenarios. This can both aid seismic interpretation and be used to extrapolate the chemical analysis away from the core

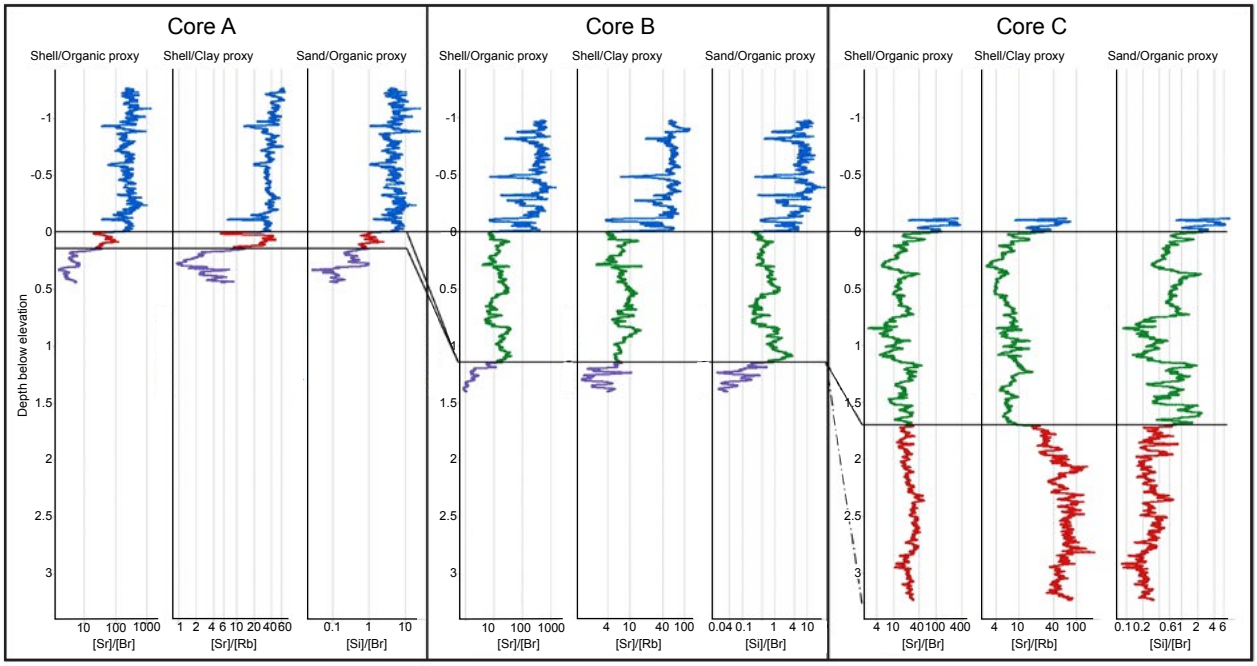

Figure 10.9 Chemostratigraphic correlation of chemo zones in wells A, B and C

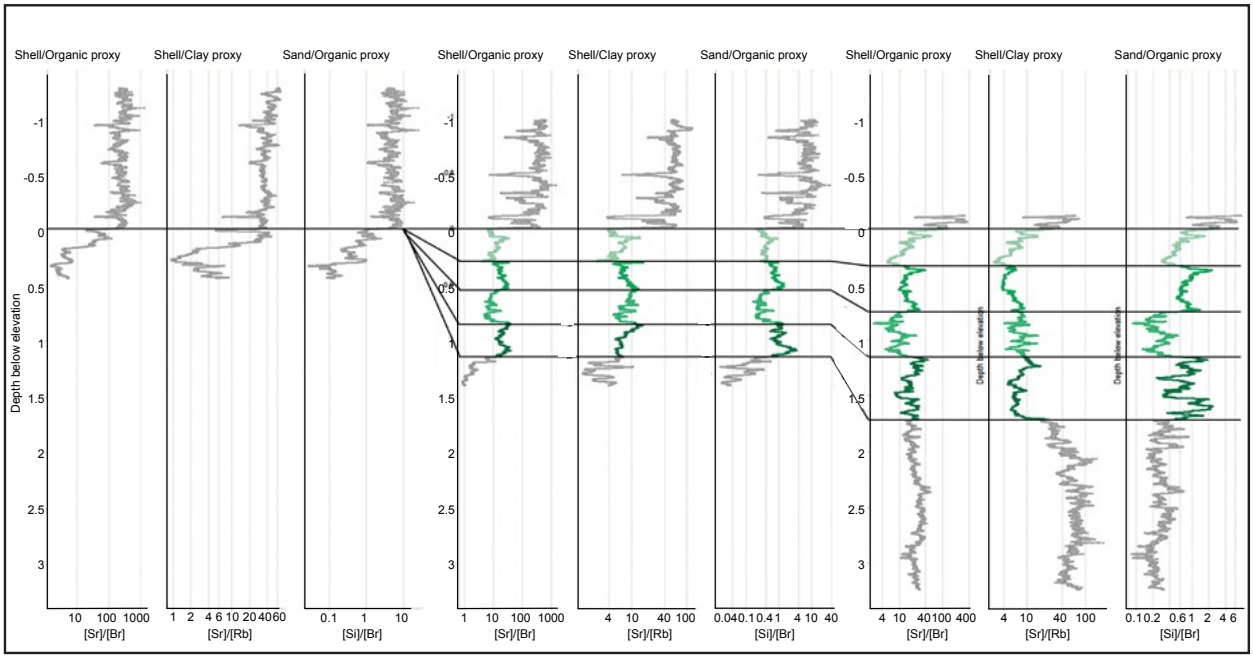

Figure 10.10 Chemostratigraphic correlation of chemo sub zones in wells A, B and C.

locations. This case study utilizes elemental and seismic data published in Gaffney *et al.* (2020) from core ELF1A, which was collected approximately 20 miles north east of core ELF19 (Figure 10.2).

Chemo zones and facies

Project core ELF1A has undergone chemostratigraphic zonation with the goal of identifying key geochemical signatures that could result from a tsunami event. Details of the investigation have been previously presented in Gaffney *et al.* (2020). Using the same method as that outlined in Case study 1, the chemical analysis was used to divide the core into six chemo zones (Figure 10.11) based on variations in:

- Sr – a proxy for shell material
- Rb – a proxy for clay
- Si – a proxy for quartz
- Zr – a proxy for detrital zircon

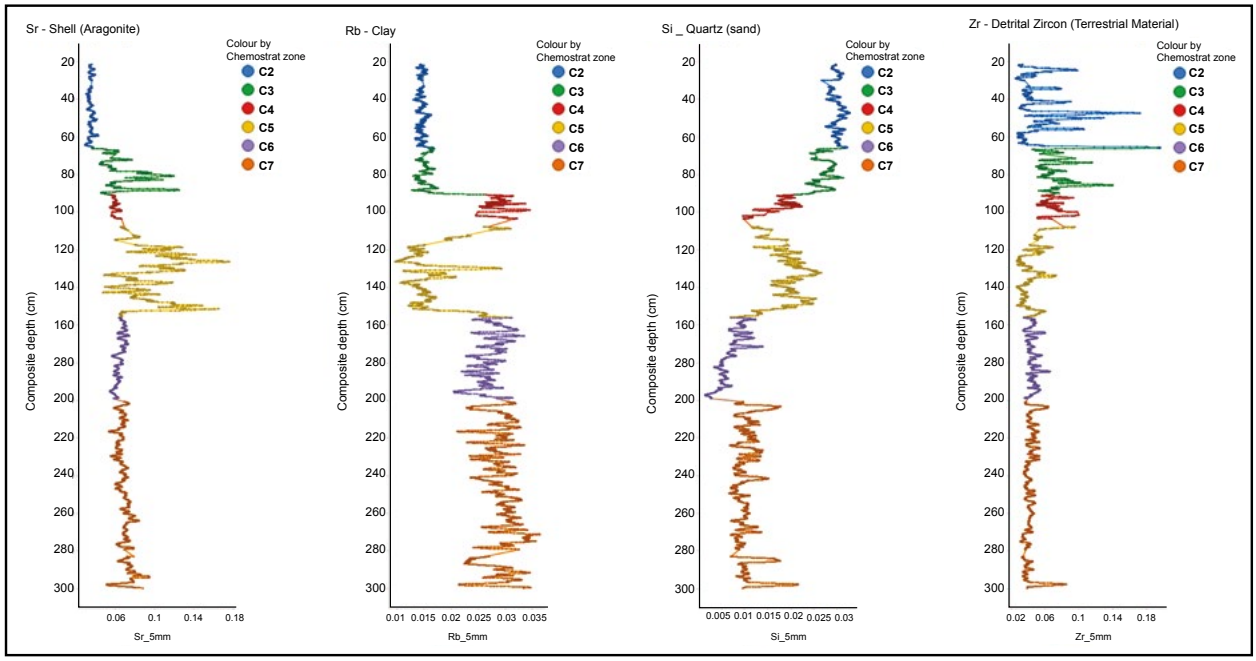

Figure 10.11 Chemostratigraphic zonation of core ELF1A (from Gaffney *et al.* 2020). Sr likely reflects the amount of shell material (aragonite) Rb likely reflects the amount of clay, Si likely reflects the amount of sand (Quartz) and Zr the amount of detrital zircon in the core.

These chemo zones have been interpreted to represent a series of chemostratigraphic facies (Chemo facies) which can be used to understand the depositional environments shown in Table 10.6 (see Gaffney *et al.* 2020 supplementary information).

Chemo zone C5 had been hypothesized to contain a Storegga tsunami deposit, and so a more detailed investigation of this zone was undertaken (Gaffney *et al.* 2020). This enabled the zone to be divided into eight separate sub zones based on changes in:

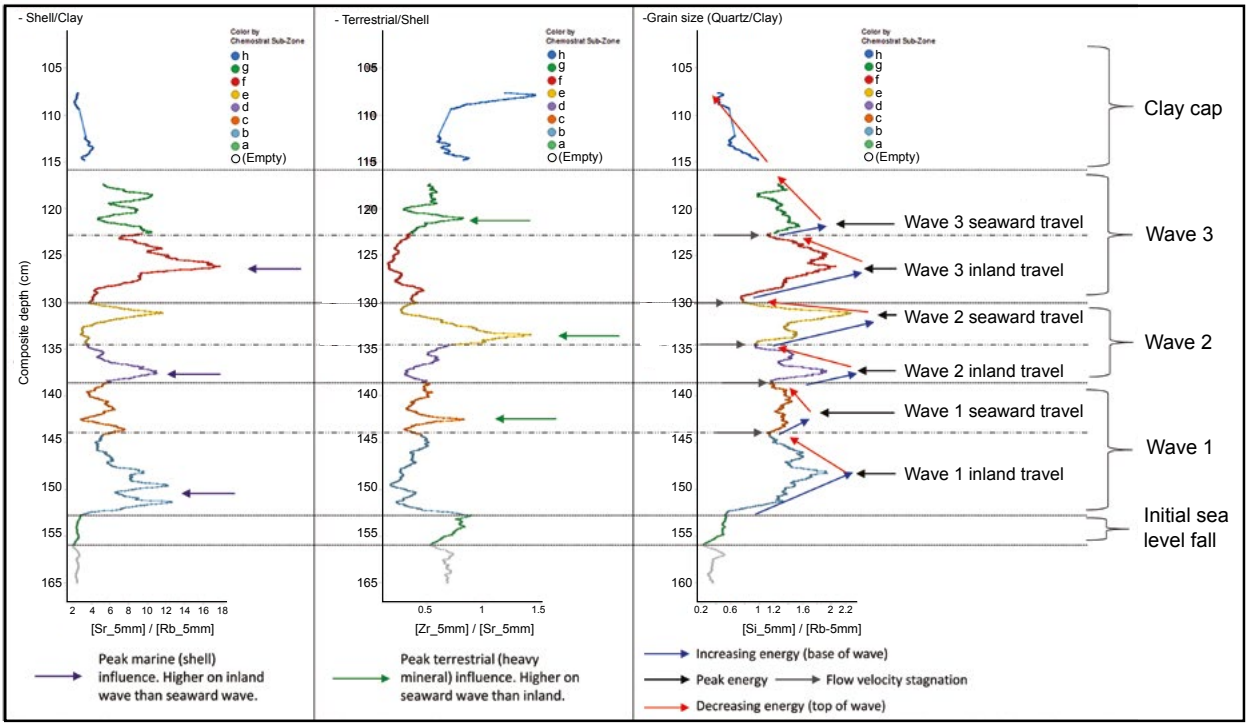

Figure 10.12 Chemostratigraphic zonation of the Stroregga tsunami deposit preserved in core ELF1A (from Gaffney *et al.* 2020).

Chemo zone	Chemo facies
C2	A clean high energy sand with little to no shell/marine material or marine influence. Several beds display high Zr/Sr values suggesting increased terrestrial derived heavy mineral sand beds.
C3	A high energy interbedded terrestrial sand and marine/shell dominated deposit.
C4	A clay/silt environment similar to that seen in units C5 and 6 with no shell material, however the moderate Zr/Sr values suggest a more terrestrial input compared to units C5 and 6.
C5	High energy/coarse material including shell/marine material. The large variation in data within C5 does suggest there is an internal stratigraphy (see Gaffney *et al.* 2020). The top of this unit shows a grading change back to values similar to those in units C6 and 7. These observations suggest this may either be a tsunami or surge deposit; an erosive base, high energy deposit bringing distal marine sediment into a previously terrestrially dominated low energy environment topped by a gradational decrease of energy.
C6	The lowest energy unit in ELF001A is dominated by clay material, little shell material and a constant balanced marine/terrestrial influence.
C7	A clay/silty unit with interbedded siltier horizons (marked by increases in Si/Rb). Little shell material and a constant balanced marine/terrestrial influence.

Table 10.6 Chemo facies identified in core ELF1A (see Gaffney *et al.* 2020 supplementary information for full discussion).

- Sr/Rb – marine signature reflecting the chemical proxy for aragonite as shell content vs clay content
- Zr/Sr – a terrestrial vs marine sediment chemical proxy based on the input of terrestrial detrital zircons compared to a marine shell signal.
- Si/Rb – grain size proxy reflecting the chemical proxy for quartz (coarser sand grain) vs clay content; the coarser-grained sediment indicates a higher depositional energy than the finer clay-sized grains

The eight chemo subzones were interpreted to represent an initial fall in sea level, overlain by deposits associated with three pulses each comprising an initial inland wave identified by its marine depositional signal, topped by a seaward wave characterized by its terrestrial signal (Gaffney *et al.* 2020). The final chemo subzone represented a clay cap, likely reflecting the post tsunami deposition of suspended fine material (Figure 10.12; reproduced from Gaffney *et al.* 2020).

This use of elemental geochemistry enabled the identification of the tsunami deposit which was dated using both C14 and OSL methods. It was postulate that the deposits were associated with the Storegga slide event (Gaffney *et al.* 2020) and represented the furthest south in the North Sea such deposits have thus far been recognised.

Linking geochemistry to seismic

Several studies have demonstrated that the ratio of the Compton and Rayleigh scattered intensity, recorded by scanning XRF tools, are affected by the average atomic number of the sample, mineralogical composition, water, organic carbon content and therefore density (Fortin *et al.* 2012, Croudace *et al.* 2006). Seismic reflection strength is also a function of the impedance contrast in velocity, in turn based on elastic moduli, and density, based on lithology/mineralogy, porosity, saturation and organic content of a material. Thus, as the acoustic impedance that produce seismic reflectors are the product of density and velocity so the Compton scattering too is a function of density and there should be a correlation between both.

Core ELF1A has both the interpreted seismic and geochemical data necessary to test this method (see Gaffney *et al.* 2020). There is a large downhole increase in density from approximately 2.6 to 3.2 chemical density units at *c.* 1.55m depth that corresponds to the base of chemo zone C5 and the tsunami deposit (Gaffney *et al.* 2020). When this is compared to the published seismic (Gaffney *et al.* 2020, Figure 10.12) this Is the same depth as the tsunami seismic reflector, suggesting that this method is valid.

Within the XRF data, there are two density changes visible at ~0.8, ~1.15 and ~2m depth. The 0.8 and 1.15m density changes occur at a similar depth to two large amplitude shallow sea floor reflectors in the seismic data (I [green] and II [purple] in Figure 10.13). The ~2m depth density change also coincides with a lower amplitude reflector (IV [black dashed], Figure 10.13). Therefore, we can use the seismic to understand the spatial extend of the chemo zones (Table 10.7). Importantly, this show how spatially limited the Storegga tsunami deposit is within the study area.

Future geochemical applications to Europe's Lost Frontiers type studies

This chapter has demonstrated how elemental chemistry can be used to recreate palaeoenvironments within the *Europe's Lost Frontiers* project. It has been shown how geochemistry can be utilised to identify variations in sediment cores (often not visible to the

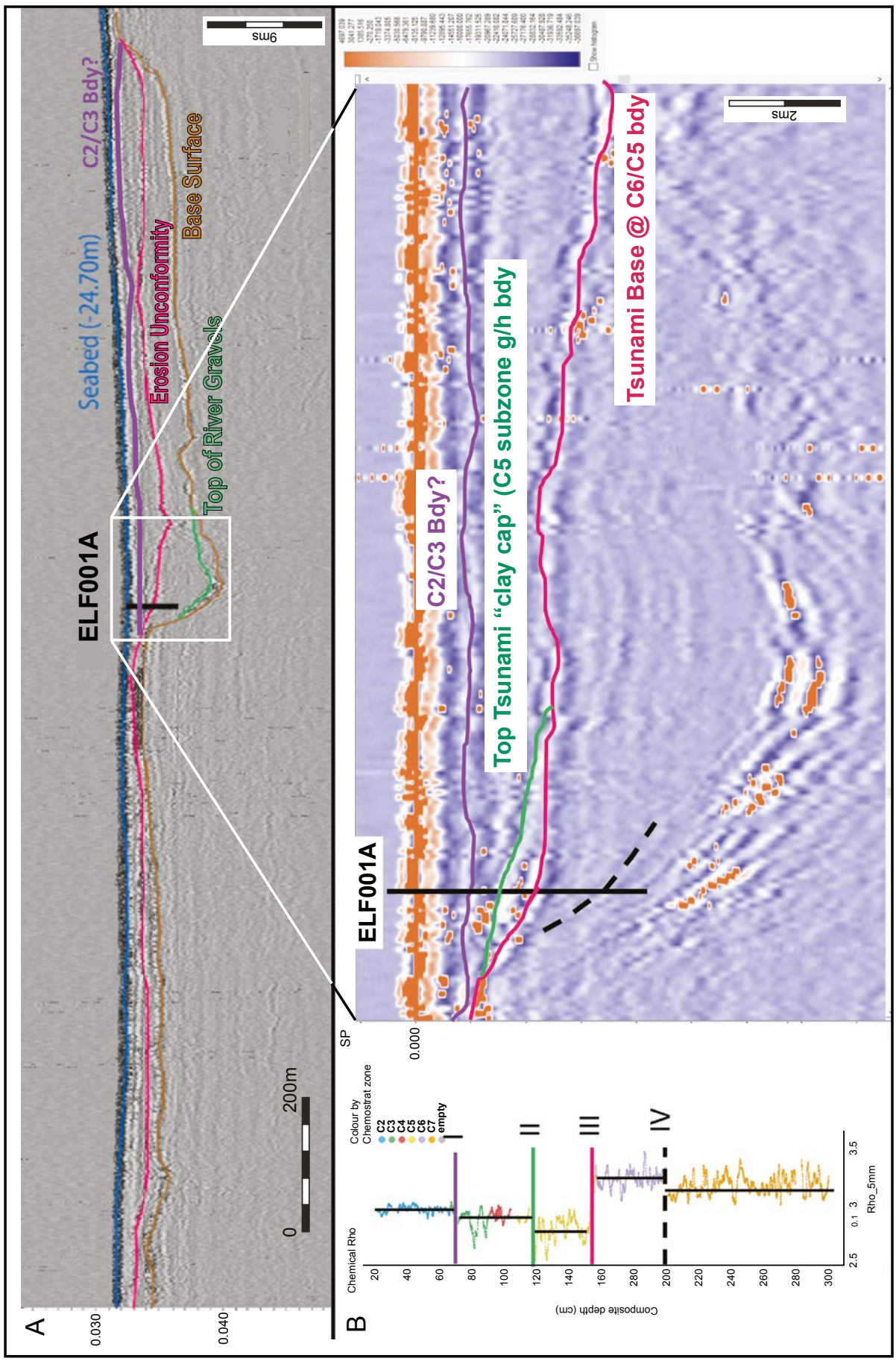

Figure 10.13 Comparison of the relative density of core ELF1A calculated from XRF data to the interpreted seismic data (from Gaffney *et al.* 2020).

Density change	Chemo zone	Chemo facies variation	Spatial extent on seismic line
I	C2-C3 Bdy	a down hole change from (C2) to sand and shell (C3) material -	laterally continuous
II	Upper C5	The transition between high energy tsunami sediments and the low energy clay cap.	Only found locally to ELF19 - suggests only a small preservation of Tsunami deposit
III	C5-C6 Bdy	Base of Storegga Tsunami deposit	laterally continuous
IV	C6-C7 Bdy	A down hole transition to a clay rich (C7) unit	hard to tell, maybe only local preservation?

Table 10.7 A summary interpretation of geochemical and seismic datasets.

eye) and to chemostratigraphically divide the core into separate chemo zones. It has been shown how the causes of these variations can be understood through statistical methods enabling chemo zones and facies to be assigned and thus in turn aid understanding of the depositional environments. The differentiation and chemostratigraphic correlation of multiple cores has then been undertaken, demonstrating how palaeosurfaces can be identified and palaeolandscapes recreated. There are of additional benefits for conducting geochemical analysis to further the understanding of palaeoenvironments that include:

- with the use of chemical signatures together with stable isotope data to link changes in paleoenvironment with changes in palaeoclimate
- identification of detrital zircon, heavy mineral and chemical provenance signatures in the cores; such studies are commonly utilised in the Carboniferous-Permian hard rock basement, below the Doggerland sediment, identifying if a sediment is sourced from the south (Variscan orogeny/bohemian massif) or north (Norway; e,g, Cram *et al.* 2014) – it is highly probable that this method could be of utility to provenance sand filled channels around Doggerland
- quantitative elemental chemistry is commonly utilised to identify the provenance of clay (e.g. Finlay *et al.* 2012) and geological materials (e.g. Bevins *et al.* 2020) in archaeological studies – could these methods be applied to lithic materials dredged from Doggerland and so both establish chemical families of lithics and potentially even correlate them to known (Present day) onshore sites?
- the chemo zones presented in this study are all linked to natural changes in the sediment record – however, could some of them be signals of human activities such as habitation? For example:
    - within North Sea oil and gas studies, the Si/Zr ratio is commonly utilised to identify flints in chalks – could this ratio be used to identify micro-debitage from knapping sites?
    - phosphorus is commonly associated with coprolite and hardgrounds – could it be used to identify phosphates caused by animal and human waste, vivianite or bone beds?
    - can Sr data be utilised to identify shell middens?

Elemental geochemistry is a powerful tool for archaeological and palaeoenvironmental studies. It can be used to identify depositional changes in any fluvial, lacustrine, marine or terrestrial setting, and correlate them across study areas, revealing palaeo- surfaces and landscapes. The wide range of modern analytical tools, from portable closed source tools that can be deployed in the field, through to lab-based scanning XRF tools that are capable of recording high vertical resolution data mean that geochemistry is a highly flexible tool suitable for application to a wide variety of settings. Furthermore, the ability to use geochemical tools to generate density data means that the results are easily linked to other investigative techniques, such as geophysics, and so aid the integration of disparate analytical datasets. Therefore, it is hoped that elemental geochemistry will become an increasingly utilised tool for studies across archaeology, palaeoenvironmental sciences and the humanities.