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Geochemical analysis for palaeoenvironmental interpretations – a case study of the English Wealden (Lower Cretaceous, south-east England)

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The elemental composition of terrigenous sediments is extremely important for interpreting the depositional conditions of sedimentary basins especially when traditional data are not available or insufficient. For the first time in the published literature, the elemental composition of the Lower Cretaceous Weald Basin (south-east England) is presented via X-ray fluorescence (XRF) and Spectral Gamma-ray (SGR) methods. The concentrations of Zr, Cr, Ni, Rb, and Sr in varying quantities suggest that the sediments may have been sourced from a stable craton while the enriched redox-sensitive elements such as Mo and Co confirm the presence of anoxic and reducing conditions at the sites of deposition. The spectral gamma-ray data show that the sandstone facies are more radioactive than the adjacent mudstone and shale and this trend is consistent with a freshwater origin. The higher quantity of thorium in relation to uranium indicates humid and hot palaeoclimatic conditions at the source areas that favoured intense weathering. The results of these analyses reinforce the importance of the geochemistry of sedimentary rocks as useful tools for understanding the depositional conditions of sedimentary basins.

Key words: elemental composition, X-ray fluorescence, spectral gamma-ray, palaeoenvironments, Lower Cretaceous, south-east England.

INTRODUCTION

The use of the geochemical composition of sedimentary rocks for interpreting palaeo- and depositional environments is well-documented (e.g., Alvarez and Roser, 2007; Pe-Piper et al., 2008; Ghasemi-Nejad et al., 2010; González-Álvarez and Kerrich, 2010; Eker et al., 2012; Garnit et al., 2012; Pi et al., 2014; Wójcik-Tabol, 2015). The elemental composition of terrigenous sediments is extremely important for interpreting the depositional conditions of sedimentary basins and may be more useful than expected when traditional data such as field observations and palaeontological examinations are not available or insufficient. The geochemical composition of terrigenous sedimentary rocks is a function of tectonic setting, provenance, weathering, transportation and diagenesis (e.g., Bhatia and Crook, 1986; Alvarez and Roser, 2007; González-Álvarez and Kerrich, 2010). Many major elements such as Fe, K, Ca, Ti and Mn in decreasing order of abundance may be affected by diagenesis or biological processes after deposition (e.g., Abanda and Hannigan, 2006; Brumsack, 2006; Wójcik-Tabol and Ślączka, 2009). Some trace elements such as Mo, U, Cr, Ni, Co and Zn are enriched in reducing sediments and are highly sensitive to redox changes (e.g., Lipinski et al., 2003; Pi et al., 2014). As a result, they are important proxies for palaeoredox reconstruction (e.g., Algeo and Rowe, 2012; Xu et al., 2012a) in various depositional environments (e.g., Elbaz-Poulichet et al., 2005). Trace elements such as Th, Zr, Co, Ti and Sc are the most immobile elements during weathering, transportation, deposition, diagenesis and are considered the most useful for determining provenance and the nature of tectonic settings of sedimentary rocks (e.g., Bhatia and Crook, 1986; Marques et al., 2011). The ratio of Th/U increases in sedimentary rocks with increasing alteration (Pe-Piper et al., 2008).

Potassium (K), uranium (U) and thorium (Th) are the dominant sources of gamma-rays in rocks. The concentrations and variations of these three elements in rocks determined by spectral gamma-ray method (SGR) present important geological and geochemical information on source rock composition, sorting during transport and deposition, grain size, clay content, modal composition of sandstone, porosity, organic carbon content, weathering at source and palaeoclimate conditions (e.g., Ruffell and Worden, 2000; Šimíček et al., 2012; Šimíček and Bábek, 2015). Potassium is common in many sediments that contain feldspar, mica, clays or chloride salts. Uranium and thorium have many host phases in sedimentary rocks and these may include clays, feldspars, heavy minerals, phosphates and organic matter. In mudrocks and argillaceous limestones, most of the U and Th are sourced from clays, organic matter, and heavy minerals (Šimíček et al., 2012; Šimíček and Bábek, 2015). Potassium is leached from feldspars and muscovite during the formation of kaolinite under hot and humid climates while thorium is concentrated during weathering. K and U are generally more soluble than Th and U is prone to mobilisation during weathering and clay mineral diagenesis (Ruffell and Worden, 2000; Schnyder et al., 2006). Depletion of K and U during weathering and palaeoweathering reflects the duration and severity of weathering (e.g., McLennan et al., 1983; Alvarez and Roser, 2007; Ghasemi-Nejad et al., 2010). Interpretation of gamma-ray emission of sedimentary rocks may

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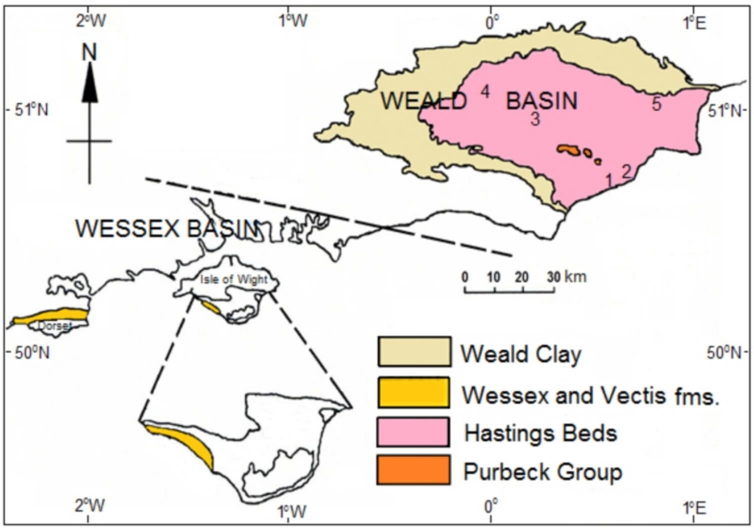

Fig. 1. Geographical locations of the Wealden strata in south-east England showing the study locations

1 – Rock-a-Nore, Old Town, Hastings; 2 – Pett Level (Haddock's Cottages and Cliff End), Fairlight, near Hastings; 3 – Northiam Quarry, Northiam; 4 – Hastingford Cutting, Hadlow Down; 5 – West Hoathly Quarry, Sharpthorne; 50°N and 51°N refer to the latitude while 2°W to 1°E refer to the longitude; modified after Goldring et al. (2005: fig 1)

sometimes become problematic where specific heavy minerals have high Th or U contents, resulting from high amounts of zircons, uraninites or thorites (Schnyder et al., 2006) while siliciclastic facies can also be complicated because of their multi-component nature (Šimíček and Bábek, 2015). It may not be possible to apply a global set of elemental discriminate for the identification of terrigenous sediment sources without a systematic investigation to evaluate the effects of diagenesis or sorting (e.g., Abanda and Hannigan, 2006; Pe-Piper et al., 2008; Wójcik-Tabol and Ślączka, 2009).

The Early Cretaceous represents an important phase in the geological record which produced episodes of accelerated global change in climate and sea level and consequently changed sedimentation style (e.g., Sladen, 1980; Ziegler, 1981; Sladen, 1983; Rawson, 1992; Taylor and Ruffell, 1993; Vandycke, 2002; Hopson et al., 2008; Föllmi, 2012). The period witnessed a change from arid/semi-arid climate and relatively high sea level in the Jurassic to humid conditions and a low sea level in the Cretaceous (e.g., Sladen, 1980, 1983; Hallam, 1984; Hallam et al., 1991; Rawson, 1992; Taylor and Ruffell, 1993). These changes ensured that sedimentation occurred in non-marine conditions in the Early Cretaceous: south-east England (e.g., Allen, 1975, 1981; Stewart, 1981a, b, 1983; Allen, 1989), south America (e.g., Anjos and Carozzi, 1988; Rodrigues et al., 1988; Legarreta et al., 1989; Scherer and Lavina, 2006; Garrido and Salgado, 2015; Ferreira et al., 2016) and China (e.g., Sha et al., 2003; Jiang and Sha, 2007; Li et al., 2013; Chen et al., 2014; Ju and Sun, 2016). The English Lower Cretaceous (Fig. 1) is used as a case study to show the geochemical composition of sediments as effective indicators of palaeoenvironments because the facies is very important geologically as described below. The Lower Cretaceous of the Weald in south-east England exposes some principal outcrops and some of the most complete successions of the lowermost Cretaceous facies in north-west Europe and beyond (e.g., Stewart, 1981a; Booth, 2005; Hopson et al., 2008; Radley and Allen, 2012). The Ashdown and Wadhurst Clay Formations (Fig. 2) provide excellent opportunity for the study of the Lower Cretaceous non-marine and fluvial-related sedimentation patterns in variety of conditions including lagoonal, deltaic and tidal that persisted prior to the Late Cretaceous greenhouse Earth (Booth, 2005; Hopson et al., 2008). These two formations also present the opportunity to study the depositional, climatic, tectonic, eustatic changes witnessed in the Lower Cretaceous in north-west Europe (Sladen and Batten, 1984; Hallam et al.,

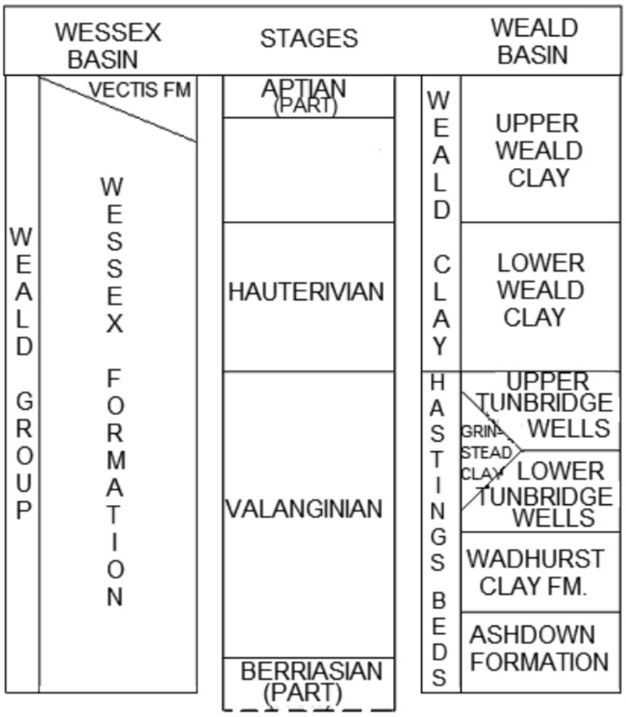

Fig. 2. Generalized stratigraphy of the Wealden sediments (part of the Lower Cretaceous) in the Weald and Wessex basins (after Allen and Wimbledon, 1991: fig. 2)

1991). Their superb exposures also make them potential analogues for studying complicated basin tectonics including basin inversion and for hydrocarbon reservoirs. Although the sedimentology and stratigraphy of the Lower Cretaceous English Wealden sediments have been studied since the early 19th century amounting to nearly 200 years of research (e.g., Fitton, 1824; Webster, 1826; Topley, 1875; Lake and Thurrell, 1974; Allen, 1975, 1981; Stewart, 1981a, 1983; Lake and Shephard-Thorn, 1987; Akinlotan, 2015), the elemental composition of these non-marine sediments is scarcely documented in the literature. For the first time in the published literature, the elemental composition of the Lower Cretaceous non-marine Weald Basin is presented via XRF and SGR methods from the Ashdown and Wadhurst Clay Fms. (Upper Berriasian–Middle Valanginian) within the Weald Basin in south-east England. The aims of this paper are to determine the elemental composition of the Wealden sediments in order to characterize the palaeo- and depositional environments of the Weald Basin and then compare with previous interpretations made from traditional datasets such as field observations and palaeontological examinations.

GEOLOGICAL SETTING

Wealden is used for the non-marine sandstones and mudstones between the Purbeck Group and the Lower Greensand of the Weald, the Isle of Wight and Dorset (Fig. 1) in south-east England. The term is also used more widely to refer to the Lower Cretaceous non-marine rocks of NW Europe (e.g., Hopson et al., 2008; Radley and Allen, 2012). The Wealden sediments in Kent and Sussex are the type area for the non-marine Wealden formations of north-west Europe and broadly equates to the Weald Basin in south-east England (Radley and Allen, 2012). The Hastings Beds (Upper Berriasian–Valanginian) in the lower section and the overlying Weald Clay (Hauterivian–Lower Aptian) make up the non-marine Wealden successions (Fig. 2) in the Weald Basin (e.g., Lake and Shephard-Thorn, 1987; Booth, 2005; Hopson et al., 2008; Radley and Allen, 2012) and represent ~25 million years of depositional history (Stewart, 1981a). The Ashdown, Wadhurst Clay, and Tunbridge Wells Sand formations (see Fig. 2) make up the Hastings Beds (Berriasian–Valanginian). The Ashdown Formation (Upper Berriasian–Lower Valanginian) is made up of fine-grained sandstones, siltstones, and mudstones with minor amounts of shale, mottled clay, lignite beds, sideritic mudstone, and sphaerosiderite nodules. These lithologies are generally arranged in rhythmic units of cyclothems and divided by thin pebble beds (Lake and Young, 1978; Lake and Shephard-Thorn, 1987; Hopson et al., 2008; Radley and Allen, 2012; Akinlotan, 2015). The Wadhurst Clay Formation (Lower–Middle Valanginian) comprises mainly soft, dark grey shales and mudstones, with minor sandstone, conglomerate, calcareous sand, clay ironstone, and lignite. All these have been changed penecontemporaneously at the surface to coloured sediments via outcrop weathering (Lake and Young, 1978; Lake and Shephard-Thorn, 1987; Hopson et al., 2008; Radley and Allen, 2012; Akinlotan, 2015). In terms of petrology and mineralogy of the sediments, the sandstones and siltstones in the two formations are mainly fine to medium-grained quartz arenites without any feldspar and rock fragments (Akinlotan, 2015). The quartz grains are generally monocrystalline. A very small amount of feldspar and rock fragment is, however, present in the Wadhurst Clay Fm. Muscovite and zircon are present in very small amounts at Haddock's Cottages. Iron stains are very common features. The mudstones and shales are dominated by illite and kaolinite with illite-montmorillonite and vermiculite. Illite-smectite is present in very small quantity in the Wadhurst Clay Fm. (Akinlotan, 2015). The overall environment of deposition of the sediments within these two formations is fluvial and non-marine. Deposition occurred under both braided and meandering river systems. The common sedimentary structures in the formations are channels, cross beddings, trough and planar laminations and slump structures. Tidal flat conditions were evident in the Ashdown Fm. while lagoonal conditions were more prominent in the Wadhurst Clay Fm. (Allen, 1975, 1981; Stewart, 1981a, 1983; Lake and Shephard-Thorn, 1987; Akinlotan, 2015).

METHODS

STUDY LOCATIONS

Twenty samples comprising seventeen mudstones and shales, and three fine-grained sandstones were sourced from across six locations from the Ashdown and Wadhurst Clay fms. (Fig. 3). The study locations were selected because they are part of the principal partial reference sections of the Wealden facies in the Weald. They represent good spread across the basin and present a mix of both coastal and inland sections to allow for the review of spatial variability in the composition of the sediments. Sampling was rationed and limited to twenty samples because of the constraints on the number of samples allowed by Natural England. This is because all the locations are either Sites of Special Scientific Interest (SSSI) and/or Geological Conservation Review (GCR) sites and are protected by law. The section at Rock-a-Nore [TQ 827 095], presents sediments from the lower part of the Ashdown Fm. at Hastings. This section is dominated by siltstones and mudstones with minor sandstones. Eight samples, mudstones, and shale were collected from this location. The outcrop at Haddock's Cottages [TQ 883 124] is in the upper section of the Ashdown Fm. and presents distinct sedimentary cycles consisting of pairs of cross-bedded sandy and silty beds. A fine-grained sandstone was collected from the accessible part of this section. The outcrops at Cliff End [TQ 888 132] fall within the uppermost part of the Ashdown Fm. and the lowermost section of the Wadhurst Clay Fm. Cross-bedded and channelized sandstones, siltstones, and mudstones that are arranged rhythmically dominate the section. Two mudstone samples were collected from the upper part of the Ashdown Fm. while two samples, mudstone and shale were collected from the lower part of the Wadhurst Clay Fm. The section at Hastingford [TQ 523 259] in the lower Wadhurst Clay Fm., consists mainly of cross-bedded medium-grained channel sands. Two samples were collected from this location. The West Hoathly Quarry [TQ 374 328 - TQ 375 329] also in the lower Wadhurst Clay Fm., is dominated by mudstone and three samples were collected in this location. One sample was collected from the mudstone unit within Northiam Sandstone at Northiam [TQ 829 253] in the upper part of the Wadhurst Clay Fm.

PORTABLE XRF (ENERGY-DISPERSIVE) METHOD

In order to determine the chemical composition of the sediments and analyse for a range of important elements to an acceptable limits of detection, energy-dispersive X-Ray Fluorescence (XRF) method was used. All the field samples were pulverised and homogenized using an agate pestle and mortar prior to XRF analysis. Trace and major element composition was determined using an *Innov-X Alpha-6500* portable X-ray

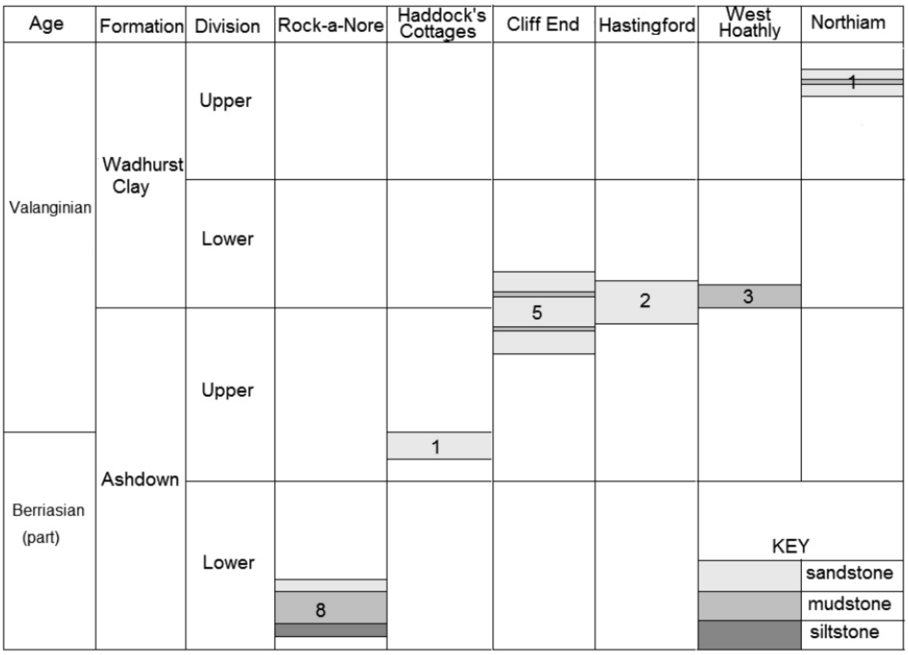

Fig. 3. Stratigraphic positions of the samples used in this study and the summary log of study locations

Each number refers to the number of samples collected at location

spectrometer (Olympus Corporation, Tokyo, Japan). This equipment provides measurements of elemental concentrations in parts per million (ppm) for about 20 elements in small samples. The equipment provides concentration of each element including a standard deviation (S.D.) value. Data output from the analysis was processed using Microsoft Excel. Data processing involves correcting for suppression or enhancement caused by the other elements for major elements. Further details of the procedures, operations and applications of XRF method have been described (Jenkins, 1974; Jenkins et al., 1982; Lee and McConchie, 1982; Williams, 1987).

In order to ensure the accuracy of the concentration of each element, the standard deviation was multiplied by three to give the appropriate detection limit for the element. Where the calculated concentration is negative, less than or equal to the standard deviation value it means the reported concentration is below the instrumental detection limit and this is removed from the spreadsheet. Some reported concentrations are greater than the error value but they are not up to three times the standard deviation values and are therefore indistinguishable statistically from the detection limit. In order to ensure the precision of the measurement for each element, each sample was measured twice and the average of the two measurements was taken. The present study includes the determination of Fe, K, Ca, and Ti as major elements and Zr, Ba, Co, Mn, Rb, Ni, Zn, Cr, Sr, Cu, Pb, As and Mo as trace elements. Elements with light atomic mass such as Mg, Al, and Si were not detected by the portable X-ray spectrometer and the applied method but may be present within the sediments. To quantify possible enrichment of the reported elements, the concentration data were normalized to avoid dilution effects in the measurements. Ti normalization was carried out using: Element/Ti (sample)/Element/Ti (shale) for each measurement. The "average shale" values of Wedepohl (1971, 1991) were used as reference background data. If the resulted value is >1, then the given element is enriched, relative to the average shale, but value <1 indicates impoverishment.

SPECTRAL GAMMA-RAY METHOD

To determine the concentrations of K, U and Th which can in turn provide useful information about clay mineral types, provenance, carbon contents and grain size within the sediments, spectral gamma-ray (Gamma Ray Spectroscopy – GRS) logging was conducted at Pett Level (Cliff End and Haddock's Cottages) and Rock-a-Nore (Figs. 1 and 3). The sites were selected for the logging because they have the best-exposed sections among all the study sites. These sites also present stratigraphically important and distinct facies of the lower and upper Ashdown Fm., the boundary between the Ashdown and Wadhurst Clay fms. and the Cliff End Sandstone. Ninety-one field GRS measurements were made with a Gamma Surveyor portable spectrometer (GF Instruments, Brno, Czech Republic) with NaI (Tl) scintillation detector diameter 3'', length 3'' (volume 6.3 in^3). It is equipped with a control unit (256 90 60 mm) for data entry and display of measurements. The equipment distinguishes the three component decay chains of potassium, uranium, and thorium by the wavelengths of their characteristic gamma emissions. Eight logging points were selected, one at Rock-a-Nore and seven at Pett Level, (see Figs. 1 and 3) to cover the different facies within the two formations. Measurement at each logging point (interval of 20 cm) was performed with full rock-detector contact on flat surface. The detector was positioned perpendicular to the section wall and parallel to bedding. The instrument converts quantitative values (counts per seconds) in the energy windows to concentrations of K (%), eU (ppm of uranium equivalent) and eTh (ppm of thorium equivalent), respectively. The measured concentrations were transferred to spreadsheet in Microsoft Excel for further analyses.

RESULTS

XRF ANALYSIS

The geochemical composition of samples from the study areas is shown in Appendix 1*. The distribution of major (Fig. 4) and trace (Fig. 5) elements is presented. Comparison of the elemental suite to the average crustal shale values (Wedepohl, 1971, 1991) and the review of Ti-normalized enrichment factors enabled the division of these elements into two categories (Table 1): enriched elements (Co, Mo, Zr, and As) and non-enriched elements (Pb, Ni, Zn, Cu, Cr, Rb and Mn). The distribution of the enriched elements across all the study sites is given in Figure 6. The variation of the concentrations with depths of some selected elements across some of the study locations is shown (Figs. 7 and 8). Although the average concentrations of Pb and Ba in study locations show that they are not enriched, their concentrations appear to be close to the values of the average crustal shale (Fig. 9). Co, Mo, Ba, and Pb have their highest values in the section at Rock-a-Nore in the lower Ashdown Fm. Zr has its highest value in the Ashdown Fm. at Haddock's Cottages. It then decreases up through the section and northwards. Enriched elements As and Ti have their maximum concentrations in the West Hoathly Quarry in the lower Wadhurst Clay Fm. Mo has its highest value in the outcrop at Northiam (Wadhurst Clay Fm.). Other locations have similar quantities of Mo. Fe has its greatest amounts at West Hoathly Quarry and Northiam in the Wadhurst Clay Fm.

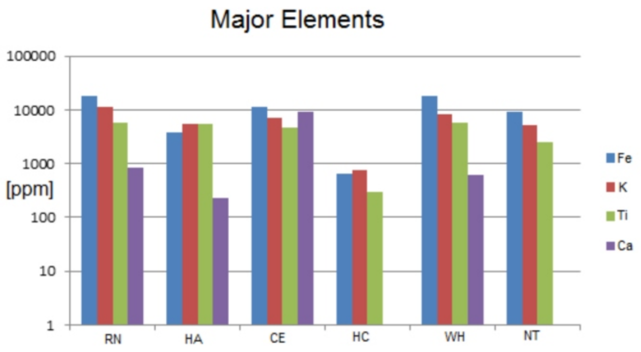

Fig. 4. The concentrations of major elements

RN – Rock-a-Nore, HA – Haddock's Cottages, CE – Cliff End (Pett Level), HC – Hastingford, WH – West Hoathly Quarry, NT – Northiam

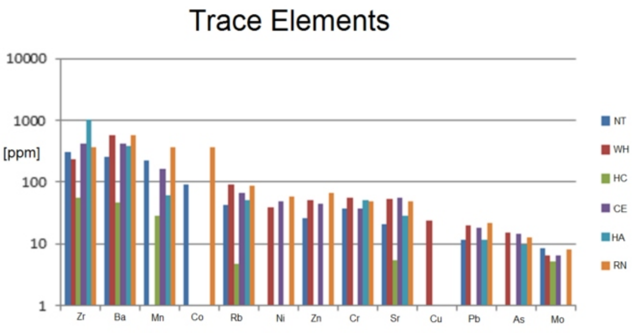

Fig. 5. The concentration of trace elements

Explanations as in Figure 4

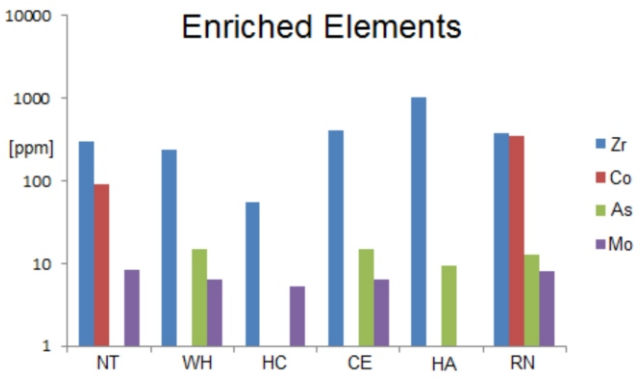

Fig. 6. The concentration of the enriched elements

Explanations as in Figure 4

SPECTRAL GAMMA-RAY ANALYSIS

The summary of the spectral gamma-ray data is presented in Table 2 and the stratigraphic distribution of the radioactive minerals is presented in Figure 10. These sediments reveal medium level of radioactivity with the following mean concentrations total gamma ray: 70.3 cps; K: 0.8%; Th: 9.5 ppm and U: 3.6 ppm. Potassium is generally higher in the sandstone compared to the mudstone and shale while thorium and uranium are generally higher in the mudstone and shale than in the sandstone although this is not a well-established trend. Overall, the sandstone facies have higher gamma-ray response compared to mudstone and shale in the two formations. The coarse-grained sandstones have higher gamma-ray response compared to finer sands. The lignite band has higher gamma-ray response than its adjacent sandstone. There is a higher gamma-ray response in the lower Ashdown Fm. at Rock-a-Nore than in the upper part of the formation at Cliff End. This trend is established in the sandstones and mudstones. The mudstone in the lower Ashdown Fm. has a higher gamma-ray response compared to the shale in the lower Wadhurst Clay Fm. The Ashdown sandstones have higher gamma-ray response compared to the Cliff End Sandstone. The lower Wadhurst Clay Fm. has a higher response than the upper part of the formation. The Cliff End Sandstone has the lowest response to K while the basal sandstone within the Wadhurst Clay Fm. has the highest response. As a whole, the Ashdown Fm. has a higher response to gamma emissions compared to the Wadhurst Clay Fm.

DISCUSSION

SOURCE ROCKS

The spectral gamma-ray data from this study reveals that thorium is concentrated at the expense of uranium. Thorium is generally concentrated during the formation of kaolinite from the weathering of feldspars and muscovite (Ruffell and Worden, 2000; Schnyder et al., 2006). The concentration of thorium during the formation of kaolinite from feldspars suggest

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* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1328

Table 1

Comparison of the average concentrations (in ppm) of elements from this study to the average crustal shale values

	(Wedepohl, 1971, 1991)	This study				Ti-EF
	Average shale	Average	N	Maximum	Minimum	
Enriched						
Co	19	269	3	377	93	14.0
Mo	2	6	23	10	3	2.79
Zr	160	365	40	1025	32	2.19
As	10	12	16	37	1	1.19
Non-enriched						
Pb	21	19	36	36	9	0.86
Ba	580	480	38	806	26	0.79
Ni	68	45	22	113	15	0.63
Zn	95	55	36	134	7	0.55
Cu	45	24	2	39	8	0.51
Cr	90	46	30	78	21	0.49
Rb	140	69	40	117	4	0.47
Mn	850	220	40	1492	26	0.24
Sr	300	44	40	145	4	0.14
Other major elements						
Fe	48000	13320	40	38785	549	0.26
K	29900	8131	40	15603	711	0.26
Ca	15700	2807	32	36176	73	0.17

N – number of measurements, Ti-EF – Ti-normalized Enrichment Factor (>1= enrichment, <1=impoverishment)

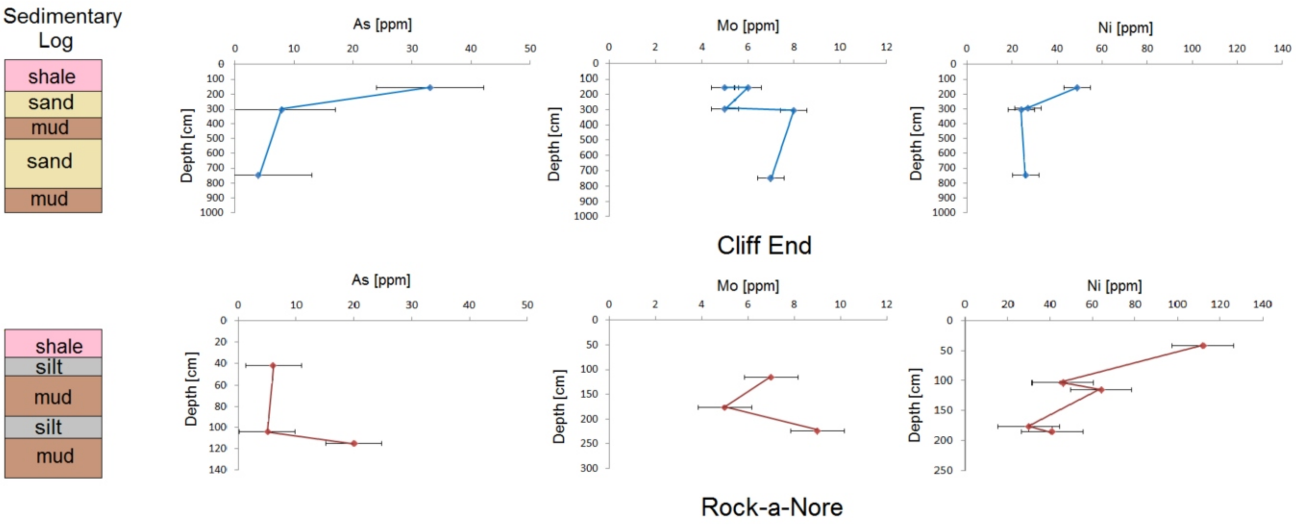

Fig. 7. Variations of As, Mo and Ni with depths at Rock-a-Nore and Cliff End

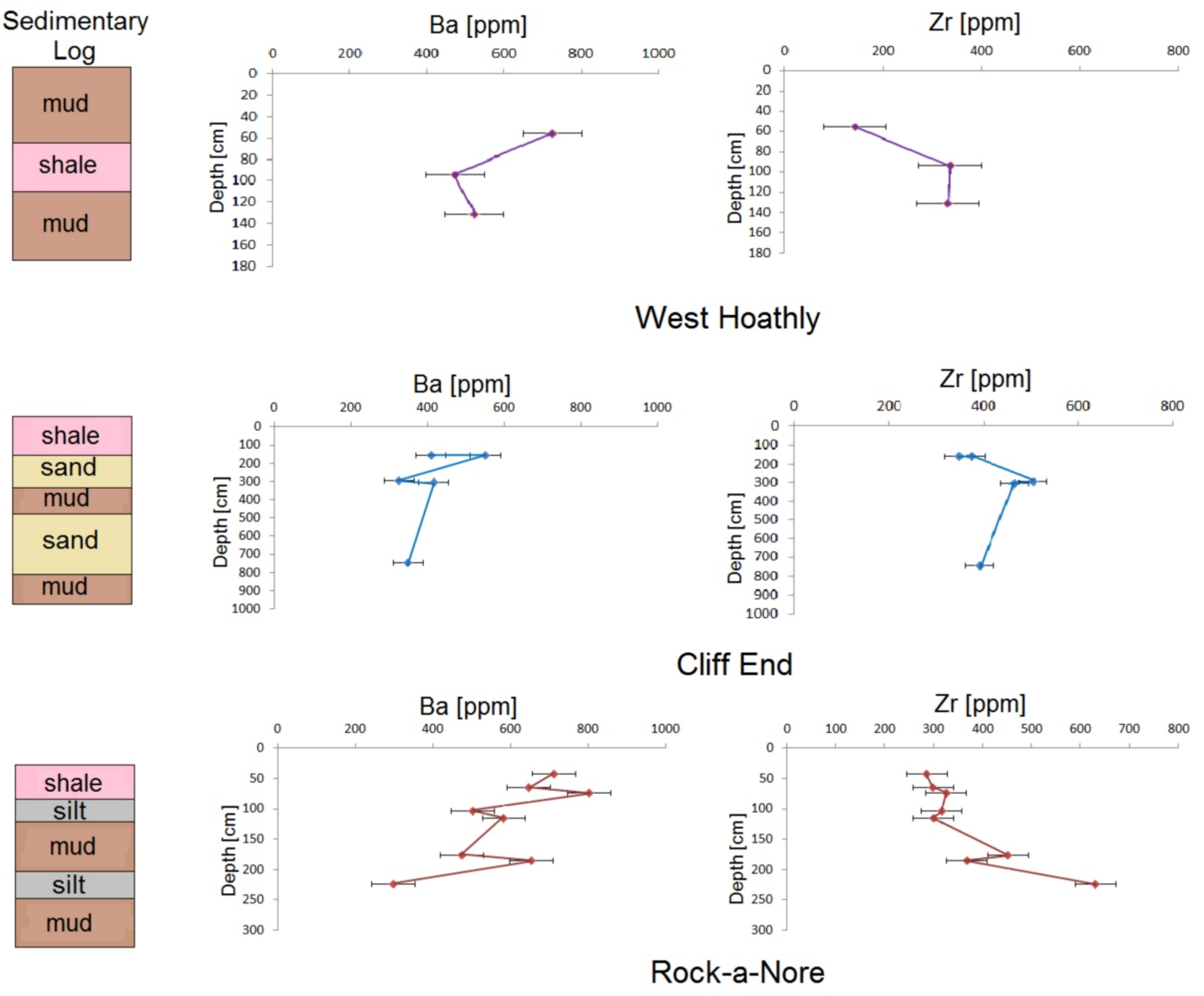

Fig. 8. Variations of Ba and Zr with depths at Rock-a-Nore, Cliff End and West Hoathly Quarry

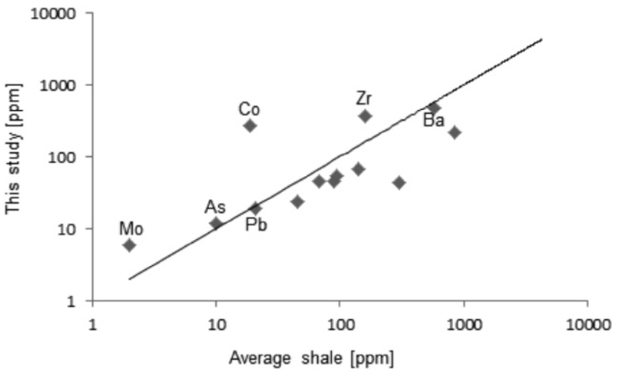

Fig. 9. Linear correlation between the concentrations of average crustal shale (Wedepohl, 1971, 1991) and those reported in this study based on Table 1

Only the enriched elements and (Pb, Ba) are labelled for emphasis

that the sediments within these two formations have been sourced mainly from granites and/or gneisses from within the source areas assuming there were primary sources. The enrichment of Zr also supports felsic sources (e.g., Alvarez and Roser, 2007). Four major possible sources have been traditionally suggested as the provenance for the sediments in the Weald Basin: London–Brabant Massif (Londinia) in the north and north-east, Armorica in the south-west, Cornubia in the west and another one towards the northern (Boreal) Sea (e.g., Kirkaldy, 1947; Allen, 1975, 1989, 1991; Radley and Allen, 2012). The main source of the sediments within the Ashdown and Wadhurst Clay fms. was the London–Brabant Massif (Londinia) in addition to minor inputs from the Armorica and Cornubia (e.g., Allen, 1975; Sladen and Batten, 1984; Akinlotan, 2015). All these sources have granitic and/gneissic materials within them and are either primarily or secondarily sourced. The London–Brabant Massif consists of Precambrian basement, strongly folded Lower Paleozoic metasedimentary and volcanic rocks, Devonian and Carboniferous rocks (Old Red Sandstone). The Armorican Massif also consists of Precambrian core of staurolite-kyanite-garnet schists, granites, New Red Sandstone (Permo-Triassic), and Jurassic volcanogenic debris. The Cornubia area was partially covered

Table 2

Summary of the field spectral gamma-ray data

	GR [cps]			K [%]			Th [ppm]			U [ppm]		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
CE 3	32.1	58.9	17.1	0.23	0.6	0.1	3.5	9.2	0.5	1.6	3.9	0.3
CE 2	82.5	110.3	37.33	1	1.8	0.1	12.5	20	3.8	4.3	7	1.1
CE 1	85.9	234	55.4	1	3.5	0.2	9.8	16.4	4.9	4	6.9	2
HAD	55.8	75.4	38.1	0.3	0.8	0	8.2	11.1	4	3.6	5.4	1
RN	95.2	130.9	47.9	1.5	3.3	0	13.4	20.2	5.8	4.3	6.6	2.4
TOTAL	70.3	234	17.1	0.8	3.5	0	9.5	20.2	0.5	3.6	7	0.3

In stratigraphical order: RN – Rock-a-Nore; HAD – Haddock's Cottages, CE – Cliff End

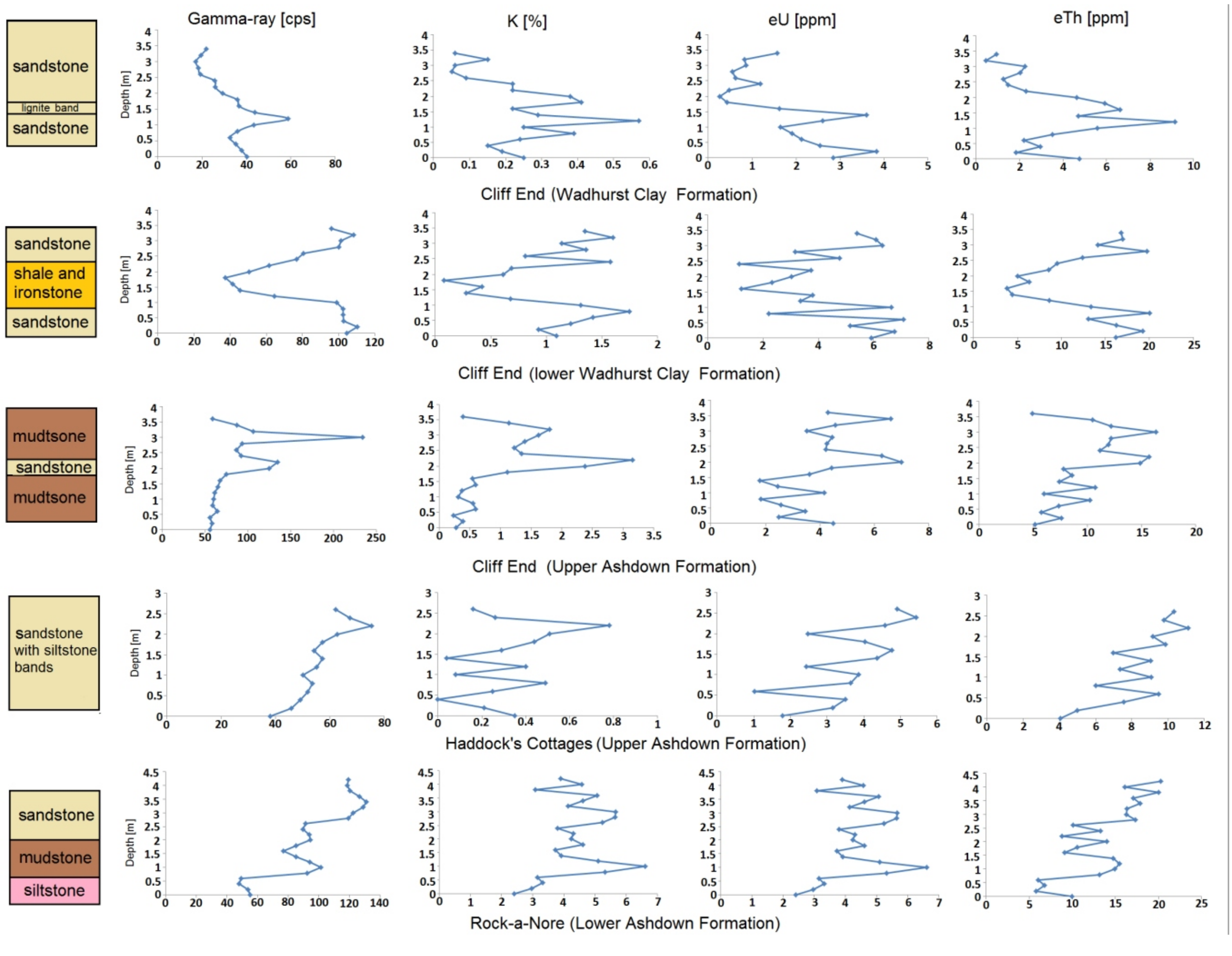

Fig. 10. Distribution of spectral gamma-ray data

The locations are in stratigraphic order

by outcrops of Permo-Triassic beds, the New Red Sandstone including some volcanic debris and Jurassic sediments (Allen, 1981, 1991; Andre, 1991). The enrichment of Th and the depletion of Ca also suggests that these source rocks were subjected to severe weathering (e.g., McLennan et al., 1983; Alvarez and Roser, 2007). Evidence from sandstone petrography and clay mineralogy also supports this interpretation. The sandstones and siltstones within Ashdown and Wadhurst Clay fms. are mainly quartz arenites and quartzose siltstones and composed mainly of quartz grains while kaolinite is a dominant clay mineral within the mudstones and makes up about one-third of the clay minerals (Akinlotan, 2015). This interpretation agrees with previous interpretations from traditional proxy such as field data (e.g., Kirkaldy, 1947; Allen, 1975, 1989, 1991; Radley and Allen, 2012).

TECTONIC SETTINGS

Bhatia and Crook (1986) used the trace elements assemblage of clastic sediments (sandstones) to determine their tectonic settings. They presented that sediments sourced from passive margin are characterized with high Zr, low Ba, Rb and Sr concentrations. This approach can be applied to the sediments within the Ashdown and Wadhurst Clay fms. which are also clastics. In the Ashdown and Wadhurst Clay fms. there is a high abundance of Zr while the concentrations of Ba, Cr, Ni, Rb and Sr are very low compared to the concentrations of average crustal shale. The concentrations of compatible and incompatible elements (Zr, Cr, Ni, Rb and Sr) in varying quantities (e.g., McLennan et al., 1983) may suggest that the sediments were sourced from passive continental margin. The composition of sandstones has also been used to decipher the tectonic settings in the source areas (e.g., Dickinson and Suczek, 1979; Bhatia, 1983; Dickinson, 1985). Dickinson (1985) demonstrated that quartzose sands (quartz-rich) with high monocrystalline to polycrystalline grains ratios and high K-feldspar to plagioclase feldspar ratios are derived from stable craton from continental interior or passive platform. Petrographic data (see below) from the Ashdown and Wadhurst Clay fms. (Akinlotan, 2015) also support the stable craton model. Petrographic descriptions of the major sand members within two formations show that the majority of sandstones and siltstones in these two formations are quartz arenites and quartzose siltstones and extremely rich in quartz. The ratio of monocrystalline quartz grains to that of the polycrystalline is rather high (approximately 99:1). In addition, only K-feldspar is identified and no plagioclase feldspar is described (Akinlotan, 2015). The above mentioned geochemical and petrographic data suggest that the sediments from the Ashdown and Wadhurst Clay fms. may have been sourced from a stable craton (Dickinson and Suczek, 1979; Bhatia, 1983; Dickinson, 1985; Bhatia and Crook, 1986). The tectonic stability of the main source of the sediments London–Brabant Massif from Devonian times has been documented by Rijkers et al. (1993). The possibility of a stable craton model is likely since a significant amount of the sediments in the London–Brabant Massif has been recycled from other sources. The interpretation on the tectonic setting in the source areas is based on limited data and is therefore open to further discussion when new data sets become available.

PALAEOCLIMATE

Elevated ratio of thorium to potassium or uranium in clays has been interpreted to reflect hot and humid palaeoclimates. Thorium is enriched during weathering in hot and humid conditions with increase in the production of kaolinite as a result of mobilising and leaching of K and U thereby concentrating thorium in the hinterland soils (Ruffell and Worden, 2000; Schnyder et al., 2006). In the current study, the concentration of thorium is considerably higher than that of uranium. The mean concentration of thorium is 9.5 ppm while that of uranium is 3.6 ppm. Considering the higher quantity of thorium in relation to uranium and taking on the model of Ruffell and Worden (2000) and Schnyder et al. (2006) into consideration, it is inferred that the palaeoclimatic conditions at the source areas were humid and hot. This climatic pattern subjected the source rocks to severe weathering which was also confirmed by the depletion of Ca (e.g., McLennan et al., 1983; Alvarez and Roser, 2007). This palaeoclimatic interpretation agrees with previous interpretations from field observations and palaeontological examinations (e.g., Kirkaldy, 1947; Allen, 1975, 1989, 1991; Radley and Allen, 2012).

DEPOSITIONAL ENVIRONMENT

The data from the spectral gamma-ray analysis from this study present evidence for freshwater environments for the Ashdown and Wadhurst Clay fms. Mudstone and shale of marine origin are expected to display higher radioactivity than the adjacent sandstone because of higher contents of organic matter that is typical of marine environments (Šimíček et al., 2012). In the Ashdown and Wadhurst Clay fms., the sandstone facies are more radioactive than the adjacent mudstone and shale and this trend is consistent with a freshwater origin for these sediments (Schnyder et al., 2006; Šimíček et al., 2012; Šimíček and Bábek, 2015). Higher gamma-ray counts may be attributed to mudstone while low gamma-ray counts may be characteristic of sandstones and conglomerates because of the effect of non-radioactive quartz, carbonate cement and pore space in the sand facies (Šimíček et al., 2012). Evidence from the lithology observed in the field and in the boreholes such as sandstones, siltstones, mudstones, shales, lignite and the geochemical composition of the sideritic ironstone (high enrichment of Fe and Mn and the low Mg/Ca ratio) also supports the freshwater and non-marine origin of these sediments (Akinlotan, 2015). These interpretation agrees with previous interpretations based on field data that the sediments within the Ashdown and Wadhurst Clay fms. were deposited under predominantly non-marine, freshwater and fluvial conditions (Kirkaldy, 1939; Allen, 1975, 1981; Stewart, 1981b, 1983; Lake and Shephard-Thorn, 1987; Hopson et al., 2008; Radley and Allen, 2012).

REDOX CONDITIONS

Trace elements such as Mo, U, V and Co are enriched in reducing sediments and are highly sensitive to redox changes. These redox-sensitive elements have been used to demonstrate anoxic environments and for palaeoredox reconstruction (e.g., Lipinski et al., 2003; Elbaz-Poulichet et al., 2005; Brumsack, 2006; Jiang et al., 2007; Xu et al., 2012b). These redox-sensitive elements Mo, U, V and Co are extremely enriched in the Ashdown and Wadhurst Clay fms. Their enrichment strongly suggests anoxic conditions at the site of deposition of the sediments and reflects the prevailing conditions in the water column at the time of deposition. In addition to these redox-sensitive elements, it has been shown that the precipitation of siderite is a direct indication of reducing conditions in such environment (e.g., Huber, 1958; Bahrig, 1989; Browne and Kingston, 1993). Huber (1958) also confirmed that siderite is stable under reducing conditions. In the Ashdown and Wadhurst Clay fms., widespread occurrence of sideritic ironstones is well documented (Taylor, 1963; Lake and Thurrell, 1974; Lake and Shephard-Thorn, 1987; Radley and Allen, 2012; Akinlotan, 2015) and their presence is a direct indication of reducing/anoxic conditions at the time of deposition. The anoxic conditions in the Wadhurst Clay Fm. reflect lagoonal conditions while in the lower Ashdown Fm. it may point to floodplain environment. Allen (1989) observed the development of anoxic lagoons within the Wadhurst Clay Fm. in East Sussex. The quantities of Co, U and Mo reveal that the highest level of anoxic conditions occurred in the lower Ashdown Fm.

before decreasing towards the boundary with Wadhurst Clay Fm. Anoxic conditions increased again in the lower Wadhurst Clay Fm. and then decreased upwards the sequence before picking up in the upper part of the formation. Based on the available data, it appears that the highest level of anoxic conditions occurred at the section at Rock-a-Nore (Fig. 1) within the lower Ashdown Fm. In the Wadhurst Clay Fm., anoxic conditions are appear to be at peak at the section at West Hoathly quarry (Fig. 1) followed by the section at the Wadhurst Clay basal beds at Pett Level and Northiam (Fig. 1).

DIAGENESIS

It is well-established that the Wealden sediments have experienced early diagenesis with a moderate degree of diagenetic alteration (Allen, 1981; Sladen, 1983; Sladen and Batten, 1984; Radley and Allen, 2012; Akinlotan, 2015). This has been demonstrated by the clay mineral assemblage and the relatively shallow depth (1.5–2 km). Clay mineral analyses reveal that the illite assemblage is dominated by 1M polymorph which seems to be detrital in origin and not diagenetic (e.g., Sladen, 1983, 1987; Akinlotan, 2015). The widespread occurrence of sideritic ironstones also confirms early diagenesis in the sediments (Lake and Thurrell, 1974; Lake and Shephard-Thorn, 1987; Akinlotan, 2015). The geothermal gradient beneath the continental crust of the United Kingdom is ~10°Ckm^{-1} (Rollin, 1995; Westaway et al., 2002). This geothermal gradient has produced insufficient heat (~15–20°C) to drive any major diagenetic alteration of the sediments or the transformation of smectite to illite-smectite in these formations. This early diagenesis is unlikely to have caused any significant changes to the geochemical composition. On the other hand, the depletion of Ca suggests that it was probably leached during this diagenetic process (e.g., McLennan et al., 1983; Alvarez and Roser, 2007).

WIDER IMPLICATIONS

Using the elemental composition of sediments for understanding the palaeoenvironmental conditions of sedimentary basins has wider implications beyond the Weald Basin. This work has shown that the elemental composition of terrigenous sediments can provide useful information about the palaeoenvironmental conditions of sedimentary basins. This has wider implications beyond the Weald Basin and the principle can be applied to other sedimentary basins elsewhere. As shown in this study the geochemical composition of the sediments has provided important information about the tectonic settings of the source areas, anoxic and reducing conditions, and palaeoclimatic conditions in the Weald Basin. The interpretations made based on the geochemical composition of sediments in the Weald Basin can be made in other sedimentary basins with similar geochemical composition. In the Weald Basin, the interpretations of the palaeoenvironments based on the geochemistry of the sediments agree with interpretations from other proxies. As a result, when traditional data sets such as field, fossil and mineralogical data are not readily available or insufficient to enable adequate interpretations, the elemental composition of sedimentary rocks will prove to be extremely useful either as supplement or primary data for understanding the palaeoenvironmental conditions of sedimentary basins. The geochemical methods used in this study, XRF and Spectral GR can also be used in other sedimentary basins and the resulting geochemical compositions will provide useful information about palaeoenvironmental conditions. The geochemical composition of sediments will provide useful information on tectonic setting, provenance, redox conditions, and weathering conditions of sedimentary basins.

CONCLUSIONS

Geochemical analyses revealed that the Ashdown and Wadhurst Clay fms. are enriched in Co, Mo, Zr, As and deficient in Pb, Ba, Ni, Zn, Cu, Cr, Rb and Mn. Redox sensitive elements such as Fe, Co, Cr, Cu, As and Mo are present in various quantities. The geochemical assemblage provides useful information on sediment provenance and depositional conditions. The concentrations of Zr, Ba, Cr, Ni, Rb and Sr in varying quantities established that the sediments may have been sourced from passive continental margin while the enriched redox-sensitive elements such as As, Mo and Co confirm the presence of anoxic and reducing conditions at the sites of deposition. Anoxic conditions peaked in the lower Ashdown Fm. and then decreased towards the boundary with Wadhurst Clay Fm. Anoxic conditions returned in the lower Wadhurst Clay Fm. and then decreased upwards the sequence. The analysis of spectral gamma-ray data shows that the sandstone facies are more radioactive than the adjacent mudstone and shale, which confirms their freshwater origin. The primary sources of the radioactive elements are likely to be the heavy minerals in the quartz grains and non-radioactive cements while secondary sources are feldspars, micas, and glauconite. The higher quantity of thorium in relation to uranium indicates humid and hot palaeoclimatic conditions at the source areas that favoured intense weathering. The geochemical composition of sediments has wider implications for understanding the depositional conditions of sedimentary basins and they will provide useful information on tectonic setting, provenance, redox conditions, and weathering conditions.

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