

Provenance, tectonic setting, source area weathering and paleo-redox condition of (late Cretaceous) Ise sandstone, Abeokuta group, Dahomey basin (SW Nigeria)

Provenance, cadre tectonique, altération de la zone source et paléo-redox du grès d'Ise (Crétacé terminal) groupe Abeokuta, bassin de Dahomey (SW Nigeria)

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Abstract. A geochemical study of the Late Cretaceous Ise sandstone of the Abeokuta Group, eastern Dahomey basin (SW NIGERIA) was carried out to infer their provenance, tectonic setting, source area weathering and paleoenvironment of deposition. Provenance studies suggest that the sediments were derived from multiple protoliths from moderate and low reliefs with felsic, intermediate and mafic compositions with contributions from recycled older sediments of interior cratonic origin. The Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW), Plagioclase Index of Alteration (PIA), Mineralogical Index of Alteration (MIA), moderate Al_2O_3 values, lower Al/K ratio, Na_2O/Al_2O_3 vs. K_2O/Al_2O_3 ; K/Na vs. Rb/Sr and Al/Na vs. CIA cross-plots and the A-CN-K ternary parameters suggests that the sandstones were derived during moderate chemical weathering of the source area. Discriminant function-based major element diagrams for the tectonic discrimination of siliciclastic sediments revealed a rift setting for the Dahomey basin. The Ise sandstones have a low Sr/Ba ratio indicating low saline water during deposition. The depositional, paleoenvironmental and paleoclimatic studies suggest that the Ise sandstone was deposited in mostly oxic to suboxic tropical humid transitional deltaic conditions under moderate transportation regime.

Keywords : Ise sandstone, Abeokuta group, provenance, tectonic setting, weathering, paleoenvironment.

Résumé. Une étude géochimique du grès de l'Ise du Crétacé supérieur du groupe Abeokuta, bassin oriental du Dahomey (SW NIGERIA) a été réalisée pour en déduire leur provenance, leur cadre tectonique, l'altération de la zone source et le paléoenvironnement du dépôt. Les études de provenance suggèrent que les sédiments provenaient de plusieurs protolithes de reliefs modérés et bas avec des compositions felsiques, intermédiaires et mafiques avec des contributions de sédiments plus anciens recyclés d'origine cratonique intérieure. Indice chimique d'altération (CIA), indice chimique d'altération (CIW), indice d'altération plagioclase (PIA), indice minéralogique d'altération (MIA), valeurs modérées d' Al_2O_3 , rapport Al / K plus faible, Na_2O / Al_2O_3 par rapport à K_2O / Al_2O_3 ; Les diagrammes croisés K / Na contre Rb / Sr et Al / Na contre CIA et les paramètres ternaires A-CN-K suggèrent que les grès ont été dérivés pendant une altération chimique modérée de la zone source. Les diagrammes des éléments principaux basés sur la fonction discriminante pour la discrimination tectonique des sédiments siliciclastiques ont révélé une configuration de faille pour le bassin du Dahomey. Les grès d'Ise ont un faible rapport Sr / Ba indiquant une faible eau saline pendant le dépôt. Les études sédimentaires, paléoenvironnementales et paléoclimatiques suggèrent que le grès d'Ise s'est déposé dans des conditions deltaïques de transition humides tropicales principalement oxygènes à suboxygènes sous un régime de transport modéré.

Mots Clés : Grès d'Ise, Abeokuta group, provenance, milieu tectonique, altération, paléoenvironnement.

INTRODUCTION

Siliciclastic sediments generally originated from continental sources and typically form near or in continental blocks away from deep oceans (Verma & Armstrong-Altrin 2013). The geochemical constituents of siliciclastic sediments are commonly used to deduce provenance, since they have a tendency to reflect parent rock composition (Bakkiaraj *et al.* 2010, Zhang *et al.* 2011, Shadan & Hosseini-Barzi 2013); to infer the tectonic setting of sedimentary basins (Pandey & Parcha 2017); to study chemical weathering and paleoclimate (Goldberg & Humayun 2010,

Elzien *et al.* 2014) and decipher paleoredox conditions (McKay *et al.* 2007). Major elements and some trace elements like Sc, Zr, Co, Hf, Cr, Y, Th and their elemental ratios are sensitive indicators of the source rocks, tectonic setting, paleoweathering conditions and paleoclimate of the clastic sedimentary rocks (McLennan *et al.* 1993, Nesbitt *et al.* 1996). Different tectonic environments have distinctive provenance features and are characterised by physicochemical markers of sedimentary processes (Karadag 2014). According to Armstrong-Altrin *et al.* (2004), sedimentary rocks of any age, derived primarily from Precambrian terranes, may be influenced by differences in parent materials. This study intends to interpret the sediment source-area weathering, provenance, tectonic setting, paleoclimate and paleo-redox

condition of the Late Cretaceous Ise sandstone of the Abeokuta Group based on major and trace element geochemistry.

GEOLOGIC SETTING AND STRATIGRAPHY

The Dahomey Basin located in West African Gulf of Guinea is an extensive basin starting from southeastern Ghana through Togo and the Republic of Benin to southwestern Nigeria (Fig. 1), where it is separated from and cut off the stratigraphically younger Niger Delta Basin (Opara 2011). Its boundary with the Niger Delta in the Eastern section is delineated by the Benin Hinge Line and Okitipupa Ridge and denotes the continental extension of the Chain Fracture Zone (Coker & Ejedawe 1987, Onuoha 1999). On the western section It is bounded by the Ghana Ridge, and has been interpreted as the extension of the Romanche Fracture Zone (Burke *et al.* 2003). The evolution of the Dahomey Basin is generally believed to be due to rifting phenomenon associated with the separation of the mega-continent called Gondwanaland—the transcurrent movements of the oceanic fracture systems during the drifting stages of separation of South America and Africa. The separation of the African and South American landmasses as a result of the continental drift led to the subsequent opening of the Atlantic Ocean during the Mesozoic Era (Storey 1995). Detail stratigraphy of the Basin has been delineated by several workers (e.g. Omatsola & Adegoke 1981, Okosun 1990). Table 1 shows the

lithostratigraphy from the oldest to the youngest according Agagu (1985). At the base is the Cretaceous Abeokuta Group—made up of the Ise Formation, Afowo Formation and Araromi Formation. Shallow marine Paleocene Ewekoro Formation deposited during transgressive episode overlies

the Abeokuta Group. The Ewekoro Formation is widespread covering a distance of about 32km from Ghana, eastwards towards the eastern margin of the basin. It finally becomes fine grained into the dominantly shelly Araromi Formation which pinches out against the western flank of Okitipupa ridge.

Table 1. Stratigraphy of the Benin Basin (After Agagu 1985)

PERIOD	Age	Lithology
Quaternary	Recent	Alluvium
	Pleistocene-Oligocene	Coastal Plain Sand
Tertiary	Eocene	Ilaro sandstone /Oshosun shales
	Paleocene	Akimbo shale/Ewekoro limestone
Cretaceous	Maastrichtian-Neocomian	Araromi shale/Afowosandstone/shale
		Ise sandstone
Precambrian Basement Complex		

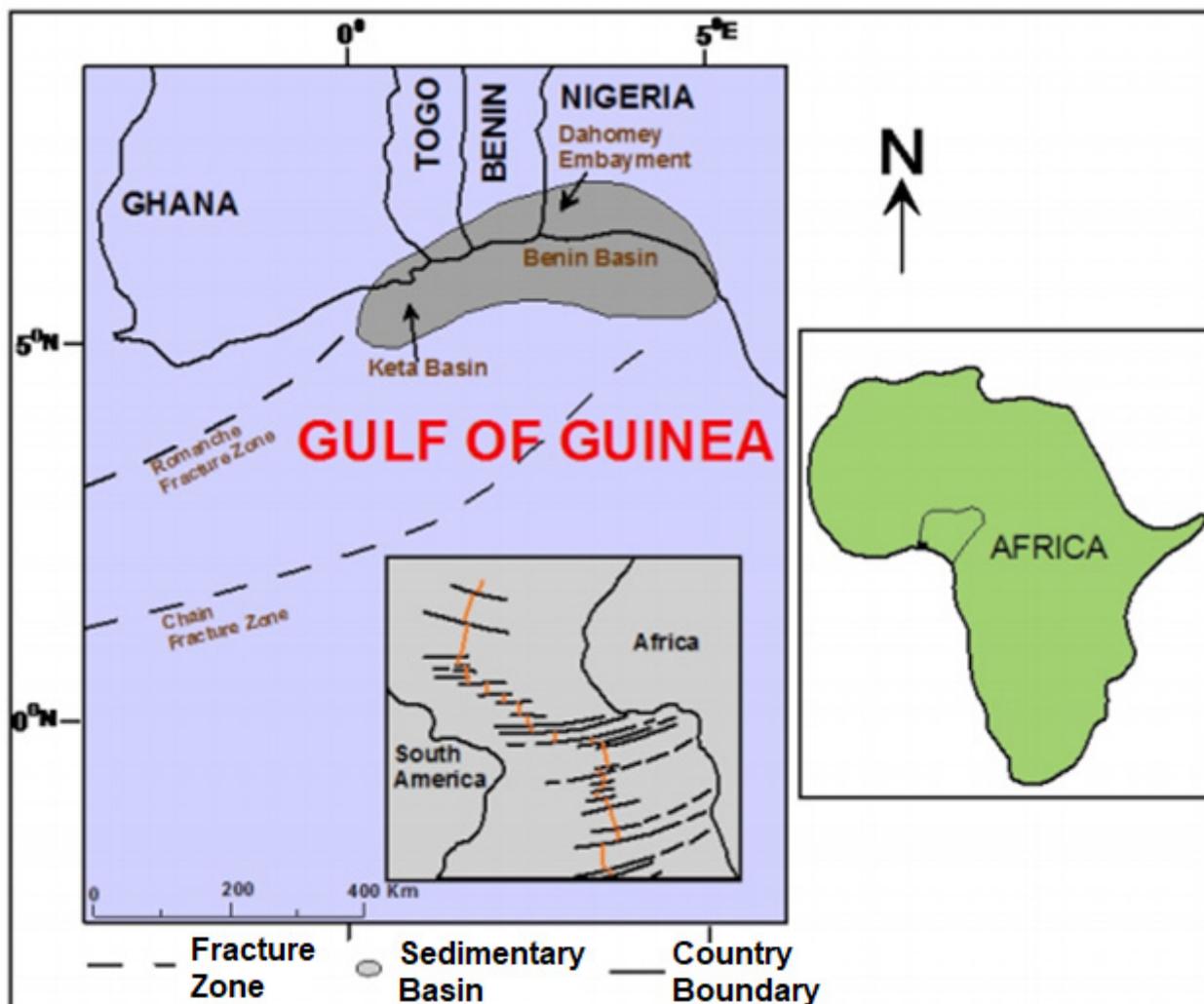


Figure 1. Map showing the location and extent of the Dahomey (Benin) Basin in the Gulf of Guinea (After Olabode 2015).

Akinbo Formation (Paleocene-Eocene) overlies the Ewekoro Formation. The Eocene Oshosun Formation overlies the Akinbo Formation and Oshosun Formation is overlain by the regressive arenaceous Ilaro Formation. Figure. 2 is a geological map of the Nigerian sector of Dahomey Basin while Figure 3 shows the study area and the sample locations.

MATERIALS AND METHODS

Fourteen samples were analyzed for major oxides using X- Ray Fluorescence (XRF) analysis at the ICP-MS Laboratory, Stellenbosch University, South Africa. Pulverised sandstone samples were analysed for major element using Axios instrument (PANalytical) with a 2.4 kWatt Rh X-ray

Tube. The detailed procedures for sample preparation for the analytical technique are reported below.

Fusion bead method for Major element analysis

- Weigh 1.0000 g \pm 0.0009 g of milled sample
- Place in oven at 110 °C for 1 hour to determine H₂O⁺
- Place in oven at 1000 °C for 1 hour to determine LOI
- Add 10.0000 g \pm 0.0009 g Claissé flux and fuse in M4 Claissé fluxer for 23 minutes.
- 0.2 g of NaCO₃ was added to the mix and the sample+flux+NaCO₃ was pre-oxidized at 700 °C before fusion.
- Flux type: Ultrapure Fused Anhydrous Li-Tetraborate-Li-Metaborate flux (66.67 % Li₂B₄O₇ + 32.83 % LiBO₂) and a releasing agent Li-Iodide (0.5 % LiI).
- Loss on Ignition (LOI) is a test used in XRF major element analysis which consists of strongly heating a sample of the material at a specified temperature, allowing volatile substances to escape or oxygen is added,
- These analytical methods yielded data for eleven major elements, reported as oxide percent by weight (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, MnO, CaO, Na₂O, K₂O, SO₃ and P₂O₅).

until its mass ceases to change. The LOI is made of contributions from the volatile compounds of H₂O⁺, OH⁻, CO₂, F⁻, Cl⁻, S; in parts also K⁺ and Na⁺ (if heated for too long); or alternatively added compounds O₂ (oxidation,

e.g. FeO to Fe₂O₃), later CO₂ (CaO to CaCO₃). In pyro-processing and the mineral industries such as lime, calcined bauxite, refractories or cement manufacturing industry, the loss on ignition of the raw material is roughly equivalent to the loss in mass that it will undergo in a kiln, furnace or smelter.

The trace and rare elemental data for this work was acquired using Laser Ablation- inductively coupled plasma spectrometry (LA-ICP-MS) analyses. The analytical procedures are as follows:

Pulverised sandstone samples were analysed for trace element using LA-ICP-MS instrumental analysis. LA-ICP-MS is a powerful and sensitive analytical technique for multi-elemental analysis. The laser was used to vaporize the surface of the solid sample, while the vapour, and any particles, were then transported by the carrier gas flow to the ICP-MS. The detailed procedures for sample preparation for both analytical techniques are as follows.

Pressed pellet method for Trace element analysis

- Weigh 8 g \pm 0.05 g of milled powder
- Mix thoroughly with 3 drops of Mowiol wax binder
- Press pellet with pill press to 15 ton pressure
- Dry in oven at 100 °C for half an hour before analysing.

The analysis yielded thirteen Trace elements: As, Ba, Ce, Co, Cu, Nb, Ni, Ti, Pb, Rb, Sr, V, Y, Zn, and Zr reported as mg/kg (ppm).

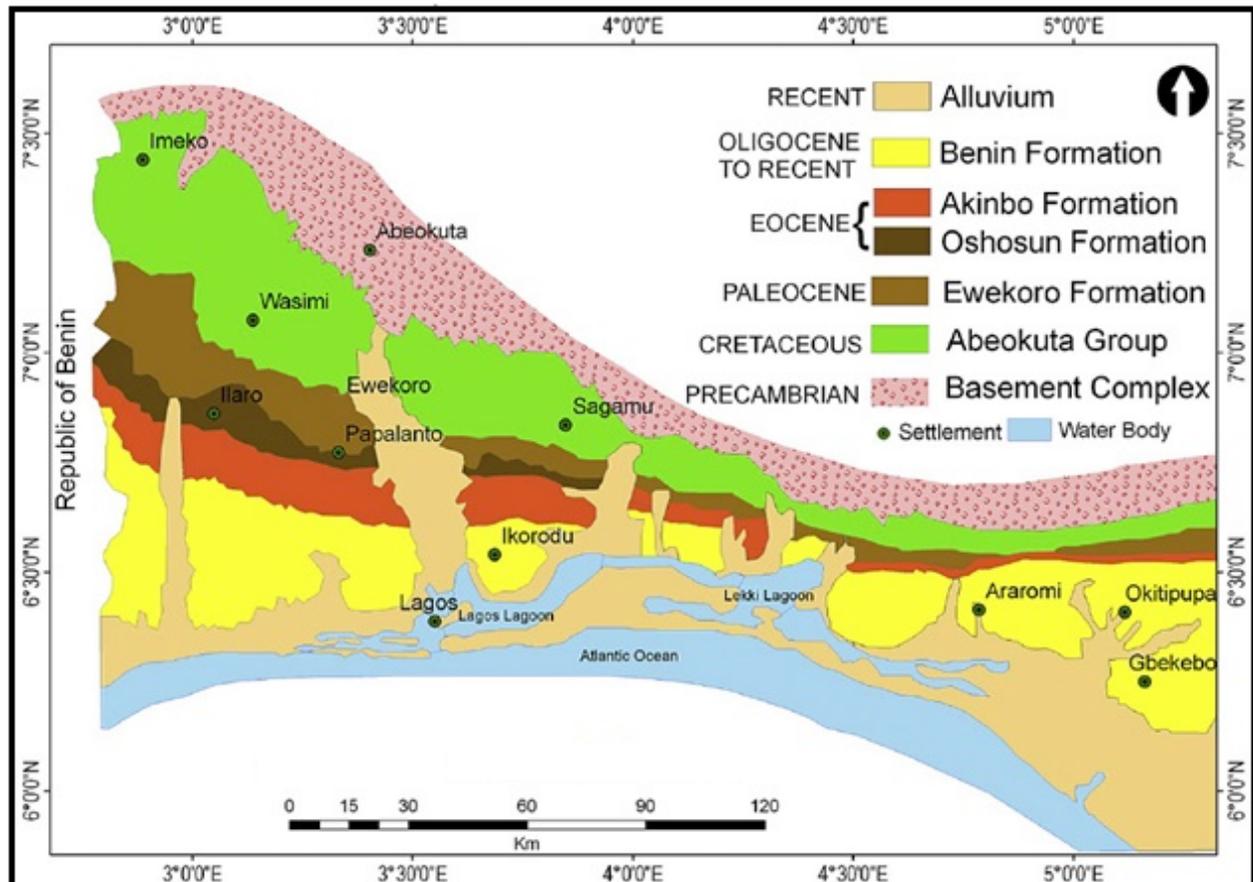


Figure. 2. Geological map of the Nigerian sector of Dahomey Basin (After Olatinsu *et al.* 2017).

RESULTS AND DISCUSSION

Source area Composition

The geochemical records of clastic sediments have been used to infer their provenance characteristics (Cullers *et al.* 1988, Condie *et al.* 1992). The high field strength elements (Zr, Hf, Y and Nb), some transition elements (e.g. Sc, Co, Cr and Ni) along with Al, Ti and Th are considered to be relatively immobile during sedimentary processes and thus are useful in discriminating source area composition of clastic sedimentary rocks (Madhavaraju & Ramasamy 2002, Armstrong-Altrin *et al.* 2004). Table 2 is the chemical concentration data of the samples under investigation. According to Feng & Kerrich (1990), high field strength elements (HFSE) are preferentially partitioned into melts during crystallization and anatexis, and are therefore enriched in felsic rocks than mafic rocks. Transition elements, on the other hand, are well-suited in magmatic processes and are highly concentrated in mafic and ultramafic rocks than felsic rocks. The enrichment of Zr, Nb, and Y among the HFSE and depletion of most of the TTE relative to UCC (Fig. 4) can be interpreted as indication of the studied sediments coming from felsic/intermediate and fractionated recycled source. The enrichments in Zr, Nb, Y and

Co suggest more evolved (felsic) material in the source rocks with minor contribution from basic rocks. Ratios such as Al/Ti, Th/Cr, Th/Co, Th/Sc, and La/Sc in clastic rocks are essentially used to infer the source rock compositions. Aluminum, Th and La are typically enriched in felsic source rocks whereas Ti, Cr, Co and Sc are relatively more concentrated in mafic rocks (Taylor & McLennan 1985, Fralick & Kronberg 1997).

There is a lack of Th and La (and other REE, except Ce) which could point to a probable intermediate source and also suggests a recycled origin; sediments that have undergone processes of sedimentation, weathering/erosion, transportation and re-sedimentation will experience loss of its elemental constituents. The degree of this loss will depend on the distance, duration and number of times that these processes occurred. Al/Ti ratios of samples range between 2.15 and 9.45 with an average of 5.2, which compares with sediments derived from mafic sources. The major element-based provenance discriminant function diagram of Roser & Korsch (1988) discriminates four major provenance categories of mafic igneous, intermediate igneous, felsic igneous, and quartzose recycled sedimentary. This discriminant function diagram shows the samples plotting in both the quartzose sedimentary

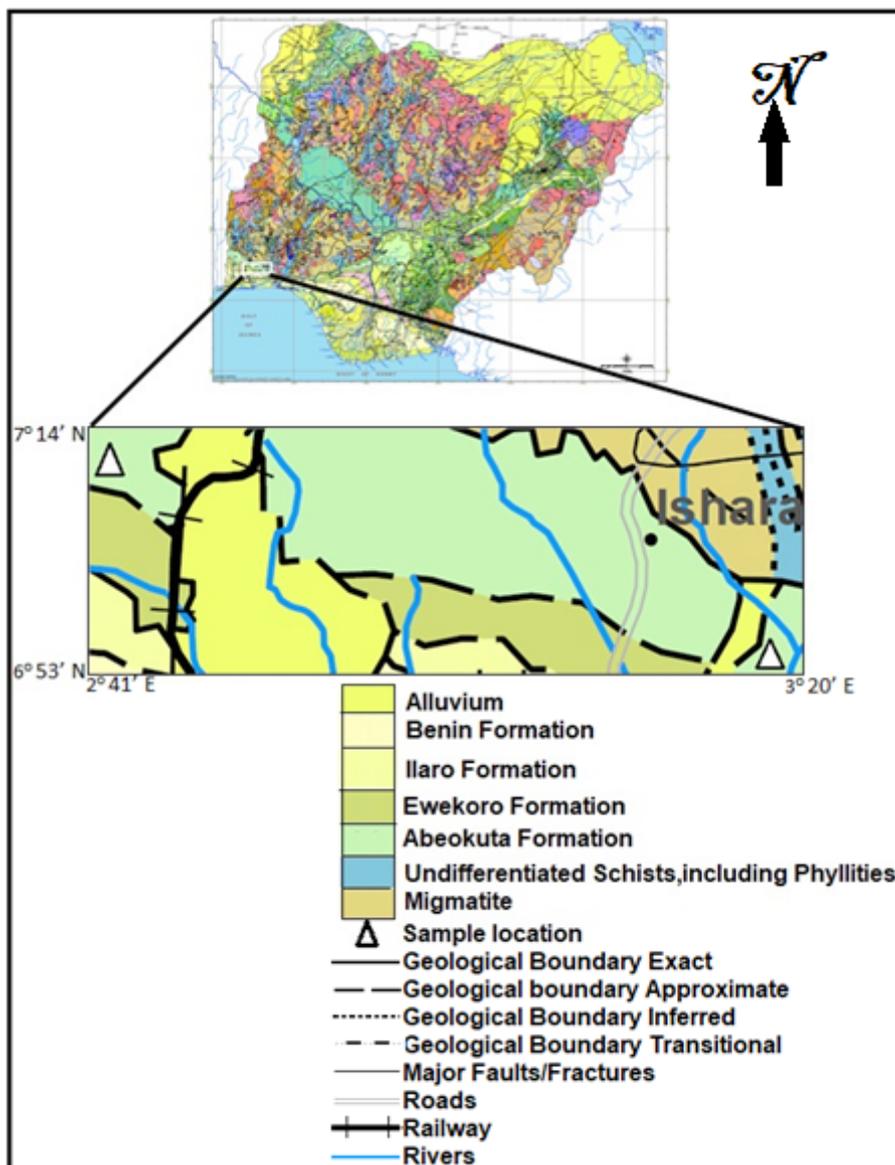


Figure 3. Geological map of the study area and sample location, modified from Nigerian Geological Survey Agency (2006).

and mafic igneous fields, which suggests a mixed source for Ise sandstones (Fig. 5). Figure 6 is another provenance discriminant function diagram by Roser & Korsch (1988), using different parameters for the function definition; this also indicates that the Ise sandstone originated from multiple sources. The concentration of zircon is used to characterize the nature and composition of source rock (Hayashi *et al.* 1997). Hayashi *et al.* (1997), stated that the TiO_2/Zr ratios are so much supportive to distinguish among three different source rock types, i.e., felsic, intermediate and mafic. The TiO_2 versus Zr plot (Fig. 7) shows the sandstones plotting mainly in the intermediate zone; this may also be due to the sandstones coming from more than one source. According to

Floyd *et al.* (1989), immobile elements, such as Ti and Ni, can be used to determine the original lithological composition of rocks and to separate immature sediments derived from a magmatic source from normal mature sediments. The Ise sandstone plots within the areas of acidic and magmatogenic greywackes (Fig. 8). The sources of a sedimentary rock suite can be determined using K versus Rb ratios that are generally comparable to standard continental crust values (Floyd *et al.* 1989). K and Rb are considered relatively mobile during diagenesis and low-grade metamorphism; figure 9 shows the samples plotting in the basic and acidic/intermediate composition zones, which suggests sediments from more than one source.

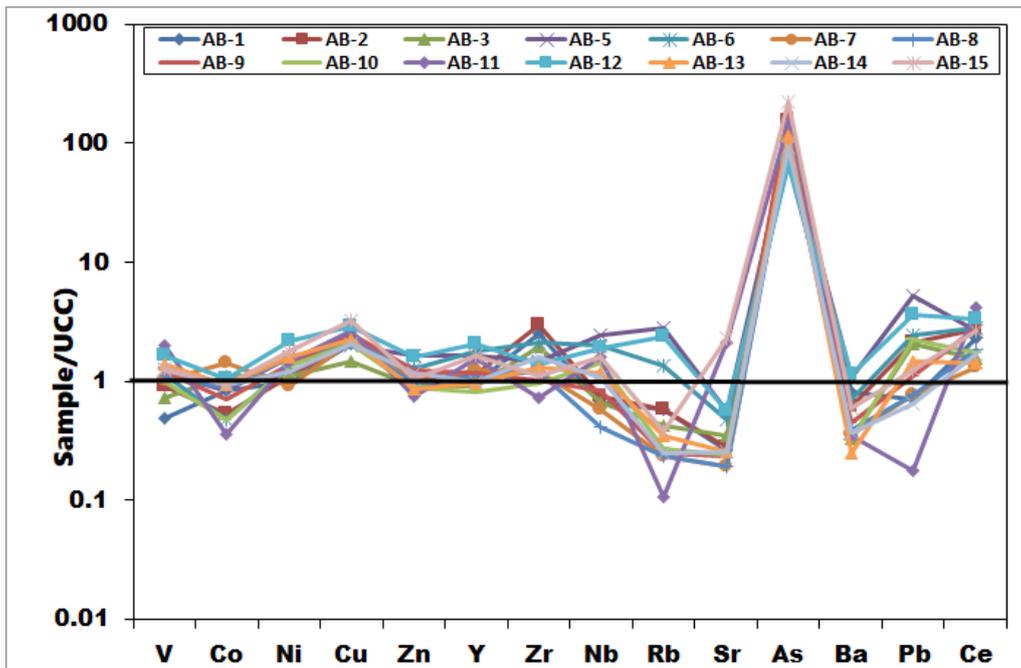


Figure 4. UCC normalized trace elements distribution of Ise sandstone samples. UCC data after Taylor & McLennan (1985; 1995)

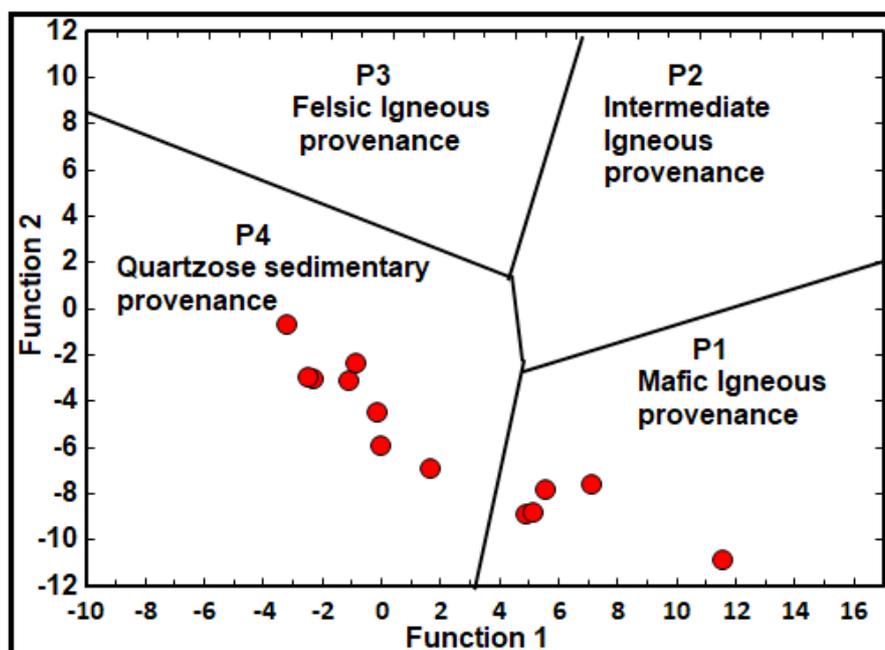


Figure 5. Major element provenance discriminant function diagram for the Ise sandstones (Roser & Korsch 1988).

Table 2: The chemical composition of Ise sandstones.

Oxides & Elements	AB-1	AB-2	AB-3	AB-5	AB-6	AB-7	AB-8	AB-9	AB-10	AB-11	AB-12	AB-13	AB-14	AB-15	UCC
SiO ₂ (%)	63.08	62.91	71.66	57.24	60.79	60.58	60.5	53.38	70.64	43.83	56.44	60.34	64.6	55.3	65.89
Al ₂ O ₃ (%)	9.14	8.37	6.88	13.52	12.5	8.43	8.53	8.36	6.05	3.62	13.84	10.78	8.37	6.93	15.17
Fe ₂ O ₃ (%)	15.35	16.57	9.21	12.59	12.26	19.18	19.24	26.09	13.03	10.49	12.46	18.27	15.6	25.6	5
MnO(%)	0.08	0.15	0.07	0.06	0.05	0.18	0.18	0.3	0.09	0.47	0.07	0.11	0.13	0.25	0.07
MgO(%)	1.56	1.58	0.98	1.93	1.89	2.61	2.53	2.55	1.21	0.61	1.87	2.36	2.19	1.87	2.2
CaO(%)	0.85	1.22	2.5	0.42	0.49	1.61	1.61	2.17	2.27	28.88	0.8	0.93	1.22	2.49	4.19
Na ₂ O(%)	1.54	1.39	1.43	0.78	1.17	1.66	1.67	1.37	1.22	1.41	0.9	1.83	1.87	1.67	3.90
K ₂ O(%)	3.34	2.72	1.97	6	3.83	0.83	0.83	0.93	0.92	0.49	4.52	1.2	1.08	1.59	3.39
TiO ₂ (%)	3.15	2.74	1.8	1.43	1.47	1.78	1.78	1.18	2.21	0.83	1.46	1.6	2.1	3.23	0.5
P ₂ O ₅ (%)	0.2	0.16	0.16	0.11	0.13	0.22	0.22	0.22	0.21	0.11	0.13	0.19	0.2	0.23	0.2
SO ₃ (%)	0.11	0.09	0.23	0.2	0.18	0.06	0.06	0.08	0.05	0.02	0.25	0.03	0.04	0.13	-
As (ppm)	215	230	144	154	102	155	154	263	166	216	103	174	138	330	1.5
Ba (ppm)	452	333	179	593	385	197	217	244	177	194	634	138	200	331	550
Ce (ppm)	146	173	99	171	179	84	118	180	111	269	211	91	109	172	64
Co(ppm)	14	9	19	14	8	24	15	12	8	6	18	16	16	16	17
Cu (ppm)	52	55	37	50	54	54	53	63	52	66	72	56	51	81	25
Nb(ppm)	8	9	8	29	24	7	5	10	17	19	23	14	13	19	12
Ni (ppm)	20	22	22	32	27	18	32	28	27	29	43	32	24	36	20
Pb (ppm)	12	36	35	90	41	13	13	19	38	3	62	25	11	21	17
Rb (ppm)	64	64	47	311	151	26	26	28	30	12	264	39	28	43	112.2
Sr (ppm)	92	96	121	199	167	68	68	82	85	746	199	90	90	805	350
V (ppm)	52	96	78	127	121	108	118	129	107	217	174	150	131	138	107
Y (ppm)	21	25	20	36	39	27	24	26	18	34	45	21	22	36	22
Zn (ppm)	88	74	64	116	91	70	68	88	63	53	112	61	82	74	71
Zr (ppm)	480	559	365	276	400	227	228	194	183	136	264	251	303	213	190

UCC: Upper Continental Crust (Taylor & McLennan 1985, 1995)

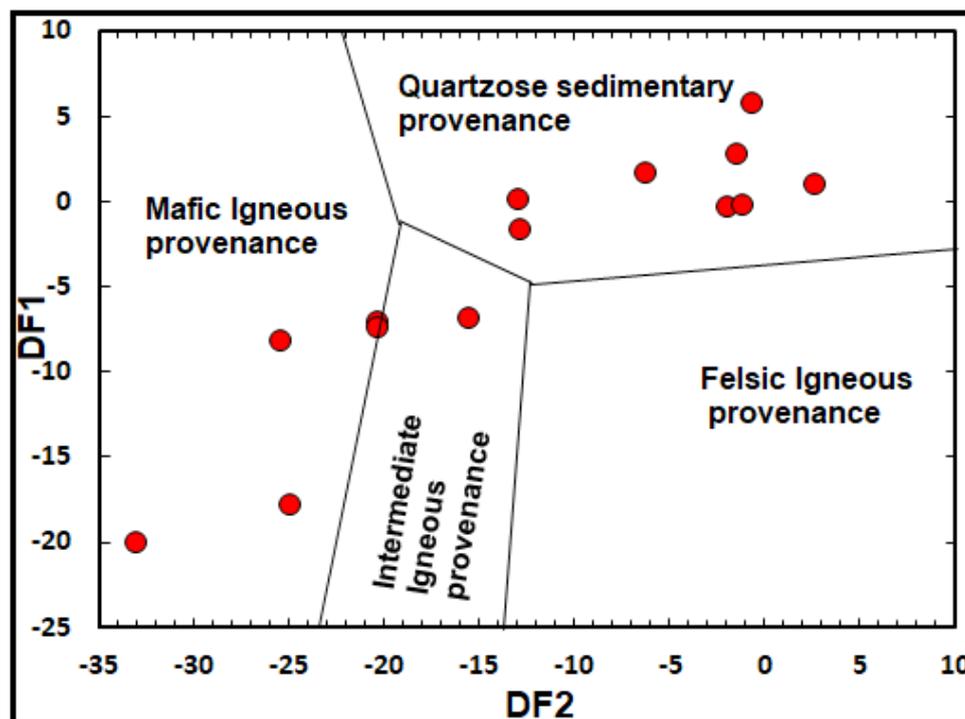


Figure 6. Major element provenance discriminant function diagram for the Ise sandstone using different discriminant function parameters (Roser & Korsch 1988).

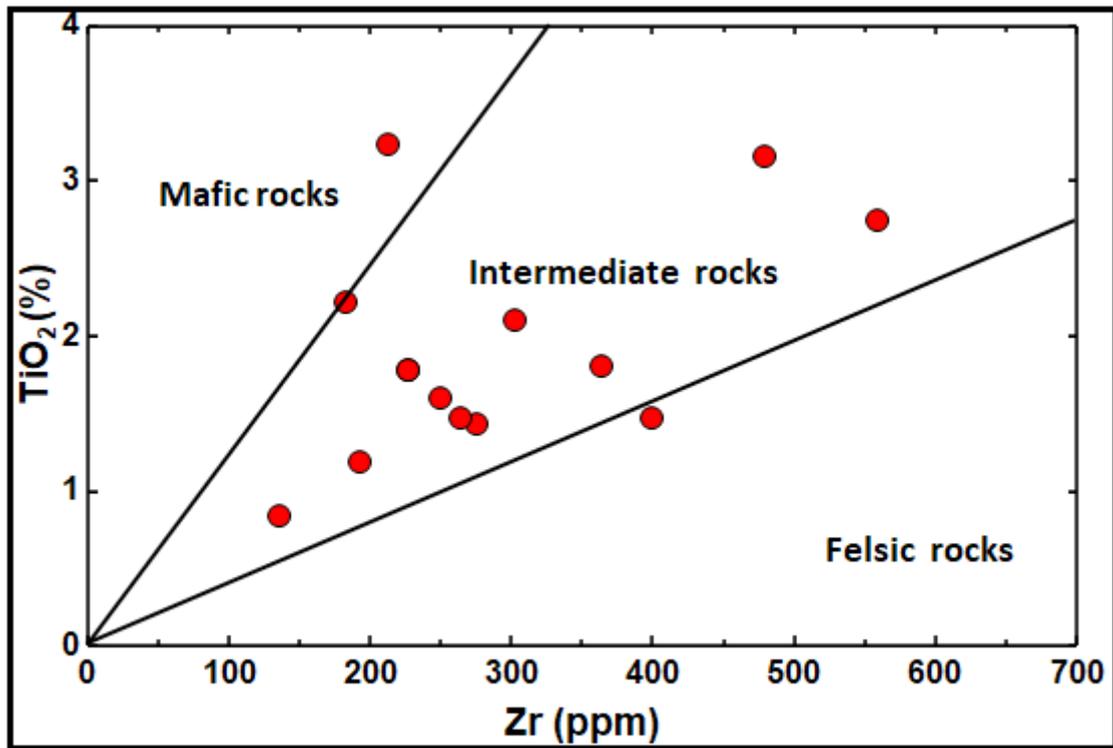


Figure 7. TiO₂-Zr plot for the sediments (Hayashi *et al.* 1997).

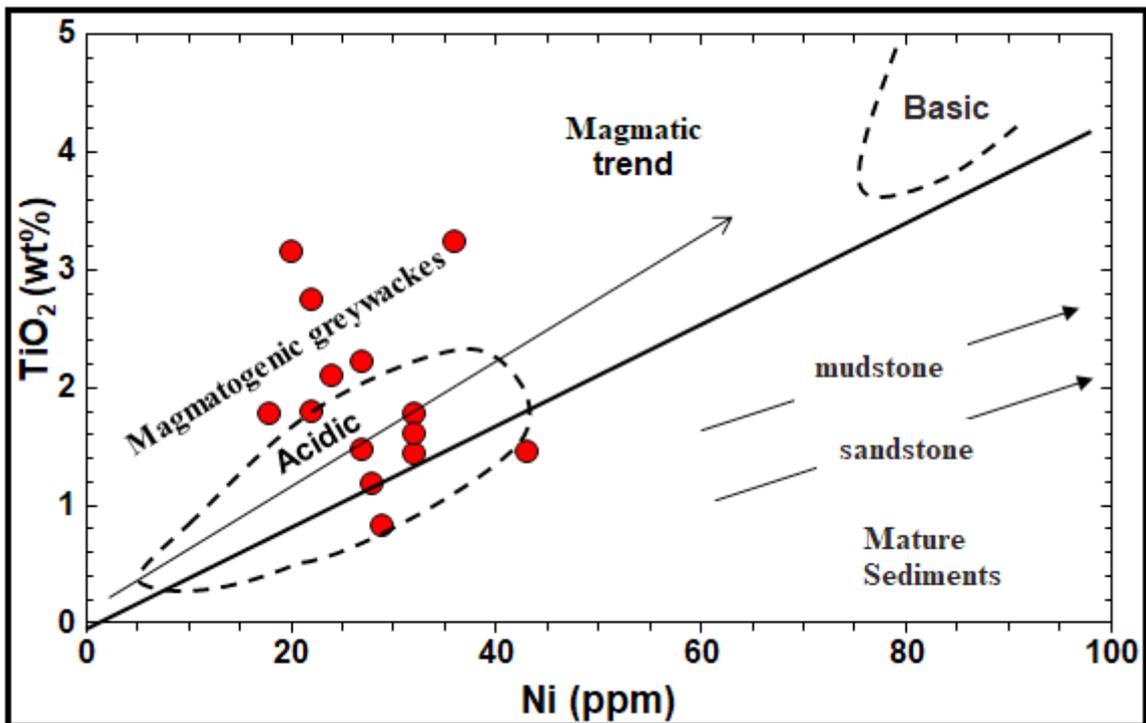


Figure 8. TiO₂ vs. Ni plot of the Ise sandstone, fields and trends after Gu *et al.* (2002), Floyd *et al.* (1989).

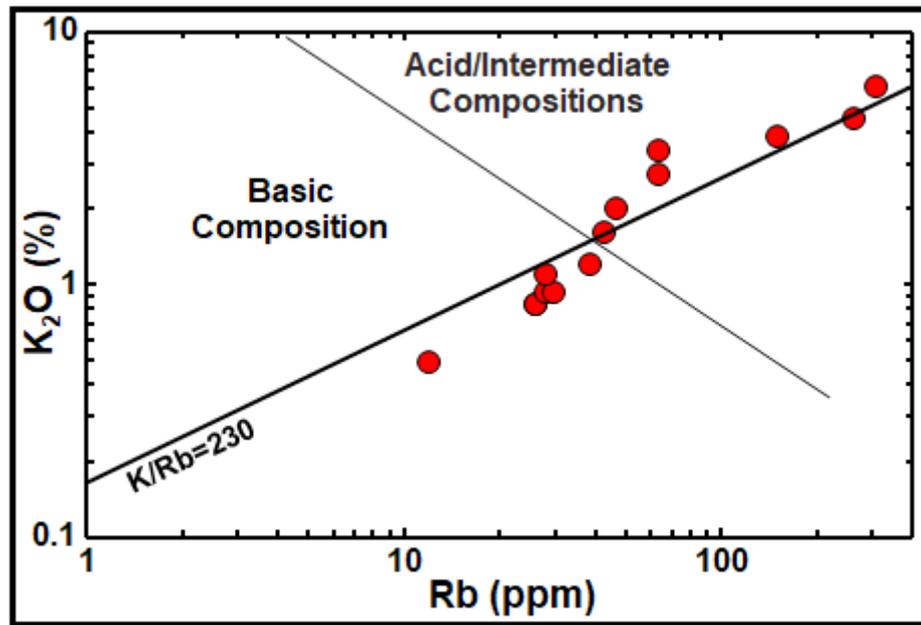


Figure 9. K_2O vs. Rb plot. Fields after Floyd & Leveridge (1987).

Weathering intensity-implication for source area composition

According to Nesbitt & Young (1989) and Nesbitt *et al.* (1996), the chemical composition of clastic sedimentary rock is principally dependent on the composition and the weathering conditions at the source rock area. The most widely used chemical index to assess the degree of chemical weathering in the source area is the Chemical Index of Alteration (CIA) proposed by Nesbitt & Young (1982). This index can be calculated using molecular proportion: $CIA = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)] * 100$. This index works correctly when Ca, Na, and K decrease as the intensity of weathering increases (Duzgoren-Aydin *et al.* 2002). The Chemical Index of Weathering (CIW) proposed by Harnois (1988) is similar to the CIA except for the exclusion of K_2O in the equation: $CIW = \text{molar } (Al_2O_3 / (Al_2O_3 + CaO + Na_2O))$. The CIA and CIW are interpreted in similar way with values of 50 for unweathered upper continental crust and roughly 100 for highly weathered materials, with complete removal of alkali and alkaline-earth elements (McLennan 1993, Mongelli *et al.* 1996). Low CIA values (i.e. 50 or less) also might reflect cool and / or arid conditions (Fedo *et al.* 1995). The degree of the chemical weathering can also be estimated using the Plagioclase Index of Alteration (Fedo *et al.* 1995); in molecular proportions:

$$PIA = [(Al_2O_3 - K_2O) / (Al_2O_3 + CaO + Na_2O - K_2O)] \times 100$$

where CaO^* is the CaO residing only in the silicate fraction. Unweathered plagioclase has PIA value of 50 while Phanerozoic shales have PIA value of 79. The CIA, CIW and PIA values for the Ise sandstone are: CIA (Av. 60%); CIW (Av. 71%); while PIA has an average of 66%, indicating a moderate degree of weathering of the source materials. Voicu *et al.* (1997), also proposed the Mineralogical Index of Alteration (MIA) as a weathering parameter evaluated as: $MIA = 2^{(CIA-50)}$. MIA values between 0 and 20% are designated as incipient, i.e. just starting; 20-40% (weak); 40-60% (moderate) and 60-100% as intense to extreme degree of weathering. The extreme value of 100% indicates

complete weathering of a primary material into its equivalent weathered product (Voicu & Bardoux 2002). MIA values for the Ise sandstone ranges from -78.95-46.27% with an average value of 20.42%, which indicates weak degree of weathering.

Figure 10 shows the weathering trend of the samples, which also confirms the moderate weathering status of the source area since the sandstones did not plot at the apex ($A = Al_2O_3$). The relatively moderate values of Al_2O_3 in the samples indicate the presence of some clay minerals; this also suggests moderate degree of weathering. The chemical composition of weathering products in a basin can be used to assess the state of chemical and physical weathering (Vital & Stattegger 2000, Singh *et al.* 2005). According to Singh *et al.* (2005), the ratio of the content of element X and Al_2O_3 in rivers basin is divided by the ratio of the same element content of upper continental crust (UCC). These elemental ratios calculated with respect to Al are used to identify and evaluate the major element mobility. The elemental ratio refers to the relative enrichment or depletion of the element, i.e., >1 indicates enrichment, <1 indicates depletion, and $=1$ indicates no change in the relative abundance of the element (Singh *et al.* 2005). The sandstone samples analyzed have values greater than 1, only Na_2O has a value less than 1. The depletion of highly mobile Na elements may be due to leaching during the formation of clay minerals during increased chemical weathering. Ca is a highly mobile element that is enriched, this may be attributable to dissolved diagenetic calcite cement or secondary enrichment sourced from overlying carbonate rocks. Si is a less mobile element and its enrichment suggests low to moderate chemical weathering; the immobile Fe and Ti and the less mobile Mg elements enrichment suggests that they may be from a common source from ferromagnesian minerals under moderate chemical weathering condition. During the formation of sedimentary particles from the crust, the very mobile Na will be removed into marine environment while more K is retained in the sediments. Rb has been considered to be primarily fixed in weathering residues and less reactive than Ca, Na, and Sr (Nesbitt *et al.* 1980). Figure

11 shows the graphical representation of ratios of K/Na vs. Rb/Sr. Almost all of the ratios are higher than UCC over a wide range, signifying low to moderate chemical weathering. This phenomenon also indicates preferential dissolution of plagioclase (Na and Sr) relative to K-feldspar (K and Rb) during the silicate weathering process (Kovács 2007). Rb is less reactive than Ca, Na, and Sr; it is considered to be primarily fixed in weathering residues (Nesbitt *et al.* 1980). According to Nesbitt & Young (1982), K/Na and Al/Na ratios

and chemical index of alteration can be used to determine the degree of chemical weathering in sediment with regards to their mobility during weathering. The Al/Na vs. CIA cross-plot (Fig. 12) shows moderate Al/Na values for the sandstones, indicating moderate weathering. Lower Al/K ratio (2.08 - 9.51; molar content) of the studied samples compared to UCC suggests that the sediments were derived during moderate chemical weathering of the source area.

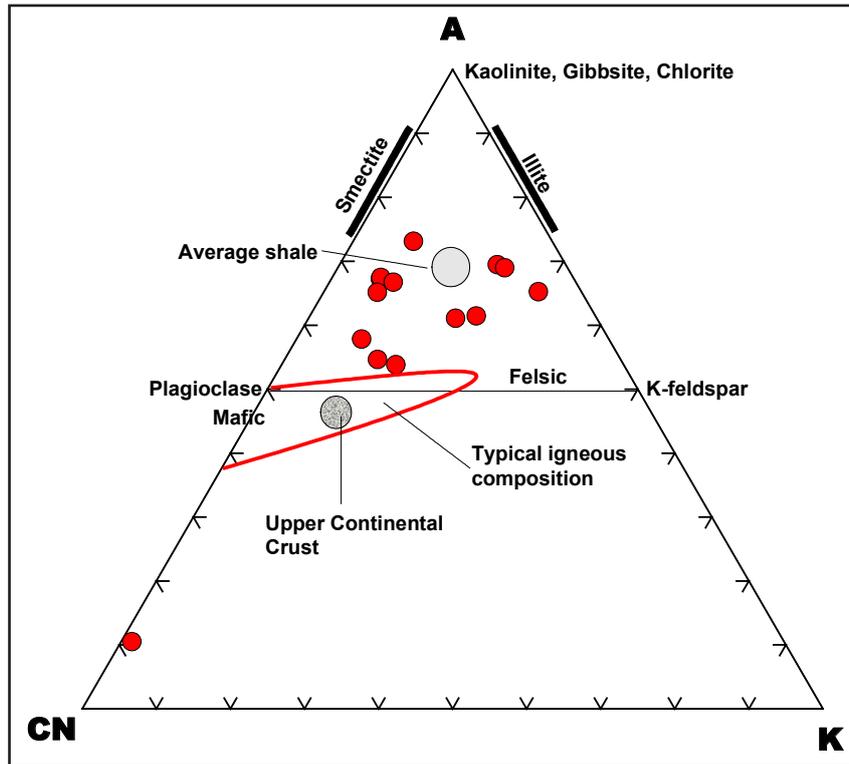


Figure 10. Ternary diagram showing the weathering trend of Ise sandstone (all in molar proportions); $Al_2O_3-CaO + Na_2O-K_2O$ (A-CN-K). UCC value from Taylor & McLennan (1985, 1995).

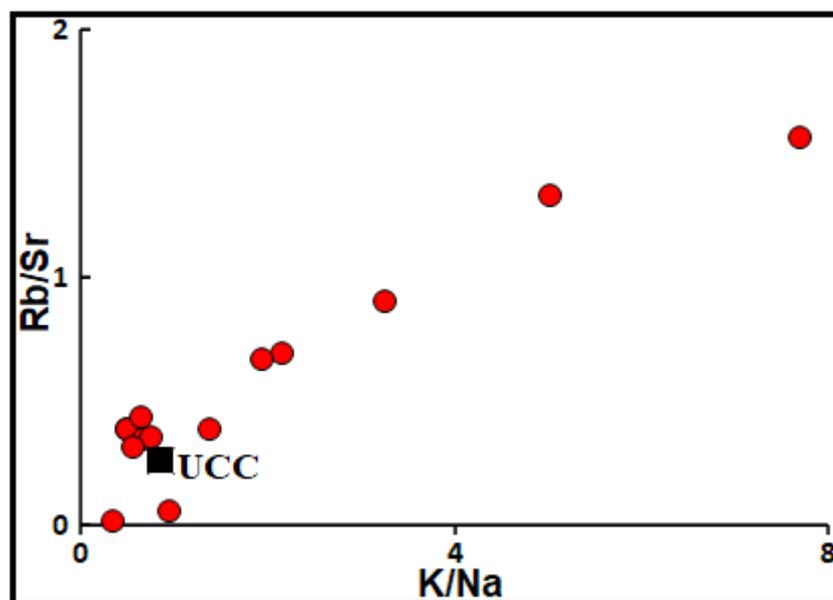


Figure 11. Rb/Sr vs. K/Na diagram indicating chemical weathering of the sandstones (after Kovács 2007).

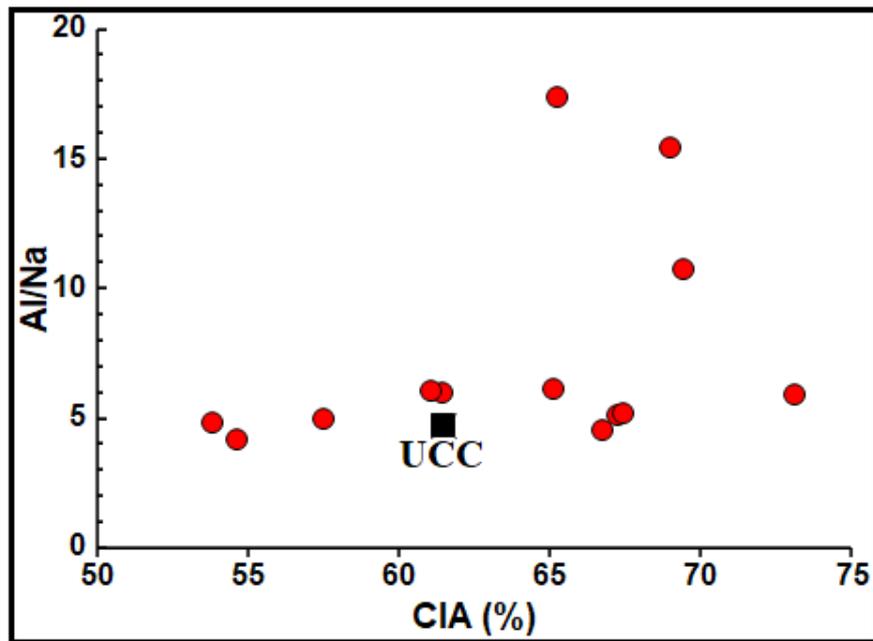


Figure 12. Relationship between Chemical Index of Alteration with Al/Na ratio in the sandstones.

Tectonic setting

According to Wang & Zhou (2013), it is usual to investigate the provenance of sediments and sedimentary rocks, but less attention is given to their tectonic setting in which the sediments were deposited (Perri *et al.* 2015), which may be due to lack of suitable tectonic discrimination diagrams

(Verma & Armstrong-Altrin 2013). The success rates of identifying plate tectonic settings of sedimentary basins using plots of Maynard *et al.* (1982), Bhatia (1983), Bhatia & Crook (1986), Roser & Korsch (1986) and Kroonenberg (1994), do not have high success rates high because they do not incorporate a coherent statistical treatment of compositional

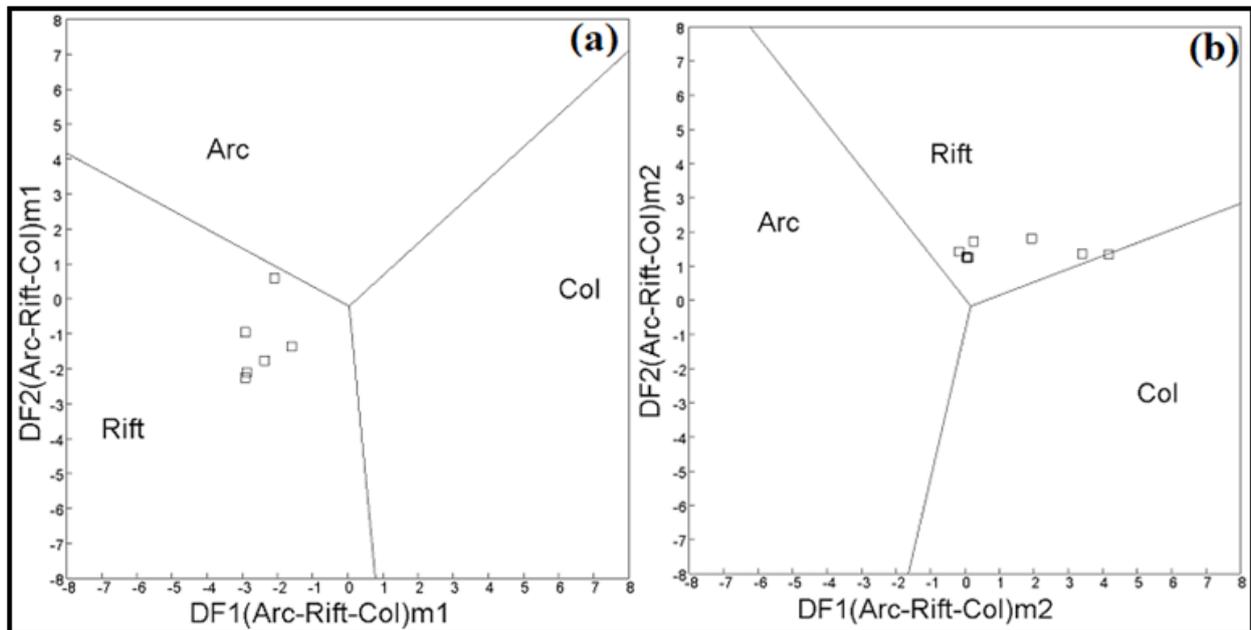


Figure 13. **a)** Discriminant function multidimensional diagram for high-silica clastic sediments (Verma & Armstrong-Altrin 2013). The subscript m1 in DF1 and DF2 represents the high-silica diagram based on loge-ratios of major elements. **b)** Discriminant function multidimensional diagram for low-silica clastic sediments (Verma & Armstrong-Altrin 2013). The subscript m2 in DF1 and DF2 represents the low-silica diagram based on loge-ratio of major elements.

data. Recently, many workers have realised the weaknesses of these traditional discrimination diagrams for clastic sedimentary rocks (Verma & Armstrong-Altrin 2013). There are better discriminant parameters available to delineate tectonic settings (Verma & Armstrong-Altrin 2016). Figures 13a and 13b are used for interpreting the tectonic setting of clastic sediments and sedimentary rocks through two new multidimensional discrimination diagrams by Verma *et al.* (2016). For each sample, the software (Tec Sand) calculates four complex discriminant functions: DF_{m1} and $DF2_{m1}$ for the high-silica diagram and $DF1_{m2}$ and $DF2_{m2}$ for the low-silica diagram, each representing linear combinations of log-ratios of all major elements. These functions determine the position of each sample within island or continental arc, continental rift, and collision/convergent settings (Verma & Armstrong-Altrin 2016). These figures (13a & b) shows all the samples plotted in the rift zone; indicating that the tectonic setting of the Ise sandstone is the rift setting.

The results obtained from these discriminant function-based multidimensional diagrams provide good evidence for the Dahomey basin rift system confirming the work of Omatsola & Adegoke (1981).

Depositional environment, Paleoclimate and Paleo-redox condition

Paleo-redox analysis is vital for distinguishing sediments depositional environment. The accrual of certain trace metals in sediments is directly or indirectly controlled by redox conditions through either a change in redox state and/or speciation (McKay *et al.* 2007). Redox-sensitive trace metals such as V, Cr, Ni, Cu, Zn, Mo, Cd, and U tend to be more soluble under oxidizing conditions and less soluble under reducing conditions, resulting in authigenic enrichments in oxygen-depleted sedimentary facies (Tribovillard *et al.* 2006). Dill (1986), have used the Ni/Co ratio as a redox indicator. Ni/Co ratios below 5 indicate oxic environments, whereas ratios above 5 indicate suboxic and anoxic environments (Jones & Manning 1994). The Ise sandstones have Ni/Co ratios between 0.72 and 4.83 (av. 2.01) indicating that the formation was deposited in oxidizing depositional condition. Ni is mainly enriched in organic-rich sediments where these metals are trapped with organic matter (Gilkson *et al.* 1985). Accumulates relative to Ni in reducing environments, where sulphate reduction is more efficient. Nickel and Vanadium are important trace elements to indicate the redox conditions during deposition as vanadium (V) is usually enriched in comparison with nickel (Ni) in anoxic marine environments (Peters & Moldowan 1993, Bechtel *et al.* 2001, Galarraga *et al.* 2008). A V/Ni ratio greater than 3 indicates that the sediments were deposited in a reducing environment, while V/Ni ratios ranging from 1.9 to 3 indicate deposition under suboxic conditions (Galarraga *et al.* 2008). The V/Ni ratios for the samples range between 2.90 and 7.48 indicating suboxic to anoxic conditions during deposition.

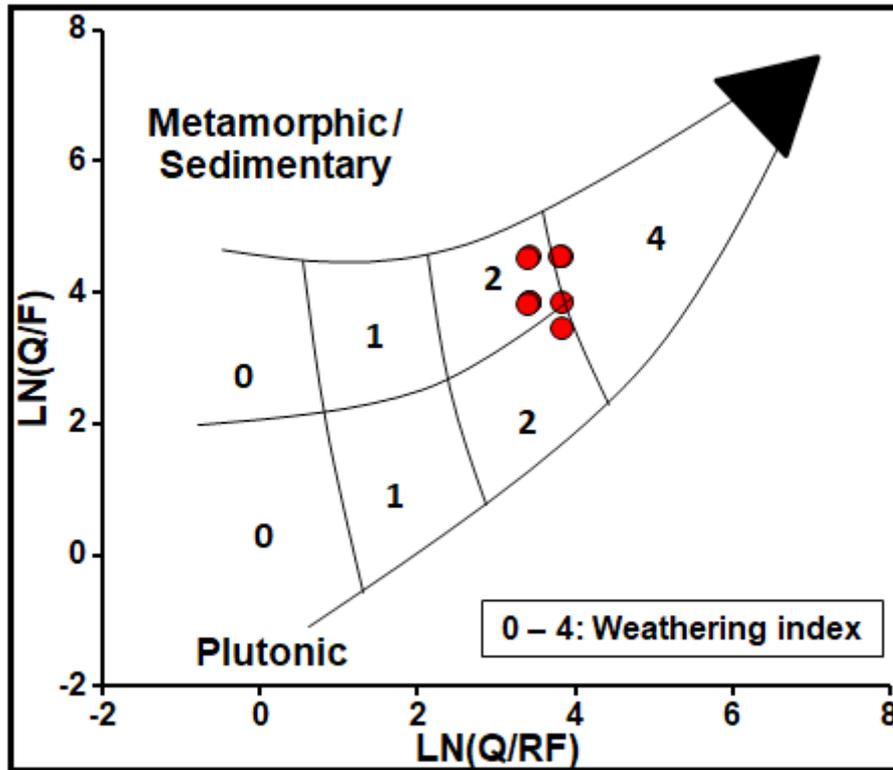
The proportionality of these two elements V/(V+Ni) is very significant to delineate information on Eh, pH and sulphide activity in the depositional environment (Madhavaraju &

Lee 2009). The V/(Ni+V) ratios below 0.46 indicate oxic environments, but ratios above 0.54 to 0.82 suggest suboxic and anoxic environments (Hatch & Leventhal 1992).

The V/ (Ni + V) ratios for the Ise sandstone range from 0.72 to 0.88 (Avg. = 0.82), which indicate suboxic environment of deposition. The Mn* value is a significant paleochemical indicator of the redox conditions of the depositional environment (Machhour *et al.* 1994, Bellanca *et al.* 1996, Cullers 2002).

The expression for calculating Mn* value is $Mn^* = \log[(Mn_{sample}/Mn_{shales})/(Fe_{sample}/Fe_{shales})]$, where the values used for the Mn_{shales} and Fe_{shales} are 600×10^{-6} and 46150×10^{-6} , respectively (Wedepohl 1978). The reduced iron and manganese form different solubilities of compounds across a redox boundary, while manganese tends to accumulate in more oxygenated conditions above the redox boundary (Bellanca *et al.* 1996). The Ise sandstones have mainly negative Mn* values (except one sample with value of 0.31) ranging from -0.73 to 0.31 with an average of -0.42. This suggests that the sandstones may have been deposited in oxic and suboxic conditions. According to Deng & Qian (1993) and Wang (1996), Sr and Ba are regarded as indicators of paleosalinity. A high Sr/Ba ratio reflects high salinity, and a low Sr/Ba ratio indicates low salinity (Deng & Qian 1993). The Ise sandstone has a Sr/Ba ratio between 0.2 and 3.85 (average 0.79), indicating low saline water during deposition and a strong continental rather than marine influence. A weathering index diagram shows the natural logarithm of quartz and feldspar ratio versus the natural logarithm of quartz and lithic fragments ratio. It can be used to determine the climatic conditions, physiology (relief) and origin of siliciclastic material (Fig. 14). The diagram is divided in two areas, regarding the rock type (metamorphic/sedimentary and plutonic). Each of these areas is divided into four fields, pointing to the climate and relief conditions. The Ise samples are grouped and plotted in the area of metamorphic/sedimentary rocks. Majority of the samples plotted in zones marked 2, while some plotted in the number 4 zone. This implies contributions from moderate and low relief under weathering conditions in tropical humid climate.

The degree of chemical weathering is a function of climate and rates of tectonic uplift (Wronkiewicz & Condie 1987). The rising chemical weathering intensity suggests the decrease in tectonic activity and/or the change of climate towards warm and humid conditions which are more favorable for chemical weathering in the source region (Jacobson *et al.* 2003). The applicability of the ratios of $SiO_2/(Al_2O_3+K_2O+Na_2O)$ for paleoclimatic condition (Suttner & Dutta, 1986) during deposition of sediments in the basin is well recognized by many workers. Figure 15 shows the samples plotting in humid-semi-humid and semi-arid climatic conditions, which reflects paleoclimatic condition during the deposition of the sandstone. Figure 16 shows the Ise sandstones classified as non-marine and deltaic sandstones and in figure 17, the sandstones plotted in the marine-terrestrial oxic to dysoxic zone; this suggests a transitional deltaic depositional environment.



Semi-quantitative weathering index		Physiography (relief)		
		High (mountain) 0	Moderate (Hills) 1	Low (plains) 2
Climate (precipitation)	(Semi) Arid and mediterranean 0	0	0	0
	Temperate subhumid 1	0	1	2
	Tropical humid 2	0	2	4

Figure 14. Log-ratio plot after Weltje *et al.* (1998). Q: quartz, F: feldspar, RF: rock fragments. Fields 1-4 refer to the semi-quantitative weathering indices defined on the basis of relief and climate as indicated in the table.

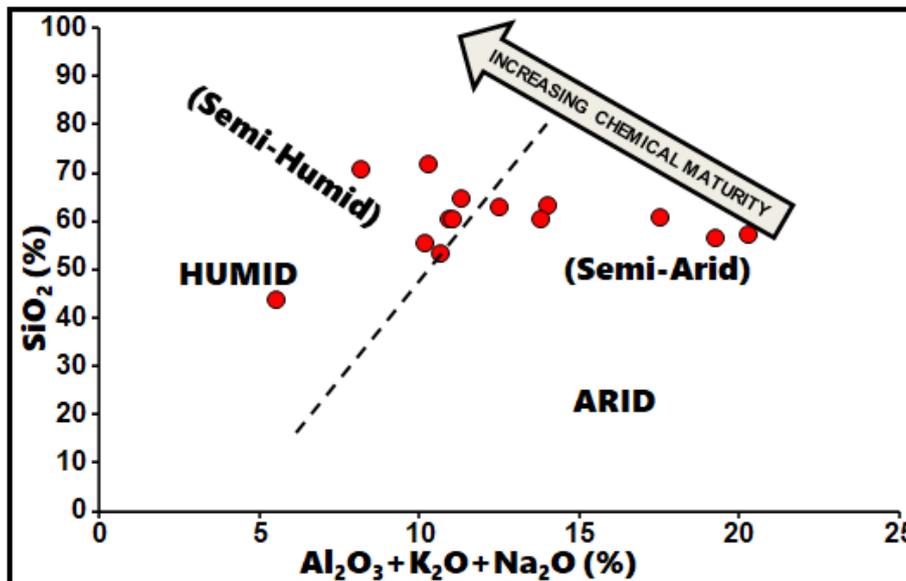


Figure 15. Bivariate plot of SiO_2 vs. $(Al_2O_3 + K_2O + Na_2O)$ to discriminate paleoclimatic condition during the deposition of the Eocene sediments (after Suttner & Dutta 1986).

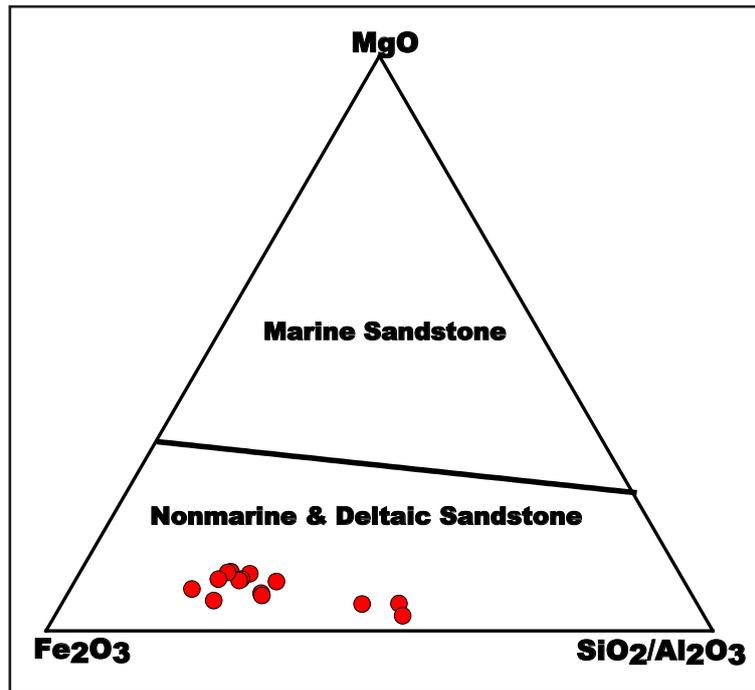


Figure 16. Ternary diagram showing characterization and differentiation of marine from nonmarine sandstones (after Ratcliffe *et al.* 2007).

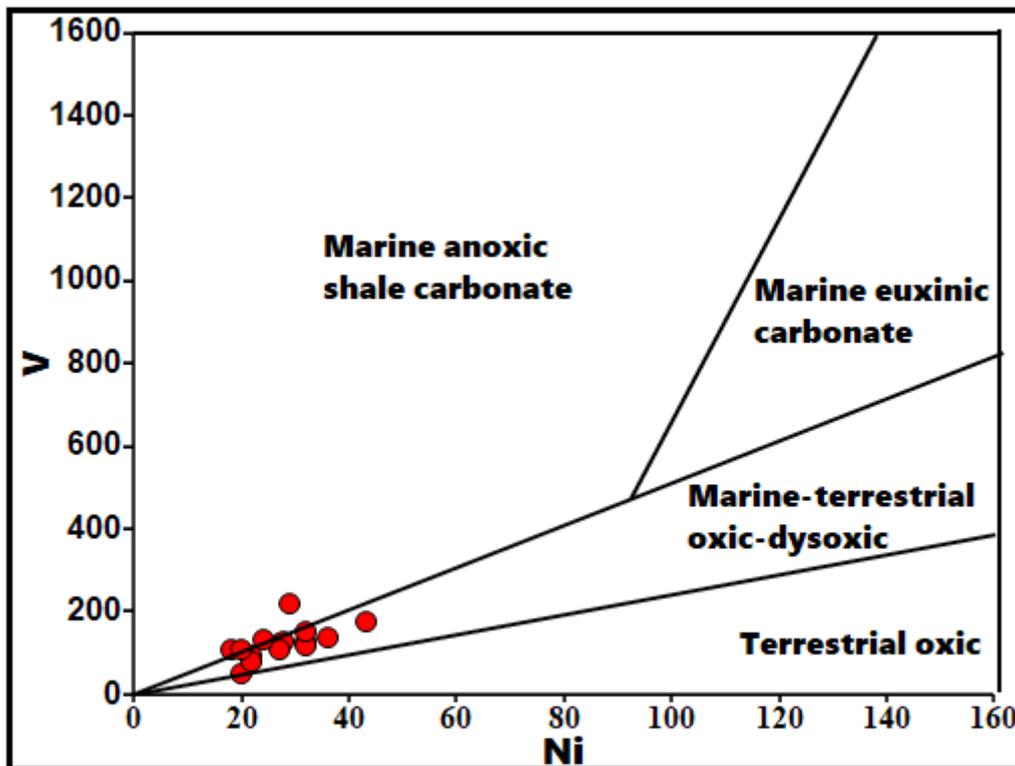


Figure 17. Cross-plot of vanadium versus nickel of the Ise sandstones (after Galarraga *et al.* 2008)

CONCLUSION

The relatively high concentrations of Fe_2O_3 and TiO_2 is an indication of iron-titanium minerals. The source area analyses of the Ise sandstone suggest that the sediments were derived from multiple protoliths from moderate and low relief. All the weathering indices indicate that the sediments were derived during moderate degree of weathering of the source materials.

The tectonic setting is of the active continental margin and passive margin types. The depositional, paleoenvironmental and paleoclimatic studies suggest that the Ise sandstone was deposited in mostly oxic to suboxic tropical humid deltaic conditions. The Ise sandstones have a low Sr/Ba ratio indicating low saline water during deposition and a strong continental rather than marine influence.

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