Geochemistry of rocks (Late Cretaceous) in the Anambra Basin, SE Nigeria: insights into provenance, tectonic setting, and other palaeo-conditions

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ABSTRACT

The geochemistry of Late Cretaceous sandstones and shales in the Anambra basin has been investigated by relatively few subsurface data-based studies, thus, there is a need for subsurface geochemical characterisation of the basin's fill provenance, tectonics, and palaeo-conditions (source rocks palaeo-weathering, palaeo-climate, and palaeo-redox). This paper presents the geochemistry of sandstones and shales from cored sections (n = 10) of the Amansioodo_1 well (located in the Anambra basin) with the intent of unravelling the provenance, tectonic setting, and palaeo-conditions. Major elements (n = 10) and the trace element concentrations of Sc, Be, V, Sr, Y, Zr, and Ba were obtained using fusion inductively coupled plasma. Trace (n = 24) and rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) concentrations were obtained using fusion mass spectrometry analytical method. Based on geochemical discrimination diagrams and element ratios such as Al2O3/TiO2, TiO2/Zr, Th/Sc, and La/Th; it is suggested that the studied samples from the Anambra Basin were derived from mixed sources (mafic, felsic, and intermediate) from the adjoining basement rocks, and recycled sediments from the Abakaliki uplift or high. The high-silica and low-silica tectonic multidimensional discrimination diagrams showed that the examined rocks might have originated from rift (69 % probability), collision (24 % probability), and continental arc (7 % probability) settings. The plagioclase index of alteration (PIA), chemical index of weathering (CIW), and chemical index of alteration (CIA) values (average > 80) of studied rock specimens indicate an intensive degree of chemical weathering of the source rocks. The plot of Al2O3 + K2O + Na2O versus SiO2, weathering indices (PIA, CIW, and CIA), and Sr/Ca and Rb/Sr ratios; as well as U, Mo, Th/U, V/Cr, V/Sc, U/Th, and Ce/Ce* all suggested warm to hot, humid and/or arid palaeo-climate in an oxic palaeo-redox condition during the accumulation of the examined samples.

1. Introduction

Insight into the provenance and tectonic setting of a sedimentary basin fill is crucial for hydrocarbon exploration/exploitation as well as other palaeo-conditions. Although the usefulness of geochemistry of sedimentary rocks in the determination of provenance, tectonic settings, and palaeo-conditions has been a global subject, its application is grossly a complex function of the nature of source rock(s), weathering intensity/duration, sedimentary recycling, diagenesis (e.g., authigenesis), and sorting (e.g., McLennan et al., 1993). The geochemical attributes of elements (major, trace, and rare earth elements, REE) in clastic sedimentary rocks are invaluable for construing provenance (Deru et al., 2007; McLennan, 2001; Taylor and McLennan, 1985), tectonic setting (Bhatia, 1983; Roser and Korsch, 1988), source rocks weathering condition (Nesbitt and Young, 1984; Fedo et al., 1995, 1996), and sedimentary depositional environment (Taylor and McLennan, 1985). Also, the geochemical composition of elements furnishes invaluable information that is germane for palaeo-climate (e.g., Lerman and Gat, 1989; Cao et al., 2012; Tao et al., 2017) and palaeo-redox (e.g., Jones and Manning, 1994; Nagarajan et al., 2007; Wignall and Myers, 1988; Wilde et al., 1996; Yang et al., 2011) reconstructions.

The Anambra Basin of southern Nigeria (lying between the NE-SW trending southern Benue Trough and the petroliferous Niger Delta, Figure 1) has been known for over a century ago as an exploration frontier for coal and decades later petroleum. Its north-western and eastern side is defined by the southwestern basement complex of Nigeria/the Bida basin and the Abakaliki anticlinorium respectively. Its post-Santonian sedimentary fill is >7,000 m at the southern part (Whiteman, 1982).

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The provenance of the sediments and the tectonic nature of the Anambra Basin have received attention for decades (Reyment, 1965; Short and Stauble, 1967; Burke et al., 1972; Murat, 1972; Nwachukwu, 1972; Hoque, 1977; Hoque and Ezepue, 1977), nevertheless, the source area and the tectonic setting are still unsettled, subjects of active deliberation. Four probable provenances have been suggested based on field evidence, petrography, and geochemistry of outcrop data set (Figure 1): (1) the eastern Precambrian basement complex rocks of Cameroon (Hoque, 1976, 1977; Hoque and Ezepue, 1977; Agumanu, 1993); (2) Campano-Maastrichtian detritus derived from the Abakaliki Anticlinorium, sequel to the Santonian uplift (Simpson, 1954; Short and Stauble, 1967; Nwachukwu, 1972; Murat, 1972; White- man, 1982; Amajor, 1987a; Tijani et al., 2010); (3) Sediments derived from the Ohan-Adamawa (Adamawa-Sarduana Massif) basement complex (Amajor, 1987a; Agumanu, 1993; Tijani et al., 2010); and (4) Sediments sourced from the Ibadan Craton (West African massif) and the Oban Massif (south-eastern, Nigeria) (Nwajeide and Reijers, 1996). Most of the aforementioned provenance studies were focused on the exposed sections of the sedimentary fills of Anambra Basin, especially the Ajali (e.g., Hoque, 1977; Hoque and Ezepue, 1977; Amajor, 1987a,b; Tijani et al., 2010; Ogala et al., 2015), Mamu (e.g., Ogungbesan, and Adedosu, 2020), Owelli sandstone (e.g., Agumanu, 1993), Enugu and Awgu (Overare et al., 2020) Formations using directional sedimentary structures or petrographic and/or geochemistry data. However, the tectonic setting of the sedimentary fills of the Anambra basin has been reported to be of passive margin, based on the surface geochemical data (e.g., Tijani et al., 2010; Ogala et al., 2015).

There have been several investigations by researchers on the geochemistry of the sedimentary successions of the Anambra Basin (e.g., Amajor, 1987b; Odoma et al., 2015; Edegbai et al., 2019; Overare et al., 2020). However, most of these studies relied heavily on rock samples obtained from road cut exposures, that are prone to sub-aerial/tropical weathering conditions for a long time. The present work made use of available core samples from the Amansiodo-1 well obtained from the repository of the Nigerian Geological Survey Agency (NGSA). This unique data set is quite desirable for this study because they are not exposed to surface conditions and were recovered from the specific interval of the
exploration well. However, published information on the provenance, tectonic setting, and other palaeo-conditions (source rock palaeo-weathering, palaeo-climate, and palaeo-redox conditions) of the sediments of the Anambra basin from subsurface geochemical data set are relatively few. In this present contribution, I complement the search for the source area, tectonic setting, and palaeo-conditions of the Anambra Basin sediments through the addition of subsurface geochemical data spanning Nkporo (Late Turonian to Early Santonian) through Ajali (Maastrichtian) Formations. In 1962 Shell D Argy (now SPDC, Nigeria) drilled a 2291 m exploration well, the Anambiosio-1 well to investigate oil and gas prospects in the Anambra Basin. This work provides core samples for this research work. The Anambiosio-1 well cuts across Ajali, Mamu, Enugu/Nkporo (with the associated lateral equivalent, Owelli Sandstones), and Agbani and Awegu Formations (Nwajide, 2013; Onuoha, 2014) of the Anambra basin (Figure 1).

2. Geological setting

2.1. Tectonic framework

The Anambra Basin is tiered up with the southern ensemble of the Benue Trough and its origin is closely related to the evolution of the Benue Trough, which is associated with the separation of Africa from the South American plate in the Mesozoic, which is the opening of the Benue Trough, which is associated with the separation of Africa from the

2.2. Stratigraphy

The sedimentary depositional history of the Anambra Basin has been presented in the light of a tripartite tectonic episode (the dominant event explained above) as conceptualized by Short and Stauble, 1967, and later affirmed by Murat (1972) and Hoque (1977). The first phase—a Pre-Santonian (Albian—Santonian) event marked by pronounced subsidence in the Abakaliki domain of the Benue Trough, while the Anambra remained a platform with mud and shallow marine deposits. The second phase (Santonian to Early Paleocene, Danian) resulted in uplifting and erosion of the Abakaliki anticlinorium have been sided due to structural inversion. The detritus generated due to the tectonic folding of the Abakaliki-Benue Belt; while the Anambra platform subsided due to structural inversion. The detritus generated due to the tectonic phase explanation above) as conceptualized by Short and Stauble, 1967, or a dominating tectonic process of wrenching (Benkelman, 1989; Maurin et al., 1986). It is known to be a folded aulacogen or a rift formed by tightly folded Cretaceous sediments intruded by numerous magmatic rocks. It is flanked to the North West by the synclinorial structure of the Anambra Basin.

3. Samples and analytical methods

Ten representative samples (shale, n = 6; and sandstone, n = 4) obtained from the cored sections of the Anamansio-1 well were analysed geochemically for major elements (oxides), trace elements, and rare earth elements (REE). As part of pre-analytical treatment, samples chipped from each core was crushed mechanically (to <2 mm), pulverized to 105 μm, and 100 g of which was packaged at the Geology Laboratory of Delta State University; and later sent for geochemical analysis at Activation Laboratories Limited in Ancaster, Ontario Canada. The whole-rock geochemical analytical assay involved major elements fusion inductively coupled plasma (FUS-ICP) (for SiO2, Al2O3, Fe2O3, MnO, MgO, CaO, Na2O, K2O, TiO2, P2O5, and LOI); trace element fusion inductively coupled plasma (for Sc, Be, V, Sr, Y, Zr, and Ba); and trace/rare earth elements mass spectrometry (FUS-MS) (for Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Nb, Mo, Ag, In, Sn, Sb, Cs, Hf, Ta, W, Ti, Pb, Th, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu). Details of the analytical procedures alongside quality checks (detection limits) are as reported in the Activation Laboratories website, www.actlabs.com and the principles of the FUS-ICP/MS methods are explained in Jarvis (1988), and Jarvis and Jarvis (1995).

4. Results

The geochemical analyses result of the major, trace, and rare earth elements (REE) for sandstones and shales from the Anamansio-1 well are presented in Tables 1, 2, and 3 and summarized/compared with geochemical standards [Upper Continental Crust (UCC) by Rudnick and Gao, 2003; North American Shale Composite (NASC) by Gromet et al., 1984; and Post-Archean average Australian Shale (PAAS) by Taylor and McLennan, 1985; McLennan 2001] in Table 4. Overare et al. (2020) worked on outcrop samples from the Awegu/Enugu shales and reported average major element compositions for SiO2 (53.7 wt.%), TiO2 (1.1 wt.%), and Al2O3 (20.80 wt. %), with the values slightly higher than the values reported in this study; while other major element compositions in their study are slightly lower. The trace/REE reported in this study are also slightly higher than those of Overare et al. (2020) except Ga, Nb, Cu, Sr, Th, Nb, Cu, Pr, and Nd. Further comparison of the average geochemical concentration of the Mamu shales with average values reported by Odoma et al. (2015) from outcrop studies revealed the major elements SiO2 (51.2 wt. %), TiO2 (1.5 wt. %), and Al2O3 (17.2 wt. %) to be slightly higher than the values reported in this study. The trace/REE compositions reported in this study for the Mamu Formation are higher than those of Odoma et al. (2015), except Nb, Ba, Cu, Sr, Y, Th, Nb, La, Ce, Nd, and Sm, that have lower values.

4.1. Major elements

Sandstones from the Anamansio-1 well have the following geochemical contents: SiO2 (69.44–94.06 wt. %, av. 83.12 wt. %), Al2O3 (1.37–14.2 wt. %, av. 5.1 wt. %), TiO2 (0.085–1.68 wt. %, av. 0.86 wt. %), Fe2O3 (3.26–15.08 wt. %, av.9.12 wt. %), and Al2O3 (20.80 wt. %), with the values slightly higher than the values reported in this study; while other major element compositions in their study are slightly lower. The trace/REE reported in this study are also slightly higher than those of Overare et al. (2020) except Ga, Nb, Cu, Sr, Th, Nb, Cu, Pr, and Nd. Further comparison of the average geochemical concentration of the Mamu shales with average values reported by Odoma et al. (2015) from outcrop studies revealed the major elements SiO2 (51.2 wt. %), TiO2 (1.5 wt. %), and Al2O3 (17.2 wt. %) to be slightly higher than the values reported in this study. The trace/REE compositions reported in this study for the Mamu Formation are higher than those of Odoma et al. (2015), except Nb, Ba, Cu, Sr, Y, Th, Nb, La, Ce, Nd, and Sm, that have lower values.
The major element geochemical concentrations of the Awgu and Enugu shales are comparable with the exceptions of Fe₂O₃ and Al₂O₃, but slightly greater than the values for the younger Mamu Formation sandstones of the Agbani, Owelli, and Ajali Formations all have high regardless of depth or age.

### Table 1. Major element concentrations (in wt. %) for the core samples from Amansiodo-1 well.

| Elements | S.N. | Am-1 | Am-2 | Am-3 | Am-4 | AvM | Am-5 | Am-6 | Am-7 | Am-8 | Am-9 | Am-10 | AvEA |
|----------|------|------|------|------|------|-----|------|------|------|------|------|-------|------|
| Oxides   |      |      |      |      |      |     |      |      |      |      |      |       |      |
| SiO₂     | 0.010 | 94.06 | 90.18 | 44.06 | 42.46 | 43.3 | 69.44 | 53.09 | 48.93 | 78.79 | 55.21 | 49.52 | 51.7 |
| Al₂O₃    | 0.001 | 0.099 | 0.085 | 1.071 | 1.152 | 1.11 | 1.576 | 1.067 | 1.422 | 0.168 | 1.011 | 1.363 | 1.22 |
| Fe₂O₃    | 0.010 | 1.370 | 1.870 | 6.640 | 8.710 | 7.67 | 14.20 | 21.94 | 16.32 | 2.960 | 20.92 | 9.710 | 17.2 |
| MgO      | 0.001 | 0.022 | 0.050 | 0.120 | 0.175 | 0.15 | 0.082 | 0.047 | 0.209 | 0.012 | 0.051 | 0.261 | 0.14 |
| CaO*     | 0.010 | 0.040 | 0.200 | 0.801 | 1.380 | 10.30 | 14.09 | 1.920 | 14.09 | 15.08 | 6.930 | 22.76 | 13.2 |
| Na₂O     | 0.010 | 0.120 | 0.210 | 0.120 | 0.17 | 0.140 | 0.840 | 0.120 | 0.145 | 0.840 | 0.090 | 0.47 |
| KO       | 0.010 | 0.100 | 0.200 | 0.420 | 0.210 | 0.32 | 0.570 | 1.650 | 0.640 | 0.150 | 1.870 | 0.290 | 1.11 |
| LOI      | 0.002 | 0.020 | 0.030 | 0.130 | 0.038 | 0.08 | 0.190 | 0.160 | 0.250 | 0.025 | 0.140 | 0.170 | 0.18 |
| Total    | 0.001 | 0.300 | 1.380 | 10.30 | 14.09 | 1.920 | 12.70 | 15.17 | 0.441 | 11.35 | 14.79 |

### 4.2. Trace elements

Trace element concentrations are presented in Table 2 and summarized in Table 4 alongside values for UCC, NASC, and PAAS for comparison. Trace element abundances in shales on average are significantly higher than those in sandstones from the Amaosiodo-1 well. Trace element average concentration values in shales thus serve as the basis for stating the enrichment/depletion of the element relative to the upper crust compositional standards. Elements such as Sc, Be, Ga, Ta, Co, Mo, Nb, U, Th, W, and Pb were slightly enriched relative to UCC, NASC, and PAAS, whereas elements like Ba, Sr, Ge, Ag, In, Bi, Cu, Sn, Cs, Rb, As, Th and Ti were depleted. Zr, Zn, V, Nb, and Cr, are strongly enriched considering the average composition of the shale samples.

### 4.3. Rare earth elements

Lanthanide concentrations (REE, from La to Lu) are presented in Table 3 and summarized in Table 4 alongside UCC, NASC, and PASC for comparison. They have comparable chondrite normalized patterns of REE to PAAS and NASC (Table 4), represented by light rare earth element (LREE) enrichment and negative Eu anomalies, an indication that the main sedimentary source(s) were continental crustal rocks. Patterns of REE show noteworthy heavy rare earth element (HREE) depletion, and (La/Yb)ₜ ratios of 7.028–9.798 (average 8.46) for sands and 7.020 to 13.39 (average 9.46) for shales (Table 4). LREE patterns on the chondrite normalization plot (Figure 2) are steep due to strong fractionation while HREE patterns are flat and not strongly fractionated. Both shale and sandstone samples exhibit distinct negative Eu anomalies ([Eu/Sm]₀ 0.599–0.665) for sands; 0.614–0.675 (average 0.66) for shales very close to that of NASC ([Eu/Sm]₀ 0.69) and PAAS ([Eu/Sm]₀ 0.64) (Table 4). The sandstones and shales revealed slightly negative Ce anomalies (Ce/Ce* of 0.851–0.965, av. 0.920 for sands; and 0.889–0.965, av. 0.930 for shales) of which the average values are less than that of NASC and PAAS (Table 4); an indication that the extent of oxidation of rocks in the provenance was lower than that of NASC, possibly because the area escaped long chemical weathering associated with tropical climate due to rapid burial and sedimentation.

### 5. Discussion

#### 5.1. Provenance

A provenance discriminant diagram (Figure 3) proposed by Roser and Korsch (1988) to discriminate quartzose sedimentary rocks from felsic, intermediate, and mafic igneous rocks was applied. Eighty percent of the samples from the Amaosiodo-1 well plotted in the P1 (mafic igneous) field, 20% in the P4 (quartzose sedimentary) field, and none in the P2 (intermediate igneous) field. The Al₂O₃/TiO₂ ratio in shales and...
sandstones has been reported to often retain their source rock composition (Garcia et al., 1994; Girty et al., 1996; Hayashi et al., 1997) as such this ratio can be used as an index of the source area. Girty et al. (1996) stated that sediments from mafic rocks have Al2O3/TiO2 ratio <14 while sediments from felsic rocks ranged from 19-28. Also, Garcia et al. (1994) and Hayashi et al. (1997) reported a range of 3-8, 8-21, and 21-70 for mafic, intermediate, and felsic sources respectively. The average of Al2O3/TiO2 ratios for shales and sandstones of the studied samples from main in the felsic igneous sandstones are of main in the felsic igneous sandstones (Hayashi et al., 1997). Figure 4b) for the studied samples indicated that the sandstones are of mafic and felsic igneous sources, and the shales plotted mainly in the felsic igneous field. Significant fractionation of TiO2 and Zr-bearing minerals usually associated with transportation and deposition of clastic rocks is a common reason for this discrepancy (Hayashi et al., 1997).

The composition of La, Sc, and Th; and their elemental ratios such as Th/Sc and La/Th are useful determinants of sediment provenance (e.g., Cullers et al., 1988; McLennan and Taylor, 1991) due to their immobile nature and abundance/concentration in felsic (La and Th) and mafic (Sc) rocks. Philips et al. (2017) stated that the Th/Sc ratios of <0.6 represent a mafic source, >0.6–1.0 typifies an andesitic composition (intermediate source), and >1.0 indicates a “continental crust enriched in incompatible elements”. The Th/Sc ratios of the study core samples ranged from 1.6 to 2.4 (average 1.92, for sandstones) and 0.51 to 0.91 (average 0.76, for shales) (Table 4). This implies that the sandstones are of andesitic composition or intermediate to felsic signatures, while the shales are mafic to andesitic composition; suggesting an overall mixed sediment source shown in the plot of Th versus Sc (Figure 4c). The La/Th ratios of the study core samples ranged from 2.80 to 5.50 have been reported to often retain their source rock composition (Garcia et al., 1994; Girty et al., 1996; Hayashi et al., 1997) as such this ratio can be used as an index of the source area. Girty et al. (1996) stated that sediments from mafic rocks have Al2O3/TiO2 ratio <14 while sediments from felsic rocks ranged from 19-28. Also, Garcia et al. (1994) and Hayashi et al. (1997) reported a range of 3-8, 8-21, and 21-70 for mafic, intermediate, and felsic sources respectively. The average of Al2O3/TiO2 ratios for shales and sandstones of the studied samples from main in the felsic igneous sandstones (Hayashi et al., 1997). Figure 4b) for the studied samples indicated that the sandstones are of mafic and felsic igneous sources, and the shales plotted mainly in the felsic igneous field. Significant fractionation of TiO2 and Zr-bearing minerals usually associated with transportation and deposition of clastic rocks is a common reason for this discrepancy (Hayashi et al., 1997).

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5.2. Plate tectonic setting

Detrital sediments are often generated under different tectonic settings alongside their inherent geochemical signature; hence the discrimination of sedimentary tectonic setting can be inferred from the chemistry of sedimentary rocks (Bhatia and Crook, 1986; Roser and Korsch, 1985, 1986). Discrimination diagrams proposed by Bhatia (1983) and Roser and Korsch (1986) have been traditionally and widely used for decades to obtain tectonic information from sediments/sedimentary rocks deposited in basins (e.g., McCann, 1988; Burnet and Quirk, 2001; Gu et al., 2002; Tijani et al., 2010; Ejeh et al., 2015; Ogala et al., 2015; Egozcue et al., 2019). Verma et al. (2016) has synthesised both the high silica and low silica diagrams and yielded the discrimination of sedimentary tectonic settings of the Anambra basin sediments. Following the adjustment of the major element oxides ([SiO₂]₀; P₂O₅ excluding loss on ignition) (Table 5) values on an anhydrous 100 % basis, TecSand separates the samples into high silica (n = 4, all sandstones) and low silica (n = 6, all shales) (Table 7). Among the high silica samples, three (Am-1, Am-5, and Am-8; see sample source/formation in Table 1) plotted in the continental rift setting with probability values of 0.999 ± 0.0097 (range 0.9644–0.9782) (Figure 5a, Table 6). The high probability value of 0.999 (~1.00) for the continental rift field implies that the probability for the other 2 fields is zero or very low. Therefore, the low probability for the lobe sample plotted in the arc field means that the sample would plot very close to the boundary of the setting which had the highest probability value, in this case, rift setting (Figure 5a). Also, for the low silica samples, four (Am-3, Am-4, Am-6, and Am-9) plotted in the rift setting with probability values of 0.702 ± 0.222 (range 0.4582–0.9912); and two (Am-7 and Am-10) plotted in collision/convergent setting with probability values of 0.9782 ± 0.0097 (range 0.9644–0.9782) (Figure 5b, Table 6). TecSand synthesised both the high silica and low silica diagrams and yielded the total samples (Σn) plotted in each field along with their total probability values (Σn prob) and percentage probability (% prob) (Table 5). Seven samples plotted in the continental rift setting with a total probability and percentage probability of 5.7153 and 69 % respectively. The two samples plotted in the collision/convergent field possessed a total probability and percentage probability of 1.9427 and 24% respectively. The sample that is plotted in the collision setting with very minimal arc settings.

### Table 3. Rare earth element concentrations (in ppm) for the core samples from Anamasiido-1 well.

| S.N. | Am-1   | Am-2   | Am-3   | Am-4   | AvM  | Am-5   | Am-6   | Am-7   | Am-8   | Am-9   | Am-10  | AvEA  |
|------|--------|--------|--------|--------|------|--------|--------|--------|--------|--------|--------|-------|
| Elements         | Pm.   | Ajali  | Ajali  | Mamu  | Mamu   | Owelli | Enugu  | Enugu  | Agbani | Awęgu  | Awęgu  |       |
| Lith.           | Sand  | Sand   | Shale  | Shale  | Shale   | Shale  | Shale  | Shale  | Shale  | Shale  | Shale  |       |
| Depth (m)       | 30.0  | 60.9   | 281.5  | 600    | 700    | 900    | 1100   | 1300   | 1779.3 | 1847.9 | 1847.9 |       |
| La              | D.I.  |        |        |        |        |        |        |        |        |        |        |       |
| Ce              | 5.700 | 5.500  | 5.800  | 5.260  | 5.600  | 4.500  | 4.100  | 4.100  | 4.100  | 4.100  | 4.100  |       |
| Pr              | 1.270 | 1.240  | 1.400  | 1.200  | 1.030  | 9.410  | 10.900 | 10.900 | 11.50  | 11.50  | 11.50  | 11.50  |
| Nd              | 4.700 | 4.400  | 5.000  | 4.075  | 4.700  | 37.00  | 42.80  | 42.80  | 42.80  | 42.80  | 42.80  | 42.80  |
| Sm              | 1.000 | 0.990  | 0.890  | 0.890  | 0.895  | 7.500  | 8.900  | 9.000  | 7.300  | 7.300  | 7.300  | 7.300  |
| Eu              | 0.170 | 0.160  | 0.169  | 0.158  | 0.164  | 1.880  | 2.000  | 2.020  | 1.570  | 1.390  | 1.650  | 1.765  |
| Gd              | 0.800 | 0.700  | 0.600  | 0.700  | 0.650  | 6.800  | 7.500  | 7.600  | 5.300  | 4.700  | 6.600  | 6.600  |
| Tb              | 0.100 | 0.100  | 0.100  | 0.100  | 0.100  | 1.200  | 1.300  | 1.200  | 0.900  | 0.800  | 1.100  | 0.100  |
| Dy              | 0.800 | 0.600  | 0.700  | 0.800  | 0.700  | 6.700  | 7.400  | 6.900  | 4.900  | 4.400  | 6.200  | 6.225  |
| Ho              | 0.200 | 0.100  | 0.150  | 0.100  | 0.125  | 1.300  | 1.500  | 1.300  | 0.900  | 0.900  | 1.200  | 1.225  |
| Er              | 0.500 | 0.300  | 0.400  | 0.500  | 0.450  | 3.700  | 4.200  | 3.800  | 2.700  | 2.500  | 3.600  | 3.525  |
| Tm              | 0.050 | 0.060  | 0.070  | 0.080  | 0.075  | 0.570  | 0.670  | 0.560  | 0.420  | 0.400  | 0.500  | 0.533  |
| Yb              | 0.500 | 0.400  | 0.400  | 0.500  | 0.450  | 3.600  | 4.200  | 3.500  | 2.600  | 2.600  | 3.300  | 0.340  |
| La              | 0.070 | 0.060  | 0.060  | 0.060  | 0.070  | 0.530  | 0.610  | 0.510  | 0.370  | 0.250  | 0.510  | 0.495  |
| Ce/Ce*          | 0.956 | 0.936  | 0.851  | 0.948  | 0.889  | 0.949  | 0.937  | 0.909  | 0.914  | 0.965  | 0.965  | 0.965  |
| Eu/Eu*          | 0.599 | 0.617  | 0.665  | 0.614  | 0.660  | 0.652  | 0.652  | 0.676  | 0.675  | 0.638  | 0.638  | 0.638  |
| (La/Yb)n        | 7.704 | 9.292  | 9.798  | 7.028  | 7.020  | 7.305  | 8.765  | 13.39  | 12.89  | 7.413  | 7.413  | 7.413  |
| ΣREE            | 27.39 | 25.32  | 25.54  | 26.62  | 24.07  | 27.04  | 22.79  | 23.16  | 22.07  | 186.0  | 186.0  | 186.0  |

Eu/Eu* = Eu/Eu/(Smn × Gd6)0.5; Ce/Ce* = 2Ce6/(La6 + Pr6); where n refers to normalization of REEs to chondrite (Formulas after Taylor and McLennan, 1985).
| Elements (n = 40) | D.L. Sandstones | Shales | UCC | NASC | PAAS |
|------------------|----------------|--------|-----|------|------|
| SiO₂ (%)        | Min. | Max. | Mean | Min. | Max. | Mean |
| TiO₂             | 0.010 | 0.085 | 0.186 | 1.011 | 1.422 | 1.181 |
| Al₂O₃            | 0.010 | 0.137 | 0.142 | 0.105 | 0.664 | 21.94 |
| Fe₂O₃            | 0.010 | 0.036 | 0.092 | 0.063 | 0.362 | 20.21 |
| MnO              | 0.001 | 0.012 | 0.082 | 0.042 | 0.261 | 0.144 |
| MgO              | 0.010 | 0.023 | 0.080 | 0.042 | 0.801 | 2.122 |
| CaO              | 0.010 | 0.050 | 0.160 | 0.099 | 0.390 | 0.329 |
| Na₂O             | 0.010 | 0.120 | 0.220 | 0.156 | 0.090 | 0.840 |
| K₂O              | 0.010 | 0.100 | 0.150 | 0.100 | 0.100 | 0.160 |
| P₂O₅             | 0.010 | 0.020 | 0.030 | 0.038 | 0.250 | 0.148 |
| Trace (ppm)      |      |      |      |      |      |      |
| Ga               | 2.00  | 0.261 | 0.040 | 0.15 | 14.00 | 29.00 |
| Nb               | 1.00  | 0.100 | 0.050 | 0.32 | 19.00 | 26.00 |
| Ba               | 3.00  | 0.230 | 0.640 | 0.27 | 91.00 | 387.0 |
| Ta               | 0.10  | 0.020 | 0.040 | 0.10 | 15.00 | 18.90 |
| Co               | 10.0  | 0.100 | 0.110 | 0.17 | 28.00 | 25.70 |
| Cu               | 10.0  | 0.100 | 0.110 | 0.10 | 20.00 | 15.00 |
| Sr               | 2.00  | 0.140 | 0.170 | 0.15 | 62.00 | 167.7 |
| V                | 5.00  | 0.120 | 0.150 | 0.13 | 123.0 | 25.70 |
| Y                | 2.00  | 0.060 | 0.070 | 0.10 | 32.00 | 37.00 |
| Th               | 0.10  | 0.016 | 0.040 | 0.10 | 15.00 | 12.30 |
| U                | 0.10  | 0.000 | 0.080 | 0.07 | 120.0 | 125.0 |
| Cr               | 20.0  | 0.300 | 0.290 | 1.70 | 151.7 | 150.0 |
| Rb               | 2.00  | 0.050 | 0.110 | 0.08 | 37.00 | 82.00 |
| Zr               | 4.00  | 0.490 | 0.760 | 0.65 | 544.0 | 210.0 |
| Hf               | 0.20  | 0.110 | 0.160 | 0.12 | 53.00 | 110.0 |
| REE (ppm)        |      |      |      |      |      |      |
| La               | 0.10  | 0.050 | 0.510 | 25.03 | 49.60 | 31.27 |
| Ce               | 0.10  | 0.100 | 0.980 | 48.84 | 95.20 | 62.78 |
| Pr               | 0.10  | 0.024 | 0.110 | 0.05 | 11.00 | 7.10 |
| Nd               | 0.10  | 0.040 | 0.420 | 0.22 | 43.10 | 27.00 |
| Sm               | 0.10  | 0.090 | 0.750 | 0.14 | 9.00 | 5.50 |
| Eu               | 0.05  | 0.016 | 0.180 | 0.158 | 1.01 | 0.88 |
| Gd               | 0.10  | 0.070 | 0.080 | 0.03 | 0.70 | 4.00 |
| Tb               | 0.10  | 0.010 | 0.120 | 0.05 | 0.10 | 0.64 |
| Dy               | 0.10  | 0.060 | 0.670 | 0.03 | 0.70 | 3.90 |
| Ho               | 0.10  | 0.010 | 0.130 | 0.06 | 0.10 | 0.83 |
| Er               | 0.10  | 0.030 | 0.370 | 0.01 | 0.10 | 2.30 |
| Tm               | 0.05  | 0.006 | 0.057 | 0.02 | 0.70 | 0.70 |
| Yb               | 0.10  | 0.040 | 0.060 | 0.01 | 0.20 | 2.20 |
| Lu               | 0.04  | 0.006 | 0.053 | 0.00 | 0.35 | 0.32 |

Index Ratios

| Elements | Sandstones | Shales | UCC | NASC | PAAS |
|----------|------------|--------|-----|------|------|
| Al₂O₃/TiO₂ | 0.176 | 0.220 | 0.116 | 0.200 | 0.127 |
| CIA | 69.23 | 96.67 | 83.46 | 83.33 | 95.51 |
| CIW | 75.00 | 97.70 | 85.52 | 90.71 | 97.94 |
| PIA | 72.70 | 95.00 | 84.43 | 87.10 | 97.9 |
| Zr/TiO₂ | 40.48 | 737.4 | 350.6 | 131.3 | 509.8 |
| Th/Sc | 0.160 | 0.240 | 0.192 | 0.052 | 0.706 |
| La/Th | 2.375 | 30.29 | 13.70 | 0.403 | 3.694 |
| Sr/Cu | 1.364 | 0.170 | 1.580 | 0.620 | 17.50 |
| Rb/Sr | 0.357 | 0.647 | 0.548 | 0.080 | 0.549 |
| Th/U | 2.130 | 3.330 | 2.783 | 1.300 | 4.160 |
| U/U | -0.070 | 0.230 | 0.058 | -1.43 | 3.970 |
| V/Cr | 0.050 | 0.400 | 0.148 | 0.750 | 1.670 |
| U/Th | 0.300 | 0.470 | 0.397 | 0.240 | 0.770 |

(continued on next page)
5.3. Source rocks palaeo-weathering and palaeo-climatic conditions

5.3.1. Impacts of modifying factors

For reliable palaeo-weathering and palaeo-climatic reconstructions, first cycle sediments are most desirable to minimize the effects of reworking (Roy and Roser, 2013; Fu et al., 2019). The chondrite normalised plots of REE for both shales and sandstones from the Amansiodo-1 well are similar (Figure 2). Though similar, the chondrite normalised plots (Figure 2) showed a clear distinction between the shales and the sandstones, due to the grain size difference and diluting effect of quartz (Taylor and McLennan, 1995). This trend is suggestive of similar source area(s) (Fu et al., 2019). However, considering the ratio Th/Sc if > 1 is as an indication of recycled or reworked sediments (McLennan et al., 1993); the sandstones ratio (Th/Sc) is > 1 while the shales ratio (Th/Sc) is < 1 (Table 4, Figure 6b). As such the sandstones having Th/Sc > 1 is an indication of recycled or reworked sediments. Suttner et al. (1981) reported that even though most ancient quartz arenites are multicyclic in origin, first cycle clastic inputs are produced in tropical climates in low relief areas. Also, there is a lack of correlation between K2O and CIA (r = -0.085, n = 10) suggesting a relatively minimal diagenetic K-metasomatism effect.

Table 4 (continued)

| Index Ratios | Sandstones | Shales | UCC | NASC | PAAS |
|--------------|------------|--------|-----|------|------|
| (La/Yb)n     | Min: 7.028 | Max: 9.798 | Mean: 8.46 | Min: 7.020 | Max: 13.39 | Mean: 9.46 |
| (La/Nb)      | Min: 1.50  | Max: 1.99  | Mean: 1.71 | Min: 1.48  | Max: 1.80  | Mean: 1.66 |
| (La/Sc)      | Min: 0.72  | Max: 1.04  | Mean: 0.89 | Min: 0.65  | Max: 1.01  | Mean: 0.88 |
| (La/Sm)      | Min: 0.37  | Max: 0.53  | Mean: 0.45 | Min: 0.30  | Max: 0.50  | Mean: 0.45 |
| (La/Gd)      | Min: 0.00  | Max: 0.00  | Mean: 0.00 | Min: 0.00  | Max: 0.00  | Mean: 0.00 |

Uau = Authigenic U, calculated as Uau = (total U) – Th/3 (after Wignall and Myers (1988), EF = enrichment factor.

5.3.2. Source rocks palaeo-weathering conditions

Chemical decomposition of rocks due to weathering results in the enrichment of Al2O3 and depletion of the alkalis (Na2O, K2O, CaO, and MgO). This situation has led to the development of various indices (Chemical index of alteration, CIA after Nesbit and Young, 1982; Chemical index of weathering, CIW after Harnois, 1988; and plagioclase index of alteration, and PIA after Fedo et al., 1995) of source rocks palaeo-weathering conditions. The palaeo-weathering conditions were ascertained based on the molar percentage of major element oxides and the formulas (Table 1) proposed by Nesbit and Young (1982), Harnois (1988), and Fedo et al. (1995) for computing CIA, CIW, and PIA indices.
respectively. The CIA average values of 89.84 (range 83.33–95.51) and 83.45 (range 69.23–96.67) were obtained for shales and sandstones of the study samples respectively (Table 4). The CIW values ranged from 90.71 to 97.94 for shales and 75 to 95.21 for sandstones (Table 4). The PIA values ranged from 87.1 to 97.9 for shales and 72.7 to 95.0 for sandstones (Table 4). The average values of CIA (89.84 for shales, and 83.45 for sands), CIW (94.41 for shales, and 85.52 for sands), and PIA (93.45 for shales, and 84.43 for sands) all indicated intense chemical

![Image](4a)

**Figure 4.** Provenance diagrams for shales and sandstones from the Amansiodo-1 well: (a) Al$_2$O$_3$–TiO$_2$ plot (after Krzeszowska, 2019), (b) Zr–TiO$_2$ plot (after Hayashi et al., 1997), (c) Sc–Th plot (after Krzeszowska, 2019), (d) Th–La plot (after Krzeszowska, 2019).

| Table 5. Adjusted major elements and log$_{10}$–transformed ratio variables for the core samples from Amansiodo-1 well. |
|---|
| Variable (major element or log$_{10}$-ratio) | High-silica [SiO$_2$]$_{adj}$ > 63% | Low-Silica [SiO$_2$]$_{adj}$ < 35% |
| (SiO$_2$)$_{adj}$ | Am-1 Am-2 Am-3 Am-4 Am-5 Am-6 Am-7 Am-8 Am-9 Am-10 |
| TiO$_2$ | 0.099 0.086 1.591 1.698 0.000 0.000 0.000 0.000 0.000 0.000 |
| Al$_2$O$_3$ | 1.382 1.886 14.34 2.99 7.382 10.10 24.99 19.20 23.55 11.31 |
| (P$_2$O$_5$)$_{adj}$ | 3.288 6.243 12.04 15.24 40.24 49.05 82.34 18.63 78.01 26.51 |
| MnO | 0.022 0.050 0.083 0.012 0.133 0.203 0.054 0.246 0.057 0.304 |
| MgO | 0.040 0.202 0.626 0.023 0.890 0.951 1.617 1.037 1.667 1.607 |
| CaO | 0.050 0.131 0.303 0.066 0.322 0.289 0.410 0.459 0.417 0.361 |
| Na$_2$O | 0.121 0.222 0.141 0.147 0.222 0.289 0.410 0.459 0.417 0.361 |
| K$_2$O | 0.101 0.202 0.575 0.151 0.467 0.244 1.879 0.753 2.105 0.338 |
| (TiO$_2$/SiO$_2$)$_{adj}$ | -6.86 -6.97 -3.79 -3.85 -3.72 -3.34 -3.91 -3.54 -3.59 -3.59 |
| (Al$_2$O$_3$/SiO$_2$)$_{adj}$ | -4.23 -3.88 -1.59 -3.28 -1.89 -1.32 -0.88 -1.10 -0.97 -1.63 |
| (Fe$_2$O$_3$)/SiO$_2$)$_{adj}$ | -3.36 -2.68 -1.76 -1.65 -0.20 0.265 -1.99 -1.13 -2.08 -0.78 |
| (MnO)/SiO$_2$)$_{adj}$ | -8.36 -7.50 -6.74 -8.79 -5.91 -5.22 -7.03 -5.46 -6.99 -5.25 |
| (MgO)/SiO$_2$)$_{adj}$ | -7.76 -6.11 -4.72 -8.14 -4.01 -3.68 -3.62 -4.02 -3.61 -3.58 |
| (CaO)/SiO$_2$)$_{adj}$ | -7.54 -6.54 -5.44 -7.10 -5.02 -4.87 -4.99 -4.83 -5.01 -5.07 |
| (Na$_2$O)/SiO$_2$)$_{adj}$ | -6.66 -6.02 -6.21 -6.30 -5.30 -5.60 -4.15 -6.01 -4.19 -6.31 |
| (K$_2$O)/SiO$_2$)$_{adj}$ | -6.84 -6.11 -4.80 -6.26 -4.65 -5.04 -4.37 -4.34 -3.38 -5.14 |
| (P$_2$O$_5$)/SiO$_2$)$_{adj}$ | -8.46 -8.01 -5.90 -8.06 -5.83 -6.75 -5.80 -5.28 -5.98 -5.67 |
| DF1 | -5.87 -3.43 -1.13 -10.7 1.641 0.333 0.339 1.476 0.620 1.315 |
| DF2 | 0.470 1.891 -0.84 -2.95 2.170 0.015 0.498 -0.99 0.311 -1.34 |
| Prob (arc) | 0.005 0.614 0.063 1.5 $^{\pm}$m 0.0004 0.2212 0.1386 0.0061 0.0889 0.0080 |
| Prob (rift) | 0.995 0.386 0.910 0.999 0.9912 0.4582 0.7213 0.0295 0.6391 0.0138 |
| Prob (Col) | 6.0 $^{\pm}$m 3.5 $^{\pm}$m 0.027 3.0 $^{\pm}$14 0.0084 0.3206 0.1401 0.9644 0.2720 0.9782 |

DF1 and DF2: Discriminant Functions 1 and 2 for samples analysed (equations for DF 1 & DF 2 are stated in Verma and Armstrong-Altrin 2013); Prob (Arc), Prob (Rift), and Prob (Col): probability values for Continental Arc, Rift (passive), and Collision tectonic settings respectively for samples analysed.
information on palaeo-climatic conditions can be obtained from trace elements such as Cr, Co, Th, U, V, Mo, Ni, and Mn, which are redox-sensitive and useful in the reconstruction of palaeo-redox conditions (Armstrong-Altrin, 2013).

5.3.3. Palaeo-climate conditions

Information on palaeo-climatic conditions can be obtained from major elements. For example, a bivariate plot of Al₂O₃ vs SiO₂ (Figure 7b) proposed by Suttner and Dutta (1986), revealed that the sediments from the study area were deposited under humid and arid climatic conditions. Although the CIA has been mostly applied for the determination of palaeo-weathering conditions of rocks, it can also be applied in palaeo-climatic reconstruction. The CIA spectra of 50–60 indicate low chemical weathering, 60–80 suggests moderate chemical weathering (in cool and/or arid climate), and 80–100 implies intensive chemical weathering (in hot and/or humid climate) (Nesbitt and Young, 1982; Fedo et al., 1995; McLennan et al., 1993). The average CIA and PIA values for all the samples examined are >80 suggesting intense chemical weathering where hot and humid climates prevailed.

Palaeo-climatic discrimination can also be obtained from trace elements that are sensitive to ancient climatic changes (e.g., Cao et al., 2012; Tao et al., 2017) such as Ba, Co, Cu, Cr, Pb, Sr, Ni, and V. Trace elemental ratios such as Sr/Cu and Rb/Sr are often used to infer palaeo-climatic conditions. Usually, Sr/Cu ratio values often increase in dry climatic conditions, and the spectra of values from 1.3 to 5.0 is an indication of warm/humid climate, while values > 5.0 reflect warm, arid climatic conditions (Lerman, 1978; Lerman and Gat, 1989; Tao et al., 2017). Conversely, Rb/Sr ratios wane in dry climatic conditions, as such low and high ratios reflect warm and cold climatic conditions respectively (Chen et al., 1999; Xu et al., 2010). The Sr/Cu ratios for the sandstone samples fall within the range of 1.36–1.70 indicating a warm humid climate, while the shales have ratios >5.0 (Table 4) indicating a hot arid climate. The low Rb/Sr ratios (0.08–0.65) for all the samples examined indicate warm climatic conditions (Table 4).
the depositional environment (Yarincik et al., 2000). Trace composition (e.g., U and Mo) and elements ratio (e.g., Th/U, V/Cr, V/Sc, and U/Th) have been used for determining palaeo-redox conditions (e.g., Wignall and Myers, 1988; Jones and Manning, 1994; Crusius et al., 1996; Wignall and Twitchett, 1996; Nath et al., 1997). Despite the usefulness of the redox-sensitive trace elements, Fu et al. (2016, 2019), emphasized the invaluable need for cautious use and in a relative sense. This is because of the problems associated with comparing their ratios directly to the threshold suggested in previous studies. Another important consideration in the use of trace elements in palaeo-redox determination is to ascertain whether they are detrital or authigenic in origin. Correlation values (Table 7), derived from cross plots of Al versus the trace elements determine if they are detrital or authigenic in origin. If a good correlation is observed and if the trace elements do not deviate too greatly from average shale (UCC) concentration, it can be inferred that the trace element is mainly detrital in origin and cannot be used for palaeo-environmental analysis. But in this study, an admixture of detrital and authigenic trace elements (Table 7) origins was observed, hence their use in palaeo-redox determination though in a relative sense, because of the diluting effects of detrital input. Also, enrichment factors (EF) were computed for the redox-sensitive elements (Mn, V, Cr, Co, Ni, Zn, Mo, Ba, U, and Cu; Table 4) based on accepted crustal average values to elucidate redox-induced enrichments or depletions. In this work, trace element ratios for palaeo-redox determination are presented in Table 4.

Wignall and Twitchett (1996) suggested that Mo composition of 5–40 ppm represents a euxinic environment. The Mo composition of all the studied samples is <5 ppm (some are below the detection limit of 2.00 ppm) with no indication of enrichment and thus oxic redox setting prevailed during their emplacement. The ratio of Th/U is an index of palaeo-redox with values 0–2 and 2–8 representing an anoxic and strongly oxidizing environment (Wignall and Twitchett, 1996). In this study, the average Th/U ratios for sandstones (2.78) and shales are >2 (i.e., between 2 - 8) representing a strongly oxidizing environment (Table 4). The V/Cr ratios of the examined samples are below 2 and therefore indicate the oxic depositional setting (Table 4). The ratio of U/Th was applied by Nath et al. (1997) to distinguish between oxic (<1.25) and suboxic to anoxic (>1.25) settings. The U/Th ratios of the samples from the Amansiodo-1 well are <1.25, they are of oxic depositional setting (Table 4). The application of trace element composition (U and Mo) and ratios (Th/U, V/Cr, U/Th) as proxies for palaeo-redox conditions of the sediments obtained from the Amansiodo-1 well all revealed oxic depositional setting.

The REE Ce is redox-sensitive and in oxic conditions, Ce$^{3+}$ is readily oxidized to Ce$^{4+}$ which is less soluble than Ce$^{3+}$ (Wilde et al., 1996). The resultant effect is a positive Ce anomaly (>0.1) in an oxidizing environment and a negative Ce anomaly (<0.1) in reducing conditions (Yang et al., 2011). Shales usually have Ce/Ce* values of ≤1 (Cox et al., 1995). The examined sandstone and shale samples have Ce/Ce* average values of 0.92 and 0.93 respectively (Table 4), greater than 0.1, and an oxidizing setting prevailed.
6. Conclusions

The geochemistry of the Upper Cretaceous rocks in the Anambra basin (SE Nigeria) was examined in this study. Generally, the stratigraphic section studied comprised mainly of shales and/or sandstone lithologies embedded in the Awgu (with the lateral equivalent, Agbani sandstone), Enugu/Nkporo (with associated lateral equivalent, Owelli Sandstone), Mamu, and Ajali Formations. Chemical elements contents, discrimination diagrams, bivariate plots, and ratio values were used to constrain the provenance, the plate tectonic setting of the sediment accumulation, the source rocks palaeo-weathering conditions, the palaeo-climate conditions, and palaeo-redox conditions. The following conclusions were reached:

- On the bases of geochemical discriminant diagrams, $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio, and bivariate plot of $\text{TiO}_2$ versus $\text{Zr}$, the sediments of the Anambra basin are mafic to intermediate and inputs from felsic sources. Therefore, a mixed source area is inferred, which is related to the surrounding basement rocks and reworked sediments from the Abakaliki high.

- The application of multidimensional discriminant diagrams proved that the plate tectonic settings of the Upper Cretaceous sediments of the Anambra basin are dominantly continental rift or passive margin, followed by collision/convergent setting with very minimal arc settings.

- The indices of source rock palaeo-weathering conditions, CIA, CIW, PIA, and the bivariate plot of CIA versus PIA showed the study samples had undergone mostly intense chemical weathering (>80), although a few had moderate weathering conditions.

- The bivariate plot ($\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O}$ versus $\text{SiO}_2$), CIA and PIA indices, and trace element ratios ($\text{Sr}/\text{Ca}, \text{Rb}/\text{Sr}$; all suggested warm to hot and humid and/or arid palaeo-climate conditions during the accumulation of the examined samples.

- The trace element composition of Uau and Mo; ratios (Th/U, V/Cr, and U/Tb), and Ce anomaly; all attest to an oxic palaeo-redox setting that may have prevailed during sediment accumulation.

Declarations

Author contribution statement

Omebhere Innocent Ejeh: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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