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Geochemical Appraisal of the Mamu Shales Exposed around Igodor in the Benin Flank of the Anambra Basin, Nigeria

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ABSTRACT: The Auchi area of Edo state which lies within the Benin flank of the Anambra Basin host shaly sediment exposures that have been classified by previous researches as units of the Mamu Formation. This study evaluated samples of this sediment from Igodor near Auchi for its geochemical and mineralogical properties, and interpreted its, depositional environment and geotectonic setting. In order to achieve this, field studies were carried out and representative samples obtained for Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analyses of major oxides, trace and rare earth elements. X-Ray Diffraction analysis was also carried out to determine the mineralogical composition. Some of the minerals determined were Aragonite and galena. Binary plots, triplots and elemental ratio plots including SiO_2/, Al_2O_3, Th/Sc, Th/Co and La/Sc , Th-Sc-Zr, and the abundance of Cr, Ni were employed to determine the provenance. The concentration of detrital indicators such as SiO_2, Al_2O_3 and TiO_2, with averages of 51.95, 25.34 and 1.39 respectively, indicate high detrital influx into the Benin Flank of the Anambra basin. SiO_2/Al_2O_3 ratios of 1.80-2.20, indicate that the shales were made up of pure kaolinite. The Ni and Cr abundance indicated a mafic and felsic provenance for the sediments, however, Th/Sc, Th/Co and La/Sc ratios show that the provenance was predominantly felsic, while the Th-Sc-Zr triplot shows that the depositional setting was passive.

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The studied area around Igodor is located in Etsako East local Government area of Edo state, Benin Flank of the Southern Anambra Basin, Nigeria. It falls within the coordinates N 07^0 27’ and E$006^0$28’. Here the Benin Flank of the Anambra Basin is exposed in several road cuts revealing both the Mamu and the Ajali Formation sediments. This study was aimed at appraising the geochemical characteristics of these sediments with a view to determining their depositional environment and provenance using sedimentological, mineralogical and geostatistical techniques. The objective is to use these proven and modern techniques to evaluate these sediments and produce a reference resource material.

Geological setting and stratigraphy: The Anambra Basin is part of the Lower Benue trough. The Post-Santonian collapse of the Anambra platform led to the emergence of several parts of the Lower and Middle Benue Basins during the Campanian – Maastrichtian and a shift in the depositional axis of sediments for the third transgressive cycle to the Anambra Basin. These sediments consist of the marine Nkporo / Enugu Formations (lateral equivalents) overlain by the deltaic successions of the Mamu Formation and the marginal marine Ajali Formation in the Anambra Basin. The Upper Cretaceous sediments are overlain by the transgressive Paleocene – Eocene shales, sandstones and siltstones of the proto -Niger Delta in the southern fringes of the Anambra Basin (Akande *et al, 2011).*

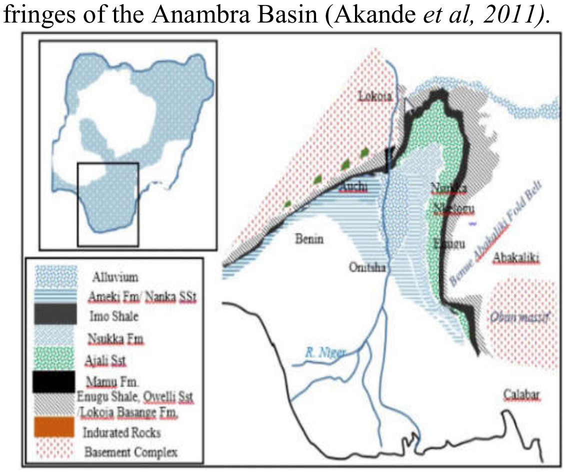

Fig 1. Anambra Basin showing the extent of the Nkporo Group and the Mamu Formation, (Modified after Murat, 1972).

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MATERIALS AND METHOD

This research involved Field Mapping, logging and sample collection of exposed road cut sediments in the study area, laboratory studies involving sedimentological, geochemical (ICP-MS) and X-Ray diffraction analyses of collected samples were done. In order to establish the qualitative and quantitative constituents of the major, minor, trace and rare earth constituents of the sediments X-ray diffraction and Inductively Coupled Plasma Mass spectrometry (ICP-MS) analyses techniques were employed.

Sample Collection: A total of Eight (8) fresh samples were collected from the exposed road cut section for this study. Sampling was done on fresh, unweathered surfaces in order to reveal the original, unaltered sedimentological and mineralogical (chemical) properties of the rocks. The samples were kept in sample bags (polythene) and later taken to laboratory for analyses.

RESULTS AND DISCUSION

Resulting from the field study, four (4) lithofacies of sandstone, siltstone, claystone and shales were determined. The results as obtained from Activation Laboratory, Ontario, Canada are presented in Tables 1, 2, 3 and 4. *Mamu Formation:*

Table 1. Percent (%) of major Oxides present in in the Benin Flank Shales using FUS-ICP

Analyte	SiO_2	Al_2O_3	Fe_2O_3(T)	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	Total
Detection Limit	0.01	0.01	0.01	0.001	0.01	0.01	0.01	0.01	0.001	0.01		0.01
Analysis Method	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP
BF1	53.7	24.42	3.77	0.012	0.39	0.05	0.06	1.18	1.536	0.14	14.54	99.81
BF 5	53.5	24.51	3.75	0.011	0.41	0.05	0.06	1.17	1.54	0.14	14.51	99.65
BF7	48.66	27.08	3.73	0.009	0.42	0.07	0.07	1.3	1.09	0.2	16.25	98.88

Table 2. Chemical composition of Benin Flank shale compared to shales from other sedimentary basins in Nigeria and Egypt

Analyte Symbol	BF1	BF 5	BF7	A	B	C	D	E	Earth's crust mean*	***Enrichment Factor
SiO2	53.7	53.5	48.66	61.26	69.94	44.91	63.30	45.80	58.53	0.92
Al2O3	24.42	24.51	27.08	16.88	10.00	15.71	18.47	16.80	13.07	1.87
Fe2O3	3.77	3.75	3.73	3.75	4.04	6.24	1.26	4.80	3.37	1.12
MnO	0.012	0.011	0.009	0.02	0.04	0.06	0.01	n.a	0.09	0.17
MgO	0.39	0.41	0.42	0.16	0.87	2.58	0.82	1.40	2.51	0.16
CaO	0.05	0.05	0.07	0.05	3.38	15.42	0.09	5.12	5.44	0.01
Na2O	0.06	0.06	0.07	0.06	0.40	0.42	0.42	0.75	2.81	0.02
K2O	1.18	1.17	1.3	1.74	1.15	2.36	2.36	0.84	2.81	0.42
TiO2	1.536	1.54	1.09	1.74	0.52	0.62	1.02	1.04	0.56	3.01
P2O5	0.14	0.14	0.2	0.08	0.17	0.46	0.46	0.62	0.15	0.91
LOI	0.14	14.51	16.25	14.2	9.21	11.1	11.6			
TOTAL	99.81	99.65	99.88	99.94	99.72	99.88	99.81			

*A = Bida Shale (Olugbenga & Olubunmi, 2012); B = Asu River group (Amajor, 1987); C = Ezeaku shale (Amajor, 1987); D = Ifon Shale (Ajayi et al, 1989); E = Abu Tator Shales, Egypt Mostafa (2005). *Average composition of sedimentary rocks. (Clark and Washington, 1924 and Taylor, 1964, in Asuen, G.O, 1984)*

Table 3. Trace Elements ICP-MS Results

Analyte Symbol	BF1	BF 5	BF7	Averages	*Earth's Crust Abundances	*Enrichment factor
V	156	155	140	122.73	190	0.65
Ba	177	175	160	336.00	340	0.99
Sr	74	74	73	94.20	360	0.26
Y	52	51	25	45.27	29	1.56
Zr	511	510	283	558.87	130	4.30
Cr	120	120	150	142.33	140	1.02
Co	12	11	10	6.87	30	0.23
Ni	< 20	< 20	30	22.00	89	0.25
Cu	20	20	10	83.33	68	1.23
Zn	50	50	50	46.67	78	0.60
Rb	68	69	79	53.47	60	0.89
Nb	29	28	20	26.60	17	1.56
Mo	3	3	3	2.60	1.1	2.36
Pb	25	23	19	17.67	9.9	1.78
Th	24.7	24.1	20.7	17.68	6	2.95
U	7.5	7.3	5.8	6.39	1.8	3.55

Table 4. Igodor: Minerals from Benin Flank Samples

BF-07			
S/N	**PEAKS**	**d=λ/2Sinø**	**Mineral**
1	P1	4.28	Arthurite
2	P2	3.50	Natrite
3	P3	2.96	Natrite
4	P4	2.75	Smithsonite
5	P5	2.66	Berborite
6	P6	2.48	Northupite
7	P7	2.33	Aragonite
8	P8	2.14	Palladoarsenide
9	P9	1.79	Galena
10	P10	1.75	Gehlenite
11	P11	1.67	Tobermorite
BF-01			
S/N	**PEAKS**	**d=λ/2Sinø**	**Mineral**
1	P1	4.28	Arthurite
2	P2	3.50	Graftonite
3	P3	2.96	Natrite
4	P4	2.75	Smithsonite
5	P5	2.66	Berborite
6	P6	2.48	Northupite
7	P7	2.41	Hemimorphite
8	P8	2.33	Aragonite
9	P9	2.14	Palladoarsenide
10	P10	1.98	Fluorite
11	P11	1.79	Galena
12	P12	1.75	Gehlenite
13	P13	1.67	Tobermorite
14	P14	1.54	Pyrope

The Mamu Formation (the Lower Coal Measure of the Geological Survey of Nigeria) overlies the Enugu Shales conformably and occurs as a narrow strip trending north-south from the Calabar Flank, swinging west round the Ankpa plateau and terminating at Idah near the Niger River (Nwajide and Reijers,1996). Its best exposures on the Benin Flank of the Anambra basin, was found along the road cuts at Igodor at Etsako East Local Government Area of Edo state. The rock units are dominantly shales, siltstones, heteroliths, fine sandstones and claystones (Plate 1).The shales are black and often splintery in intervals up to 2m in thickness. They are interlaminated in most sections with fine sandstones and siltstones. The sandstones are dominantly fine to medium grained. In some horizons, siltstones and fine sandstones are laterally transitional. It is very dark in colour, and alternate with siltstones and fine sands with rootlets, indicative of a coal swampy environment of deposition. These observations also agree with that of Akaegbobi, 1999; Nwajide and Reijers, 1996a. Elemental concentrations in sediments result from the competing influences of provenance, weathering, sorting, and sediment diagenesis (Quinby-Hunt et al., 1991). The major oxides results presented in table 1 form the basis for the mineralogical and geostatistical interpretation of the major oxides. The Trace and rare earth elements were also determined by ICP-MS analysis (See Table 3). These were used to determine the provenance and the tectonic setting of these sediments. The studied shales show enrichment of elements that are chemically resilient and are associated with terrigenous influx, such as SiO_2, Al_2O_3 and TiO_2 (See Table 2). These elements can survive throughout intensive chemical weathering and diagenesis (Cullers, 2000). Their concentration in sediments is used as a measure of detrital input. The major constituents of the studied shale samples do not vary greatly from one location to another. The SiO_2, Al_2O_3 and TiO_2 tend to form together the main constituents of the studied shales and are normally related to clays. The SiO_2, Al_2O_3 and TiO_2 show both strong positive and negative correlation in most of the samples (Table 5). This indicates that the major constituents SiO_2, Al_2O_3 and TiO_2 of the studied shale samples are dominantly terrigenous in origin but might have originated from different sources. The average of Al_2O_3 content in the Mamu shales of the Benin Flank is 25.53 with enrichment factor of 0.97 (Table.2). High concentration of alumina is a good indicator of detrital influx. This result shows high detrital influx as indicated by the high alumina content with enrichment factor of 1.87, supported by the high TiO_2 enrichment factor of 1.12 (Table 2). In order to determine the clay type SiO_2/Al_2O_3 ratio was used. According to Felix (1977), SiO_2/Al_2O_3 ratio is used for determining the presence of pure montmorrillonite (2.80 to 3.31) and pure kaolinite (about 1.18) in sediments. It was discovered that the clay type in these shales is of pure Kaolinite therefore roads constructed in this area will last longer than if the clay type was mixed with montmorrilonite. According to Ahmed, 1997, enrichment of Fe_2O_3 in shales could be attributed to their formation under reducing condition with high input of non-reactive iron to the Basin. Therefore the depositional environment of the Benin Flank of the Anambra Basin with average Fe_2O_3 content of 3.75% and enrichment factor of 1.11 could be said to be a reducing one.

Table 6. SiO_3/Al_2O_3 Ratio

SiO_3/Al_2O_3 Ratio		
LOCATION	RATIO	CLAY TYPE
Mamu Shales from Beni Flank of the Anambra Basin	1.80-2.20	Kaolinite

Cr and Ni abundance in siliciclastic sediments is usually considered a useful provenance tool. Wrafter and Graham (1989), stated that high Cr and Ni content are mainly found in ultramafic rock-derived sediments. Therefore it could be said that the provenance of the sediments from the Benin Flank of the Anambra Basin were from mafic and felsic source rocks (Table 7). However, elemental ratio plots show that the sediments where predominantly from a felsic source (Table 8). Th-Sc-Zr plots indicate that the sediments where from passive margin.

Table 5: Correlation Matrix for studied Mamu Formation shales.

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	*V*	*Cr*	*Co*	*Ni*	*Cu*	*Zn*	*Rb*	*Sr*	*Y*	*Zr*	*Nb*	*Mo*	*Ba*	*Pb*	*Th*	*U*
SiO_2	1.00																									
Al_2O_3	-1.00	1.00																								
Fe_2O_3	-0.73	0.78	1.00																							
MnO	0.76	-0.73	-0.35	1.00																						
MgO	-0.97	0.98	0.85	-0.68	1.00																					
CaO	-0.82	0.84	0.74	-0.68	0.79	1.00																				
Na_2O	0.93	-0.90	-0.59	0.76	-0.91	-0.57	1.00																			
K_2O	0.80	-0.77	-0.36	0.69	-0.77	-0.34	0.96	1.00																		
TiO_2	0.60	-0.65	-0.85	0.40	-0.66	-0.89	0.32	0.04	1.00																	
P_2O_5	-0.95	0.97	0.86	-0.70	0.95	0.94	-0.78	-0.59	-0.82	1.00																
V	-0.93	0.92	0.66	-0.65	0.94	0.57	-0.98	-0.93	-0.36	0.80	1.00															
Cr	0.88	-0.84	-0.42	0.69	-0.82	-0.47	0.97	0.98	0.15	-0.68	-0.96	1.00														
Co	-0.83	0.82	0.63	-0.49	0.86	0.41	-0.93	-0.90	-0.24	0.68	0.96	-0.91	1.00													
Ni	0.00	0.03	0.13	-0.14	-0.06	0.56	0.34	0.53	-0.62	0.25	-0.36	0.42	-0.51	1.00												
Cu	0.92	-0.89	-0.46	0.74	-0.86	-0.57	0.97	0.96	0.24	-0.75	-0.95	0.99	-0.88	0.29	1.00											
Zn	-0.90	0.93	0.95	-0.55	0.97	0.78	-0.80	-0.62	-0.76	0.94	0.85	-0.68	0.80	0.00	-0.71	1.00										
Rb	-0.94	0.96	0.90	-0.66	0.97	0.90	-0.79	-0.59	-0.82	0.99	0.82	-0.67	0.72	0.18	-0.74	0.97	1.00									
Sr	-0.26	0.19	-0.40	-0.30	0.11	-0.16	-0.46	-0.67	0.58	-0.04	0.41	-0.65	0.39	-0.54	-0.60	-0.12	-0.09	1.00								
Y	0.71	-0.74	-0.76	0.53	-0.70	-0.98	0.41	0.16	0.96	-0.88	-0.43	0.29	-0.28	-0.66	0.40	-0.74	-0.85	0.35	1.00							
Zr	0.97	-0.95	-0.56	0.81	-0.89	-0.79	0.91	0.83	0.48	-0.88	-0.89	0.90	-0.77	-0.02	0.95	-0.77	-0.85	-0.43	0.65	1.00						
Nb	-0.46	0.41	-0.04	-0.41	0.41	-0.09	-0.73	-0.89	0.41	0.17	0.70	-0.83	0.73	-0.77	-0.76	0.23	0.17	0.86	0.29	-0.54	1.00					
Mo	0.62	-0.68	-0.99	0.28	-0.76	-0.70	0.46	0.22	0.88	-0.79	-0.54	0.28	-0.51	-0.20	0.32	-0.89	-0.84	0.54	0.76	0.43	0.18	1.00				
Ba	0.97	-0.98	-0.86	0.66	-1.00	-0.79	0.90	0.76	0.66	-0.95	-0.94	0.82	-0.86	0.06	0.85	-0.97	-0.97	-0.10	0.70	0.89	-0.40	0.77	1.00			
Pb	-0.41	0.47	0.85	0.04	0.60	0.29	-0.40	-0.24	-0.54	0.50	0.51	-0.25	0.60	-0.23	-0.23	0.75	0.60	-0.44	-0.35	-0.20	0.01	-0.86	-0.62	1.00		
Th	-0.67	0.65	0.35	-0.40	0.68	0.14	-0.87	-0.94	0.09	0.44	0.89	-0.91	0.93	-0.73	-0.85	0.57	0.47	0.64	0.02	-0.66	0.91	-0.22	-0.68	0.40	1.00	
U	-0.57	0.56	0.41	-0.25	0.63	0.04	-0.79	-0.85	0.08	0.38	0.83	-0.80	0.92	-0.80	-0.73	0.58	0.43	0.48	0.09	-0.51	0.83	-0.30	-0.64	0.56	0.97	1.00

Table 7. Cr and Ni abundance

	Cr abundance	Ni abundance	
	Enrichment Factor (EF)		Provenance
Benin Flank of the Anambra Basin	1.02	0.25	MFIC & Felsic rocks

Table 8. Elemental Ratios for Benin Flank Mamu Shales

Sample No.	La	Sc	**La/Sc**	Th	Co	**Th/Co**	Th	Sc	**Th/SC**
BF1	86.80	19.00	**4.57**	24.70	12.00	**2.06**	24.70	19.00	**1.30**
BF 5	86.10	19.00	**4.53**	24.10	11.00	**2.19**	24.10	19.00	**1.27**
BF7	79.00	17.00	**4.65**	20.70	10.00	**2.07**	20.70	17.00	**1.22**

Table 9. Th/Sc, Th/Co and La/Sc ratios for Benin Flank sediments

	Benin Flank Shales	**[1]Range of sediments**	
		Felsic rocks	**Mafic rocks**
Th/Sc	1.22-1.30 (Felsic)	0.84-20.5	0.05-0.22
Th/Co	2.06-2.19 (Felsic)	0.69-19.4	0.04-1
La/Sc	4.53-4.65 (Felsic)	2.5-16.3	0.43-0.86

[1] *Cullers (1994, 2000), Cullers and Podkovyrov (2000), Cullers et al., (1988)*

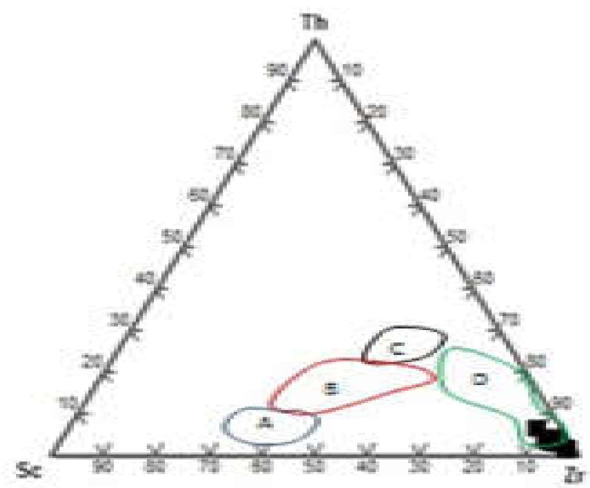

Fig 2: Th-Sc-Zr/10 discrimination diagram (taken from Bhatia and Crook, 1986) for studied Mamu shales from Benin Flank. The fields are: A - Oceanic island–arc, B - Continental island–arc, C - Active continental margin, D - Passive margin

Clay minerals can be used as stratigraphic markers and environmental indicators. The type of clay minerals found in shale is a function of provenance and diagenetic history. Depositional environment has a considerable influence on the clay mineralogy through early mineral transformations in the basin of deposition, (Russell, 1970). The XRD results reveal that the minerals are predominantly silicate minerals. The presence of a minerals such as Aragonite which is unstable and can be reworked by gravity flows as well as galena (a lead glance) which probably arrived at the Benin Flank from the Abakaliki Anticlinorium support the detrital influx of these sediments into this region.

Conclusion: The present study enabled the understanding of the inherent geochemical properties of the Mamu shales exposed at the Benin Flank of the Anambra Basin. From the study, concentration of SiO_2, Al_2O_3 and TiO_2 indicate high detrital influx into the Benin Flank of the Anambra basin. SiO_2/Al_2O_3 ratios indicate that the shales were made up of pure kaolinite. The Ni and Cr abundance indicated a mafic and felsic provenance, however, Th/Sc, Th/Co and La/Sc ratios show that the provenance was predominantly felsic, while the Th-Sc-Zr ratio shows that the depositional setting was passive.

REFERENCES

Akande, SO; Ojo, OJ; Adekeye, OA (2011). Stratigraphic Evolution and Petroleum Potential of Middle Cretaceous Sediments in the Lower and Middle Benue Trough, Nigeria: Insights from New Source Rock Facies Evaluation. *Petroleum Technology Development Journal*. 1. 2-30.

Ahmed, HA (1997). Mineralogical and geochemical studies of the black shales intercalated with phosphorite deposits at Abu Tartur area Western Desert, Egypt: M.Sc. thesis, Ain Shams Uni. Cairo, Egypt, p.284.

Akaegbobi, IM; Boboye, AO (1999). Textural Structural Features and Micrfossil Assemblage Relationship as a delineating Criteria for the Stratigraphic Boundary between Mamu Formation and Nkporo Shale within the Anambra Basin, Nigeria. *NAPE Bulletin,* 14 (2), 193-207.

Asuen, GO (1984). Major and Minor elements of some British Carboniferous coals and their relationships to coal type. PhD Thesis, Organic Geochemical Unit, Department of Geology, University of Newcastle Upon Tyne. p. 246-266.

Bhatia, MR; Crook, KAW (1986). Trace element characteristics of greywackes and Tectonic setting discrimination of sedimentary basins. *Contrib. Mineral. Petrol.* 92, 181–193.

Clark; Washington (1924) and Taylor (1964): in Asuen, G.O (1984). Major and Minor elements of some British Carboniferous coals and their relationships to coal type, PHD thesis, p. 213-214.

Murat, RC (1972): Stratigraphy and Palaeogeography of the Cretaceous and Lower Tertiary of southern Nigeria. In: T.F.J. Dessauvagie and Whiteman (eds.), African Geology, Ibadan University Press, Nigeria, p.251-266.

Nwajide, CS; Reijers, TJA. (1996). The Geology of the Southern Anambra Basin, in: T.J.A. Reijers (ED.) selected chapter in Geology sedimentary geology and sequence stratigraphy of the Anambra Basin, *SPDC publication*, p. 133-148.

Russell, CA (1970). Geochemistry and halmyrolysis of clay minerals, Rio Ameca, Mexico. *Geochim. Cosmochim. Acta,* V. 34, 893-907.

Taylor, SR; McLennan S (1985).The Continental Crust: Its Composition and Evolution: Blackwell, Oxford, p. 312 .

Quinby-Hunt, MS; Wilde, P; Berry, WBN (1991). The provenance of low-calcic black shales. *Mineralium Deposita* 26, 113-121.

Wrafter, JP; Graham, JR (1989). Ophiolitic detritus in the Ordovician sediments of South Mayo Ireland: *Journal of the Geological Society, London*, 146, 213-215.