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GEOCHEMICAL AND INDUSTRIAL CHARACTERISTICS OF PHOSPHATE-BEARING ROCKS IN SEVEN LIBYAN AREAS

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Abstract: Libya has an abundance of mineral resources, (such as phosphate deposits), but its economy is largely reliant on gas and oil. In this work, the phosphate-bearing rocks in the Al Fuqaha, Sabha, Idri, Hasi Anjiwal, Tikiumit, Wadi Tanezzuft, and Anay sheets are evaluated for their geochemical and industrial characteristics. The phosphate-bearing rocks are detected in a variety of formations, including the Melaz Suqran Formation (Late Ordovician), the Akakus Formation (Late Silurian), the Awainat Wanin Formation (Middle-Late Devonian), the Marar Formation (Early Carboniferous), the Assedjefar Formation (Early Carboniferous), the Zarzaitine Formation (Late Permian-Early Triassic), and the Zimam Formation (Late Cretaceous-Late Paleocene). According to the findings, there are three different types of phosphate-bearing rocks: (1) Phosphorite rocks; (2) Phosphatic rocks; and (3) Phosphatized rocks. Most of the phosphorite samples are mainly derived from marine origin, while the remaining samples are mainly resulted from detrital input. The phosphatic rocks are of low quality, whereas the phosphorites range in quality from medium to high. Although the Marar Formation in Tikiumit Sheet satisfies all fertilizer industry standards, the Fe_2O_3 content requires treatment. Artificial bone can be made from the Awainat Wanin Formation in Sabha Sheet, but only after the Ca/P ratio has been processed to the proper level.
Keywords: Phosphorites, Fertilizer Industry, Artificial Bone, Libya.

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1. Introduction

The following are the main settings where phosphate minerals can be found: (1) Marine deposits (francolite, dahllite, and collophane); (2) Igneous deposits (fluorapatite and hydroxyapatite); (3) Metamorphic deposits (fluorapatite and hydroxyapatite); (4) Biogenic deposits (hydroxyapatite and carbonate hydroxyapatite); and (5) Weathered deposits (fluorapatite) (Straaten, 2002). Numerous industries, including the fertilizer, chemical, medical, and food sectors, use phosphate minerals. Egypt, Tunisia, Algeria, and Morocco are the primary producers of phosphate in North Africa.

Libya's economy is primarily dependent on oil and gas, despite the country's abundance of mineral resources, including phosphate deposits. A number of Libyan areas, including the Al Fuqaha, Sabha, Idri, Hasi Anjiwal, Tikiumit, Wadi Tanezzuft, and Anay sheets (Figure 1), contain phosphate-bearing rocks (Galecic, 1984; Parizek et al., 1984; Protic, 1984; Radulovic, 1984; Roncevic, 1984; Seidl and Rohlich, 1984; Woller, 1984). The Melaz Suqran Formation (Late Ordovician) contains 109,000 tons of phosphate deposits in the Tikiumit Sheet (World Atlas, 2019). Assessing the geochemical and industrial characteristics of the phosphate-bearing rocks in the seven Libyan areas mentioned above

(Figure 1) is the goal of this work. It should be noted that we did not find any publications pertaining to this topic upon reviewing the earlier works.

2. Research Method

The major oxide data found in the Al Fuqaha, Sabha, Idri, Hasi Anjiwal, Tikiumit, Wadi Tanezzuft, and Anay sheets (Galecic, 1984; Parizek et al., 1984; Protic, 1984; Radulovic, 1984; Roncevic, 1984; Seidl & Rohlich, 1984; Woller, 1984) were used by the authors. There are 20 samples of the phosphate-bearing rocks. In order to prevent confusion, the authors have adjusted the sample numbers in this work due to their similarity in the studied sheets.

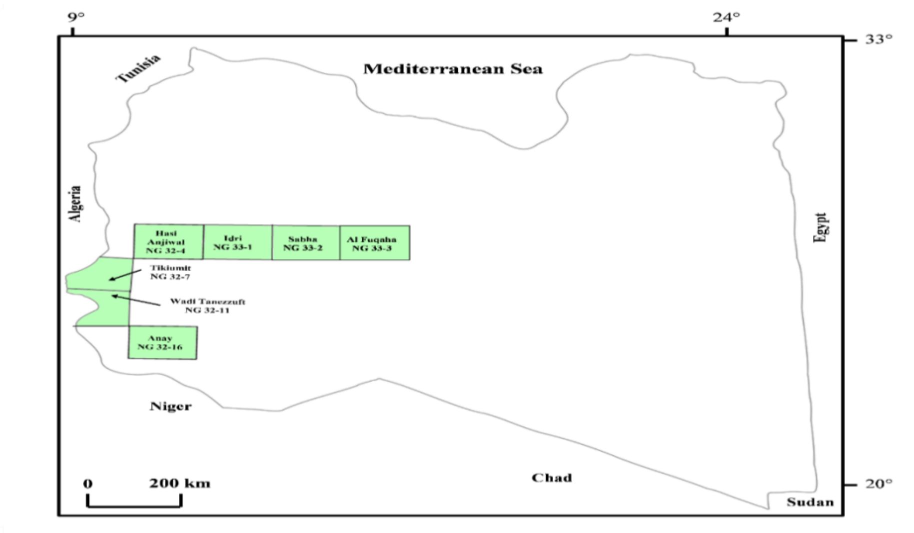

Figure 1. Location map of the studied areas

3. Results and Discussion

3.1. Geochemical Characteristics

Twelve major oxides are included in the chemical data, as indicated in Tables (1a,b&c). The phosphate-bearing rocks are found in the Melaz Suqran Formation (Late Ordovician), the Akakus Formation (Late Silurian), the Awainat Wanin Formation (Middle-Late Devonian), the Marar Formation (Early Carboniferous), the Assedjefar Formation (Early Carboniferous), the Zarzaitine Formation (Late Permian-Early Triassic), and the Zimam Formation (Late Cretaceous-Late Paleocene) (Figure 2). Fluorapatite is the type of apatite in the phosphate nodules of the Melaz Suqran Formation (Protic, 1984). Samples P3, P4, P7, P13, P14, P15, P16, P17, and P18 have K2O concentrations below 0.2%, which may be traces of marine water that was confined in the sediments during deposition. The SiO2 concentration varies significantly (5.71-64.17%). Abou El-Anwar et al. (2017) confirmed that a high SiO2 content in phosphate deposits is a sign of biogenic origin. In samples P1, P3, P4, P10, P12, P15, and P18 the CaO concentration ranges from 20.23 and 44.02%, reflecting the calcareous nature of these samples. According to Khan et al., (2012), the CaO/P2O5 ratio in pure carbonate fluorapatite is approximately 1.54, whereas the most reactive phosphate deposits have a ratio between 3.5 and 5 (Khasawneh et al., 1980). The higher CaO/P2O5 ratio in samples P1, P10, and P17 (1.98-7.05) compared with samples P3, P4, P5, P6, P7, P8, P9, P15, P16, and P18 (0.65-1.4) indicates an excess of calcite or dolomite cement to the phosphate-bearing rocks. The MgO/CaO ratio for dolomite is roughly 0.72 (Lorenz and Gwosdz, 2003). Samples P3, P4, P5, P7, P8, P9, P10, P15, P16, P17, and P18 have very low MgO/Cao ratios (0.003-0.1), indicating little to no dolomitization. On the other hand, the presence of dolomite in samples P1 and P6 is evident from the high MgO/Cao ratio (0.57-0.72). Three types of phosphate-bearing rocks were distinguished by Pettijohn (1957) according to the P2O5 content: (1) Phosphorite rocks (P2O5 exceeds 19.5%); (2) Phosphatic rocks (P2O5 varies from 9.8 to 19.5%); and (3) Phosphatized rocks (P2O5 varies from 3 to 9.8%). Samples P8 and P12 are categorized as phosphatic rocks, whereas samples P3, P4, P15, P16, and P18 are confirmed to be phosphorite rocks (Table 2). The phosphatized rocks comprise the remaining samples.

Table 1a. Chemical analysis data of major oxides (concentration in wt%) of the studied phosphate-bearing rocks (after Galecic, 1984; Parizek et al., 1984; Protic, 1984; Radulovic, 1984; Roncevic, 1984; Seidl and Rohlich, 1984; Woller, 1984)

Sheet	Area	Formation	Sample No. in the sheets	Sample No. in this work	Lithology	SiO_2	TiO_2	Al_2O_3	$Fe_2O_{3\,total}$
Al Fuqaha	SW of Qararat Al Hirah	Zimam	36	P1	Dolostone	25.26	0.15	1.72	4.65
Sabha	WSW of Khasm An Niqwi	Awainat Wanin	18	P2	Sandstone	18.37	0.51	9.41	51.33
	NW of Aqar		20	P3	Conglomerate	17.62	0.12	3.86	16.00
	WSW of Khasm An Niqwi		21	P4	Conglomerate	24.13	0.70	6.28	2.02
	N of Bir Al Ghalmayah		25	P5	Conglomerate	15.97	0.65	6.00	49.18
	WSW of Tarut		28	P6	Oolite	20.86	0.51	11.33	46.59
	NNW of Qarat Al Baddadah		33	P7	Conglomerate	18.57	0.39	5.15	48.35
	N of Ash Shab		34	P8	Conglomerate	11.42	0.39	6.03	44.48
	NNW of Qarat Al Baddadah	Marar	41	P9	Conglomerate	19.00	0.53	5.40	49.50
Idri	Wadi Ash Shati	Awainat Wanin	39	P10	Oolite	5.71	0.21	4.15	45.64
Hasi Anjiwal	WNW of Hasi Anjiwal	Zarzaitine	26	P11	Sandstone	64.17	-	1.35	16.20
	SW of Bir Intalkhata	Assedjefar	27	P12	Sandstone	50.95	-	1.80	3.25
Tikiumit	S of Taramhi	Melaz Suqran	19	P13	Sandstone	42.64	-	10.63	26.10
	W of Hagh Naql	Melaz Suqran	20	P14	Sandstone	40.04	-	0.48	35.75
	W of Wadi Wayn Kah Janit	Melaz Suqran	23	P15	Concretions	12.41	-	5.12	6.62
	SE of Bir Tikiumit	Marar	24	P16	Concretions	8.93	-	1.52	4.30
	Bir Tazibzabin	Marar	25	P17	Concretions	45.60	-	0.56	35.90
	Wadi Ann Aramas	Assedjefar	26	P18	Concretions	21.60	-	2.27	4.58
Wadi Tanezzuft	Tin Alkharmah	Akakus	37	P19	Sandstone	8.05	0.56	4.58	59.40
Anay	SW of Wadi Talmisayn	Assedjefar	37	P20	Sandstone	44.05	0.75	9.36	8.10

Table 1b. Chemical analysis data of major oxides (concentration in wt%) of the studied phosphate-bearing rocks (after Galecic, 1984; Parizek et al., 1984; Protic, 1984; Radulovic, 1984; Roncevic, 1984; Seidl and Rohlich, 1984; Woller, 1984)

Sheet	Area	Formation	Sample No. in the sheets	Sample No. in this work	Lithology	MnO	MgO	CaO	Na_2O
Al Fuqaha	SW of Qararat Al Hirah	Zimam	36	P1	Dolostone	0.21	12.60	22.08	0.14
Sabha	WSW of Khasm An Niqwi	Awainat Wanin	18	P2	Sandstone	3.37	0.14	1.45	0.08
	NW of Aqar		20	P3	Conglomerate	1.14	0.61	27.95	0.10
	WSW of Khasm An Niqwi		21	P4	Conglomerate	0.42	0.10	29.87	0.26
	N of Bir Al Ghalmayah		25	P5	Conglomerate	1.16	0.41	9.18	0.10
	WSW of Tarut		28	P6	Oolite	0.51	2.47	3.44	0.45
	NNW of Qarat Al Baddadah		33	P7	Conglomerate	0.41	0.23	5.42	0.21
	N of Ash Shab		34	P8	Conglomerate	0.00	0.26	13.12	0.44
	NNW of Qarat Al Baddadah	Marar	41	P9	Conglomerate	0.47	0.25	5.36	0.23
Idri	Wadi Ash Shati	Awainat Wanin	39	P10	Oolite	3.52	0.36	20.23	0.97
Hasi Anjiwal	WNW of Hasi Anjiwal	Zarzaitine	26	P11	Sandstone	0.83	0.12	9.15	0.40
	SW of Bir Intalkhata	Assedjefar	27	P12	Sandstone	0.83	1.07	23.52	0.43
Tikiumit	S of Taramhi	Melaz Suqran	19	P13	Sandstone	-	1.65	7.73	0.06
	W of Hagh Naql	Melaz Suqran	20	P14	Sandstone	-	0.10	10.56	0.03
	W of Wadi Wayn Kah Janit	Melaz Suqran	23	P15	Concretions	-	0.18	39.54	0.03
	SE of Bir Tikiumit	Marar	24	P16	Concretions	-	0.26	44.02	0.04
	Bir Tazibzabin	Marar	25	P17	Concretions	-	0.34	6.06	0.06
	Wadi Ann Aramas	Assedjefar	26	P18	Concretions	-	0.70	35.68	0.03
Wadi Tanezzuft	Tin Alkharmah	Akakus	37	P19	Sandstone	0.48	2.50	8.75	0.06
Anay	SW of Wadi Talmisayn	Assedjefar	37	P20	Sandstone	-	1.17	16.70	0.93

Table 1c. Chemical analysis data of major oxides (concentration in wt%) of the studied phosphate-bearing rocks (after Galecic, 1984; Parizek et al., 1984; Protic, 1984; Radulovic, 1984; Roncevic, 1984; Seidl and Rohlich, 1984; Woller, 1984)

Sheet	Area	Formation	Sample No. in the sheets	Sample No. in this work	Lithology	K_2O	P_2O_5	Cl	SO_3
Al Fuqaha	SW of Qararat Al Hirah	Zimam	36	P1	Dolostone	0.23	3.13	<0.05	0.51
Sabha	WSW of Khasm An Niqwi	Awainat Wanin	18	P2	Sandstone	0.36	3.29	0.04	0.65
	NW of Aqar		20	P3	Conglomerate	0.17	25.00	0.06	0.77
	WSW of Khasm An Niqwi		21	P4	Conglomerate	0.17	26.22	0.19	4.00
	N of Bir Al Ghalmayah		25	P5	Conglomerate	0.30	7.69	0.15	1.97
	WSW of Tarut		28	P6	Oolite	0.51	3.13	0.40	0.25
	NNW of Qarat Al Baddadah		33	P7	Conglomerate	0.14	8.30	0.17	1.88
	N of Ash Shab		34	P8	Conglomerate	0.25	11.61	0.48	2.65
	NNW of Qarat Al Baddadah	Marar	41	P9	Conglomerate	0.47	7.34	0.43	2.55
Idri	Wadi Ash Shati	Awainat Wanin	39	P10	Oolite	0.47	5.80	0.71	2.90
Hasi Anjiwal	WNW of Hasi Anjiwal	Zarzaitine	26	P11	Sandstone	0.51	5.02	0.68	0.08
	SW of Bir Intalkhata	Assedjefar	27	P12	Sandstone	0.38	13.62	0.50	-
Tikiumit	S of Taramhi	Melaz Suqran	19	P13	Sandstone	0.12	4.16	0.35	-
	W of Hagh Naql	Melaz Suqran	20	P14	Sandstone	0.06	6.14	0.25	-
	W of Wadi Wayn Kah Janit	Melaz Suqran	23	P15	Concretions	0.06	29.62	0.35	-
	SE of Bir Tikiumit	Marar	24	P16	Concretions	0.08	31.50	0.36	-
	Bir Tazibzabin	Marar	25	P17	Concretions	0.10	3.06	0.70	-
	Wadi Ann Aramas	Assedjefar	26	P18	Concretions	0.06	26.30	0.52	-
Wadi Tanezzuft	Tin Alkharmah	Akakus	37	P19	Sandstone	0.35	3.06	-	-
Anay	SW of Wadi Talmisayn	Assedjefar	37	P20	Sandstone	1.15	6.95	0.38	-

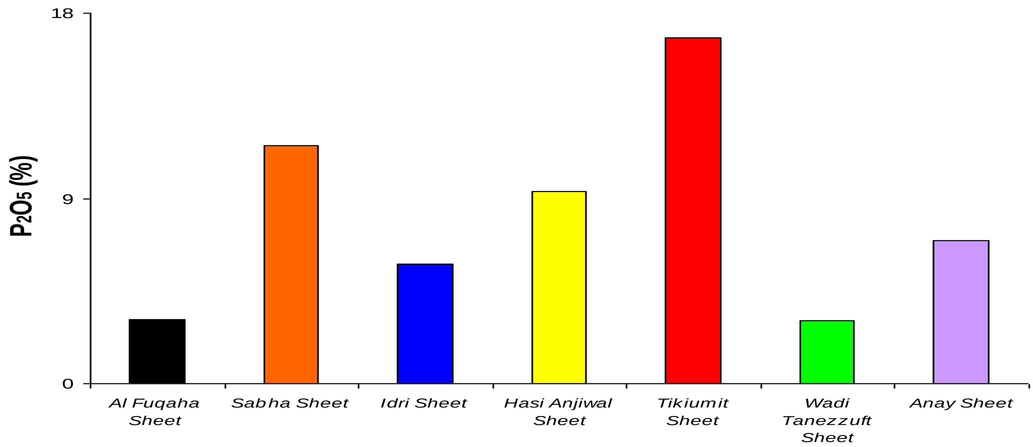

Figure 2. Average P_2O_5 concentration in the studied phosphate-bearing rocks

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Table 2. Chemical classification of the studied phosphate-bearing rocks (classes after Pettijohn, 1957)

Formation	Sample No.	P_2O_5 (%)	Class
Zimam	P1	3.13	Phosphatized rocks
Awainat Wanin	P2	3.29	Phosphatized rocks
	P3	25.00	Phosphorite rocks
	P4	26.22	Phosphorite rocks
	P5	7.69	Phosphatized rocks
	P6	3.13	Phosphatized rocks
	P7	8.30	Phosphatized rocks
	P8	11.61	Phosphatic rocks
Marar	P9	7.34	Phosphatized rocks
Awainat Wanin	P10	5.80	Phosphatized rocks
Zarzaitine	P11	5.02	Phosphatized rocks
Assedjefar	P12	13.62	Phosphatic rocks
Melaz Suqran	P13	4.16	Phosphatized rocks
Melaz Suqran	P14	6.14	Phosphatized rocks
Melaz Suqran	P15	29.62	Phosphorite rocks
Marar	P16	31.50	Phosphorite rocks
Marar	P17	3.06	Phosphatized rocks
Assedjefar	P18	26.30	Phosphorite rocks
Akakus	P19	3.06	Phosphatized rocks
Assedjefar	P20	6.95	Phosphatized rocks

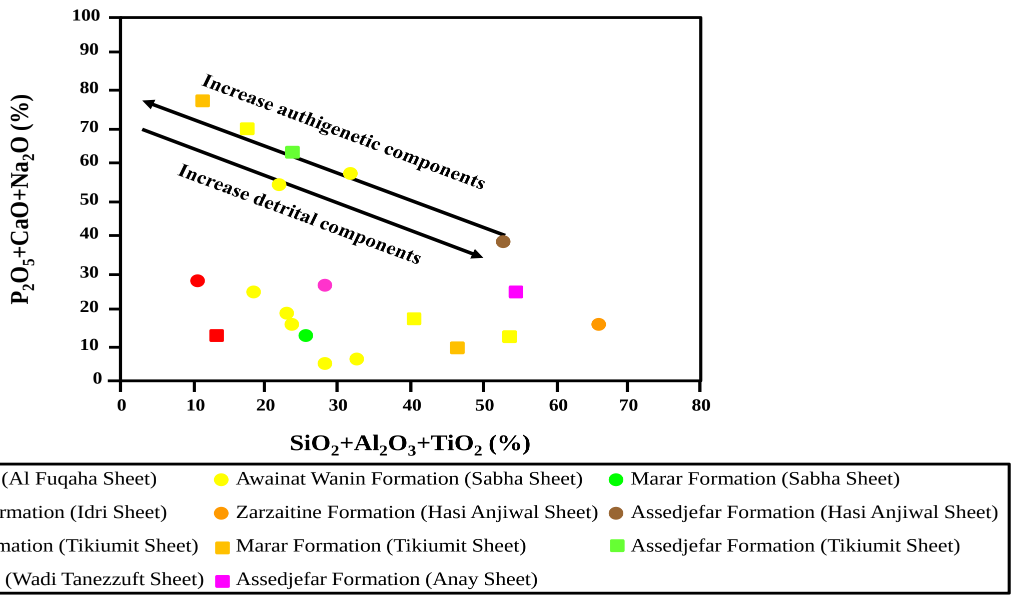

Figure 3. Binary plot of $SiO_2+Al_2O_3+TiO_2$ vs. $P_2O_5+CaO+Na_2O$ showing the origin of the studied phosphate-bearing rocks (fields after Ahmed et al., 2022).

The binary plot of $SiO_2+Al_2O_3+TiO_2$ (terrestrial components) versus $P_2O_5+CaO+Na_2O$ (authigenic components) (Fig. 3) suggests that most of the phosphorite samples (P4, P15, P16, and P18) are primarily precipitated from marine input, while the majority of the remaining samples are detrital in origin.

3.2. Industrial Characteristics

Three categories of phosphate ores are distinguished based on the P_2O_5 content: (1) Low-grade ore (P_2O_5 ranges from 12 to 16%); (2) Intermediate-grade ore (P_2O_5 ranges 17 to 25%); and (3) High-grade ore (P_2O_5 ranges 26 to 35%) (Ozer et al., 2000; Sengul et al., 2006; Aydin et al., 2010). It is evident from the prior classification that the phosphate ores should contain at least 12% P_2O_5. Consequently, samples with a P_2O_5 content of less than 12% were not included in the evaluation of the quality of the studied phosphate-bearing rock. The quality of the phosphorite samples (P3, P4, P15, P16, and P18) ranges from medium to high, while the quality of the phosphate rock sample (P12) is low (Table 3). Global agriculture is currently fertilized by phosphate fertilization, which is based on phosphorite ore (e.g., Zhang *et al.*, 2019). The phosphate ores must have the following characteristics in order to be used in the fertilizer industry: (1) P_2O_5 content >30%; (2) CaO/P_2O_5 ratio <1.6; (3) MgO content <1%; and (4) The content of Al_2O_3 and Fe_2O_3 should not exceed 2.5% (Sengul et al., 2006; Heidarpour, 2009). With the exception of Fe_2O_3 content, sample P12 (Marar Formation in Tikiumit Sheet) satisfies all of the aforementioned requirements (Table 4), suggesting that treatment is required prior to use in the fertilizer industry. The Ca/P ratio in calcium phosphate is essential for evaluating artificial bone (e.g., Liu et al., 2008). To enhance juxtaposed bone growth surrounding orthopedic implants, such as knee and hip prostheses, hydroxyapatite (HA) with a Ca/P ratio of 1.67 is utilized (Kay, 1988). Tricalcium phosphate (TCP) with a Ca/P ratio of 1.5 is used as injectable cements and drug delivery systems to repair bone defects (Kumta et al., 2005). Samples P3, P4, P12, P15, P16, and P18 have Ca/P ratios of 1.8, 1.84, 2.79, 2.15, 2.25, and 2.19, respectively. This suggests that samples P3 and P4 (Awainat Wanin Formation in Sabha Sheet) can be utilized in the field of artificial bone, but only after the Ca/P ratio has been adjusted through processing.

Table 3. Industrial classification of the studied phosphate-bearing rocks (classes after Ozer et al., 2000; Sengul et al., 2006; Aydin et al., 2010)

Formation	Sample No.	P_2O_5 (%)	Quality
Awainat Wanin	P3	25.00	Intermediate
	P4	26.22	High
Assedjefar	P12	13.62	Low
Melaz Suqran	P15	29.62	High
Marar	P16	31.50	High
Assedjefar	P18	26.30	High

Table 4. Values of fertilizer industry requirements in sample P12 (Marar Formation in Tikiumit Sheet)

Formation	Sample No.	P_2O_5	CaO/P_2O_5	MgO	Al_2O_3	Fe_2O_3
Marar	P16	31.50	1.40	0.26	1.52	4.30

4. Conclusions

This study assesses the geochemical and industrial characteristics of the phosphate-bearing rocks in seven Libyan areas. The phosphate-containing rocks are found in a number of different formations. All types of phosphate rocks are present in the study areas. Marine input is the likely origin of most phosphorite samples, while the remaining samples appear to be of detrital origin. The phosphorites are characterized by medium to high quality, while the phosphatic rocks belong to the low-quality class. The Fe_2O_3 content needs to be treated even though the Marar Formation in Tikiumit Sheet meets all fertilizer industry requirements. It is possible to use the Awainat Wanin Formation in Sabha Sheet in the field of artificial bone, but only after the Ca/P ratio has been suitably adjusted.

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