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## The physical, mineralogical, and geochemical properties of the recent sediments at Thi-Qar Governorate, Iraq

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### Abstract

The study aimed to determine the physical, mineralogical, and geochemical properties in Thi-Qar and to determine the chemical weathering, chemical maturity and paleoclimate in the study area. Mineralogical, geochemical, and grain size analyses of samples were obtained from sediments of selected areas within Thi-Qar Governorate (Al-Aslah, Nasiriyah Refinery, Tall Al-Laham, and Grarraf) and have been examined. Texture analysis was performed on all samples using British, American, and folk standards specifications. The results were as follows: a high rate of silt and sand, with an even higher percentage of clay.

The X-ray diffraction technique distinguishes non-clay minerals from clay minerals. The non-clay minerals represented quartz, calcite, dolomite, and feldspar; they are light minerals, as they were in varying proportions, which explains them chemically.

The diagnosed clay minerals in the area were kaolinite, montmorillonite-chlorite mixed layer, montmorillonite, illite, and palygorskite. Inductively Coupled Plasma Mass Spectrometry analysed the significant elements of oxides. The results show an increase in silica compared to the other oxides because silica is considered a substantial component of clay minerals and quartz. The high loss in ignition percentage was due to the evaporation of the water molecules in the clay minerals' crystalline structure and the breakdown of the carbonate structure. The chemical index of alteration values indicates that moderate chemical weathering and low chemical maturity affect the study area sediments, as it reflects the semi-arid climate during the deposition process.

**Keywords:** Clay minerals; South of Iraq; Mesopotamia; Paleoclimate; Recent sediments.

دراسة الخصائص الفيزيائية، المعدنية، والجيوكيميائية للرواسب الحديثة في محافظة ذي قار، العراق

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الخلاصة

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هدفت الدراسة إلى تحديد التوزيع الفيزيائي والمعدني والجيوكيميائي في محافظة ذي قار وتحديد التجوية الكيميائية والنضج الكيميائي والمناخ القديم في منطقة الدراسة. وتم إجراء دراسات معدنية وجيوكيميائية وتحليل الحجم الحبيبي على رواسب مناطق مختارة ضمن محافظة ذي قار (الإصلاح، مصفاة الناصرية، تل اللحم، والغراف). كذلك قد تم إجراء تحليل النسيج على جميع العينات طبقاً للمواصفات القياسية البريطانية والأمريكية وحسب الشروط القياسية لفولك. وكانت النتائج التي تم الحصول عليها على النحو التالي: نسبة عالية من الطمي والرمل مع نسبة أعلى من الطين. تقوم تقنية حيود الأشعة السينية بتمييز المعادن غير الطينية عن المعادن الطينية. وتمثل المعادن غير الطينية الكوارتز والكالسيت والدولوميت والفلسبار والهاليت. وهي معادن خفيفة، إذ كانت بنسب متفاوتة، وهو ما يفسر وجودها كيميائياً. المعادن الطينية التي تم تشخيصها في المنطقة هي الكاولينيت، طبقة مختلطة من المونتموريلونيت-كلوريت، المونتموريلونيت، الإليت، وباليجورسكايت. وقد قام مطياف الكتلة البلازمية المقترنة بالحث بتحليل العناصر المهمة للأكاسيد، وأظهرت النتائج زيادة في السليكا مقارنة بالأكاسيد الأخرى لأن السليكا تعتبر مكوناً مهماً للمعادن الطينية والكوارتز. وكان ارتفاع نسبة مفقودات الحرق بسبب تبخر جزيئات الماء في البنية البلورية للمعادن الطينية وانهايار بنية الكربونات. يشير مؤشر التغير الكيميائي إلى أن منطقة الدراسة تتأثر بالتجوية الكيميائية المعتدلة وانخفاض النضج الكيميائي حيث يعكس المناخ شبه الجاف أثناء عملية الترسيب.

## 1. Introduction

According to the tectonic setting, the Thi-Qar Governorate is located within the Euphrates Subzone within the Mesopotamian Zone on the unstable shelf [1]. The recent sediments in the Mesopotamian Zone contain clay and silt-rich alluvial layers from the Euphrates River covering the Thi-Qar Governorate [2]. Thi-Qar Governorate is situated about 358 Km southwest of Baghdad on the banks of the Euphrates River. Its outer borders are Basra, Muthanna, Missan, Diwaniyah, and Kut governorates, with desert plains covering the governorate topographically.

This study covered the Thi-Qar Governorate, which includes five districts: Nasiriyah, Souq Al-Shuyukh, Al-Shatrah, Al-Rifai, and Al-Chibayish, and all parts of the Governorate. The Holocene Epoch is of great interest because it supplies a recent analogue for the paleoenvironments and geological processes. These sediments and landforms supply important clues about the changes due to the last shift from the glacial to the nonglacial climatic mode.

The location was previously studied by [3], which studied the physical, chemical and mineralogical properties of subsurface recent sediment in Thi Qar Governorate/ South Iraq; the grain size analysis showed that most of those sediments were muddy, while the mineralogical study showed that the prevalent non-clay minerals were quartz, calcite, dolomite, feldspar, gypsum, and halite. Montmorillonite, kaolinite, chlorite, illite, palygorskite, and the mixed layer minerals montmorillonite-chlorite are prevalent clay minerals in the area.

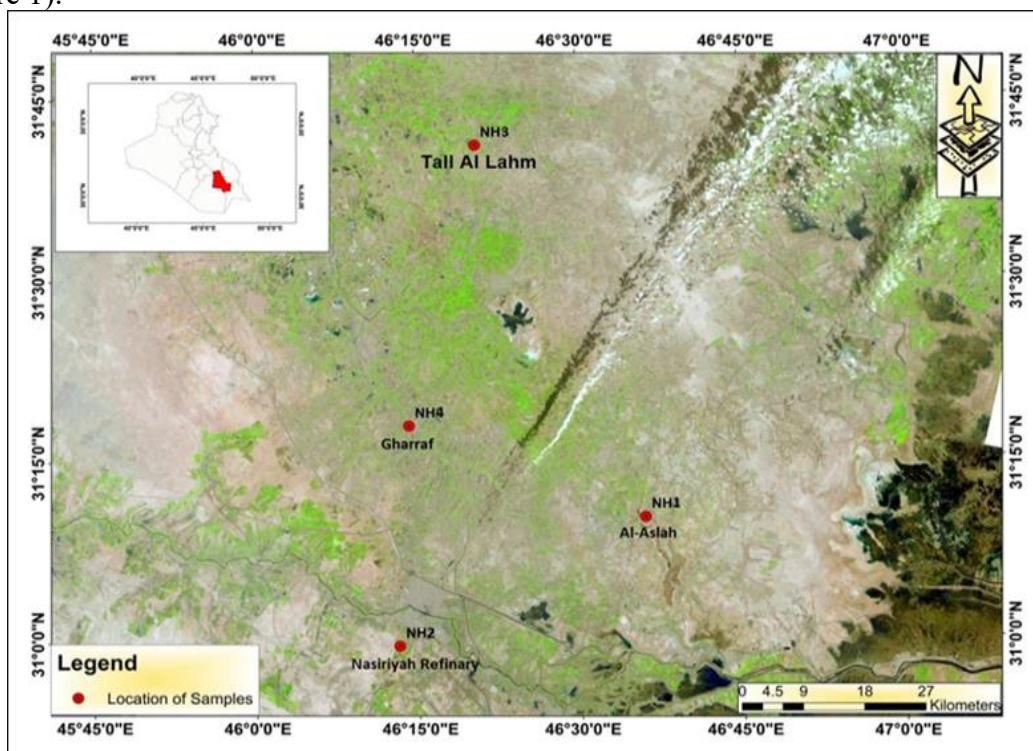
The chemical results showed increased silica and a lack of alumina and alkaline oxides. [4] studied the physical, mineralogical, and geochemical properties along the highway connecting Basra, Nasiriyah and Muthana cities. The results of the physical study showed that sediments of the studied area consisted of sandy silt and silt with a small amount of clay. The results of the mineralogical research showed the presence of clay minerals mixed layer (montmorillonite-illite), illite, palygorskite and kaolinite, and the non-clay minerals calcite, quartz, halite, and gypsum with a trace of sylvite.

[5] studied the quaternary sediments and determined the light and heavy minerals in Basrah, Thi-Qar and Missan governorates south of Iraq. The physical test results showed three types of sediment: silt, sandy silt, and silty sand. The light minerals were dominated by carbonate, quartz, chert, evaporates, feldspar and light muscovite.

## 2. Materials and Methods

### 2.1 Study area

The exact location of the study area is within Thi-Qar Governorate, to the south of Iraq, between latitude ( $30^{\circ} 59' - 31^{\circ} 41' N$ ) and longitude ( $46^{\circ} 13' - 46^{\circ} 36' E$ ); its sediments originate from the quaternary period and the Mesopotamian plane; it composed of marine, delta, and river deposits and can be specified by their vertical and horizontal facies variation [6]. Moreover, the study area is in an unstable zone, specifically in the Euphrates Zone [7] (Figure 1).



**Figure 1:** Study area Map showing sampling points.

### 2.2 Sampling and Analysis

The fieldwork was accomplished in October/2022 in the main study area sites (industrial, agricultural, commercial, and residential). Four samples were taken from different sites in Thi-Qar Governorate (Al-Aslah, Nasiriyah refinery, Tall Al-Laham, and Gharraf) (Figure 1) at a depth about 5 cm after being selected by hand and then placed in marked polyethene bags as shown in which represents the locations of the collected samples within the study area. The texture analysis was carried out for all samples using the hydrometer method in the Department of Geology laboratories at the College of Science, University of Basrah. The type of hydrometer that was used was Hydrometer, 152H, Franc, according to [8], [9], and [10]. At the Australian Laboratory Services (ALS) laboratory group in Seville, Spain, the chemical analysis was carried out for all samples using inductivity coupled plasma spectrometry (ICP-MS) to determine the concentration of the major elemental oxides  $SiO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$ ,  $CaO$ ,  $MgO$ ,  $Na_2O$ ,  $K_2O$ , and  $TiO_2$ , in addition to LOI. Mineralogical analysis was carried out by X-ray diffractometer (XRD) to identify the clay and non-clay minerals in bulk and oriented mount samples.

The analysis was conducted using a Cu K $\alpha$  source operated with a tube voltage of 40 kV over angles of 20° to 60° 2 $\theta$  for the bulk mounts and (5° to 35° 2 $\theta$ ) for the oriented mounts at a scanning speed of 2° 2 $\theta$ /min. A randomly oriented bulk powder mount and three oriented glass slide mounts, including non-treated, treated with ethylene glycol at 60°C for two hours and heated at 500°C for two hours, were prepared according to the procedures described by [9] [10] and [11]. All basal reflection peaks of minerals in each XRD profile were identified and interpreted according to [8] and [13].

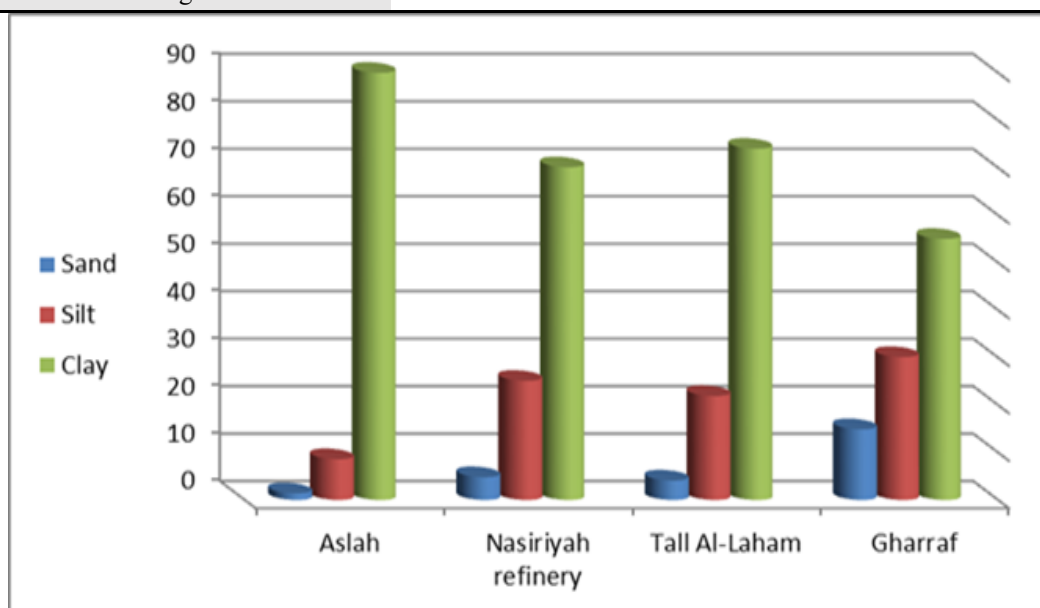
### 3. Results and Discussion

#### 3.1 Grain size analysis

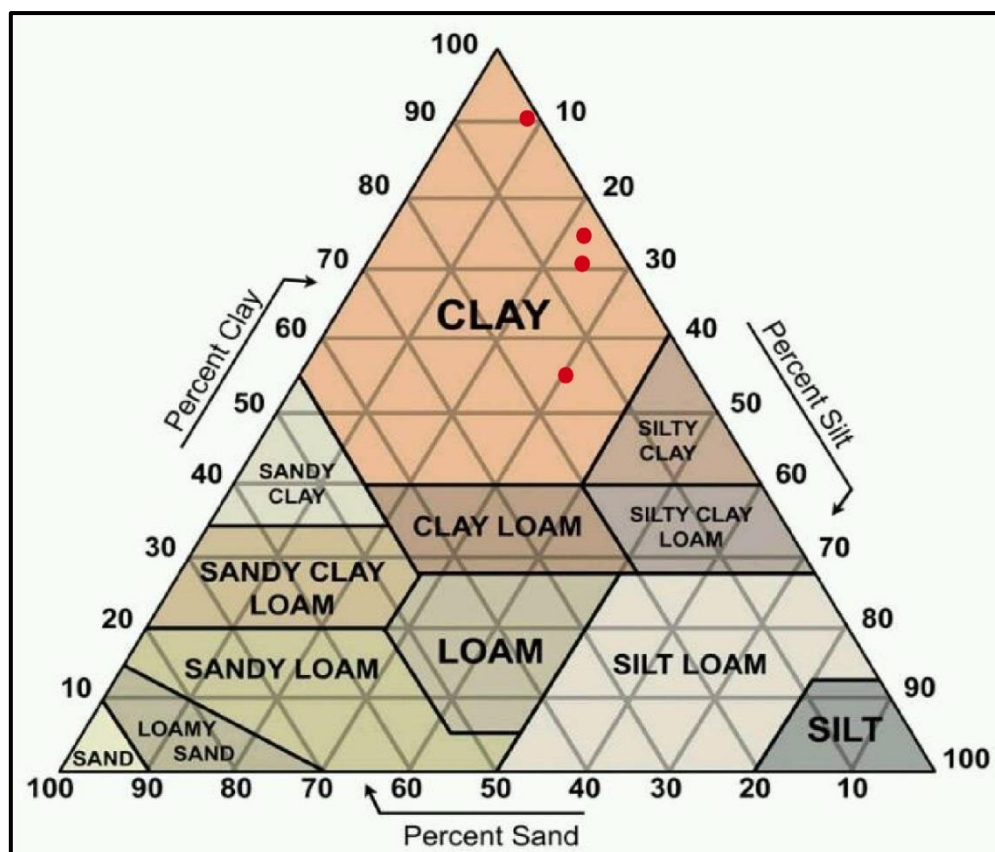
The test was accomplished for the muddy part according to the [8], [9], and [10], where the 63-micron sieve was used to separate the sand from the mud, and the Hydrometer used for the texture analysis for all the samples of the study area (Table 1; Figure 2) the results show that the study area contains clay ranging between 55% and 90%, with an average of 72.2%, which is the highest value and refers to very low sedimentation conditions [14], [15]. The clay content refers to the grain size fraction comprising particles smaller than 63 microns. On the other hand, chemical analysis provides the actual compositional values. The silt ranged between 8.6% and 30.1%, with an average of 21.4%, and the sand ranged between 1.4% and 14.9%, with an average of 6.3%. Moreover, all the samples show clay texture (Table 1; Figure 3).

**Table 1:** Grain size analysis and texture results

Sample No.	Sand	Silt	Clay	Texture
Al-Aslah	1.4	8.6	90	Clay
Nasiriyah refinery	4.8	25.1	70.1	Clay
Tall Al-Laham	4.1	21.9	74	Clay
Gharraf	14.9	30.1	55	Clay
Average	6.3	21.4	72.2	



**Figure 2:** Graph of grain size analysis



**Figure 3:** Classification triangle of sediment texture (after Folk, 1980).

### 3.2 Mineralogy

The XRD technique is used to distinguish the clay minerals and non-clay minerals after the separation of bulk samples and the oriented samples (treated with heat at 550°C, treated with ethylene glycol, and non-treated samples), as shown below:

#### 3.2.1 Non-Clay minerals

The sediments of Thi-Qar Governorate are rich in silica, an essential mineral in the clay fraction and is also considered the main component of the sand represented by quartz ( $\text{SiO}_2$ ). The percentage of quartz ranged between 40% and 50% (Table 2; Figure 4). In contrast, the major peak is at d-space 3.3 Å, and the minor peak is at d-space 4.2 Å.

Carbonate minerals are characterized by calcite and dolomite minerals, where calcite ( $\text{CaCO}_3$ ) appears in the major reflection 3.03 Å and the minor reflection 2.8 Å the percentage of calcite ranged between 31.2% and 52.02% (Table 2; Figure 4) and the rate of dolomite ranged between 1.32% and 9.93% (Table 2; Figure 4) Feldspar ( $\text{KAlSi}_3\text{O}_8$ ) appears in the main reflection 3.2 Å the percentage of feldspar ranged between 2.8% and 7.3% (Table 2; Figure 4), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) appears in the main reflection 8 Å the percentage of gypsum ranged between 3.69% and 4.6% (Table 2; Figure 4).

**Table 2:** Non-clay mineral percentage in the study area

Sample	Quartz	Calcite	Dolomite	Feldspar	Gypsum	Average
Al-Aslah	40	52.02	1.32	2.8	3.69	99.83
Nasiriyah refinery	41.5	42	9.22	7.3	-	100
Tall Al-Laham	45.2	51.16	-	3.6	-	99.96
Gharraf	50.3	31.2	9.93	3.8	4.6	99.83

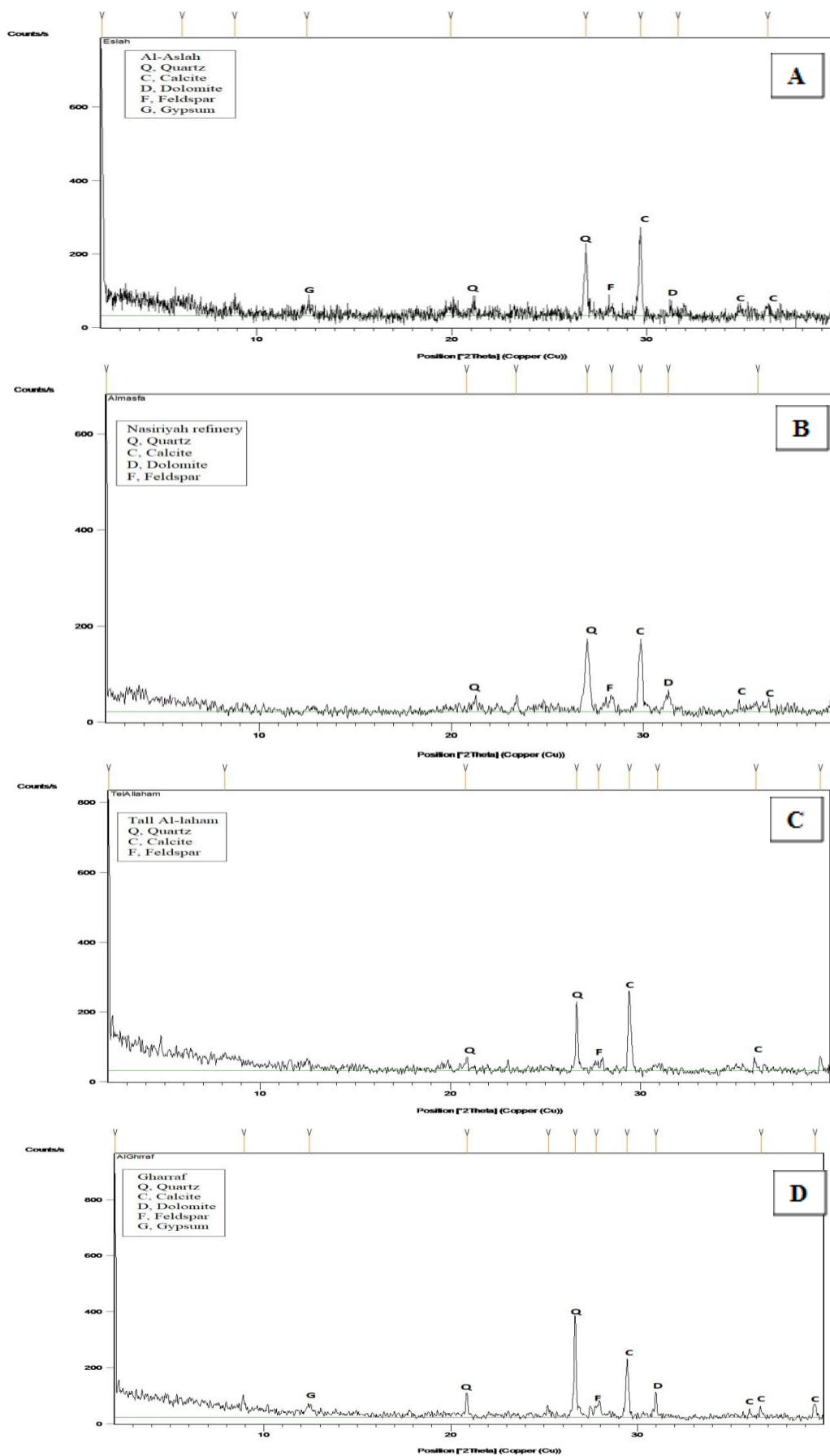


Figure 4: A, B, C, and D- X-ray diffraction reveals the bulk sample in the study area

### 3.2.2 Clay minerals

Clay minerals diagnosed in the study area (Table 3; Figure 5) represented by kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , which appears in the main basal reflection  $7.15 \text{ \AA}$ , peak collapse when heated above  $550^\circ\text{C}$ , and unaffected during treatment with ethylene glycol, the percentage of kaolinite ranged between 17% and 21.45% (Table 3; Figure 5). Kaolinite is formed by the weathering of igneous and metamorphic rocks affected by the moist climate, acidic water, and good discharge movement [11], [16].

Montmorillonite  $(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2.n\text{H}_2\text{O}$  which appears in the main basal reflections  $14.4 \text{ \AA}$ , and  $5.03 \text{ \AA}$ , the percentage of montmorillonite ranged between 37.17% and 45.36% (Table 3; Figure 5). montmorillonite affected by heating due to losing water molecules between mineral layers; as a result its basal reflection shifted to  $10 \text{ \AA}$ , the mineral is formed in low moisture, low acidity environment, and semi-arid climate by the high magnesium igneous, sedimentary, and metamorphic rocks erosion and chemical weathering, it is also formed by the alterations in volcanic ash [11], [16].

Illite  $(\text{K}, \text{H}_2\text{O}) (\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si Al})_4\text{O}_{10}((\text{OH})_2.\text{H}_2\text{O})$ , which appears in the main basal reflection  $10 \text{ \AA}$ , isn't affected when treating the sample with ethylene glycol but is little affected when heated to  $550^\circ\text{C}$  [10], the percentage of illite ranged between 18.5% and 25.74%. Illite is formed in arid areas, is rich in potassium content, and is found in a highly alkaline environment [17], [18].

Palygorskite  $(\text{Mg}, \text{Al})_2\text{Si}_4\text{O}_8(\text{OH}).4\text{H}_2\text{O}$  appears in the main basal reflection  $10.5 \text{ \AA}$ . Palygorskite isn't affected when treated with ethylene glycol, but declines and is slightly shifted when heated to  $550^\circ\text{C}$ . The percentage of palygorskite ranged between 10.31% and 20.5% (Table 3; Figure 5). Palygorskite is formed in an alkaline, rich in magnesium and silicon environment [19], [20].

A montmorillonite-chlorite mixed layer appears in the main basal reflections  $4.7\text{\AA}$  and  $7.1\text{\AA}$ ; this type of mineral has uneven basal reflections, which lie between the normal reflection values of these minerals. The values and intensity of these minerals' reflections depend on the proportionate presence of both combined minerals [21]. The percentage of montmorillonite-chlorite mixed layers ranged between 3.55% and 7.43% (Table 3; Figure 5).

**Table 3:** Clay mineral percentage in the study area.

Sample	Kaolinite	Montmorillonite	Illite	Palygorskite	Montmorillonite – Chlorite mixed layer	Avg.
Al-Aslah	17.8	39.48	19	19.81	3.55	99.64
Nasiriyah refinery	17	36.15	20.2	20.5	5.92	99.77
Tall Al-Laham	17.6	37.17	18.5	19.31	7.3	99.88
Gharraf	21.45	45.36	25.74	-	7.43	99.98

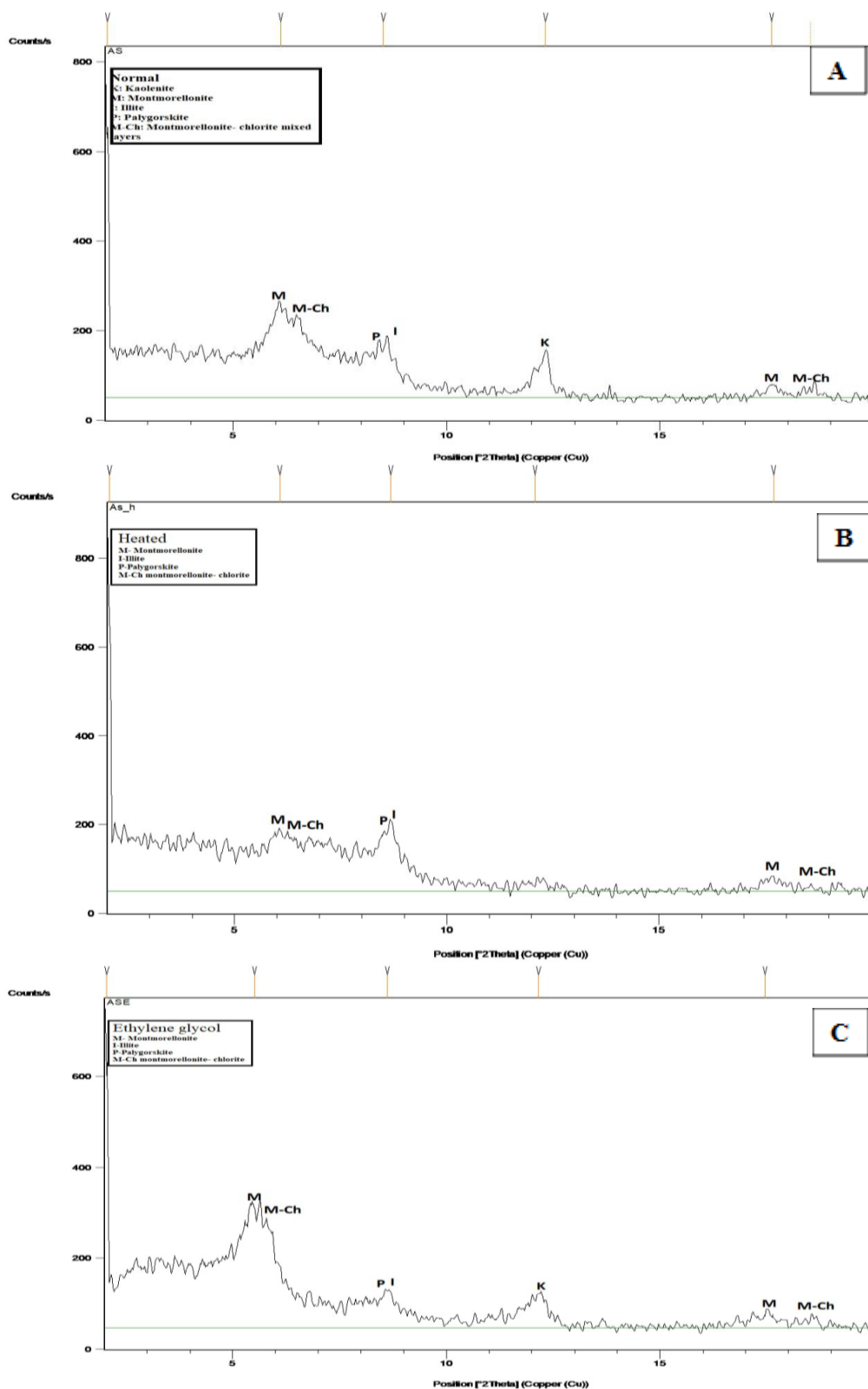


Figure 5: A, B, and C- X-ray diffraction reveals clay minerals in the study area

### 3.3 Geochemistry

#### 3.3.1 SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>

Silica has the highest concentration value of all the oxides. The source of silica is quartz, feldspar and clay minerals, with its extent between 31.1 and 37.7% (Table 4) the reported silica percentage appears lower than quartz percentage because the analysis includes the rate

of loss on ignition (LOI), which reduces the apparent silica content and the chemical analysis are actual compositional values, as silicon is combined with oxygen, and quartz percentage are semi-quantitative consists of multiple elemental components [18]. As silica content is a major component in the clay minerals' crystalline structure [21], and this is expressed by the positive correlation coefficient with clay forming minerals (aluminium, iron, and potassium oxides) and an inverse correlation with CaO, and MgO (Table 5) because of the difference in depositional environments [23].

Aluminum oxide ranges between 10.5 and 11.7% (Table 4), and its presence is associated with being the main component of clay minerals; its distribution is affected by the amount of clay minerals, which is positively correlated with potassium (Table 5) due to its presence in illite and feldspar mineral [24], [25], and negative correlation with CaO, and MgO (Table 5) because of the difference in depositional environments [23].

Iron oxide percentage ranged between 4.92 and 6.4 (Table 4). Iron positively correlated with silica, aluminium and titanium (Table 5). due to its existence in montmorillonite and montmorillonite-chlorite minerals [26] and positively correlated with potassium oxides (Table 5), which means its presence in the crystalline structure of illite minerals or similar sources [27], [28].

### 3.3.2 CaO, MgO, and LOI

The percentage of calcium oxide ranges between 14.1 and 15.9% (Table 4), which is considered to be high due to its presence as a major component of calcite, dolomite and gypsum minerals [27], [29] and this explained by the negative correlation with clay minerals oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ) (Table 5).

The percentage of magnesium oxide ranges between (5.28 and 6.42%) (Table 4), which is high due to the presence of magnesium as a major component of dolomite, palygorskite, and montmorillonite minerals [30], [31], this explained by the strong positive correlation with CaO and weak negative correlation with clay minerals oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ) (Table 5).

The percentage of Los on ignition (LOI) ranged between 16.2 and 19.5% (Table 4), resulting from the adsorbing of water on clay particles caused by the breaks of carbonate structure (calcite and dolomite) and release of carbon dioxide in addition to the volatile gasses released during burning, such as sulfates  $\text{SO}_3$  as well as the molecular water ( $\text{H}_2\text{O}^+$ ,  $\text{OH}^-$ ) that evaporates from the clay minerals crystalline structure [32], and for this reason LOI correlate with strong positive correlation with ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , CaO, MgO).

### 3.3.3 $\text{Na}_2\text{O}$ , $\text{K}_2\text{O}$ , and $\text{TiO}_2$

Sodium oxide percentages ranged between 0.9 and 2.5% (Table 4); sodium exists in claystone as a replaceable ion in clay minerals [33] since it is absorbed on the surfaces of clay minerals when the acidic function increases, such as montmorillonite mineral [34].

Potassium oxide ranged between 1.31 and 1.43% (Table 4). Its existence is related to the presence of illite minerals. Also, potassium exists as a replaceable ion or is adsorbed on the clay minerals layers surfaces [26], in addition to its existence in the feldspar minerals, as shown in the strong correlation with ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ).

The percentage of titanium oxide ranged between 0.54 and 0.58% (Table 4). Titanium exists as small crystals of heavy minerals, such as rutile minerals, in the internal layers of clay minerals, which refers to the strong positive correlation with ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ). Titanium also replaces magnesium in octahedral layers of palygorskite because of the convergence of their ionic radius [35], which is explained by the strong positive correlation with MgO.

**Table 4:** The concentrations of major oxides in the study area in ppm.

Element	UCC	Al-Aslah	Nasiriyah refinery	Tall Al-Laham	Gharraf	Range	Average
SiO <sub>2</sub>	66	31.7	31.7	31.1	37.7	31.1-37.7	33.05
Fe <sub>2</sub> O <sub>3</sub>	5	6.08	5.73	6.42	4.92	4.92-6.42	5.79
Al <sub>2</sub> O <sub>3</sub>	15.2	11.1	11.7	10.5	10.9	10.5-11.7	11.05
TiO <sub>2</sub>	0.5	0.549	0.546	0.585	0.553	0.546-0.585	0.56
CaO	4.2	15.7	14.1	15.9	14.9	14.1-15.9	15.15
MgO	2.2	6.09	6.35	6.42	5.28	5.28-6.42	6.04
Na <sub>2</sub> O	3.9	2.38	0.934	1.87	2.51	0.934-2.51	1.92
K <sub>2</sub> O	3.4	1.31	1.27	1.43	1.33	1.27-1.43	1.34
LOI		19.5	17.3	17.4	16.2	16.2-19.5	17.60
CIA		67.36	79.98	69.27	66.00	66-79.98	70.65

\*UCC: Upper Continantal Crust

\* CIA: Chemical Index of Alteration

**Table 5:** Correlation coefficient of major oxide.

	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	LOI
SiO <sub>2</sub>	1								
Fe <sub>2</sub> O <sub>3</sub>	0.930	1							
Al <sub>2</sub> O <sub>3</sub>	0.922	0.849	1						
TiO <sub>2</sub>	0.482	0.559	0.825	1					
CaO	-0.754	-0.575	-0.835	0.654	1				
MgO	-0.175	-0.288	-0.139	0.349	0.637	1			
Na <sub>2</sub> O	0.532	-0.255	-0.633	0.087	0.625	0.668	1		
K <sub>2</sub> O	0.537	0.563	0.930	0.975	-0.256	-0.173	0.307	1	
LOI	-0.643	0.624	0.606	-0.159	0.459	0.458	0.120	0.142	1

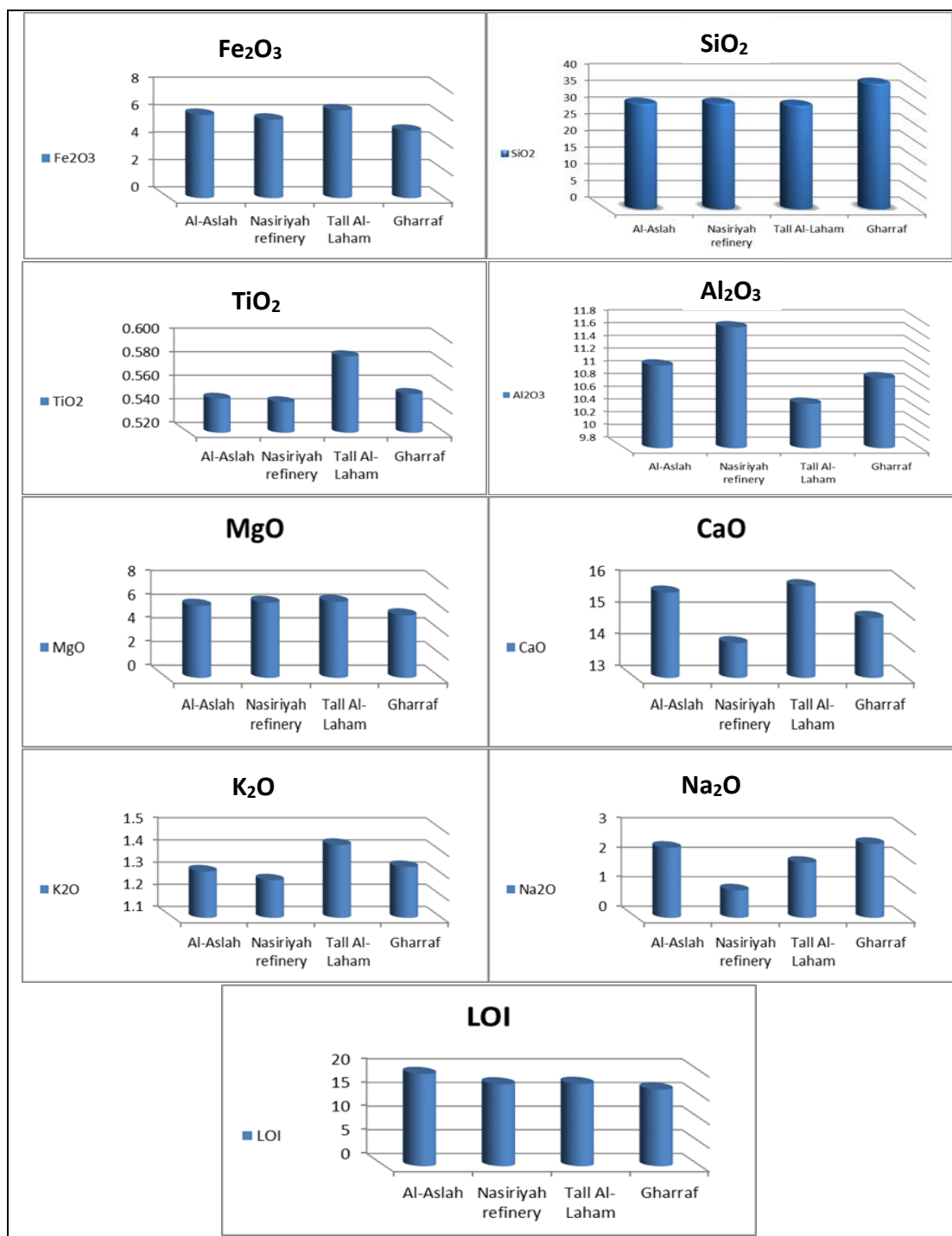


Figure 6: Major oxide distribution in the study area

### 3.4 Chemical weathering

The Chemical Index of Alteration (CIA) is generally used to indicate weathering and alteration of the source area. CIA was proposed by [36], and the following formula calculates it:

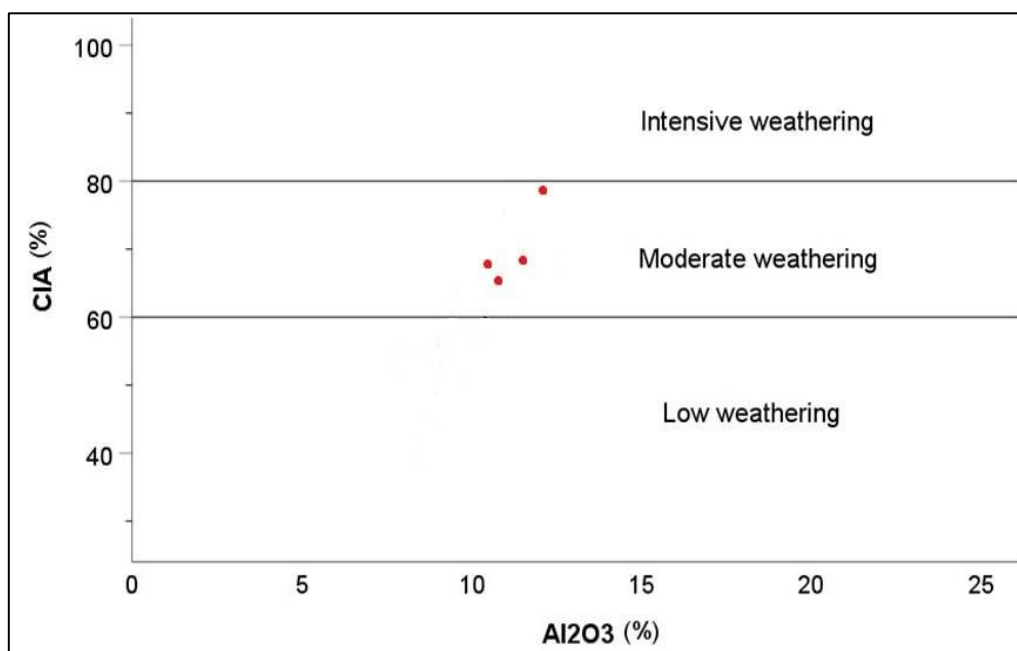
$$CIA = [Al_2O_3 / (Al_2O_3 + CaO * + Na_2O + K_2O)] \times 100 \quad (1)$$

Where (CaO\*) equal to:-

$$CaO * = 0.35 * 2 (Na_2O \%) / 62 \quad (2)$$

When the CIA is less than 60, this means low chemical weathering; 60-80 is identified as moderately chemical weathering, and if the CIA is more than 80, it is defined as intensive

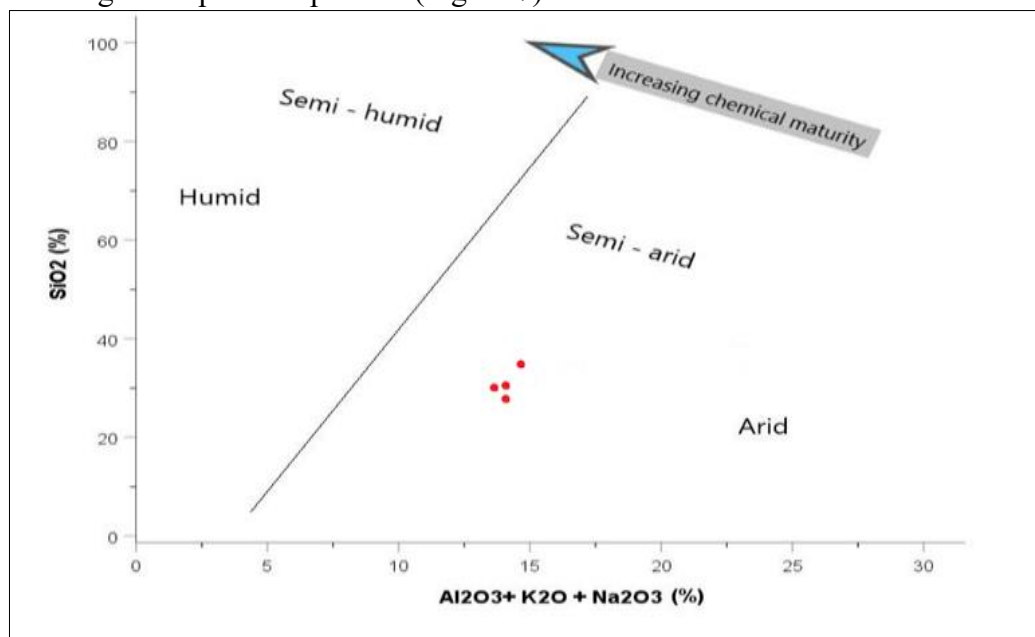
chemical weathering [36]. CIA values ranged between 66 and 79.98 (Table 4); the values were plotted on the CIA versus  $\text{Al}_2\text{O}_3$  graph [38], which confirms that the samples were affected by moderate chemical weathering (Figure 6).



**Figure 6:** CIA vs.  $\text{Al}_2\text{O}_3$  diagram for the chemical weathering of the studied samples according to [38]

### 3.5 Maturity and Paleoclimate

The proportion of the element's major oxides in the sediments of the study area is used to indicate chemical maturity. Then it is used as an indicator and guide to the ancient climate using oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ ) versus  $\text{SiO}_2$  diagram [39]. It is clarified that the sediments of the study have a low chemical maturity, as it reflects the nature of the semi-arid climate during the deposition process (Figure 7).



**Figure 7:**  $\text{SiO}_2$  versus ( $\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O}$ ) diagram shows paleoclimate conditions and chemical maturity according to [39]

#### 4. Conclusions

Thi-Qar sediments are composed of calcite, quartz, gypsum, and dolomite minerals and are composed of clay minerals, montmorillonite, illite, kaolinite, palygorskite, and montmorillonite-chlorite mixed layer. Grain size analysis shows that the study area sediments consist of a high percentage of clay compared with the low sand, which was low, and the sediments of the study area show clay texture.

Major oxides demonstrate varied relationships and correlation coefficients, which refer to the various sediment components, sedimentary conditions, and origins. The percentage of silica was the highest compared to other oxides, in addition to the increase in the rate of salts in the area. The loss percentage on ignition (LOI) was high due to the high carbonate content and clay texture. The study area is affected by moderate chemical weathering and has a low chemical maturity due to the semi-arid climate during the deposition process.

Finally, due to the wide distribution of these deposits, the studied areas can be utilized for brick manufacturing, provided that the quantity and thickness of these deposits are adequately assessed.

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