Mineralogical , Crystal Structure and Chemical Composition Characterization of Iraqi Natural Rich-Bauxite Mineral Clays

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Abstract
This study provides the mineralogical and compositional characterization of locally natural mineral clay deposits of Iraq which have been converted from hydrated aluminum silicate as their parents, grafted and enclosing rocks. The mineral assemblage of the raw clays of these primary deposits has been determined to include disordered bauxite , boehmite, quartz , gibbsite, calcite, in addition to trace amounts of other mineral clays like hematite and anatase. Such results have been investigated using powder x-ray diffraction, x-ray fluorescence, thermo gravimetric analysis, differential thermal analysis, infrared spectroscopy, and technical chemical analysis. Crystal structure and chemical composition of this bauxite rich mineral clays also have been performed to attribute that influence the industrial usage of Iraqi natural mineral clays are highlighted.

Introduction:
Mineral clays are the interest material to deal with and the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with limited amount of water, among of these materials are hydrated aluminum silicates. They are very stable during catalytic treatment processes. They have surface endowed with weakly acidic and basic sites. The catalyst is able to maintain a high specific surface area up to about look, if transition metals ions are present[1]. They are prepared by adding small amount of the active materials especially metal oxides to the surface of the porous solid support. The most important solid supports are alumina oxides, silica gel, MgO, TiO_2, ZrO_2, aluminum silicates, zeolite, activated carbon and ceramics [2] .

Fortunately such materials are occurred naturally in massive quantities in the world and especially in several cities 0f Iraq [3] .As a result of that, application of Iraqi raw minerals in petroleum refining was the interest of many workers, and recently, the natural Iraqi mineral clays have been investigated and applied in petroleum fractionation[4] . Accordingly, and in continuation of investigating the chemical composition and structural properties of Iraqi raw materials, the present study is considered. It deal with bauxite – rich mineral clays naturally occurring around Al-Anbar governorate / Iraq .

Experimental :
A- Sources and collections of samples :
Natural minerals clay, obtained from area around Al-Hussainiat area at Al- Anbar governorate / Iraq, were purified from carbonate and bicarbonate compounds chemically by 25% HCl and used as a natural clay samples. These samples were pale yellow in color have (120-150 mesh ASTM). Individual samples weighed from 1.0 to 3.0 kg ; and were thoroughly mixed before their coning and quartering to obtain representative samples. At each sampling site, parent rock, samples were also collected. For x-ray diffraction analysis and bulk mineralogy, the raw sample was powdered by agate mortar and agate tama mill.

B- Methods of study :
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The identification of clay minerals and their alteration products was carried out by the power diffraction method, which carried out using Phillips x-ray diffraction equipment model pw /1710 with monochromatic, Cu-radiation (λ=1.54178 A^o) at 40 k.v, 35 m.A. and scanning speed 0.02 ^{o}/sec. were used. The reflection peaks between $2\theta = 2^o$ and 60 ^{o}, corresponding spacing (d, A^o) and relative intensities (I / I^o) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files. Meanwhile x-ray fluorescence spectrophotometer was employed for natural clays on Phillips / PW 2404 analysis and the absorption spectra were recorded on FTIR 4100 JASCO spectrophotometer using KBr disk [5] .

The thermal analysis was by means of Schimadzu DTA-50H , and TGA-50H. Each powdered sample was heated by 10 ^{o} C /min. up to 1100^o C with α-Al_2O_3 as a reference material. Temperature, weight change in wt., and the thermal behavior of the sample is recorded on the chart.

The above technical studies were performed at ministry of petroleum, the Egyptian mineral resources authority, central laboratory sector/ Egypt.

Results & Discussion:
A. Chemical analysis : -
The results of chemical analysis provide information on the mineralogical composition of the samples, both on the amount of the primary mineral and on amount and nature of any other minerals present in the sample. However, such interpretation of the chemical analysis requires additional information, primarily crystallographic information from x-ray analysis. Further clues are provided by the results of dissolution experiments, thermal analysis and spectral analysis. Chemical analysis of the suite of clay samples were performed by means of x-ray fluorescence and traditional chemical analysis techniques, like atomic absorption spectra and flame photometry and shown in Table (1). It seems that natural samples compose of different oxides most of them related to mineral rocks and clays suggested to be used as absorbent catalysts like silica, alumina, iron oxide, calcium, magnesium and potassium oxides [6]

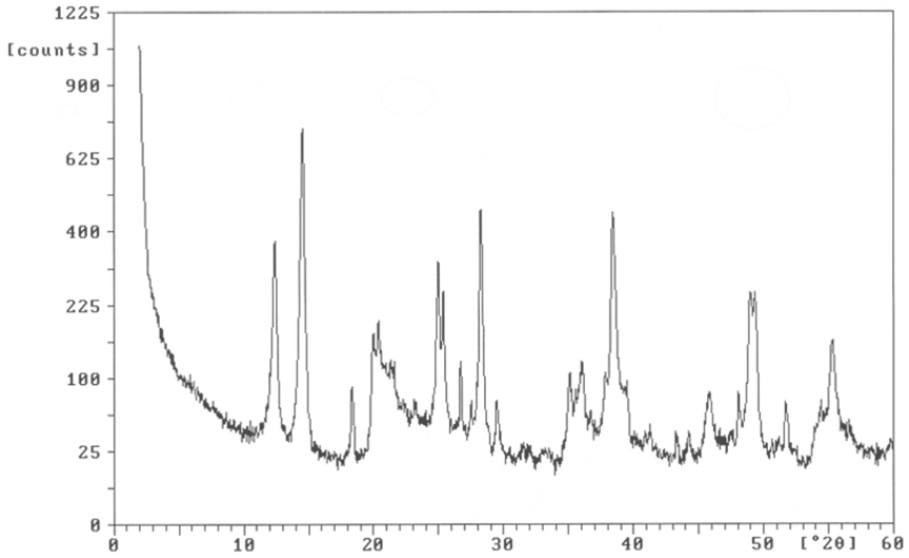
Table(1): Chemical composition of natural clay sample

$\%SiO_2$	$\%Al_2O_3$	%MgO	%CaO	$\%Na_2O$	$\%K_2O$	$\%Fe_2O_3$	$\%TiO_2$	$\%SO_3$	LOI
25.30	49.41	0.60	5.95	3.55	0.70	1.20	4.09	1.20	5.33

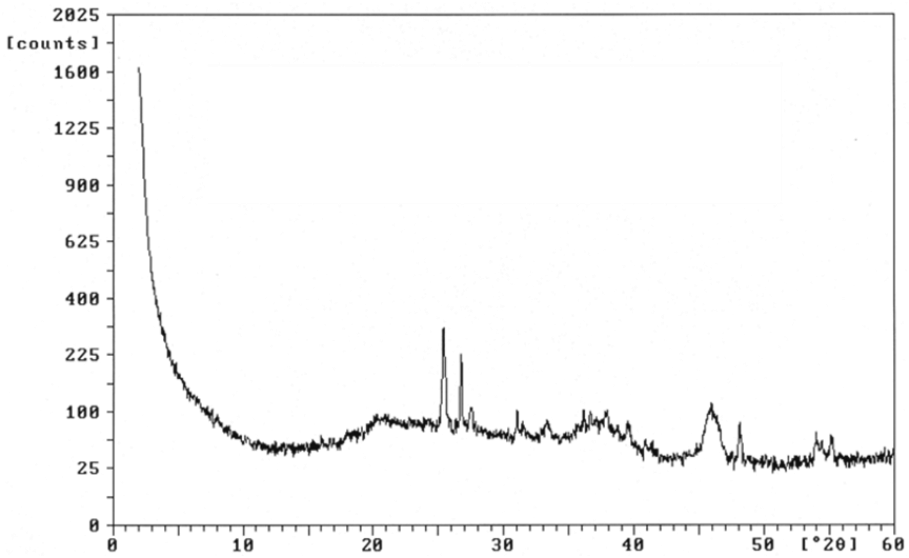
B. Structural investigation :

The mineralogy of sedimentary clays and rocks and their related compounds may be determined on the bases of x-ray diffraction, x-ray fluorescence, dehydration characteristics, thermal analysis, infrared absorption …… etc [7]. Many rock and clay materials are composed of more than one mineral, and the minerals may be mixed in several ways. It is well known that careful x-ray diffraction studies reveals the presence of mixed layer structures and frequently indicate the nature and the relative abundance of the units that are mixed.

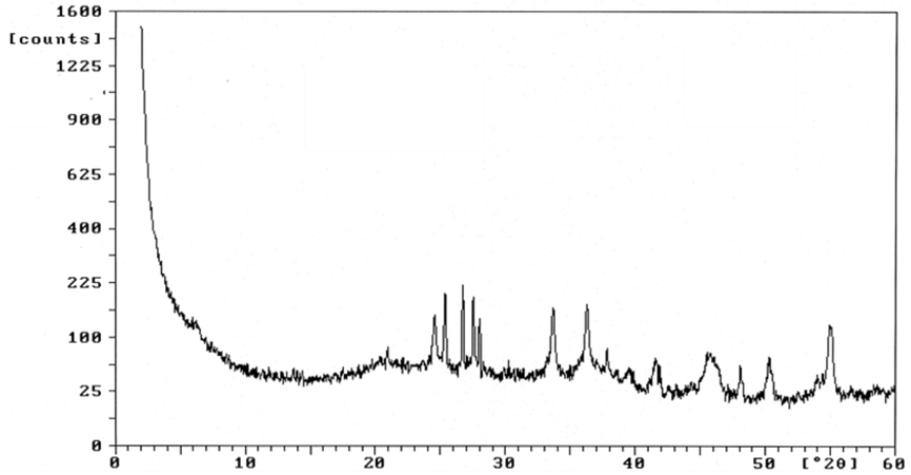
Accordingly, such technique has been applied for the bauxite clay samples under investigation . Powder x-ray diffraction patterns ,which include in addition to natural bauxite ,the sample which has been heated to 700°C and that which has been doped with chromium oxides and heated to 550°C ,are shown in Figures(1-3).



Figure(1): Powder x-ray diffraction pattern of natural clay sample



Figure(2): Powder x-ray diffraction pattern of clay sample heated to 700° C



Figure(3): Powder x-ray diffraction pattern of doped clay sample heated to 550^{o} C

Powder x-ray diffraction patterns of these three samples reflect the presence of the minerals reported in Table(2).

Table(2): Mineral clays percentage from XRD analysis in the clay samples

Natural Bauxite		**Natural Bauxite heated to ^{o}700**		**Graft Bauxite heated to ^{o}550**	
Minerals	**%**	**Minerals**	**%**	**Minerals**	**%**
Boehmite AlO(OH)	Major	Quartz SiO_2	Major	Eskolite Cr_2O_3	Major
Kaolinite $Al_2Si_2O_5(OH)_4$	Minor	Anatase TiO_2	Minor	Quartz SiO_2	Major
Calcite $CaCO_3$	Trace	Dolomite $CaMg(CO_3)_2$	Minor	Boehmite AlO(OH)	Minor
Gibbsite $Al(OH)_3$	Trace	-----	-----	-----	-----

Such mixed units of clay minerals identified by their clearly first highest peaks. Meanwhile, other trace minerals like haloysite ,anatase , rutile , quartz ,dolomite ,hematite , kaolinite proposed to be present but through their minor reflection peaks[8] . Inter planar spacing of the above major mixed unites of clay minerals are presented in Tables(3-5).

Moreover, it is of interest that powder x-ray diffraction might be used to calculate the percentage values of the above relative minerals [9] . From the calculated area under the highest peak of each mineral, it is clear that boehmite presents as 42.3% of the investigated clay sample dropped to 30% when such sample heated to 550 ^{o}C and disappeared on heating the sample to 700 ^{o}C .This result indicate the transforming of both mineral to α –Al_2O_3 in the range of (540-580 ^{o}C) .Other minerals like crystalline silica and anatase appeared on heating the clay sample to certain temperature and reflect the perfect crystallanity of these minerals on calcinations . Meanwhile, other minerals appear to be present in different percentages .

It is obvious that rocks and clays are porous in character and should held water molecules as a hydration and geometrical water. Both TG & DTA were used to determine the purity level and to help identify contaminants or impurities.TG analysis allowed quantitative estimation of the clay minerals present in the sample of the art methods[10] . Determination of loss on ignition (LOI) provided an approximate across check on the TG figures. Therefore, TG & DTA were employed to study the hydration phenomenon and the results were presented in Figures (4 & 5).

Table (3); Interplanar spacings for contributing phases in natural clay sample

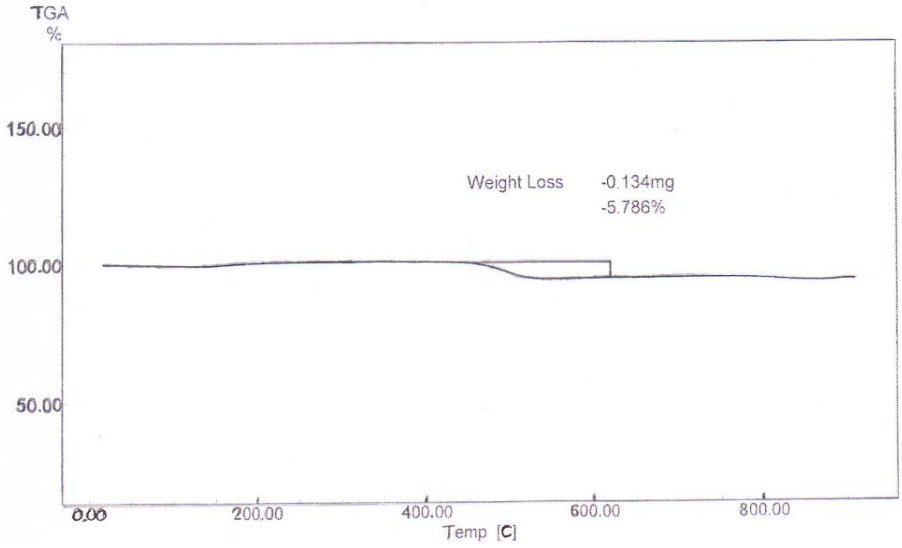
Crystalline phase	hkl	2θ°	d values (A^O)	peak width (1/2 2θ)	Peak int. (counts)
Kaolinite	001	12.4	7.124	0.100	217
Boehmite	020	14.5	6.08	0.180	671
Gibbsite	002	18.3	4.842	0.100	62
Hallosite	11-,02-	20.0	4.445	0.180	142
Gibbsite	100	20.3	4.361	0.060	193
Kaolinite	111	21.4	4.144	0.400	90
Kaolinite	021	23.1	3.843	0.200	48
Kaolinite,Anatase	002,101	24.9	3.568	0.100	303
Anatase,Kaolinite	101,002	25.3	3.514	0.120	225
Quartz	101	26.6	3.344	0.120	112
Rutile	110	27.5	3.247	0.120	50
Boehmite	120	28.5	3.160	0.100	445
Calcite	104	29.4	3.036	0.100	49
Dolomite	104	31.9	2.807	0.800	9
Hematite	104	33.2	2.701	0.640	6
Hallosite	13-	35.0	2.561	0.240	88
Kaolinite, Calcite	131,110	36.1	2.491	0.320	92
Gibbsite	021	36.7	2.452	0.200	40
Boehmite	140	38.4	2.348	0.100	416
Calcite	202	43.3	2.091	0.240	17
Anatase	200	48.1	1.895	0.160	59
Boehmite	051	48.9	1.864	0.140	222
Boehmite	200	49.3	1.848	0.240	207
Kaolinite	004	51.6	1.772	0.160	49
Kaolinite	241	54.3	1.689	0.240	42

Table(4); Interplanar spacings for contributing phases in clay sample heated to 700°C

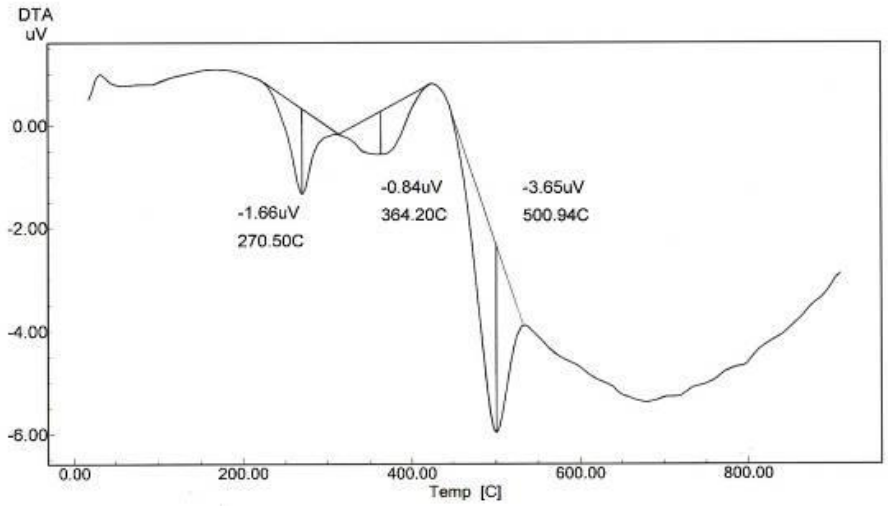
Crystalline Phase	**hkl**	**2Θ**	**d Value A^o**	**Peak Width ½ 2Θ**	**Peak int. (counts)**	**I / I_1**
Anatase	101	25.3	3.515	0.160	234	100
Quartz	101	26.7	3.341	0.080	204	87.4
Rutile	110	27.5	3.242	0.160	40	17.0
Dolomite	104	31.04	2.888	0.120	40	17.0
Hematite	104	33.3	2.691	0.320	25	10.7
Kaolinite	131	36.1	2.488	0.120	50	21.5
Quartz	110	36.6	2.456	0.120	52	22.1
Anatase, Kaolinite	004,003	37.8	2.380	0.240	49	20.9
Quartz	102	39.8	2.281	0.320	32	13.9
Kaolinite	203,132	45.8	1.983	0.560	66	28.0
Calcite	108	47.5	1.915	0.240	6	2.7
Anatase	200	48.09	1.895	0.060	53	22.8
Dolomite	009	53.9	1.701	0.240	34	14.4
Anatase	211	55.09	1.669	0.240	29	12.5

Table (5); Interplanar spacings for contributing phases in doped clay sample heated to 550° C

Crystalline Phase	hkl	2Θ	d-Value A°	Peak Width ½ 2Θ	Peak int. (counts)	I / I_1
Montmorillonite	001	6.3	13.940	0.480	13	5.8
Quartz	100	20.9	4.252	0.120	28	12.7
Eskolaite	012	24.5	3.629	0.160	85	38.1
Anatase,Kaolinite	101,002	25.3	3.515	0.140	164	73.8
Quartz	101	26.7	3.343	0.120	222	100
Rutile	110	27.5	3.248	0.120	149	67.0
Boehmite	120	28.0	3.191	0.140	90	40.7
Eskolaite	104	33.7	2.661	0.160	119	53.5
Eskolaite	110	36.2	2.480	0.200	135	60.6
Anatase,Kaolinite	004,003	37.8	2.382	0.120	48	21.4
Quartz	102	39.5	2.284	0.400	18	8.3
Eskolaite	113	41.6	2.172	0.120	38	17.3
Kaolinite	203,132	45.4	1.997	0.400	44	19.6
Anatase	200	48.0	1.895	0.120	31	14.1
Eskolaite	024	50.2	1.818	0.120	45	20.2
Anatase	211	54.8	1.675	0.120	96	43.3
Boehmite	151	55.0	1.669	0.160	92	41.5
Eskolaite	122	58.6	1.577	0.640	7	3.0



Figure(4): TG curves of clay sample



Figure(5): DTA curves of clay sample

In general and in referring to the literature [11] ,it appears that TG and endothermic DTA peaks at approximately 170^{o} C correspond to the removal of the absorbed water in the bauxite mineral sample which present in the investigated clays. Therefore, it looks to represent the hydration phenomenon

which is usually occurred in the range (130-170 ^{o}C) .Moreover, it is obvious that there are two endothermic peaks at 270 and 364 ^{o}C related to the change of gibbsite to boehmite mineral. Finally ,it looks that 4th TG and DTA curves at 500 ^{o}C might represent the transformation of boehmite to α –Al_2O_3 material [12] .

Finally , it is of interest to investigate both, the migration and elimination of the held water molecules in addition to the mineralogy of the clay sample under investigation by infrared absorption technique Therefore, a range of 400-4000 cm^{-1} in frequency was applied and the spectra revealed several absorption bands including those at 1080 and 790 cm^{-1} which are attributed to the Si-O stretching and bending vibrations [13] . Moreover, the absorption bands located at 429 and 474 cm^{-1} are definitely characteristic of Al-O and Fe-O absorptions respectively , whereas the absorption bands at 1431 and 876 cm $^{-1}$ are attributed to stretching and bending of – CO_3 group which were shown before treatment of the sample and disappear after the acidic treatment. Also there is absorption bands at 1636 cm $^{-1}$ and in the range 3440-3687 cm^{-1} which are related to the structural (OH) group. Such absorptions show a significance variance in the position and sharpness of the vibration up on heating the samples in the range of 120-550 ^{o} C, which is related to the dehydration phenomena [14].

Conclusions:

The mineralogical attributes of Iraqi natural mineral clay deposits studied by XRD, XRF, TG, DTA, IR and traditional chemical techniques corroborate the presence of platy disordered boehmite ,gibbsite , quartz, and calcite . There is general increase of boehmite mineral in some fractions as shown by XRD analysis that gave content of 42.3%. Such deposits appeared to be important for industrial uses, chemical bleaching may be required to remove the unwanted minerals in addition to the thermal activation.

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دراسة التركيب المعدني والبلوري والتكوين الكيميائي للاطيان العراقية الطبيعية الغنية بمعدن البوكسايت

رجب عود بكر ، موفق خزعل الراشدي ، عمر موسى رمضان

قسم الكيمياء ، كلية التربية ، جامعة الموصل ، الموصل ، العراق

(تاريخ الاستلام: 4 / 10 / 2011 ---- **تاريخ القبول:** 2 / 4 / 2012)

الملخص :

تبين هذه الدراسة الخصائص المعدنية والتركيبية لرواسب من معادن طينية طبيعية محلية من العراق مشتقة من صخور المصدر والتي هي اطيان سيليكات الالمنيوم المائية حدث لها تعرية جوية مع مرور الزمن فضلا عن الاطيان المطعمة وذات العلاقة. وقد تم تحديد التركيب المعدني لهذه الرواسب الأولية لتشمل البوكسايت ، والبوهيمايت ،والكوارتز ، والجيبسايت ، والكالسايت فضلا عن كميات قليلة من معادن طينية أخرى مثل الهيميتايت والاناتيس. تم الحصول على هذه النتائج باستخدام تقنيات حيود الأشعة السينية للمسحوق وفلورة الأشعة السينية والتحاليل الحرارية الوزنية والتفاضلية وطيف الأشعة تحت الحمراء فضلا عن آليات التحاليل الكيميائية التقليدية. ان الصفات التركيبية البلورية والمكونات الكيميائية لهذه المعادن والتي تم دراستها أيضا سلطت الأضواء على احتواء هذه الرواسب على كميات كبيرة من معدن البوكسايت وبالتالي إلى أهمية مثل هذه الرواسب في المجالات الصناعية.