# Indirect Evaluation of Chemical Composition in Illite/ Smectite Interstratification and its Application in Paleoenvironment of Deposition

**Faraj H. Tobia**
*S.E. of Geological Survey and*
*Mining( GEOSURV)*
*Baghdad*

**Khalid J. Aswad**
*Department of Geology*
*College of Science*
*Mosul University*

(Received 18/6/2006 , Accepted 15/7/2007)

## ABSTRACT

A total number of 22 samples representing the Jurassic Formations (Hussainiyat, Amij and Muhaiwir) from the clastic units were collected and used for mineralogical studies.

X-ray diffraction studies have proved that kaolinite is the dominant clay mineral, the mixed layer illite/ smectite is randomly interstratified and rich in K-poor illite. Based on x-ray pattern decomposition of 001 reflection in conjunction with the chemical analysis of the clay fractions, it has been found that there is a difference in K replacement by $H_2O$ between illite of the southern parts, having the formula of $[H_2O_{1.2}K_{0.3}Al_4(Al_{0.3}Si_{7.7})O_{20}(OH)_4]$, and the illite of the northern parts $[H_2O_{0.9}K_{0.6}Al_4(Al_{0.6}Si_{7.4})O_{20}(OH)_4]$.

Based on illite/ smectite composition there is a variation in pH of the deposi-tional environments and the intense weathering between northern and southern parts of the Formations. The variations have been deduced from the clay mineral assemblages.

---

# التقييم غير المباشر للتركيب الكيميائي في الالايت/ السمكتايت متداخل الطبقات وتطبيقاته في بيئة الترسيب

**فرج حبيب طوبيا**
*الشركة العامة للمسح*
*الجيولوجي والتعدين*
*بغداد*

**خالد جلال اسود**
*قسم علوم الأرض*
*كلية العلوم*
*جامعة الموصل*

## الملخص

تم جمع ٢٢عينة حاوية على الأطيان ممثلة لتكاوين النظام الجوراسي (حسينيات وعامج ومحيور) من الوحدات الفتاتية بغية دراستها من الناحية المعدنية.

اثبتت دراسات حيود الاشعة السينية ان الكاولينايت هو المعدن الطيني السائد، وان معدن الالايت/ السمكتايت متداخل الطبقات ذات تداخل عشوائي (randomly stratified) وغني بمعدن الالايت الفقير بالبوتاسيوم. استناداً الى تفسير انماط الاشعة السينية للانعكاس ٠٠١ وبالارتباط مع التحليل الكيميائي للاجزاء الطينية، وجد انه هناك اختلاف في كمية البوتاسيوم الذي يحل محل الماء بين الالايت في الاجزاء الجنوبية للتكاوين التي لها الصيغة [$H_2O_{1.2}K_{0.3}Al_4(Al_{0.3}Si_{7.7})O_{20}(OH)_4$] وبين الالايت في الاجزاء الشمالية للتكاوين ذات الصيغة [$H_2O_{0.9}K_{0.6}Al_4(Al_{0.6}Si_{7.4})O_{20}(OH)_4$].

استناداً الى وجود الاختلاف في تركيب الالايت/ السمكتايت هناك تباين في قيم الأس الهيدروجيني لبيئات الترسيب وفي شدة التجوية بين الاجزاء الشمالية والجنوبية للتكاوين المدروسة، كذلك تم استنتاج هذه الاختلافات من تجمعات المعادن الطينية.

## INTRODUCTION

The Jurassic System (Hussainiyat, Amij, Muhaiwir and Najmah Formations) in western desert of Iraq (Figure 1) is characterized by the alternations of clastic (lower parts) and carbonate (upper parts) units. Generally, the clastic units are composed of claystone and sandstone with intercalation of carbonate facies (marl, clayey limestone…etc.) especially in the northern parts of Amij and Muhaiwir Formations and with ironstone especially in Hussainiyat Formation (Al-Mubarak and Amin, 1983; Jassim *et al.*, 1984, 1986; Al-Naqib *et al.*, 1986; Al-Sengary, 1987; Ismail, 1996; Tobia, 2005).

It is evident from a recent study (Tobia, 2005) that there is a variation in the depositional environment of the northern from the southern parts of the Hussainiyat, Amij and Muhaiwir Formations, due to the variation in pH and Eh and also the more effect of the sea water on the northern part. The variation has been deduced from mineral chemistry and its assemblages.

As the chemistry of the clay minerals is very sensitive to the environmental changes (from weathering and transportation to the deposition), the current study focused on the clay fractions of the clastic units of above mentioned Formations. The clastic units are composed mainly of kaolinite with illitic clays. However, the illitic clays are usually mixed layer with the illite making up to 80% of the clay layer with the smectite making the rest. Aja and Rosenberg (1992) have suggested that the illite/ smectites have four distinct compositions: $K_{0.29}/O_{10}(OH)_{2\ (S)}$, $K_{0.5}/O_{10}(OH)_{2\ (IS)}$, $K_{0.69}/O_{10}(OH)_{2\ (ISII)}$ and $K_{0.85}/O_{10}(OH)_{2\ (I)}$ with the illite- rich forms being more stable at elevated temperatures. There are many difficulties for the direct evaluation of the composition of illite interstratifications, and in order to overcome these difficulties an indirect evaluation is carried out. The aim of this study, however, is to relate the K for $H_2O$ substitution, and to extrapolate the pH conditions.

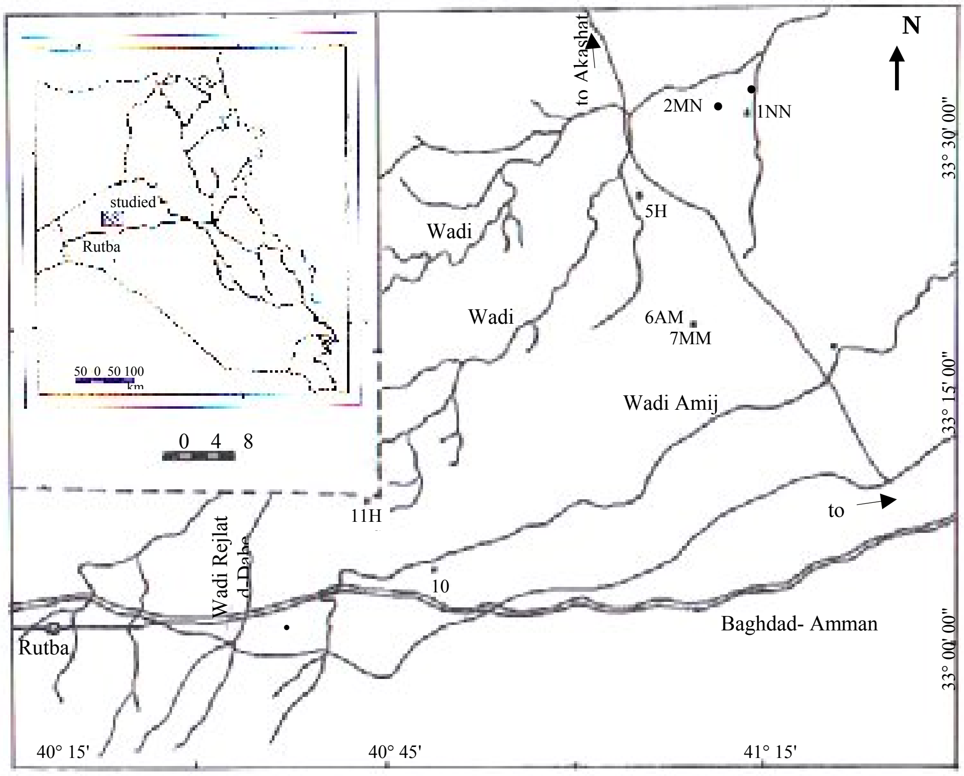


Fig. 1: Location of study area. Enlarged map showing positions of the sections and boreholes.

## Materials and Methods

100g of each studied sample (22 samples from 7 sections and 2 bore-holes) were grounded in a porcelain mortar. The clay fractions (<2µm) and bulk samples were analyzed for K contents using a Flame Photometer 410 of Sherwood Company. The clay fraction was separated by pipette method described by Folk (1974). The suspensions of these fractions were dried on glass slides. The clay samples in oriented mounts were run under three separate conditions: air dried, ethylene glycol treatment and heating to 550°C for 1 hour. X-ray diffraction patterns of oriented aggregates were examined by Philips PW 1410 Spectrophotometer, equipped with a monochromatic CuKα radiation at 40kV and 20mA.

The peaks of the clay minerals were identified, and the layer sequence of illite/ smectite interstratification was quantified by using the curves developed by Tomita and Takahashi (1985) based on intersecting d-values of illite/ smectite for 001and 002 reflections. The intersection point represents $P_{SI}$ (y-axis) and $P_{IS}$ (x-axis). $P_{SI}$ is probability that an illite layer succeeds smectite layer where the first layer is smectite; $P_{IS}$ is probability that a smectite layer succeeds an illite layer where the first layer is illite.

From the $P_{SI}$ and $P_{IS}$, the probability of illite layer $P_I$ and the probability of smectite layer $P_S$ follow the following equations ( Brindley and Brown, 1980) and thus could be drawn:

$$P_I + P_S = 1$$
$$P_{II} + P_{IS} = 1$$
$$P_{SS} + P_{SI} = 1$$
$$P_{IS} = P_S P_{SI} / P_I$$

## RESULTS AND DISCUSSION

X-ray diffractograms of separated clay fraction (<2µm) of some selected claystone samples are shown in Figure 2. Mineralogically, the study shows that kaolinite is the dominant mineral in clay fractions. The illite/ smectite mixed layers (randomly interstratified structures) with non-integral peaks at positions intermediate between the peaks from the individual mineral layers, are lesser extending in Hussainiyat, Amij and Muhaiwir and absent in Najmah Formation. The other clay minerals are in minor amounts, these are palygorskite which is limited in the northern parts of Amij and Muhaiwir and chlorite in Amij but in lesser amount in Najmah.

The percentage of each clay mineral was calculated (Table 2) using area under curve of the diffractogram peaks and the probability junction.

The proportion of illite (in illite/ smectite interstratification) varies between 73.9% in the upper part of the southern section (Hussainiyat Formation) to 93.2% in the upper of the middle section (Amij Formation). Relative proportions of illite and smectite within the I/S phases show no clear trends with increasing depth and age (Table 2). This points to the possibility that the smectite to illite transformation did not occur in situ or the illite/ smectite interstratification is of model B, where, Stixrude and Peacor (1997) found two models of illite/ smectite interstratified clay mineral: model A views as stacking of layers identical to end member illite and smectite layers, implying discrete and independently formed unit, whereas model B views the clays as composed of crystallites with a unique structure that maintains coherently over much greater distances. The total energy of the model B is 2.3 kJ atom$^{-1}$mol$^{-1}$ lower than that of model A. The latter has less stability; however, this energy difference can be traced to structural distortions in model A due to local charge imbalance. Hence, the studied illite/ smectite interstratifications of model B, is the more stable one.

Figure 3 shows the dispersive relationship between the illite% and K content; the existence of molecular water ($H_2O$) which occupies unfilled interlayer positions, is partially responsible for weakening and dispersion of the statistical correlation between illite% and K content in the studied clay fraction.

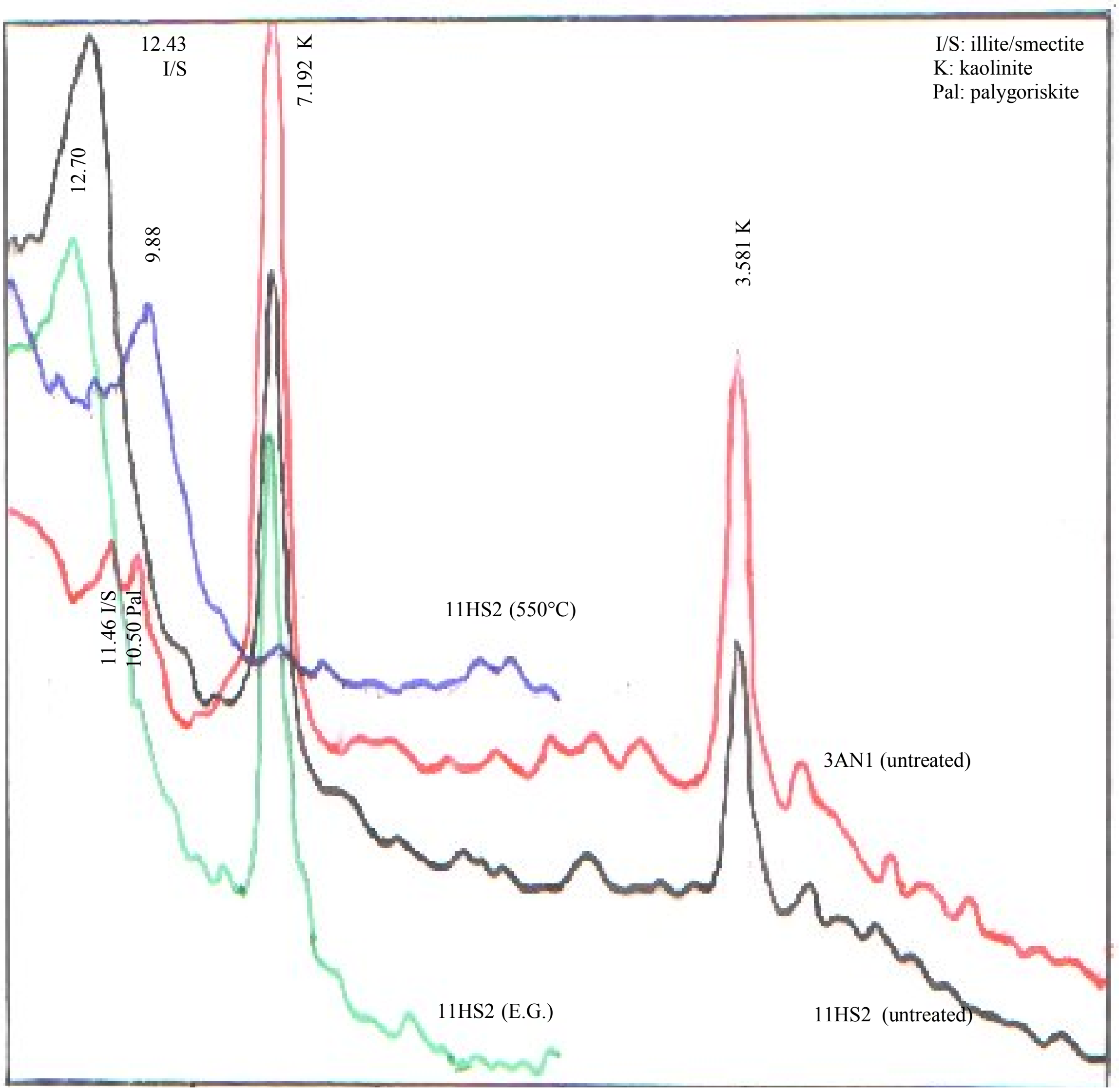


Fig. 2: X-ray diffractograms of separated clay fraction (<2µm) of some selected samples from the clastic units of Jurassic System/ Iraqi western desert.

Brown and Norrish (1952) suggested that the deficiency of $K^+$ ions is partly the result of $H_2O^+$ substitution in the interlayer region. However, Hower and Mowatt (1966, cited in Brindley and Brown, 1980) concluded that the excess $H_2O^+$ in illite is present as neutral $H_2O$ trapped in non-expandable layers. Interstratification of illite with smectite layers will decrease the average number of interlayer cations and increase the water content. The high value of $H_2O$ in excess of that required for the hydroxyl ions $[O_{10}(OH)_2]$ is surface sorbed water, either physically or chemically sorbed by so called broken bonds, and/ or as molecular water occupying interlayer positions not filled by $K^+$ and equivalent ions (Brindley and Brown, 1980).

Table 1: The probability of succession of illite and smectite layers and the frequency of occurrence of illite and smectite layers of selected claystones and calcareous claystones of Iraqi western desert.

| Sample no. | $P_{IS}$ | $P_{SI}$ | $P_S$ | $P_I$ | Sample no. | $P_{IS}$ | $P_{SI}$ | $P_S$ | $P_I$ |
|---|---|---|---|---|---|---|---|---|---|
| **2MN2** | ٠.٠٧٨ | ٠.٨٠٨ | ٠.٠٨٨ | ٠.٩١٢ | **6AM9** | ٠.١٢١ | ٠.٩٨٣ | ٠.١١٠ | 0.890 |
| **2MN3** | ٠.١٢١ | ٠.٩٥٩ | ٠.١١٢ | ٠.٨٨٨ | **10AS1** | ٠.٠٧٩ | ٠.٨٠٠ | ٠.٠٩٠ | ٠.٩١٠ |
| **7MM3** | ٠.٢٢١ | ٠.٩٦٣ | ٠.١٨٧ | ٠.٨١٣ | **10AS3** | ٠.١٥٠ | ٠.٨١٧ | ٠.١٥٥ | ٠.٨٤٥ |
| **3AN1** | ٠.١٥٠ | ١.٠٠٠ | ٠.١٣٠ | ٠.٨٧٠ | **10AS6** | ٠.١٤٢ | ٠.٩٥٨ | ٠.١٢٩ | ٠.٨٧١ |
| **3AN2** | ٠.١٤٢ | ٠.٩٨٢ | ٠.١٢٦ | ٠.٨٧٤ | **10AS8** | ٠.١٤٢ | ٠.٨٦٣ | ٠.١٤١ | ٠.٨٥٩ |
| **3AN4** | ٠.١١٠ | ١.٠٠٠ | ٠.١٠٠ | ٠.٩٠٠ | **5HN2** | ٠.١٣٠ | ٠.٩٧٣ | ٠.١١٨ | ٠.٨٢٢ |
| **6AM1** | ٠.١٨٨ | ٠.٧٨٨ | ٠.١٩٣ | ٠.٨٠٧ | **5HN3** | ٠.١٤٢ | ٠.٩١٨ | ٠.١٣٤ | ٠.٨٦٦ |
| **6AM4** | ٠.١٣٣ | ٠.٩٣٣ | ٠.١٢٥ | ٠.٨٧٥ | **11HS2** | ٠.٢٠٠ | ٠.٧٨٣ | ٠.٢٠٣ | ٠.٧٩٧ |
| **6AM5** | ٠.١٤٢ | ٠.٨٨٣ | ٠.١٣٩ | ٠.٨٦١ | **11HS6** | ٠.٢٨٣ | ٠.٨٠٠ | ٠.٢٦١ | ٠.٧٣٩ |
| **6AM6** | ٠.١٥٠ | ٠.٨٧٨ | ٠.١٤٦ | ٠.٨٥٤ | **1C/7** | ٠.٢٠٠ | ١.٠٠٠ | ٠.١٦٧ | ٠.٨٣٣ |
| **6AM8** | ٠.٠٥٨ | ٠.٨٠٠ | ٠.٠٦٨ | ٠.٩٣٢ | **124/2** | ٠.٢٤٠ | ١.٠٠٠ | ٠.١٩٤ | ٠.٨٠٦ |

$P_{IS}$: probability that smectite layer succeeds illite layer, first layer is illite.
$P_{SI}$: probability that illite layer succeeds smectite layer, first layer is smectite.
$P_S$: frequency of occurrence of smectite layer.
$P_I$: frequency of occurrence of illite layer.

The illite: illite/smectite ratio with formula unit of K based on $K_n/O_{20}(OH)_4$ was plotted to determine the chemical formula of the illite and the $H_2O$ content that replaces K cations. It is obvious from Figure 4 that the mixed layer (I/S) in the southern parts for the studied Formations contains illite of higher $H_2O$ than the northern parts. The $K/H_2O$ ratio ranges from 1:9 to 3:7 in the southern parts; while, it is from 3:7 to 5:5 in the middle and northern parts, i.e. with an average chemical formula $[H_2O_{1.2}K_{0.3}Al_4(Al_{0.3}Si_{7.7})O_{20}(OH)_4]$ in the southern parts and $[H_2O_{0.9}K_{0.6}Al_4(Al_{0.6}Si_{7.4})O_{20}(OH)_4]$ in the northern parts, and as a short hand may be written as $K_{0.30}/O_{20}(OH)_4$ and $K_{0.6}/O_{20}(OH)_4$, respectively.

Table 2: Relative clay mineral abundance and $K_2O$ contents in bulk and clay fraction samples from clastic units of Jurassic System in Iraqi western desert.

| sample no. \ Wt% | kaolinite | illite/ smectite | illite (inters.) | smectite (inters.) | palygorskite | chlorite | $K_2O$ (bulk) | $K_2O$ (in clay) |
|---|---|---|---|---|---|---|---|---|
| **2MN2** | ٨٠ | ٢٠ | ١٨.٣ | ١.٧ | X | | ٠.٩١ | ١.٥٧ |
| **2MN3** | ٧٨.٤ | ٢١.٦ | ١٩.٢ | ٢.٤ | X | | ٠.٦٠ | ٣.٢٣ |
| **7MM3** | ٨٢.٢ | ١٧.٨ | ١٤.٥ | ٣.٣ | | | ٠.٩٠ | ٢.٢٢ |
| **3AN1** | ٨٤.٤ | ١٥.٦ | ١٣.٦ | ٢.٠ | X | | ٠.٥١ | ٣.٤٠ |
| **3AN2** | ٧٨.٥ | ٢١.٥ | ١٨.٨ | ٢.٧ | X | X | ٠.٨١ | ٣.٠٩ |
| **3AN4** | ٧٧.٢ | ٢٢.٨ | ٢٠.٥ | ٢.٣ | X | X | ٠.٨٤ | ١.٦٩ |
| **6AM1** | ٨٨.٦ | ١١.٤ | ٩.٢ | ٢.٢ | | | ١.٣٠ | ٢.٤٦ |
| **6AM4** | ٧٨.٩ | ٢١.١ | ١٨.٥ | ٢.٦ | | | ١.٤٢ | ٣.٠٤ |
| **6AM5** | ٨١.٣ | ١٨.٧ | ١٦.١ | ٢.٦ | | X | ٠.٩٢ | ٣.٢١ |
| **6AM6** | ٧٥.٩ | ٢٤.١ | ٢٠.٦ | ٣.٥ | | | ١.٢٦ | ٣.١١ |
| **6AM8** | ٧٢.٢ | ٢٧.٨ | ٢٥.٩ | ١.٩ | | | ٠.٦٧ | ٣.٣٥ |
| **6AM9** | ٨٤.٧ | ١٥.٣ | ١٣.٦ | ١.٧ | | X | ٠.٦١ | ٣.٢٥ |
| **10AS1** | ٨٨.٤ | ١١.٦ | ١٠.٦ | ١.٠ | | | ٠.٨٢ | ١.٦٢ |
| **10AS3** | ٨٥.٤ | ١٤.٦ | ١٢.٣ | ٢.٣ | | X | ٠.٦٨ | ١.٨١ |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **10AS6** | ٨٥.٤ | ١٤.٦ | ١٢.٧ | ١.٩ | | | ٠.٨١ | ١.٨١ |
| **10AS8** | ٧٨.٦ | ٢١.٤ | ١٨.٤ | ٣.٠ | | | ٠.٩١ | ١.٨٨ |
| **5HN2** | ٦٠.٠ | ٤٠.٠ | ٣٥.٣ | ٤.٦ | | | ١.٧٤ | ٣.٢١ |
| **5HN3** | ٦٧.٧ | ٣٢.٣ | ٢٨.٠ | ٤.٠ | | | ١.٣٨ | ٣.٢٨ |
| **11HS2** | ٣٧.٠ | ٦٣.٠ | ٥٠.٢ | ١٢.٨ | | | ٠.٨٥ | ١.٤٥ |
| **11HS6** | ٣٥.٧ | ٦٤.٣ | ٤٧.٥ | ١٦.٨ | | | ٠.٦٩ | ١.٥٧ |
| **1C/35/7** | ٥٠.٤ | ٤٩.٦ | ٤١.٣ | ٨.٣ | | | ٣.٥٠ | ٣.٥٠ |
| **124/24/2** | ٤٥.٥ | ٥٤.٥ | ٤٣.٩ | ١٠.٦ | | | ٣.٤٥ | ٠.٦٣ |

x: the mineral is present but in minor amounts (<5%).

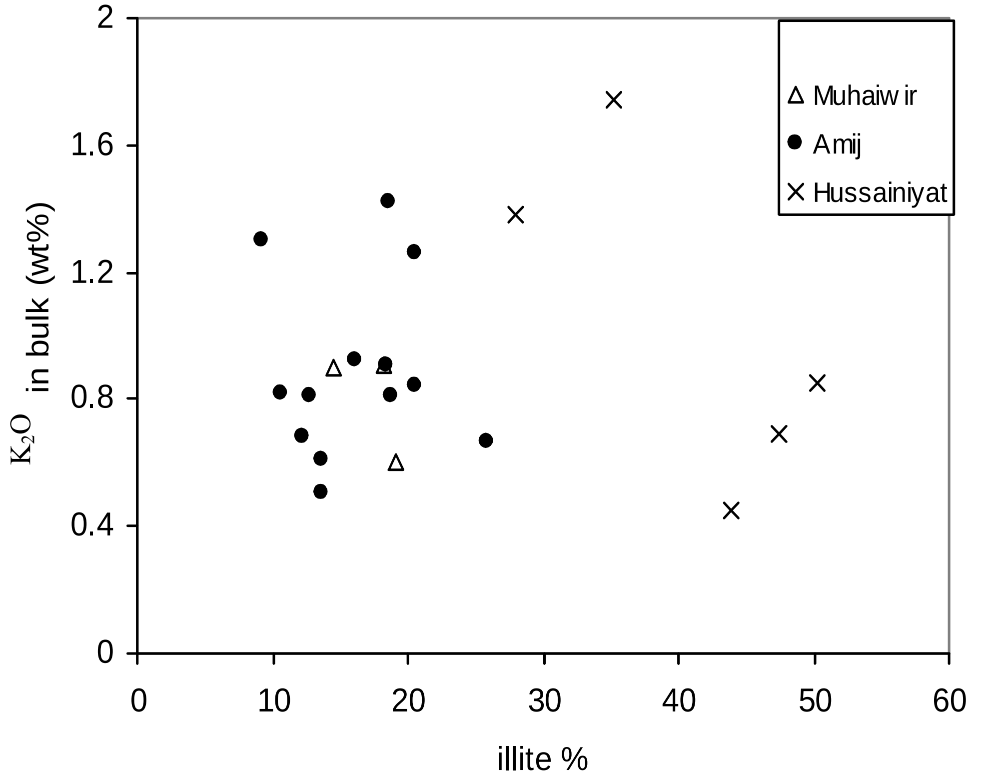


Fig. 3: The relationship of illite% (from XRD) vs. $K_2O$ weight percent (from chemical analysis) in the clay fractions (<2µm) of the clastic units of Jurassic System, Iraqi western desert.

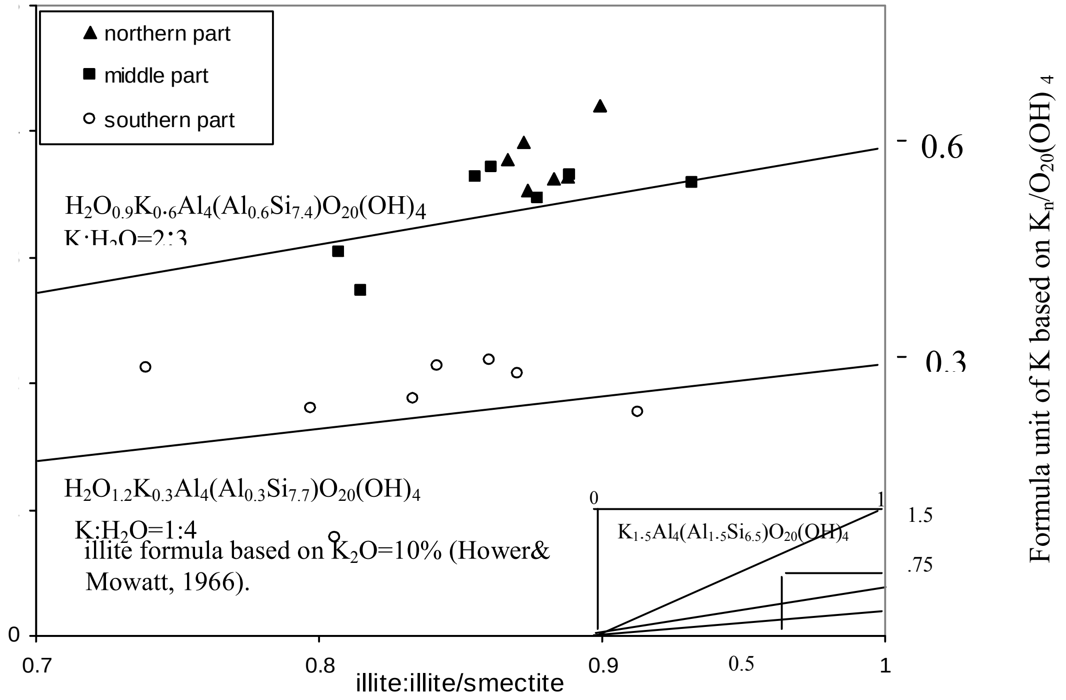
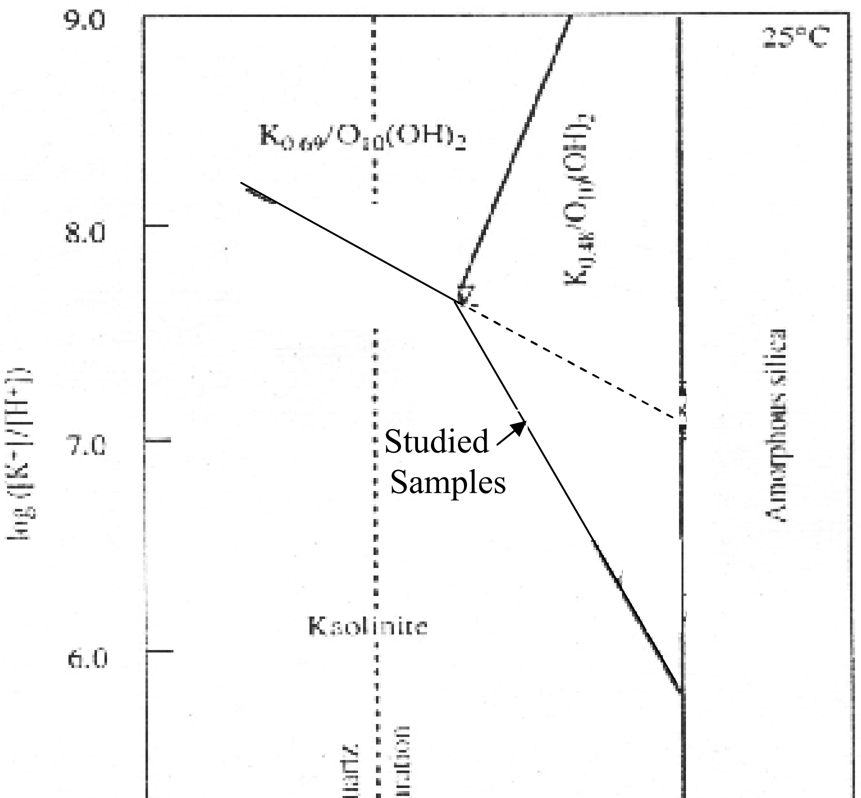


Fig. 4: Relationship between K and illite: illite/smectite in the clay fractions of clastic units of Jurassic System/ Iraqi western desert.

The suggested formula ($K_{0.30}/O_{20}(OH)_4$ and $K_{0.6}/O_{20}(OH)_4$) can be plotted on Figure 5 in order to extrapolate the pH of the media that deposited such clay minerals. It is clear that the $\log([K^+]/[H^+])$ has a range from about 6.0 to 7.5, therefore, the expected pH values in the southern and northern parts are nearly 6.7 and 8.2, respectively. This conclusion can be supported by the presence of palygorskite and dolomite in the northern parts that favors alkaline conditions; however, the former minerals are absent in the southern parts, at least in the clastic units.



## CONCLUSIONS

The mixed layer illite/ smectite in the studied samples is randomly inter- stratified and rich in illite. There is deficiency of $K^+$ ions which might be the result of $H_2O$ substitution in the interlayer. The difference of illite formula in the southern from northern parts was used to predict the paleoenvironment such as pH values.

## REFERENCES

Aja, S.U., and Rosenberg, P.E., 1992. The thermodynamic status of compositionally-variable clay minerals: A discussion, *Clays Clay Miner.*,Vol. 40, No.3, pp.292-299.

Aja, S.U., Rosenberg, P. E. and Kittrick, J.A., 1991a. Illite equilibria in solutions: I.Phase relationships in the system $K_2O$-$Al_2O_3$-$SiO_2$-$H_2O$ between 25 and 250°C, *Geochim. Cosmochim. Acta*, Vol.55, pp. 1353-1363.

Al-Mubarak, M. and Amin, R.M., 1983. Regional mapping of the eastern part of the western desert and the western part of south desert, part 1, *GEOSURV*, Iraq, (internal report).

Al-Naqib, S.Q., Kalaf, L.S., Yakta, S.A. and Taha, Y.M., 1986. Detail geological survey of Rutba-Kilo 160 area, *GEOSURV*, Iraq, (internal report).

Al-Sengary, A.A., 1987. Stratigraphic study of Jurassic rocks in Rutba area, *Unpub. Ph.D. Thesis*, University of Baghdad, 211p. (in Arabic).

Brindley, G.W. and Brown, G.,1980. Crystal structure of clay minerals and their X-ray identification, *Mineralogical Society Monograph*, No.5, London,495p.

Brown, G. and Norrish, K., 1952. Hydrous micas, *Miner. Magaz.*, Vol.29, pp.929-932.

Folk, R.L., 1974. Petrology of sedimentary rocks, *Hamphill Publ.Co.*,Texas, 182p.

Jassim, S.Z., Karim, S., Al-Mubarak, M., Basi, M. and Munir, J.,1984. The final report on the regional geological survey of Iraq, Vol.3, Stratigraphy, *GEOSURV*, Iraq, (internal report).

Ismail, S.A.,1996. Mineralogy and geochemistry of the clastic rocks of Amij Formation, Western Iraq, *Unpub. Ph.D. Thesis*, University of Baghdad, 120p. (in Arabic).

Langmuir, D., 1997. Aqueous environmental geochemistry, *Prentice Hall*, New Jersey, 600p.

Newman, A.C.D. and Brown, G.,1966. Chemical changes during the alteration of mica, *Clay Minerals*, 6, 297.

Stixrude, L. and Peacor, D.R.,2002. First-principle study of illite-smectite and implication for clay mineral systems, *Nature*, Vol.420, pp.165-168.

Tobia, F.H., 2005. Mineralogy and geochemistry of the clastics of Jurassic System in Iraqi western desert, *Unpub. Ph.D. Thesis*, University of Mosul, 220p. (in Arabic).

Tomita, K. and Takahashi, H.,1985. Curves for quantification of mica/smectite and chlorite/smectite interstratifications by X-ray powder diffraction, *Clays Clay Miner.,* Vol.33, No.5, pp.379-390.