Epigenetic Alunites In The Ga’ara Kaolinitic Mudrocks, In The Western Desert Of Iraq

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ABSTRACT

Epigenetic alunite occurs in the kaolinitic mudrocks of the Ga’ara Formation (Permocarboniferous) at the Ga’ara Depression, western desert of Iraq. The alunite occurs: at the contact between the mudrock horizons and the Quaternary slope sediments, in association with calcite and gypcrete, and along some kaolinitic mudrock layers found at shallow depths (few tens of metres). The alunite is milky white, fine and powdery in the form of isolated to subcontinuous nodules, or as white spots about one millimeter in diameter embedded in the mudrock layers. XRD studies and chemical analysis revealed that kaolinite is the main clay mineral constituent in the host rocks as well as in the alunitic mudrocks. Illite and/or mixed-layer illite-smectite are present as traces except in one locality where illite is present in the host rock in significant amount. Non-clay constituents are also minor such as quartz, goethite, anatase and secondary gypsum. SEM studies revealed two varieties of alunite based on shape namely rhombic and acicular. The rhombic variety is more frequent and is likely to be K-alunite as the K$_2$O:Na$_2$O ratio in the alunitic claystone ranges from 2.8 to 7.1:1 (mean 4.9:1). Alunization took place by groundwater activity as a result of the reaction of dilute sulphate solution with clay minerals during the Quaternary with no evidence of sulphuric acid.

INTRODUCTION

Alunite is aluminium sulphate group containing hydroxyl of K, Na, NH$_4$, H$_2$O or Ca in their structure giving rise to several mineral species, namely alunite, natroalunite, ammonioalunite and schlossmacherite respectively (Novak, F., J. Jansa and I. Prachař, 1994; Jambor, J.L., 1999). The large cations form an isomorphous series, of which alunite KAl$_7$(SO$_4$)$_3$(OH)$_$_$_2$ is the most common in nature (Brophy, G.P., et al., 1962; Parker, R.L., 1962). Sizeable deposits are becoming economically considered as a new raw material for the production of alumina, sulphuric acid, coagulants and aluminium chlorides (Cherkasov, G.N., 1989).

Two genetic types of alunite are known hydrothermal or sedimentary. The former occur as a product of hydrothermal alteration of volcanic rocks (Cherkasov, G.N., 1989; Lombardi, G. and S.M.F. Sheppard, 1977) whereas the latter is either a diagenetic product (Goldbery, R., 1978; Goldbery, R., 1980; Rouchy, J.M. and C. Pierre, 1987; Khalaf, F.I., 1990) or epigenetic (King, D., 1953; Keller, W.D., et al., 1967; Ross, C.S., et al., 1968; Aswad, K.J., et al., 1995). So far, in all cases, alunite of both origins is formed by the reaction of sulphuric acid (generated by the oxidation of H$_2$S or metallic sulphides) with Al-minerals. In the present case there is no evidence of sulphuric acid source or H$_2$S and the metallic sulphides are very limited in there occurrences.

Adams and Hajek (1978) carried out a set of solution experiments in which crystalline alunite was precipitated from dilute solutions of various concentrations of sulphate and potassium at different pHs and aging of precipitates at 50°C for 18 weeks. Gypsum was present in some precipitates. They found that alunite was the dominant mineral in the precipitate even with K/Al mole ratio of 0.1. Their experiments revealed that K ions in the aging solution were highly effective in transforming amorphous basaluminite into crystalline alunite even with as little as 0.01 M K in solution.

Lopez-Aguayo and co-workers (1977) presented data on stability of alunite and jarosite showing that there precipitation is governed by pH of their corresponding hydroxide and alunite forms at higher pH values. They also concluded that the main factors controlling the equilibrium relations of the different phases in the K$_2$O-Al$_2$O$_3$-SiO$_2$-SO$_3$-H$_2$O system are: temperature, pH, [K$^+$] and [SO$_4^{2-}$].
This study presents a new occurrence of alunite associated with some Permocarboniferous kaolinitic mudrocks. In addition to field occurrence and mineralogy, the origin of the alunite is discussed. A new mechanism is proposed here to explain the genesis of alunite without sulphuric acid.

**Geological Setting:**

Alunite is found in the Ga’ara depression associated with mudrocks of the Ga’ara Formation (Permocarboniferous). The Ga’ara depression is an erosional depression located about 50 kilometres north of Rutba Town in the Western Desert of Iraq (Fig. 1). The depression is part of the Rutbah Uplift and falls within the Arabian platform.

The strata exposed on the southern rim of the depression and its floor constitutes the oldest exposed lithostratigraphic unit (Permocarboniferous and Upper Triassic successions). They dip very gently south-southeastwards (Fig. 2) and were first affected by the Late Kimmerian orogeny (Tamar-Agha, M.Y., et al., 1997). On the other hand the strata cropping out on the northern, eastern and western rims of the depression are younger (Upper Cretaceous-Paleogene). They overlie the older strata with angular unconformity and dip very gently northwards.

The age of the Ga’ara Formation, extends from Late Carboniferous to Early Permian (Ctyroky, P., 1973; Nader, A.D., et al., 1993; Nader, A., et al., 1994). The upper part (mostly exposed or found at shallow depths), in which the alunite is present, belongs to the Early Permian-Autunian (Nader, A.D., et al., 1993).

The Ga’ara Formation is a mature siliciclastic unit consisting of repeated fining-upwards sequences of fluvial origin. Generally each cycle comprises sandstone, siltstone and mudrocks. The mudrocks are white, pale grey and varicoloured kaolinitic claystone and silty claystone with occasional iron oxyhydroxides (such as crusts, pisoliths, concretion and stains) and organic remains (plant debris and rootlets). Red, purple and orange mottles of different size are characteristic of the majority of the mudrock horizons. They represent the overbank deposits of meandering streams (Tamar-Agha, M.Y., 1986; Tamar-Agha, M.Y., 1993).

Quaternary deposits extensively cover the floor of the Ga’ara depression and the surrounding pediments (Tamar-Agha, M.Y., 1996). These deposits are polygenetic such as slope, aeolian, fluvial and pedogenic origins. Calcrite and gypcrete are conspicuous features of the Quaternary deposits in the Ga’ara depression and the former is more prominent. The calcrite forms an extensive blanket, which is thick on the floor (up to five metres) and thin on the slopes or even disappear. Calcrite is also formed between the gravel of the older terraces. Gypsification occurs below the calcrite horizons, underneath the older terraces, and at the contact between the Ga’ara Formation and the overlying Quaternary deposits.

**MATERIALS AND METHODS**

Seven mudrock samples were collected from seven localities (Sufi, South Sufi, North Wadi Tayyarah, West Wadi Tayyarah, Duekhla, East Afaif and East Wadi Tayyarah) representing the host rocks (Fig. 1). Six alunitic mudrock samples were collected from four of these localities: Sufi, South Sufi, North Wadi Tayyarah and West Wadi Tayyarah (Fig. 1).

Powdered samples of the whole rocks were pressed in an aluminium holder in order to investigate their mineralogy by X-ray diffractometry. The clay fraction (<2 μm) was separated from coarser fraction by dispersion in distilled water with mechanical stirrer, without using any dispersant agent, and finally extracted by standard sedimentation methods after Stoke’s law at room temperature following the procedures recommended by Carver (1971). Three oriented smears on glass slides were prepared for the <2 μm fraction of each sample, using the technique suggested by Gipson (1966). One sample remained in an air-dried state; the second was glycolated (in an ethylene glycol bath for 24 hours at 60°C); the third was heated to 550°C (heated samples were left for two hours after stabilizing the temperature). The four smears were run in the Philips X-ray Diffractometer PW 1965/60 (20 mA, 40 KV, Cu-Ni Kα, at 1°20/minute speeds). Some air-dried smears were repeated in the range 24-26° 2θ at speed 1°40/minute to distinguish chlorite from kaolinite. Crystallinity index of kaolinite were measured using the method described by Hinckley (1963) whereas degree of disordering was estimated by comparing the diffractograms with a set-up model consisting of four classes representing different degrees of disorder (Tamar-Agha, M.Y., & N.A. Al-Sa’adi, 1993). Six of the studied samples, representing both the alunitic mudrocks and the host rocks were studied using scanning electron microscopy (SEM).

Wet chemical analyses were carried out in the Laboratories of the State Company of the Geological Survey and Mining - Baghdad. The maximum possible error was 5% for major elements and 10% for minor elements. The analytical methods followed were: SiO₂ by gravimetry, Al₂O₃ and TiO₂ by colorimetry (using Technicon Autoanalyser) and titration for higher values, Fe₂O₃, CaO, MgO by atomic absorption spectrophotometry (AAS, using Pye Unicam SP 1900) and Na₂O and K₂O by flame photometry.

Approximate mineral proportions were estimated from chemical analysis and X-ray diffractometry of bulk samples since the major and minor elements are controlled by their mineral affinities. These constituents are
controlled by kaolinite, illite, goethite, quartz, anatase and gypsum. Kaolinite, quartz, goethite, anatase and gypsum were calculated using their stoichiometric formulae whereas illite was calculated using the following formula (28): K₂O + Na₂O: 7.02% SiO₂: 49.78%, Al₂O₃: 26.35%, MgO: 2.75% and Fe₂O₃: 4.3%. In the alunitic claystone, alunite proportion is calculated from the formula K₂O + Na₂O: 11.4%, Al₂O₃: 37%, SO₃: 38.6% and H₂O: 13%.

Mode Of Occurrence Of Alunite:

Alunite is found in the Ga‘ara mudrocks in two settings. The first is near surface, few decimeters to few metres deep, at the contact between the mudrocks of the Ga‘ara Formation and the Quaternary deposits, especially on the slopes (Fig.3). Alunite is usually associated with gypsum crystals and their frequency progressively decreases away from the contact. The gypsum crystals are fine to medium size (0.5-6 mm). The second setting is the presence of alunite in some mudrock layers at shallow depths (Fig.4) such as in South Sufi, Sufi, West Tayyarah and North Tayyarah deposits. The depth of these occurrences is up to 60 metres (deeper drillings are not available). Alunite occurs along fractures or contacts with the interbedded porous and friable sandstone but is commonly devoid of gypsum crystals. Its occurrence is stratigraphically controlled, found at many levels within a given mudrock layer or in many successive mudrock layers.

The alunite is milky white, fine, powdery and friable occurring as isolated to subcontinuous nodules, about 1-10 cm in diameter or as white spherical spots about one millimetre in diameter. The spots are either isolated and disseminated in the mudrock layers or clustered together forming in some places thin lamina.

![Fig. 1: Location map.](image)

Mineralogy And Geochemistry:

The results of chemical analysis of the host rocks reflect mudrocks of high maturity, where SiO₂, Al₂O₃, Fe₂O₃, TiO₂ and loss on ignition comprise more than 97% of the chemical constituents (Table 1). The calculations of mineral proportions and the XRD diffratograms revealed that kaolinite is the main clay mineral constituent in the host rocks as well as in the alunite-bearing rocks (Table-2 and Fig.5). Kaolinite is characterized by its basal reflection 7.16 angstrom (001) and 3.58 angstrom (002). It is not affected by glycolation but peaks disappear at heating to 550 °C (Fig. 5). Illite in the host rock is generally subordinate although it occurs in significant amount in the South Sufi deposit (about 27%). However in the alunitic mudrocks, the illite is nearly absent (Fig.5) and the majority of the K₂O is present in the alunite. Non-clay constituents are quartz, goethite, anatase, and secondary gypsum in addition to some organic matter (plant debris).
Table 1: Chemical analysis of the host rocks and alunitised claystones.

<table>
<thead>
<tr>
<th>Constituent</th>
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<th>4</th>
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<th>6</th>
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Table 2: Approximate mineral proportions based on chemical composition.

A. Host rocks:

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<th>Sample number</th>
<th>kaolinite</th>
<th>Illite</th>
<th>Quartz</th>
<th>Anatase</th>
<th>Goethite</th>
<th>Gypsum</th>
<th>Total</th>
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<tr>
<td>7</td>
<td>83</td>
<td>4</td>
<td>10</td>
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<td>-</td>
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B. Alunitic rocks:

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The values obtained for the measurements of the crystallinity index of the kaolinite in the host rocks ranges from 0.3 to 0.5 which indicate poor degree of crystallinity. These kaolinites showed also high state of disordering. SEM studies support the XRD results with respect to the development of kaolinite crystal faces as they look all battered faces (Fig. 6).

Alunite was identified on X-ray (Cu Kα) diffractograms by the presence of its characteristic peaks at 5.70, 4.95, 3.51 (sometimes covered by kaolinite 002 reflection), 2.99, 2.88, 2.28, 2.2, 1.9 and 1.75Å. In the nodules, which are frequent at the contact zone between the mudrocks and the Quaternary deposits, alunite is the main mineral with minor proportions of gypsum and quartz (Fig. 5). Otherwise alunite occurs in lower proportions associated with kaolinite, quartz and goethite.

SEM studies revealed two varieties of alunite based on shape namely rhombic and acicular (Fig. 5). Chemical analyses showed that both the host rocks and the alunitic claystone are higher in K₂O than Na₂O (table 1). The K₂O content ranged from 0.08 to 1.9% (mean 0.7%) in the host rocks whereas the Na₂O content ranged from 0.07 to 0.7% (mean 0.48%) in the alunitic claystone. The K₂O:Na₂O ratio in the host rocks ranged from 0.3 to 5.3:1 (mean 2.7:1), yet, it ranged from 2.8 to 7:1 (mean 4.9:1) in the alunitic claystone.

The two morphological varieties observed by SEM and deduced from chemical analysis are probably alunite and schloessmacherite (i.e. hydronium alunite). The diagnosis of the two varieties needs to be verified by further analysis and scrutiny. Availability of illite in the host rocks seems to control the kind of alunite that develops, i.e. whether it is a K or H₂O type. Khalaf (10) differentiated the K-alunite from the hydronium-alunite using Energy dispersive X-ray analysis. He found that the former is rhombic in shape and the latter is needle-shaped.
Fig. 2: Geological map of the study area.

Fig. 3: Schematic diagram of the sequence in the Sufi area illustrating the mode of occurrence of alunite.
Fig. 4: Schematic diagram of the sequence in West Tayyarah area illustrating the mode of occurrence of alunite in subsurface sections.

**Genesis Of Alunite:**

Alunite is known to be formed by secondary processes such as hydrothermal or supergenic activities (29). Hydrothermal alunite is usually produced by alteration of volcanic rocks (5&6). The supergenic alunite are diagenetic (Goldbery, R., 1978; Goldbery, R., 1980; Rouchy, J.M. and C. Pierre, 1987; Khalaf, F.I., 1990) or epigenetic (King, D., 1953; Keller, W.D., et al., 1967; Ross, C.S., et al., 1968; Aswad, K.J., et al., 1995). Alunite of both types is believed to have formed by the reaction of sulphuric acid generated by the oxidation of H₂S or metallic sulphide with Al-bearing minerals.

Alunite in the present study is restricted in occurrence to the mudrock horizons of the Ga’ara Formation, either in juxtaposition with the Quaternary deposits or along the weakness zones, such as the contact with the associated porous sandstone, fractures and joints. It infrequently has a replacive relationship with the clays and usually associated with gypsum, especially when occurring with the Quaternary sediments. It is believed that in both settings, alunite was formed by the reaction of dilute solution from groundwater with available Al-bearing sources such as kaolinite, illite and amorphous aluminium hydroxide.

Mineralogical and geochemical studies revealed that kaolinite is the predominant clay mineral present in the studied rocks with minor illite and mixed-layer mineral. The clay minerals were formed by intense hydrolytic weathering, at least in two stages, the first was in the hinterland and the second was at the depositional site during later pedogenesis. XRD and SEM studies revealed that the kaolinite is poorly crystalline, disordered and have battered crystal faces. Some amorphous aluminium hydroxide is expected to be formed but in limited amount. However, about 5-10% of the alumina in these mudrocks was leached in 5% sulphuric acid (Tamar-Agha, M.Y., 1986).

Sulphuric acid, hydrogen sulphide or metallic sulphides are not available in the system but instead dilute sulphate solution is evident. Metallic sulphides are infrequent, especially in the nearby areas. Chemistry of both meteoric groundwater, from shallow hand-dug wells, and the Ga’ara aquifer reveals that they are both sulphate group water and are neutral to weakly alkaline (Radosevic, L., 1981). The source of aluminium is the disordered kaolinite, illite and possibly some amorphous aluminium hydroxide. Availability of a clay host is of utmost importance for the formation of alunite, as no alunite is recorded in the sandstone. Alunite with occasional gypsum is formed in areas with available alumina otherwise gypsum is formed only. Gypsum is precipitated by the evaporation of ascending dilute sulphate solution, rising to the capillary zone by a mechanism such as the evaporative pumping. Ca²⁺ and SO₄²⁻ are the dominant ions in the groundwater (Radosevic, L., 1981). The nature of distribution of the alunitic white spots, as solitary, grouped with sometimes coalesce to form patches indicates that they are replacive and affect the clay minerals only. Jarosites were not encountered in association with alunite in the studied sequence although plenty oxyhydroxides are present, probably because simultaneous precipitation of alunite and jarosite requires lower pH value (Lopez-Aguayo, F., et al., 1977).
Fig. 5: X-ray diffractograms of host rocks and alunitic claystones.
Fig. 6: Figure 6. SEM photographs of host rocks and alunites: a) kaolinitic mudrock showing anhedral kaolinite flakes with some altered to alunite (†). b) Flaky anhedral kaolinite with alteration to acicular alunite (ac) and rhomb alunite (r), note the high porosity in comparison to the host rocks. c) acicular (ac) and rhomb alunite (r) occurring together in the same sample, kaolinite flakes show alteration to acicular alunite, sometimes in radial form. d) alunite as white spot in the kaolinitic mudrock outlined by dashed line. e) details of the alunite in the white spot showing stacked subhedral rhombs.

Alunite in both settings was formed by the reaction of dilute solutions (from groundwater) with available clay minerals (kaolinite and illite) and amorphous aluminium hydroxide, as follows:

$$\begin{align*}
(K,Na)AlSi_3O_10(OH)_2 + 4H_2O + 2SO_4^{2-} & \rightarrow (K,Na)Al(SO_4)_2(OH)_6 + 3SiO_2 + 2H_2O \\
\text{illite} & \text{alunite}
\end{align*}$$

$$\begin{align*}
3Al_2Si_2O_5(OH)_4 + 4H_2O + 4SO_4^{2-} + 4Ca^{2+} & \rightarrow 2(H_3O)Al(SO_4)_2(OH)_6 + 6SiO_2 + H_2O + 4CaO \\
\text{kaolinite} & \text{alunite}
\end{align*}$$

$$\begin{align*}
6Al(OH)_3 + 4H_2O + 4SO_4^{2-} & \rightarrow 2(H_3O)Al(SO_4)_2(OH)_6 + 8H_2O \\
\text{amorphous} & \text{alunite}
\end{align*}$$

Adams and Hajek (1978) carried out a set of solution experiments in which crystalline alunite was precipitated from dilute solutions of various concentrations of sulphate and potassium at different pHs and aging of precipitates at 50°C for 18 weeks. Gypsum was present in some precipitates. They found that alunite was the dominant mineral in the precipitate even with K/Al mole ratio of 0.1. Their experiments revealed that K ions in the aging solution were highly effective in transforming amorphous basaluminite into crystalline alunite even with as little as 0.01 M K in solution.
Conclusions:
The alunite within the Permocarboniferous Ga’ara mudrocks is replacive, affecting the clay minerals only. They are of groundwater epigenetic non-hydrothermal origin and of Quaternary age. Alunitization occurred by the reaction of dilute sulphate solution (groundwater) with the clay minerals. Sulphuric acid need not necessarily be available for the formation of alunite. Availability of illite controls the kind of alunite that is produced, i.e. whether it is K or H₂O type.

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