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Occurrences and Origin of Alunite, South Jordan

Talal Mohammad Al-Momani
Department of Earth and Environmental Sciences, Faculty of Science,
Yarmouk University, Irbid-Jordan

Abstract: The objectives of this study are to explain the possible mode of origin and to record the occurrences of the alunite in the lower part of the Shale Member, South Jordan. Alunite was characterized by field work, SEM, XRD and XR Microanalyzer. The results of the field, chemical and mineralogical studies indicated that the alunite occurs as small fine-grained white spots along bedding planes within the lower part of the Shale Member, South Jordan. The sulfur trioxide (SO₃) is related to the presence of gypsum and alunite. Iron sulfides (source of sulfur) could be originally produced by mineral replacement of chitinous tests of graptolites in oxygen deficient marine environment.

Key words: Alunite, shale, graptolite, Jordan, origin, SEM, XRD, sulfur

INTRODUCTION

Alunite or Alumstone, a mineral first observed in the 15th century at Tofla, near Rome-Italy, where it is mined for the alum. Alunite is a very fine hydrous sulfate mineral with hydroxyl in its structure. The formula for pure alunite is $KAl_3(SO_4)_2(OH)_6$. It has a rhombohedral crystal structure.

Alunite was recorded for the first time in Jordan by Khoury (1987) in the kaolinite bed of the Kurnub Sandstone Formation of the Lower Cretaceous age. Khoury (1987) indicated that alunite is possibly formed as a result of both diagenetic and supergene processes. Sulfuric acid originated from the oxidation of pyrite. The source of potassium is the result of hydrolysis reactions of feldspars and illite-muscovite. The reaction of such water with kaolinite could form alunite.

In general, different types of alunite were investigated by many authors in different areas around the world, mainly in Turkey, Italy and Australia. Frost *et al.* (2006a) discussed a Raman spectroscopic study of alunites. They mention that the minerals are characterized by well-defined hydroxyl stretching patterns, which give two groups of hydrogen bonds with calculated hydrogen bond distances of 2.90 and 2.84Å. Frost *et al.* (2006b) discussed a thermogravimetric study of the alunites of sodium, potassium and ammonium.

They mention that three mechanisms of decomposition are observed (a) dehydration, (b) dehydroxylation and (c) desulphation. The thermal decomposition of the three alunites is different. Küçük and Yildiz (2006) studied the decomposition kinetics of mechanically activated alunite ore in air atmosphere by thermogravimetry. They

concluded that it can be verified that alunite decomposes in two steps, which are dehydration and desulphation. Mutlu *et al.* (2005) studied the geochemistry and origin of the Şaphane alunite deposit, Western Anatolia, Turkey. They mention a replacement type alunite deposit occurs in the studied area.

The objectives of this study are to explain the possible mode of origin and to record the occurrences of the alunite in the lower part of the Shale Member, South Jordan. This will enhance the understanding of nature of alunite in the lower part of the Shale Member, South Jordan.

LOCATION AND GEOLOGICAL SETTING OF THE STUDIED AREA

The investigated area is situated in southern Jordan. The area is located about 100 km east of Aqaba at a distance of 20 km to the southeast of Ad-Disa Village (Fig. 1).

The oldest rocks, which crop out in the study area, are of paleozoic age. Three formations are cropping out in the study area, with a general dip towards the southeast. These are from bottom to the top: Bedded brownish weathered sandstone formation; Graptolite sandstone formation and Sabellarifex sandstone formation, respectively.

Graptolite sandstone formation covers most of the studied area in scattered outcrops and at the surface. It is subdivided into the shale member and the sandstone-siltstone member. The shale member, which belongs to the lower part of the graptolite sandstone formation, consists of kaolinite of various colors, which range from light gray, dark gray, violet, brown-red and red. It is intercalated by

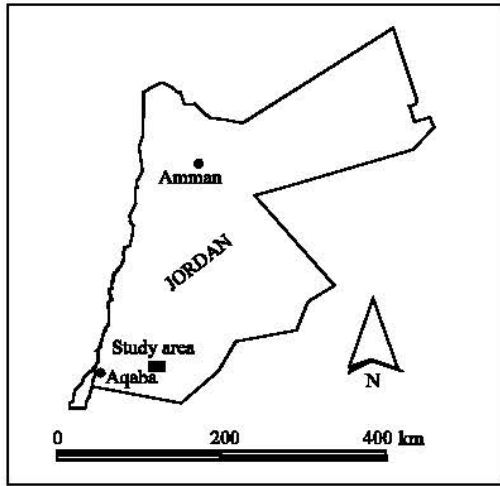


Fig. 1: General map showing the study area



Fig. 2: White Alunite patches, mainly along the bedding planes

few thin beds (10-20 cm) of ferruginous and hard siltstone. The kaolinite deposits are the essential constituents of the shale member. Alunite is present as white soft separated patches mainly along the bedding planes (Fig. 2). Graptolite sandstone formation contains well-preserved graptolites (*Didymograptus* sp., Fig. 3).

Sampling and laboratory techniques: Field work was carried and focused on Shale Member in March-April 2005. Sixteen samples were collected from the lower part of the Shale Member in accordance to the lithological variations.

Scanning Electron Microscopy (SEM) analyses on the selected samples were carried out using (SEM FEI Quanta 200-Holland) and chemical analyses of spot samples carried out using EDAX XR Microanalyzer at the Department of Earth and Environmental Sciences, Yarmouk University, Irbid, Jordan. The mineralogy of the samples was determined by X-ray powder diffraction

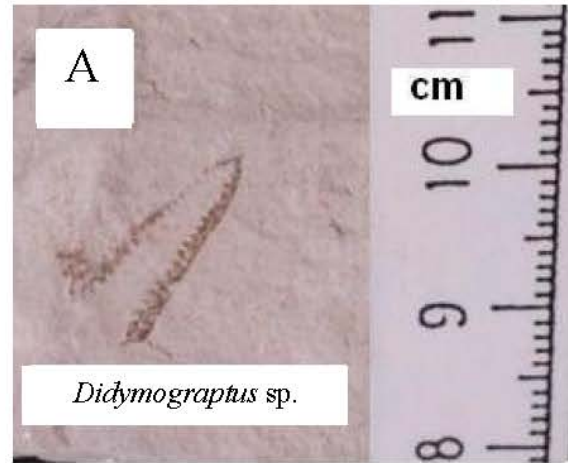


Fig. 3: Well preserved graptolites (*Didymograptus* sp.)

(XRD). The random samples were scanned from (2 to 65) degree 2θ using $\text{Cu K}\alpha$ radiation at 35 kV and 25 mA with a Philips-Xpert MPD diffractometer available at the laboratories of Natural Resources Authority (NRA), Amman Jordan.

RESULTS AND DISCUSSION

The Scanning Electron Microscopy (SEM) photomicrographs (Fig. 4) indicated the presence of rhombohedral idiomorphic alunite crystals within the kaolinite beds, South Jordan.

The results of the X-ray diffraction analyses for the bulk rock samples are shown in Fig. 5a-c). The results indicated that the identified clay and non-clay minerals are kaolinite, quartz, alunite, muscovite, gypsum and hematite (Fig 5a). Kaolinite, quartz, muscovite and alunite are present in all samples (Fig. 5a-c). In addition, the results of the X-ray diffraction analyses of the bulk rock samples indicated that kaolinite and quartz are the most abundant minerals. Alunite is present as a minor component.

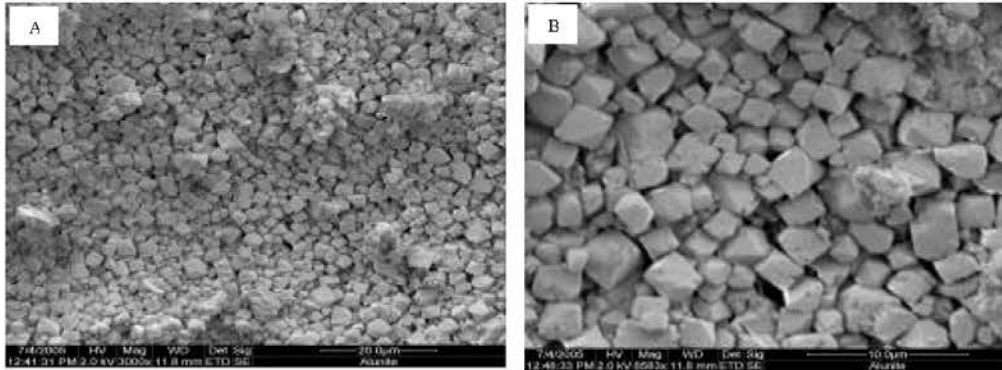


Fig. 4: Scanning electron micrograph showing aggregates of rhombohedral idiomorphic Alunite

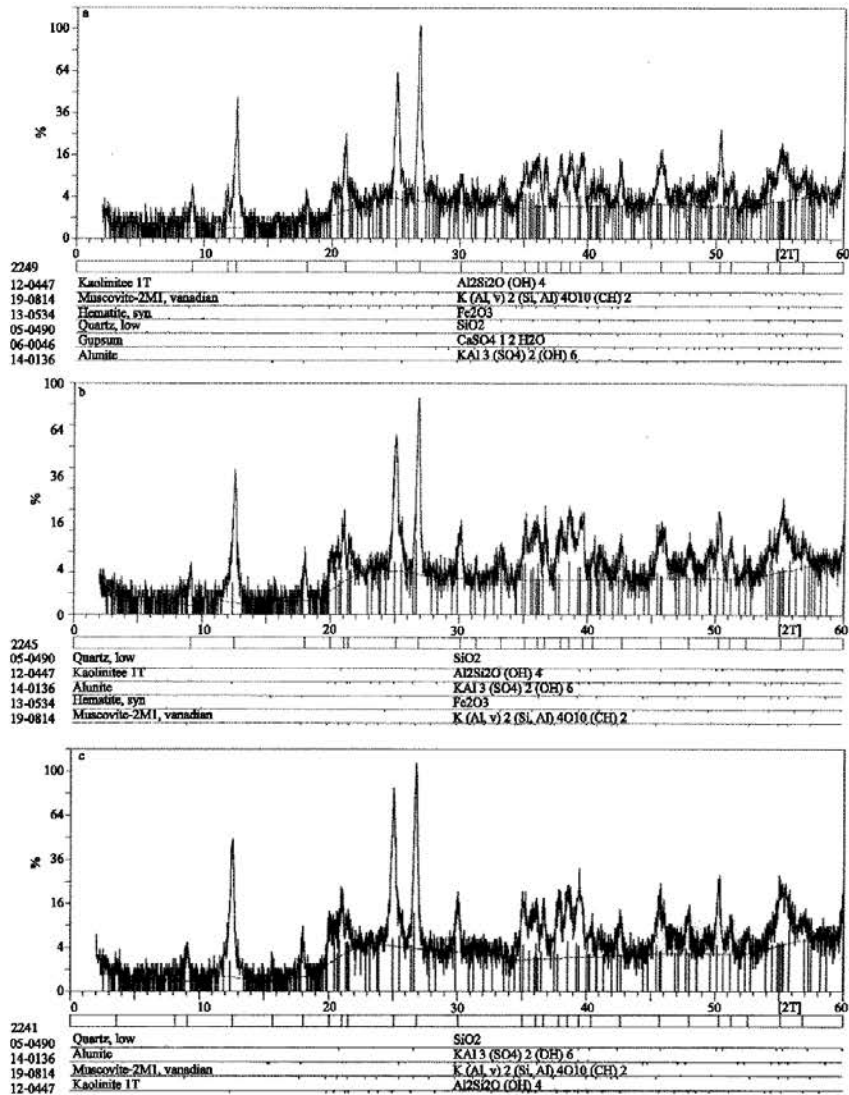


Fig. 5: Typical X-ray diffractograms of the bulk rock samples

Table 1: Results of chemical analysis of the analyzed white spot alunite samples

Sample No.	Al ₂ O ₃ (%)	SO ₃ (%)	K ₂ O (%)
1	36.82	31.48	10.37
2	38.98	33.51	7.05
3	38.06	37.40	7.86
4	42.46	35.96	5.89
5	40.93	41.43	5.81
6	38.67	41.17	9.89
7	41.25	38.20	8.15
8	34.44	41.19	12.17
9	34.64	39.11	13.17
10	40.57	37.86	9.92
11	37.68	39.65	13.36
12	32.30	41.74	14.69
13	32.36	40.05	14.40
14	36.20	41.75	13.08
15	33.87	40.03	15.92
16	34.49	40.28	12.06
Minimum	32.30	31.48	5.81
Maximum	42.46	41.75	15.92
Average	37.11	38.80	10.86
Pure Alunite	36.92	38.66	11.37

Gypsum is identified as a filling material in joints and fractures. Hematite is present in a few samples in low concentrations (Fig. 5b).

The chemical composition of the analyzed spot samples is given in Table 1.

The important major oxides (Al₂O₃, SO₃ and K₂O) are usually present in all of the studied spot samples as major chemical constituents of alunite.

The contents of Al₂O₃, SO₃ and K₂O range from 32.30 to 42.46%, 31.48 to 41.75% and 5.81 to 15.92%, respectively. The results indicated that the average chemical composition of the analyzed spot samples (37.11 Al₂O₃, 38.80 SO₃ and 10.86% K₂O) is equivalent with the important major chemical constituents of pure alunite (36.92% Al₂O₃, 38.66% SO₃ and 11.37% K₂O).

The results of the field, chemical and mineralogical (XRD and SEM) studies indicated that the alunite occurs as minor constituents in clay beds of the lower part of the Shale Member, South Jordan. The Shale Member which belongs to the lower part of Graptolite Sandstone Formation contains well-preserved graptolites (*Didymograptus* sp. Fig. 3). The occurrence of well preserved graptolite molds indicate that shale was deposited in a quite marine environment (deep marine depositional environment).

Graptolites are marine organisms usually form simple and chitinous colonies, belong to the order Graptoloidea. They are considered as index fossils and are used for stratigraphic correlation and for age determination. They have particularly played an important role as stratigraphical markers for Silurian and Ordovician periods being worldwide in distribution. Graptolites have short vertical range in time, abundance and show rapid



Fig. 6: Broken *Didymograptus* can be confused with uniserial straight *Monograptus*

evolution in their species. In most cases, *Didymograptus* consists of two symmetrical branches diverging from at any angle between 0 to 180° (Fig. 3a) and are characteristic to a pelagic (epiplanktonic) marine environment. It is important to note that broken *Didymograptus* can be confused with uniserial straight *Monograptus* (Fig. 6) (McKinney, 1991; Aiyengar and Prasad, 1996; Moore *et al.*, 1997).

The sulfur trioxide (SO₃) content (Table 1) is related to the presence of gypsum and alunite (Fig. 5). Iron sulfides (source of sulfur) could be originally produced by mineral replacement of chitinous tests of graptolites (Fig. 3) in oxygen deficient marine environment. Alunite is a very fine sulfate mineral (KAl₃(SO₄)₂(OH)₆), secondary precipitation of alunite is present in voids and along the bedding planes. The formation of alunite within the clay beds indicates the presence of a sulfur source, which is a possibly sulfide.

CONCLUSIONS

Iron sulfides (pyrite; FeS₂) could be originally produced by the mineral replacement of the chitinous tests of graptolites in oxygen-deficient marine environment and pyrite could be the source for sulfur. The oxidation of pyrite and the formation of sulfuric acid could explain the possible source for the (SO₄)⁻ group, which is presented in the alunite and/or gypsum.

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