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ORIGINAL PAPER

Occurrence of diagenetic alunites within karst cavity infill of the Dammam Formation, Ahmadi, Kuwait: an indicator of hydrocarbon gas seeps

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Abstract Alunite minerals occur as white powdery lumps and laminated coloured deposits within cavity and solution channel infill of the palaeokarst zone of the Upper Eocene Dammam Formation. This formation is exposed in a quarry located on the Al Ahmadi ridge within the Greater Burgan oil field in southern Kuwait. Field occurrences and sedimentary structures of the alunite deposits were described. Collected samples were petrographically described, and their mineralogy and geochemistry were determined using X-ray diffraction and X-ray fluorescence, respectively. Microfabrics were investigated using SEM, revealing that they are primarily composed of fibrous alunogen (hydrous aluminium sulphate) and pseudo-cubical K-alunite (hydrous potassium aluminium sulphate). Their mode of occurrence suggests a hypogenetic origin, where sulphide gases associated with hydrocarbon gases reacted with an Al-rich solution leached from clay minerals and feldspars of the cavity-fill muddy sand sediments. The hydrocarbon gases may have seeped from subsurface petroliferous formations within the Greater Burgan oil field along vertical fractures. This study suggests that these acidic seeps may have played a role in the development of the palaeokarst zone of the Dammam Formation.

Keywords Alunite · Dammam Formation · Gas seeps · Burgan · Kuwait

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Introduction

Alunites are iso-structural sulphate minerals having a composition with the general formula $AR_3(SO_4)_2(OH)_6$, where A refers to a large cation in 12-fold coordination (Na, K, Pb, NH_4, H_3O Sr, Ba, La, Ce) and R is Al and Fe with minor amounts of Cu and Zn in octahedral coordination (Sato et al. 2009). This group includes alunite [$KAl_3(SO_4)_2(OH)_6$], natroalunite [$NaAl_3(SO_4)_2(OH)_6$], basic aluminium sulphate or hydronium alunite [$(H_3O)Al_3(SO_4)_2(OH)_6$], and alunogen ($Al_2(SO_4)_3{\cdot}16H_2O$); however, alunite is the most abundant in nature. The mineralogical investigation, nomenclature, classification, and genesis of alunites have attracted the interest of many scientists (Taguchi 1961; Goldbery 1980; Hill and Forti 1986; Chitale and Gtiven 1987; Khalaf 1990; Rye et al. 1992; Polyak and Goven 1996; Mutlu et al. 2005; Hassan and Baioumy 2007; Sato et al. 2009; Hikov et al. 2010; Wray 2011).

Minerals of the alunite group form under low-pH (0.8–5.3) conditions from sulphate fluids with high oxygen potential (Kelepertsis 1989; Long et al. 1992; Rye et al. 1992; Polyak and Goven 1996; Mutlu et al. 2005; Hikov et al. 2010). Two genetic types of alunite have been identified: hydrothermal and diagenetic. Hydrothermal alunite is developed by the alteration of acidic volcanic rocks, whereas diagenetic alunites are formed in potassium- and aluminium-rich sedimentary deposits. In both cases, the genesis of alunite is attributed to the reaction between potassium- and aluminium-rich rocks and sulphuric acid, which is generated by the oxidation of gaseous or metallic sulphides (Lombardi and Sheppard 1977; Hall 1978). Diagenetic alunites have been reported in the USA, Hungary, Australia, Greece, and the Middle East (Stephenson 1946; King 1953; Bayliss 1964; Keller et al. 1967; Ross et al. 1968; El-Sharkawi and Khalil 1977; Goldbery 1978; Hall 1978; Rouchy and Pierre 1987; Kelepertsis 1989; Scott 1990; Khalaf 1990; Al-Momani

2007). Stracher and Taylor (2004) and Stracher et al. (2005) reported the association of alunite and other sulphate mineralisation with S-based and hydrocarbon gas compounds at coal mine gas vents in Pennsylvania and Inner Mongolia. Alunite group minerals within cave sediments have been reported from only a small number of localities (Hill and Forti 1986; Polyak and Goven 1996). The present paper describes new occurrence of diagenetic alunite minerals in the infill of cavities of a palaeokarst zone of the upper Dammam Formation exposed in a quarry at the Al Ahmadi area in Kuwait. This report also discusses the minerals' genesis and relevance to possible petroleum gas seeps.

Geologic setting

Kuwait lies on the northwestern side of the Arabian Gulf, extending between latitudes 28° 30′ N and 30° 05′ N and longitudes 46° 33′ E and 48° 30′ E. It is bordered to the north and northwest by Iraq and to the south and southwest by Saudi Arabia. The area of Kuwait constitutes a part of the interior homocline of the Arabian Peninsula where Eocene to Recent rocks are exposed. The surface of Kuwait is generally flat and is mostly carved into a partially calcretised sequence of clastic deposits of Mio-Pleistocene age, known locally as the Kuwait Group.

Tectonically, Kuwait is situated near the eastern margin of the Arabian Plate where several structural elements are recognised. The Kuwait Arch is the most prominent structural element in Kuwait and contains the largest oil pools (Burgan, Magwa, Ahmadi, Bahara Sabriyah, Raudhatain, and Wafra oil fields) (Abdullah et al. 1997). These oil fields are mostly anticlinal structures cut by swarms of near-vertical normal faults which are mostly founded on basement horsts. The Al Ahmadi ridge, an asymmetrical north-northwest-trending anticline with a topographic height of 100 m, is related to Zagros orogeny, and it overprints the Kuwait Arch trend.

Deep-seated faults that extend from the deep Triassic Minjur Formation to the highly fractured Eocene Dammam Formation were recognised within Burgan and Ahmadi oil fields (Carman 1996). Strong smell of sulphur and free crystallised sulphur on the surface at some locations within the Burgan oil field indicate gas seepage (Connan et al. 1999). The oil of some reservoirs (Wara, Burgan, and Minagish Formations) in the Burgan Field has an average sulphur concentration of 3.0 % (Abdullah and Connan 2002).

The sedimentary sequence in Kuwait is represented by a thick section of predominantly shallow marine sediments dominated by platform carbonates that range in age from Triassic to Pleistocene. Major episodes of uplift and erosion occurred during the Early Jurassic, Late Cretaceous, and Oligocene. These episodes are manifested by the occurrence of well-recognised unconformities. The Dammam Formation has a thickness of approximately 225 m in the synclinal area to the west of the Al Ahmadi (29″ 05′ N, 48″ 04′ E) ridge and over 350 m to the east of the ridge. The thickness along the Al Ahmadi ridge is almost constant at 200 m. A karstification zone was recognised within the topmost part of the Dammam Formation, which delineates a major disconformity with the overlying Mio-Pleistocene Kuwait Group clastic deposits (Owen and Nasr 1958; Milton 1967; Burdon and Al-Sharhan 1968; Khalaf et al. 1989; Khalaf and Abdullah 2013). The studied alunite deposits have been recognised within exposures at an operating quarry located at the Al Ahmadi area, southeast Kuwait (Fig. 1). An approximately 25-m-thick section of the topmost part of the middle Eocene Dammam Formation and the basal part of Kuwait Group clastics is exposed in this quarry (Fig. 2).

Field observations

The thickness of the Dammam palaeokarst zone exposed in the Al Ahmadi quarry ranges between 2.4 and 9.8 m. Its surface is extensively eroded (Fig. 3a). It is formed of fractured and severely disturbed chertified dolomicritic rocks in which bedding and chert bands are difficult to follow. Most fractures are oriented vertically or sub-vertically, and some have been widened by dissolution, forming solution channels. Karstification is manifested by the occurrence of abundant cavities and solution channels. Most of these cavities are filled with siliciclastic mud and muddy sand deposits.

Alunite commonly occurs as white chalky powdery lumps associated with the muddy sediments infilling the karst cavities (Fig. 3b). These lumps range in size from a few centimetres to tens of centimetres and are usually located where the infill material makes contact with the cavity walls. Chalky alunitic material occurs in association with siliciclastic and detrital dolomite deposits as the infill of solution channels (Fig. 3c). The dolomitic walls of most of the karst caves are weathered to white chalky powdery alunite. Alunite also occurs as thinly laminated elongated lenses at the bottom of the muddy sand infill of large karst cavities. Lamination is attributed to variations in colour rather than texture, where thin laminae of purple, red, and white with diffused contacts constitute the alunite lenses (Fig. 3d). Randomly oriented fractures, ranging in width between a few millimetres to centimetres, within the muddy sand host sediments are usually filled with displacive fibrous gypsum. Some fractures are cemented with white chalky alunite and appear as white dendritic veinlets.

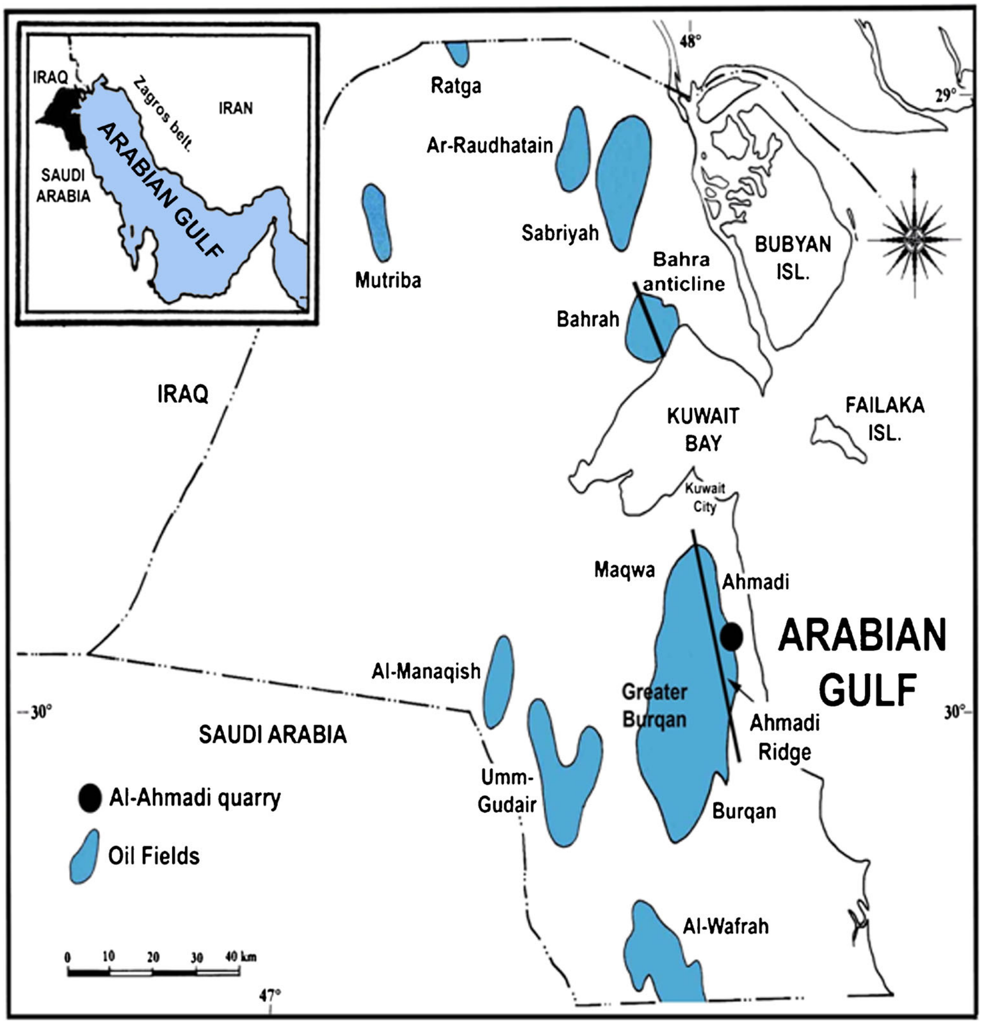


Fig. 1 Location map

Petrography

Karst cave and fracture infilling alunite is often a soft friable mixture of very fine white powder and siliciclastic grains, whereas laminated coloured alunite is composed of siliciclastic grains floating in relatively hard and compact alunite cement. It was difficult to prepare thin sections of the chalky powdery alunite lumps; therefore, parts of the lump were investigated using a binocular microscope. The alunite lumps are formed of a mixture of siliciclastic grains and very fine-grained whitish material. The siliciclastic grains are mostly of medium sand size and consist of quartz and feldspars. Microscopic investigation of thin sections of coherent coloured alunitic samples revealed that they are composed of poorly sorted quartz and feldspar grains that range in size from fine sand to granule size, cemented by microcrystalline alunite. The latter has a very low birefringence and displays a flow pattern around the siliciclastic framework grains (Fig. 3e). The quartz and feldspar grains are severely corroded, particularly along the fractures in quartz and cleavage in feldspars. Thin veinlets of blocky gypsum cross-cut the alunitic groundmass. Fine-grained particles of iron oxides (<10 μm) are abundant in the alunite cement of the reddish and brownish alunitic deposits. A few minute globules (<0.3 mm) of authigenic chalcedony are scattered within the alunitic groundmass.

Mineralogy

X-ray diffraction analysis of the studied samples confirmed the occurrence of K-alunite and alunogen (Table 1). K-alunite is indicated by its characteristic peaks of the following *d*-spacing (Å): 4.95, 3.50, 2.98, 2.28, and 1.90. Alunogen is identified by its prominent peak at 4.48 Å. K-alunite and alunogen are the most abundant components of the white powdery material. The average relative frequencies of K-alunite and

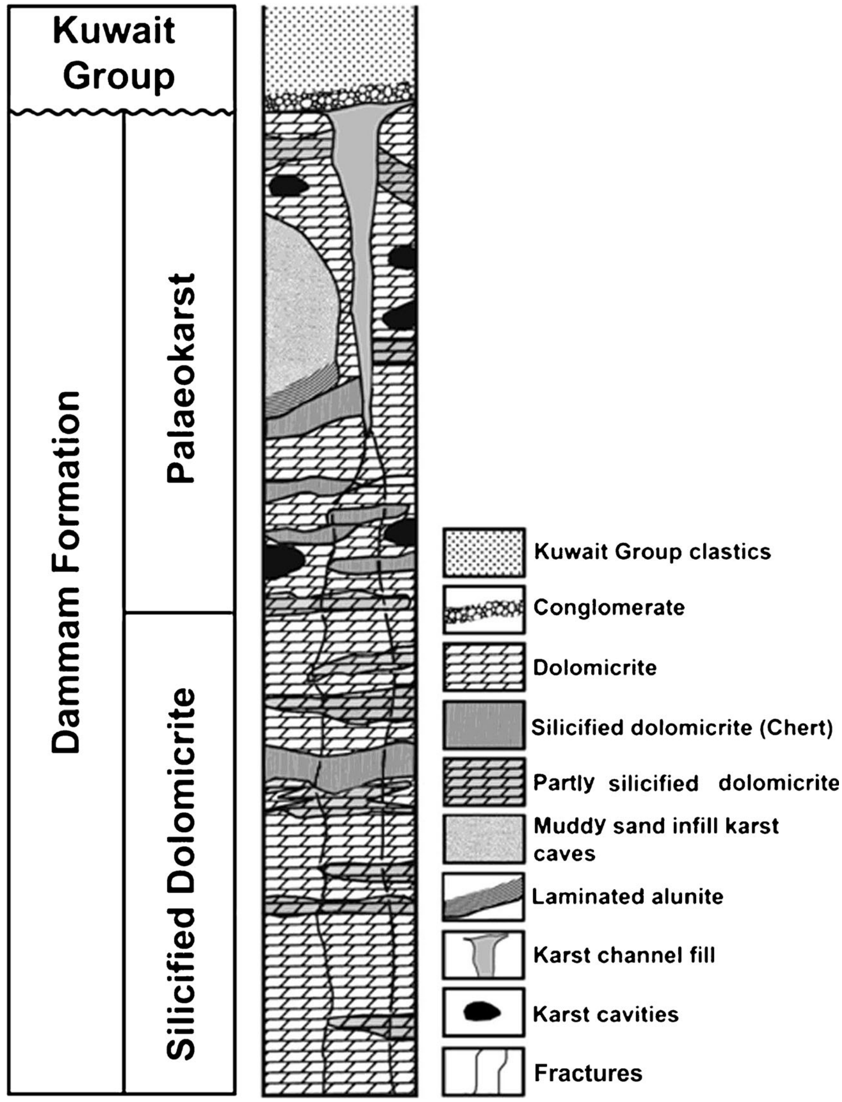


Fig. 2 Lithological sequence of the exposed Dammam Formation at Al Ahmadi quarry

alunogen are 27 and 20 %, respectively, in the white powdery alunite and 13 and 10 %, respectively, in the laminated coloured alunite. The difference in the amount of K-alunite and alunogen minerals is attributed to the relative abundance of the clastic framework grains. Dolomite only occurs in association with the white powdery alunite, with an average contribution of 10 %.

SEM investigation of the white powdery material revealed that it consists of clustered aggregates of alunite cementing the framework grains of the host sediments (Fig. 4a). These aggregates consist of a mixture of alunogen and K-alunite (Fig. 4b). Alunogen occurs as microaggregates of interwoven fibres. Alunogen fibres may reach up to 1 μm in length and 80 nm in width (Fig. 4c), and some are arranged in a radial fan pattern (Fig. 4d). K-alunite occurs as well-formed euhedral pseudo-cubes of approximately 2 μm in length (Fig. 4e). It was also noticed that the white powdery alunite is mixed with dolomite. The latter occurs as hollow dolomite, where the crystal core has dissolved and the outer zone has resisted dissolution (Fig. 4f). An insoluble residue of hollow dolomite crystals (dolomite crystal hash) is associated with the alunite material. Some of the hollow dolomite crystals are stuffed by alunite (Fig. 4g). Long fibres similar to that of palygorskite were observed, occurring in bundles covering some of the hollow dolomite crystals (Fig. 4h).

Geochemistry

Chemical analysis has confirmed the occurrence of alunite minerals within the studied samples (Table 2). The average concentrations of Al_2O_3 and SO_3 in the white powdery and coloured laminated materials are 22.88 and 21.38 % and 10.23 and 9.61 %, respectively. This result indicates that the ratio of Al_2O_3 to SO_3 is close to 1:1, which is similar to that of alunite

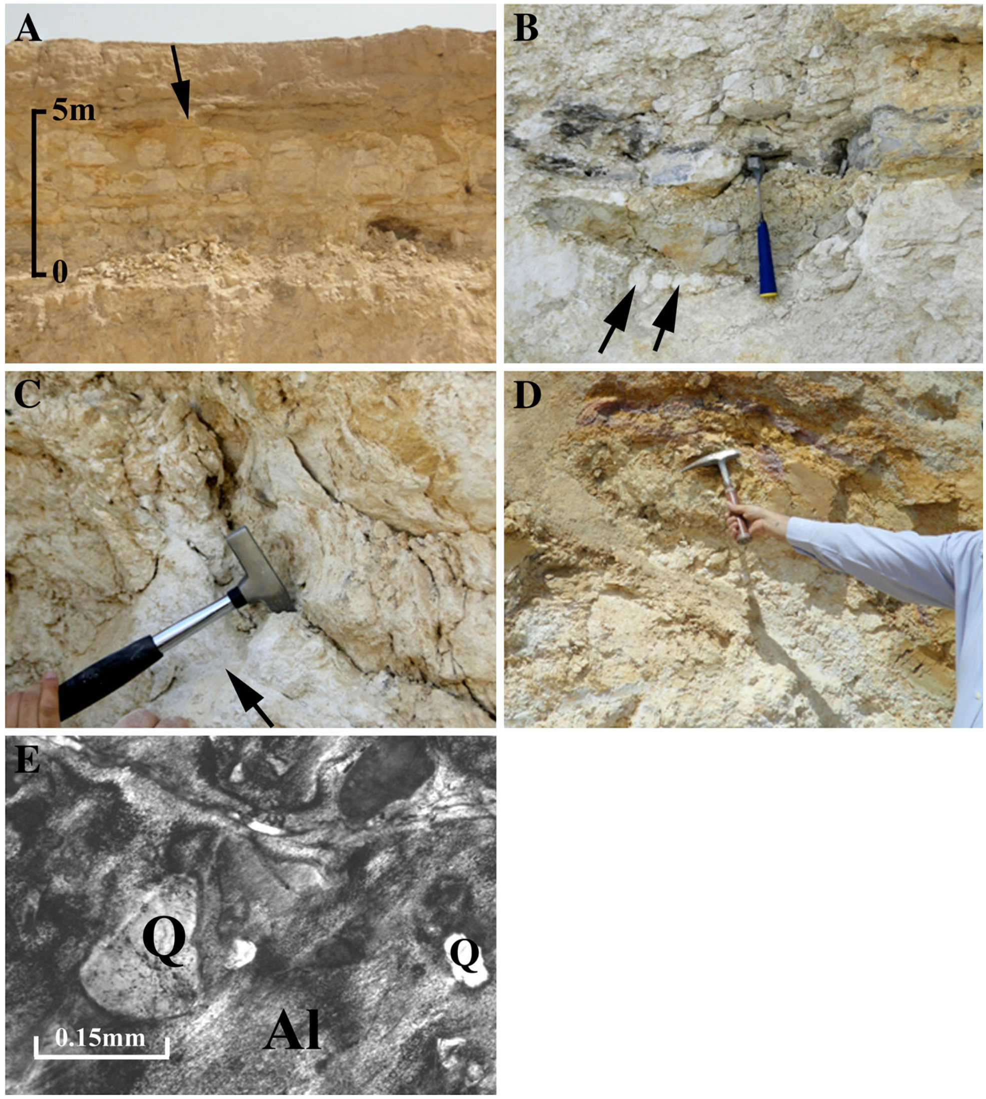


Fig. 3 **a** Karst surface of the upper Dammam Formation (*arrow*) exposed along the rock cut wall within the Al Ahmadi quarry. **b** White powdery alunite lumps (*arrows*) associated with the muddy sand infilling karst cavities. **c** Fracture widened by dissolution and filled with white, powdery alunite (*arrow*). **d** Laminated coloured alunite at the bottom of muddy sands infill a large karst cave. **e** Photomicrograph of chalky alunite with quartz grains (*Q*) floating in the microcrystalline alunite groundmass (*Al*)

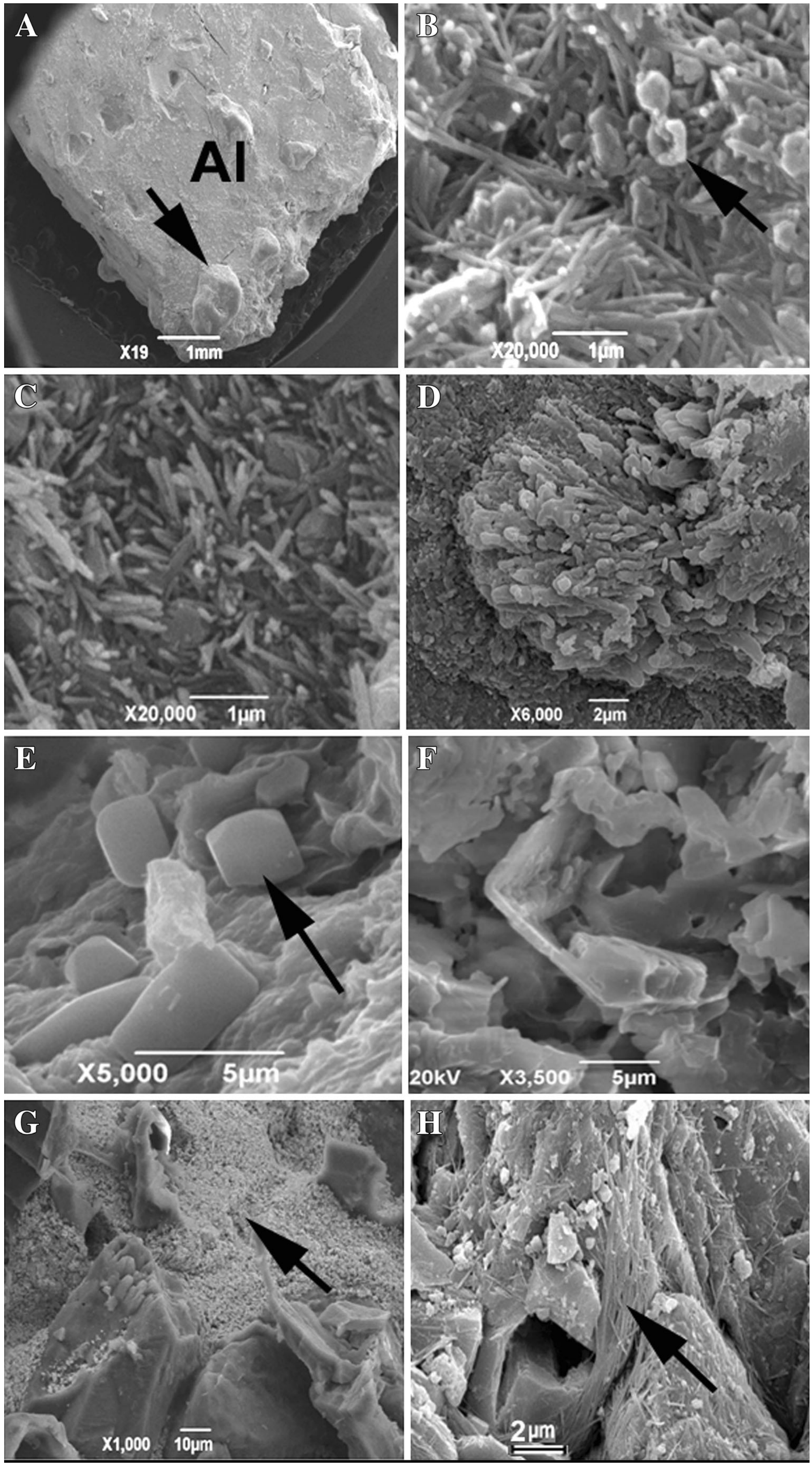
(Khalaf 1990; Hassan and Baioumy 2007). The high concentration of silica reflects the abundance of siliciclastic grains in the coloured alunite and authigenic silica in the white powdery alunite. The ratio of K_2O to Al_2O_3 is less than that of K-alunite, which may be attributed to the fact that alunitic material occurs as a mixture of K-alunite and alunogen. Concentrations of Mg and Ca reflect the occurrence of dolomite. The higher concentration of Mg relative to Ca is attributed to the occurrence of palygorskite (Mg Al silicate). The concentration of iron oxide is relatively high in the laminated coloured alunite (5.26 % on average).

Table 1 XRD analysis results

	White powdery alunitic deposits (n=10)		Laminated alunitic sediments (n=10)	
	Range	Average	Range	Average
Quartz	15–45	31	85–60	70
Dolomite	5–30	10	–	–
Feldspar	5–10	6	10–5	7
Gypsum	0–5	4	–	–
Alunite	20–40	27	20–10	13
Alunogen	15–30	20	0–15	10

Discussion

Field investigation and mineralogical and geochemical analyses confirmed the occurrence of alunite minerals within the upper Dammam karst caves and solution channels. Alunite minerals are mainly represented by alunogen (hydrous aluminium sulphate) and K-alunite (hydrous potassium aluminium sulphate). Khalaf (1990) reported the occurrence of alunite within calcretic and gypcretic succession of Kuwait Group clastics in southern Kuwait. However, the present study


A
Al
X19 1mm
B
X20,000 1µm
C
X20,000 1µm
D
X6,000 2µm
E
X5,000 5µm
F
20kV X3,500 5µm
G
X1,000 10µm
H
2µm

◀ **Fig. 4** SEM images of alunite. **a** Alunite lump fragment showing siliciclastic grains (*arrow*) floating in the alunite groundmass (*Al*). **b** Enlarged view showing the interwoven mat of alunogen fibres, including scattered pseudo-cubes of K-alunite (*arrow*). **c** Fibrous habit of the alunogen. **d** Fan-shaped radial fibrous alunogen crystals. **e** Well-formed euhedral pseudo-cubes of K-alunite (*arrow*). **f** Skeleton of a hollow dolomite rhomb and accumulation of hollow dolomite rhombs. **g** Hollow dolomite crystal stuffed with alunite powder (*arrow*). **h** Bundle of fibrous palygorskite (*arrow*) wrapping around a hollow dolomite rhomb

reports for the first time the occurrence of alunites within the karst caves and solution channels of the upper Dammam Formation. The occurrence of these alunites may be attributed to the reaction between potassium- and aluminium-rich sediments and/or acidic sulphate-rich solutions. The latter could have been generated by the oxidation of hydrogen sulphide associated with hydrocarbon gas seeps (Lombardi and Sheppard 1977; Hall 1978; Polyak and Goven 1996; Wray 2011). Variations in the texture between the white powdery alunites and coloured laminated alunites may reflect differences in their development processes. It is suggested that the white powdery alunite lumps have been developed by the precipitation of alunite minerals as a result of the reaction between acidic sulphate-rich solution and an Al-rich leachate. Sulphur is provided as sulphur oxide (SO_2), which may be formed by the oxidation of H_2S gas. The latter may have reached the upper Dammam Formation in association with hydrocarbon gas seepage along vertical fractures within the Greater Burgan oil field. The expulsion of hydrocarbon gases and their seeps within the highly fractured Dammam Formation may have occurred in the time since the Oligo-Miocene (Brennan 1990; Abdullah et al. 1997). SO_2 dissolves in water, forming sulphuric acid, which leaches Al from clay minerals (illite and montmorillonite) disseminated within the dolostone rocks as well as from the karst cavity-fill siliciclastic deposits. The occurrence of K-alunite could be attributed to the presence of limited amounts of K within the Al leachate.

Table 2 Major oxides of the studied alunite (wt%)

	White powdery material		Coloured laminated material	
	Range	Average	Range	Average
SiO_2	37.5–50.0	42.69	66.0–68.1	67.22
Al_2O_3	18.4–26.2	22.88	8.47–12.3	10.23
MgO	0.52–1.86	1.02	1.42–1.91	1.76
CaO	0.22–1.05	0.5	0.24–0.28	0.26
Na_2O	2.27–3.26	2.82	1.42–1.75	1.58
K_2O	4.80–9.28	6.81	3.00–4.15	3.67
TiO_2	0.05–0.19	0.09	0.12–0.19	0.17
P_2O_5	0.11–0.65	0.44	0.11–0.26	0.22
Fe_2O_3	0.55–2.49	1.35	2.95–5.88	5.26
SO_3	18.2–24.76	21.38	9.30–10.0	9.61

The occurrence of coloured laminated alunite as lenses at the bottom of greenish muddy sand infill of large karst cavities may suggest an in situ alteration of the muddy matrix to alunite. The occurrence of iron oxide inclusions within the alunite groundmass may indicate the concurrent precipitation of these two minerals.

The association of dolomite crystal hash and iron oxide inclusions with the alunite deposits may be interpreted as due to their transportation by an alunite-supersaturated solution prior to the precipitation of the authigenitic alunite.

The occurrence of diagenetic alunite within the karst caves and solution channels triggered an argument regarding the genesis and development of the karstification of the upper Dammam Formation, namely whether it is epigenetic or hypogenetic. The epigenetic karstification is usually controlled by meteoric water, whereas hypogenetic karstification is facilitated by ascending acidic fluids (Bakalowich et al. 1987; Ford and Williams 1989; Forti 1996; Galdenzi 1997; Klimchouk 2007). Some hypogenetic caves are related to deep oil deposits (Hill 1987). Differentiation between epigenetic and hypogenetic karst is generally difficult (Klimchouk 2009). The karstification of the upper Dammam Formation has been argued to be epigenetic (Khalaf 2011); however, the role of ascending fluids and gases should not be ruled out. The occurrence of alunite may support the partial role of the hypogenetic affinity of the Dammam karst.

Conclusions

1. Alunite minerals represented by diagenetic K-alunite and alunogen occur as cavity and solution channel infill within the palaeokarst zone of the upper Dammam Formation exposed in a quarry located on the Al Ahmadi ridge within the Greater Burgan oil field in southern Kuwait.
2. Their mode of occurrence suggests a hypogenetic origin in which sulphide gases associated with hydrocarbon gases reacted with Al leachate from clay minerals and feldspars of the muddy sand infill cavities.
3. The occurrence of alunite may be used as an indicator of hydrocarbon gas seeps along fractures from underneath petroliferous formations. A partial hypogenetic affinity of the upper Dammam karst is possible.

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