SULFUR ISOTOPES GEOCHEMISTRY OF THE BITUMINOUS FATHA EVAPORATES IN FATHA FORMATION, HIT–ABU JIR AREA, WESTERN IRAQ

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ABSTRACT

Fatha Formation (Middle Miocene) in Hit area, western Iraq was targeted for this study. Pure gypsum, bituminous gypsum and native sulfur were investigated for $\delta^{34}S$, FTIR and SEM to define the historical scenario of the paleo-environment and the relationship between sulfur, bitumen and evaporates (gypsum and anhydrite). SEM along with FTIR clarified that the bitumen were injected into the gypsum under high stress generated from the basin hydrodynamic pressure. The pure gypsum samples are enriched in heavy sulfur isotope and characterized by narrow range of $\delta^{34}S$ values (22.5 – 23.52 ‰) indicating a primary gypsum formed by direct precipitation from saline without bacterial activity. The lighter sulfur values (14.13 – 14.42 ‰) in the sulfur samples of the Abu-Jir area indicate a bacterial reduction of gypsum into native sulfur. The difference between $\delta^{34}S$ values in sulfur deposits in the Abu-Jir area (14.13 – 14.42 ‰) and in the Mishraq Mine (9.51 ‰) is clearly attributed to the remnant of gypsum as impurities within sulfur deposits in the Abu-Jir area. The bitumen sample has depleted in $\delta^{34}S$ value (-2.57 ‰), whilst the bituminous gypsum samples have enriched (22.07 – 24.11 ‰). This high variation reflects the highly isotopic fractionation between oxic and anoxic environments.

Keywords: Sulfur isotope, Sulfates, Bitumen, Gypsum, Abu-Jir, Fatha Formation

INTRODUCTION

The Fatha Formation represents a closed shallow basin which had been isolated from the Tethys Sea during the Middle Miocene. Basically, gypsum is an evaporate mineral usually precipitates in closed or semi-closed shallow water. It is a good seal for the oil reservoirs. Hydrocarbons can penetrate into such this seal to some extent, when subject to enormous pressure (Awadh and Hussien, 2015). This penetration caused

changing the original conditions that was prevailing before penetration. In early Archean sedimentary rocks, most sulfides and the rare sulfates have δ^{34}S-values near 0‰ (Cameron, 1982). The evidence for the activity of sulfate-reducing bacteria in the present day, δ^{34}S values (40 – 60 %) between bacteriogenic sulfide and marine sulfate in the sedimentary environments (Hoefs, 2009). The sulfur isotopic composition in the original solution based on the supplying external sources, and fractionation by geochemical and biological processes (Strauss, 1997). The lagoon-filling brine was highly enriched in calcium and sulfate; consequently, an ordinary evaporation led to the gypsum precipitation. The isotopic differentiation occurred during and after deposition led ultimately to variance in the light and heavy isotopes values. Organic-rich zones are certainly rich in heavy sulfur isotope (Longinelli and Flora, 2007). In the anoxic environments, the sulfate-reducing bacteria are stimulated to the metabolism and consuming oxygen. Consequently, sulfur will be released. This paper is going to discuss the nature of gypsum precipitation, the historical scenario of sulfur partitioning in the restricted lagoon that had been isolated from the Tethys Sea in Iraq during the Middle Miocene, the bacterial role in sulfur formation, and clarify the relationship of sulfur with both of gypsum and bitumen.

MATERIALS AND METHODS

A total of nine samples (Three pure gypsum samples, one sample of bitumen-rich gypsum, two bituminous gypsum samples, one bitumen sample, one sample from Mishraq native sulfur deposits, and two sulfurous gypsum samples from Abu-Jir deposits) were collected from the area extended between Hit and Abu-Jir village (Fig. 1). Some bituminous samples were split into two parts, where the bitumen has manually separated from the whole sample in order to investigate each part individually. This procedure is a good idea to understand in which fraction elements can be concentrated. All samples were investigation by the Fourier Transform Infrared Spectrophotometry (FTIR), Shimadzu instrument at the Environmental Laboratory University of Baghdad to identify the hydrocarbon species of bitumen impregnated in gypsum samples. These samples were also analyzed for sulfur isotopes (δ^{34}S). The sulfur from troilite of the Vienna-CDT (V-CDT) instead of Canyon Diablo troilite iron meteorite (CDT) has been used as a new international standard reference material (Hoefs, 2009). The sulfur isotopic analyses performed in Washington State University (Laboratory for biotechnology and bioanalysis) Sulfur was extracted by combustion using method stated by Chakrabarti (1978) and Yanagisawa and Sakai (1983). The results were expressed in delta notation by equation below:

$$\delta^{34}S\ sample(\text{‰}) = [(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard} - 1] \times 1000$$

The isotope composition in the Abu-Jir sulfur deposits was compared to the native sulfur deposit of the Mishraq mine. These isotope data are adopted to determine the origin of the native sulfur deposits in Abu-Jir area. Geological map and sampling sites were drawn using GIS software.

GEOLOGY

The Fatha Formation (Middle Miocene) is of lagoon evaporitic facies, mainly consists of gypsum and anhydrite interbedded with limestone, marl and relatively fine grained clastics (Buday, 1980). In the study area, it forms the top of the stratigraphic succession as Mesa and Kuesta land scape near Hit area, conformable overlying the Euphrates Formation. It has variable thickness in the central basin, the thickness is up to 900 m; whilst less than 15 m in the study area (around Hit area). It is of wide distribution in Iraq covering the marginal areas of the Stable Shelf and almost all of the whole Unstable Shelf. Injana Formation overlies Fatha Formation near Karbala and Najaf areas. The formation has lateral changes in lithology from gypsum to marly limestone toward the southern part of the basin. Due to this change the Nfayil Formation (Middle Miocene) is recommended. (Fig. 1). The Nfayil Formation is recently added to the stratigraphic column of Iraq. It composed of siltstone, green marlstone and sandstone conformably with the Injana Formation. Their exposures appear from Hit to the Bahr Al-Najaf area in the north westerly of Tar Al-Najaf. The depositional environment is shallow marine water (Sissakian, 1997), with normal to high saline water with clear oscillation in the sea level. The lithofacies indicates that the Nfayil is little deeper than the Fatha Formation. Some hydrocarbon seepages (bitumen and H_2S gas) associate the sulfurous spring water, while others are independent bitumen seeps (Fig. 1). So, these distinct phenomena can be easily seen on surface intruded with rocks or associated spring water in the study area. These seepages were considered as a reflection of the NW – SE trend of the Abu-Jir Fault Zone (AJFZ). The interaction among Abu-Jir Fault Zone with Euphrates and Fatha basins appears as bitumen seepages and sulfurous water springs as evidence for recent activity along Anah-Abu Jir Fault (Sissakian and Deikran, 2009). Oil seeps were generated from planktonic kerogen partially mixed with the terrestrial material belong to source rock older than Jurassic and Cretaceous rocks (Awadh *et al*., 2015). These seeps are characterized by non-waxy oil originated from the marine organic source deposited under anoxic conditions (Awadh and Hussien, 2015).
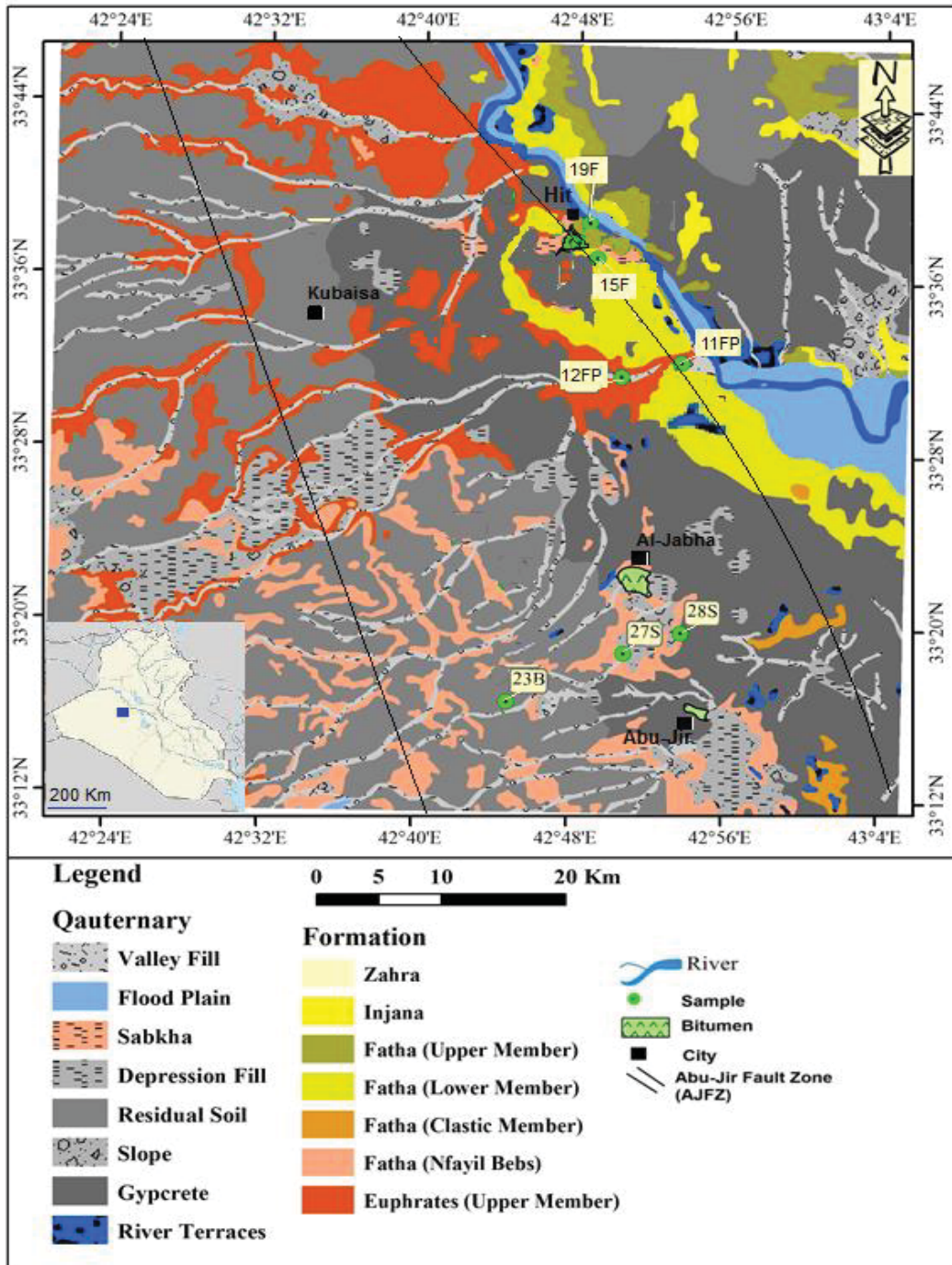
Fig. 1: Geological and location map of the study area displays sampling sites along the AJFZ (after IGS, 1995), the approximate boundary of AJFZ installed in this map based on Awadh *et al*. (2013)

RESULTS AND DISCUSSION

1. Hydrocarbon Species and Sulfur in Gypsum

For detailed study, particularly, organic compounds hosted in evaporate of Fatha Formation (Fig. 2), the FTIR technique was, therefore used. Bonds (S-O$_3$ and OH) in gypsum were clearly identified based on the standard figure of pure gypsum identified by Salisbury *et al*. (1987). FTIR revealed that the gypsum of Fatha Formation is composed of pure gypsum (Fig. 3A) and bitumen-rich gypsum (Fig. 3B). The wavelengths located at 3547.09 and 3404.36 cm^{-1} represents stretching vibrations of the H$_2$O molecules in the gypsum. Two transmittance spectrum peaks for O-H bending vibration modes (1687 and 1622 cm^{-1}) in the gypsum spectrum. The presence of two peaks in gypsum indicates that there are two crystallographic distinct types of water. One type of water is linked with sulfate ions by hydrogen bonding. The other one is directly linked to calcium ions. Sulfate ion is identified by the strong band centered around 1128 cm^{-1} which splits into two components at around 1141.95 and 1116.78 cm^{-1} along with the small peaks at 669.3 and 601.79 cm^{-1} that are assigned to the stretching and bending modes of sulfate Figures (3A and B). The hydrocarbon species in bitumen as well as sulfur are clearly displayed. Their wavelength positions were identified in Figure (3B) based on the standard identification table.

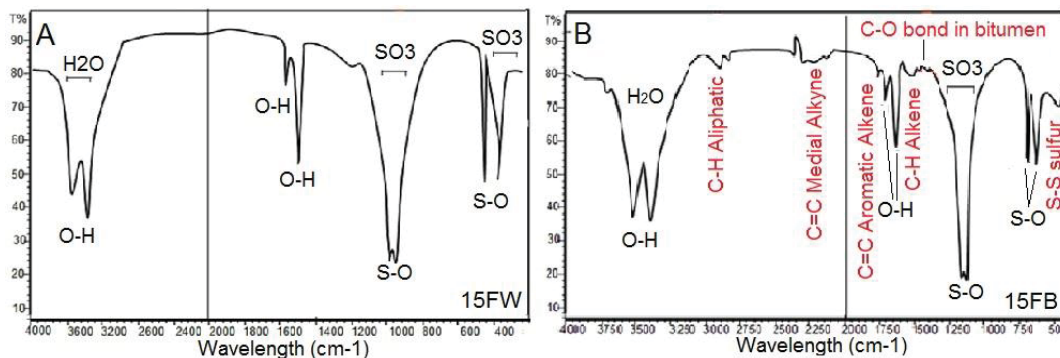**Fig. 2: Field photo shows bituminous gypsum in the Fatha Formation near Hit area**

Fig. 3: FTIR transmittance spectra of pure gypsum (A); and bitumen-rich gypsum (B)

2. Sulfur Isotope Geochemistry

The $\delta^{34}S$, and values of the pure gypsum, bitumen-rich gypsum, bituminous gypsum and native sulfur from the Mishraq mine and Abu-Jir area along with their lithological description of the samples are listed in Table 1. The $\delta^{34}S$ compositions in the pure gypsum samples are characterized by narrow range (22.5 – 23.52 ‰) enriched by heavy sulfur isotope. Currently, seawater maintains a constant $\delta^{34}S$ value of 21‰ (Fig. 4); and the $\delta^{34}S_{SO4}$ value in evaporites is approximately equal to the $\delta^{34}S_{SO4}$ value in seawater (Paytan *et al*., 1998). So, it was concluded, that the Middle Miocene seawater has $\delta^{34}S$ close to its value in evaporates. Consequently, $\delta^{34}S$ values in pure gypsum indicate a primary gypsum that had been chemically precipitated from marine water with no bacterial activity. The relative proportion of sulfate (SO_4^2) and sulfide (S^{2-}) is a control factor on $\delta^{34}S$ value in the seawater. Since the two species of sulfur $(SO_4^{2-}$ and $S^{2-})$ are present in the seawater, so the sulfate marine deposits provide with a historical scenario of the relative partitioning of the sulfur isotopes between the oxidized and reduced reservoirs through time.

Table 1: $\delta^{34}S$ values lithology area and formation of the samples

S. No	lithology	Area (Fm)	$\delta^{34}S$
11FB	Pure gypsum	Hit (Fatha)	22.75
12FB	Pure gypsum	Hit (Fatha)	23.52
15F	Pure gypsum	Hit (Fatha)	22.87
15FB	Bitumen-rich gypsum	Hit (Fatha)	22.50
19FW	Bituminous gypsum	Hit (Fatha)	22.07
19FB	Bituminous gypsum	Hit (Fatha)	24.11
Ranges			22.07 – 24.11
23B	Bitumen	Hit (Fatha)	-2.57
SM	Native Sulfur	Mishraq (Fatha)	9.51
27S	Sulfurous gypsum	Abu-Jir	14.42
28S	Sulfurous gypsum	Abu-Jir	14.13

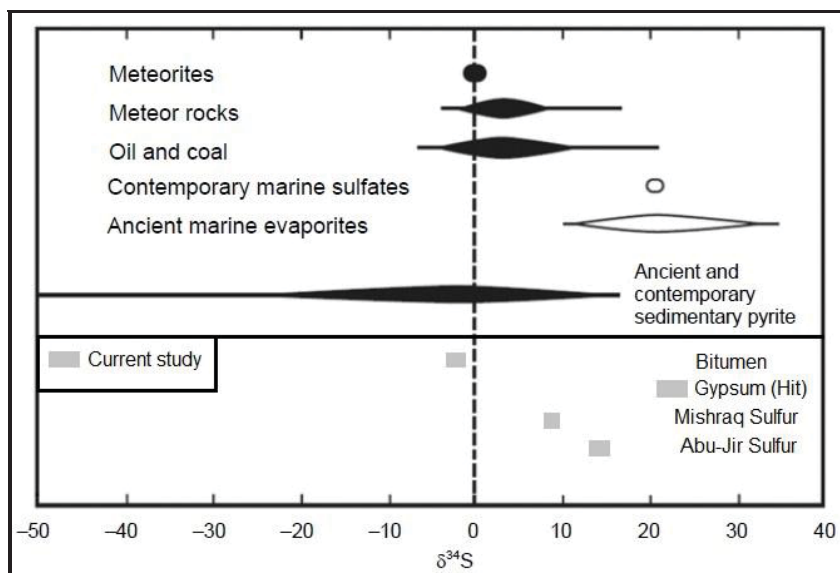**Fig. 4: δ³⁴S variations of different important sulfur reservoirs materials by Seal (2006) and Chervyatsova *et al.* (2016), and the data of current study of the sulfur isotopic composition in bitumen, gypsum, Mishraq sulfur deposit and Abu-Jir sulfur deposits**

The dark color in gypsum samples reflects the bitumen content (Fig. 2). In Hit area, the bacterial activity seems weaker than in Abu-Jir due to the oxidized conditions, as the gypsum did not generate native sulfur, and this is evident from the comparable $\delta^{34}S$ (22.07 – 24.11 ‰) in the bituminous gypsum samples to those of pure gypsum. Accordingly, the $\delta^{34}S$ values in gypsum occupy a place lies within the ancient marine evaporate, and similar to contemporary marine sulfates (Fig. 4) with little enrichment in heavy isotope. In the ancient marines (Early Paleozoic to Permian), the $\delta^{34}S$ values vary from +30‰ to +10‰. Any shift reflects net fluxes of light sulfur generated during bacterial reduction of oceanic sulfate to the reservoir of reduced sulfide in sediments, thus increasing the ^{34}S-content in the remaining oceanic sulfide reservoir. Conversely, a net return flux of the light sulfide to the ocean during weathering decreases marine sulfate $\delta^{34}S$-values (Beaudoin *et al*., 1994). The isotopic differentiation had been occurred in bitumen of Hit area, in native sulfur of the Abu-Jir area and Mishrq mine. The isotopic differentiation led ultimately to variance in the light and heavy isotopes values. The sulfur isotope values, in the bitumen of Hit area (-2.57‰), in Abu-Jir (14.13 – 14.42 ‰) and in Mishraq mine (9.51‰) indicate a biogenic origin rich in the light sulfur. The sites that in which hydrocarbons such as Hit and Abu-Jir areas are

characterized by euxenic conditions, in particularly, hydrodynamic organic-zones located near the spring waters. Such these sites are certainly rich in light sulfur isotope (Longinelli and Flora, 2007). The chemical reaction under anoxic conditions starts firstly by breaking S-O bond converting sulfate to sulfite (Goldhaber and Kaplan, 1974). The heavy sulfur (^{34}S) becomes depleting in sediments and euxinic waters up to 70‰ (Jørgensen *et al*., 2004), so as H_2S is extremely depleted in ^{34}S. The common genera (*Desulfovibrio* and *Desulfotomaculum*) of sulfate-reducing bacteria (SRB) (Buchanan and Gibbons, 1974); adopted under anaerobic and aerobic environments (Wargin *et al*., 2007). H_2S gas is an evidence of the presence of SRB (Gibbson, 1990), where it is predominant in the study area. Consequently, the sulfate reduction is processed SRB can be grouped in two genera, Desulfovibrio desulfotomaculum (Buchanan and Gibbons, 1974). Later, these genera destroyed the calcium sulfate to sulfide (Krikland and Evans, 1980). So, similar reaction led to reduce gypsum and anhydrite to sulfide as shown by equation below:

$$CH_4 + SO_4^{2-} + 2H^+ = H_2S + CO_2 + 2H_2O$$
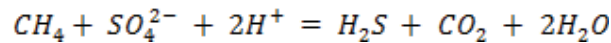
In marine environments, the metabolism of reducing bacteria is based on sulfate ion concentration and reducing conditions (Jorgensen, 1983). Methane (CH_4) and H_2S associated the oil seeps resulted in reducing conditions. The shift of stable sulfur isotope toward negative (from 24.11 to – 2.57 ‰) indicates a bacterial reduction process, where Stemmerik *et al*. (1988) mentioned that the bacterial reduction of sulfate to sulfide yields an enrichment of – ^{34}S values of H_2S that reflecting the degree of reduction. The reduction process was demonstrated by two evidence. The first evidence is the oxygen deficiency was detected by the clustering of the bacterial colonies on bitumen and sulfur surfaces in which SRB had increased (Fig. 5). The high salinity of the sulfurous spring waters in the study area represents the second evidence, where Awadh and Abdul Al-Ghani (2014) mentioned the salinity rise during high evaporation in the Middle Miocene lagoon, this rise in salinity caused a decrease in the solubility of oxygen in the brine (Kinsman *et al*., 1973). The temperature is a control factor for fractionation. SRB can tolerate temperatures from -1.5 to over 100 °C and salinities from fresh water to brines (Canfield *et al*., 2006). The reduction of aqueous sulfates by organic compounds can occurs at temperatures as low as 100 °C (Krouse *et al*., 1988, and Machel *et al*.,

1995). Awadh and Al-Ankaz (2016) demonstrated that the temperature of the ascending hydrocarbons-bearing fluids in the study area is 35 °C.
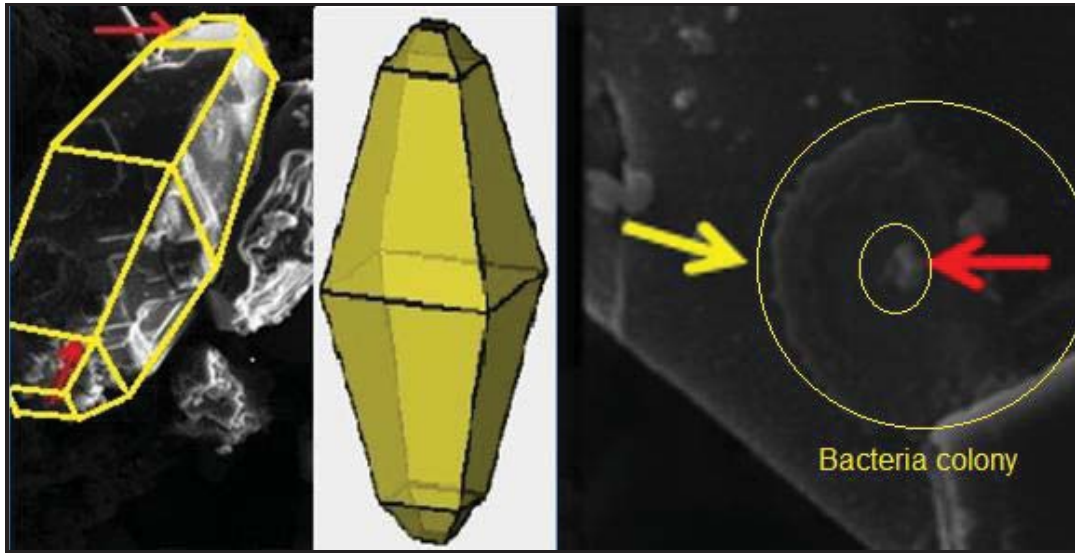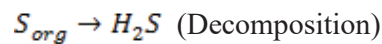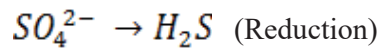

Fig. 5: SEM image displays an Orthorhombic-Dipyramidal crystal (500 µm) of native sulfur discovered in the Abu-Jir sulfur deposits bears a tiny cluster of bacterial colonies

Finally, the field observations and the isotopic data indicate that the biochemical reactions including oxidation, reduction, assimilatory reduction and decomposition are processes currently still ongoing (Fig. 6) as shown below:

$$SO_4^{2-} \rightarrow H_2S \quad \text{(Reduction)}$$

$$SO_4^{2-} \rightarrow S_{org} \quad \text{(Assimilatory reduction)}$$

$$S_{org} \rightarrow H_2S \quad \text{(Decomposition)}$$

There is no evidence to prove oxidation ($H_2S \rightarrow H^0 + SO_4^{2-}$) occurred.
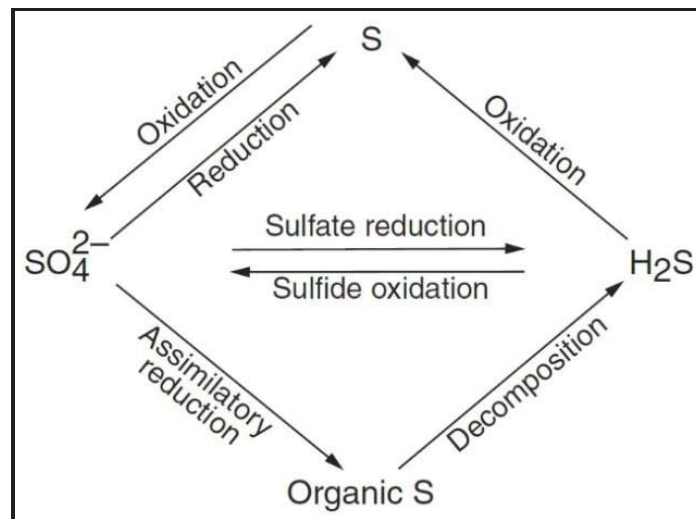
Fig. 6: Biochemical cycles of sulfur (after Cravotta, 1997)

CONCLUSIONS

The findings from this study summarized as:

1. Two crystallographic types of water incorporated in gypsum were detected by FTIR spectra; one distinct type of water is linked with sulfate ions by hydrogen bonding, whilst, the other one is directly linked to calcium ions.

2. The sulfur isotope composition in the gypsum of Fatha Formation is closely reflected marine sulfate. So, it is a primary gypsum precipitated chemically as a directly precipitation form oversaturated solution that had been isolated as a lagoon from marine water without bacterial action. This was demonstrated by the narrow range of $\delta^{34}S$ values (22.5 – 23.52 ‰).

3. The isotopic shift toward light sulfur enrichment (14.13 – 14.42 ‰) in the sulfur samples of the Abu-Jir area indicates a bacterial reduction of gypsum into native sulfur.

4. The native sulfur deposits were formed as a result of the SRB action which is the main process that led to the reduction of the marine sulfate forming native sulfur in Abu-Jir area.

5. The negative value of $\delta^{34}S$ (-2.57‰) in the bitumen sample indicates a high role of SRB due to the presence of hydrocarbons which is suitable conditions for the anaerobic bacteria activity.

6. H_2S generates as a result of the anaerobic bacterial sulfate reduction processes, ongoing on gypsum, anhydrite and hydrocarbons in the hydrodynamic zones.

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