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Physics



Physics Procedia 55 (2014) 41 - 45

Eigth International Conference on Material Sciences (CSM8-ISM5)

# The study of the groundwater by using the <sup>34</sup>S and <sup>18</sup>O of the sulphates-S<sup>18</sup>O<sub>4</sub> isotopes

Sadek Awad\*

Lebanese university, faculties of agronomy and sciences, MCEMA laboratory, Beirut, Lebanon

## Abstract

The stable isotope of the sulphur atom (<sup>34</sup>S) and the <sup>18</sup>O of the sulphates (S<sup>18</sup>O<sub>4</sub>) give information about the type of the mineralisation of the groundwater existing during the water seepage. The decrease of the concentrations in dissolved SO<sub>4</sub><sup>2-</sup> (meq/L) versus the increase of  $\delta^{18}$ O (‰ vs. SMOW) of the sulphates (S<sup>18</sup>O<sub>4</sub><sup>2-</sup>) confirms a partial reduction of the dissolved sulphates in the water. The Under-saturated waters versus the gypsum do not cause the precipitations of the sulphates. The study of  $\delta^{34}$ S (‰ CD) vs. Cl<sup>-</sup> (mg/L) indicates high variations in  $\delta^{34}$ S (‰ CD) for weak difference in the Cl<sup>-</sup> (mg/L) content, this is due to the reduction of the dissolved sulphates. Concerning the Jurassic water in Lebanon, an oxidation of the sulphide can take place.

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Key words: sulphur 34; mineralisation; sulphates; Bekaa; Lebanon.

## 1. Introduction

Thirteen (13) samples of water were analyzed to measure the isotopic content in oxygen-18 of the dissolved sulphates ( $\delta S^{18}O_4^{2-}$  ‰ vs. SMOW (Standard Mean Oceanic Water)). The isotopic contents vary between -4.41 and 9.80 ‰ vs. SMOW (Table 1). A reduction of the dissolved sulphates takes place in the aquifer of Cenomanian to obtain sulphuric formations (H<sub>2</sub>S) with a tendency to dissolve the gypsum after

\* Corresponding author. Tel.:+961-3-711629; fax:+961-8-801100. *E-mail address*:sadekawad@yahoo.fr

1875-3892 © 2014 Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/). Peer-review under responsibility of the Organizing Committee of CSM8-ISM5 doi:10.1016/j.phpro.2014.07.007 the saturation in calcite and dolomite. In consequence, the dissolved sulphates in water coming from the dissolution of gypsum will be subjected to a reduction in the deeply aquifer (Cenomanian) [1].

Site	Date	Reference	Nature	δ <sup>18</sup> O %° (vs VSMOW)	δ <sup>18</sup> O <sub>(SO4)</sub> %° (vs VSMOW)	δ <sup>34</sup> S %° CD	Cl <sup>-</sup> meq/L	SO4 <sup>2-</sup> meq/L
Mount-Lebanon								
Jdita	05/04/2003	C1	Well	-7.74	2.62	-20.46	0.17	0.20
Nabi eila	07/04/2003	C4	Well	-7.64	4.48	-12.78	0.25	0.24
Wadi el karm	10/04/2003	A6	Well	-9.33	9.80	-5.47	0.15	0.29
Bekaa								
Rayack	05/04/2003	C5	Well	-8.08	6.08	12.13	0.34	0.52
Zabboud	09/04/2003	A8	Well	-7.26	2.21	-	0.65	0.13
Anti-Lebanon								
Aîta el Foukhar	19/04/2004	D9	Well	-6.59	3.00	-9.79	0.32	1.23
Aîta el Foukhar	19/04/2004	Al Arich (\$26)	Spring	-7.75	7.24	-11.62	0.35	0.21
Al Dakoui	17/04/2004	D7	Well	-6.13	4.42	2.34	1.16	0.59
Bakka	18/04/2004	D8	Well	-7.02	4.26	-	0.32	0.81
El khedr	05/04/2003	C10	Well	-7.21	0.27	-8.35	0.25	0.22
Mdoukha	19/04/2004	D6	Well	-6.13	-4.41	-	0.34	0.23
Nabi Chit	05/04/2003	C8	Well	-8.18	5.95	3.32	0.21	0.21
Orsal	09/04/2003	A9	Well	-8.86	5.08	0.80	0.21	0.14

**Table 1:**  $\delta^{34}$ S and  $\delta^{18}$ O (SO4) of the groundwater in the valley of Bekaa.

## 2. The sulphur-34 and oxygen-18 of the sulphates

The decrease in the concentration of dissolved  $SO_4^{2^-}$  (meq/l) according to the increase in  $\delta^{18}O$  (‰ vs. SMOW) of the sulphates ( $S^{18}O_4^{2^-}$ ) (Figure 1) can confirm the existence of a partial reduction of the dissolved sulphates in the water. This phenomenon of reduction of the sulphates is possible especially for the confined aquifers of jurassic and cenomanian. The variation of  $\delta^{18}O$  (‰ vs. SMOW) of the sulphates according to the  $\delta^{18}O$  of the molecule of water (Figure 2) confirms the absence of the precipitation of the sulphates.

When the time of residence of the water in the aquifers increases, the water will become more impoverished in  $\delta^{18}$ O of the sulphates and more rich in  $\delta^{18}$ O of the molecule of water. The undersaturated water in gypsum (I.S << 0) does not allow the precipitation of the sulphates.

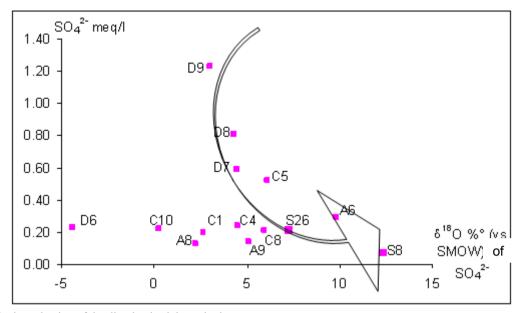


Figure 1: the reduction of the dissolved sulphates in the water.

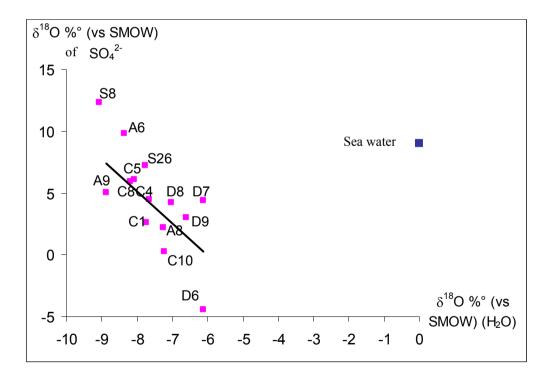


Figure 2: the relation between the isotopic contents in oxygen-18 of the sulphates and of the molecule of water (‰ vs. SMOW).

#### 3. Origin of the mineralization

The hypothesis of an oxidation of the pyrite / marcasite is possible, this ferric geological formation exists in the basic sandstone formation of the inferior Cenomanian (C<sub>1</sub>) [2]. The study of the isotopic contents in  $\delta^{34}$ S (‰ CD) vs.  $\delta^{18}$ O of the sulphates (SO<sub>4</sub><sup>2-</sup>) (‰ vs. SMOW) (Figure 3) indicates a tendency to an oxidation of the sulphurs. In other side, the study of  $\delta^{34}$ S (‰ CD) vs. Cl<sup>-</sup> (mg/L) indicates a strong variation in  $\delta^{34}$ S (‰ CD) for a weak difference in Cl<sup>-</sup> (mg/L) (Figure 4), that gives an idea about the existence of a reduction of the dissolved sulphates [3].

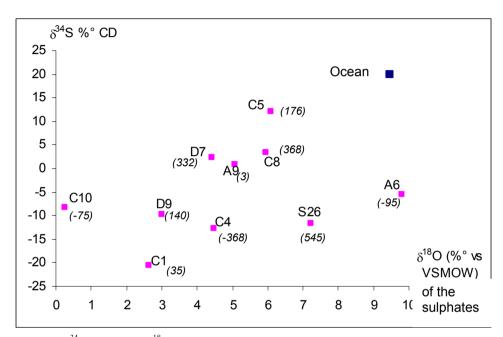
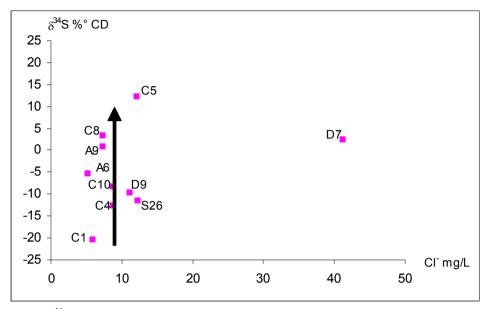


Figure 3 : The study of  $\delta^{34}$ S (‰ CD) vs.  $\delta^{18}$ O (‰ vs. VSMOW) of the sulphates, with the indication of the Eh (mv).

In the Jurassic aquifer, an oxidation of the sulphurs can take place. For the cenomanian aquifer, an oxidation of the sulphurs can occur when there are an oxidizing zone, and a reduction of the sulphates in confined aquifer condition. The origin of the sulphates can be the oxidation of the sulphurs or/and the dissolution of the sulphated minerals coming from the use of the fertilizers for the agriculture zone. The high isotopic contents in  $\delta^{34}$ S (‰ CD) and the enrichment in dissolved sulphates for the water of the Eocene and Neogen aquifers, confirm the pollution of these aquifers by the superficial irrigation's water.



**Figure 4 :** The study of  $\delta^{34}$ S (‰ CD) vs. Cl<sup>-</sup> (mg/L)

### 4. Conclusion

The origin of the sulphates in the water comes from :

- 1) the dissolution of the sulphated formations existing in the aquifers (Gypsum in the Cenomanian)
- 2) the dissolution of sulphated minerals coming from the fertilizers (Eocene, Neogen and locally for the Cenomanian)
- 3) the oxidation of the sulphurs (Pyrite / Marcasite in superior Jurassic and inferior Cretaceous).

#### Acknowledgements

My gratitude and acknowledgements to : Mr. Laurent DEVER—Professor in the University of Paris-Sud, Mr. Mustapha MROUEH Professor in the Lebanese University, all the members of IDES laboratory (Interactions and Dynamic of the Environnements of the Surface), O.N.L (Office National of Litani), METEO Liban in the Bekaa (Haouch el Omara), the faculty of agronomy, the faculty of sciences in Lebanon, NCSR (National Council of the Scientific Research).

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