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## The sources and evolution of sulfur in the hypersaline Lake Lisan (paleo-Dead Sea)

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### Abstract

$\delta^{34}\text{S}$  values in gypsum are used to evaluate the fate of sulfur in the hypersaline Lake Lisan, the late Pleistocene precursor of the Dead Sea (70–14 ka BP), and applied as a paleo-limnological tracer. The Ca-chloride Lake Lisan evolved through meromictic periods characterized by precipitation of authigenic aragonite and holomictic episodes characterized by enhanced gypsum precipitation. The lake deposited two major gypsum units: the “Lower Gypsum unit” (deposited at ~56 ka) showing  $\delta^{34}\text{S}$  values of 18–20‰, and the “Upper Gypsum unit” (deposited at 17 ka) displaying significantly higher  $\delta^{34}\text{S}$  values of 26–28‰. Laminated and disseminated gypsum, residing within the aragonite, exhibit  $\delta^{34}\text{S}$  values in the range of –26‰ to 1‰.

The isotopic composition of the gypsum was dictated by freshwater sulfate input that replenished the upper layer of the lake (the mixolimnion), bacterial sulfate reduction (BSR) that occurred under the anoxic conditions of the lower brine (the monimolimnion), and mixing between these two layers. During meromictic periods, the sulfate reservoir in the lower brine was replenished by precipitation of gypsum from the upper layer, and its subsequent dissolution due to sulfate deficiency induced by BSR activity. This process describes a “sulfur pump” mechanism and its effect on  $\delta^{34}\text{S}$  in the water can be modeled by a modified Rayleigh distillation equation. Steady state  $\delta^{34}\text{S}$  values (~40‰) were reached in the lower brine after long meromictic periods. Following overturn episodes, induced by diminishing freshwater input and lake level decline, large quantities of  $\delta^{34}\text{S}$  enriched gypsum precipitated.

The negative  $\delta^{34}\text{S}$  values in laminated and disseminated gypsum provide evidence for BSR activity in the lower brine that removed isotopically depleted sulfides from the water column, causing significant isotopic enrichment of remaining sulfate. Following the lake desiccation, the sediments were exposed and the latter sulfides oxidized and re-crystallized as gypsum. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** sulfur isotopes; bacterial sulfate reduction; Lake Lisan; Rayleigh distillation; brines

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## 1. Introduction

The isotopic composition of sulfur in open water bodies is dominated by the rate of sulfur input from external sources, and changes in the rate of geochemical processes and removal fluxes within the water body, including the deposition of sedimentary sulfides and sulfates, and bacterial sulfate reduction (BSR) [1–6]. Of the above, the latter has the most significant effect on the isotopic composition of water column sulfate under anoxic conditions. The development of anoxia in open water bodies is typical of estuarine stratified water columns, where BSR tends to occur continuously resulting in sulfate isotopic enrichment, and lowered sulfate concentrations. In closed system environments the BSR and sulfate enrichment can follow the Rayleigh distillation curve [1–6].

Here, we discuss the fate of sulfur in the paleo-Dead Sea (Lake Lisan) lacustrine system that follows a modified track of sulfate isotopic enrichment and Rayleigh distillation scheme. The Dead Sea brine evolved from an ancient Ca-chloride brine [7] (a general summary of closed-basin brines is given in [8,9]). This brine is highly enriched in calcium and relatively depleted with respect to sulfate, and involves an uncommon mechanism of gypsum precipitation. It has been suggested that the precipitation of massive gypsum layers in Lake Lisan was induced by major lake level falls and water column overturns, that occurred during arid periods in the region [10]. The purpose of this work is to study the sulfur system and the gypsum precipitation mechanism in Lake Lisan, and its significance as a paleo-limnological tracer. We use the sulfur isotopic composition in saline and fresh waters and in various types of gypsum to evaluate the sulfur sources and initial isotopic composition as well as the processes that influenced its isotopic and chemical evolution. On the basis of this data we present a conceptual model describing the sulfur cycle under the particular limnological–geochemical configuration of Lake Lisan.

## 2. Geological setting

### 2.1. Lakes and brines in the Dead Sea basin

Several water bodies occupied the tectonic depressions along the Dead Sea rift during the Quaternary

(Fig. 1). These water bodies evolved from the ancient (probably Pliocene) Sedom lagoon that derived its chemical constituents from evaporated seawater that ingressed into the rift valley and interacted with the carbonate wall rocks of the ancient Dead Sea basin, leading to dolomitization and production of Ca-chloride brine [7,11–13]. This brine is relatively low in

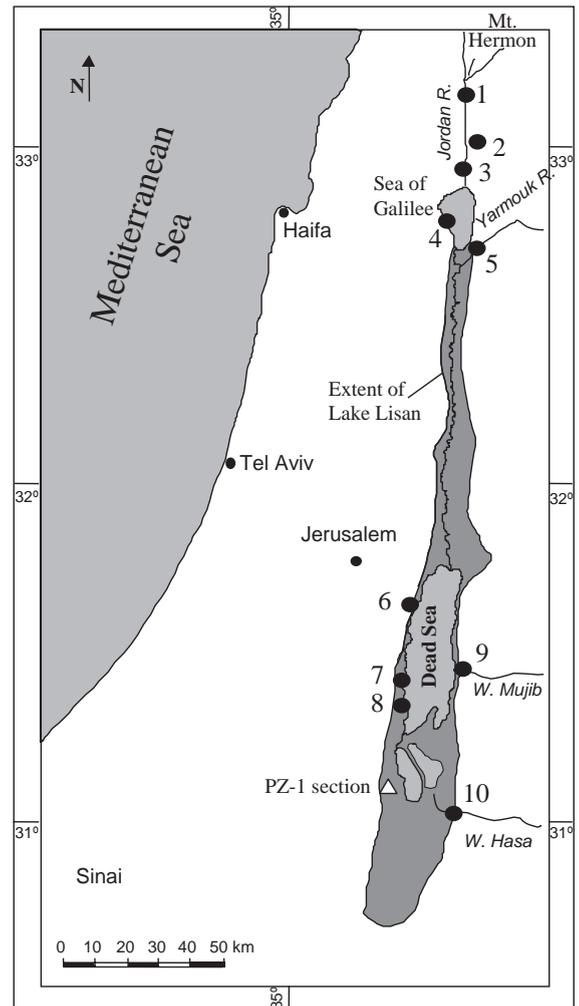


Fig. 1. Location map of sampling sites along the Dead Sea basin–Jordan Valley. Maximum extent of Lake Lisan is marked in grey. Sediments were sampled in the Perazim Valley (PZ-1 section, marked by  $\Delta$ ). Water sampling sites are marked in numbers as follows: 1, Jordan River at Yosef Bridge; 2, Golan Springs; 3, Jordan River at Arik Bridge; 4, Hamme Tiberias; 5, Hamat Gader (Yarmouk River); 6, Enot Zuquim (brackish); 7, En-Kedem/En Shalem saline springs; 8, En Gedi spring (freshwater); 9, Wadi Mujib; 10, Wadi Hasa.

$\text{HCO}_3$  and  $\text{SO}_4$  and is characterized by  $\text{Ca}/(\text{SO}_4+\text{HCO}_3)>1$  (equivalent ratio) [7,11,13]. After the disconnection of the Sedom lagoon from the open sea, the limnological and geochemical history of the now closed and terminal water bodies was controlled by the interaction between the brine and freshwater input from the drainage area of the Dead Sea basin [14].

The volume of the freshwater input, and the lakes' limnological configuration (e.g., stratified vs. homogeneous lakes) reflect the climatic–hydrological history of the region, which fluctuated during the Quaternary between arid to semiarid conditions [10,14–17]. These changes were correlated to the global climate records of Greenland ice and deep-sea cores [10,14,16,18].

The depth of the northern basin of the Dead Sea is  $-730$  msl. The water level of the late Pleistocene Lake Lisan fluctuated between  $-160$  msl (highest stand during the last glacial maximum) to less than  $-450$  msl (at the end of the Pleistocene) [14–17]. For comparison, the water level of the Dead Sea is significantly lower, fluctuating around  $-400$  msl during most of the Holocene.

During times of enhanced rain precipitation, lake level rose and a stratified water column developed. To maintain stratification, a positive or balanced water balance was required, i.e. evaporation was compensated by at least the equivalent amount of freshwater inflow. Stability and thickness of the stratification must have been sufficient as not to allow time and winds to cause significant mixing of the upper layer (mixolimnion) with the lower brine (monimolimnion). A change to a negative water balance resulted in water level drop and a decrease in the thickness of the upper layer. The consequent increase in salinity and density of the upper waters weakened the stability of stratification, leading to overturn and mixing of the entire water column. Such an overturn was recorded in the Dead Sea in 1979 [19] following several hundreds of years of stable stratification [20], that were terminated by a sharp lake level drop that began in the 1960s [21]. Prior to overturn, the thickness of the upper water column was 40 m [22]. Since then the lake is mostly holomictic, experiencing annual stratification and overturn. Short meromictic periods (3–4 yr) develop following particularly rainy winters [22–25].

In Lake Lisan, changes in lake level and mode of stratification are reflected in several geochemical parameters such as the  $\text{Sr}/\text{Ca}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios [10,14,26,27] and the two limnological configurations (stratified and mixed) are characterized by specific sedimentation. The Ca-chloride composition of the brine, along with the bi-carbonate and Ca content of the runoff water (draining carbonate terrains) led to saturation of the upper (mixed) layer of the lake with respect to  $\text{CaCO}_3$  (similar to modern conditions). Saturation with respect to  $\text{CaCO}_3$  was maintained through annual precipitation of aragonite whose crystallization, rather than calcite, was controlled by the high  $\text{Mg}/\text{Ca}$  ratio of the brine [10,28]. The slight excess of bi-carbonate over calcium in the runoff water required that aragonite precipitation consumed some calcium from the brine. However, because the brine was highly enriched in calcium, this had little effect on its concentration. Sulfate that reached the lake with the runoff water accumulated in the upper layer, which was initially under-saturated with respect to gypsum. Provided sufficient time of lake stratification and sulfate accumulation, gypsum saturation was eventually attained. Alternatively, gypsum saturation could have also been achieved as lake level declined and the salinity of the upper water layer increased. Nevertheless, relatively a few gypsum layers are found in Lake Lisan sediments, while those that are found were interpreted to have precipitated during overturn events [10]. According to Stein et al. [10], these gypsum layers, however, cannot account for the total calculated supply of sulfate to the lake. They speculated that the missing sulfate must be present in the form of disseminated gypsum within the Lisan formation.

## 2.2. The Lisan formation at Perazim valley

The Lisan formation (Fm.), deposited between  $\sim 70$  to 14 ka BP [14,18,29,30], is exposed in the Dead Sea basin from south of the Dead Sea, to the Sea of Galilee in the north (Fig. 1). The formation comprises primarily of three lithologies: aragonite, gypsum and silty detritus (made mainly of quartz, calcite, and some dolomite and clay). Aragonite appears in laminated sequences where  $\sim 1$  mm laminae alternate with silty–detritus ones. The aragonite precipitated chemically from the lake, whereas the detritus laminae are

mainly eolian quartz and calcite, and erosion products of the rock cover from the Dead Sea rift shoulders [14,31,32]. It is important to note that in none of the previous studies of the Lisan Fm., have pyrite or other sulfide phases been identified in the sediments [26,27,32,33].

In the Perazim Valley, west of Mt. Sedom diapir, several sections of Lisan Fm. have been measured and described in details [18,29,32,34–37]. Here we focus on the PZ-1 section (Fig. 2), which was divided into three stratigraphic members. The Lower Member consists mainly of “alternating aragonite–detritus laminae” (“*aad*” facies) and is topped by three thick (10–20 cm) gypsum layers (“Lower Gypsum unit”)

that can be correlated over a large distance in the Dead Sea basin [37]. The Middle Member contains more abundant clastic beds (sand, silt and clay) alternating with *aad* sequences and some gypsum. The Upper Member comprises mainly the *aad* facies with massive gypsum layers at the top (“Upper Gypsum unit”).

U-series dating of Lisan aragonite obtained by TIMS provides a high-resolution chronology of the PZ-1 section [18,29]. The ages range between 70 ka BP at the bottom to 14 ka BP at the top of the section. The Lower Gypsum unit precipitated at 56 ka BP and the upper one at 17 ka BP (Fig. 2). The boundaries between the Lower, Middle and Upper Members, coincide with the transitions from marine isotopic stages

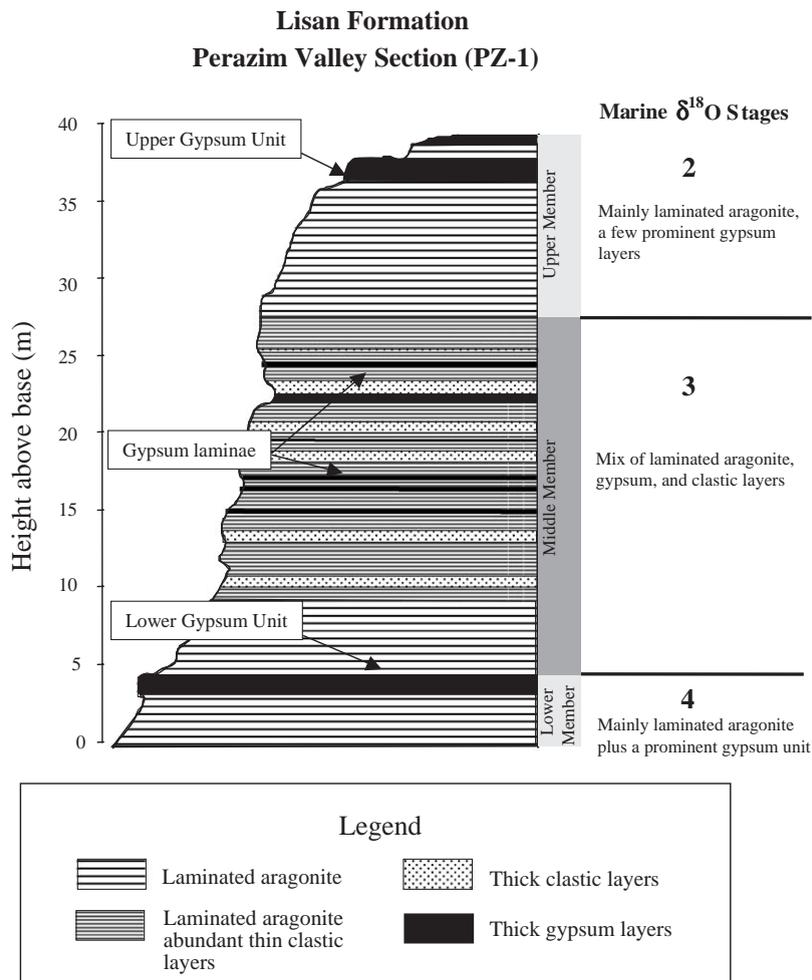


Fig. 2. Lithology and stratigraphy of the PZ-1 section at the Perazim Valley (after Hasse-Schramm et al. [18]). The Lower Gypsum unit and the Upper Gypsum unit are the main gypsum units in the section, while thin gypsum laminae are abundant throughout the Middle Member.

(MIS) 4, 3 and 2 in the global record, respectively. The *aad* sequences that characterize the Lower and Upper Members, were deposited during high lake-level conditions, corresponding to the colder MIS 4 and 2, respectively, while the abundant clastic layers of the Middle Member reflect lower lake-stand conditions that prevailed during the warmer MIS 3 [14,18].

### 3. Methods

The different types of gypsum that appear in the Lisan PZ-1 section (discussed in Section 4.2) were dissolved in de-ionized water, filtered, and the  $\text{SO}_4$  precipitated as  $\text{BaSO}_4$ . The precipitate was then collected on a Whatman<sup>®</sup> ashless filter paper (#42), thoroughly washed with de-ionized water and burned at 850 °C. The  $\text{BaSO}_4$  was introduced into a sulfur vacuum extraction line at the Geological Survey of Israel, where  $\text{SO}_2$  gas was produced and separated following the procedure described by Coleman and Moore [38]. The  $\text{SO}_2$  gas was collected in gas ampoules, which were shipped to the British Geological Survey where the isotopic analyses were carried out on a VG Sira II mass spectrometer. The overall analytical reproducibility is  $\pm 0.2\%$  as determined on repeated replicates of laboratory internal standard. The international reference material NBS-127 gave an average of  $\delta^{34}\text{S}=20.4\%$  ( $n=5$ ).

Water samples were treated according to the procedures described by Stein et al. [10] and Gavrieli et al. [39]. Samples were collected directly into double-seal polyethylene bottles and refrigerated. Before further treatment they were filtered to remove suspended particles.  $\text{SO}_4$  concentrations in the water and brine samples were measured in the Geological Survey of Israel using an ICP-AES (Perkin Elmer Optima 3300).

### 4. Results

#### 4.1. $\delta^{34}\text{S}$ values in waters from the drainage area of Lake Lisan

The sulfur isotopic compositions of various waters from the drainage area of the lake are required to constrain the composition of the freshwater input

and saline water (representing the brines) inputs. Table 1 lists  $\delta^{34}\text{S}_{\text{SO}_4}$  values of representative water samples from the drainage basin of the Dead Sea. The sampling sites are marked in Fig. 1. It can be assumed that most of these sources were also relevant during the Lisan period (~70–14 ka BP), when the lake was significantly larger than the present Dead Sea. A major water source to Lake Lisan was probably the upper Jordan River, which originates from the springs discharging at the foot of Mt. Hermon. The Jordan River was sampled at Yosef Bridge before it enters the artificially dried Hula basin. The  $\delta^{34}\text{S}$  value obtained there was 13.7‰ reflecting contributions of subsurface Triassic gypsum [40,41]. Nissenbaum [41] reported lower values of 6.5–10.6‰ for the upper Jordan River. Further downstream, the Jordan River receives water from the springs of the Golan Heights (basaltic aquifers and streams), which exhibit values of  $\delta^{34}\text{S}=12\text{--}13\%$ . None of these water sources are suspected of being contaminated and therefore their isotopic composition should represent the late Pleistocene solutions. The southern leg of the Jordan River between the Sea of Galilee and the Dead Sea was not sampled because its current base flow is not of natural composition [42].

Other major freshwater sources that drained into Lake Lisan include the Yarmouk River, the major

Table 1  
 $\delta^{34}\text{S}$  values in major water sources in the drainage area of the Dead Sea and Lake Lisan

Water source	Date	$\delta^{34}\text{S}$ (‰)	$\text{SO}_4$ (mg/l)
North Jordan River (Yosef Bridge)	7/1994	13.7	26 [10]
Golan basaltic springs	9/2000	11.9–12.7	4–8
Jordan River before Sea of Galilee (Arik bridge)	3/1994		21 [10]
Sea of Galilee (surface)	7/1996	11.8	52 [10]
Yarmouk River	3/2002	10.4 [42]	77 [42]
Dead Sea	1997	14.5 [39]	494 [39]
Wadi Mujib	3/1996	6.9	60
Wadi Hasa	3/1996	5.5	120
Dead Sea saline springs	1996– 1997	~22 [39]	~1000 [39]
En Gedi spring (En Shulamit)	5/1996	9.6 [39]	28 [39]
Enot Zuqim (freshwater spring)	10/1996	4.8 [39]	78 [39]

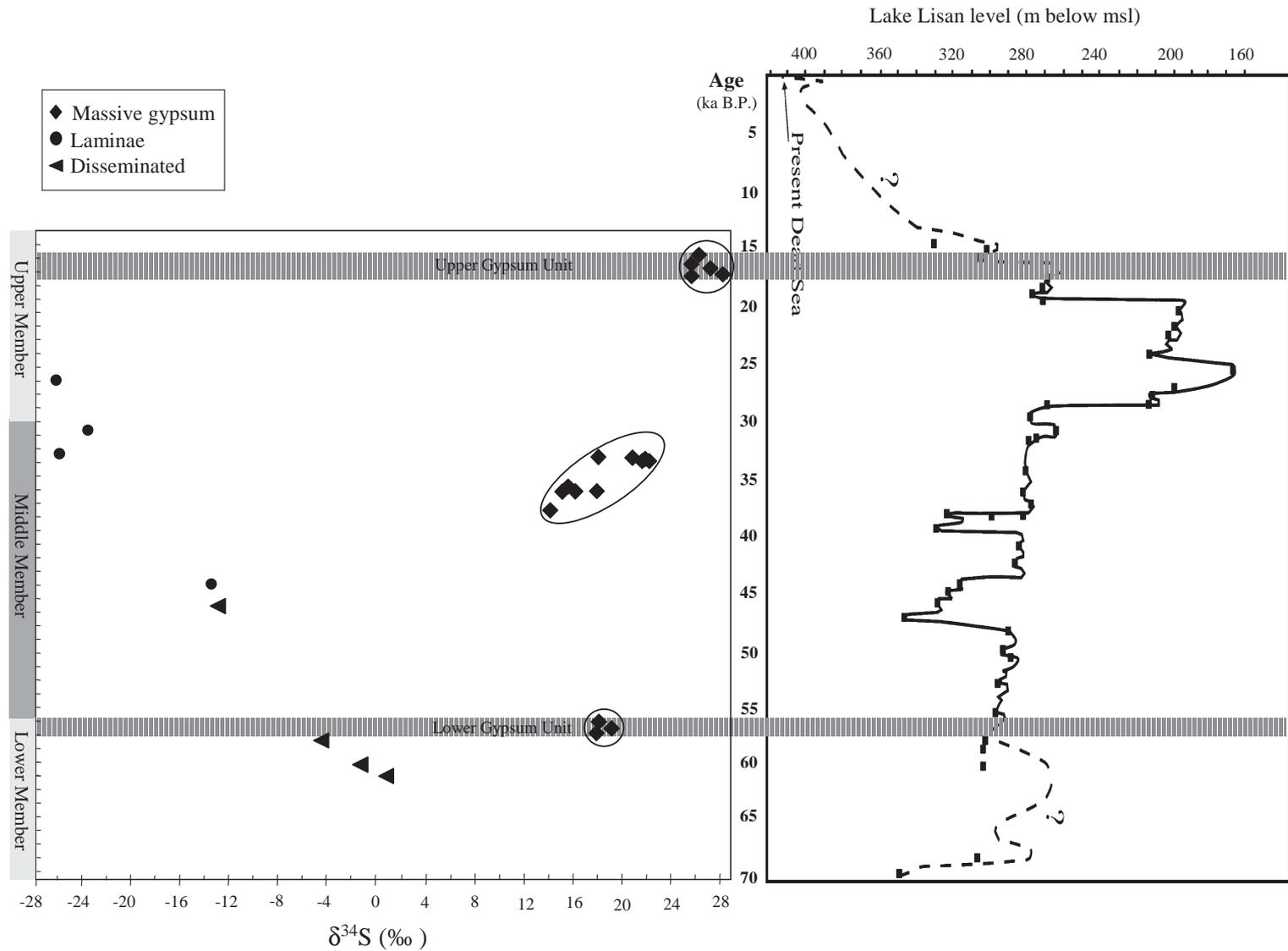


Fig. 3. Variations in  $\delta^{34}\text{S}$  values along the PZ-1 section. The main gypsum units display  $\delta^{34}\text{S}$  values in the range of 14–28‰, whereas the disseminated and gypsum laminae have depleted  $\delta^{34}\text{S}$  values in the range of –26‰ to +1‰. Also shown is the reconstructed level curve of Lake Lisan (modified after Bartov et al. [16]). The Upper Member was deposited during high-stand period; the Middle Member during low stands. The deposition of the main gypsum units occurred following water column overturn during arid periods and water level drop.

tributary of the Lower Jordan River south of the Sea of Galilee ( $\delta^{34}\text{S}=10.4\text{‰}$ ), Wadi Mujib ( $\delta^{34}\text{S}=6.9\text{‰}$ ) and Wadi Hasa ( $\delta^{34}\text{S}=5.5\text{‰}$ ), the latter two discharging directly to the Dead Sea from the Edom Mountains to the east. The wadis on the western escarpment have no base flow and are characterized by winter flashfloods. Freshwater springs, such as En Gedi and the brackish water at Enot Zuqim, yielded sulfur isotopic composition in the range of 4.7–9.6‰ [39], typical to waters of carbonate terrains in Israel.  $\delta^{34}\text{S}$  values in rainwater from the Dead Sea basin area lie in the range of 0.6–8.5‰ [43–45].

Another water source in the Dead Sea–Jordan basin are thermal saline springs, such as Hamme Tiberias at the Sea of Galilee, Hamat Gader in the Yarmouk River, and En-Shalem and En Kedem springs located on the shores of the Dead Sea. These springs have sulfur isotopic compositions in the range of 22–23‰ [39,46]. Based on hydrological considerations, their chemical composition, low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\delta^{34}\text{S}$  values, it has been suggested that some of the saline springs are diluted remnants of the Sedom Ca-chloride brine that percolated into the Cretaceous wall rocks of the basin and remained there for a substantial time period [10,39,47]. These, or chemically similar brines had limited contribution to the chemical budget of Lake Lisan [10].

#### 4.2. $\delta^{34}\text{S}$ values in gypsum samples from the Lisan PZ-1 section

Samples for the present study were collected from the three distinct types of gypsum that appear in the PZ-1 Lisan section: (1) massive and laminated gypsum units that are 10–20 cm in thickness (the major gypsum units are marked in Fig. 2), (2) thin (less than 5 mm) gypsum laminae, which are abundant in the Middle Member of the formation, (3) disseminated gypsum, extracted by water leaching of aragonite laminae.

The  $\delta^{34}\text{S}$  values of the gypsum samples from the PZ-1 section are illustrated in Fig. 3 and are listed in Table 2 along with the lithological description of the samples. The Lower Gypsum unit (~4 m above the base of the formation) is characterized by  $\delta^{34}\text{S}=18\text{--}20\text{‰}$  while the Upper Gypsum unit (capping the Upper Member) displays significantly more  $^{34}\text{S}$  enriched compositions of  $\delta^{34}\text{S}=26\text{--}28\text{‰}$ . Gypsum

Table 2  
 $\delta^{34}\text{S}$  of sulfates in sediments of the Lisan Formation

Sample	Height (cm)*	Lithology	$\delta^{34}\text{S}$ (‰)
<i>Upper Member</i>			
IG-1A	3826	Laminated (4–6 mm) gypsum	26.4
IG-4	3776	Massive gypsum	25.7
IG-3	3770	Laminated gypsum	27.1
IG-2	3769	Alternating gypsum and detritus	27.1
IG-10	3690	Massive gypsum	28.5
IG-11	3671	Mainly laminated gypsum with detritus	25.7
<i>Middle Member</i>			
IG-12	2909	Red laminae, mostly halite with some gypsum	–26.1
IG-15	2540	Gypsum laminae with halite within aragonite	–23.5
IG-17	2380	Gypsum laminae	–25.9
IG-18	2335	Laminated gypsum	18.0
IG-19	2335	Laminated gypsum	21.8
IG-20	2330	Laminated gypsum	20.7
IG-21	2327	Laminated gypsum	22.2
IG-21a	2327	Laminated gypsum	22.2
IG-21b	2327	Laminated gypsum	21.8
IG-22	2325	Laminated gypsum	21.9
IG-23	2119	Gypsum and detritus	15.8
IG-24	2092	Laminated gypsum	18.0
IG-25a	2090	Columnar gypsum within detritus	16.2
IG-25b	2090	Gypsum and detritus	15.0
IG-26	1950	Columnar gypsum within detritus	14.1
IG-27	1412	Gypsum laminae	–13.4
L-8-T	1247	Disseminated in aragonite	–12.8
<i>Lower Member</i>			
IG-31	450	Laminated gypsum	18.3
IG-30	390	Massive gypsum	19.3
IG-29	330	Laminated gypsum	17.9
L-3	290	Disseminated in aragonite	–4.4
L-7	82	Disseminated in aragonite	–1.1
PZ-1-0	0	Disseminated in aragonite	0.9

\* Height refers to elevation above base line of PZ-1 section in Fig. 2.

layers from the Middle Member yielded  $\delta^{34}\text{S}$  values in the range of 14–22‰. The gypsum laminae and the disseminated gypsum are characterized by negative  $\delta^{34}\text{S}$  values in the range of –26‰ to –13‰ and –13‰ to +1‰, respectively. The  $\delta^{34}\text{S}$  values of the thick gypsum layers appear to increase from bottom to top of the section, while combined, the disseminated and thin laminae of gypsum seem to form a negative trend.

## 5. Discussion

### 5.1. $\delta^{34}\text{S}$ values in the ancient Dead Sea brine

The  $\delta^{34}\text{S}$  isotopic value of the ancient brine in the Dead Sea basin was dictated by the composition of the Sedom lagoon, which was filled by seawater that entered the basin during the Pliocene. The evaporated seawater precipitated gypsum, interacted with the Cretaceous wall rocks of the basin, dolomitized them, precipitated more gypsum and returned to the lagoon as Ca-chloride brine [7,11,13,39]. Precipitation of gypsum involves only limited fractionation of sulfur isotopes whereby  $^{34}\text{S}$  is enriched in the solid phase leading to slight isotopic depletion in the residual solution ( $\Delta^{34}\text{S}=1.65\text{‰}\pm 0.12\text{‰}$ ; [4,48]). The Sedom Fm. salts display  $\delta^{34}\text{S}$  values of 16.5–20.8‰ [11], i.e., the same to somewhat depleted values relative to Neogene seawater (~21‰; [2,49]), most likely indicating some contribution of freshwater in the early stage of the lagoon history.

After the disconnection of the Sedom Lagoon from the open sea, BSR at the bottom of the lakes and mixing between the Sedom brine and freshwater could have modified the sulfur isotopic composition. Indeed, BSR has been identified in the modern Dead Sea and its sediments when the lake was still stratified [33,45]. Thus, changes in the  $\delta^{34}\text{S}$  values that characterize the lacustrine bodies in the Dead Sea basin have been governed by the sulfate content and  $\delta^{34}\text{S}$  values in the inflowing freshwater, in the brines, the product of their mixing, and processes within the lakes.

### 5.2. $\delta^{34}\text{S}$ of the inflowing sulfate

The relative contributions of the freshwater sources to the Dead Sea/Lake Lisan were estimated by Stein et al. [10] on the basis of strontium isotopes and chemical composition of the Lisan aragonite and contributing solutions. They suggested that northern Jordan River and runoff waters from the basin shoulders contributed about 1:1 mixture of the freshwater entering the lake. Applying this ratio, and considering the sulfate concentration of the various freshwater sources (~20–120 mg/l; Table 1), the sulfur isotopic composition of freshwater sulfate that flowed into Lake Lisan was in the range of 6–14‰ (Table 1).

The saline springs, with high sulfate concentrations, could contribute sulfate with enriched isotopic values (~22‰; Table 1; [39]) to the lake. However, it was argued that the saline springs could have only limited contribution to the chemical budget of the lake [10]. Moreover, considering the isotopic composition of the saline springs, changes in their relative sulfate contribution cannot account for the isotopic enrichment of the Upper Gypsum unit nor for the isotopic depletion of the disseminated gypsum.

For the discussion and the conceptual model that follows we assume an inflowing sulfate average isotopic composition of 10‰. While this composition may be offset by a few per mill either way, it would not change the results of the proposed model and the conclusions regarding the unique sulfur cycle that operated in Lake Lisan.

### 5.3. Sulfate in the modern Dead Sea brine and in Lake Lisan

Sulfate concentration in the Ca-chloride brines of the Dead Sea basin (modern Dead Sea water and saline springs on the lake margins) is limited by the high Ca concentration and gypsum saturation: the more saline and Ca-rich the brine is, the lower is its sulfate concentration.

In the modern Dead Sea (TDS=340,000 mg/l) the high calcium content (18,000 mg/l) and gypsum saturation dictate sulfate concentration of only 450–500 mg/l. Even at these relatively low sulfate concentrations, the brine is somewhat over-saturated with respect to gypsum but kinetic factors limit its precipitation [50,51]. Higher sulfate concentrations in the Dead Sea brines were reported in the 1950s. At that time, the Dead Sea was still a stratified lake, with a relatively dilute upper layer (TDS=300,000 mg/l, Ca=16,400 mg/l; [22]). The lower Ca concentration enabled a higher sulfate concentration of ~580 mg/l, while still maintaining saturation with respect of gypsum. As the Dead Sea level declined, the salinity of the upper layer as well as Ca concentration increased, and gypsum precipitated from the brine [22]. Because of the extremely low  $\text{SO}_4/\text{Ca}$  ratio in the brine, the precipitation of gypsum lowered the  $\text{SO}_4$  concentration, while Ca concentration continued to increase along with the overall salinity.

The Ca-chloride brine of the Dead Sea and Lake Lisan, and the freshwater sources derived from the carbonate terrain in the drainage basin, have different  $\text{SO}_4$  and Ca contents, but rather similar  $\text{HCO}_3$  abundances [10]. Thus, when the calcite-saturated freshwater enters the aragonite-saturated lake, its  $\text{HCO}_3$  is removed from the upper water layer as aragonite. Most of the calcium that precipitates as aragonite is also derived from the freshwater. Yet, because there is some excess of  $\text{HCO}_3$  over Ca in the inflowing freshwater (i.e.  $\text{Ca}/\text{HCO}_3 < 1$ ), some contribution of Ca from the brine is also required. Thus, Ca concentration remains nearly unchanged, or decreases as a function of the dilution of the upper water column. On the other hand, as long as gypsum does not precipitate from the upper water column, sulfate accumulates and its concentration rises.

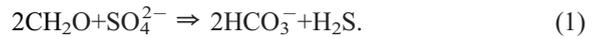
The saline springs around the Dead Sea, which are saturated with respect to gypsum, have a salinity approximately half that of the Dead Sea, and contain lower Ca and higher sulfate concentrations (about 11,500 and 1000 mg/l, respectively; [39]). These compositions probably resemble those of Lake Lisan, whose salinity ranged between a third and a half that of the Dead Sea [27,32,52].

The differing isotopic ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios) and chemical (Sr/Ca ratios) compositions of aragonites and the corresponding disseminated salts in the Lisan Fm. provide evidence for the preservation of difference in compositions between the upper and lower water bodies during stratified periods [10,14,26,27]. This does not imply that some diffusion and mixing between the two waters did not take place at the interface and transition layer. In fact, it is possible that some gypsum precipitated at this interface due to mixing between the relatively sulfate-rich upper layer, and more concentrated and calcium-rich lower waters. However, we consider this process to be minor as it still enabled the two water bodies to develop a different chemical and isotopic signature over a prolonged time period. As will be discussed hereafter, this is particularly true of the sulfur isotopic composition.

#### 5.4. Bacterial sulfate reduction

Bacterial sulfate reduction (BSR) is a major process that can change the sulfate isotopic composition

of the brine. This process takes place under anoxic conditions following the very simplified overall reaction:



BSR is accompanied by isotopic fractionation whereby preferential reduction of  $^{32}\text{SO}_4$  results in the remaining sulfate becoming typically enriched in  $^{34}\text{S}$ . The fractionation associated with BSR varies over a wide range of 5‰ to (–46)‰ [53–59] and is dependent on various factors, including temperature, rate of reduction, bacteria species, and availability of sulfate. Under closed system conditions and known fractionation factor, the evolving isotopic composition of the remaining sulfate follows a Rayleigh distillation equation which can be approximated by [3]:

$$\delta^{34}\text{S} = \delta^{34}\text{S}_i + 1000(\alpha - 1)\ln f \quad (2)$$

where:  $f$  is the fraction of sulfate remaining in solution;  $\delta^{34}\text{S}_i$ ,  $\delta^{34}\text{S}$  are the initial and measured  $\delta^{34}\text{S}_{\text{SO}_4}$ , respectively; and  $\alpha$  is the sulfur fractionation factor.

During stratification, anoxic conditions develop in the lower brine as oxygen is consumed through the oxidation of organic matter, which sinks to the deep water from the upper layer. Once all or most of the oxygen has been consumed, the oxidation of the remaining organic matter continues through bacterial reduction of nitrate, Mn- and Fe-oxyhydroxides and sulfate [60 and references therein]. Prolonged stratification periods, lasting tens to a few thousands of years are possible in deep saline lakes such as Lake Lisan and the Dead Sea, when freshwater inflow dilutes the upper waters and the salinity of the upper layer is significantly lower than that of the lower brine. As mentioned above, during meromictic periods limited mixing probably occurs across the transition layer. Nevertheless, the composition of the lower brine during meromictic periods changes very little. At the same time, it is likely to develop anoxic conditions which favor BSR activity. Indeed, prior to the 1979 overturn, the lower water body of the Dead Sea contained  $\text{H}_2\text{S}$  [22,33,45], and coexisting sulfate and sulfides showed sulfur isotope fractionation of 25–30‰, suggesting  $\text{H}_2\text{S}$  production by BSR [33,45]. Similar sulfur isotope fractionations were found in various hypersaline springs and groundwater around

the Dead Sea [33,39] as well as in sediments of the Dead Sea [45,61], indicating that BSR can thrive in the hypersaline environment of the Dead Sea brine system. Some of these anoxic groundwaters have chemical compositions very similar to the Dead Sea water, yet their sulfate isotopic composition is highly  $^{34}\text{S}$  enriched, attaining values as high as  $\delta^{34}\text{S}=60\text{‰}$  [39].

Evidence for the occurrence of BSR in Lake Lisan is provided by the isotopic composition of the disseminated gypsum and the thin gypsum laminae. The occurrence of these gypsum types in the sediments, in addition to the massive gypsum layers, was previously suggested by Stein et al. [10] on the basis of mass balance calculations (i.e., the “missing” sulfate). The low  $\delta^{34}\text{S}$  values of both ( $-13\text{‰}$  to  $+1\text{‰}$  in the disseminated gypsum and  $-26\text{‰}$  to  $-13\text{‰}$  in the thin gypsum laminae; Table 2; Fig. 3) indicate that the sulfate sulfur is of biogenic origin. In fact, the most depleted  $\delta^{34}\text{S}$  values may point to further isotope fractionation during bacterial disproportionation of sulfur intermediate products produced during anoxygenic phototrophic oxidation of  $\text{H}_2\text{S}$  [59,62,63]. On the other hand, the more enriched  $\delta^{34}\text{S}$  values determined for the disseminated gypsum could be an analytical artifact. During the dissolution of the disseminated salts, some aragonite also dissolves, thereby contributing sulfate that coprecipitated with the aragonite from the upper layer. As outlined below, this aragonite-derived sulfate is probably characterized by isotopic composition closer to the freshwater sulfate composition, i.e.,  $\delta^{34}\text{S} \approx 10\text{‰}$ , and far removed from the depleted compositions found in the thin gypsum laminae or measured in the disseminated gypsum. The source of the isotopically depleted  $\delta^{34}\text{S}$  values of the thin gypsum laminae and disseminated gypsum is discussed in the following sections.

### 5.5. The “sulfur pump” in Lake Lisan

Due to the high salinity of Lake Lisan, the contribution of most incoming ions to the salt budget of the water column was generally relatively small, enabling the preservation of the ionic ratios typical to the original Ca-chloride brine [10]. The unique Ca-chloride composition dictated a swift removal of the relatively large quantities of bi-carbonate that entered the

lake and at the same time the accumulation of entering sulfate in the upper layer (Fig. 4a). Periods of positive water balance resulted in lake level rise, development of relatively dilute upper water column and the maintenance of prolonged water column stratification. The build-up of sulfate concentrations in the upper layer is imperative for the precipitation of massive gypsum layers during the following overturn events. Given enough time and sulfate input, the upper layer eventually attained saturation with respect to gypsum. From this stage onward, additional freshwater inflow to the lake would result not only in precipitation of aragonite, but also with that of gypsum (Fig. 4b). However, the isotopic composition of the laminated

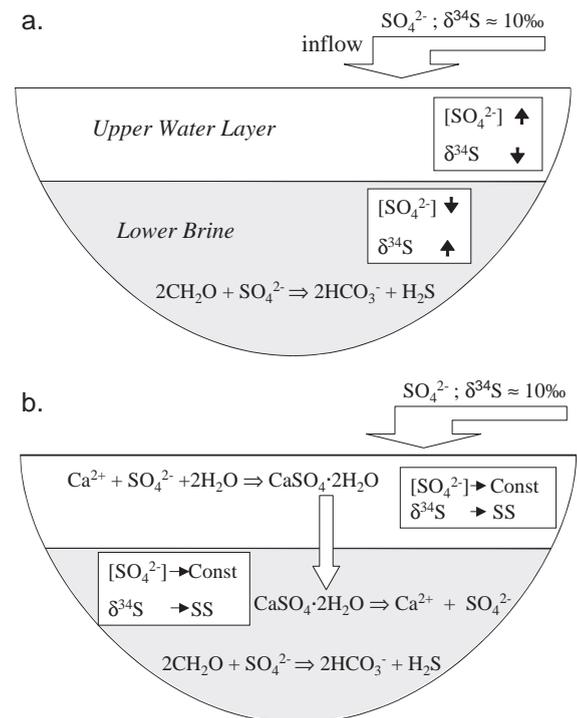


Fig. 4. Schematic representation of the “sulfur pump” model. Arrows denote trends of increasing (upward) or decreasing (downward)  $\text{SO}_4$  concentrations or  $\delta^{34}\text{S}$  values: a) Onset of stratification. Sulfate from inflowing freshwater accumulates in the upper water layer while sulfate is consumed in the lower brine through bacterial sulfate reduction (BSR). b) Full operation of the “sulfur pump”. The upper water layer attains saturation with respects to gypsum, which crystallizes and precipitates to the lower brine where it dissolves. BSR consumes sulfate but its concentration rises due to gypsum dissolution until saturation with respect to gypsum is reached.  $\delta^{34}\text{S}$  rises until steady state isotopic composition (SS), defined by Eq. (4), is attained.

and disseminated gypsum, characterized by  $\delta^{34}\text{S}$  values of  $-26\text{‰}$  to  $+1\text{‰}$ , which are much lower than  $\delta^{34}\text{S}_{\text{SO}_4}$  in the freshwater ( $\sim 10\text{‰}$ ) or in the brine, are not consistent with direct deposition of gypsum from the upper water layer to the sediments. More likely, these depleted isotopic compositions reflect sulfide production by BSR as argued above. To resolve this problem we propose a mechanism termed the “sulfur pump”.

The rate of oxygen consumption in the lower brine during stratified periods depends largely on the supply of organic matter from above. It is reasonable to assume that by the time gypsum begins precipitating from the upper layer, the lower brine has already developed anoxic conditions and BSR is active. Intensive BSR in the lower brine would decrease the sulfate concentration in the brine, which may become under-saturated with respect to gypsum. Gypsum that precipitates from the upper layer and sinks through the lower brine is then susceptible to dissolution. Accordingly, the inflowing sulfate is transported via continuous gypsum precipitation from the upper layer to the lower brine where it re-dissolves. Concurrent BSR in the lower brine results in  $^{34}\text{S}$ -depleted sulfide and  $^{34}\text{S}$ -enriched sulfate (Fig. 4b). This “sulfur pump” can work as long as sulfur supply and gypsum precipitation from the upper layer continues. When the rate of gypsum precipitation from the upper layer and its dissolution in the lower brine outweighs the rate of sulfate reduction, sulfate concentration recovers. Eventually the lower brine attains its original sulfate concentration, and becomes saturated with respect to gypsum. Reduction of sulfate at this stage is compensated by gypsum dissolution, while the excess gypsum reaches the bottom sediments.

Anoxic conditions and the “sulfur pump” will prevail for some time even after a change to a negative water balance, and will cease only when overturn occurs and the entire water column oxidizes. Prior to the overturn, gypsum will precipitate from the upper layer as an evaporitic mineral, in response to increasing salinity, and less due to sulfate inflow. Sulfate concentration will decrease as the general salinity and Ca content increases, and the upper layer approaches a chemical composition similar to that of the lower brine. At this stage, the most significant difference between the two water layers could be their sulfate content and isotopic composition. The

“sulfur pump”, by its nature, leaves little evidence in the sedimentary record of the Lisan Fm., and its identification relies on the interpretation of  $\delta^{34}\text{S}$  values in the various types of gypsum.

Massive gypsum precipitation occurs during overturn, when the gypsum-saturated upper and lower water bodies mix and out-salting occurs. The  $\delta^{34}\text{S}$  composition of the gypsum will be that of the mixed water body which in turn depends on the relative volumes, concentrations and isotopic compositions of the two water layers before the overturn. This “overturn gypsum” should have higher  $\delta^{34}\text{S}$  values compared to gypsum precipitating pre-overturn from the upper layer. The latter might not be present at all in the sediments since it may have dissolved in the lower brine, or at the bottom of the lake, as might have been the case for the Dead Sea [22,33].

It has been suggested that gypsum precipitation took place during meromictic periods due to some mixing across the transition layer between the water bodies [10]. The isotopic composition of this gypsum would represent a mixture between the two water bodies at proportions that are different than during full overturn or when gypsum precipitates solely from the upper water column, and may therefore smear the change in the isotopic signal expected during the transition from a stratified to a homogeneous water column.

### 5.6. Sulfide precipitation and oxidation

Stein et al. [10] showed, based on mass balance considerations, that not all the sulfate that reached Lake Lisan precipitated in the form of the massive gypsum layers. They suggested that this “missing” sulfate, which according to them precipitated due to mixing and grazing of the interface between the lower and upper water layers, is present in the Lisan Fm. in the form of disseminated gypsum. The isotopic data presented in this paper indicates that the “missing” sulfate was first reduced to sulfide and only then removed from the water column.

The  $^{34}\text{S}$  depleted sulfides were most probably removed from the lake system through precipitation of Fe-sulfide phases and burial in the sediments. The high sedimentation rate of Lake Lisan decoupled these phases from the aqueous system soon after deposition. Thus, during water column mixing and oxidation the

reduced sulfides were not susceptible to oxidation and therefore were not recycled back to the brine. This enabled the preservation of an enriched isotopic composition also after overturn and oxidation.

Oxidation of the Fe-sulfides (whether pyrite, greigite or any other sulfide mineral or amorphous phase), occurred following the lake desiccation and sediment exposure. Such oxidation involves only minor isotopic fractionation [59,64,65], enabling the preservation of the original depleted values. Given the abundance of calcium in the exposed sediments, the oxidized sulfur quickly precipitated and formed the disseminated and thin laminae of gypsum. Though no Fe–S species were identified in the Lisan Fm., their occurrence was reported in the Holocene Dead Sea sediments [61]. Thus, contrary to the Lisan Fm., the freshly exposed Holocene sediments have not yet undergone full oxidation and still contain the original reduced phases.

### 5.7. Deviation from Rayleigh distillation process

The “sulfur pump” describes an open system mechanism that causes the isotopic composition of the sulfate in the lower brine to deviate from a simple Rayleigh distillation behavior described by Eq. (2). Rather, we consider a “modified Rayleigh distillation process” for an open system, previously suggested by Gavrieli et al. [39] for the groundwater around the Dead Sea. In this process, the fractionation between the reactant sulfate and product sulfide remains constant, and the sulfate content of the lower brine does not change. At each time step of the modified Rayleigh distillation the reservoir of sulfur in the lower brine is replenished by the dissolving sulfate and attains the following sulfur isotopic composition:

$$\delta^{34}\text{S} = \delta^{34}\text{S}_i + 1000(\alpha - 1)\ln(1 - F) + \delta^{34}\text{S}_{\text{precipitate}} \cdot F \quad (3)$$

where:  $\delta^{34}\text{S}_i$  is the S–SO<sub>4</sub> isotopic composition of the reservoir (the lower brine) prior to current BSR time step;  $F$  is the fraction of sulfate that is reduced;  $\delta^{34}\text{S}_{\text{precipitate}}$  is the S–SO<sub>4</sub> isotopic composition of the sulfate that replenishes the reservoir (i.e., the gypsum that precipitates from the upper layer and dissolves in the lower brine).

Eq. (3) is plotted in Fig. 5 for different  $\delta^{34}\text{S}_i$  compositions and with  $\alpha=0.97$  ( $\Delta_{\text{H}_2\text{S}}^{\text{SO}_4}=30\text{‰}$ ). The latter value is based on a fractionation factor that characterized the meromictic Dead Sea prior to the 1979 overturn and is similar to the values found in the hydrothermal springs around the Dead Sea [39,45,61]. It can be assumed that the BSR in Lake Lisan was accompanied by the same fractionation factor. With time, continuous BSR leads to a steady state sulfur isotopic composition, as observed in Fig. 5 and defined by Gavrieli et al. [39]:

$$\delta^{34}\text{S}_{\text{ss}} = \delta^{34}\text{S}_{\text{precipitate}} + \Delta_{\text{H}_2\text{S}}^{\text{SO}_4} \quad (4)$$

where:  $\delta^{34}\text{S}_{\text{ss}}$  is the steady state isotopic composition;  $\Delta_{\text{H}_2\text{S}}^{\text{SO}_4}$  is the isotope fractionation associated with the BSR.

### 5.8. The evolution of sulfur in Lake Lisan

The steady state  $\delta^{34}\text{S}$  values of the lower brine are dictated completely by the BSR fractionation factor and the isotopic composition of the replenishing sulfate, and are not affected by the initial isotopic composition of the brine (Fig. 5). Based on present-day  $\delta^{34}\text{S}$  values in the main freshwater sources in the Dead Sea drainage system (Table 1), the waters entering Lake Lisan were in the range of  $\delta^{34}\text{S}=6\text{--}14\text{‰}$ . Under prolonged stratification and sulfate influx, the upper layer would approach the isotopic composition of this inflowing sulfate. Thus, following Eq. (4) and Fig. 5, the steady state  $\delta^{34}\text{S}$  values of the lower brine during prolonged stratification periods could have attained values as high as  $\sim 40\text{‰}$  and still remain saturated with respect to gypsum. The steady state composition is attained when 3–4 times the original amount of dissolved sulfate have been reduced (Fig. 5).

In the following discussion, we assume that the lower brine occupied the deepest depression in the basin and its volume could not have been significantly different than that of the present day Dead Sea (present water level of  $-420$  msl), and therefore we use the Dead Sea properties as representative of those of Lake Lisan’s lower brine. The sulfate reservoir of the Dead Sea amounts to  $\sim 6$  g/cm<sup>2</sup> [10]. Assuming: 1. sulfate concentrations in incoming freshwater of 20–120 mg/l, and 2. an annual freshwater influx of 2–5 m/cm<sup>2</sup>

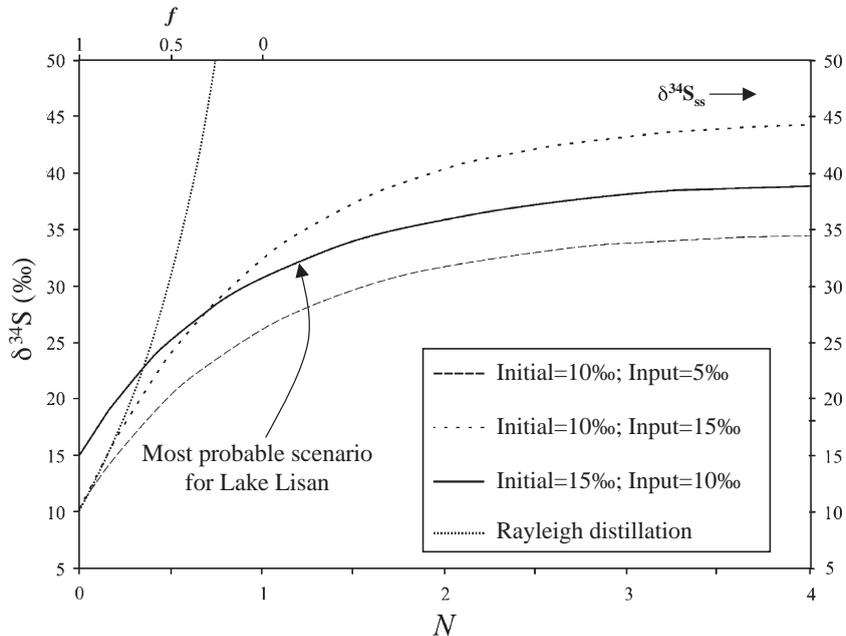


Fig. 5. Changes in  $\delta^{34}\text{S}$  composition of sulfate in open systems where bacterially reduced sulfate is replenished by sulfate input (e.g. gypsum dissolution), thereby maintaining constant sulfate concentration. The calculations are based on a fractionation factor of 30‰ with initial sulfate compositions of 10‰ and 15‰, and sulfate inputs of 5‰, 10‰ and 15‰ (Eq. (3)). Note that the  $\delta^{34}\text{S}_{\text{ss}}$  (Eq. (4)) is approached when the equivalent of 3–4 times the initial sulfate content has been reduced. The  $\delta^{34}\text{S}_{\text{ss}}$  depends only on the fractionation factor and the input values. Assuming an initial isotopic composition of a Dead Sea like brine (~15‰) and an input composition of 10‰ (see text), the designated graph describes the most probable scenario for Lake Lisan. The  $\delta^{34}\text{S}_{\text{ss}}$  value for Lake Lisan is approximately 40‰. Higher  $\delta^{34}\text{S}_{\text{ss}}$  values can be attained through input of more enriched sulfate. The units at the bottom abscissa ( $N$ ) are the number of times the original sulfate content was replaced. The latter may also represent time units, depending on the residence time of sulfate in the lake (see text). The units at the upper abscissa indicate the fraction of sulfate (between  $f=1$  and  $f=0$ ) according to the Rayleigh distillation in a closed system.

[10], then the residence time of sulfate in the Dead Sea is in the range of 100–1500 yr. Thus, the time it would take the lower brine to reach a steady state composition, assuming it is reached when the amount of sulfate reduced is about four times the original dissolved sulfate (Fig. 5), may range between 400 and 6000 yr. These time periods could be somewhat longer in the case of Lake Lisan because its lower brine could have been slightly dilute relative to present day Dead Sea conditions. Thus, the lower Ca concentrations would allow higher  $\text{SO}_4$  concentrations at gypsum saturation, and the arrival time to steady state could be longer accordingly.

Since the precipitation of the Upper Gypsum unit occurred after at least ~10 ka of high water level stand (27–17 ka BP; [18,66]), suggesting prolonged meromictic conditions, it is reasonable to assume that prior to its deposition the water column approached steady state values. In contrast, the deposition of the Lower

Gypsum unit took place at ~5 ka BP following ~5 ka of aragonite–silty detritus deposition, which in turn came after a major depositional hiatus at ~61 ka BP [18]. Between 61 and 56 ka BP water level was much lower than during the long meromictic period preceding the deposition of the Upper Gypsum unit [16,18]. Therefore it is not clear whether the ~5 ka time interval preceding the deposition of the Lower Gypsum unit represents a stable period during which prolonged stratification was established.

The difference between the  $\delta^{34}\text{S}$  values of the Lower Gypsum unit and the isotopically heavier Upper Gypsum unit could therefore reflect the following scenarios:

1. The steady state isotopic composition (described by Eq. (3) and Fig. 5) was not reached in the lower brine prior to the deposition of the Lower Gypsum unit because of frequent mixing events during

lower lake stands. This would result in a less effective or no BSR operation in the lower brine. Alternatively, a  $\sim 5$  ka meromictic period, that might have preceded the Lower Gypsum unit deposition, might have been too short to attain steady state conditions.

2. During the high stand period of 27–17 ka BP, the amount of organic matter supplied from the upper water layer to the lower brine and available for BSR was higher. This is due to an increase in bioactivity enabled by the lowered salinity of the upper water column and from increased inflow of detrital material. This organic matter could support enhanced BSR activity in the lower waters prior to the deposition of the Upper Gypsum unit. Increased bioactivity in the Upper Member period is supported by higher  $\delta^{13}\text{C}$  values in corresponding aragonite laminae compared to the Lower Member [67,68].

The behavior of the sulfur cycle in Lake Lisan, as illustrated by the “sulfur pump” mechanism, is a direct result of the lake’s unique Ca-chloride composition. The accumulation of sulfate from freshwater sources results in attainment of gypsum saturation in the upper water column. Once this is achieved, any additional incoming sulfate would lead to gypsum crystallization and sinking to the lower brine where it is susceptible to dissolution. Accordingly, the replenishment of the sulfate reservoir in the lower water column does not require any additional mass transfer (i.e., water circulation) to the lower waters.

In many non-closed-system anoxic water bodies, such as the Black Sea, sulfate removal by reduction is compensated at least partially through water circulation (Mediterranean Sea water, in the case of the Black Sea). Despite long periods of anoxia, sulfate concentration remain steady but at lowered levels, while the isotopic values are enriched but do not reach the steady state values described by Eq. (4) [69–72 and references therein]. In contrast, sulfate reduction in closed systems, as proposed for example in “snowball earth” models, follows the Rayleigh distillation curve. Accordingly, the sulfate is progressively exhausted to a minimum and reaches extremely high isotopic values [73–75].

It is only in a Ca-chloride environment, such as Lake Lisan, that the open system behavior of constant

flux of sulfate to and from the water body, and concurrent “closed system” characteristics of the lower water layer can coexist. Sulfate replenishment is provided in the form of solid gypsum, requiring no water circulation. Such a unique setting enables the attainment of enriched isotopic composition without depletion of the sulfate reservoir.

## 6. Conclusions

- a) Lake Lisan, the late Pleistocene precursor of the Dead Sea (70–14 ka BP), evolved through cycles of stratifications, overturn episodes and periods of relatively well-mixed water column. In the present study,  $\delta^{34}\text{S}$  in gypsum has been established as a paleo-limnological tracer that can be used to constrain modes of lake configuration.
- b) Three distinct types of gypsum appear in the PZ-1 Lisan Fm.: massive and laminar gypsum layers ( $\delta^{34}\text{S}=14\text{--}28\text{‰}$ ), thin gypsum laminae ( $\delta^{34}\text{S}=(-26)\text{--}(-13)\text{‰}$ ), and disseminated gypsum ( $\delta^{34}\text{S}=(-13)\text{--}1\text{‰}$ ).
- c) The  $\delta^{34}\text{S}$  value in the gypsum is dictated by the composition of the freshwater sulfate input to the upper water layer, bacterial sulfate reduction (BSR) in the lower brine and the degree of mixing between the two water layers. Freshwater input is characterized by  $\delta^{34}\text{S}$  values of 6–14‰, while  $\delta^{34}\text{S}_{\text{SO}_4}$  in the lower brine is significantly higher, due to BSR.
- d) Evidence for BSR is provided by negative  $\delta^{34}\text{S}$  values of the disseminated gypsum and thin gypsum laminae (–26‰ to +1‰). This gypsum is the product of oxidation of the sulfide that was deposited during stratified-anoxic periods in the lake’s history. Oxidation took place after the exposure of the sediments, during low stands, such as those that prevailed during the Holocene.
- e) We propose a “sulfur pump” mechanism, whereby gypsum precipitates from the upper layer and re-dissolves in the anoxic lower brine where BSR operates. This process enables a steady state sulfate concentration and isotopic composition in the lower brine. The steady state  $\delta^{34}\text{S}$  value is defined by the composition of the inflowing freshwater sulfate as well as the fractionation associated with the BSR (30‰ in the Dead Sea brine system).

Thus, the lower brine may attain sulfur isotopic composition as high as ~40‰, following prolonged stratification, and yet remain saturated with respect to gypsum.

- f) Two limnological configurations are revealed by the  $\delta^{34}\text{S}$  values in Lake Lisan gypsum: (I) Prolonged stratification and efficient “sulfur pump” operation that enables attainment of steady state values. This scenario is illustrated by the high  $\delta^{34}\text{S}$  values (26–28‰) of the Upper Gypsum unit (at 17 ka BP). (II) Mixed water column or relatively short stratification periods that prevented the system from attainment of steady state values. This scenario is illustrated by a moderate change in the  $\delta^{34}\text{S}$  values (18–20‰) of the Lower Gypsum unit (at 56 ka BP) relative to the freshwater value.
- g) The occurrence of BSR is well documented in many natural aqueous environments around the world. However, contrary to other long-term stratified-anoxic environments, the unique composition of the Ca-chloride brine in Lake Lisan enabled both isotopic enrichment and concurrent maintenance of the original sulfate concentrations in the water column.

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