

# The Influence of the Dead Sea Water Decline on the Concentration Changes of Lithium and Strontium Trace Elements

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**Abstract:-** The Dead Sea is the lowest unique closed basin on the globe, which has the highest water salinity of 349 g/Kg, where the average ocean water salinity is 35 g/Kg. The basin is occupying about 625 Km<sup>2</sup> with an elevation of 431m below the mean sea level. The total dissolved solids (TDS) in this brine water reaches 379.6 g/L, and the brine density is 1.224 Kg/L. The trace elements have been recently occupied a large important in industrial researches; one of these important elements is Lithium (Li). It is a vital element in many recent industries and technologies, mainly the solar energy storage systems. The Dead Sea water content of Lithium ranges between 17 and 19 ppm and the calculated geological reserve is 5.4 million metric tons. This reserve is enough to supply the world demands for about 160 years according to the world consumption inventory. It is found that the Lithium concentration in the return waters from Arab Potash Company (APC) reached 30 ppm. This retained water can be enriched with Li by natural evaporation up to 65 ppm. The Shock Heat method was used to raise the concentration of Lithium in the residual brine where, an average of 180 ppm was achieved. But, the Lithium content in the precipitated salts is reached up to 49.6 ppm. A strong combination was found between both elements of Lithium and Strontium in all evaporation stages.

**Keywords:-** Dead Sea, Lithium, Density, Shock Heat.

## I. INTRODUCTION

The water of the Dead Sea contains many industrial compounds; the most important exploited commodities among them are Potash, Bromine and Magnesium. The

arid climate in the Dead Sea region causes shrinkage of the water basin, where the inflow waters are much less than the evaporation rates. This decrease of the water level leads to increase the concentration of many elements. Therefore, different minerals started to precipitate, as Halite and some Gypsum. The Potash companies are fruitfully recruited this free solar energy to evaporate the brine waters in artificial ponds to precipitate Carnallite. Consequently, this process concentrates the Lithium and other rare elements in the residual brine.

The worldwide propagation of the renewable resources of energy technologies, such as solar system, increased the demand on the rare earth elements such as Lithium. This element is involved in energy manufactured items, essentially for electric and hybrid vehicles batteries, rechargeable and disposable batteries. Lithium uses are estimated as follows: batteries 39%, ceramics and glass 30%; lubricating greases 8%; continuous casting mold flux powders and polymer production 5% each, air treatment 3% and other uses 10% [1]. The worldwide estimated Lithium resources are about 39 million tons (Mt), this amount will provide the highest proposed demands of 20 Mt for the period 2010 to 2100 [2].

Lithium brine deposits contribute for about 75% of the world's Lithium production. The main Lithium compounds naturally available in the natural brine waters are; Lithium bromide (LiBr), Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), Lithium chlorate (LiClO<sub>3</sub>), Lithium chloride (LiCl) and Lithium fluoride (LiF). The worldwide production of Lithium from brine waters is summarized in table 1. The lowest commercial concentration of Lithium was reported in the Qaidam Basin Salt Lake in China as 150 ppm [3].

Location	Li (ppm)	Reference
Clayton Valley, USA	400	[4]
Salar de Atacama, Chile	1500	[4]
Salar de Hombre Muerto, Argentina	550	[4]
Salar de Olaoz, Argentina	500	[5]
Salar de Rincon, Argentina	330	[6]
Zhabuye Salt Lake, China	750	[3]
Qaidam Basin Salt Lake, China	150	[3]

Table 1:- The main worldwide average concentration of Lithium productive areas.

This research is an effort to evaluate the existing (Li) element and its minerals in the Dead Sea water, the origin of Lithium will be discussed as well. The Shock Heat method is new technique implemented in this research to raise the concentration of Lithium and the accompanied trace element Strontium (Sr) and the rare earth element Yttrium (Y) in the Dead Sea water. This method depends on immediate expose of the brine water to a pre-heated atmosphere, the procedure involve five stages.

## II. METHODOLOGY

The experimental approaches for the chemical analyses of the Dead Sea water were achieved by two different methods: The first method is the direct sampling of the Dead Sea waters and the surrounding possible sources, which are the hot springs and the precipitation of dried springs, the nearby deep aquifer wells, the sinkholes water and soils. This procedure enables to detect the origin of Lithium present in the brine. The second method depends on the laboratory experiments implemented to increase the concentration of Lithium and other trace elements in the brine. This was achieved by the Shock Heat method that contains five consecutive phases; starting the first phase, the oven temperature is elevated to above 300 °C, then the brine is placed in the pre-heated oven for about 6 hours. This period is enough to evaporate about 17% of the water and precipitate most of the Halite and a small amount of Gypsum as it cools to the room temperature. In the second phase, the deposited salts are removed from the brine and consequently, the residual brine returned to the pre-heated oven. This phase continues for about 2 hours to achieve 30% evaporation level, where the rest of the Halite and Gypsum are precipitated in accompany with some Carnallite, Bischofite and other Mg minerals. The third phase includes the 50% evaporation level. Then the 75% evaporation level contains the highest concentration of Li. The last phase of 90% evaporation level showed a decrease of Li contents due to the fact that the precipitated salts capture the Li in its structure. Therefore, the best stage to stop the process is the 75% evaporation stage (4<sup>th</sup> stage), which involves the isolation of the residual dense brine that contains the high Lithium concentration. The evaporation levels above the 75% showed a decreasing concentration of Li. Sampling of the brine during the five phases was achieved and investigated by Quantima GBC Scientific Equipment (ICP-OES) device. The precipitated minerals through the five different phases were sampled and investigated by means of X-Ray

Powder Diffraction (XRD). This device is characterized by scanning  $\theta=2^{\circ}$ - $65^{\circ}$ , the radiation tube is Cu-2K, reproducibility of  $\pm 0.0001^{\circ}$  and accuracy  $\leq \pm 0.0001^{\circ}$  [7]. The search indexing programs ICDD's Sieve for PDF-2 is designed to search and identify unknown materials. Identification is achieved by comparing the X-Ray diffraction pattern from unknown samples with reference database [8]. The S4 pioneer Bruker AX5 GmbH X-Ray Fluorescence Spectrometer (XRF) with the software Spectra Plus is utilized as a powerful analytical technique that analyzes the range from Beryllium to Uranium. The accuracy depends on the sample preparation; this includes the grinding for a final size  $\leq 200$  meshes. Particular problems of accuracy may arise due to X-ray absorption and special line overlap [9]. Sampling of the brine during the five phases was investigated by Quantima GBC Scientific Inductively Coupled Plasma (ICP-OES) device, which is a multi-element analysis technique with precision of  $\pm 1.0\%$  [10]. For the accuracy purposes, the Atomic Absorption Spectrometry (AAS) was implemented to compare the gained results from the ICP investigations. This technique involves the absorption of light ranges between 0.150 A to 3.000 A by free atoms of an element. It is applied for elements with a specified wave length within the range between 185–760 nm [11]. The device has a great sensitivity to detect small amounts as low as 1 ppm. Therefore, the reliability of AAS is adequate for the detection of Lithium (Atomic number 3, Atomic mass 6.941 and primary wave length 670.8 nm) in the Dead Sea waters.

## III. RESULTS AND DISCUSSION

The ICP analyses of the Dead Sea brine water that simulates the cases of each ten years interval indicates that the Lithium contents are low and slightly varies with time as far as the intensive water loss is naturally going on. The results revealed that the Lithium concentration is stable and will not show any significant commercial increments. It is ranging between 17 ppm and 23 ppm (Table 2). The investigated samples confront interference problems, which can be reduced by implementing high resolution spectrometers or using inter element correction factor. Other physical problems are viscosity and density; these problems can be reduced by dilution. The chemical problem facing ICP analyses is ionization of Na, K, Rb and Cs. This problem can be minimized by dilution, control plasma or calibration [12].

Year	2016	2026	2036	2046	2056	2066
Evaporation %	0.00	3.33	6.66	10.00	13.33	16.67
Li (ppm)	17	18	21	21	22	23

Table 2:- The ICP analyses of Lithium in the Dead Sea water for ten years interval.

The precipitated salts at each evaporation level representing the ten years interval were analyzed using the XRD technique to identify their mineral composition. The prepared salt samples for the XRD tests are rapidly affected by the atmospheric humidity, and this complicates the procedure of testing. Therefore, special steps are

introduced to improve the results. The samples were directly investigated individually to control over the atmospheric conditions. This technique also confronts another two main problems in identifying Lithium minerals; the first is the crystallization degree, where amorphous texture can't be realized. The second is the low

presences of this element under the threshold limit of detection. The conducted results using the XRD analyses revealed that only Halite mineral is precipitated through all different stages of evaporation and the Lithium minerals do not precipitate at these evaporation levels that in total represented the 17% evaporation level.

The XRF analyses can't be used as a valuable tool in determining the presence of Lithium and its amounts, because Lithium atomic number (3) is below the device detection limits.

The 'Shock Heat' method was utilized for evaporating water to different levels in stepwise, starting from 17%, 30%, 50%, 75% and 90% evaporation water levels. Therefore, the mixtures of fine crystallized precipitated salts, which have different saturation points, are rapidly formed. As a result of suddenly reaching the saturation point of different constituent minerals, a specified mineral will deposit on its specific point. For example, Sodium chloride "Halite point" occurs at the present water level, thus Halite precipitates at the present

normal atmospheric temperature; this indicates that the specific point of Halite is reached at present conditions. Consequently, the Dead Sea water is saturated with  $\text{Na}^+$  and  $\text{Cl}^-$  ions. While, calcium sulphate (Gypsum) precipitates after 17% evaporation level; this means that the brine is saturated with respect to calcium and sulphate, the "Carnallite point" is started at 30% evaporation level. Consequently, the magnesium chlorides start to form at the 50% evaporation level. But in the 'Shock Heat' method different minerals reach their specific point simultaneously and precipitate at the same time.

The precipitated salt samples were dried until their weight is constant using high temperature that reaches 300 °C. This process was repeated for salts precipitated at each different evaporation levels, and the precipitated salts at each level was sampled and analyzed by the XRF and XRD methods. The XRF result presented in table 3 revealed that  $\text{Na}^+$  decreases continuously by increased water evaporation level. This is due to continuous Halite precipitation in all stages of evaporation including the atmospheric temperature.

Evaporation Level	Na	Ca	K	Mg	Si	S	P	Al	Fe	Br	Cl
0%	39.50	0.69	0.11	0.41	0.47	0.15	0.24	0.21	0.06	0.05	58.10
17%	19.60	6.69	3.09	8.29	0.85	0.05	0.07	0.39	0.07	1.90	58.80
30%	7.10	6.89	1.12	17.90	0.08	0.04	0.04	0.02	0.03	1.62	56.10
50%	3.60	5.49	11.30	19.60	0.10	0.12	0.02	-	0.03	2.49	56.80
75%	3.31	5.12	9.47	19.70	0.08	0.12	-	-	0.03	2.90	59.10
90%	0.65	9.30	0.40	25.60	0.09	0.04	-	-	0.04	3.87	59.60

Table 3:- The XRF results of main elements % in the Dead Sea water at different evaporation levels

The XRF analyses were conducted for the brine water taken from the artificial ponds of APC, the results were equivalent to the waters of 50% evaporation levels,

this means that the extraction of Lithium and other rare earth elements should be started from this level, thus to reduce the cost (Table 4).

Brine Source	Na	Ca	K	Mg	Br	Cl
Dead Sea	39.50	0.69	0.11	0.41	0.05	58.10
Pond C1-1	1.57	9.77	1.77	26.70	1.86	57.80
Pond C1-2	0.89	8.45	3.39	23.90	2.58	59.70

Table 4:- The XRF results of main elements % in the Dead Sea water and Potash Company ponds

The presence of different elements in the brine waters of the APC ponds compared with their percentages in the Dead Sea water (Figure 1).

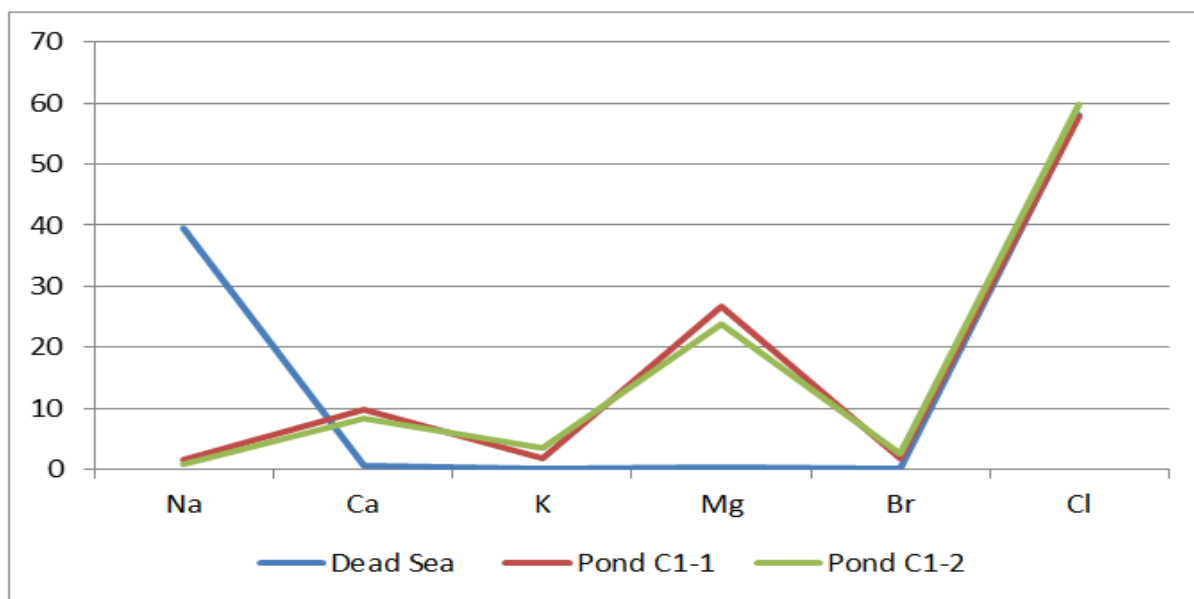


Fig 1:- Comparison between the element components of Dead Sea water and the brine of ponds C1-1 and C1-2.

The XRD results presented in table 5 illustrates that the Lithium compounds were found in the precipitates of the last two evaporation levels. Therefore, the Dead Sea will precipitate Lithium compounds after 225 years, which

is in case of continuous water balance deficit of one billion cubic meters per year, assuming that the total present volume of the water in the Dead Sea basin is equal 300 billion cubic meters.

Evaporation Level	Halite	Tachyhydrite	Carnallite	Bischofite	Chlorocalcite	Kalicinite	Lithium Hydroxide
00%	100	-	-	-	-	-	-
17%	76.46	15.76	7.78	-	-	-	-
30%	42.55	26.48	15.59	15.38	-	-	-
50%	21.94	19.26	13.57	22.61	22.62	-	-
75%	0.82	12.81	15.35	19.55	36.47	-	15
90%	-	-	4.58	13.55	23.37	42.10	16.39

Table 5:- The XRD results of the precipitated Lithium compounds at different evaporation levels.

Consequently, the residual water in each evaporation level was tested using the ICP device. Then, in order to detect the accuracy of these results, the obtained results were confirmed through comparing them with the obtained results for the same samples using the AAS analyses (table

6). It was found that the Strontium concentration is proportionally increases with respect to the Lithium concentration. Therefore, the ICP analyses were conducted for both elements in different stages of evaporation, and the gained results emphasized this result.

Evaporation level %	Li (ppm) ICP	Li (ppm) AAS	Li (ppm) Average	Sr (ppm) ICP	Li : Sr Ratio
0	17	21	19	370	1:19.5
17	18	22.3	20.15	390	1:19.4
30	25	28	26.5	530	1:20.0
50	30	37.3	33.65	680	1:20.2
75	161	180	170.5	3100	1:18.2
90	104	111	107.5	1887	1:17.6

Table 6:- The Strontium and average Lithium concentration ratio at different evaporation levels.

The Lithium to Strontium ratio in the Dead Sea water is calculated to be 1: 19.5 with reference to the conducted results by the two different testing devices ICP and AAS. The average of the Lithium concentration is 19 ppm, while

the Strontium concentration is 370 ppm. This is a good indicator for the precision of the other results (Table 6), (Figure 2).

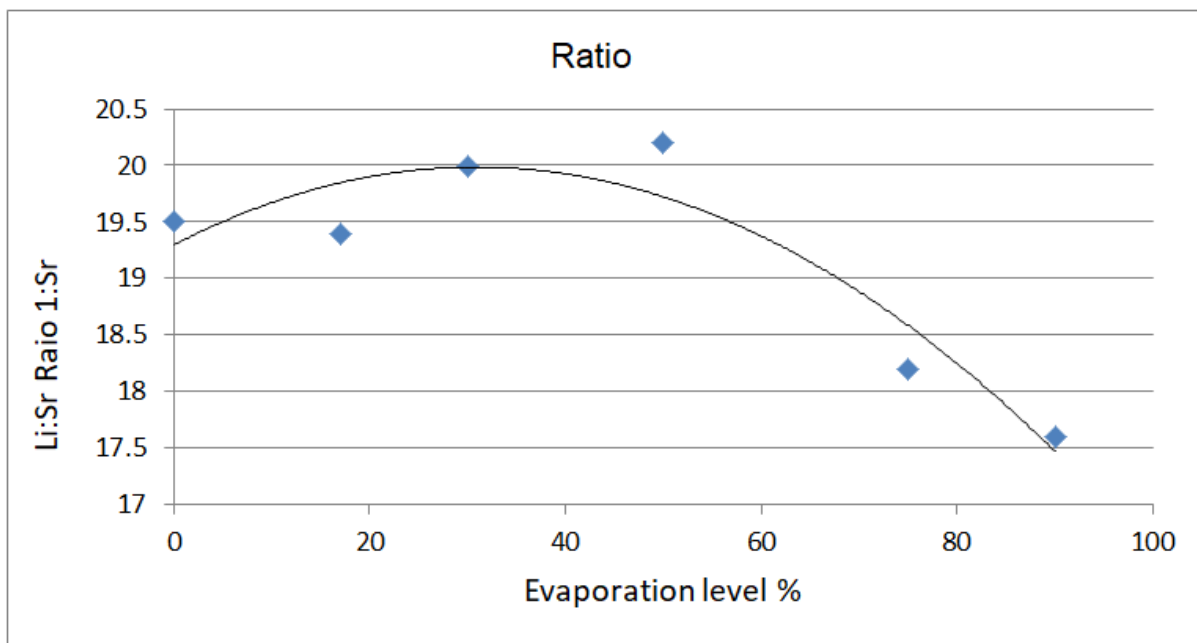


Fig 2:- The Lithium: Strontium ratio at successive evaporation % levels.

The comparison of the obtained results for the Lithium concentration at the different evaporation levels showed that the values of the AAS analyses are always higher than that of the ICP analyses, Figure 3. Even it is known that the AAS device is more accurate, because it

depends on the wave length of the element and there for avoid the problems of interference, but the averages of both readings were used as an end result for the comparison with the presence of Strontium in the same samples.

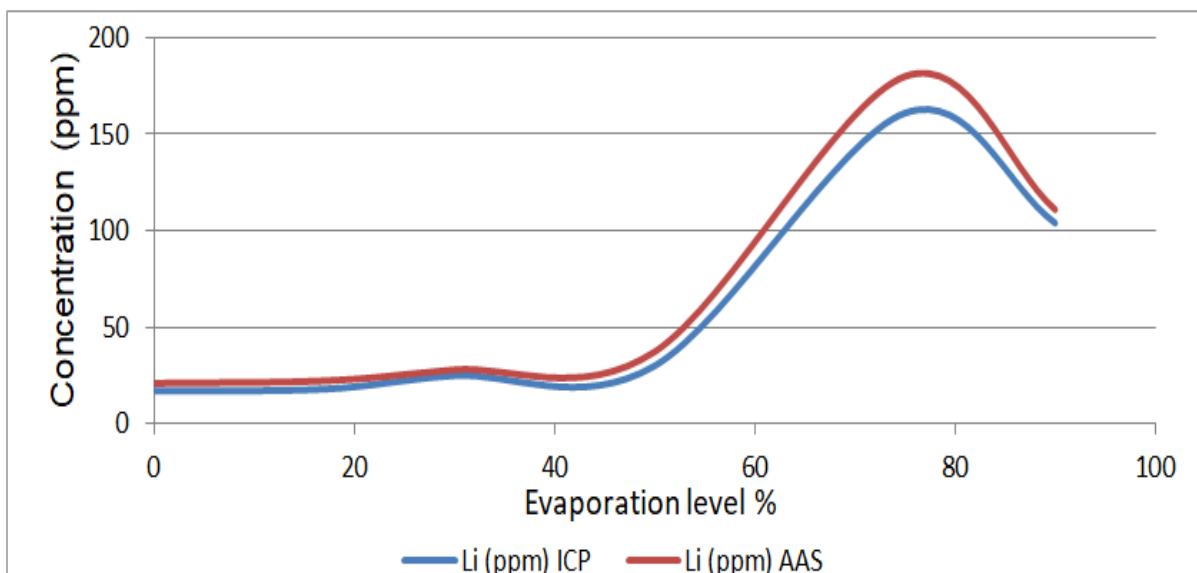


Fig 3:- Comparison between concentrations of lithium at different evaporation levels by different analyses methods (ICP and AAS).

➤ *Lithium in the Retained Water Brine*

The Dead Sea water passes into several stages in the Potash Company within the Potash industry process. The end product after the extraction of different salts is the

return water. The composition of these waters is studied in this research by means of ICP and AAS methods were the conducted results are represented in table 7.

Evaporation level %	Li (ppm) ICP	Li (ppm) AAS	Li (ppm) Average	Sr (ppm) ICP	Li : Sr Ratio
0	17	21	19	370	01:19.5
17	20	22	21	413	01:19.7
30	50	51	51	1010	01:19.8
50	68	70	69	1250	01:18.1
70	111	111	111	2138	01:19.3
75	170	170	170	3300	01:19.4
90	70	70	70	1350	01:19.3

Table 7:- The Li and Sr amounts in the return water.

The water taken from the APC evaporation ponds (C-1) was analyzed and the results indicated the presence of Li within the range between 23 to 40 ppm (Table 8).

Evaporation level %	Li (ppm) Average	Sr (ppm) ICP	Li : Sr Ratio
15	25	460	1:18.4
20	28	530	1:18.9
25	29	620	1:21.4
30	30	660	1:22.0
40	31	740	1:23.9
50	35	810	1:23.1
55	40	950	1:23.8

Table 8:- Li ppm in the brine water of pond C-1.

The extracted salts were dried for 6 hours at 300 C; the XRD results are shown in table 9.

Evaporation Level	Bischofite $MgCl_2 \cdot 6H_2O$	Magnesium Hydroxide Chloride $ClHMgO+2$	Sinjarite $CaCl_2 \cdot 2H_2O$
00%	**	***	-
10%	**	***	-
20%	***	***	-
30%	***	***	-
50%	***	***	-
70%	*	***	***

Table 9:- The XRD results of the precipitated Lithium compounds in the Dead Sea Returned water at different evaporation levels.

The Bischofite mineral continuously precipitated until 50% evaporation level where, the Mg decreased notably due to the precipitation of Bischofite and other Mg minerals. Thereafter, Ca minerals started to form such as Sinjarite.

The ICP results for the concentration of Lithium by evaporation under atmosphere conditions in natural

environment indicated that the optimal concentration reaches 55 ppm. The natural evaporation levels of 55%, 70% and 90% are presented in table 10 where, it shows that the concentrations of Lithium and Strontium are still comparable with the obtained results via the Shock Heat method. The ratio between Lithium to Strontium is about 1:20 in all different evaporation levels.

Evaporation %	0.00	55	70	90
Li (ppm)	29	36	43	65
Sr (ppm)	578	750	900	1300
Li : Sr	1:19.9	1:20.8	1:20.9	1:20

Table 10:- The AAS results of natural evaporation of ponds brine water

The precipitated minerals detected by the XRD analyses revealed that the dominant Lithium containing mineral at the 55% evaporation level is Lithium Chloride Magnesium Chloride Hydrate (Li Cl) (Mg Cl<sub>2</sub>) (H<sub>2</sub>O)<sub>7</sub> (Fig. 4).

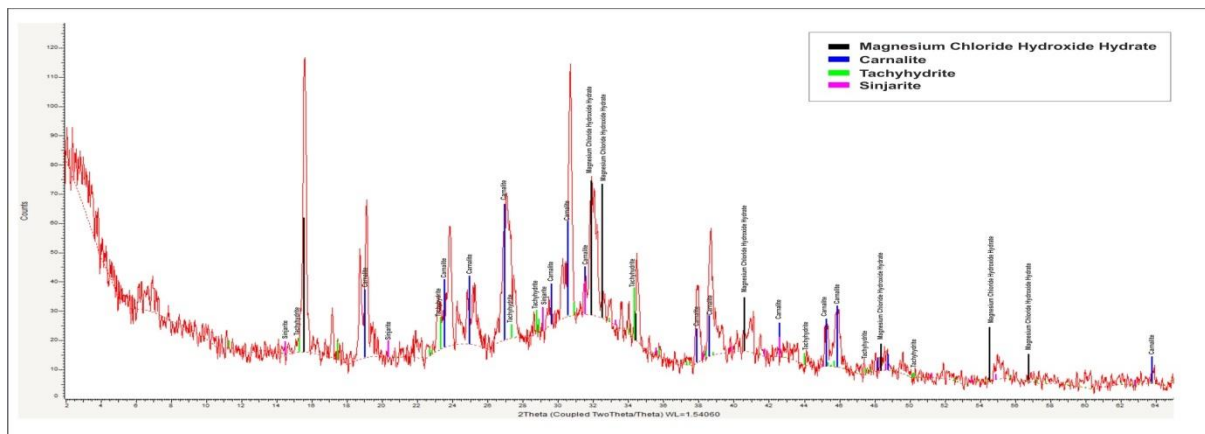


Fig 4:- The 55% evaporation level.

The investigations revealed that the dominant Lithium mineral precipitated at 70% natural evaporation level is Lithium Manganese Oxide Hydrate (Li Mn O<sub>4</sub> 3H<sub>2</sub>O) (Fig. 5).

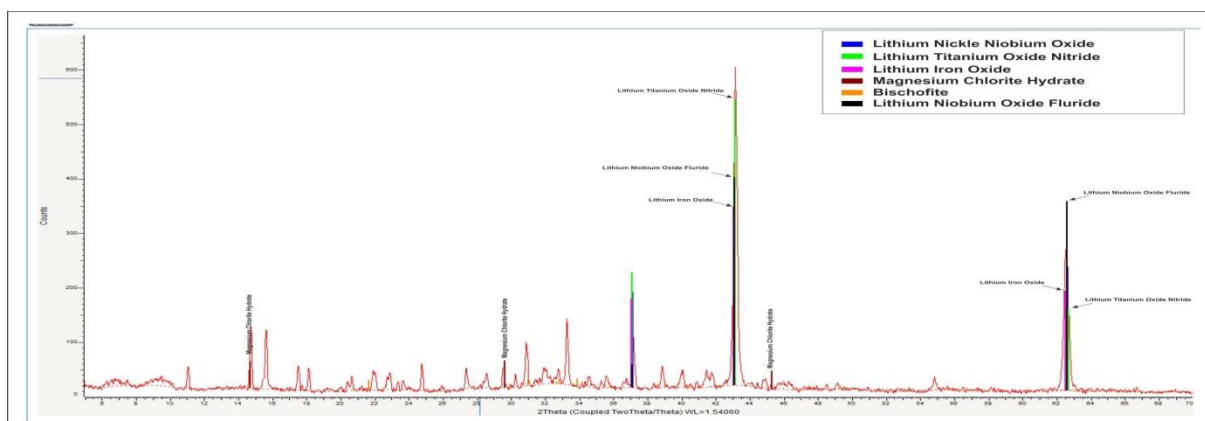


Fig 5:- The 70% evaporation level

The dominant Lithium mineral precipitated at 90% evaporation level is Lithium Titanium Oxide Nitride (Li<sub>0.11</sub> Ti<sub>0.89</sub> O<sub>0.58</sub> N<sub>0.72</sub>) (Fig. 6).

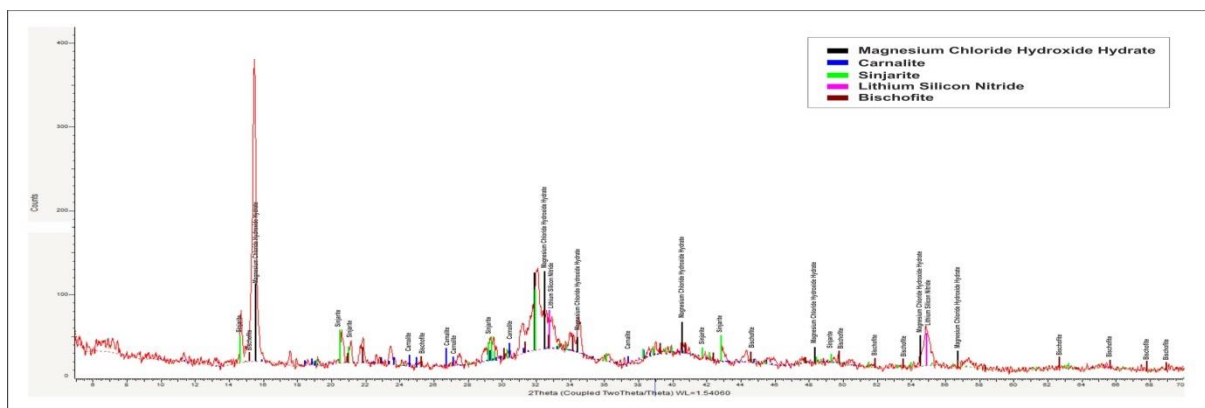


Fig 6:- The 90% Evaporation level

➤ *Origin of Lithium in the Dead Sea water*

In order to determine the origin of the Lithium present in the Dead Sea waters, all expected sources were sampled and analyzed. These sources include the Ma'in – Zara hot spring that emerges from the deep aquifer system. The hot springs are believed to be influenced by the convection currents occur in the deep aquifer system, but also it may be influenced by the surrounding volcanic rocks. In addition, the soils and salts deposited by the dried seasonal springs were analyzed. The sandstone deep

aquifer system, which is juxtaposes the shoreline were taken into consideration by analyzing the pumping wells waters in the vicinity of the Dead Sea located to the south of Haditheh Area. Meanwhile, the water and soils of the sinkholes were sampled and investigated. The sinkhole waters contain partially the rain waters and stream waters that may bring the eroded materials from the surrounding country rocks, whereas many of them are invaded by the Dead Sea waters. The locations of the collected samples are illustrated in figure 7.

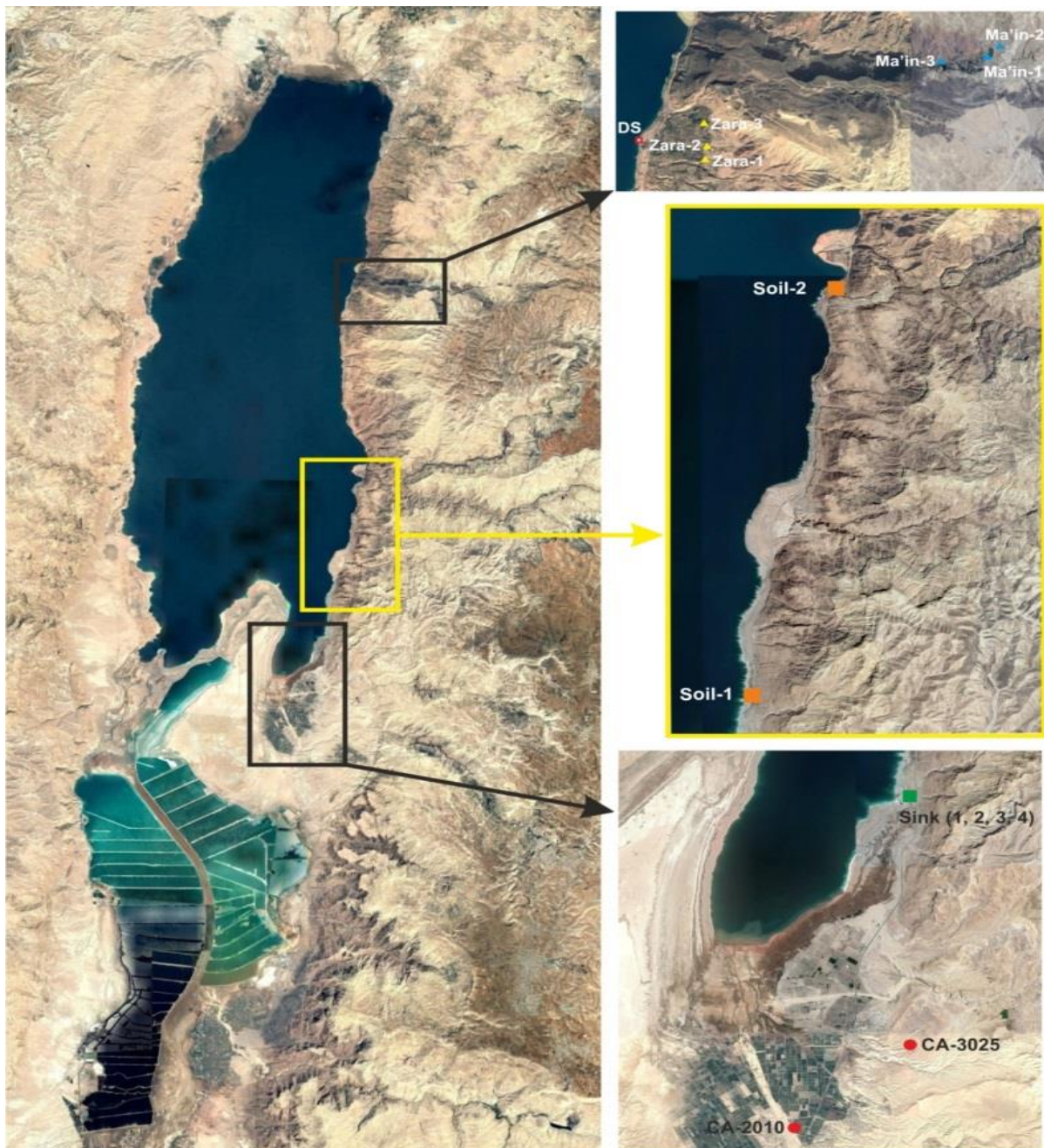


Fig 7:- Location map of the collected water, soils and salt samples

The collected samples from the hot springs of Ma'in and Zara areas were analysed by the ICP device. The results indicated that the major elements are; Ca, Mg, K, Si and Na. Other elements include Mn, V and Ti (Table 11).

The results also indicate the presence of some rare earth elements in different springs, such as Ti, As, Co and Cr. These elements may be weathered from the adjacent volcanic bodies in the area.



Sample	Al	Ca	K	Mg	Mn	Si	Ti	Na	Cu	Ni	Pb	Zn	As	Co	Cr	V
Ma'in1	-	53.1	11.6	15.4	0.1	7.4	5.1	105.0	-	0.1	0.2	<0.1	0.3	0.1	0.1	3.6
Ma'in2	0.1	52.9	11.7	13.8	0.1	7.7	4.8	103.7	-	<0.1	-	<0.1	-	0.1	<0.1	3.5
Ma'in3	-	43.1	18.7	11.1	0.1	8.2	5.0	86.3	-	<0.1	-	<0.1	<0.1	<0.1	<0.1	3.5
Zara1	0.1	88.0	28.0	17.0	-	-	-	150.0	-	-	-	-	-	-	0.1	<0.1
Zara2	0.1	97.0	31.0	18.0	-	-	-	157.0	-	-	0.6	-	-	-	0.1	<0.1
Zara3	-	94.0	34.0	18.0	0.7	-	-	175.0	-	-	-	-	-	-	0.1	0.1

Table 11:- The ICP analyses of spring's water near the Dead Sea (ppm)

The analyses of Lithium revealed that the Dead Sea waters contains between 17-19 ppm. The concentration of Lithium in the sinkholes samples showed 17-22 ppm, except the sample (sink 1), which gives 7 ppm that indicates the water in the sinkholes are the same as the Dead Sea water. The hot springs of Ma'in and Zara areas showed 0.1-0.2 ppm. Meanwhile, the deep aquifer system water represented by the samples from the Potash Company wells (CA2010, CA3025) showed Lithium concentration between 0.1 to 0.3 ppm (Table 8). Therefore, it is conspicuous that the waters of the deep wells are sharing the same water sources with the Ma'in – Zara hot spring.

The Lithium presence in the spring water of Zara2 has been concentrated by means of the 'Shock Heat' method. The gained results at 90% evaporation level of ten liters water showed an increase of the Lithium concentration from 0.1 ppm to 3.6 ppm. On the other hand,

by the same procedure used to concentrate Lithium in ten liters of the water sample taken from Ma'in2 spring, the process is used to evaporate 75% of the water by the 'Shock Heat'. The results revealed an increase in the Lithium concentration from 0.2 ppm to 1.01 ppm. Therefore, it is most possible that the origin of the Lithium element is the deep aquifer system, where the waters percolate and come out in the form of hot springs. In addition, it is presented in the water of the wells pumping from the same reservoir of the sandstone deep aquifer. The notable temperatures of the waters in both the hot springs and the water of the investigated wells have the same range, between 42 °C to 46 °C. The other strong evidence supporting the hypotheses of the Lithium origin to be the sandstone deep aquifer system is the average Lithium: Strontium ratio calculated for the gained results presented in table 12. The ratio is 1:19.88, which is coincided with the ratio previously calculated for the Dead Sea water.

Sample	DS	Sink1	Sink2	Sink3	Sink4	Zara1	Zara2	Zara3	Ma'in3	CA2010	CA3025
Li	17	7	18	17	22	0.1	0.1	0.1	0.2	0.1	0.3
Co	1	1.7	-	0.5	-	-	-	-	-	-	-
Sr	338	125	326	334	397	2.5	2.6	2.5	2.9	1.7	5.4
Ce	11	-	-	-	-	-	-	-	-	-	-

Table 12:- The ICP analyses of spring's water near the Dead Sea (ppm)

The investigated samples of the soils and salts (Soil 1 and Soil 2) collected from the dried springs above the Dead Sea shoreline via XRD analyses revealed that the abundant minerals are; the Quartz  $\text{SiO}_2$ , Kaolin  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , Coquimbite  $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ,  $x \sim 0.5$  and Saponite  $(0.5\text{Ca},\text{Na})_{0.3}(\text{Mg},\text{Fe}^{++})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_{2-4}(\text{H}_2\text{O})$ .

The samples taken from the sinkhole Sink 1 indicated that the dark lamina contains Quartz, Kaolin and Pyrite, while the white crystalline deposits samples Sink 2, Sink 3 and Sink 4 contains mainly Halite (table 13). The source of Pyrite in sample Sink 1 is attributed to the deep aquifer hot waters that are rich in pyrite, these waters are invaded into the sinkholes as a result of the regression of the salt – fresh water interface.

Sample	Halite	Quartz	Kaolinite	Pyrite	Coquimbite	Saponite
Soil 1	-	71.7	12.17	-	14.66	1.46
Soil 2	-	83.38	12.67	-	3.95	-
Sink 1	-	61.44	5.39	33.17	-	-
Sink 2	100	-	-	-	-	-
Sink 3	100	-	-	-	-	-
Sink 4	100	-	-	-	-	-

Table 13:- The Semi - Quantum analyses of the XRD results of the Dead Sea precipitates

The investigations of the soil samples taken from the dried spring (Soil 1 and Soil 2), using the XRF device showed that the major constituent oxides are silicon oxides  $\text{SiO}_2$ , iron oxides  $\text{Fe}_2\text{O}_3$  and aluminum oxides  $\text{Al}_2\text{O}_3$  (Table 14).

Item	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{MnO}$	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_2\text{O}_5$	$\text{Na}_2\text{O}$	$\text{SO}_3$	L.O.I
Soil 1	4.74	0.42	0.49	0.23	0.006	1.60	10.90	64.50	0.051	0.21	0.73	15.60
Soil 2	14.5	1.12	0.32	0.55	0.006	0.45	5.57	55.80	0.101	-	0.80	19.40

Table 14:- The XRF analysis of the major oxides (%) in dried springs soil and salt samples

The analyses of the consisting elements of the precipitated salts in the sinkholes Sink 2, Sink 3 and Sink 4 revealed high percentages of Na and Cl, which are the main components of Halite. This is the normal precipitated mineral from the Dead Sea waters under the present atmospheric conditions (Table 15).

Item	Na	K	Ca	Mg	Mn	Fe	Ti	Al	Si	S	Cl
Sink 2	47.3	0.45	3.24	1.56	-	-	0.05	0.12	1.33	0.065	45.88
Sink 3	38.7	0.55	5.37	1.38	0.014	0.51	0.07	0.94	2.62	0.077	49.4
Sink 4	42.2	0.15	0.93	1.19	-	0.07	-	0.14	0.39	0.102	54.7

Table 15:- The XRF analyses of the elements (%) in the sinkhole salts

The AAS device was implemented to detect the presence of Lithium and other trace elements in the collected samples from the dry spring soils represented by Soil 1 and Soil 2. The results revealed a high content of Lithium, Cobalt, Cesium and strontium. This is a good indicator that endorses the origin of Lithium to be the hot

springs water, which is the deep aquifer system water. The other three sinkholes samples (Sink 2, Sink 3 and Sink 4) showed low contents of Lithium and relatively low contents of the other elements, which are Cobalt, Cesium and Strontium (Table 16).

Item	Li	Co	Sr	Ce	Cr	Ni	Pb	Mn	Zn
Soil 1	20	25	74	60	<0.1	0.4	-	2	0.3
Soil 2	8	4	243	45	<0.1	0.1	-	5	0.5
Sink 2	3	4	53	16	<0.1	<0.1	<0.1	0.4	0.3
Sink 3	4	4	58	14	<0.1	<0.1	-	0.2	<0.1
Sink 4	0.7	5	12	27	<0.1	<0.1	0.2	0.6	0.1

Table 16:- The chemical analyses AAS of trace elements (ppm) in soils and salts

#### IV. CONCLUSIONS

The Lithium content in the Dead Sea brine is ranges between 17 to 19 ppm which is believed to be enriched through successive continuous cycles of inflow and evaporation along thousands of years from the inflow waters in the surrounding areas. The origin of Lithium and other trace elements in the Dead Sea water are mostly the adjacent hot spring waters that emerged from the deep aquifer system.

The Lithium is a high soluble element in water therefore; it was not precipitated within the recent time in the Dead Sea basin. Vast amounts of Lithium are present in the Dead Sea brine water; it is estimated to reach 5.4 million metric tons that are potential and economically feasible.

The ‘Shock Heat’ method revealed an interesting procedure to concentrate Lithium from the Dead Sea water to reach 180 ppm in the residual water through successive evaporation levels and the precipitated salts contained 49.6 ppm.

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#### REFERENCES

- [1]. United States Geological Survey (USGS), 2017. Mineral Commodity Summaries.
- [2]. Paul W. Gruber, Pablo A. Medina, Gregory A. Keoleian, Stephen E. Kesler, Mark P. Everson, Timothy J. Wallington, 2011. Global Lithium Availability, A Constraint for Electric Vehicles?, DOI: 10.1111/j.1530-9290.2011.00359.x
- [3]. Shengsong, Y., 1986. The hydrochemical features of salt lakes in Qaidam Basin. *Chinese Journal of Oceanology and Limnology*, vol. 4, No. 4: 383-403.
- [4]. Garrett, D.E., 2004. *Handbook of Lithium and Natural Calcium Chloride, their deposits, processing, uses and properties*. Elsevier Academic Press, pp. 476.
- [5]. Houston, J. and Gunn, M., 2011. Technical report on the Salar de Olaroz Lithium – Potash project, Jujuy Province, Argentina. NL 43 – 101 report prepared to Orocobre Ltd. [http://www.orocobre.com/PDF/31 Jan 12-2011%20May%20NL43-101%201aroz.pdf](http://www.orocobre.com/PDF/31%20Jan%2012-2011%20May%20NL43-101%201aroz.pdf).
- [6]. Pavlovic, P. and Fowler, J., 2004. Evaluation of the potential of Salar de Ricon brine deposit as a source of Lithium, Potash, Boron and other mineral resources. Final report prepared for Admiralty Resources NL and Argentina Diamonds Ltd.

- [7]. BRUKER-X-Ray Diffraction D4 Endeavour (XRD), 2003. Operators Manual.
- [8]. International Center Diffraction Data (ICDD), 2003. PDF2.
- [9]. <http://www.speciation.net/Database/Instruments/Bruker-AXS-GmbH/S4-PIONEER--XRF-Spectrometer-i638>
- [10]. GBC, 2010. Inductively Coupled Plasma (ICP-OES), Methods manual, Part Number 01-0093-01.
- [11]. SPECTRA<sup>plus</sup>, 2003. Software Package for X-Ray Spectrometers, Version 1.6. Operators Manual.
- [12]. Ruth E. Wolf, 2005. What is ICP-MS? and more importantly, what can it do?, USGS/CR/CICT.