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Geochemistry of Calcium Sulphate Rocks of Fat`ha Formation at Four Localities within Nineveh District, Northern Iraq (with emphasis on strontium distribution)

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ABSTRACT

Strontium distribution within (90) calcium sulphate samples (20 anhydrite, 25 massive gypsum, 25 selenite and 20 fibrous gypsum) from Fat'ha Formation (Middle Miocene) at four selected localities in northern Iraq were investigated. The study revealed that there was a loss of (182 ppm, 15.50%) strontium during the hydration of anhydrite to gypsum. This loss is attributed to the incapability of monoclinic structure of gypsum to hold all the released strontium from anhydrite. Massive gypsum contains almost twice and (3.46) times strontium than selenite and fibrous gypsum respectively. These differences are related to the different mode of formation of each type. There is a negative correlation between crystal size of gypsum and strontium content. The relationship is linear on a logarithmic scale. Estimated partition coefficients of strontium (K_{Sr} G) for the three typs of gypsum are all equal to (0.20) at an estimated temperature and brine concentration of (32ºC) and (X3.4) respectively. Estimated partition coefficient for anhydrite is (0.4) at an estimated temperature and brine concentration of (35ºC) and (X7.5) respectively. Multivariate discriminant analyses proved that strontium is the most discriminating element between (anhydrite and gypsum) and between (massive gypsum, selenite and fibrous gypsum).

جيوكيمياء صخور كبريتات الكالسيوم لتكوين فتحة في أربعة مناطق ضمن محافظة نينوى شمال العراق (وأهمية توزيع السترونتيوم)

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الملخص

تم دراسة توزيع السترونتيوم في (90) نموذجا من كبريتات الكالسيوم (20 أنهايدرايت، 25 جبسوم كتلي، 25 سلينايت و 20 جبسوم اليافي) تابعة لتكوين فتحة (المايوسين الاوسط) في أربعة مناطق مختارة من شمال العراق. وقد أوضحت الدراسة بان هناك فقدان في السترونتيوم مقداره (182ج م م، 15.50%) عند تميه الانهايدرايت الى الجبسوم، ويعزى هذا الفقدان إلى عدم قابلية تركيب الجبسوم الأحادي الميل على احتواء جميع السترونتيوم المتحرر خلال عملية التميه. ويحتوي الجبسوم الكتلي على الضعف تقريبا و(3.46) مرة سترونتيوم مقارنة بالسلينايت والجبسوم الاليافي على التوالي. ويعزى هذا الفرق الى طريقة التكوين المختلفة لكل نوع من انواع الجبسوم. وهناك ارتباط سالب بين حجم بلورة الجبسوم ومحتواها من السترونتيوم وهذه العلاقة خطية عند استعمال المقياس اللوغارتمي. ان أقيام معامل التوزيع (Partition coefficients) التقديرية للأنواع الثلاثة من الجبسوم تكون متساوية وتساوي(0.20) عند درجة حرارة تقديرية مقدارها (32° سليزية) وتركيز السائل المالح (brine) التقديري (X3.4). والقيمة التقديرية لمعامل التوزيع للانهايدرايت هي (0.40) عند درجة حرارة تقديرية (35° سليزية) وتركيز السائل المالح (X7.5). واظهر التحليل الفرزي المتعدد المتغيرات بأن السترونتيوم هو اكثر المتغيرات فرزا بين (الجبسوم والانهايدرايت) وبين (الجبسوم الكتلي والسلينايت والجبسوم الاليافي).

INTRODUCTION

A total number of (90) calcium sulphate samples (20 anhydrite, 25 massive gypsum, 25 selenite and 20 fibrous gypsum) were collected from four localities belonging to the Fat'ha Formation (Middle Miocene) at northern Iraq. The lithology consists of alternations, in cyclic fashion, of calcium sulphates, marls and carbonates. Samples of two localities (Mishraq and Mosul Dam) consist of borehole cores, while samples of the other two (Batnaya and Shaikh Ibrahim) are from natural exposures (Fig. 1). Sample distributions within the localities are given in (Table 11).

Mishraq samples (7 gypsum and 10 anhydrite) were taken from bore hole number (53/III), having a total thickness of about (182 m.). The bore hole section is given in (Alkawaz, 1980) and in (Aljubouri and Alkawaz, 2006). Gypsum and anhydrite make up about (46%) of total sediments. However, they are undifferentiated and both are reffered to as gypsum in the section.

Mosul dam samples (6 gypsum and 10 anhydrite) were taken from bore hole number (61 MP1), having a total thickness of about (220m.). Gypsum and anhydrite make up about (21.5) of total sediments (8.5% gypsum and 13% anhydrite). The bore hole section is given in (Aljubouri and Khattab, 1993).

Shaikh Ibrahim samples consist of (6 massive, 12selenite and 20 fibrous gypsum).

This section has a thickness of about (554 m). The gypsum makes up about (56%) of total sediments. The section is given in (alkawaz, 1980) and in (Aljubouri and Alkawaz, 2006).

Batnaya samples consist of (6 massive and 13 selenite) and the section has a thickness of about (33m.). The gypsum makes about (50%) of total sediments. The section is described in details in (Mohammad Ali, 2009).

The purpose of this work is to determine the mineral phases within each type of calcium sulphate; to give a brief geochemistry of the major oxides (CaO, SO_3 and H_2O^+), minor oxides (SiO_2 and MgO) and the trace elements (Al, K and Fe) and to study the geochemistry of strontium. This includes its distribution within the four types, estimation of partition coefficient of each type and multivariate dicriminant analysis for the two groups anhydrite and gypsum and for the three groups massive gypsum, selenite and fibrous gypsum.

The choice of four localities for the present study was to facilitate the sample collections of different forms of calcium sulphate (anhydrite, massive gypsum, selenite and fibrous gypsum). It was not possible to collect all forms of calcium sulphate from one or even two localities.

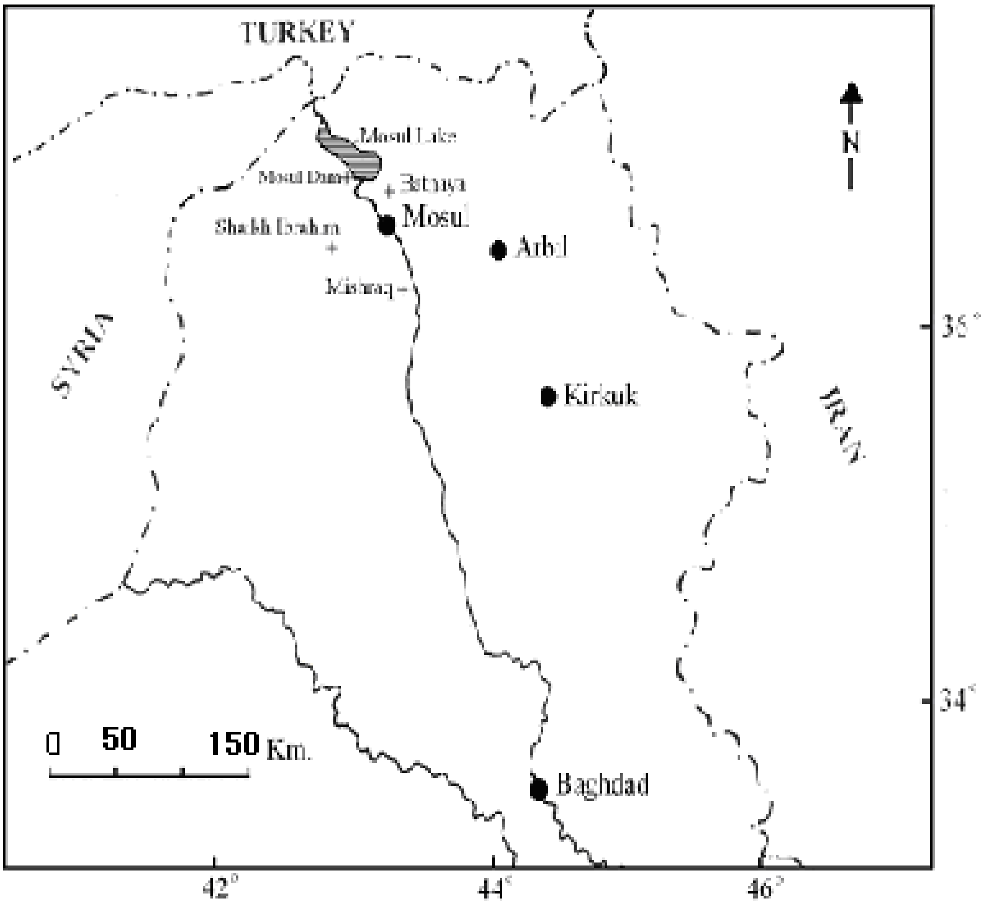

Fig. 1: The Studied Localities (+)at Northern Iraq.

ANALYTICAL PROCEDURES

The oxides (CaO, SO_3, MgO and SiO_2) and the trace elements (Al, K, Fe and Sr) were analyzed using a Philips (PW 1450) X-ray spectrometer using the pressed powder pellet method (Norrish and Hutton, 1964; Leake *et al.,* 1969). Water of crystallization (H_2O^+) was analyzed by heating one gram of powdered sample at (300ºC) for one hour. Insoluble residue (I.R.) was determined by dissolving (10 g) of powdered sample in (10%) hydrochloric acid, filtering and drying out the precipitate and weighing. All these analyses were carried out at the Department of Geology, College of Science, University of Mosul, Iraq.

The results of average chemical analyses for the four calcium sulphate rocks are given in (Table 1). The results of all (90) samples are given in (Table 10 A, B, C and D).

Table 1: Average Chemical Composition of the Four Types of Calcium Sulphate Rocks (Data from Table 10)

***Oxide/Element**	**Ahhydrite **(n=20)**	**Massive gypsum (n=25)**	**Selenite (n=25)**	**Fibrous gypsum (n=20)**
CaO	40.40	32.51	32.53	32.58
SO_3	57.50	46.35	46.45	46.39
H_2O^+	0.96	20.22	20.32	20.33
I. R.	0.16	0.13	0.12	0.13
MgO	0.16	0.15	0.06	0.02
Total	99.18	99.36	99.48	99.15
Al	290	257	249	297
K	44	36	27	37
Fe	477	370	360	365
Sr	1175	749	382	216

*Oxides in wt%; elements in ppm. **n=number of samples.I.R. = Insoluble Residue.

NORMATIVE CALCULATIONS

Normative calculations are used in the present study to work out the percentages of mineral phases that have previously been identified by x-ray diffraction analyses and/or inferred from chemical analyses. The method of calculation has been used by the author on gypsum rocks (Aljubouri, 1993; Aljubouri and Sulayman, 1996; Aljubouri, 1999).

Gypsum ($CaSO_4.2H_2O$) is first calculated from (H_2O^+), (Gypsum%= H_2O^+ * 4.778). Clay minerals are next calculated by assigning all (Al or Al_2O_3) to clay minerals. From the x-ray diffraction of marl sediments associated with calcium sulphates (Aljubouri and Al-Kawaz, 2006, 2008). The contents of clay minerals in gypsum or anhydrite are calculated using the following relationship:

Clay minerals=Al * 8.7746 or Al_2O_3 * 4.644

The amount of clay minerals in calcium sulphates of the present study (0.23 – 0.26%) is too small to warrant a detailed explanation of the method of calculation.

Quartz and iron oxide (SiO_2 and Fe_2O_3) are then calculated after subtracting (SiO_2 and Fe_2O_3) in the clay minerals from total (SiO_2 and Fe_2O_3) respectively in (Table 1). Both amounts are less than (0.05%) and considered negligible.

Dolomite is calculated after subtracting (MgO) in the clay minerals from total (MgO) and the remaining is converted to dolomite (Dolomite%=MgO * 4.5746).

Anhydrite was then calculated after subtracting (CaO) in gypsum and in dolomite from total CaO) and converting the remaining (CaO) to anhydrite.

Celestite ($SrSO_4$) is not calculated, since anhydrite contains no celestite (Aljubouri, 1972), that is all (Sr^{+2}) is in isomorphous substitution for (Ca^{2+}). On the other hand, the three types of gypsum contain rather small amounts (less than 0.1%) of strontium which could be incorporated within the monoclinic structure, either replacing (Ca^{2+}) or within the intersticial sites of water molecules (Kushnir, 1980). The results of mineral phases in the four types of calcium sulphates are given in (Table 2).

Table 2: Mineral Phases in the Four Types of Calcium Sulphate Rocks (Data from Table1).

Phase	**Anhydrite**	**Massive Gypsum**	**Selenite**	**Fibrous Gypsum**
Gypsum	4.59	96.61	97.09	97.14
Anhydrite	93.95	2.20	2.11	2.07
Dolomite	0.65	0.61	0.20	0.26
Clay Minerals	0.26	0.23	0.22	0.26
Total	99.45	99.65	99.62	99.73

These results show that anhydrite contains small amounts (4.59%) of gypsum, due to partial hydration. Gypsum, on the other hand, contains smaller amounts (2.1% average) of anhydrite, either as remnants (especially in massive gypsum) due to incomplete hydration or due to partial dehydration of gypsum. Anhydrite and gypsum both nearly always contain small amounts of dolomite.

The presence of gypsum in anhydrite and anhydrite in gypsum and dolomite in both, has been proved by the present author through the use of x-ray diffraction analysis and petrographical study of calcium sulphate rocks of the same age as the present study (Aljubouri, 1993, 1999). The very small amounts of clay minerals (0.24% average) in gypsum and anhydrite represent marl impurities within calcium sulphates.

GEOCHEMISTRY

CaO, SO_3 and H_2O^+:

These three oxides constitute the bulk of calcium sulphate compositions of the present study. In anhydrite they make up (98.86) while in the three types of gypsum, they make up more than (99%, Table 1), indicating the very high purity of these rocks within the studied localities.

The theoretical (CaO/SO_3) ratio in all cacium sulphate minerals is (0.700). In the rocks of the present study, this ratio is (0.7033, 0.7040, 0.7013 and 0.7017) for anhydrite, massive gypsum, selenite and fibrous gypsum respectively (Table 1). The slight departure in the ratio from the theoretical is due to the presence of dolomite (Table 2). That is, not all (CaO) is within calcium sulphate minerals. After subtracting (CaO) in dolomite, the ratios for all the four types of calcium sulphates becomes (0.700), indicating again the high purity of the rocks and the correctness of analyses.

SiO_2, MgO, Al, K and Fe:

These oxides and elements, with the exception of most MgO, make up the marl studied rocks is very small (less than 0.5%) and consists mainly of clay minerals, with traces of quartz and iron oxide.

Most SiO_2 (>75%) is within the clay minerals and the remaining is in the free silica, in the mineral quartz. Most (MgO) (72-88%) is within the chemical or carbonate fraction in dolomite and the remaining is within the clay minerals, mainly in chlorite.

Aluminium is distributed within the clay minerals according to their ratios in the associated marl (Illite 73.7; chlorite15.0; kaolinite 9.0 and montmorillonite 2.3%) (Aljubouri and Al-Kawaz, 2006, 2008).

Potassium is almost restricted to elite while most Fe_2O_3 (61-70%) is in the free iron oxide (haematite) and the remaining is within the clay minerals.

THE STUDIED LOCALITIES

The average composition of major and minor oxides (CaO,SO_3,$H2O^+$,SiO_2 and MgO) and the trace elements (Al, K, Fe and Sr) for the four studied localities are shown in (Table 3). For the comparison of concentration of minor and trace elements at the studied localities and to eliminate the dilution effect due to the introduction of water of crystallization (H_2O^+) in calcium sulphate, the ratio of (oxide,element /CaO) is taken, rather than their absolute concentrations.

The major oxides (CaO,SO_3 andH_2O^+) show relatively very small variations in concentrations, especially CaO, at the four studied localities (Table3) indicating that gypsum composition nearly always exhibit relatively small departure from the ideal composition (Aljubouri,1972,Hurlbut and Klein,1977,Berry, *et al.,* 1983).

In anhydrite samples, (CaO) at Mishraq is lower and (SO_3) is higher in concentrations than at Mosul Dam. The probable cause for this is that (MgO) is lower (0.13%) at Mishraq than at Mosul Dam (0.2%). Lower (MgO) indicates the near absence of dolomite causing the lowering in the total (CaO) with an apparent increase in (SO_3). In the absence of dolomite the ratio of (CaO/SO_3) approaches the theoritical of (0.700) and that is the case for Mishraq anhydrite (Table 3and 4).

The ratio of (SiO_2/CaO) at the four localities for the four types of calcium sulphate is about (0.004) (Table4) indicating that anhydrite and gypsum of the present study contain similar amounts of clay minerals and quartz as impurities.

The ratio of ($Al*10^{-4}$/CaO) in anhydrite and massive gypsum of Mosul Dam and Mishraq and in selenite of Batnaya is lower than that of massive gypsum of Batnaya and massive gypsum,selenite and fibrous gypsum of Shaikh Ibrahim (Table 4), indicating a possible precipitation of sum aluminium with the chemical fraction as Al-Sulphates or in the mineral Alunite ($KAl_3(SO_4)2$ (OH)6 (in ppm.) as suggested by (Aljubouri, 1972). The ratio of ($K*10^{-4}$/CaO) shows significant variations among the four types of calcium sulphate at the four localities. It is rather low at Batnaya selenite (0.49) and Mosul Dam anhydrite (0.62); higherb at Shaikh Ibrahim and Batnaya massive gypsum (0.80 and 0.96 respectively) and considerably higher at the other localities with other types of calcium sulphate (Table4). These variations reflect the mobile nature of potassium and its possible prescence in the chemical fraction, as well as in the detrital fraction within the clay minerals. However, due to the very high solubility of potassium evaporate minerals, the amount precipitated with gypsum would be very small (in ppm.)

The ratio of ($Fe*10^{-4}$/CaO) does not show much variotations within the four types of calcium sulphate at the four localities, ranging from (10.48) for anhydrite at Mishraq to (13.12) for anhydrite at Mosul Dam. (Table 4). These differences possibly reflect small variations of iron oxide concentrations in calcium sulphate at the studied localities

The ratio of ($Sr*10^{-4}$/CaO) shows a distinct variation in the four types of calcium sulphate at the four localities, reflecting the variable distribution of strontium in calcium sulphate minerals, being rather low in selenite and fibrous gypsum, higher in massive gypsum and still higher in anhydrite (Table 4).

However, massive gypsum of Mosul Dam has the highest ratio of (32.73) and this is due to the presence of one sample (36) with very high strontium concentration of (2957ppm) (Table 10B) and the number of samples is only six, leading to rather high average (1065ppm) (Table 3). In any case strontium distribution is discussed bellow in more details

With the exception of anhydrite at Mishraq locality, the ratio of (CaO/SO_3) is higher than the theoretical of (0.700) due to the presence of small amounts of dolomite (Table 2), being rather low in massive gypsum and selenite of Batnaya and in selenite and fibrous gypsum of Shaikh Ibrahim localities (Table 4).

Table 3: Average Concentrations of Major and Minor Oxides and Trace Elements for the Four Types of Calcium Sulphate at the Studied Localities (Data from Tables 10 and 11).

Oxides% Elements ppm	**Mosul Dam**		**Mishraq**		**Batnaya**		**Shaikh Ibrahim.**		
	Anh n=10	M.Gyp. n=6	Anh.n=10	M.Gyp.n=7 .	M.Gyp..n=6	Sel. n=6	M.Gyp .n=13	Selenite. n=12	F.Gyp. n=20
CaO	40.62	32.54	40.26	32.53	32.41		32.54	32.56	32.55
SO_3	57.09	46.13	57.90	46.21	46.18	46.39	46.20	46.47	46.39
H_2O+	0.97	20.28	0.96	19.99	20.45	20.24	20.19	20.40	20.33
SiO_2	0.16	0.13	0.16	0.12	0.13	0.14	0.14	0.12	0.13
MgO	0.20	0.11	0.13	0.14	0.12	0.05	0.24	0.07	0.08
Total	99.04	99.19	99.41	98.99	99.29	99.38	99.31	99.62	99.48
Al	290	252	289	232	277	210	272	276	297
K	25	39	63	49	31	16	26	38	37
Fe	533	390	422	344	385	312	366	411	365
Sr	1209	1065	1140	612	691	435	646	324	216

Anh.=Anhydrite; M. Gyp.=Massive Gypsum; Sel.=Selenite; F. Gyp.=Fibrous Gypsum in= Number of Samples.

Table 4: Oxide, Element*/CaO and (CaO/SO_3) Ratios for the Four Types of Calcium Sulphate at the Studied Localities

Ratio	Mosul Dam		Mishraq		Batnaya		Shaikh Ibrahim		
	Anh.	M.Gyp.	Anh.	M.Gyp.	M.Gyp.	Sel.	M.Gyp.	Sel	F.Gyp
SiO_2/CaO	0.0039	0.004	0.0040	0.0037	0.0040	0.0043	0.0043	0.004	0.0040
MgO/CaO	0.0049	0.0034	0.0032	0.0043	0.0037	0.0015	0.0074	0.002	0.0025
Al/CaO	7.14	7.74	7.18	7.13	8.55	6.45	8.36	8.48	9.12
K/CaO	0.615	1.20	1.57	1.51	0.96	0.49	0.80	1.17	1.14
Fe/CaO	13.12	11.99	10.48	10.58	11.88	9.58	11.25	12.62	11.21
Sr/CaO	29.76	32.73	28.32	18.81	21.32	13.36	19.85	9.95	6.64
CaO/SO3	0.7115	0.7054	0.695	0.7033	0.7018	0.7019	0.7043	0.701	0.7017

* = Elements x 10^{-4} . Anh.=Anhydrite;M.Gyp.=Massive Gypsum; Sel.=Selenite; F.Gyp.=Fibrous Gypsum. (Data from Table 3).

STRONTIUM DISTRIBUTION

Strontium distribution within anhydrite and the three types of gypsum (massive, selenite and fibrous) of the present study and some other areas of the world are given in (Table5). It is clear that these concentrations are within the range of reported values by other authors as shown in the table. In fact, the average for anhydrite (1150 ppm) and gypsum (750 ppm) of Baja California (USA) (Butler, 1973), are very close to the averages of the present study (1175 and 747 ppm respectively).As far as the author is aware, the only reported values for Sr in selenite are those of (Butler, 1973) at Abu Dhabi. The range and average are very close to those of the present study (Table 5). On the other hand, the only reported values for Sr in fibrous gypsum are those of the author (Aljubouri, 1972) and also with similar range and average to those of the present study. The rather low strontium averages for anhydrite (850 ppm) and gypsum (423 ppm) of (Al-Marsoumi, 1980, Table 3) are due to the use of atomic absorption for Sr analysis, where the "signal" is suppressed by the presence of sulphate ions (Watson, 1985).

On the other hand, the low strontium average (610 ppm) for gypsum of (Abdul-Hamid, 1983) is due to the incorporation of selenite and fibrous gypsum samples in the chemical analysis of strontium (personal communication).

Anhydrite, on an average, always contains more strontium than massive gypsum. On hydration, all anhydrite constituents of oxides, minor and trace elements, would be diluted by (20.93%) which is the theoretical (H_2O^+) content of gypsum. In the present study, anhydrite contains (1175 ppm) strontium and on hydration (i.e. conversion to gypsum) strontium content of the resulting gypsum should be (929 ppm), but in fact massive gypsum of the present study, which is secondary in origin, in relation to anhydrite (Aljubouri, 1993) contains only (747ppm). This means that, there is a loss of (182 ppm; 15.5%) of strontium which has gone into solution on hydration of anhydrite. This loss is usually interpreted as due to the incapability of monoclinic structure of gypsum to hold all the released strontium from the hydration of anhydrite (Aljubouri, 1972; Kushnir, 1980).

Table5: Strontium Distribution in some Calcium Sulphate Rocks, Compared with Present Study. Ranges and Averages are in ppm.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Calcium sulphate	Present Study	Aljubouri, 1972	Al-Marsoumi, 1980	Butler, 1973	Butler, 1973	Abdul-Hamid, 1983	Muller *et al.*, 1990	Playa *et al.* 2007
Anhydrite	839-1990 (1175) (n=20)	1141-1626 (1494) (n=7)	400-4400 (850) (n=5)	880-5220 (2260) (n=36)	990-1240 (1150) (n=5)	896-1979 (1252) (n=10)	1070-1603 (1303) (n=6)	---
Massive Gypsum	498-2957 (747) (n=25)	544-1340 (1171) (n=81)	50-2720 (423) (n=68)	450-1240 (900) (n=12)	710-840 (750) (n=5)	245-819 (610) (n=50)	---	691-1353 (1118) (n=10)
Selenite	208-614 (382) (n=25)	---	---	210-570 (410) (n=6)	---	---	---	---
Fibrous Gypsum	103-321 (216) (n=20)	154-197 (172) (n=11)	---	---	---	---	---	---

1. Fat'ha Formation, Middle Miocene, Northern Iraq.
2. Keuper Marl, Triassic, England.
3. Fat'ha Formation, Middle Miocene, Northern Iraq.
4. Recent Sabkha, Abu Dhabi, UAE.
5. Recent Sabkha, Baja California, USA.
6. Dhiban Formation, Lower Miocene, Sinjar, Northern Iraq.
7. Upper Miocene, Messinian evaporites, western Mediterranian Sea.
8. Late Jurassic-Early Cretaceous, Gulf of Carpentaria, Australia. (1175). Average of analysis; n=number of samples

Massive gypsum contains almost twice (1.96) strontium than selenite and (3.46) times than fibrous gypsum (Table 1).

These differences can not be structural, since the three forms of gypsum are monoclinic. However, their modes of formations are different. Massive or alabastrine gypsum constitutes more than (95%) of the three types and in the Fat'ha Formation (Middle Miocene), it may reach a thickness of more than (50) meters in one cycle. It is believed to have been formed in an almost closed basin according to the reflex theory of (King, 1947; Aljubouri and Sulayman, 1996).

Selenite, on the other hand, is usually found in irregular cavities and on the surfaces of gypsum beds and nodules; its formation is post-depositional from circulating groundwaters rich in calcium and sulphate ions. Fibrous gypsum, usually found within horizontal dilation cracks, from few to (15) cm. in height. It is also post-depositional and precipitated from groundwaters (Aljubouri, 1972).

The difference in strontium concentration within the three types of gypsum is a function of its concentration in the original brine, from which its host gypsum was precipitated. This is clearly shown in (Table 8) where the estimated concentration is expressed as the ratio of $(Sr^{2+}/Ca^{2+})L$ in brine. This ratio progressively decreases from massive gypsum (1.51×10^{-2}) through selenite (0.80×10^{-2}) to fibrous gypsum (0.48×10^{-2}), in accordance with a decrease in strontium concentrations from (747 ppm) and (382 ppm) to (216 ppm) respectively.

Higher strontium concentration means higher degree of supersaturation or higher growth rate, resulting in smaller crystal size. On the other hand, lower strontium concentration leads to slower growth rate and resulting into relatively large crystal size. This negative correlation between crystal size and strontium concentration was first reported by (Butler, 1973) for Sr in gypsum samples from Abu Dhabi and confirmed by (Kushnir, 1980) for Sr in gypsum samples from Bardawil sabkha in northern Sinai. In the present study, this relationship is clearly shown in figure (2 A and B) and in (Table 6). The logarithmic plot gives a good linear trend with the following equation:

$$\text{Log } Y = -0.298 * \text{log size } (X) + 3.6686 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq. 1}$$

Where (Y) represents the concentration of strontium in gypsum.

Using this equation, it is possible to calculate strontium concentration in any of the three forms of gypsum, from crystal size.

Table 6: Relationship Between Crystal Size and Strontium Content.

A **Type of Gypsum**	**Average Crystal Size (mm)**	**Average Sr (ppm)**
Massive Gypsum	0.5	747
Selenite	5	382
Fibrous Gypsum	30	216
B **Type of Gypsum**	Log Size	Log Sr
Massive Gypsum	2.67	2.87
Selenite	3.70	2.58
Fibrous Gypsum	4.48	2.34

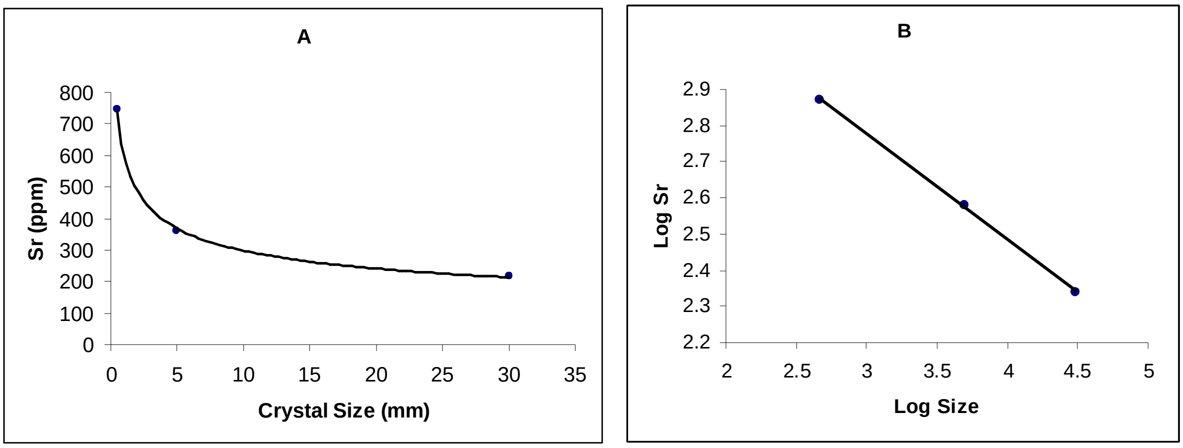

Fig.2: Relationship between Crystal size and Strontium Contents in the three Types of Gypsum. (A) Normal scale, (B) logarithmic scale. (Data from Table 6).

Partition coefficient of strontium K_{Sr} :

Partition coefficient of strontium (K_{Sr}) is the ratio of strontium to calcium (Sr^{2+}/Ca^{2+}) in the solid calcium sulphate, gypsum (G) or anhydrite (A) divided by same ratio in the liquid (L) or in the brine (Butler, 1973).

$$K_{Sr}(G/A) = \frac{(Sr^{2+}/Ca^{2+})G/A}{(Sr^{2+}/Ca^{2+})L} \quad \text{..................................Eq. 2}$$

Because of the partitioning of (Sr^{2+}) between solute and precipitated minerals, the ratio (Sr^{2+}/Ca^{2+}) in pore brines in an evaporate environment plays a dominant role in determining the concentration of strontium in precipitated gypsum (Sr G) and in anhydrite (Sr A).

Partition coefficient of strontium is affected by three main factors: the temperature, brine concentration and the degree of supersaturation or the growth rate.

The increase in temperature tends to lower the partition coefficient, while the higher the concentration of the brine the higher the partition coefficient. The increase in growth rate (or the degree of supersaturaion) increases the partition coefficient (Kushnir, 1980).

Estimation of partition coefficient of Strontium:

It is not so easy to estimate the partition coefficient of strontium in gypsum ($K_{Sr}G$) and anhydrite (K_{Sr} A) in old rocks, since diagenesis and phase transformations (gypsum⇆anhydrite) might have affected the final concentration of strontium in these rocks. Also, it is not so easy to estimate the ratio of (Sr^{+2}/Ca^{+2})L of brine of older rocks.

However, the work of (Butler, 1973) on the partition coefficient of strontium in gypsum and anhydrite of recent sabkha environment at Abu Dhabi coast (UAE), encouraged him to estimate an average (Sr^{2+}/Ca^{2+}) L of brine fluid for each average value of strontium in gypsum or anhydrite of Permian and Zechstein age (Table7).

Table 7: Estimated Ratio of (Sr^{2+}/Ca^{2+}) L in the Brine for Strontium Content in Gypsum and Anhydrite Rocks of Permian and Zechstein Age (Butler, 1973).

Location	**Age**	**Gypsum Average Sr %**	**Estimated (Sr^{2+}/Ca^{2+})L**
W. Oklahoma	Permian	0.100	2.0 x 10^{-2}
	Permian	0.086	1.9 x 10^{-2}
S.W. Oklahoma	Permian	0.038	0.8 x 10^{-2}
		Anhydrite	
Germany	Permian	0.243	2.3 x 10^{-2}
	Zechstein	0.217	2.0 x 10^{-2}
	Zechstein	0.204	1.9 x 10^{-2}

Using these figures, two linear equations, one for gypsum and the other for anhydrite, relating the average (Sr G/A) with the ratio (Sr^{2+}/Ca^{2+})L in brine or in groundwater could be deduced.

For gypsum:

Y (Sr^{2+}/Ca^{2+}) L*10 $^{-2}$= 19.355 * (Sr G) + 0.065 ....Eq. 3

For anhydrite:

Y (Sr^{2+}/Ca^{2+}) L*10^{-2} = 10.2564 * (Sr A) - 0.1923 ……………………..Eq. 4

After calculating (Sr^{2+}/Ca^{2+}) L and using (Table 1) and equation (2), a value of (K_{Sr} G/A) for the rocks of the present study, could now be calculated. The results for the three types of gypsum (massive, selenite and fibrous gypsum) and for anhydrite of (Sr^{2+}/Ca^{2+})L and (K_{Sr} G/A) are given in (Table8).

Table 8: Partition Coefficients of strontium (K_{Sr}) for three types of Gypsum and Anhydrite of rocks of the present study.

Calcium Sulphate	**Sr wt%**	***(Sr^{2+}/Ca^{2+}) G/A**	****(Sr^{2+}/Ca^{2+})L**	**K_{Sr} G/A**
Massive Gypsum	0.0747	0.32 x 10-2	1.51 x 10^{-2}	0.20
Selenite	0.0382	0.16 x 10-2	0.80 x 10^{-2}	0.20
Fibrous Gypsum	0.0216	0.093 x 10^{-2}	0.48 x 10^{-2}	0.20
Anhydrite	0.1175	0.41 x 10^{-2}	1.01 x 10^{-2}	0.40

* ratio in gypsum (G) or in anhydrite (A). ** ratio in brine (L).

From this table, it could be seen that the three different types of gypsum have virtually the same partition coefficient (K_{Sr} G) of (0.20) at the same estimated temperature of (32ºC) and estimated brine concentration of (X 3.4). On the other hand, anhydrite partition coefficient (K_{Sr} A) is (0.40) twice as that of gypsum at higher temperature (35ºC) and much higher brine concentration (X 7.5).

It is also noted that strontium concentration within the three types of gypsum, progressively increases with an increase in the ratio of (Sr^{2+}/Ca^{2+}) L in brine or in groundwater. Although the ratio (Sr^{2+}/Ca^{2+}) L for massive gypsum (1.51×10^{-2}) is higher than that for anhydrite (1.01×10^{-2}), but anhydrite is precipitated rather than gypsum, due to the higher temperature (35ºC) and higher brine concentration (X 7.5). Butler (1973, figure 8, p.442) showed that partition coefficient of anhydrite was more than twice that of gypsum and the decisive factor in the precipitation of either of them is the brine concentration.

STATISTICAL ANALYSIS

Multivariate discriminant analysis (Chyi *et al.,* 1978) was used on anhydrite and massive gypsum, to find out the most discriminating element between the two groups. The analysis was also used on the groups (massive gypsum, selenite and fibrous gypsum) to find out if they are actually three distinct groups on the basis of the chemical analysis of their major and minor oxides and trace elements.

In the case of anhydrite and gypsum, the obvious discriminating oxides (CaO, SO_3 and H_2O^+) were removed from the analysis. CaO and SO_3 are theoretically (20.93%) each more in anhydrite than in gypsum, while (H_2O^+) is zero in theoretical anhydrite and is (20.93%) in theoretical gypsum. The results of standardized discriminant function coefficients are given in (Table 9 A and B).

It is clear from (Table 9 A) that strontium is the most discriminating element between anhydrite and gypsum, with a coefficient of (+0.786). It is also the most discriminating element, with a coefficient of (+0.841) between the three types of gypsum (Table 9 B). That is, massive gypsum, selenite and fibrous gypsum are three distinct groups on the basis of their strontium contents.

Table 9: Standardized Canonical Discriminant Function Coefficients for the four groups of calcium sulphates:

A- Anhydrite and gypsum:

Oxide/Element	**Function 1**
Sr	0.786
Fe	0.250
MgO	- 0.066
K	0.489
Al	0.334
SiO_2	- 0.581

B- Massive Gypsum, Selenite and Fibrous Gypsum:

Oxide/Element	**Function 1**	**Function 2**
Sr	0.841	- 0.196
Fe	0.053	- 0.016
MgO	0.463	0.226
K	0.268	0.410
Al	- 0.186	0.497
SiO_2	- 0.433	- 0.009
H_2O^+	- 0.515	- 0.312
SO_3	- 0.416	- 0.842
CaO	- 0.002	0.602

Table 10A: Chemical Analyses of Anhydrite (n=20).

Oxides in wt%, elements in ppm; n=number of samples

Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
CaO	40.34	40.31	40.8	40.13	40.19	40.01	40.32	40.07	40.09	40.38	40.44	40.69	39.18	41.68	41.26	41
SO_3	57.85	58.3	57.83	58.27	58.03	57.78	57.37	57.38	57.89	58.3	58.4	57.38	56.3	55.97	56.69	56.98
H_2O^+	0.76	0.88	0.61	0.61	0.82	0.60	1.75	1.68	1.27	0.58	1.28	0.38	3.71	0.63	0.48	0.60
SiO_2	0.14	0.12	0.16	0.16	0.14	0.14	0.12	0.27	0.25	0.12	0.16	0.16	0.14	0.18	0.18	0.13
MgO	0.06	0.1	0.05	0.05	0.14	0.17	0.2	0.22	0.1	0.17	0.06	0.17	0.2	0.09	0.14	0.23
Total	**99.55**	**99.31**	**99.45**	**99.22**	**99.32**	**98.70**	**99.76**	**99.62**	**99.60**	**99.55**	**100.34**	**98.78**	**99.53**	**98.55**	**98.75**	**98.94**
Al	30.9	381	400	150	260	100	300	422	250	322	300	245	288	310	296	287
K	23	33	37	38	88	85	63	109	87	66	35	35	20	26	38	18
Fe	200	328	176	176	457	562	679	726	328	586	211	562	655	316	468	773
Sr	953	1025	1208	1194	1215	1251	884	1956	879	839	905	1295	1230	1070	1670	1043

Table 10B: Chemical Analyses of Massive Gypsum (n=25).

ample Number	21	22	23	24	25	26	27	28	29	30	31	32	33	34
CaO	32.72	32.54	32.58	32.31	32.47	32.43	32.68	32.42	32.56	32.45	32.2	32.48	32.36	32.77
SO_3	46.38	46.06	46.29	46.02	46.27	46.33	46.09	46.32	46.31	45.99	45.97	45.9 3	46.58	46.05
H_2O^+	19.8	19.8	19.91	20.25	20.14	19.89	20.11	20.31	20.18	20.81	20.53	20.49	20.38	19.99
SiO_2	0.12	0.21	0.2	0.08	0.06	0.07	0.12	0.14	0.23	0.11	0.08	0.05	0.15	0.06
MgO	0.04	0.03	0.11	0.03	0.07	0.6	0.07	0.03	0.05	0.1	0.14	0.21	0.17	0.07
Total	**99.06**	**98.64**	**99.09**	**98.69**	**99.01**	**99.32**	**99.07**	**99.22**	**99.33**	**99.46**	**98.92**	**99.16**	**99.14**	**98.9**
Al	375	126	124	151	273	357	220	273	370	254	204	350	208	332
K	34	101	111	10	5	12	41	66	37	23	13	30	17	20
Fe	270	279	259	366	400	429	405	421	341	481	340	450	277	363
Sr	699	683	716	638	518	509	521	498	647	727	625	625	1026	658

Sample Number	41	42	43	44	45	Mean
CaO	32.58	32.65	32.5	32.54	32.41	32.51
SO_3	46.42	45.98	46.13	46.19	46.18	46.16
H_2O^+	20.06	20.43	20	19.86	20.49	20.22
SiO_2	0.13	0.22	0.09	0.16	0.08	0.13
MgO	0.2	0.33	0.05	0.5	0.11	0.15
Total	**99.39**	**99.61**	**98.77**	**99.94**	**99.27**	**99.17**
Al	259	290	283	334	252	257
K	28	38	11	23	19	36
Fe	390	419	321	315	311	370
Sr	672	617	552	582	574	747

Oxides in wt%, elements in ppm;   n=number of samples

Table 10C:Chemical Analyses of Selenite (n=25).

Sample Number	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
CaO	32.43	32.47	32.49	32.54	32.41	32.64	32.81	32.71	32.63	32.66	32.67	32.4	32.4	32.46	32.5
SO_3	46.42	46.65	46.79	46.37	46.18	46.42	46.66	46.53	46.49	46.22	46.43	46.12	45.77	46.55	46.58
H_2O^+	20.3	19.89	19.89	20.6	20.37	20.2	20.15	20.53	19.9	20.4	20.39	20.25	20.19	20.09	20.32
SiO_2	0.17	0.16	0.15	0.16	0.16	0.15	0.16	0.16	0.16	0.16	0.05	0.06	0.06	0.06	0.09
MgO	0.11	0.01	0.05	0.1	0.01	0.03	0.05	0.02	0.04	0.13	0.07	0.06	0.02	0.01	0.11
Total	**99.43**	**99.18**	**99.37**	**99.77**	**99.13**	**99.44**	**99.83**	**99.95**	**99.22**	**99.57**	**99.61**	**98.89**	**98.44**	**99.17**	**99.6**
Al	375	20.7	172	219	166	280	94	104	249	218	252	395	187	309	235
K	14	19	18	10	14	18	10	18	15	17	17	16	25	27	43
Fe	302	291	284	284	275	321	282	286	461	319	279	298	377	338	563
Sr	463	471	499	482	464	473	473	461	464	472	327	302	307	298	239

Sample Number	66	67	68	69	70	Mean
CaO	32.63	32.76	32.44	32.92	32.61	32.56
SO_3	46.74	46.53	46.11	46.48	46.98	46.39
H_2O^+	19.82	20.32	20.23	20.81	20.51	20.32
SiO_2	0.09	0.08	0.11	0.12	0.18	0.12
MgO	0.11	0.12	0.02	0.06	0.12	0.06
Total	**99.39**	**99.81**	**98.91**	**100.39**	**100.4**	**99.45**
Al	242	352	328	303	195	249
K	26	15	10	59	69	27
Fe	372	295	236	337	381	360
Sr	562	614	363	254	355	382

Oxides in wt%, elements in ppm; n=number of samples

71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89
32.34	32.84	32.41	32.4	32.37	32.68	32.73	32.75	32.38	32.34	32.66	32.43	32.3	32.69	32.65	32.56	32.62	32.68	32.
46.1	46.76	46.15	46.2	46.00	46.77	46.63	46.67	46.3	46.25	46.2	46.19	45.9	46.46	46.23	46.46	46.53	46.65	46.
20.57	19.7	20.33	20.5	20.57	20.08	20.44	20.17	20.66	20.65	20.23	20.33	20.62	19.98	20.52	20.33	20.35	20.27	19.
0.15	0.15	0.06	0.06	0.06	0.06	0.06	0.06	0.14	0.14	0.13	0.12	0.23	0.17	0.16	0.26	0.27	0.15	0.1
0.06	0.12	0.07	0.13	0.02	0.11	0.02	0.06	0.03	0.08	0.05	0.06	0.26	0.06	0.07	0.03	0.05	0.11	0.1
99.22	**99.57**	**99.02**	**99.29**	**99.02**	**99.70**	**99.88**	**99.71**	**99.51**	**99.46**	**99.27**	**99.13**	**99.31**	**99.36**	**99.63**	**99.64**	**99.82**	**99.86**	**99.**
282	362	196	298	375	225	215	238	179	180	332	412	415	210	217	386	440	349	311
10	15	27	36	40	41	27	63	22	75	61	54	84	27	21	29	30	14	15
448	362	337	476	385	455	449	441	304	286	304	297	261	275	399	341	505	406	301
319	321	224	233	163	164	165	164	260	164	185	183	207	181	188	239	237	224	173

Table 10D: Chemical Analyses of Fibrous Gypsum (n=20).

Table 11: Sample locations and the type of calcium sulphate of the present study.

Locality	**Sample Number**	**Calcium sulphate**
Mishraq	1,2,3,4,5,6,7,8,9,10	Anhydrite
	21,22,23,24,25,26,27	Massive gypsum
Batnaya	28,29,30,31,32,33	Massive gypsum
	46,47,48,49,50,51,52,53,54,55,56,57,58	Selenite
Mosul Dam	11,12,13,14,15,16,17,18,19,20	Anhydrite
	34,35,36,37,38,39	Massive gypsum
Shaikh Ibrahim	40,41,42,43,44,45	Massive gypsum
	59,60,61,62,63,64,65,66,67,68,69,70	Selenite
	71,72,73,74,75,76,77,78,79,80,81,82,83,84,85,86,87,88,89,90	Fibrous gypsum

Oxides in wt%, elements in ppm; n=number of samples

CONCLUSIONS

The present study concludes at the following points:
Anhydrite always contains small amounts of gypsum due to partial hydration while gypsum always contains smaller amounts of anhydrite either due to partial dehydration or as remnants of incomplete hydration.

On hydration of anhydrite, there is a loss of (182 ppm, 15.58%) of strontium in the resulting gypsum. This loss is attributed to the incapability of monoclinic structure of gypsum to hold all the released strontium.

Massive gypsum contains almost twice and (3.46) times strontium as selenite and fibrous gypsum respectively. These differences are due to the different mode of precipitation of each type.

Estimated partition coefficients of the three types of gypsum are all equal to (0.20) at an estimated temperature and brine concentration of (32ºC) and (X 3.4) respectively. Estimated partition coefficient for anhydrite is (0.40) at an estimated temperature and brine concentration of (35ºC) and (X7.5) respectively.
There is a negative correlation between crystal size of gypsum and its strontium content and the relationship is linear on a logarithmic scale.

Multivariate discriminant analyses proved that strontium is the most discriminating element between (anhydrite and massive gypsum) and between (massive gypsum, selenite and fibrous gypsum).

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