

Origin and geochemistry of Miocene marine evaporites associated with red beds: Great Kavir Basin, Central Iran

HOSSAIN RAHIMPOUR-BONAB^{1*}, ZEINAB SHARIATINIA¹ and MICHAEL G. SIEMANN²

¹*School of Geology, University College of Science, University of Tehran, Tehran, Iran*

²*Technische Universität Clausthal, Institut für Mineralogie und Mineralische Rohstoffe, Adolph-Roemer Str. 2A, 38678 Clausthal-Zellerfeld, Germany*

During the Cenozoic numerous shallow epicontinental evaporite basins formed due to tectonic movements in the Northern Province of the Central Iran Tectonic Zone (the Great Kavir Basin). During the Miocene, due to sea-level fluctuations, thick sequences of evaporites and carbonates accumulated in these basins that subsequently were overlain by continental red beds. Development of halite evaporites with substantial thickness in this area implies inflow of seawater along the narrow continental rift axis. The early ocean basin development was initiated in Early Eocene time and continued up to the Middle Miocene in the isolated failed rift arms. Competition between marine and non-marine environments, at the edge of the encroaching sea, produced several sequences of both abrupt and gradual transition from continental wadi sediments to marginal marine evaporites in the studied area. These evaporites show well-preserved textures indicative of relatively shallow-brine pools. The high Br content of these evaporites indicates marine-derived parent brines that were under the sporadic influence of freshening by meteoric water or replenishing seawater. However, the association of hopper and cornet textures denotes stratified brine that filled a relatively large pool and prevented rapid variations in the Br profile. Unstable basin conditions that triggered modification of parent brine chemistry prevailed in this basin and caused variable distribution patterns for different elements in the chloride units. The presence of sylvite and the absence of Mg-sulphate/chlorides in the paragenetic sequence indicate SO₄-depleted parent brine in the studied sequence.

Petrographic examinations along with geochemical analyses on these potash-bearing halites reveal parental brines which were a mixture of seawater and CaCl₂-rich brines. The source of CaCl₂-rich brines is ascribed to the presence of local rift systems in the Great Kavir Basin up to the end of the Early Miocene. Copyright © 2007 John Wiley & Sons, Ltd.

Received 11 July 2006; revised version received 6 November 2006; accepted 13 November 2006

KEY WORDS marine evaporite; halite; Iran; geochemistry; Miocene

1. INTRODUCTION

Tectonic movements in the Northern Province of the Central Iran Tectonic Zone (i.e. the Great Kavir Basin) during the Cenozoic have formed numerous shallow epicontinental evaporite basins (Rahimpour-Bonab and Kalantarzadeh 2005). During this time due to sea-level fluctuations thick sequences of evaporites, carbonates and red beds accumulated in these basins. For example, in the middle Miocene, development of restricted marine conditions led to a facies change, from shallow marine carbonates to thick evaporite sequences (M1 member), which are the subject of this study. These evaporite deposits contain variegated thick sections of alternating very thin halite, and some potash layers, ~1 cm thick. While halite and sylvite are the main primary constituents,

*Correspondence to: H. Rahimpour-Bonab, School of Geology, University College of Science, University of Tehran, Tehran P.O. Box: 14155-6455 Iran. E-mail: rahimpour@khayam.ut.ac.ir

primary Mg-sulphate minerals are absent. Polyhalite ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) is the main secondary phase that displays a close relationship with anhydrite nodules in the primary halite. The geochemistry of these evaporites and the origin of polyhalite which is a common constituent of many ancient evaporite sequences, especially in the Permian and Neogene (Sonnenfeld 1984) are the main subjects of this paper. Seemingly, due to its kinetic factors, polyhalite could form easier than other K-Mg-sulphate minerals in ancient and Recent environments (Schulze 1970; Sonnenfeld 1984). Other studies on the origin of this mineral in modern environments include the Ojo de Liebre Lagoon, Mexico (Holser 1966b; Pierre and Fritz 1984; Pierre 1985); the sabkha of el Melah de Zarzis, Tunisia (Perthuisot 1971, 1975) and Lake Tuz Golu, Turkey (Irion and Muller 1968). It seems that brine-rock interactions were the responsible mechanisms for making the early diagenetic polyhalite in the primary halite (e.g. Hardie 1968; Schulze 1970; Braitsch 1971; Estefan *et al.* 1980; Hardie 1984; Ordóñez *et al.* 1994), or being oversaturated with respect to MgSO_4 and K_2SO_4 (e.g. Braitsch 1971; Langbein 1987; Hovorka 1992; Schreiber and Walker 1992). One possible process for polyhalite formation is anhydrite alteration (Langbein 1987; Hovorka 1992; Schreiber and Walker 1992).

In this paper our aims are to illustrate the geochemical variations during the formation of primary and secondary evaporite minerals (with a focus on the polyhalite) and to define the diagenetic history of the studied evaporites.

2. GEOLOGY AND STRATIGRAPHY

In Iran evaporite deposits of the Eocene, Oligocene and Miocene rocks are mainly situated in the Central Iran Tectonic Zone (Kalhor 1961; Stocklin 1968; Rahimpour-Bonab and Alijani 2003; Rahimpour-Bonab and Kalantarzadeh 2005; Rahimpour-Bonab *et al.* in press). Tectonic movement in the late Cretaceous to late Cenozoic in the Northern Province of the Central Iran Tectonic Zone (i.e. the Great Kavir Basin) led to the development of shallow epicontinental basins suitable for extensive carbonate/evaporite deposition. In fact, during the Cenozoic, the Great Kavir Basin was an intracontinental rift basin (Stocklin 1974) filled with several kilometres-thick series of Eocene to Recent marine and continental sediments. These sediments are mainly composed of evaporites, carbonates and red beds. Tectonic activity evidenced by the horst and graben structures that underlie the Kavir Basin (Stocklin 1974) formed numerous shallow depressions.

In the Great Kavir Basin, these shallow-water settings developed under arid climatic conditions, suitable for the formation of widespread evaporite deposits (Jackson *et al.* 1990). Toward the depocentres of the Great Kavir Basin, the thickness of chloride and potash beds increases progressively and reaches about 3000 m where they are elevated in many areas as huge salt domes (Jackson *et al.* 1990). As a whole, the Great Kavir Basin, particularly near its centre (Figures 1 and 2), is filled with younger Oligocene deposits including Lower Red Formation (LRF), the Miocene Qom Formation and Upper Red Formation (URF). The evaporite units in the URF are widespread throughout Central Iran and are confined to the M1 and M3 members (Figure 3). The M1 member (from bottom to top) consists of alternations of chlorides with thin potash beds (Figure 4) which are overlain by gypsum layers and fossil-bearing carbonates and toward the top they are replaced by continental siliciclastic deposits. The chloride unit of M1 member which is more than 800 m in thickness, is very well-bedded, strongly variegated and shows alternations of various colours in different scales. This unit is composed of the following paragenetic assemblage: primary minerals include halite, gypsum, sylvite and carnallite ($\text{MgCl}_2 \cdot \text{KCl}_2 \cdot \text{H}_2\text{O}$). Whereas, based on the petrographic examinations, secondary minerals are polyhalite ($2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$), langbeinite ($2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$), d'ansite (MgNa_{21}) (Cl_3SO_4) (SO_4)₉, anhydrite (CaSO_4), plus minor amounts of dolomite and ankerite. In addition, some tiny particles of reworked volcanoclastic minerals are present in the studied thin sections.

Towards the uppermost part of the chloride unit the pure halite and sylvite beds gradually change to an alternation of halite and gypsum that signals the end of halite deposition. In this part of the section about 50 m of gypsum, composed of vertically aligned primary vertical crystals (fibrous), overlies the chloride unit with sharp contact. These sulphate beds are overlain by a marine, fossil-bearing, carbonate unit approximately 30 m in thickness.

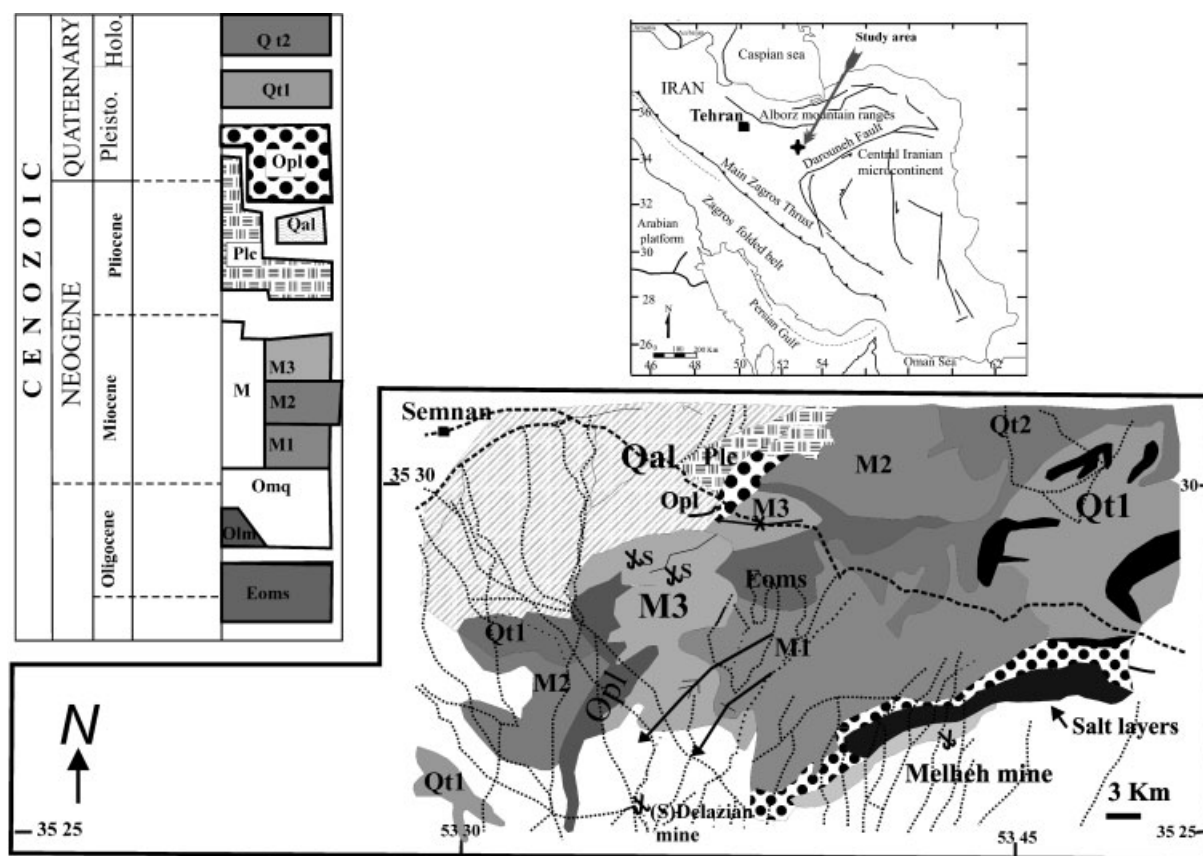


Figure 1. Location and geology maps of the study area.

This unit, which is the subject of the present study, crops out in the Central Iran Tectonic Zone with enormous thickness and include chlorides, carbonates and sulphate beds. Seemingly, these sequences formed as a facies mosaic of lagoonal and salina evaporites (mainly halite beds) admixed with wadi siliciclastics that sharply overlies the Qom Formation. The facies patterns and geochemistry of potash-bearing halite sequences of the M1 member in the NW of the Central Iran Tectonic Zone have been studied earlier by Rahimpour-Bonab and Kalantarzadeh (2005).

3. MATERIALS AND METHODS

In this study 200 samples were collected from outcrop and boreholes of the Melheh salt pit (Figures 3 and 4) for petrographic and geochemical studies. Bulk sample mineralogy was determined by optical microscopy and XRD analyses (10 samples in the University of Barcelona by J. J. Pueyo and 42 samples in the Department of Mineralogy, Clausthal Technical University). The microanalysis of frozen primary fluid inclusions trapped in halite (Cryo-SEM-EDS) was carried out by D. I. Cendón at the University of Barcelona (Ayora *et al.* 1994; Cendón *et al.* 2004).

Trace, minor and major elements (K, Ca and Mg) have been measured by AAS in Tehran University. The Br and SO₄ contents of 20 samples were measured by use of Metrohm ion chromatograph with chemical suppression for the anions at the Department of Mineralogy, Clausthal Technical University. All samples were acidified to a pH

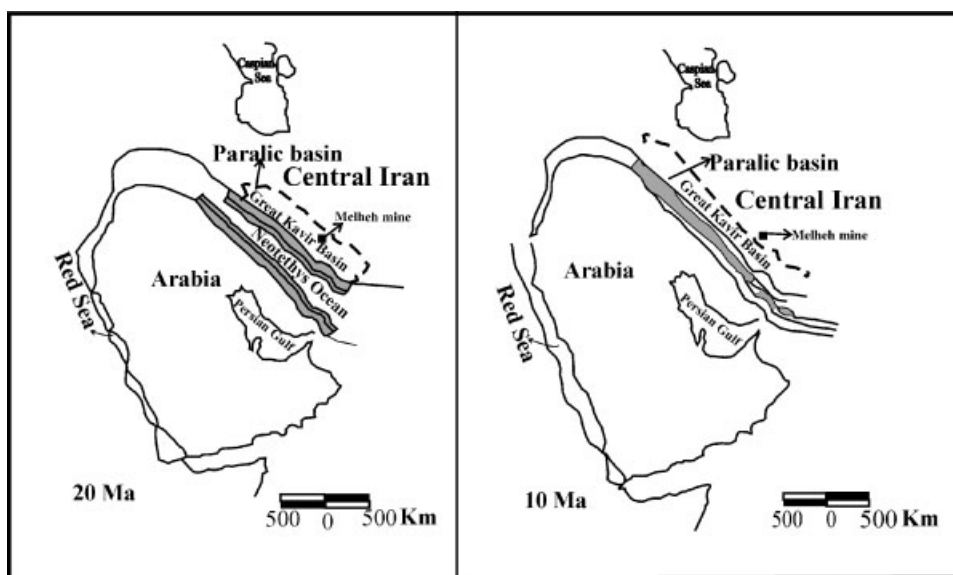


Figure 2. Palaeogeographic maps of the study area from 20 to 10 Ma that shows the Neotethys Ocean connection to the Great Kavir Basin in the Miocene (during salt deposition). This shallow paralic basin which periodically covered the Great Kavir Basin, had direct connection with the Neotethys Ocean and was the site of thick evaporite deposition during the middle Miocene (Modified from McQuarrie *et al.* 2003).

Period	Epoch	Stage	Formation	Lithology Description(Scale: 1:30,000)
Quaternary			Alluvial Deposits	
Pleistocene		Zaunclean	Hezardarre Fm.	Conglomerate containing volcanic, tuff and chert pebble size, well rounded fragments(CU)
Miocene	Upper		M3	Very thin salt beds or laminae Alternating gypsum and green to grey mudstone fine beds brown fine bedded sandstone with conglomerate intercalations, volcaniclastics which in part is limey
			M2	Some limestone beds Alternating green mudstone or shale and gypsum with ostracods and Chara stems Alternating grey to tan sandstones and cavernous microconglomerates due to dissolution of mud clasts
	Middle		M1	Conglomerate containing volcanic fragments Alternating red to grey siltstone to limey siltstones and sandstones with red to green-grey mudstones Limestone with bivalves (<i>Dreissensidea</i> and <i>Mytilidea</i>) and red algae Gypsum with vertical growth textures (acicular crystals)
				Variegated pure salt rock, fine beds
	Lower	Burdigalian Aquitainian	Qom Fm.	Marl and gypsum Fossil-bearing limestone includes <i>Millioides</i> , <i>Miogypsina</i> , green and red algae, echinoderms (<i>Scaevola</i>), corallids, bryozoa fragments
Oligocene				Alternating green and red beds of sandstone and conglomerate with intercalation of clay and gypsum
				Limey tuff with brachiopods, bivalves and nummulites Gypsum
Eocene				Evaporites alternating with some carbonates and volcanics

Figure 3. Stratigraphic column of the studied section (adapted from Jackson *et al.* 1990).

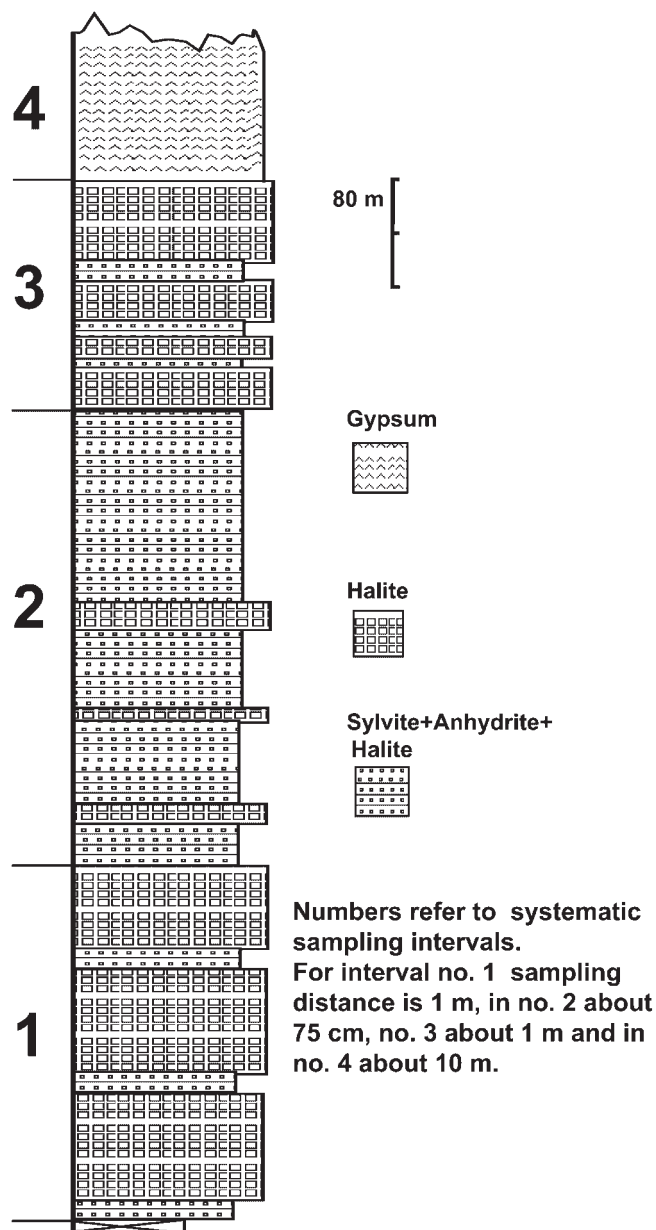


Figure 4. Vertical measured log section through the chloride unit (lower part of Member 1, Upper Red Formation) that shows the position of sample localities in the Melheh salt pit. Samples were systematically collected.

of 2.6. Accuracy and reproducibility were investigated. Accuracy as well as precision was tested against an in-house reference material (halite with known concentration of Br-analysed in different laboratories in Germany). Precision is ± 2 ppm and reproducibility ± 1 ppm. The additional 51 samples were analysed for their Br content in the University of Barcelona by XRF. The limit of detection is about ± 5 ppm Br in the halite. To measure the Br contents of halite samples, they were first crushed and flushed with ethanol to allow brines retained in fluid inclusions, or in the inter-crystalline space, to be liberated (Moretto 1988). For all instances, this methodology ensures that the ion which is analysed mainly represents that of the solid fraction.

4. RESULTS

4.1. Petrography

The thickness of the chloride unit (lowermost part of the M1 member) (Figures 3 and 4) reaches over 800 m and has very different variety of colour spectra, for example from very dark black to white in sylvite layers and red, green, violet, blue coarse-grained crystals in halite beds. It seems that alteration of volcanoclastic fragments had caused the variety of colour ranges in halite crystals (Sonnenfeld 1995).

The paragenetic sequence of these potash-bearing salts is a mixture of halite and sylvite as primary salts, and gypsum, anhydrite, polyhalite, langbeinite, d'ansite, ankerite and dolomite as secondary minerals. Generally, secondary potash minerals have been found in the samples that contain both anhydrite nodules and potash (either as mineral or inclusions) minerals. Primary textures in the halite, such as cornet, are present in well-preserved samples and are indications of growth in shallow-brine pools (Figure 5) (Dellwig 1955; Wardlaw and Schwerdtner 1966; Llewellyn 1968). They contain abundant primary fluid inclusions. The cornet texture suggests that precipitation occurred from denser brine (stratified) on the floor of a shallow-brine pool. A brine body like this would generally show decreasing temperature gradient (Braitsch 1971) and higher saturation with respect to sylvite. The hopper halite crystals (Figure 6) in the sylvinite horizons also indicate precipitation on the bottom of a deeper brine pool. In the Melheh mine, similar to other cases described in the literature (e.g. Peryt and Kovalevich 1997), the presence of the hopper and platy textures of halite in the sylvinite horizons could be attributed to this process. An ordered cyclicity in the sylvinite horizons, formed by alternating sylvite beds and include primary halite and sylvite beds, could be observed in the Melheh salt pit. In some samples granular textures typical of primary sylvite, with greyish colour, enclose the halite grains and lack any burial textures (Figure 7).

Anhydrite is present in many samples from halite and sylvinite layers as circumgranular films (Figure 8) and in many cases nodules that plugged the halite microkarst. In some of the samples, secondary potash minerals such as polyhalite, d'ansite and langbeinite, replace anhydrite nodules (Figures 9 and 10). In this case, polyhalite appears as replacement of anhydrite (Figure 9) and along the halite crystal boundaries (Figure 10). In some samples, tiny crystals of diagenetic ankerite-dolomite are associated with anhydrite (Figure 11) and polyhalite. Daughter minerals include halite and sylvite and have frequently been observed in the halite crystals as inclusions (Figure 12). These solid inclusions in the sylvite-bearing halite crystals reflect the brine evolution to the potash saturation stage.

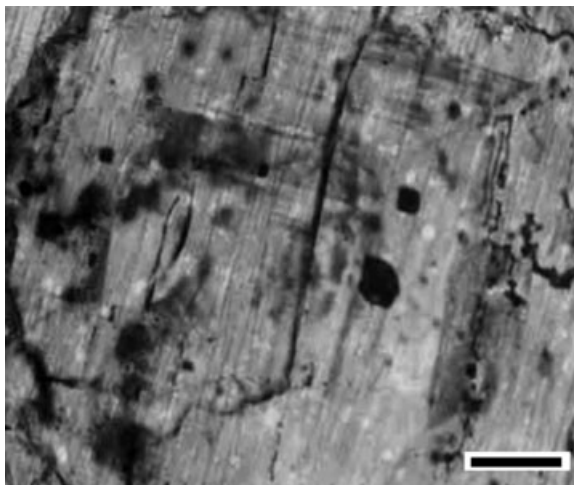


Figure 5. Thin section photomicrograph of halite crystals showing cornet texture, chloride unit, M1 member (PPL, scale bar is 2 mm).

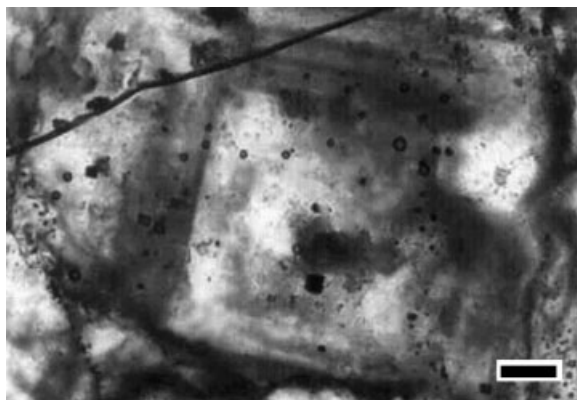


Figure 6. Thin section photomicrograph showing hopper texture in halite beds, sylvinite horizon, M1 member (PPL, scale bar is 2 mm).

4.2. Geochemistry

To investigate brine chemistry and evolution, the concentration of Br, Ca, Mg, K and SO_4^{2-} in bulk samples were analysed (Tables 1 and 2). Among these ions bromine is an important trace element in chemically precipitated marine chloride sediments (Siemann 2003). This is because Br geochemistry provides evidence of the depositional conditions, salinity fluctuations and brine evolution during halite and sylvite deposition. The Br content of the halite layer in the studied area varies from 60 to 140 ppm (Table 2) and rises to 200–305 ppm in the potash beds.

The Ca, Mg and K contents of bulk samples vary closely and follow a relatively similar trend with depth and reach their maximum in the potash-bearing horizons, but SO_4^{2-} does not show such a correlation (Tables 1 and 2, Figure 13). The K values vary from 10 to 325 ppm while Ca concentration varies from below the detection level up to 500 ppm. The Mg concentration ranges from 93 to 377 ppm and SO_4^{2-} from 0.21 to 6.1%.

5. DISCUSSION

Hardie (1984) suggested that potash deposits containing primary sylvite and carnallite and lacking MgSO_4 salts may have precipitated from Na-Ca-Mg-K-Cl brines. By progressive seawater evaporation and concentration (up to

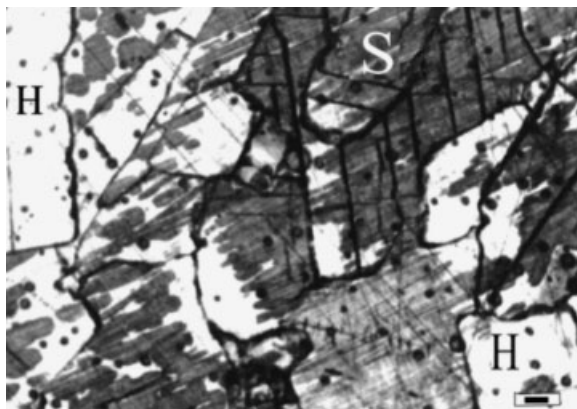


Figure 7. Granular textures typical of primary sylvite, with greyish colour that enclosed the halite grains and lack any burial textures, sylvinite horizon, M1 member (PPL, scale bar is 2 mm)(H= halite, S= sylvite).

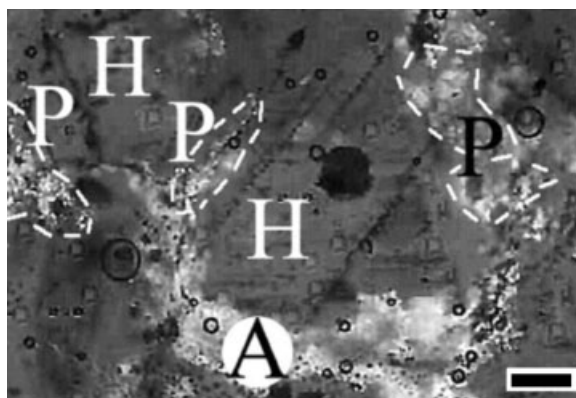


Figure 8. Polyhalite as replacement of anhydrite shaping circumgranular films around halite crystals, chloride unit, M1 member (PPL, scale bar is 2 mm)(P = polyhalite films around halite (H) crystals, A = anhydrite nodules).

70–100 times) depletion in SO_4 and Ca occurs in the remaining brine. This brine will be relatively enriched in Mg, K and Br.

Modern seawater analyses show that during seawater evaporation and its evolution to the bittern salt deposition, the remaining brine becomes progressively depleted in MgSO_4 , but enriched in KCl and CaCl_2 , as illustrated in

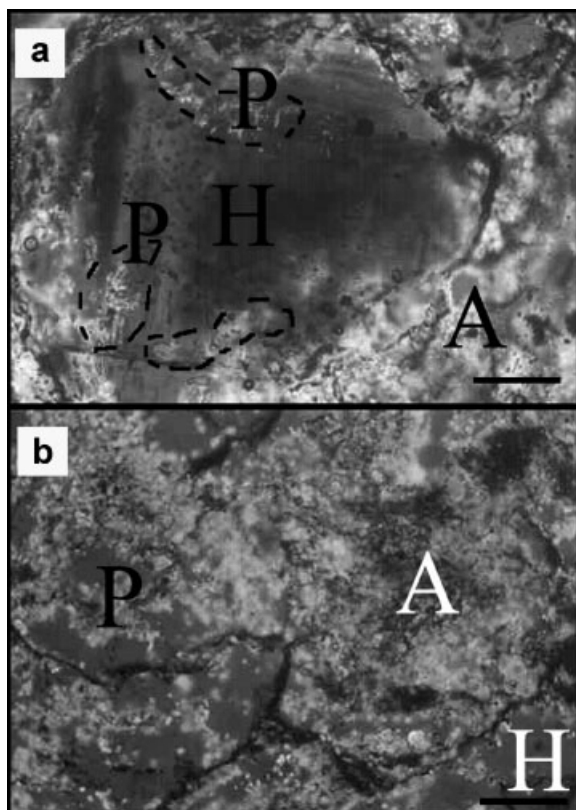


Figure 9. a- Replacement of anhydrite films by polyhalite along grain boundaries of hopper halite, b- Replacement of secondary anhydrite nodules by polyhalite, sylvinite horizon, M1 member (XPL, scale bar is 2 mm)(H = hopper halite, A = anhydrite, P = polyhalite).

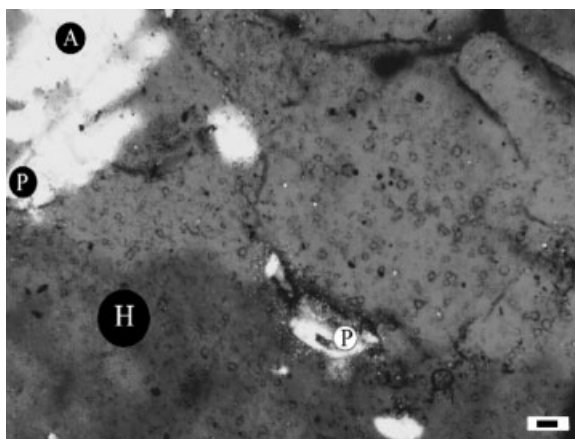


Figure 10. Closer view of tiny polyhalite crystals that replaced anhydrite (A) along grain boundaries of halite (H) crystals (surroundings). Polyhalite crystals are present only in minor amounts, sylvinite horizon, M1 member (XPL, scale bar is 0.5 mm)(P=polyhalite).

Figure 14. The Br concentration in halite is a function of both seawater composition and the degree of evaporation. In other words, the partition coefficient for Br in halite does not only depend on the concentration of Br in brine and on the concentration of MgCl_2 , but other components in brine, such as SO_4 , K and Cl ions, could affect this factor (e.g. Braitsch and Herrmann 1963). Moreover, Siemann (2003) pointed out that the presence of SO_4 at an early stage of halite saturation has the maximum influence in decreasing Br incorporation in the halite crystals. Subsequent to precipitation of the SO_4 ions an important influence was caused by the presence of K ions followed by HCO_3 (Siemann 2003). This is due to ion pair formation that inhibits their contribution (K and Br) in the halite formation. Thus, in such evaporite sequences, the Br partition coefficient decreases with increasing ions concentrations, that means increasing SO_4 and K content has important influence on the $^{\text{halite}}D_{\text{Br}}$.

Generally, detailed Br profiles are employed for revealing different processes such as steady state regimes in lagoons (Kühn 1968; Hite 1974), brine dilution by fresher inflows (Wardlaw and Schwerdtner 1966; Kühn and Hsu 1974) and major flooding events (Holser 1966a; Decima 1978; Kühn and Hsu 1978; Fisher and Kreitler 1983). Since diagenetic events could strongly modify Br profiles (Tucker and Cann 1986), a detailed petrographic examination has been carried out prior to any geochemical sampling.

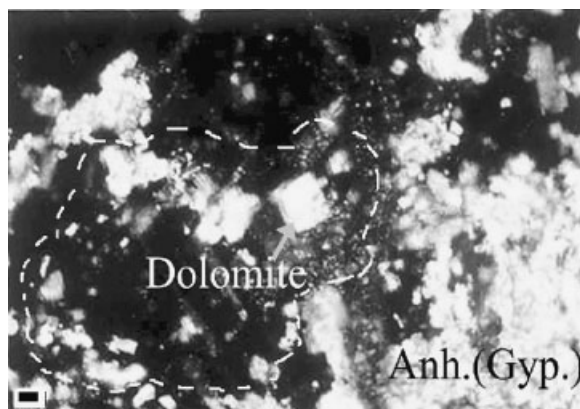


Figure 11. Dolomite and ankerite around anhydrite nodules. Their disposition suggest that they formed from the remaining Mg-bearing brines, chloride unit, M1 member (XPL, scale bar is 0.5 mm).

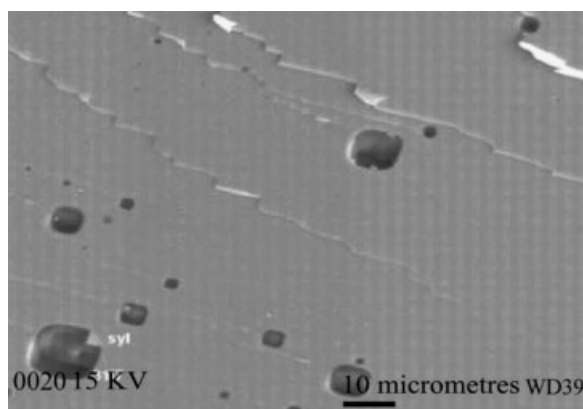


Figure 12. Sylvite inclusions within primary halite. Photo provided by Cryo-SEM-EDS method of frozen fluid inclusions, sylvinite horizon, M1 member (photo courtesy of D.I. Cendón).

Table 1. Major ions concentrations in chloride unit samples

Depth (m)	K (ppm)	Ca (ppm)	Mg (ppm)
0	176	144	94
2.5	125	126	95
5	200	0	96
7.5	20	19	196
10	175	12	97
12.5	130	63	132
15	230	10	111
17.5	180	51	116
20	260	60	208
22.5	215	504	250
25	325	5	377
27.5	195	103	133
30	55	249	150
32.5	30	0	200
35	60	156	155
37.5	156	24	106
40	178	85	125
42.5	260	24	93
45	220	60	165
47.5	85	86	170
50	100	0	110
52.5	35	0	110
55	32	0	110
57.5	30	0	121
60	70	0	125
62.5	43	2	130
65	20	0	131
67.5	50	0	132
70	33	0	133
72.5	45	0	127
75	10	0	156
77.5	11	0	160

Table 2. Br and SO₄ ions concentrations in chloride unit samples

Sample No.	Br (ppm)	SO ₄ %	Sample No.	Br (ppm)	SO ₄ %
1A	140	0.77	23	220	3.08
1	105	—	24	205	0.74
2	100	—	25	199	0.75
3	112	—	26	204	—
4	137	—	27	257	0.80
5	138	—	29	171	0.04
6	124	—	30	195	0.60
7	160	—	31	114	—
7a	100	—	32	226	—
8	158	—	34	216	0.21
11	198	—	35	203	—
12	179	—	36	86	0.61
13	176	3.14	37	208	—
13–1	156	—	38	184	—
13–2	162	—	39	197	2.06
14	143	0.89	40	—	215
15	186	—	41	—	204
16	232	2.94	42	222	6.10
17–1	163	—	43	211	—
17–2	205	—	44	219	—
18	195	—	45	224	—
19–1	182	—	46	50	0.67
20	168	—	47	242	1.19
21	197	—	48	208	—
22	190	—	49	197	—
			64	168	—

The Br content of the halite layer in the studied area at the Melheh salt pit varies from 60 to 140 ppm (Table 2) and rises to 200–330 ppm in the potash beds. In the study area periodic influxes of seawater into the basin caused variations in potash content of sylvinite deposits (Figure 15) producing fluctuations of low (60 ppm) and high Br (>200 ppm) contents. It seems that the maximum Br content of 305 ppm observed in some bittern salts (presence of sylvite) is an indication of concentrated brine near to the point of carnallite crystallization. Apparently, vertical variations in potash content (Figure 15) were due to periodic brine freshening. In the potash-bearing units, alternating bands of low and high Br halite are also indicative of this localized refreshment. In addition, partial freshening of sylvite-saturated brine may also have produced density stratification in the brine mass. The bottom brine layer was saturated with respect to potash minerals, while the overlying layer was saturated with halite. This long-lasting brine stratification caused deposition of halite beds on the potash-bearing units (Raup 1970; Lowenstein and Spencer 1990).

Distinctive vertical variations in Ca, Mg, K, SO₄ and Br contents of primary halite samples (Figure 13) are mainly caused by changes in the evaporation conditions, such as brine freshening events and the degree of evaporative concentration. However, according to observed cyclicity in the chloride section of these evaporites, these brine freshening events caused by fresh seawater, were short-lived (probably weeks or months). Generally, the Mg and K concentration in brines could be used as a reasonable indicator for the degree of evaporation (Figure 16), because they behave as conservative elements during evaporative concentration of brine until consumed by the solid phase (for K before the precipitation of sylvite or carnallite, and for Mg before the precipitation of Mg sulphates or chlorides). In samples with high Mg content, the slope of the Mg-Ca curve is parallel with the stoichiometry of polyhalite which is an indication of polyhalite (Figure 17 and Table 1). This also indicates mixing of anhydrite (or gypsum) with Ca-bearing polyhalite.

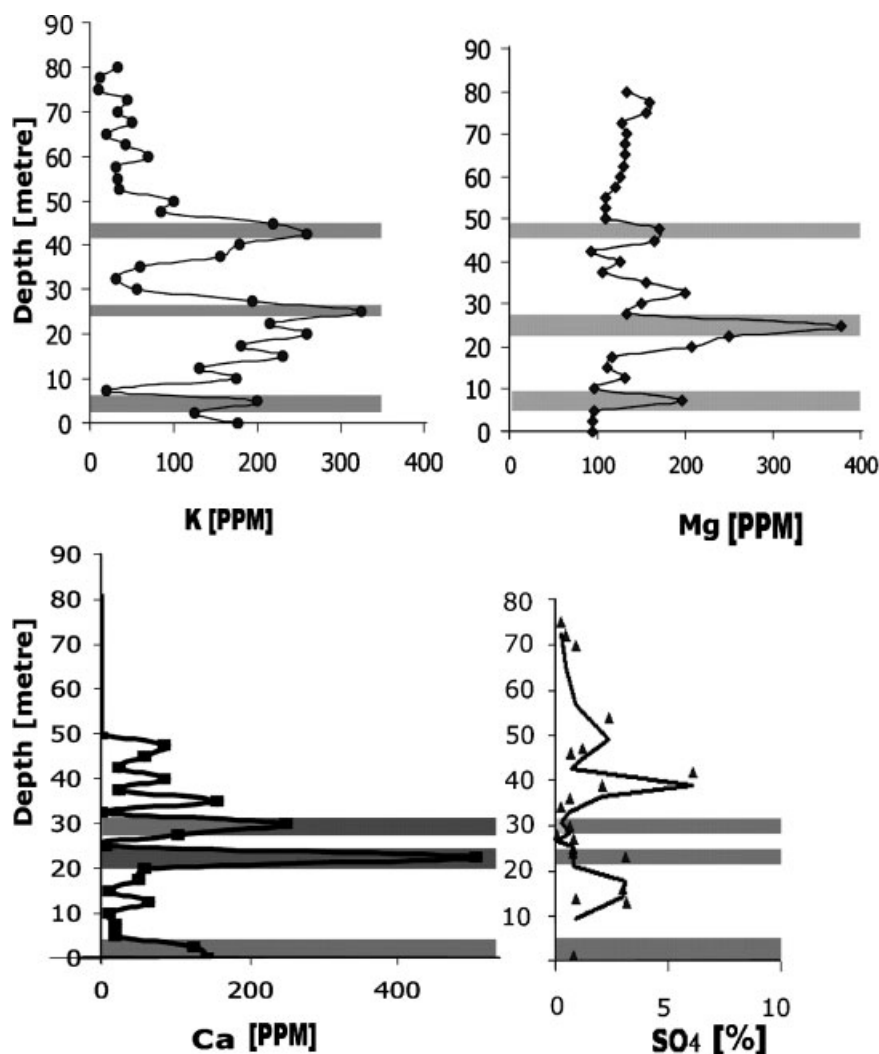


Figure 13. Geochemical variations of some important ions during evaporation in the whole-rock samples of the chloride unit, M1 member. Grey bars show potash-bearing horizons in the studied section.

In some samples, gradual replacement of anhydrite microcrystals (or nodules) by polyhalite could be observed (Figures 9 and 10). The partial alterations of diagenetic sulphate minerals suggest chemical reactions with Mg-rich brines (Schulze 1960; Holser 1966b; Pierre and Fritz 1984; Hardie 1990; Ayora *et al.* 1994; Fanlo and Ayora 1998; Peryt *et al.* 1998; Sánchez-Moral *et al.* 1998). Therefore, the early diagenetic (replacement) polyhalite crystals formed by the reactions between penetrating K-Mg-SO₄ brines and earlier gypsum, anhydrite or glauberite, beneath the surface of the brine pool by capillary force (Hardie 1990; Sánchez-Moral *et al.* 1998). The sylvite dissolution could supply such very concentrated brines (Harvie *et al.* 1984; Johnson 1997; Peryt *et al.* 1998). Ankerite and dolomite crystals are present as a by-product of the gradual replacement of anhydrite by polyhalite. During late stages of seawater evaporation and concentration, due to halite precipitation, remaining brines became depleted in SO₄, Mg, and Ca and enriched in K, and Br. These enriched brines are able to alter earlier sulphate minerals to polyhalite (Schulze 1960; Holser 1966b; Pierre and Fritz 1984), as could be seen in the Br-rich halite layers of the studied area.

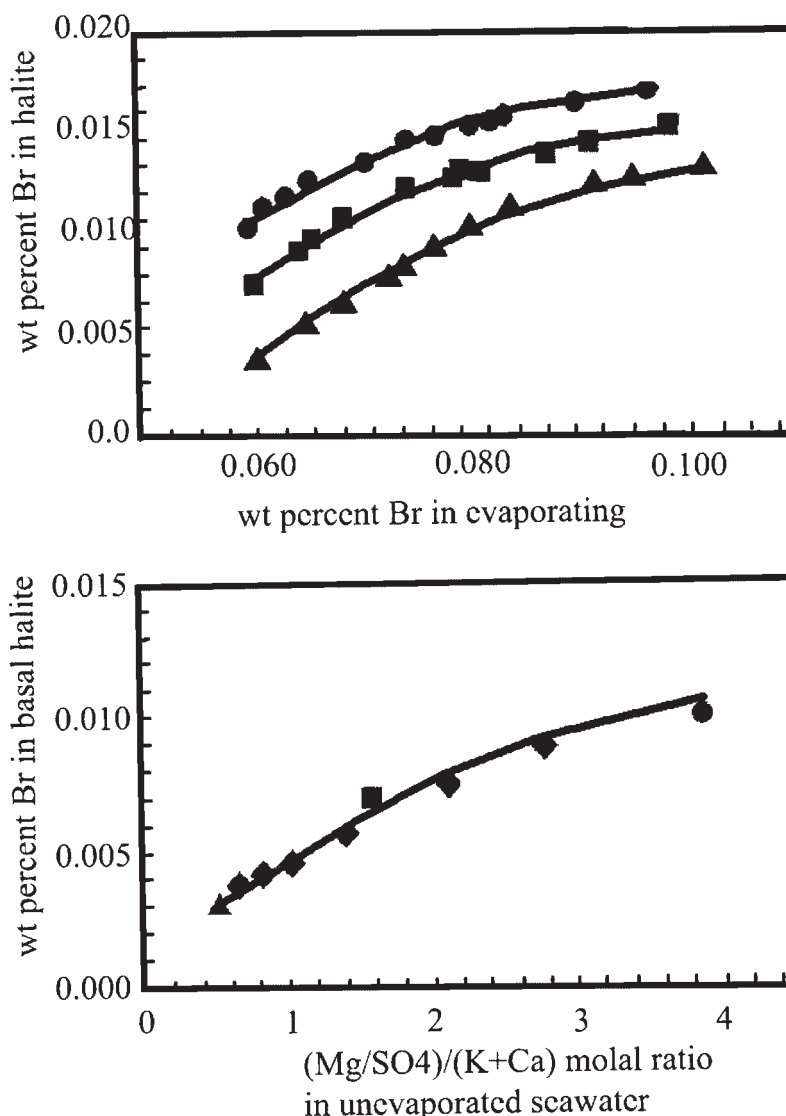


Figure 14. Experimentally developed distribution of Br with respect to the variations of the $(\text{Mg} + \text{SO}_4)/(\text{K} + \text{Ca})$ molar ratio. The progressive increase in $\text{Mg} + \text{SO}_4$ and in KCl and CaCl_2 enriched with increasing the degree of evaporation (Siemann 2003).

Based on studies in modern seawater environments, reflux is not able to disturb stratified large brine pools and produce short term fluctuations in the Br-profiles of evaporite deposits (Lowenstein and Spencer 1990). In this situation, the bottom brine layer is saturated with respect to last stage evaporite minerals, while the overlying layer is halite saturated. Therefore, such brine stratification would cause alternating deposition of halite beds with hopper texture on the potash-bearing units (Raup 1970; Lowenstein and Spencer 1990), as seen in the studied area.

Mineral paragenesis and geochemistry of studied evaporites indicate that the simple seawater evaporation pattern as suggested by Cendón *et al.* (2004) for the Middle Miocene evaporite of Badenian is not the case here. Therefore, regarding solute proportion (Table 2), in the Great Kavir Basin, the normal sequence of evaporite deposition is complicated by leakage of CaCl_2 brines through rift systems (Rahimpour-Bonab *et al.* in press). This process could have depleted SO_4 ions in the parent brine. Continuous reduction in SO_4 concentration during this process, explains

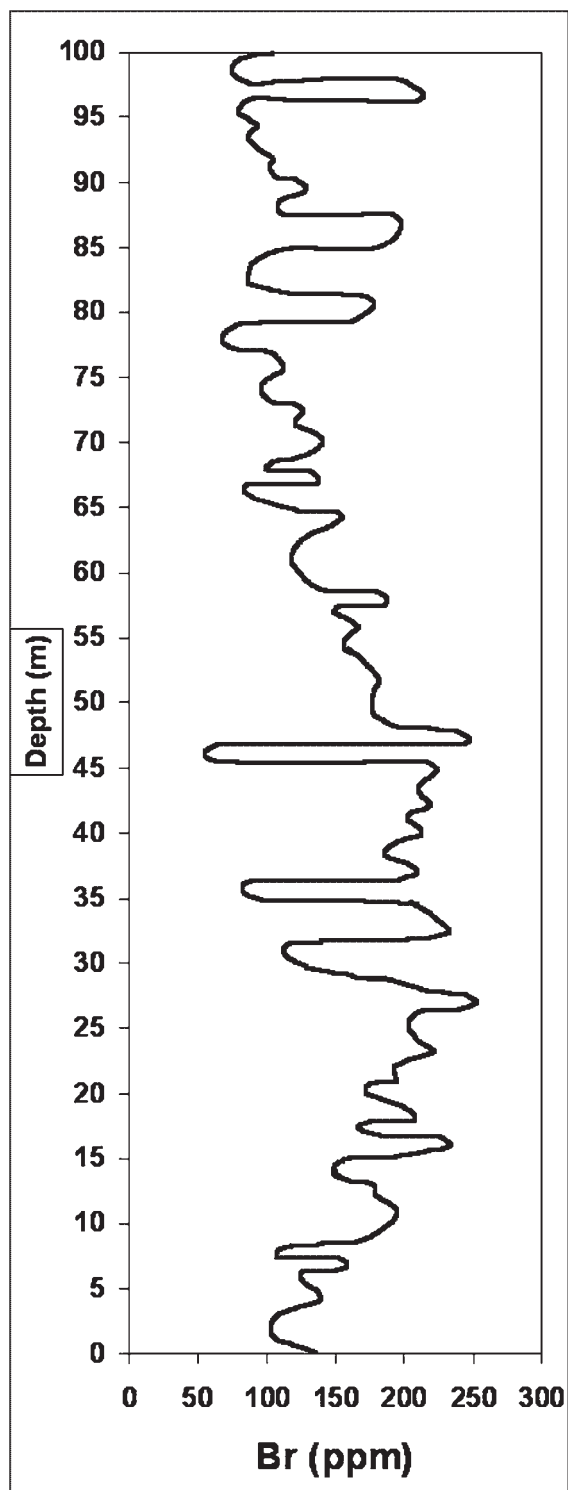


Figure 15. The vertical Br profile of the chloride unit that shows delicate fluctuations due to brine evolution.

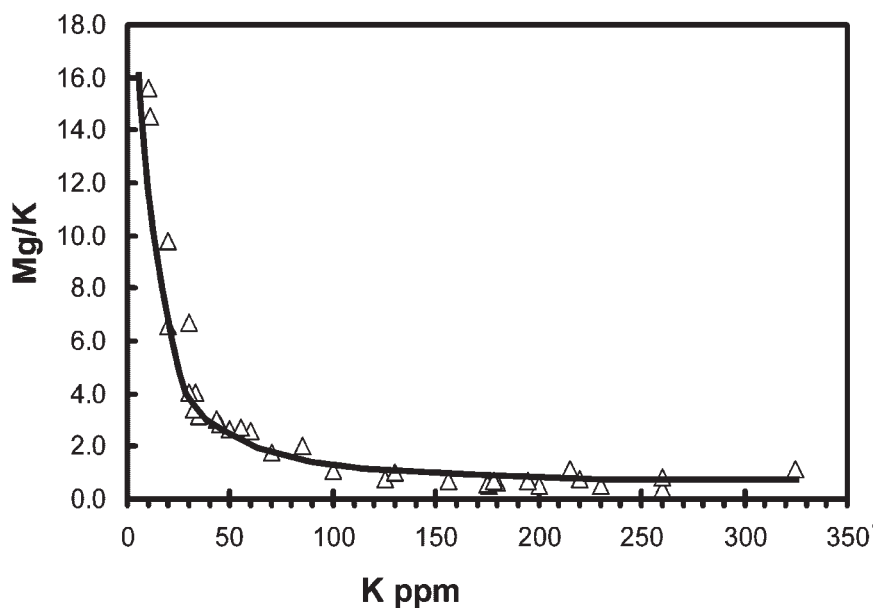


Figure 16. Mg/K versus K variation curve that shows the degree of evaporation and onset of K consumption due to potash mineral crystallization from brine.

the lack of primary polyhalite in our sequence and its absence in solid inclusions in the primary halite. A similar observation was reported by Ayora *et al.* (1994) in the study of the South Pyrenean Cenozoic basin. The SO_4 content in the halite samples was too low to allow precipitation of Mg-sulphates. Two main hypotheses have been suggested to explain depleted values of SO_4 in these samples: (1) bacterial sulphate reduction, and (2) addition of Ca to the basin and subsequent removal of SO_4 by precipitating Ca-sulphates (Ayora *et al.* 1994).

6. CONCLUSIONS

The general salinity crisis in the Great Kavir Basin of Oligocene and Miocene times has been caused by the development of a prolonged period of widespread, and thick, evaporitic potash-bearing deposits in Iran. Among them, salt deposits in the north of the Great Kavir Desert, with their considerable thickness, show well-preserved textures indicative of relatively shallow-brine pools. In addition, the presence of sylvite in the paragenetic sequence indicates probable SO_4 depletion in the parent brine. The Br geochemistry indicates marine-derived parent brines that were under sporadic influence of freshening by meteoric or fresh seawaters. Moreover, based on mineralogical and geochemical data, influx of CaCl_2 -rich brines through active rift systems of Neogene times into the Great Kavir Basin, exerted important influence on the brine chemistry. This may have triggered SO_4 depletion and the lack of primary Mg-sulphate minerals in the studied section. Distribution patterns of various elements in the chloride unit suggest unstable basin conditions that were able to modify the parent brine chemistry. Absence of Mg-sulphate/chlorides in the studied sequence reveal a low quantity of SO_4 in the parent brine. The important evidences for a marine origin of the parent brine in the studied area are the high values of Br (average 180 ppm) and K (90 ppm) of bulk samples.

In conclusion, the development of halite evaporites with substantial thickness (hundreds to thousands of metres) in the studied area suggests initial inflow of seawater along the narrow continental rift axis of the incipient ocean basin, initiated in Early Eocene time and continued up to the Middle Miocene in the isolated failed rift arms. Discontinuous and alternating deposition of normal marine sediments (e.g. Qom Formation) on these continental sediments and marginal marine evaporites (LRF) demonstrate the full influx of the sea and the flooding of the

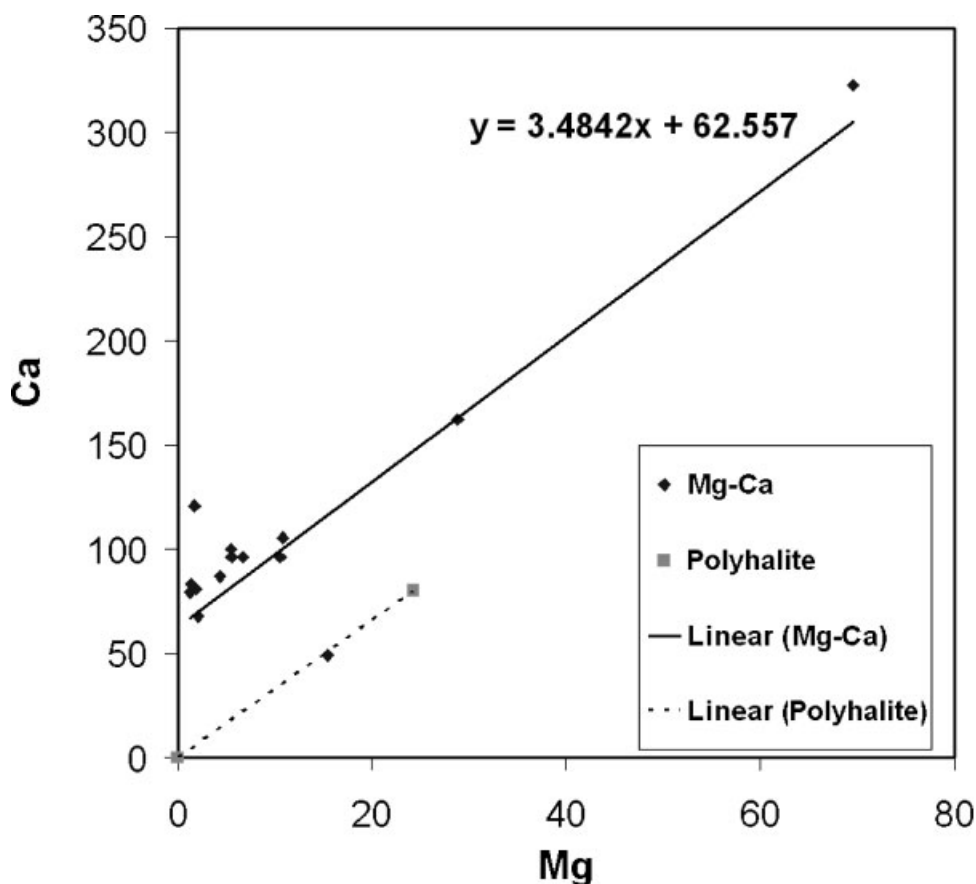


Figure 17. The Mg-Ca diagram for halite samples that indicates mixing of anhydrite (or gypsum) with Ca-bearing polyhalite.

subsiding margins of the divergent continents. This competition between marine and non-marine environments, at the edge of the encroaching sea, produced several sequences of both abrupt and gradual transition from continental wadi sediments to marginal marine evaporite in the studied area. This finally led to the accumulation of marine evaporites of M1 of URF that, in turn, are gradually replaced by red beds of continental sediments of M2 and M3.

ACKNOWLEDGEMENTS

This paper is produced by a grant to the first author from University of Tehran, which is appreciated. B. C. Schreiber and D. I. Cendón provided invaluable comments and suggestions to an earlier draft, for which we are sincerely grateful. We also thank J. J. Pueyo and D. I. Cendón for their help with the geochemical analyses. Constructive and perceptive reviews by C. Kendal, T. M. Peryt and I. D. Somerville are gratefully acknowledged.

REFERENCES

- Ayora C, Garcia-Veigas J, Pueyo JJ. 1994. The chemical and hydrological evolution of an ancient potash-forming evaporite basin as constrained by mineral sequence, fluid inclusion composition, and numerical simulation. *Geochimica et Cosmochimica Acta* **58**: 3379–3394.

- Braitsch O. 1971.** *Salt Deposits, Their Origin and Composition*. Springer: Berlin.
- Braitsch O, Herrmann AG. 1963.** Bromine geochemistry of salt deposits, II: during the formation of primary Sylvite and Carnallite. *Geochimica et Cosmochimica Acta* **28**: 1081–1109 (in German).
- Cendón DI, Peryt TM, Ayora C, Pueyo JJ, Taberner C. 2004.** The importance of recycling processes in the Middle Miocene evaporite basin (Carpathian foredeep): palaeoenvironmental implications. *Palaeogeography, Palaeoclimatology, Palaeoecology* **212**: 141–158.
- Decima A. 1978.** Initial data on the bromine distribution in the Miocene salt formation of southern Sicily. *Memoir of Geological Society of Italy* **16**: 39–43.
- Dellwig LF. 1955.** Origin of Salina salt of Michigan. *Journal of Sedimentary Petrology* **25**: 83–93.
- Estefan SF, Awadalla FT, Yousef AA. 1980.** Solar evaporation of Qarun Lake brine. *Salt Research Industry* **16**: 1–11.
- Fanlo F, Ayora C. 1998.** The evolution of the Lorraine evaporite basin: implications for the chemical and isotope composition of the Triassic ocean. *Chemical Geology* **149**: 135–154.
- Fisher RS, Kreidler CW. 1983.** Bromide content of halite in core from upper and lower San Andres, Glorieta, and upper and lower Clear Fork Formations, Doe-Gruy Federal no. 1 Rex White Well, Randall County, Texas. *The University of Texas at Austin, Bureau of Economic Geology, Geological Circular* **83**: 125–127.
- Hardie L. 1968.** The origin of the recent non-marine evaporite deposit of Saline Valley California. *Geochimica et Cosmochimica Acta* **32**: 1279–1301.
- Hardie L. 1984.** Evaporites: marine or non-marine? *American Journal of Science* **284**: 193–240.
- Hardie L. 1990.** The roles of rifting and hydrothermal CaCl₂ brines in the origin of potash evaporites: a hypothesis. *American Journal of Science* **290**: 43–106.
- Harvie CE, Moller N, Weare JH. 1984.** The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25°C. *Geochimica et Cosmochimica Acta* **48**: 723–751.
- Hite RJ. 1974.** Evaporite deposits of the Khorat Plateau, northeastern Thailand. In *Fourth International Symposium on Salt*, Coogan AH (ed.). Geological Society Northern Texas: 135–146.
- Holser WT. 1966a.** Bromide geochemistry of salt rocks. In *Proceeding of the Second International Symposium on Salt*, Rau JL. Northern Ohio Geological Society, v. 2: Cleveland Ohio: 248–275.
- Holser WT. 1966b.** Diagenetic polyhalite in Recent salt from Baja California. *American Mineralogist* **51**: 99–109.
- Hovorka SD. 1992.** Halite pseudomorphs after gypsum in bedded anhydrite—clue to gypsum—anhydrite relationships. *Journal of Sedimentary Petrology* **62**: 1098–1111.
- Irion G, Muller G. 1968.** Huntite, magnesite and polyhalite of Recent age from Tuz Golu Turkey. *Nature* **220**: 1309–1310.
- Jackson MPA, Cornelius RR, Craig CH, Ganster A, Stocklin J, Talbot CJ. 1990.** Salt diapirs of the Great Kavir, Central Iran. *Geological Society of America Memoir* **177**: 1–139.
- Johnson KA. 1997.** Evaporite karst in the United States. *Carbonates and Evaporites* **12**: 2–14.
- Kalhor R. 1961.** Geology of Neogene Formation in Varamin-Garmsar Area and Evaluation of Abardej Nose. Unpublished National Iranian Oil Company, Geological report No.233: 17 p.
- Kühn R. 1968.** Geochemistry of the German potash deposits. *Geological Society of America* **88**: 427–504.
- Kühn R, Hsu KJ. 1974.** Bromine content of Mediterranean halite. *Geology* **2**: 213–216.
- Kühn R, Hsu KJ. 1978.** Chemistry of halite and potash salt cores, DSDP sites 374 and 376, Leg 42A, Mediterranean Sea. In *Initial Reports of the Deep Sea Drilling Project*, Kidd RB, Worstell PJ (eds.). US Government Printing Office, 4: part 1 613–619.
- Langbein R. 1987.** The Zechstein sulphates: the state of the art. *Lecture Notes in Earth Sciences* **156**: 56–59.
- Llewellyn PG. 1968.** Dendritic halite pseudomorphs from the Keuper Marl of Leicestershire, England. *Sedimentology* **11**: 293–297.
- Lowenstein TK, Spencer RJ. 1990.** Syndepositional origin of potash evaporites; petrographic and fluid inclusion evidence. *American Journal of Science* **290**: 43–106.
- McQuarrie N, Stock JM, Verdel C, Wernicke BP. 2003.** Cenozoic evolution of Neotethys and implications for the causes of plate motions. *Geophysical Research Letters* **30**: SDE 6-1.
- Moretto R. 1988.** Observations on the incorporation of trace elements in halite of Oligocene salt beds, Bourg-en-Bresse Basin, France. *Geochimica et Cosmochimica Acta* **52**: 2809–2814.
- Ordóñez S, Sánchez-Moral S, García del Cura MA, Rodríguez Badiola E. 1994.** Precipitation of salts from a Mg²⁺, Na⁺, SO₄²⁺, Cl⁻ playa lake brines: endorreic saline ponds of La Mancha (Central Spain). *Society of Economic Mineralogists and Paleontologists Special Publications* **50**: 61–71.
- Perthuisot JP. 1971.** Recent Polyhalite from Sebkhah el Melah (Tunisia). *Nature Physical Science* **232**: 186–187.
- Perthuisot JP. 1975.** The Sabkha el Melah in the Zarzis. Genesis and evolution in a paralic basin. School of normal superior, Paris (In French).
- Peryt TM, Kovalevich VM. 1997.** Association of re-deposited salt breccias and potash evaporites in the lower Miocene of Stebnyk (Carpathian foredeep, west Ukraine). *Journal of Sedimentary Research* **67**: 913–922.
- Peryt TM, Pierre C, Gryniv SP. 1998.** Origin of polyhalite in the Zechstein (Upper Permian) Zarada platform (northern Poland). *Sedimentology* **45**: 565–578.
- Pierre C. 1985.** Polyhalite replacement after gypsum at Ojo de Liebre Lagoon (Baja California, Mexico): an early diagenesis by mixing of marine brines and continental waters. In *Sixth International Symposium on Salt*, Schreiber BC, Harner L (eds). I, 257–265.
- Pierre C, Fritz B. 1984.** Replacement processes of both gypsum and polyhalite: example of the south-oriental of the Ojo de Liebre (Baja California, Mexico). *Review of the Dynamic Geology and Physical Geography* **25**: 157–166.
- Rahimpour-Bonab H, Alijani N. 2003.** Petrography, diagenesis and depositional model for potash deposits of the north Central Iran, and use of bromine geochemistry as a prospecting tool. *Carbonates and Evaporites* **18**: 19–28.
- Rahimpour-Bonab H, Kalantarzadeh Z. 2005.** Origin of the secondary potash deposits; a case from Miocene evaporites of NW central Iran. *Journal of Asian Earth Sciences* **25**: 157–166.
- Rahimpour-Bonab H, Shariatnia Z, Siemann MG.** Role of rifting in evaporite deposition in the Great Kavir Basin. In *Evaporites*, Schreiber BC (ed.). Journal of Geological Society, London, (In Press).

- Raup OB. 1970.** Brine mixing: an additional mechanism for formation of basin evaporites. *AAPG Bulletin* **54**: 2246–2259.
- Sánchez-Moral S, Ordonez S, Delcura MAG, Hoyos M, Canaversa JC. 1998.** Penecontemporaneous diagenesis in continental saline sediments- Bloeditization in Quero playa lake (La Mancha, Central Spain). *Chemical Geology* **149**: 189–204.
- Schreiber BC, Walker D. 1992.** Halite pseudomorphs after gypsum: a suggested mechanism. *Journal of Sedimentary Petrology* **62**: 61–70.
- Schulze G. 1960.** Stratigraphic and genetic vertical variations in the bromine of Zechstein evaporite deposits. *Freiberger Forschungsheft* C83.
- Schulze G. 1970.** Polyhalite genesis in Deutsche Zechstein Salt. *Geology* **16**: 310–317.
- Siemann MG. 2003.** Extensive and rapid changes in seawater chemistry during the Phanerozoic, evidence from Br contents in basal halite. *Terra Nova* **15**: 243–248.
- Sonnenfeld P. 1984.** *Brines and Evaporites*. Academic Press: Orlando; pp. 613.
- Sonnenfeld P. 1995.** The colour of rock salts-a review. *Sedimentary Geology* **94**: 267–276.
- Stocklin J. 1968.** Salt deposits of the Middle East. *Geological Society of America IWC Special Paper* **88**: 157–181.
- Stocklin J. 1974.** Possible ancient continental margins in Iran. In *The Geology of Continental Margins*, Burk CA, Drake CL (eds). Springer-Verlag: New York: 873–887.
- Tucker RM, Cann JR. 1986.** A model to estimate the depositional brine depths of ancient halite rocks: implications for ancient subaqueous evaporite depositional environments. *Sedimentology* **33**: 401–412.
- Wardlaw NC, Schwerdtner WM. 1966.** Halite–anhydrite seasonal layers in the Middle Devonian Prairie Evaporite Formation, Saskatchewan, Canada. *Geological Society of America Bulletin* **77**: 131–342.