

Fluid inclusion studies in modern halite from the Inagua solar saltwork

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The composition of evaporated seawater and fluid inclusions in recently precipitated marine halite from the solar saltwork on Great Inagua, Bahamas, has been analyzed in order to test whether there is a difference between the composition of the parent brines and the trapped inclusion fluids. The concentration of Na, K, Mg, Ca, Cl, SO₄, and Br was determined by micro extraction ion chromatography, and the concentration of B, Rb and Li by micro extraction ICP-MS. Fluid inclusions from the center of hopper crystals have homogeneous compositions identical with that of the parent brine, whereas network inclusions from the marginal parts of the crystals containing stronger evaporated brines have a different composition compared to the parent brine (open pore space?). Although possibly an artificial effect due to sample storage, this also might be important for halite from environments with high evaporation rates and temporarily desiccation.

1. AIMS

With the development of several new micro techniques for single fluid inclusion analysis, the investigation of palaeo seawater chemistry and secondary mineral reactions in salt deposits by studying brine inclusions in marine halite has become very topical [1-5]. These studies are based on the assumption that the trapped fluid has the same composition as the brine participating in the salt forming process. According to our knowledge, there are no investigations on fluid inclusion compositions in marine halite precipitated from evaporated seawater to confirm this assumption. Solar saltworks are a suitable place for this kind of study, because at the same time evaporated seawater, precipitated halite and trapped fluid inclusions can be investigated.

2. FIELD AREA AND SAMPLES

The solar saltwork of Great Inagua, Bahamas, [6] was selected because its halite crystals are several millimeters to centimeters in size and contain fluid inclusions larger than 200 µm in diameter.

The reservoir system with brine densities from 1.024 g/cm³ at the seawater inlet to about 1.214 g/cm³ in the final reservoir feeds 61 halite crystallizers or salt pans (A1 to Y; total pan area: 9 km²).

Crystallizer brines with a density above 1.248 g/cm³ are drained and discharged to the ocean. Each crystallizer will be drained and refilled approximately three times a year and the precipitated halite is harvested after reaching a thickness of 20 cm. A small layer of salt floor is left in the crystallizer.

At each sampling location density, pH, brine temperature, air temperature, and humidity were measured in the field. The parent brine in the salt pan and halite crystals growing on the floor were sampled. The parent brines diluted by SERALPUR water (resistivity <17.5 megohms/cm) at a ratio of 1:20 were stored in NALGENE bottles. The bottles were sealed to prevent further evaporation. At each location, one split of halite crystals was stored in 250 ml polypropylene bottles covered with parent brine, whereas a second split of crystals was dried with tissues and stored in plastic bags.

3. METHOD

Fluid inclusions >200 µm were opened by a mechanical drill. 0.1 to 1 µl of inclusion brine were carefully extracted with a microsyringe [7-8, Lazar, von Borstel]. For ion chromatography SERALPUR water was added (~1:2000). The concentration of Na, K, Mg, Ca, Cl, SO₄, and Br of the fluid inclusions and the parent brines were determined

Table 1 Major species concentrations of fluid inclusions in samples E4, F2, and G2.

	Sample F2						Sample G2						Sample E4					
	Na	K	Mg	Ca	Cl	SO ₄	Na	K	Mg	Ca	Cl	SO ₄	Na	K	Mg	Ca	Cl	SO ₄
F.I.	79.6	4.4	13.4	n.d.	155	22.2	51.4	10.2	27.3	n.d.	142	36.7	30.7	13.3	39.1	0.4	130	59.6
F.I.	82.3	4.2	12.2	n.d.	155	20.4	64.6	7.0	19.4	n.d.	142	29.5	35.4	14.8	43.8	0.7	143	68.8
F.I.	73.0	5.6	15.9	n.d.	150	24.2	62.0	8.6	24.9	n.d.	154	37.8	33.4	19.0	54.9	0.3	161	64.1
F.I.	76.8	4.7	14.4	n.d.	152	22.2	53.8	7.9	23.5	n.d.	136	34.4	28.6	18.4	56.1	0.2	171	76.0
F.I.	72.7	5.9	16.6	n.d.	150	24.9	48.4	10.0	31.2	n.d.	141	44.1	26.0	16.3	52.5	0.7	188	45.8
F.I.	80.6	4.5	13.3	n.d.	170	23.1	56.9	8.5	25.7	n.d.	145	42.6	13.5	5.9	52.2	0.4	166	29.8
F.I.	80.7	4.5	13.6	n.d.	158	21.2	57.1	8.0	24.0	n.d.	141	39.3	14.9	2.3	51.2	0.5	157	25.8
F.I.	80.6	4.5	13.3	n.d.	161	22.0	59.5	8.5	26.3	n.d.	151	40.4						
x	78.3	4.8	14.1	n.d.	156	22.5	56.7	8.6	25.3	n.d.	144	38.1	26.1	12.9	50.0	0.5	159	52.8
asd	3.7	0.6	1.5		7	1.5	5.4	1.1	3.4		5.9	4.7	8.7	6.4	6.2	0.2	18.9	19.5
rsd	4.7	12.8	10.5		4.3	6.6	9.5	12.4	13.4		4.1	12.3	33.3	49.6	12.4	41.5	11.8	36.9
n	8	8	8		8	8	8	8	8		8	8	7	7	7	7	7	7
brine	78.8	4.9	12.0	0.5	165	22.2	58.6	8.9	29.5	0.4	155	40.3	58.1	8.0	25.6	0.3	149	38.4
dev %	0.7	2.3	-17.4		5.2	-1.5	3.2	3.5	14.3		7.1	5.5	55.1	-61.7	-95.2	-71	-7.0	-37.6

Concentrations in g/kg brine, F.I.=fluid inclusion, x=average, asd=absolute standard deviation, rsd=relative standard deviation in %, n=number of analyses, dev%=difference between average F.I. composition and parent brine, n.d.= not determined

with a precision between 2 and 7 % using a Dionex 500 instrument. For inductively coupled plasma mass spectrometry [9], a Re/In-standard, 3 times distilled HNO₃ and 3 times distilled water were added to the extracted brine (dilution ~1:200). The concentration of Li, B, and Rb of the inclusion fluids and the parent brines were measured with a precision of 7 to 11 % using a FISIONS Plasmaquad 2+ combined with a micro-nebulizer system (Micro Mist, Glass Expansion).

4. RESULTS

Two types of fluid inclusions were observed: one type of inclusions is trapped in the center part of hoppers, whereas network like inclusions occur in the more marginal parts of the crystal. The latter inclusions form a system of connected chambers separated by delicate and not always complete walls.

Fluid inclusions in samples F2 and G2 were extracted from the center of hoppers, whereas in sample E4 network inclusions were opened and analyzed. Table 1 contains the concentration of the major species in fluid inclusions and parent brines for crystallizers F2, G2, and E4. The average value (x), the absolute standard deviation (asd), the relative standard deviation in % (rsd), and the number of analyses (n) are also included for the fluid inclusion compositions in F2, G2, and E4. For comparison, the deviation between average fluid inclusion composition and parent brine is added (dev%). Table 2 lists the same items for trace element analyses.

The standard deviation (rsd) of the major species (Table 1) varies from 4.3 % for Cl to 12.8 % for Mg for 8 analyzed fluid inclusions in sample F2 and between 4.1 % for Cl and 13.4 % for Mg for 8 inclusions in sample G2. This is roughly within the range of 2 and 7 % determined for the reproducibility.

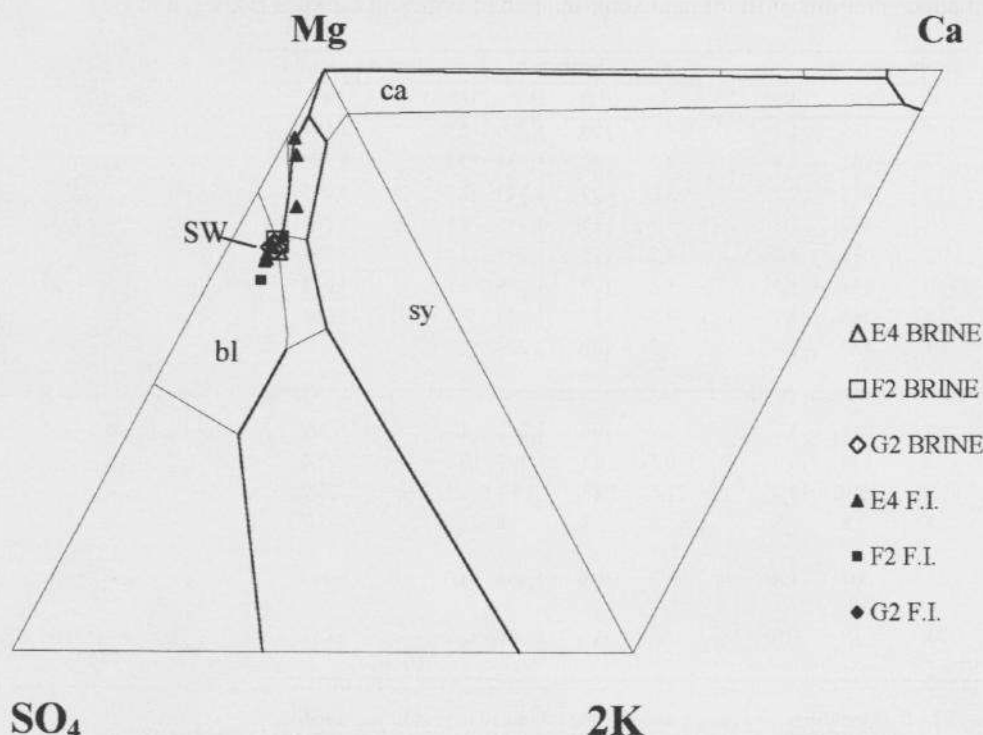


Figure 1 Jaenecke diagram with fluid inclusion and parent brine compositions at 25 °C. SW=seawater, bl=bloedite, ca=carnallite, sy=sylvite

lity of the micro extraction IC method. In comparison to that, the standard deviation for 7 inclusions in E4 (Table 1) varies between 11.8 % for Cl and 49.6 % for K.

A similar picture is observed for the trace elements (Table 2) with standard deviations of 11.0 % for B and 19.4 % for Rb in sample F2, and 6.5 % for Rb and 15.1 % for Br in sample G2. This is in fair agreement with the reproducibility of 7 to 11 % for the micro extraction ICP-MS method. On the other hand, the standard deviation for Br in sample E4 is 26.7 % based on the analysis of 7 fluid inclusions. This demonstrates clearly that the compositions of fluid inclusions in F2 and G2 are homogeneous, whereas the network inclusions in E4 are heterogeneous in composition.

Looking at the deviation between the composition of the parent brine and the average fluid inclusion,

this becomes even more obvious: In crystallizer F2 this deviation (Table 1) varies between 0.7 and 17.4 % for the major species, and crystallizer G2 shows a similar range between 3.2 and 14.3 %, whereas crystallizer E4 shows a deviation between the composition of the least evaporated fluid inclusion and the parent brine of about 50 % for most major species (Tables 1, 3). Trace element deviations of the composition of the parent brine and the average inclusion fluid range from 6 to 23 % for samples F2 and G2, whereas the Br concentration of the parent brine and of the least evaporated fluid inclusion in E4 show a deviation of 55%. Again, this indicates that the compositions of the network inclusions in E4 differ significantly from the composition of the parent brine.

Table 3 contains degrees of evaporation (DE) calculated on the basis of elements that are not re-

Table 2 Trace element concentrations of fluid inclusions and parent brines in samples E4, F2, and G2.

	Sample F2				Sample G2				Sample E4
	Li	B	Br	Rb	Li	B	Br	Rb	Br
F.I.	2.6	68	785	1.7	4.6	106	1,706	2.9	2,194
F.I.	2.1	57	762	1.4	3.3	90	1,135	2.5	2,365
F.I.	3.0	77	968	2.2	3.6	99	1,445	2.7	3,045
F.I.	2.6	67	820	1.8	3.8	110	1,146	2.8	3,266
F.I.	2.9	72	1,015	1.8	4.2	118	1,469	3.0	3,558
F.I.	2.3	60	841	1.5	3.8	109	1,209	2.8	4,073
F.I.	2.1	58	763	1.2	4.5	127	1,224	3.1	4,664
F.I.	2.1	61	535	1.4	3.7	109	1,244	2.8	
x	2.5	65	811	1.6	3.9	108	1,322	2.8	3,309
asd	0.4	7	146	0.3	0.5	11	199	0.2	884
rsd	14.9	11.0	18.0	19.4	11.5	10.3	15.1	6.5	26.7
n	8	8	8	8	8	8	8	8	7
brine	2.0	53	1,007	1.4	3.7	98	1,464	2.6	1,419
dev %	-23	-23	19	-16	-6	-11	10	-9	-133

Concentrations mg/kg brine, F.I.=fluid inclusion, x=average, asd=absolute standard deviation, rsd=relative standard deviation in %, n= number of analyses, dev%=difference between average F.I. composition and parent brine

Table 3: Degrees of evaporation (DE) and Jaenecke units for seawater and samples E4, F2, and G2

Sample	DE _{Mg}	DE _K	DE _{Li}	DE _B	DE _{Br}	DE _{Rb}	DE	Mg	2K	SO ₄	m(H ₂ O)	2NaCl	C.B.
seawater							1.0	69.0	6.5	24.5	70,700	305	
F2-brine	11	12	13	13	12	13	12 ± 1	70.3	7.4	22.3	6,720	206	-11.4
F2-F.I.	9	12	11	11	14	11	11 ± 2	63.7	8.1	28.2	7,160	221	-1.9
G2-brine	19	21	21	23	19	23	21 ± 2	69.5	7.3	23.2	3,705	82	0.3
G2-F.I.	22	22	20	21	21	21	21 ± 1	69.9	6.6	23.6	3,195	73	0.3
E4-brine	27	27			28		27 ± 1	69.5	7.3	23.2	3,705	82	3.1
E4-F.I.	40	44			44		43 ± 2	67.3	7.1	25.5	1,689	28	0.1
E4-F.I.	47	52			49		49 ± 2	67.0	7.0	26.0	1,431	29	1.7
E4-F.I.	61	69			66		65 ± 4	71.4	7.7	20.9	1,171	23	9.6
E4-F.I.	64	69			72		68 ± 4	69.3	7.1	23.6	1,083	19	-1.0
E4-F.I.	58	59			75		64 ± 9	76.4	7.4	16.2	1,317	20	-5.8
E4-F.I.	53	20			92			85.1	3.0	11.9	1,611	12	-4.8
E4-F.I.	51	7			78			88.1	1.2	10.7	1,737	14	-0.4

C.B.=charge balance, F.I.=fluid inclusion

moved in significant amounts during the evaporative concentration of seawater due to the precipitation of halite, like K, Mg, B, Br, and Li. The average DE's of fluid inclusions in sample F2 and G2 are 11 ± 2 and 21 ± 1 , respectively. This is in excellent agreement with the values of 12 ± 1 and 21 ± 2 determined for DE in the parent brines of F2 and G2. For E4 the fluid inclusions compositions cover a range of DE between 43 ± 2 and 68 ± 4 , which is clearly different from the DE of 27 ± 1 determined for the parent brine. The great variation in the DE's determined from Mg, K, and Br in the final three inclusions of E4 indicates the beginning precipitation of potash minerals.

This can also be seen from the Jaenecke units of the fluid inclusion compositions. Non-evaporated seawater shows values of $Mg=69.0$, $2K=6.5$ and $SO_4=24.5$. This ratio does not change during evaporative concentration of seawater unless potash minerals start to precipitate.

The Jaenecke units of the parent brines and the average fluid inclusion compositions of F2 and G2 are similar to those for seawater (see Table 3, Figure 1). This also true for the first four inclusions of sample E4 with values of Mg ranging from 67.0 to 71.4, of 2K between 7.0 and 7.7, and of SO_4 between 20.9 and 26.0. The ratios of the last 3 fluid inclusions of E4 (Table 3) shift clearly from $Mg=76.4$, $2K=7.4$, $SO_4=16.2$ to $Mg=88.1$, $2K=1.2$, $SO_4=10.7$.

Evaporated and with halite saturated seawater prior to potash precipitation shows a range of $m(H_2O)$ values between 7,070 and 1,260 and of 2NaCl-values between 305 and 22. The $m(H_2O)$ values of 6,720 in the parent brine and 7,160 in the average fluid inclusion of F2 demonstrate an early stage of evaporation just at the beginning of halite precipitation, whereas the $m(H_2O)$ values of 3,705 in the parent brine and 3,195 in the average fluid inclusion of G2 indicate twice the concentration factor compared to F2. This is consistent with the results of DE calculations for these samples (see above). The $m(H_2O)$ -values of fluid inclusions in E4 cover a range between 1,737 and 1,083 compared to 3,705 in the parent brine. The 2NaCl-values (Table 3) of fluid inclusions and parent brines also fit in the overall pattern.

In summary, this indicates clearly that inclusion compositions from hopper centers like in samples F2 and G2, are identical with the composition of the parent brine. In these samples there are also no significant differences between the fluid inclusion compositions from halite samples dried in tissues and samples covered with parent brine. On the other hand, the network inclusions from the marginal parts of the crystals in E4 are much stronger evaporated than the parent brine. The least evaporated inclusion fluid in sample E4 with a degree of evaporation of 43 is comparable to the strongest evaporated parent brines in the crystallizers, whereas the most evaporated fluid inclusion compositions in E4 show real degrees of evaporation well above 65. No comparable compositions are found among the crystallizer brines. Unfortunately, these network inclusions were taken from a tissue dried sample, and a sample of halite stored in parent brine was not available for this crystallizer. Thus, it cannot be decided whether the difference between the compositions of the fluid inclusions and the parent brine in E4 is due to storage or whether the network inclusions showed these unusual high degrees of evaporation already at the time of sampling. Even if the observed difference is due to storage, this also might be important for fluid inclusions in halite precipitated in shallow lagoons with high evaporation rates and temporarily desiccation.

5. CONCLUSIONS

- (1) The composition of fluid inclusions in centers of hoppers of modern halite is identical to the composition of the evaporated parent brine. This validates the reliability of the approach to reconstruct the seawater composition in ancient evaporite basins with the help of homogeneous fluid inclusion compositions in marine halite.
- (2) There also seems to be evidence, that the pore space in marginal crystal parts is not completely closed and, if kept dry, the inclusion fluids might evaporate further.
- (3) This may result in a considerable heterogeneity of fluid inclusion compositions on a millimeter

to centimeter scale in single halite crystals. In this case the chemistry of the parent brine cannot be constrained by analyzing fluid inclusion compositions in halite.

- (4) Heterogeneous fluid inclusion compositions in halite may potentially serve as an indicator for the evaporite deposition in a shallow basin with temporarily desiccation.

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