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The geochemistry of brines and minerals from the Asse Salt Mine, Germany

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Abstract—The chemistry and stable isotopes (^{18}O, D) of highly concentrated chloride brines and minerals from the Asse salt mine in the north of the Federal Republic of Germany were studied. Chemical data indicate the occurrence of three types of brines: (a) Mg-Cl type, of carnallitite origin with Li $<$ 30 mg/kg; (b) Na-Cl type brines, of rock salt origin, with Li $>$ 100 mg/kg; and (c) almost pure $MgCl_2$-type brines with Li $>$ 100 mg/kg. The first group may be subdivided into brines with Li $<$ 4.0 mg/kg and brines with Li between 18 and 30 mg/kg. Lithium is shown to be an efficient complementary tool in tracing the origin of the brines. The complex evolution of carnallitite-type brines is discussed in detail. Isotopic data of brines that were sampled directly from seepages (presumably unaltered) indicate that these brines are not a mixture with relatively fresh ground water from the overburden sediments. The stable isotope composition (^{18}O and D) of hydration water in carnallite, kieserite and polyhalite sampled from the Asse mine were also studied. It is shown that water extracted from the so-called primary carnallite is isotopically different from water extracted from secondary carnallite. The isotopic fractionation factors for ^{18}O and D between carnallite hydration water and mother solution were studied in the laboratory. Assuming that crystallization water of the so-called primary carnallite samples is not altered, the isotopic composition of the mother solution is evaluated.

INTRODUCTION

IN THE former salt mine Asse near Wolfenbüttel, scientists of the Institut für Tieflagerung of the Gesellschaft für Strahlen und Umweltforschung have been concerned, since 1965, with investigations on potentialities and risks of the final disposal of radioactive wastes in salt formations. Salt mining began at Asse with the sinking of the Asse 1 shaft between 1899 and 1907. Between 1906 and 1908 the shaft Asse 2 was sunk to a depth of 765 m. Initially, potash salt was mined exclusively. In 1916 mining of rock salt began. Because of a crisis in the German potash industry after World War I, mining of potash salt was discontinued at the end of 1925 and all further mining was restricted to rock salt. This was discontinued for economic reasons in 1964. Since 1965, the mine has been used as a research facility by the GSF.

As shown in Fig. 1, the Asse mine is an excavation within the Asse salt anticline which is a folded multicycle evaporitic sequence of Permian (Zechstein) age. The salt structure consists essentially of the Stassfurt series (Z2), the Leine series (Z3) and a small part of the Aller series (Z4). A general description of the internal stratigraphy of the Asse structure is given by ESSAID and KLARR (1982). The main rock salt units of the series contain 90–100 wt% halite (NaCl), 0–5 wt% polyhalite [$Ca_2K_2Mg(SO_4)_4 \cdot 2H_2O$], 0–5 wt% anhydrite ($CaSO_4$) and 0–5 wt% kieserite ($MgSO_4 \cdot H_2O$). The only potash salt formation in the Asse mine is the carnallitite (K2C): This unit is part of the Stassfurt series and contains about 56 wt% of the mineral carnallite ($KMgCl_3 \cdot 6H_2O$), 27 wt% halite, 14 wt% kieserite, 2 wt% anhydrite and ±1 wt% sylvite (KCl). The chemical composition of the brines indicates with which of the two above mentioned formations they have been in contact.

Rock salt as a host rock for radioactive wastes has both advantages and disadvantages. Its shielding ability and its thermal and mechanical properties are advantages, whereas its high solubility could be seen as a possible disadvantage. During the last 100 years of salt mining activities in Germany, several mines have been flooded. Mining experience has shown

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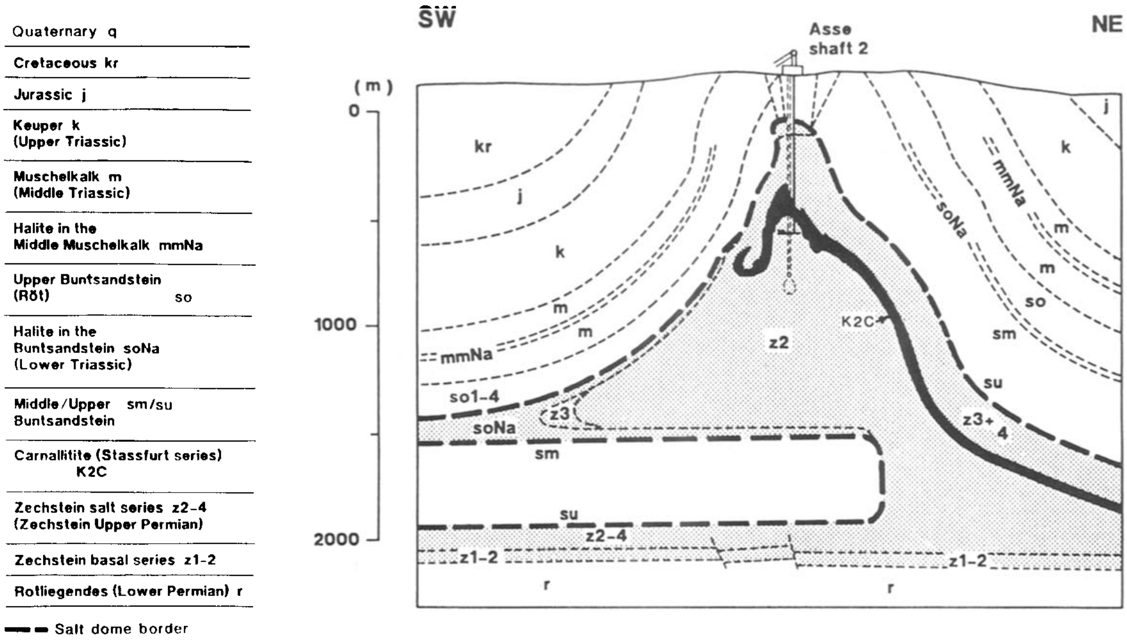

FIG. 1. Geological cross section through the Asse structure (after KLARR, 1986).

that even minor seepages with very low influx rates over the years can suddenly develop into an uncontrolled inflow, which may lead to the complete flooding of the mine. Radionuclides stored in such flooded mines could be transported to the biosphere. However, brines found in salt mines are not necessarily linked with fresh groundwater. Brines may originate from metamorphic processes in salt formations or from mining activities. An additional category of brines may originate from the disposal of heat-producing high-level wastes which leads to the liberation of hydration water from certain salt minerals. The knowledge of the origin of brine in such salt mines is essential for nuclear waste disposal.

Most of the brines in the Asse mine are found at the 750 m level below surface. These brines originate from unknown sources and most of them drain into ditches dug into the salt rock at the galleries. BRAITSCH (1971) claims that it is not possible to trace back the origin of brines in salt formations because they are most probably altered. In the present study the authors attempted to define the immediate source of the brines collected from the Asse mine by means of combining major ion chemistry, Li content and stable isotopes (^{18}O, D) of the brines and of the adjacent minerals.

An effort was first made to establish suitable analytical procedures for the determination of both D and ^{18}O in the brines and the hydration water of different minerals. A further insight into the possible origin of the brines in question was gained through experimental work in which the partition coefficient of Li as well as the isotopic fractionation factors for ^{18}O and D between carnallite and its mother solution were determined.

SAMPLING

Sampling was carried out in 1983, 1985 and 1986. Brines were filtered and tightly sealed in 100 ml glass bottles. During the sampling procedure, temperature and density were measured. Rock samples were enclosed in 250 ml beakers.

Brines

Brines from seepages are of special interest. They are the least altered brines because cooling and contact to the air in the mine can be avoided. Where seepages occurred, holes of 2.5 cm diameter and 2–3 m length were drilled and sealed. In some of these drill holes brines accumulated at a very slow rate, about 1 l/a. The brines TVF-4A, TVF-4B, 3542 and 3543 were sampled in this way at the 800 m level in the mine. Most of the brines, however, were collected from open pools. All these pools are natural or artificial depressions in the floor of galleries. The pools 750/1 to 750/26 are located at the 750 m level (Fig. 2), 775/4 and 800/1 are located at the 775 m and 800 m levels, respectively. Some pools at the 750 m level occasionally flood and the brines migrate to neighboring pools at lower elevation. From time to time some of the pools are pumped and the brines transferred to the bottom of the mine and stored in a larger pool. Brine No. 850/1 was sampled from such an accumulation pool.

Between 90 and 150 m^3 of brines accumulate per year in the open pools (KLARR, 1981). For the safety of the mine it is important to trace back the origin of these brines.

Samples 761 and 762 were collected from circulating formation waters in the gypsum cap rock of the Asse salt structure. The samples were obtained from a surficial borehole drilled into the cap rock. These brines were included in this study to show an example of the chemical and isotopic composition of waters from outside the salt dome.

Mineral samples

Two generations of carnallite, primary and secondary, are easily observed. Primary carnallite (TICP) contains

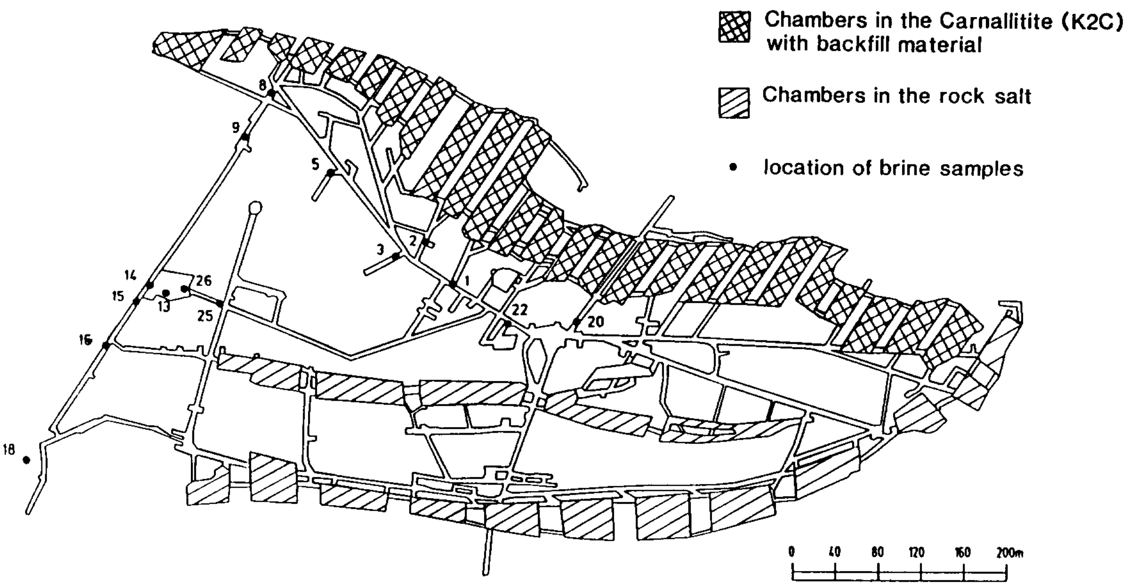

Fig. 2. Plan of the 750 m level in the Asse salt mine.

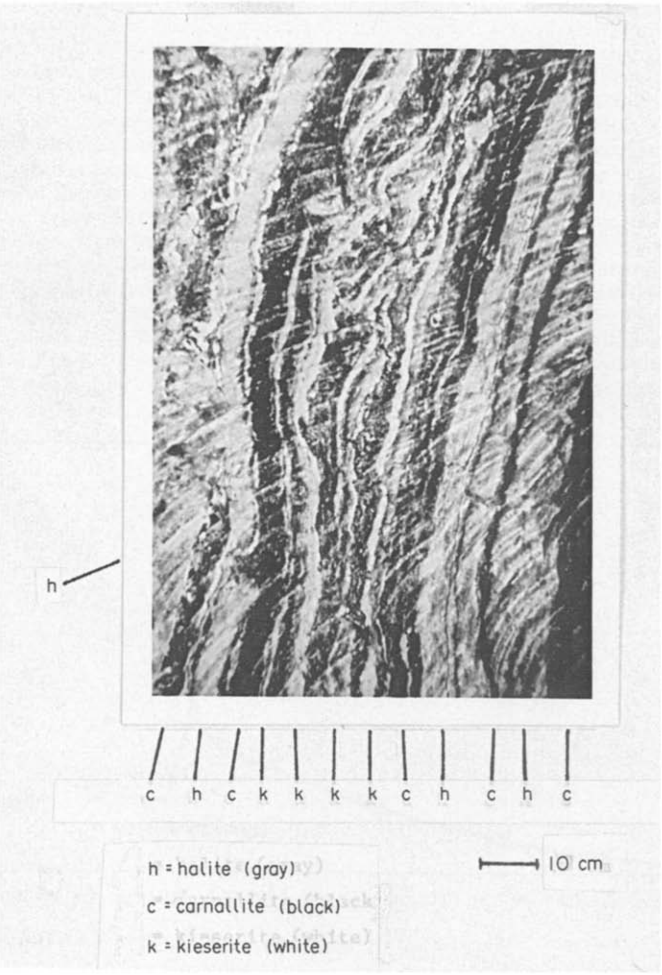

Fig. 3. The carnallitite formation K2C of the Stassfurt series in the Asse mine.

trace amounts of hematite and shows a characteristic reddish-brown iridescence. The term primary is inferred from BRAITSCH (1971) who discussed this formation extensively. According to SIEMEISTER (1961), BORCHERT and MUIR (1964) and BRAITSCH (1971) carnallite is an important primary mineral in the Zechstein salt formation, but much less common as a secondary product. In the Asse the original layered sedimentary texture is still preserved. The primary carnallitite formation (K2C) is characterized by alternating thin bands of halite, carnallite and kieserite (Fig. 3). During the uplift of the Asse salt structure, the carnallitite formation was partially brecciated. The fragments are cemented by secondary carnallite (TICS). This secondary carnallite plays a minor role. It is characterized by color differences as compared with the adjacent, primary carnallite. It is either reddish or colorless. Kieserite (TIK) was sampled from the K2C layer. Polyhalite (Pol) was sampled from the Na2 and Na3 layers, the main rock salt unites in Z2 and Z3, respectively. Mineral identification was by means of XRD. Several mineral samples are from a 3 m core, denoted CLV-3, which was drilled vertically into a carnallitite breccia at the 710 m level.

ANALYSIS

For $\delta^{18}O$ determination, the brines were equilibrated for 64 h in 5 ml glass vials, with CO_2 gas under a pressure of 600 torr and in a temperature controlled water bath at 18°C. Measurements were performed with a GD-150 mass spectrometer. This analytical procedure for ^{18}O determination in brines is routinely performed by the GSF laboratories.

A special technique had to be developed for $\delta^{18}O$ determination of the water of crystallization of carnallite. Natural carnallite samples often contain variable amounts of sylvite and halite. In the presence of dissolved $MgCl_2$, the solubility of both halite and sylvite decreases. Thus, it is difficult to determine when all of the carnallite is dissolved. In natural carnallite samples we obtained complete dissolution of the solid (including halite and sylvite) only when the ratio between crystallization water to distilled water was approximately 1:3. Such a solution cannot be used for ^{18}O determination in natural carnallite because the ratio of crystal water to "foreign" water in this mixture is too low and hence the resulting analytical error is too high. As a consequence, another analytical procedure for the determination of ^{18}O in the hydration water of carnallite had to be developed.

SLROWY and TITTEL (1958) found that Mg(OH)Cl is formed when carnallite is heated above 150°C (at about 180°C and at atmospheric pressure carnallite decomposes). Hence, upon heating to high temperatures, the water released from the carnallite may not represent the original crystallization water. However, we found that while heating to 125°C under vacuum for 12 h, >99% of the original water is extracted and only minute amounts of HCl are produced. This was verified by the low pH (<2.5) measured in these samples. This was also the procedure adopted here for the determination of ^{18}O in hydration water of carnallite samples. The distillate was collected in a dry ice–acetone trap.

Hydration water from kieserite, polyhalite and gypsum was extracted by heating to 450°C for 48 h and collecting the water vapor in a dry ice trap. Because bischofite is extremely soluble, ^{18}O in its hydration water was determined in a solution prepared by dissolving the mineral in a minimum volume of distilled water of known isotopic composition.

Preparation of brines and mineral crystallization water for D determination was performed by a slight modification of the COLEMAN *et al.* (1982) procedure, i.e. reaction of the water with Zn grains at 475°C within a closed tube. We introduced the brine or an appropriate amount of the powdered mineral (dried previously under vacuum at room temperature) directly into the tube. We used 1000 mg Zn grains (BDH product) per ~10 ml of water. The larger amount of Zn grains was required to overcome the "poisoning effect" by Cl, which is significant in the high-Cl brines being examined here. We examined the reliability of this technique by comparing δD determined in crystallization water by this technique to that determined by a different procedure. Thus, D determined for $MgCl_2 \cdot 6H_2O$ crystals (Merck product) by this technique was found to be −44.3‰ (SMOW). By comparison, δD determined for the water of crystallization in a 1:1 solution of this salt in water of known isotopic composition was −46‰ ± 3 ‰. In a second experiment we found practically identical results (a difference of 2‰) for hydration water in carnallite, in the water extracted from the carnallite (at 120°C under vacuum) and by introducing the carnallite directly into the "Coleman tube". The measurements performed are of unequal quality. In the case of ^{18}O the reproducibility range is between 0.15‰ for fresh water and ~1‰ for high-$MgCl_2$ brines. In the case of δD reproducibility varies from 0.4‰ to ±3‰, depending, possibly, on the efficiency of cleaning of the Zn grains before reaction. In general, the reproducibility for δD determination in hydration water of powdered mineral samples was

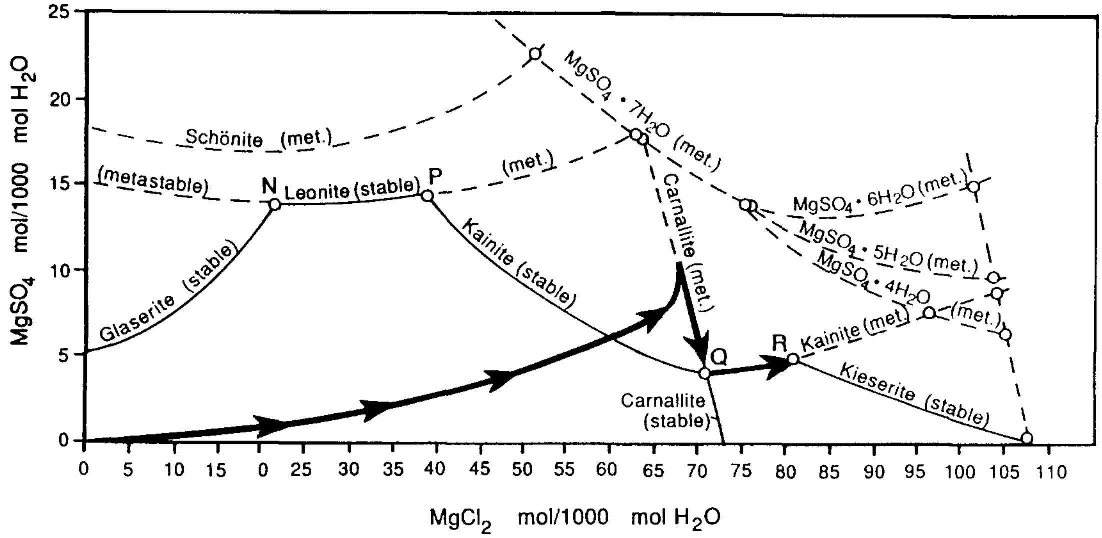

FIG. 4. Reaction path of a carnallitite dissolution experiment in the Asse mine.

better than for solutions: The δD measurements were performed using an M-86 mass spectrometer. Chemical analysis of the minerals was performed by dissolving 40 g of solid samples in 40 ml conc. HNO_3 followed by 1000 ml distilled water. Magnesium, K, SO_4 and Li were determined by ICP, Na by AAS. Calcium in NaCl-rich solutions was measured by EDTA titration, whereas in $MgCl_2$-enriched solutions it was measured by ICP. Chloride was measured by $AgNO_3$ titration. Chemical and XRD analyses were performed by the laboratories of the Institut für Tieflagerung of the GSF in Braunschweig, F.R.G.

RESULTS

The physical parameters and the chemical composition of the brines in the Asse mine are shown in Tables 1 and 2, respectively. Chemical data for rock samples appears in Table 3.

Isotopic data for the brines and their grouping according to isotopic parameters are shown in Table 4. Table 5 shows isotopic data for the hydration water of different minerals; this table also includes the predominant mineral in the samples and the depth of sampling. To examine the possible interaction (moisture exchange that may cause isotopic alteration) between the ambient air in the mine and carnallite hydration water we have examined samples from core CLV-3. The results appear in Table 5. Figure 5 presents, in a comprehensive way, the isotopic data for brines, hydration water of minerals and some additional isotopic data.

The yellow and brown color of the brines is due to the presence of Feoxy-hydroxides which are probably derived from interaction with primary or secondary carnallite. Color data could be of importance for the interpretation of the origin of the brines and are therefore presented in Table 1. The so-called carnallite mineral samples mostly contain other minerals. Sylvite (KCl), which is a common mineral in carnallite samples, cannot be identified by X-ray diffraction in the concentrations found here. Hence, the mineralogical composition of these samples was defined by evaluating the chemical data (Table 3) regarding the rock samples. The following procedure was adopted; we assumed that all of the Na is found in halite and that SO_4 appears as $MgSO_4$ H_2O mineral, the surplus of K over Mg (with respect to carnallite) was attributed to sylvite. It was calculated that sylvite and halite (and sometimes kieserite) constitute between 3 to 19% of the bulk carnallite samples (Table 3).

DISCUSSION

Major ion chemistry

The analyses from Table 2 were evaluated with two different computer programs. One was written by H. ABERCROMBIE and R. SPENCER and the other, EQ_3NR, by WOLERY. WOLERY (1953) presents the basic

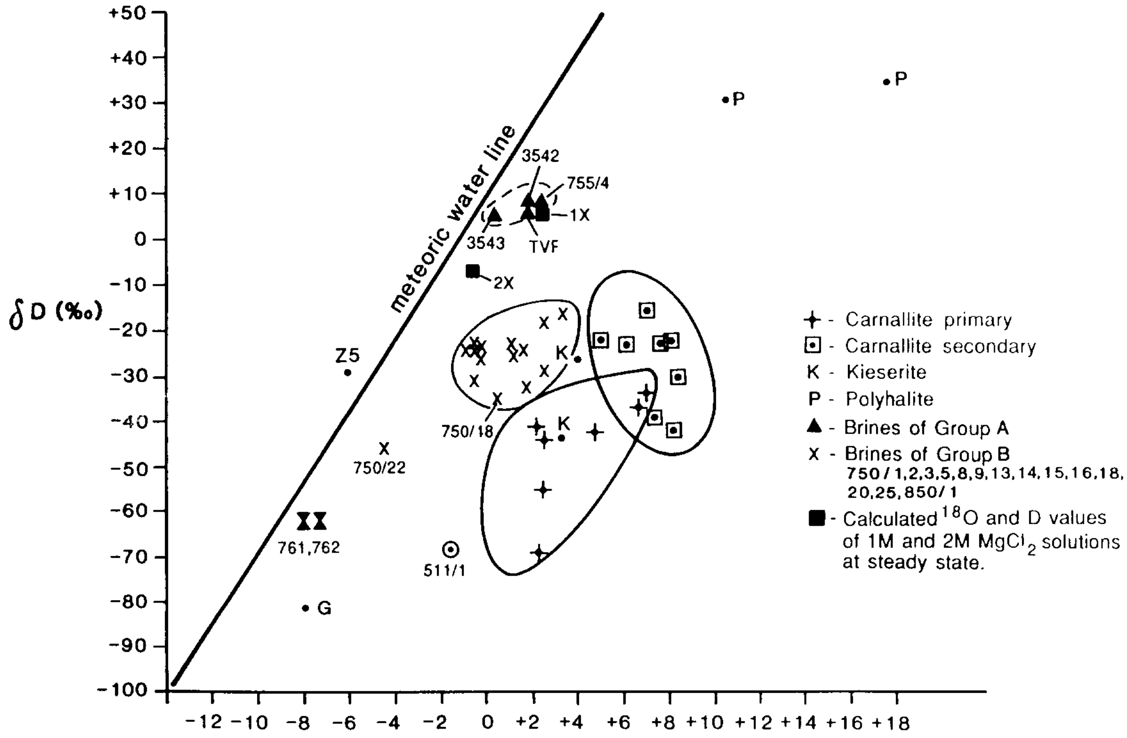

FIG. 5. $\delta^{18}O$ vs δD in brines and hydration water of various minerals of the Asse mine. $\delta^{18}O$ results for brines are corrected according to SOFER and GAT (1972).

Table 1. Description and physical parameters of brines

Sample No.	Description of sampling site	Color of brine	Temperature (°C) measure in field	Density g/cm^3 25°C
511/1	open pool	colorless	28.2	1.3548
750/1	open pool	yellow	26.2	1.3389
750/2	open pool	yellow	34.0	1.3017
750/3	open pool	strong brown	33.0	1.3397
750/5	open pool	pale brown	35.2	1.3506
750/8	open pool	pale yellow	35.4	1.3034
750/9	open pool	pale yellow	35.2	1.3179
750/13	open pool	pale yellow	29.7	1.3217
750/14	open pool	pale yellow	34.7	1.3275
750/15	open pool	pale yellow	31.6	1.3654
750/16	open pool	strong yellow	32.2	1.3574
750/18	open pool	pale brown	33.5	1.3545
750/20	open pool	pale yellow	25.6	1.3051
750/22	open pool	colorless	24.4	1.3131
750/25	open pool	yellow	28.8	1.3444
750/26	open pool	pale yellow	30.7	1.3487
775/4	seepage	pale yellow	34.7	1.3400
850/1	assembling pool	yellow	34.7	1.3138
TVF4A	seepage	colorless	32.5	1.2370
TVF4B	seepage	colorless	32.5	1.2360
3542	seepage	colorless	33.0	1.2530
3545	seepage	colorless	34.0	1.2370
761	cap rock brine	colorless	20.0	1.202
762	cap rock brine	colorless	20.0	1.202

Table 2. Chemical composition of brines: mg/kg of solution for Li, g/kg for major ions

Sample No.	Li	Ca	Na	K	Mg	SO_4	Cl	Total dissolved salts	Reaction error (%)
511/1	187.0	*	1.1	0.5	87.4	6.5	262.7	358.5	1.78
750/1	0.9	*	2.1	1.7	84.2	24.5	240.7	353.2	1.65
750/2	2.2	*	5.0	8.5	83.7	20.1	252.9	370.2	1.56
750/3	0.6	*	1.8	1.3	86.6	18.8	251.9	360.5	1.77
750/5	4.4	*	1.3	0.8	88.0	8.7	264.6	363.5	2.16
750/8	2.0	*	5.7	10.8	73.9	20.2	227.5	338.2	1.71
750/9	19.5	*	3.7	4.9	80.8	17.2	240.6	347.3	1.47
750/13	26.0	*	2.8	2.9	82.8	22.7	239.1	350.3	1.45
750/14	27.0	*	2.7	2.9	82.1	22.0	239.6	349.3	1.87
750/15	30.0	*	1.2	0.6	90.6	21.2	256.5	370.2	0.98
750/16	28.2	*	1.2	0.7	91.6	16.2	261.7	371.3	0.71
750/18	101.5	*	1.3	0.7	93.1	11.6	265.6	372.4	0.11
750/20	1.2	*	5.1	7.9	73.8	25.6	226.9	339.3	3.25
750/22	0.6	0.4	58.7	7.4	19.6	5.5	154.6	246.2	1.16
750/25	18.3	*	1.9	1.2	87.1	24.2	242.2	356.7	0.36
750/26	28.1	*	1.9	1.2	81.8	23.0	247.6	355.5	4.31
775/4	28.6	*	4.2	1.2	72.7	25.4	201.8	305.3	0.12
850/1	11.7	*	3.7	5.0	79.9	22.1	234.3	345.0	1.48
TVF–4A	152.3	0.8	50.0	29.0	30.7	5.6	173.1	289.3	1.30
TVF–4B	170.4	0.8	49.8	32.3	25.8	5.3	176.8	290.0	1.20
3542	107.7	*	24.5	25.4	47.0	5.3	193.7	295.9	0.26
762	1.0	0.9	99.0	1.8	3.1	6.3	153.0	264.1	3.20

* = concentration <0.05 g/kg solution.

No chemical analyses of the samples 3543 and 761 from Table 1 are available.

Table 3. Chemical data for rock samples and calculated mineralogical composition; mg/kg of dried rock for Li, g/kg for major ions

Sample No.	Na	K	Li	Ca	Mg	Cl	SO_4	Calculated weight-% of mineral based on the water soluble fraction (>99%) carnallite	halite	sylvite	kieserite
TICP-4	46.24	218.00	<4	*	118.20	615.91	0.28	82.5	11.8	05.3	0.0
TICP-5	11.15	223.0	<4	*	138.50	625.63	0.27	96.8	03.1		
TICP-6	26.71	218.96	<4	*	130.41	622.44	0.10	91.1	06.8	01.6	
TICS-3	36.32	220.40	<4	*	123.42	617.56	0.91	90.0	06.9	03.4	
TICS-4	28.10	223.9	<4	*	127.04	618.73	0.82	88.7	07.1	03.8	
TICS-5	27.42	222.11	<4	*	124.73	569.13	55.22	77.4	07.0	08.9	06.9
TIK-2	0	9.93	<4	*	198.03	10.08	781.78			1.9	98.0
RC			4	>99%	carnallite						

* Average Ca concentration samples is 2.07 g/kg.

Table 4. Isotopic data for brine samples (‰SMOW)

Sample No.	$\delta^{18}O$ measured (‰)	δ^{18*} corrected (‰)	δD measured (‰)
511/1	−5.5	−1.5	−67.3
750/1	−4.4	−0.5	−24.6
750/2	−3.6	−0.3	−25.6
750/3	−4.4	−0.4	−24.0
750/5	−4.4	−0.3	−23.2
750/8	−3.9	−0.5	−31.3
750/9	−2.5	+1.2	−22.4
750/13	−1.3	+2.5	−28.7
750/14	−2.1	+1.7	−24.1
750/15	−0.7	+3.5	−15.7
750/16	−2.2	+2.0	−32.4
750/18	−3.7	+0.6	−34.9
750/20	−4.1	−0.7	−23.6
750/22	−6.1	−4.4	−46.5
750/25	−1.4	+2.6	−17.4
750/26	−1.3	+2.5	—
775/4	−0.6	+2.7	+7.4
850/1	−2.4	+1.3	−25.3
TVF-4A	+0.5	+1.8	+5.0
TVF-4B	+0.5	+1.8	+5.0
3542	−0.1	+2.0	+8.1
3543	+0.1	+0.4	+5.0
761	−8.4	−8.3	−62.5
762	−8.5	−8.4	−62.6

* Corrected to concentration terms according to Sofer and Gat (1972).

— = not determined.

Table 5. Isotopic data for hydration water in mineral samples.

Sample No.	Predominant mineral	Depth of sampling (m below surface)	δ^{18}O of hydration water	δ^{18}D of hydration water
TICP-1	P. carnallite		+2.4	−54.7
TICP-2	P. carnallite		+6.7	−36.5
TICP-3	P. carnallite		+4.7	−42.3
TICP-4	P. carnallite	553	+2.2	−69.0
TICP-5	P. carnallite	574	+2.2	−40.9
TICP-6	P. carnallite	700	+2.5	−43.9
TICP-8	P. carnallite		+7.0	−33.7
TICP-10	P. carnallite			−46.9
TICS-1	S. carnallite		+8.2	−42.0
TICS-2	S. carnallite		+7.0	−15.6
TICS-3	S. carnallite	553	+8.3	−29.1
TICS-4	S. carnallite	553	+7.6	−22.7
TICS-5	S. carnallite	700	+7.3	−39.5
TICS-6	S. carnallite			−21.0
3052*	S. carnallite	750		−41.3
RC	S. carnallite			−37.0
CLV-3*	carnallite	0.0†	+5.1	−21.7
CLV-3*	carnallite	0.1†		−21.5
CLV-3*	carnallite	0.2†	+8.1	−21.6
CLV-3*	carnallite	1.0†	+6.1	−23.1
CLV-3*	carnallite	2.7†		−21.4
CLV-3*	carnallite	0.2†		−20.4
CLV-3*	carnallite	1.2†		−24.2
CLV-3*	kieserite	2.65†		−58.1
TIK-1	kieserite		+3.3	−43.3
TIK-2	kieserite	700	+3.9	−25.9
T-1‡	bischofite			−35.1
VEIN	bischofite			−31.3
TIP-7	polyhalite		+17.7	+35.2
TIP-8	polyhalite		+10.6	+30.3
TIP-10	polyhalite			+18.3
G	gypsum		−7.9	−81.8

P = primary.
S = secondary.
* Samples taken from a 3m core (Core CLV-3).
† Distance (cm) from wall surface.
‡ Taken from a fissure filling.
G = gypsum sampled from a vertical fissure within the sedimentary layers overlying the Asse salt anticline.

Table 6. Affinities and saturation state of brines calculated with the EQ3NR program; Affinities in kcal. Saturation state −undersaturated, +oversaturated, ±0.500 kcal = approximately saturated, s = approximately saturated, ss = oversaturated

Sample No.	511/1	750/1	750/2	750/3	750/5	750/8	750/9	750/13	750/14	750/15
Anhydrite	−0.732	−0.107 s	−0.150 s	−0.024 s	−0.491 s	−0.879	−0.601	−0.240 s	−0.431 s	+0.260 s
Bischofite	−0.123 s	−0.277 s	−0.279 s	−0.050 s	−0.066 s	−1.070	−0.605	−0.374 s	−0.563	+0.139 s
Carnallite	−0.215 s	+0.279 s	+1.255 ss	+0.449 s	+0.147 s	+0.277 s	+0.452 s	+0.459 s	+0.197 s	+0.265 s
Epsomite	−1.108	−0.328 s	−0.520	−0.521	−0.952	−0.471 s	−0.527	−0.373 s	−0.364 s	−0.489 s
Gypsum	−1.657	−0.977	−1.066	−1.002	−1.449	−1.475	−1.343	−1.072	−1.180	−0.819
Halite	−0.228 s	+0.052 s	+0.613 ss	+0.145 s	−0.073 s	+0.083 s	+0.140 s	+0.148 s	−0.018 s	+0.075 s
Hexahydrite	−0.833	−0.080 s	−0.249 s	−0.218 s	−0.660	−0.360 s	−0.343 s	−0.144 s	−0.176 s	−0.137 s
Kainite	−1.229	+0.090 s	+0.968 ss	+0.056 s	−0.701	+0.819 s	+0.134 s	+0.247 s	+0.015 s	−0.084 s
Kieserite	+0.160 s	+0.777 ss	+0.724 ss	+0.908 ss	+0.417 s	−0.189 s	+0.191 s	+0.618 ss	+0.377 s	+1.242 ss
Leonhardite	−0.682	+0.017 s	−0.106 s	−0.014 s	−0.475 s	−0.538	−0.376 s	−0.85 s	−0.201 s	+0.165 s
Pentahydrite	−0.762	−0.036 s	−0.182 s	−0.121 s	−0.572	−0.453 s	−0.364 s	−0.119 s	−0.193 s	+0.011 s
Polyhalite	−4.778	−0.882	+0.946 ss	−0.918	−3.330	−0.960	−1.123	−0.498 s	−1.071	−0.921
Sylvite	−1.490	−0.842	+0.136 s	−0.900	−1.185	−0.051 s	−0.341 s	−0.565	−0.638	−1.273

n.d. = not determined
* Glauberit −0.2585.

framework and mathematical basis for EQ_3NR. Changes since 1983 are documented internally within the latest public release (August 1987) available from the National Energy Software Center, Argonne National Laboratory, Argonne, Illinois, U.S.A. WOLERY (1983) together with PITZER (1973) effectively describe the options used for the computations, done in accordance with the August 1987 release, reported here. Both programs use the specific ion interaction approach (PITZER, 1973) with the parameters for 25°C of HARVIE and WEARE (1980) and HARVIE *et al.* (1984). The saturation indices were calculated by the Abercrombie and Spencer program and the affinities and the saturation state by the EQ_3NR program. In the EQ_3NR program mineral phases with affinities in the ranges of -0.5 and $+0.5$ are considered as approximately saturated, although negative values indicate undersaturation and positive values oversaturation (see Tables 6 and 7). Affinity = $RT \log Q/K$, where Q = ion activity product and K = equilibrium (or solubility) product. In the Abercrombie and Spencer program the saturation state is indicated by Sat. ind = 1.00. The affinities and the approximate saturation state for all the brines calculated with the EQ_3NR program are listed in Table 6. Three examples listed in Table 7 show that the calculations with the Abercrombie and Spencer program and the EQ_3NR program are in reasonably good agreement. In the EQ_3NR program calculations Ca concentration was set to 5 mg/kg when not specified in Table 2, and pH was set to 6.0. The assumptions made for Ca concentration in the calculations made by the Abercrombie and Spencer program differed from those for the EQ_3NR runs. Therefore, results for anhydrite and gypsum differ between these two calculations. This difference will cause comparatively minor differences for other minerals by affecting activity coefficients.

Based on major ion chemistry and color data, we suggest three types of brines in the Asse mine: (a) the rock salt type samples TVF-4A, TVF-4B, and 3542; (b) the carnallitite-type, samples 750/1-750/26 and 850/1; and (c) the highly $MgCl_2$-enriched colorless brine 511/1. Sample 3543 listed in Table 1 and Fig. 5 belongs chemically and isotopically to the rock salt brines.

(a) *Rock salt type brines*

These brines occur as seepages from the sulfate (anhydrite and polyhalite) bands in the main rock salt formation Na 2β (Hauptsalz) at the 800 m level in the Asse mine. This 200 m thick formation is composed of coarse grained, colorless or cloudy halite crystals with 1–3 mm thick sulfate bands. These bands are often intensely folded and separated by about 10 cm thick almost pure halite bands. The porosity of the anhydrite-polyhalite bands is higher than that of the compact rock salt. Therefore, brines can accumulate in the sulfate layers.

The brines TVF-4F and TVF-4B are close to saturation with respect to the minerals halite, anhydrite, gypsum and sylvite. Brine 3542 is saturated with respect to halite and almost saturated with respect to sylvite. None of these brines is even close to saturation with respect to polyhalite, even though the Mg^{2+} and K^+ concentrations of these solutions most probably stem from polyhalite dissolution.

(b) *Carnallitite-type brines*

The major ion chemistry of all the carnallitite-type brines indicates that these brines during their chemical evolution had contact with halite, carnallite and kieserite. These minerals are present in the carnallitite rock formation K2C as well as in the backfill material which was emplaced more than 50 years ago in the chambers dug in the carnallitite formation K2C. After mining the carnallitite material was transported to a factory, where KCl was separated. Following this industrial process the solid residue of essentially kieserite, halite, some unconverted car-

Table 6. *Continued*

750/16	750/18	750/20	750/22	750/25	750/26	775/4	850/1	3542	TVF–4A	TVF–4B	762*
+0.172 s	+0.025 s	−0.792	−4.558	−0.050 s	−0.397 s	−1.097	−0.549	−2.553	+0.313 s	+0.163 s	+0.340 s
+0.197 s	+0.236 s	−1.127	−4.351	−0.213 s	−0.555	−1.452	−0.709	−2.621	−3.277	−3.659	−5.477
+0.444 s	+0.503 ss	+0.010 s	−4.285	+0.164 s	−0.312 s	−1.584	+0.316 s	−1.302	−2.040	−2.463	−6.258
−0.666	−0.876	−0.307 s	−6.159	−0.338 s	−0.314 s	−0.290 s	−0.375 s	−1.572	−1.862	−1.975	−3.033
−0.940	−1.109	−1.360	−4.587	−0.947	−1.139	−1.540	−1.252	−2.810	+0.113 s	+0.018	+0.178 s
+0.123 s	+0.203 s	−0.024 s	−0.254 s	+0.044 s	−0.221 s	−0.396 s	+0.067 s	+0.031 s	+0.191 s	+0.015 s	+0.024 s
−0.297 s	−0.495 s	−0.210 s	−6.331	−0.077 s	−0.129 s	−0.255 s	−0.211 s	−1.630	−1.949	−2.089	−3.194
−0.073 s	0.219 s	+0.086 s	−7.910	−0.045 s	−0.464 s	−1.415	+0.176 s	−1.618	−2.193	−2.368	−5.589
+1.184 ss	+1.020 ss	−0.109 s	−7.572	+0.848 ss	+0.408 s	−0.466 s	+0.227 s	−2.307	−2.768	−3.048	−4.383
+0.041 s	−0.135 s	−0.418 s	−7.073	+0.047 s	−0.160 s	−0.586	−0.282 s	−2.147	−2.523	−2.718	−3.916
−0.133 s	−0.320 s	−0.318 s	−6.707	−0.020 s	−0.149 s	−0.425 s	−0.251 s	−1.893	−2.241	−2.408	−3.559
−1.168	−1.811	−0.807	n.d.	−0.926	−1.961	−4.068	−0.793	−6.031	−0.566 s	−0.949	−5.345
−1.152	−1.131	−0.262 s	−1.333	−1.020	−1.155	−1.530	−0.373	−0.079 s	−0.161 s	−0.202 s	−2.179

Table 7. Saturation indices (Sat. Ind), affinities in kcal (Aff.) and saturation state (State) of three brines from open pools. Saturation indices calculated with the Abercrombie and Spencer program and affinities and saturation state with EQ3NR

Sample No.	511/1			750/13			850/1		
	Sat. Ind.	EQ3NR		Sat. Ind.	EQ3NR		Sat. Ind.	EQ3NR	
Minerals		Aff.	State		Aff.	State		Aff.	State
Anhydrite	3.14E − 08	−0.732		8.37E − 08	−0.240	s	7.60E − 08	−0.549	
Bischofite	1.00E + 00	−0.132	s	4.84E − 1	−0.324	s	3.69E − 01	−0.709	
Carnallite	8.69E − 01	−0.215	s	1.78E + 00	0.459	s	2.11E + 00	0.316	s
Epsomite	—	—		—	0.373	s	—	−0.375	s
Gypsum	8.61E − 09	−1.657		3.14E − 08	−1.072		3.16E − 08	−1.252	
Halite	7.45E − 01	−0.228	s	1.06E + 00	0.148	s	1.20E − 00	0.067	s
Hexahydrite	—	—		—	0.144	s	—	−0.211	s
Kainite	—	—		—	0.247	s	—	0.176	s
Kieserite	1.76E + 00	0.160	s	2.48E + 00	0.618	ss	1.81E + 00	0.227	s
Leonhardite	—	—		—	0.085	s	—	−0.282	s
Bentahydrite	—	—		—	0.119	s	—	−0.251	s
Sylvite	8.29E − 02	−1.490		3.51E − 01	−0.565		5.47E − 01	−0.373	s
Polyhalite	—	—		—	−0.498	s	—	—	

— = not determined.
s = approximately saturated.

nallitite and some entrapped brine was transported back to the mine and used as a backfill. This was necessary in order to mechanically support the empty chambers in the carnallitite formation. There is no need for backfilling in rock salt chambers. Chambers with backfilling material are indicated in Fig. 2. Half of all the open pools at the 750 m level in the mine are located along the old backfilled chambers in the carnallitite formation. This is a strong indication that the brines entrapped in the backfill are still seeping out and accumulating in the nearby gallery.

However, there are also other possible origins for some of the brines in the open pools. Some may have originated in the carnallitite formation itself. An additional part of these brines certainly stems from the interaction of atmospheric moisture with the exposed carnallite in the mine. During the summer months with high relative humidity the hygroscopic carnallite absorbs moisture from the ventilation and dissolves. When the relative humidity decreases, these brines evaporate and leave thick white efflorescences on the walls and the bottom of the galleries in the carnallitite formation. Major components of the efflorescences are carnallite and bischofite. Bischofite will be dissolved even more readily than carnallite when the relative humidity increases again, and will yield relatively large amounts of $MgCl_2$ brines [1 mole bischofite ($MgCl_2 \cdot 6H_2O$) contains 6 moles of crystallization water, see also discussion in the section "Effects of evaporation and changing relative humidity"].

Brine 750/22 is sometimes used for mining operations and may, hence, be mixed with fresh water. We have included this brine in the frame of this research in order to show the effect of fresh water on the chemical and isotopic parameter. Brine pool 850/1 served several years ago as an accumulation pool for all the brines in the mine. Here all the brines of the above mentioned possible origins are mixed.

The calculation of the thermodynamic state of the brines show for most analyses an undersaturation with respect to NaCl and KCl and an oversaturation with respect to $MgCl_2$ and $MgSO_4$. To make sure that no analytical errors were made, all the brines from the open pools were sampled again in 1987 and reanalyzed. This was necessary as the 1983 samples were totally consumed. As expected, the analyses of the new samples were not identical with the old ones, but in all cases the same trends were confirmed. The undersaturation with respect to NaCl and KCl and the oversaturation with respect to $MgCl_2$ and $MgSO_4$ are real. In other words, most of the brines in the Asse mine are non-equilibrium solutions. The reason for the undersaturation with respect to halite (in some cases up to 3 times) and large oversaturation with respect to carnallite and kieserite (many analyses are 5–8 times the saturation value for kieserite) can be explained by the evaporation and precipitation processes which take place in the open pools. The effects of cooling, evaporation and changes in relative humidity will be discussed later.

Chemical evolution of brines in contact with halite, carnallite and kieserite

Halite, carnallite and kieserite are the main minerals in the carnallitite formation K2C. These minerals are also present in the backfill material in the Asse mine. Water or a NaCl-saturated solution in contact with these minerals will eventually be saturated with respect to all three minerals. Final stable equilibrium will be reached at point R in the five-component system $NaCl–KCl–MgCl_2–Na_2SO_4$ (Braitsch, 1971). The chemical composition of the R solution is shown in Table 8.

Table 8. R- and Q-solution at 25°C [after D'ANS (1933) and AUTENRIETH and BRAUNE (1959)]

	R-solution	Q-solution	
Solid phases	halite	halite	(NaCl)
	carnallite	carnallite	($MgCl_2 \cdot KCl \cdot 6H_2O$)
	kainite	kainite	($KCl \cdot MgSO_4 \cdot 2.75H_2O$)
	kieserite	sylvite	(KCl)
Density g/cm^3	1.311	1.292	
Composition g/kg solution			
Mg^{2+}	81.97	67.35	
Na^+	3.32	7.29	
SO_4^{2-}	27.72	18.50	
K^+	7.05	17.12	
Cl^-	230.17	203.61	
H_2O	649.77	680.13	

By dissolving carnallite, the NaCl-saturated solution rapidly attains KCl saturation. The further dissolution of carnallite and kieserite leads to increasing $MgCl_2$ and $MgSO_4$ contents in the solution and to precipitation of sylvite and halite. $MgSO_4$ and KCl in the solution react and form kainite. When the solution has reached saturation with respect to sylvite, carnallite and kainite, it has the composition of a Q solution (Table 8). This solution, however, is not yet in equilibrium with kieserite. Therefore, kieserite dissolution will continue. Kieserite contains crystallization water which is released during the dissolution. This water can dissolve more carnallite which again sets free more crystallization water from the carnallite. When the solution has reached saturation with respect to kieserite, the chemical composition is that of an R solution. By the time the solution has reached the composition R, all the previously precipitated sylvite from the incongruent carnallite disintegration has reacted with $MgSO_4$ to form kainite. Thus, kieserite is a solid phase of the R solution, but not sylvite. When a potash bed contains both sylvite and kieserite, the chemical composition of the solution will drop at point Q and stay there as long as kieserite and sylvite are available. KCl and $MgSO_4$ in the solution will continuously react and precipitate kainite. Eventually, one of the two components will be consumed or will not be exposed to the solution any more. Where sylvite is present in excess, the solution will be a Q solution. Where kieserite is predominant, an R solution will be formed. In the Asse mine the final equilibrium solution is an R solution. A large-scale dissolution experiment in the Asse mine at 35°C showed that a NaCl-saturated solution in contact with the carnallitite formation K2C reached KCl saturation within 24 h. Afterwards, only the $MgCl_2$ and $MgSO_4$ values of the solution continued to rise. On the 7th day saturation with respect to kainite was reached. The newly formed kainite was detected by X-ray diffraction. After 23 d the highest Mg^{2+} and sulfate values were recorded (Fig. 4). Due to the formation of kainite, the $MgSO_4$ content in the solution began to drop and the solution started to get closer to point Q. After approximately 300 d the composition of the solution began to approach point Q. The only possible further evolution of the solution is from point Q along the stable kainite path towards point R. The cause for this indirect evolution of the solution is (Fig. 4) the formation of a metastable solution with respect to carnallite in the field of kainite supersaturation. A quantitative description of the reaction of a NaCl-saturated solution in contact with carnallite and kieserite up to point Q and R is given by SANDER and HERBERT (1987). The reaction path of the solution up to point Q and farther to point R is reproducible with the computer program EQ3NR/EQ6 (CLOKE, HERBERT and KHABIRI, 1987).

The above described processes take place in the carnallitite formation K2C as well as in the backfill material in the Asse mine. The resulting solution has a chemical composition between the points Q and R, or exactly the composition of an R solution when final equilibrium is reached. A brine sampled in 1984 from a newly drilled borehole in a backfilled chamber at the 750 m level in the Asse mine had a chemical composition very close to point R. Through major ion chemical composition alone it is not possible to tell if such a solution was formed in the carnallitite formation K2C or in the backfill material. If this solution migrates from the source rock and accumulates in a nearby open pool in the halite rock formation Na2β, it is subjected to the effects of cooling, evaporation and changing relative humidities.

Cooling effect

NaCl has a very low temperature coefficient of solubility which is reduced by the presence of KCl and may even be negative. However, in the presence of high concentrations of $MgCl_2$ it is always positive. Sylvite has a very large temperature coefficient of solubility (even in the presence of dissolved NaCl) which is reduced by the addition of $MgCl_2$. Carnallite has a positive temperature coefficient of solubility. Kieserite, however, has a negative temperature coefficient of solubility between 25–35°C and hence dissolves upon cooling within this temperature range. In many brine samples stored at a temperature of about 20°C we found approximately 1 g of precipitate (essentially carnallite) per ~50 ml of brine. It is therefore expected that precipitation of essentially carnallite and some sylvite plus halite (but not kieserite) takes place during brine outflow from the surrounding rocks (with average temperatures of 35°C) into the mine (with temperatures around 30°C depending on the location in the mine). The formation of some secondary carnallite may be due to such a mechanism. Cooling during outflow alters the composition of the brine and increases the Mg/K and SO_4/K ratio.

Effects of evaporation and changing relative humidity

Chemical alteration of the brines due to evaporation during flow and storage in the pools is a common effect in the mine. Evaporation of a solution with a composition around point R results in precipitation of carnallite and kieserite, thus increasing the Mg/K and SO_4/K ratios in the residual solution. A complete evaporation results in the precipitation of large amounts of bischofite. Bischofite and carnallite often form thick crusts at the bottom of the pools. Sometimes, during dry seasons, the brines are completely evaporated. Rising relative humidities lead to a partial redissolution of the precipitated minerals. Preferentially, bischofite, carnallite and kieserite, the most hygroscopic minerals, are dissolved.

The combined effects of cooling, evaporation and redissolution due to changing air humidities lead to the observed chemical compositions. There is often no time for chemical equilibrium to be reached, because of the continuously changing relative humidity, (the relative humidity depends on the ventilation air, which is brought into the mine from above ground), but also because the solutions do not have sufficient contact with NaCl and KCl. The direct contact with the halite is obstructed by the thick crust of precipitates and most of the KCl is bound in kainite.

This discussion shows that the carnallitite-type brines may have originated either from the K2C formation or the backfill material and that they have undergone complex alteration processes. All of these brines except for 511/1 are colored, indicating the occurrence of Fe oxy-hydroxides in the various amounts. Brine 511/1 is a high-$MgCl_2$ colorless brine at saturation with respect to bischofite, slightly oversaturated with respect to kieserite and slightly undersaturated with respect to halite and carnallite. It has a very different isotopic composition from all other brines.

LITHIUM AS A POSSIBLE TRACER FOR THE ORIGIN OF BRINES

A further insight into the origin of these brines is obtained by studying some aspects of Li in the system. Dissolved Li is considered as conservative during the evaporation of sea water. Its co-precipitation with halite is considered to be negligible, hence it is expected to be found in relatively high concentration during the major post-halite precipitation stages of evaporating sea water. HERRMANN (1959) found great variability in the Li concentration in different brines with identical chemistry that were sampled from the Zechstein Formation. Thus, the interpretation of Li data in such brines is somewhat problematic. HERRMANN (1959) reviewed the literature and showed that in the Zechstein sequence only the Salztone (the argillaceous layer overlying the potash deposit, K2C) in the normal sequence contains significant amounts of dissolved Li. BRAITSCH (1971, p. 265) claims that definite examples of residual solutions from the evaporation of sea water in this sequence are unknown, however, they should be characterized by high Li content. He further claims that the Salztone may contain altered residues of such solutions.

Concentrations of Li in the brines vary from <1.0 mg/kg to 180 mg/kg (presented in Table 2). The one obvious conclusion that can be drawn from the data is that the brines can be subdivided according to Li concentration into three distinctive groups: (1) up to 4.4 mg/kg; (2) between 18.3 to 30 mg/kg and (3) >100 mg/kg. All rock salt type brines plus the brines 511/1 and 750/18 contain >100 mg/kg Li. All other carnallitite-type brines belong to groups 1 or 2. The carnallitite-type brine 775/4 that was sampled from a seepage contains 28.6 mg/kg Li and falls into group 2. The fact that this brine can be assumed to have undergone minimum alteration processes suggests that group 2 is not a mixture of groups 1 and 3 within the mine itself but an "authentic" group.

At the 750 m level, Li in the brines appears to be related to the location of the pool within the mine. Brines 750/1, 2, 3, 5, 8 and 20 belong to group 1 and are located at the galleries leading to the chambers filled with backfill material, whereas brines 750/9, 13, 14, 15, 16, 25 and 26 belong to group 2 and are located elsewhere. This suggests that at different parts of the mine, at the 750 m level, carnallitite-type brines may originate from different sources. The low-Li brines (<4.3 mg/kg) are probably derived from the backfill material, which slowly releases the moisture brought in from outside during the industrial process. The carnallitite-type brines of group 2, with Li between 18.3 to 30 mg/kg, could be derived directly from the carnallitite unit K2C.

To what extent is Li really a conservative element in a brine–rock system such as is found in the Asse mine and can it serve as a tracer for the origin of such brines? In an attempt to solve these questions, we have performed experiments in which we determined the partition coefficient of Li between high Mg–K–Cl brines and carnallite samples precipitated from these brines. The brines chosen were: (a) an artificial carnallite sample and its contact solution; (b) a brine sampled from the mine during 1985 and carnallite crystals precipitated from it; and (c) brine and carnallite taken from the evaporation ponds at the southern part of the Dead Sea with Li 27 mg/kg. The artificial carnallite samples were prepared by slow evaporation of a solution containing 80M $MgCl_2$ and 20M KCl per 1000M H_2O (and Li spiked as LiCl). Evaporation was carried out at 45–55°C over several days and was followed by stirring at 20°C ± 3 for an additional 7 d. Assuming equilibrium co-precipitation of Li with carnallite, a homogeneous distribution coefficient (defined as the ratio between Li/Mg in the solid over the respective ratio in the mother solution) of 0.149 is obtained for Li between carnallite and the contact brine. This value is an average of 0.142, 0.149 and 0.156, obtained for the partition coefficients in the three samples examined.

It is true that the value of partition coefficients derived under experimental conditions could be equal to or higher than the equilibrium partition coefficient (McIntire, 1963). However, two of the samples of brine plus carnallite were taken from the field where precipitation of carnallite was rather slow and hence equilibrium co-precipitation may have been approached. Hence we refer to the average value of partition coefficient measured by us of 0.149 as an equilibrium value.

The Li concentration of a pure secondary carnallite sample, denoted in Table 3 as RC, is 4 ppm (more or less the detection limit for Li in carnallite samples). Assuming that this carnallite sample was precipitated from a brine containing 85000 ppm dissolved Mg (an approximation for Mg in Cl brines during carnallite precipitation), and assuming that the partition coefficient is equal to 0.149, this brine should have had a Li content of >28 ppm. This implies that it could precipitate only from carnallitite-type brines with Li greater than this value, i.e. groups 2 or 3, but could not precipitate from a carnallitite-type brine of group 1 which we believe is released from the backfill material.

Again, assuming that the equilibrium coefficient is equal to 0.149, it is possible to evaluate the Li concentration in the brine from which the so-called primary carnallite had precipitated. The Li in TICP sample is 4 ppm, hence, in this old brine it was <28 ppm.

The high Li contents (>100 ppm) of the NaCl-type brines sampled from anhydrite bands in the rock salt may derive from a possible contact of these brines with Li-rich clay minerals. Variable amounts of clay minerals occur in the Decksteinsalz Na2r and in the Graue Salzton T3 in the Asse mine. These formations overlie the carnallitite formation K2C.

ISOTOPIC MEASUREMENTS IN BRINES AND CRYSTALLIZATION WATER

Brines

Isotopically, four groups of brines are observed in the Asse mine (Fig. 5 and Table 4) although two are represented only by single points; a fifth group shows the isotopic composition of two brines sampled from the cap rock. The groups are: (1) the rock salt and the carnallitite-type (775/4) emerging from a seepage with positive δD values; (2) the carnallitite-type, in open pools with intermediate δD values; (3) brine 750/22 with relatively negative values of both δ^{18}O and δD; (4) brine 511/1 with an extremely negative δD value. A fifth group that is presented in Fig. 5 are brines 761 and 762, that were sampled from the cap rock and not from the mine itself, with α^{18}O and δD values close to the meteoric water line.

Most of the brines sampled in the mine came from open pools, are as defined above from the carnallitite-type, and isotopically belong to group 2. The average δD value for this group is −23‰ (range from −17‰ to −34‰) and the average δ^{18}O value is +1.0‰ (range from −0.7‰ to +3.5‰). By comparison, the average isotopic values obtained by Knauth and Beeunas (1986) for fluid inclusions within halite crystals (presumably primary) taken from the Palo Duro salt (Permian age) are similar and are $\delta^{18}O = +2‰, \delta D = -15‰$. Nevertheless, we doubt our isotopic results for group 2 because one would expect vapor exchange processes to alter the original isotopic composition of the brines in open pools. For the same reason, we assume that only group 1 brines that were sampled from seepages are not altered. This effect was also demonstrated by Knauth, *et al.* (1980) for brine samples from the Weeks Island mine, Gulf Coast, U.S.A.

In the presence of high salt concentrations the activity of the water aH_2O (the ratio of saturation vapor pressure of the solution over that of pure water) is 1.0. The equilibrium humidity of a carnallitite-type brine is 33% at 25°C (inferred from D'Ans, 1933). The humidity of the air ventilated into the mine varies seasonally, depending on the atmospheric humidity and temperature. In winter the apparent humidity of the ambient air in the mine could be rather low due to lower average atmospheric humidity and to large temperature gradients prevailing between the atmosphere and the ambient air in the mine. Flow of brines to pools is therefore reduced due to evaporation. In summer the average humidity of the ambient air in the mine is relatively high and a net influx of water molecules from the air to the brines is likely to take place, as has been pointed out. Highly hygroscopic salts, such as bischofite formed by the evaporation of brines during winter, may redissolve in summer. Back transport of water molecules is most probably less emphasized in less saline solutions (such as 750/22) where the activity of water (aH_2O) in the brine is higher.

Gonfiantini and Fontes (1963) calculated the steady-state $\delta^{18}O$ and δD values of 1M and 2M $MgCl_2$ solutions while exposed to atmospheric moisture with $\delta^{18}O = -12‰$, $\delta D = -80‰$, and humidity 80%. We have plotted these data in Fig. 5 (solid squares) as point 1*x* representing the 1M and point 2*x* representing the 2M $MgCl_2$ solutions. Most of the brines found in the Asse mine are more saline than the 2M $MgCl_2$ solution; in addition, the calculated $\delta^{18}O$ and δD of atmospheric moisture within the mine are approximately −17‰ and −130‰, respectively. This implies that, due to vapor exchange processes, brines in the mine are at steady state and would acquire an even more depleted isotopic composition than is represented by the 2M $MgCl_2$ value (point 2*x*). During the summer, when there is a net influx of water from the ambient air to the brines, even more depleted steady state isotopic values are predicted. We assume, therefore, that the original isotopic composition of the brines, i.e. before exposure to the ambient air, has been shifted to lighter values during migration and storage within the open pools. Moreover, it could well be that the isotopic values of brines from group 2 are approximately the steady state values with the ambient air in the mine.

Brine 775/4 is a carnallitite-type brine, but is an exception because it was sampled from a seepage, hence it is assumed to have undergone minimal vapor exchange processes. Its isotopic composition is heavier, in δD, than all of the carnallitite-type brines that were sampled from open pools and is similar to that of the rock salt type brines (group 1). This brine is assumed to represent the original isotopic composition of carnallitite-type brines that emerge from the carnallitite formation (but not from the backfill material).

Brine 511/1 has the most depleted δD value (Fig. 5), and is therefore distinctively different from other brines in the mine. Brine 750/22, which is used for mining activities, has an isotopic composition which is intermediate between that of group 2 and the local ground water (761, 762 in Fig. 5).

Mineral crystallization water

The δD and $\delta^{18}O$ values from the crystallization water of carnallite rock samples plotted in Fig. 5 display a large range of values. However, most secondary carnallite samples, TICS, CLV-3, are enriched in D and ^{18}O, as compared to the so-called primary carnallite samples (TICP). The average δD and $\delta^{18}O$ values for the TICP samples are −42.6‰ and +4.62‰, respectively, whereas those for secondary carnallite samples are −22.0‰ and +7.55‰, respectively. Thus, isotopically, it is possible to distinguish between secondary and primary carnallite samples.

The theoretical water content expected for pure carnallite ($KMgCl_3 \cdot 6H_2O$) is 38.9%. Thus the water content expected for a bulk secondary carnallite sample is about 33% because these samples contain 10–15% of foreign anhydrous minerals (Table 4). We have extracted about 42% (±2%) water from these samples, implying that the 9% difference in water content must be attributed to non-chemically bound water, such as inclusion water or grain boundary water. From the primary carnallite samples, however, we extracted between 29 and 35% water; this is about the amount expected from the bulk mineral samples. It is reasonable, therefore, that isotopic determinations for primary carnallite samples represent crystallization water, whereas those of secondary carnallite represent a mixture of physically bound water and crystallization water.

A brine originating from the dissolution by fresh ground water of primary carnallite (which constitutes most of the carnallite in the Asse) and which has not undergone isotopic alteration due to vapor exchange processes, would acquire an isotopic composition between that of the TICP samples and that of the ground water (761, 762). Except for brine 750/22, there are no such brines in the 750 m level of the mine. Thus, stable isotope data do not indicate that brines are formed due to dissolution of carnallite by fresh ground water.

Deuterium and ^{18}O values for hydration water in kieserite ($MgSO_4 \cdot 1H_2O$) are scattered (Table 5). Kieserite samples were found to contain 3–4% more water than the theoretical content (about 13%). A possible explanation is that kieserite is less soluble than carnallite and in the presence of water it may "sorb" the water to become an $MgSO_4$ mineral with a higher hydration number. The isotopic data for polyhalite are distinctly different from carnallite and kieserite. Hydration water of polyhalite samples are characterized by relatively positive values on the δD–$\delta^{18}O$ diagram (Fig. 5).

Rock fissures in stratigraphic units overlying the salt anticline are often filled with gypsum. Isotopic determination of one such gypsum sample showed $\delta D = -81.8‰$ and $\delta^{18}O = -7.9‰$. By comparison, local groundwater has −62‰ and −8.5‰, respectively. Considering the appropriate isotopic fractionation between gypsum and mother solution (Gonfiantini and Fontes, 1963) the meteoric origin of the hydration water is verified.

Measurements of δD and $\delta^{18}O$ values in the Zechstein brines and in carnallite hydration waters have been performed previously. Schmiedel (1982) sampled carnallite and various types of brines from potash mines in the DDR. For what he termed "old residual brines" he found an average of +6.2‰ (ranging between +0.3‰ and +8.6‰) for $\delta^{18}O$, and an average of +7‰ (ranging from −9 to +27) for δD. For the hydration water in carnallite samples he found an average of +8.6‰ (ranging from +5.0‰ to +14.0) for $\delta^{18}O$ and −34‰ (ranging from −47‰ to −17‰) for δD. Vogel (1974) found an average $\delta^{18}O$ of +5.5‰ for the hydration water of carnallite samples taken from the Werra series (Lower Zechstein). Zuber (1979) determined a value of −36.9‰ for δD

in one sample of carnallite taken from the Zechstein Formation in Poland. In general, the isotopic data for crystallization water in carnallite samples quoted from the literature are similar to the results presented here.

Stable isotope analyses are used to distinguish waters from different origins as well as to study reactions with local rock minerals. As a consequence, the presumed equilibrium isotopic fractionation factor during the exchange of water between crystallization water of carnallite and its contact solution were studied here. Three artificial carnallite samples used for this determination were prepared by the procedure described above in dealing with Li. The isotopic fractionation factor α is defined as: $\alpha = R$ crystal water/R mother solution, with $R = D/H$ or $^{18}O/^{16}O$, in concentration terms. The $\alpha^{18}O$ value, reported below, represents an average for three brine-contact solution samples, whereas the αD value includes six additional samples that precipitated from Asse brines during storage at about 20°C. It was found that $\alpha^{18}O = 1.005\ (\pm 0.002)$ and $\alpha D = 0.979\ (\pm 0.0025)$.

The experimentally defined isotopic factors were used to evaluate the isotopic composition of the mother solution from which the primary carnallite minerals, found in the mine, were precipitated, assuming equilibrium precipitation. The primary carnallite of the Stassfurt series is claimed (by BRAITSCH, 1971) to be indeed primary and not an alteration product. Several theories exist with regard to the maximum temperature that prevailed in the Zechstein sequence since its formation. These theories have been used to explain specific mineral assemblages in this sequence. From 72 to 100°C, under closed conditions, (i.e. the vapor released remains in contact with the solid) it is expected that between 1 and 2 molecules of water out of 6 molecules in its unit cell would be released from the carnallite. In the laboratory we extracted two (out of 6) water molecules at 90°C under atmospheric pressure from a pure carnallite sample (sample RC) and found no isotopic effects between the released water and the residual crystal water. If, indeed, partial dehydration of the primary carnallite ever took place, then the opposite process of back hydration should also be taken into account (because the average mol ratio of H_2O to $MgCl_2$ in the primary carnallite samples is close to 6). We do not attempt to solve these types of questions here, but the fact that our δD and $\delta^{18}O$ values in crystallization water of carnallite samples are close to those quoted in the literature for the hydration water of Zechstein carnallite samples elsewhere may indicate that the $\delta^{18}O$ and δD values in the mother solutions were similar. Assuming that the crystal water of the so-called primary carnallite represents equilibrium with the mother solution, the solution at isotopic equilibrium was calculated and presented in Fig. 5 as point Z5. This point could represent the isotopic composition of the mother brines at the stage of primary carnallite precipitation.

SUMMARY

Two major groups of brines in the Asse mine are distinguished. Except for some brines that will be discussed later in this summary, these two groups are distinctly different in major ion chemistry and in Li content. The first group is the rock salt type that was sampled from seepages within the Na2β rock salt formation. The second group is the carnallitite-type brines that can further be subdivided into those with Li <4 ppm and those with Li between 18 and 30 ppm.

We suggest that brine 775/4 that was sampled from a seepage, with its Li content of 28 ppm, and isotopic composition that is heavier, in δD, than the 750 m level carnallite-type brines in the open pools is, in fact, derived from the Carnallite Formation K2C. We noticed that the low Li (<4 ppm) containing brines are situated in open pools in the galleries leading to chambers with backfill material. Hence, we argue that the low Li containing brines originate from the backfill material, whereas the 18–30 ppm group are derived from the carnallite formation.

Brine 511/1 has a unique isotopic and chemical composition and is colorless. It is an almost pure $MgCl_2$ solution saturated with respect to bischofite, has an extremely depleted D value (Fig. 5), and contains 187 mg/kg Li. Summer dissolution of bischofite veins by the ambient air is a probable source of this brine. Brine 750/18 seems, isotopically and chemically, to be sort of intermediate between brine 511/1 and the carnallite-type brines that are derived from the carnallitite formation. Isotopic data for brines in open pools (which constitute most of the brines accumulating in the Asse mine) seem to be altered. The isotopic compositions of these brines may very well be near the steady state value expected due to interaction with the ambient air. Hence, except for cases of very recent mixing with local groundwater such as the case of brine 750/22 which is used for mining activities, isotopic data cannot serve to trace the origin of such brines. However, isotopic data may add valuable information for unaltered brines.

Isotopic data of crystallization water in the so-called primary carnallite samples examined in the Asse mine are similar to those of crystallization water of carnallite samples quoted in literature for the Zechstein formation elsewhere. This may have an implication on the genesis of this formation.

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