Pergamon

Geochimica et Cosmochimica Acta, Vol. 66, No. 8, pp. 1387–1399, 2002
Copyright © 2002 Elsevier Science Ltd
Printed in the USA. All rights reserved
0016-7037/02 $22.00 + .00

PII S0016-7037(01)00857-2

Henry's and non-Henry's law behavior of Br in simple marine systems

MICHAEL G. SIEMANN[1,*] and MICHAEL SCHRAMM[1,†]

[1]Technische Universität Clausthal, Institut für Mineralogie und Mineralische Rohstoffe, A.-Roemer-Strasse 2A, 38678 Clausthal-Zellerfeld, Germany

(*Received May* 22, 2001; *accepted in revised form October* 17, 2001)

Abstract—Experimental studies for the partitioning of Br as a trace element between aqueous and solid solutions were carried out in simple marine systems. The evaporation experiments were performed at 25°C and 1 atm in the systems of halite (NaCl), sylvite (KCl), kainite ($KMgClSO_4 \cdot 2.75H_2O$), carnallite ($KMgCl_3 \cdot 6H_2O$), and bischofite ($MgCl_2 \cdot 6H_2O$). The partition coefficients for the systems investigated are constant only at a restricted concentration range. For concentrations lower than 100 to 300 μg Br/g aqueous solutions, D_{Br} increases with decreasing concentrations. Various evaporation experiments indicate that this observation is not due to kinetic effects (evaporation rates). To find a link between the partition coefficient and the Henry's law behavior, the activity coefficients of the trace components in the solid solutions were recalculated from the experimentally derived data. It can be shown from these calculations that constant activity coefficients or Henry's law behavior is reached for higher mole fractions of the trace component in the solid solution in halite and sylvite and thus correspond to constant partition coefficients. For bischofite and carnallite, Henry's law behavior is restricted to the lower mole fractions, where D_{Br} is not constant. This behavior is caused by the activity of the trace component in the aqueous solution, which is powered by the stoichiometric factor of this component in the Br–end-member solid solution. For halite, sylvite, and kainite, this factor equals 1 and is 2 for bischofite and 3 for carnallite. However, it is thus impossible to correlate Henry's law behavior with constant partition coefficients for solid solution systems where the stoichiometric factor of the trace component is greater than 1. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

The behavior of Br as trace element in evaporating seawater and diagenetic reactions of evaporites is of prime importance for geochemical studies in marine chemical sediments. The number of marine minerals incorporating Br instead of Cl in their lattice is limited. During the course of evaporation of seawater, halite (NaCl) is the first and most abundant Cl mineral precipitated. Other relevant minerals are sylvite (KCl), kainite ($KMgClSO_4 \cdot 2.75H_2O$), carnallite ($KMgCl_3 \cdot 6H_2O$), and bischofite ($MgCl_2 \cdot 6H_2O$) as the last-stage precipitate. All these minerals can be of primary as well as of secondary origin in evaporite bodies. The conservative vertical distribution in the oceans, the high concentration of 0.84 mmol/kg H_2O (Bruland, 1983), and one of the highest residence times of 1.0×10^8 (Chester, 2000) to 7.9×10^8 yr (Taylor and McLennan, 1985) in the oceans makes Br the most important trace element in chemically precipitated marine Cl sediments.

The behavior of Br during the evaporation and its partitioning between aqueous solutions and halite has often been studied under laboratory conditions as well as in natural environments (see Siemann and Schramm (2000) for a compilation and evaluation of existing data). In contrast to the large number of articles dealing with halite, investigations on other marine Cl minerals are rare. With rare exceptions (Stoessell and Carpenter, 1986), the general opinion during the last decades was that the partition coefficient of Br (D_{Br} equals the percentage of Br in solid solution divided by the percentage of Br in aqueous solution) in these minerals precipitated from simple aqueous solutions is constant. This was recently questioned on the basis of thermodynamic considerations by Siemann and Schramm (2000), who showed that the incorporation of Br into halite can be thermodynamically described as an extreme form of solid solutions. Furthermore, it was shown that these parts of the solid solution system cannot be calculated satisfyingly by means of ideal, regular, or the usual subregular solid solution models.

The main problem of handling the incorporation of trace elements in crystals as an extreme form of solid solutions is that they are thermodynamically described by activities and activity coefficients that cannot be measured directly. The general equation for a solid solution system is

$$a = X \cdot \lambda \tag{1}$$

where a denotes the activity, X the mole fraction, and λ the activity coefficient. It is generally assumed that the extreme ends of a solid solution system ($X_{trace} \rightarrow 0$ or $X_{major} \rightarrow 1$) can be described by Raoult's or Henry's laws. For ideal systems, the activity coefficient is 1, and thus the activity equals the mole fraction. This behavior is known as Raoult's law and is generally applied for $X_{major} \rightarrow 1$. For the thermodynamics of the trace component in the solid solution systems ($X_{trace} \rightarrow 0$), λ_{trace} is assumed to be constant but not 1, and it is generally known as Henry's law behavior.

In previously published studies, different and nonconstant partition coefficients of Br in halite were found (Siemann and Schramm, 2000) and commonly explained by kinetic effects related to different crystallization rates. The aim of this study is to examine the observed nonconstant behavior of the partition coefficient of Br in halite and in other marine Cl minerals and

---

* Author to whom correspondence should be addressed (michael.siemann@tu-clausthal.de).

† Present address: Bundesanstalt für Geowissenschaften und Rohstoffe, Referat Salzgeologie, Stilleweg 2, 30631 Hannover, Germany.

Table 1. Analytical results of the crystallization experiments in the system NaCl-NaBr-H_2O.[a]

	Aqueous solution				Solid solution					
Run	Br	σ	Cl	Na	Br	σ	Cl	Na	$^{\text{halite}}D_{Br}$	σ
1	0.0060	0.0002	16.0	10.2	0.0018	0.0002	60.7	39.3	0.295	0.037
2	0.0061	0.0001	15.9	10.2	0.0017	0.0001	60.7	39.3	0.283	0.014
3	0.0065	0.0001	15.9	10.4	0.0020	0.0001	60.7	39.3	0.314	0.013
4	0.0119	0.0002	16.3	10.3	0.0022	0.0001	60.7	39.3	0.189	0.011
5	0.0120	0.0001	15.9	10.0	0.0025	0.0001	60.7	39.3	0.209	0.009
6	0.0125	0.0002	15.8	10.2	0.0025	0.0001	60.7	39.3	0.202	0.011
7	0.0205	0.0002	16.0	10.1	0.0035	0.0001	60.7	39.3	0.170	0.005
8	0.0207	0.0001	15.8	10.3	0.0033	0.0000	60.7	39.3	0.161	0.003
9	0.0209	0.0001	15.7	10.0	0.0032	0.0000	60.7	39.3	0.154	0.002
10	0.0295	0.0004	15.9	10.2	0.0044	0.0000	60.7	39.3	0.150	0.002
11	0.0295	0.0002	15.8	10.1	0.0041	0.0001	60.7	39.3	0.138	0.002
12	0.0298	0.0002	15.8	10.3	0.0044	0.0000	60.7	39.3	0.147	0.001
13	0.0583	0.0002	15.7	10.2	0.0076	0.0002	60.7	39.3	0.131	0.003
14	0.0593	0.0002	15.8	10.3	0.0084	0.0001	60.7	39.3	0.142	0.002
15	0.2863	0.0024	15.7	10.4	0.0381	0.0003	60.6	39.3	0.133	0.002
16	0.5736	0.0043	15.8	10.1	0.0804	0.0008	60.6	39.3	0.140	0.002
17	2.9149	0.0218	14.6	10.3	0.4092	0.0088	60.3	39.2	0.140	0.003
18	2.9382	0.0223	14.4	10.1	0.3470	0.0081	60.4	39.3	0.118	0.003
19	5.9011	0.0127	13.1	10.0	0.7306	0.0189	60.1	39.2	0.124	0.003
ER										
0.42	0.0206	0.0004	15.7	10.2	0.0036	0.0001	60.7	39.3	0.173	0.002
0.87	0.0211	0.0003	15.7	10.2	0.0033	0.0001	60.7	39.3	0.157	0.002
1.04	0.0204	0.0002	15.8	10.1	0.0033	0.0003	60.7	39.3	0.164	0.004
1.06	0.0205	0.0002	15.7	10.2	0.0035	0.0001	60.7	39.3	0.172	0.003
1.40	0.0214	0.0006	15.7	10.2	0.0035	0.0001	60.7	39.3	0.165	0.002
1.44	0.0219	0.0009	15.7	10.2	0.0036	0.0001	60.7	39.3	0.165	0.004
2.05	0.0206	0.0001	15.8	10.1	0.0034	0.0001	60.7	39.3	0.166	0.001
2.15	0.0212	0.0014	15.7	10.1	0.0035	0.0001	60.7	39.3	0.167	0.004
2.33	0.0206	0.0002	15.7	10.2	0.0034	0.0001	60.7	39.3	0.163	0.002
2.94	0.0214	0.0005	15.8	10.3	0.0035	0.0001	60.7	39.3	0.162	0.002
3.34	0.0219	0.0002	15.8	10.1	0.0038	0.0002	60.7	39.3	0.172	0.003
3.80	0.0213	0.0003	15.7	10.2	0.0036	0.0001	60.7	39.3	0.170	0.002
4.20	0.0205	0.0001	15.7	10.2	0.0033	0.0003	60.7	39.3	0.161	0.005
5.29	0.0219	0.0006	15.7	10.2	0.0037	0.0003	60.7	39.3	0.171	0.006
5.31	0.0228	0.0003	15.9	10.0	0.0038	0.0001	60.7	39.3	0.166	0.002
8.22	0.0223	0.0004	15.7	10.2	0.0039	0.0001	60.7	39.3	0.173	0.002
19.63	0.0202	0.0002	15.6	10.4	0.0033	0.0003	60.7	39.3	0.162	0.004

[a] All values are given in mass%. σ denotes the standard deviation of eight measurements. The partition coefficient $^{\text{halite}}D_{Br}$ = mass% $Br_{\text{solid solution}}$/= mass% $Br_{\text{aqueous solution}}$ and its calculated standard deviation are also listed. The lower part of the table contains the experimental data of the evaporation of one aqueous solution at different evaporation rates (ER), calculated as g H_2O-loss per day. The concentrations of Cl and Na in the crystals are calculated from the Br contents and the stoichiometry. See text for analytical details.

the dependence of the partition coefficient on kinetic effects. Furthermore, we sought to find a link between Henry's law and constant partitioning of Br in the systems investigated.

2. MATERIALS AND METHODS

2.1. Evaporation Experiments

All experiments were carried out in thermoconstant incubators at 25 ± 1°C. To minimize the incorporation of fluid inclusions, previously described crystallization methods (Yamaguchi et al., 1998; Siemann and Schramm, 2000) were applied. Nearly saturated aqueous solutions were placed in Erlenmeyer flasks that were sealed with stretchable laboratory plastic tape. To achieve slow evaporation rates of no more than 1 to 3 g H_2O loss per day, the plastic tape was punctured with a hole 5 mm in diameter. To produce ~1 g of crystals, the flasks were placed for several weeks in the incubator. Because of our experience that inclusion-free crystals cannot be produced if the solution is stirred, the flasks were left untouched until the end of the experiment.

To check for vertical concentration gradients in the flasks, several samples were taken at different depths from the brines via the needle of a syringe to avoid stirring the solution. The Br concentrations were constant in the range of analytical reproducibility. In addition, the unavoidable vibrations of incubators during cooling or heating also avoided any concentration gradients in the brines. The crystals were sampled with a plastic sieve. After grinding, they were immediately washed with pure ethanol (halite and sylvite) or acetone (kainite, bischofite, and carnallite) to flush away any brine that might have come from the destroyed fluid inclusions. After this procedure, the powders were air dried. All aqueous solutions were synthesized by means of Merck p.a.-grade chemicals and demineralized water (0.055 μS cm^{-1}). After the dissolution of the chemicals, the solutions were cleaned with 0.45-μm filters to remove dust and impurities that originated from the chemicals.

For the halite system, 19 evaporation experiments were carried out using NaCl and NaBr; the latter ranged from 1 to 1000 mmol/kg H_2O. In addition to the 19 evaporation experiments with different Br contents, one nearly NaCl-saturated 30-litres solution containing ~200 μg Br/g was synthesized. Seventeen aliquots of this solution were evaporated at different rates ranging from 0.42 to 19.63 g H_2O loss per day by varying the open surface of the evaporating solution. The results for this system are listed in Table 1. For the sylvite system, a total of 28 nearly saturated solutions were evaporated with Br concentrations ranging from 0.2 to 150 mmol KBr/kg H_2O. The solutions were made

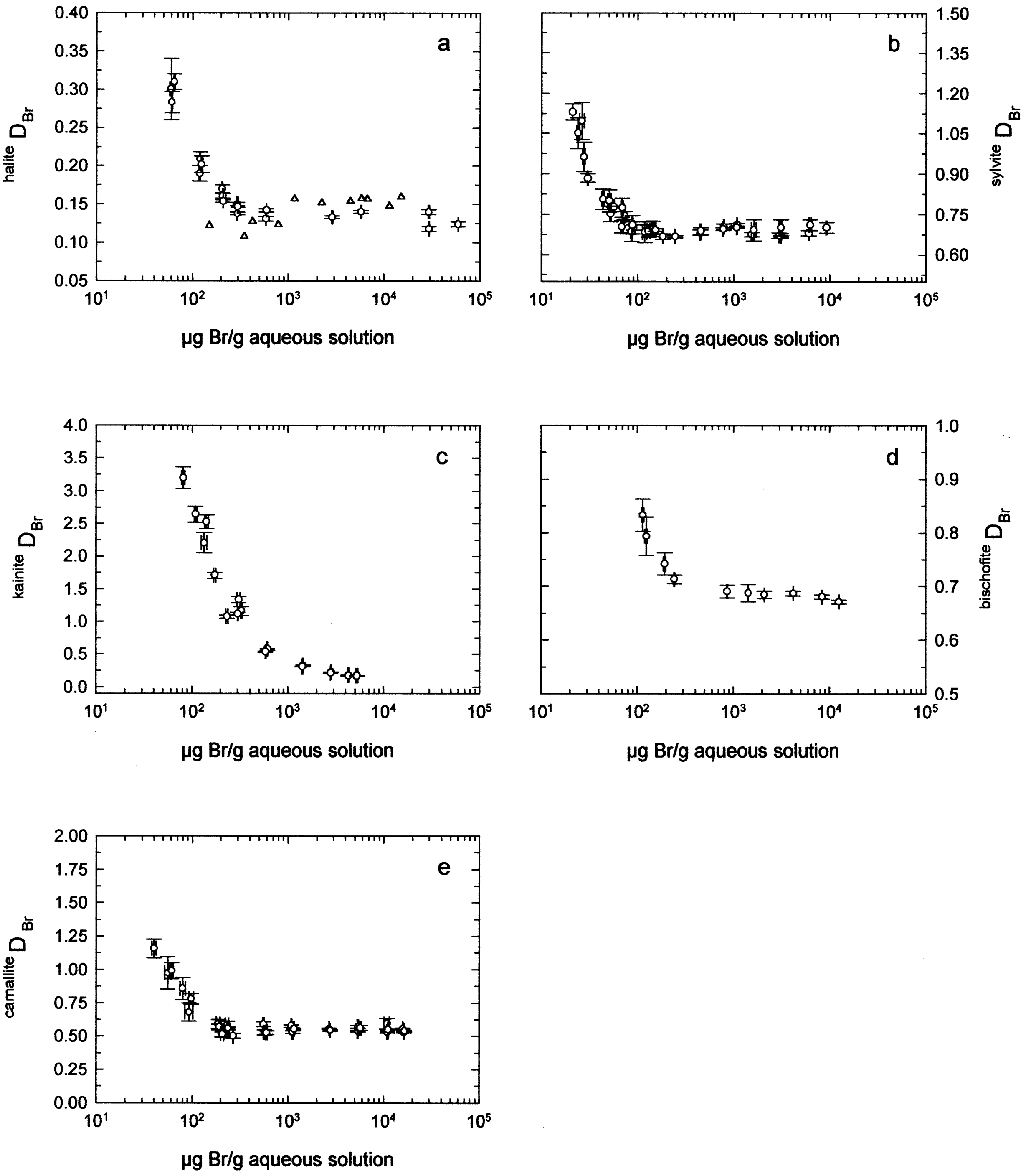

Fig. 1. The partition coefficient of Br in halite (a), sylvite (b), kainite (c), bischofite (d), and carnallite (e) as a function of the concentration of Br in the aqueous solution, obtained from crystallization experiments in simple binary solutions at 25°C. The error bars indicate the standard deviation of eight measurements. The data are listed in Tables 1 to 5. The triangles in (a) indicate the results presented in former studies (Siemann and Schramm, 2000).

of KCl and KBr. The nearly kainite-saturated solutions were produced by use of KCl, KBr, $MgCl_2 \cdot 6H_2O$, and $MgSO_4 \cdot 7H_2O$. The Br in the saturated solutions ranged from 1 to 90 mmol/kg H_2O. For the synthesis of the bischofite solutions, $MgCl_2 \cdot 6H_2O$ and $MgBr_2 \cdot 6H_2O$ were used, varying the Br concentration in the solution from 2 to 200 mmol/kg H_2O. In the carnallite experiments, KCl, $MgCl_2 \cdot 6H_2O$, and $MgBr_2 \cdot 6H_2O$ were used with a range of the Br contents in the aqueous solutions of 1 to 400 mmol/kg H_2O. The concentrations of the solutions at saturation stage are listed in Tables 1 to 5.

2.2. Analytical Methods

The chemical composition of the solutions and the crystals were analyzed by ion chromatography. Major anions and cations in the

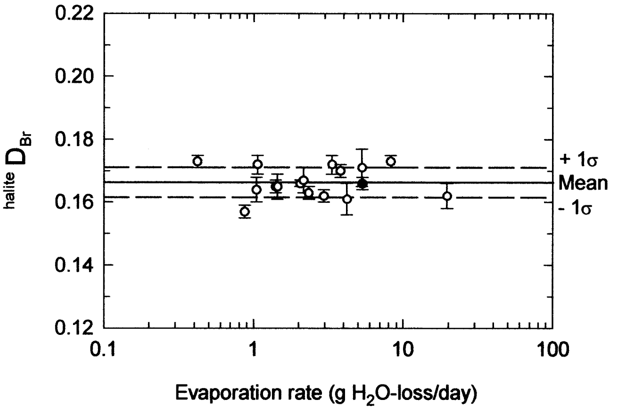

Fig. 2. The partition coefficient of Br in halite at different crystallization speeds. The data were obtained by evaporating 17 aliquots of a nearly NaCl-saturated solution containing 0.01 mol NaBr/kg H_2O. The data are listed in the lower part of Table 1. The aliquot plotted as black circle was left in the incubator sealed for more than 18 months and showed no alteration of the Br concentration in the crystals and brine.

solutions were measured simultaneously after dilution by a factor of 5000 to 10,000 by use of a Metrohm ion chromatograph with chemical suppression for the anions. All samples were acidified to a pH of 2.6. Accuracy and reproducibility were investigated by analyzing the North Atlantic Standard Seawater (NASS4) international reference sample (n = 50). The accuracy was better than 1% (relative) for all elements except for K (<4% relative). The relative standard deviation for the analysis of the reference sample was <1% except K (<3%). The electroneutrality parameter was better than 1% for all measurements. Br in the solutions and crystals was analyzed in neutral solution after they were diluted 1:1000. Accuracy as well as reproducibility was better than 1% measured against an in-house halite reference sample. The calibration for the Br quantification was strongly adapted to the Cl concentration of the solution or crystal. Because chemical suppression of the anion chromatographic system usually improves the detection limit by a factor of four (Schäfer et al., 1996), the quantitation limit for our system was at 20 μg Br/g halite. The density of the brines was measured with a DMA 38 density meter at 25°C right after the separation. Before dissolving the crystals, they were analyzed by laser Raman spectroscopy (Siemann and Ellendorff, 2001) and X-ray powder diffraction (Siemann, 1993).

3. RESULTS

3.1. NaCl-NaBr

The results of the evaporating experiments in the system NaCl-NaBr-H_2O are listed in Table 1 and plotted in Figures 1a and 2. Br in the aqueous solution ranged from 60 μg Br/g solution to 5.9 wt% Br. The corresponding partition coefficients varied systematically from 0.295 to 0.124. For concentrations greater than 300 μg Br/g aqueous solution, the partition coefficient was constant at a mean value of 0.133 ± 0.009. For lower Br values, the partition coefficient increased with decreasing concentration in the aqueous solution. At the NaCl saturation stage, the density of the solution was 1.199 ± 0.001

Table 2. Analytical results of the crystallization experiments in the system KCl-KBr-H_2O.[a]

	Aqueous solution				Solid solution					
Run	Br	σ	Cl	K	Br	σ	Cl	K	$^{sylvite}D_{Br}$	σ
1	0.0024	0.0001	12.5	13.8	0.0025	0.0001	47.6	52.4	1.05	0.06
2	0.0026	0.0001	12.5	13.8	0.0029	0.0001	47.6	52.4	1.10	0.07
3	0.0027	0.0001	12.5	13.8	0.0026	0.0001	47.6	52.4	0.96	0.05
4	0.0051	0.0002	12.5	13.8	0.0040	0.0002	47.6	52.4	0.80	0.04
5	0.0052	0.0001	12.6	13.7	0.0039	0.0001	47.6	52.4	0.75	0.03
6	0.0068	0.0002	12.5	13.7	0.0048	0.0001	47.6	52.4	0.70	0.02
7	0.0069	0.0002	12.5	13.6	0.0053	0.0002	47.6	52.4	0.77	0.04
8	0.0087	0.0002	12.5	13.8	0.0059	0.0003	47.6	52.4	0.69	0.04
9	0.0088	0.0001	12.5	13.9	0.0062	0.0003	47.6	52.4	0.71	0.03
10	0.0118	0.0006	12.3	14.0	0.0081	0.0001	47.6	52.4	0.68	0.04
11	0.0130	0.0004	12.5	13.8	0.0089	0.0001	47.6	52.4	0.69	0.02
12	0.0146	0.0006	12.5	13.8	0.0101	0.0001	47.6	52.4	0.69	0.03
13	0.0152	0.0001	12.5	13.8	0.0105	0.0001	47.6	52.4	0.69	0.01
14	0.0183	0.0002	12.5	13.8	0.0122	0.0002	47.6	52.4	0.67	0.01
15	0.0244	0.0001	12.5	13.9	0.0163	0.0001	47.6	52.4	0.67	0.01
16	0.0448	0.0006	12.5	13.9	0.0305	0.0002	47.6	52.4	0.68	0.01
17	0.0452	0.0004	12.5	13.8	0.0311	0.0005	47.6	52.4	0.69	0.01
18	0.0770	0.0003	12.4	13.8	0.0535	0.0004	47.6	52.4	0.70	0.01
19	0.0786	0.0007	12.4	13.6	0.0552	0.0007	47.6	52.4	0.70	0.01
20	0.1069	0.0003	12.4	13.8	0.0749	0.0003	47.6	52.4	0.70	0.01
21	0.1076	0.0001	12.4	13.9	0.0765	0.0005	47.6	52.4	0.71	0.01
22	0.1616	0.0085	12.3	13.8	0.1110	0.0023	47.6	52.4	0.69	0.04
23	0.2979	0.0029	12.4	14.0	0.1999	0.0029	47.6	52.4	0.67	0.01
24	0.3073	0.0110	12.2	13.8	0.2165	0.0030	47.6	52.4	0.70	0.03
25	0.3112	0.0013	12.2	13.6	0.2084	0.0023	47.6	52.4	0.67	0.01
26	0.6022	0.0054	11.9	13.8	0.4122	0.0051	47.6	52.4	0.68	0.01
27	0.6214	0.0160	11.6	14.0	0.4382	0.0093	47.6	52.4	0.71	0.02
28	0.9209	0.0051	11.6	13.8	0.6444	0.0221	47.6	52.4	0.70	0.02

[a] All values are given in mass%. σ denotes the standard deviation of eight measurements. The partition coefficient $^{sylvite}D_{Br}$ = mass% $Br_{solid\ solution}$/= mass% $Br_{aqueous\ solution}$ and its calculated standard deviation are also listed. The concentrations of Cl and K in the crystals are calculated from the Br contents and the stoichiometry. See text for analytical details.

Table 3. Analytical results of the crystallization experiments in the system $KMgClSO_4 \cdot 2.75\ H_2O$-$KMgBrSO_4 \cdot 2.75\ H_2O$-$H_2O$.[a]

	Aqueous solution						Solid solution							
Run	Br	σ	Cl	SO_4	K	Mg	Br	σ	Cl	SO_4	K	Mg	$^{kainite}D_{Br}$	σ
1	0.0081	0.0003	18.7	3.67	1.37	6.90	0.0258	0.0009	14.5	39.3	15.99	9.94	3.199	0.171
2	0.0109	0.0003	18.8	3.66	1.36	6.93	0.0288	0.0010	14.5	39.3	15.99	9.94	2.641	0.121
3	0.0134	0.0009	18.7	3.67	1.37	6.91	0.0295	0.0008	14.4	39.3	15.99	9.94	2.205	0.156
4	0.0141	0.0006	18.7	3.66	1.36	6.90	0.0358	0.0005	14.4	39.3	15.99	9.94	2.530	0.105
5	0.0173	0.0004	18.8	3.68	1.36	6.91	0.0296	0.0003	14.4	39.3	15.99	9.94	1.709	0.046
6	0.0232	0.0004	18.7	3.68	1.37	6.90	0.0250	0.0003	14.4	39.3	15.99	9.94	1.077	0.025
7	0.0300	0.0001	18.7	3.67	1.37	6.91	0.0334	0.0006	14.3	39.3	15.99	9.94	1.115	0.022
8	0.0308	0.0012	18.6	3.66	1.36	6.93	0.0411	0.0002	14.3	39.3	15.99	9.94	1.336	0.051
9	0.0329	0.0004	18.6	3.67	1.36	6.91	0.0381	0.0023	14.2	39.3	15.99	9.94	1.159	0.071
10	0.0585	0.0004	18.7	3.66	1.36	6.91	0.0316	0.0004	14.2	39.3	15.99	9.94	0.540	0.007
11	0.0614	0.0004	18.7	3.67	1.37	6.90	0.0353	0.0008	14.2	39.3	15.99	9.94	0.575	0.013
12	0.1420	0.0005	18.6	3.68	1.37	6.93	0.0440	0.0002	14.1	39.3	15.99	9.94	0.310	0.002
13	0.1446	0.0009	18.6	3.66	1.36	6.91	0.0478	0.0008	14.1	39.3	15.99	9.94	0.330	0.006
14	0.2794	0.0014	18.6	3.67	1.36	6.91	0.0593	0.0004	14.0	39.3	15.99	9.94	0.212	0.002
15	0.2825	0.0002	18.6	3.66	1.36	6.93	0.0635	0.0007	14.0	39.3	15.99	9.94	0.225	0.002
16	0.4264	0.0028	18.4	3.66	1.37	6.93	0.0776	0.0006	13.9	39.3	15.99	9.94	0.182	0.002
17	0.4268	0.0026	18.5	3.68	1.36	6.91	0.0737	0.0004	13.8	39.3	15.99	9.94	0.173	0.001
18	0.5245	0.0103	18.4	3.66	1.36	6.91	0.0881	0.0007	13.7	39.3	15.99	9.94	0.168	0.004
19	0.5258	0.0137	18.5	3.67	1.37	6.91	0.0924	0.0008	13.6	39.3	15.99	9.94	0.176	0.005

[a] All values are given in mass%. σ denotes the standard deviation of eight measurements. The partition coefficient $^{kainite}D_{Br}$ = mass% $Br_{solid\ solution}$/= mass% $Br_{aqueous\ solution}$ and its calculated standard deviation are also listed. The concentrations of Cl, SO_4, K, and Mg in the crystals are calculated from the Br contents and the stoichiometry. See text for analytical details.

g cm^{-3}. When compared with previous experiments, the new data presented here were achieved at much lower concentrations.

In the lower part of Table 1, the results of the evaporation of 17 aliquots of a single brine at different rates are listed. The concentration of Br at saturation stage was 212 ± 8 μg Br/g solution. The evaporation speed, calculated from the loss of water, varied by a factor of ~50 and ranged from 0.42 to 19.63. Despite of this large range of experimental evaporation rates, the obtained partition coefficient of Br in halite was constant at 0.166 ± 0.005.

3.2. KCl-KBr

The results of the experiments in the system KCl-KBr-H_2O are listed in Table 2 and plotted in Figure 1b. The obtained pattern of the partition coefficient of Br in sylvite was very close to that of halite. A constant partition coefficient of 0.690 ± 0.014 was only obtained for concentrations greater than ~70 μg Br/g aqueous solution. For lower concentrations of Br, increasing partition coefficients were observed. The density of the solutions at saturation stage was 1.178 ± 0.002 g cm^{-3}.

3.3. $KMgClSO_4 \cdot 2.75\ H_2O$-$KMgBrSO_4 \cdot 2.75\ H_2O$

Unlike the experiments for halite and sylvite, for the concentrations of Br in the system $KMgClSO_4 \cdot 2.75\ H_2O$-$KMgBrSO_4 \cdot 2.75\ H_2O$-$H_2O$ of 81 to 5258 μg Br/g aqueous solution, no constant partition coefficients was observed (Table 3 and Fig. 1c). The obtained data for $^{kainite}D_{Br}$ ranged from 0.176

Table 4. Analytical results of the crystallization experiments in the system $MgCl_2 \cdot 6\ H_2O$-$MgBr_2 \cdot 6\ H_2O$-H_2O.[a]

	Aqueous solution				Solid solution					
Run	Br	σ	Cl	Mg	Br	σ	Cl	Mg	$^{bischofite}D_{Br}$	σ
1	0.0114	0.0003	25.6	8.77	0.0095	0.0003	34.9	12.0	0.833	0.030
2	0.0124	0.0004	25.7	8.77	0.0098	0.0003	34.9	12.0	0.793	0.036
3	0.0192	0.0005	25.6	8.79	0.0143	0.0002	34.9	12.0	0.742	0.021
4	0.0242	0.0002	25.6	8.76	0.0173	0.0001	34.9	12.0	0.714	0.008
5	0.0861	0.0003	25.4	8.77	0.0594	0.0010	34.8	12.0	0.690	0.012
6	0.1423	0.0007	25.5	8.78	0.0978	0.0022	34.8	12.0	0.687	0.016
7	0.2086	0.0004	25.4	8.77	0.1428	0.0014	34.8	12.0	0.685	0.007
8	0.4180	0.0006	25.2	8.76	0.2872	0.0019	34.6	12.0	0.687	0.005
9	0.8327	0.0023	24.8	8.79	0.5666	0.0027	34.3	12.0	0.681	0.004
10	1.2460	0.0048	24.4	8.77	0.8365	0.0024	34.1	12.0	0.671	0.003

[a] All values are given in mass%. σ denotes the standard deviation of eight measurements. The partition coefficient $^{bischofite}D_{Br}$ = mass% $Br_{solid\ solution}$/= mass% $Br_{aqueous\ solution}$ and its calculated standard deviation are also listed. The concentrations of Cl and Mg in the crystals are calculated from the Br contents and the stoichiometry. See text for analytical details.

Table 5. Analytical results of the crystallization experiments in the system $KMgCl_3 \cdot 6\ H_2O$-$KMgBr_3 \cdot 6\ H_2O$-H_2O.[a]

	Aqueous solution					Solid solution						
Run	Br	σ	Cl	K	Mg	Br	σ	Cl	K	Mg	$^{carnallite}D_{Br}$	σ
1	0.0040	0.0002	34.0	0.85	11.2	0.0046	0.0001	38.3	14.1	8.75	1.158	0.070
2	0.0056	0.0004	34.0	0.86	11.0	0.0054	0.0005	38.3	14.1	8.75	0.974	0.122
3	0.0061	0.0002	34.0	0.85	11.1	0.0060	0.0003	38.3	14.1	8.75	0.990	0.060
4	0.0080	0.0005	34.0	0.86	11.0	0.0068	0.0005	38.3	14.1	8.75	0.856	0.085
5	0.0093	0.0009	34.0	0.85	11.0	0.0064	0.0002	38.3	14.1	8.75	0.680	0.067
6	0.0098	0.0005	34.0	0.84	11.3	0.0076	0.0000	38.3	14.1	8.75	0.780	0.040
7	0.0188	0.0009	34.0	0.86	11.1	0.0111	0.0004	38.3	14.1	8.75	0.592	0.034
8	0.0192	0.0003	34.0	0.85	11.2	0.0110	0.0003	38.3	14.1	8.75	0.570	0.020
9	0.0207	0.0007	34.0	0.85	11.1	0.0107	0.0002	38.3	14.1	8.75	0.515	0.020
10	0.0234	0.0009	34.0	0.84	11.0	0.0137	0.0003	38.3	14.1	8.75	0.584	0.027
11	0.0238	0.0005	34.0	0.84	11.1	0.0134	0.0002	38.3	14.1	8.75	0.560	0.010
12	0.0269	0.0001	34.0	0.86	11.3	0.0135	0.0005	38.3	14.1	8.75	0.503	0.017
13	0.0558	0.0008	34.0	0.86	11.1	0.0329	0.0009	38.3	14.1	8.75	0.590	0.018
14	0.0568	0.0009	34.0	0.85	11.0	0.0299	0.0013	38.3	14.1	8.75	0.530	0.020
15	0.0598	0.0012	34.0	0.84	11.1	0.0315	0.0004	38.3	14.1	8.75	0.527	0.012
16	0.1090	0.0007	33.9	0.84	11.2	0.0629	0.0010	38.2	14.1	8.75	0.577	0.010
17	0.1122	0.0016	33.9	0.85	11.0	0.0596	0.0004	38.2	14.1	8.75	0.530	0.010
18	0.1160	0.0007	33.9	0.86	11.2	0.0644	0.0008	38.2	14.1	8.75	0.555	0.008
19	0.2700	0.0010	33.8	0.85	11.3	0.1501	0.0009	38.1	14.1	8.75	0.556	0.004
20	0.2777	0.0019	33.8	0.84	11.1	0.1511	0.0011	38.1	14.1	8.75	0.544	0.005
21	0.5403	0.0019	33.5	0.87	11.2	0.2909	0.0023	38.0	14.1	8.75	0.538	0.005
22	0.5413	0.0084	33.5	0.84	11.0	0.3093	0.0004	38.0	14.1	8.75	0.571	0.009
23	0.5699	0.0176	33.5	0.85	11.2	0.3202	0.0021	38.0	14.1	8.75	0.562	0.018
24	1.0855	0.0689	32.9	0.84	11.1	0.6437	0.0043	37.7	14.1	8.75	0.593	0.038
25	1.0960	0.0091	32.9	0.85	11.1	0.5824	0.0027	37.7	14.1	8.75	0.531	0.005
26	1.1169	0.0047	32.9	0.86	11.0	0.6151	0.0006	37.7	14.1	8.75	0.551	0.002
27	1.5905	0.0030	32.4	0.88	11.2	0.8842	0.0083	37.4	14.1	8.75	0.556	0.005
28	1.6330	0.0028	32.4	0.85	11.1	0.8658	0.0077	37.4	14.1	8.75	0.530	0.005
29	1.6511	0.0124	32.4	0.84	11.3	0.8907	0.0003	37.4	14.1	8.75	0.539	0.004

[a] All values are given in mass%. σ denotes the standard deviation of eight measurements. The partition coefficient $^{carnallite}D_{Br}$ = mass% $Br_{solid\ solution}$/= mass% $Br_{aqueous\ solution}$ and its calculated standard deviation are also listed. The concentrations of Cl, K, and Mg in the crystals are calculated from the Br contents and the stoichiometry. See text for analytical details.

up to 3.199. At saturation stage, the density of the solutions was 1.276 ± 0.007 g cm^{-3}.

3.4. $MgCl_2 \cdot 6H_2O$-$MgBr_2 \cdot 6H_2O$

The region of constant partition coefficients in the system $MgCl_2 \cdot 6H_2O$-$MgBr_2 \cdot 6H_2O$-H_2O was comparably small and was only observed for concentrations greater than ~800 μg Br/g aqueous solution (Table 4 and Fig. 1d). Here, the $^{bischofite}D_{Br}$ was 0.684 ± 0.007. As in the systems discussed above, the partition coefficient increased for decreasing Br concentration in the solution. The density of the bischofite-saturated brines was 1.326 ± 0.007 g cm^{-3}.

3.5. $KMgCl_3 \cdot 6H_2O$-$KMgBr_3 \cdot 6H_2O$

For the carnallite system $KMgCl_3 \cdot 6H_2O$-$KMgBr_3 \cdot 6H_2O$-H_2O (Table 5 and Fig. 1e), constant partition coefficients of

Table 6. Logarithm of the solubility product, log K_r, and the calculated standard molar Gibbs energies of formation, $\Delta_f G^0_m$, at T = 298.15 K and p^0 = 101,325 Pa for the investigated minerals.

Mineral	Formula	log K_r	$\Delta_r G^0_m$ (kJ/mol)	Source for log K_r[a]
Halite	NaCl	1.561	−384.3	Mean of a, b, c, d, e, and f
Br-Halite	NaBr	2.965	−349.0	Mean of d, e, and g
Sylvite	KCl	0.900	−408.6	a
Br-Sylvite	KBr	1.069	−380.4	c
Kainite	$KMgClSO_4 \cdot 2.75\ H_2O$	−0.193	−2266.3	a
Br-Kainite	$KMgBrSO_4 \cdot 2.75\ H_2O$	−0.535	−2240.8	Own solubility data
Bischofite	$MgCl_2 \cdot 6\ H_2O$	4.455	−2114.8	a
Br-Bischofite	$MgBr_2 \cdot 6\ H_2O$	5.283	−2055.4	Own calculations from h
Carnallite	$KMgCl_3 \cdot 6\ H_2O$	4.330	−2529.3	a
Br-Carnallite	$KMgBr_3 \cdot 6\ H_2O$	6.222	−2436.5	Own calculations from h

[a] Sources are as follows: a, Harvie et al. (1984); b, Helgeson et al. (1978); c, Robie et al. (1978); d, Wagman et al. (1982); e, Weast (1990); f, Woods and Garrells (1987); g, Stoessell and Carpenter (1986); h, Boeke (1908).

Table 7. Single electrolyte solution parameter values used for the calculations in the investigated systems.

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Source[a]
Na	Cl	0.0765	0.2644	0.0000	0.00127	a
Na	Br	0.0973	0.2791	0.0000	0.00110	b
Na	OH	0.0864	0.2530	0.0000	0.00440	a
K	Cl	0.0484	0.2122	0.0000	−0.00084	a
K	Br	0.0569	0.2212	0.0000	−0.00180	b
K	SO_4	0.0450	0.7793	0.0000	0.00000	a
K	OH	0.1298	0.3200	0.0000	0.00410	a
Mg	Cl	0.3524	1.6815	0.0000	0.00519	a
Mg	Br	0.4327	1.7528	0.0000	0.00308	b
Mg	SO_4	0.2210	3.3430	−37.23	0.02500	a
Mg	OH	0.0000	0.0000	0.0000	0.00000	a
H	Br	0.1960	0.3564	0.0000	0.00820	b
H	Cl	0.1775	0.2945	0.0000	0.00080	a
H	SO_4	0.0298	0.0000	0.0000	0.0438	a

[a] Sources are as follows: a, Harvie et al. (1984); b, Pitzer (1979).

0.55 ± 0.01 were obtained for concentrations greater than $\sim$100 μg Br/g solution. As in all other systems investigated, decreasing concentrations of Br in the aqueous solution led to increasing partition coefficients. The carnallite-saturated brines had a density of 1.288 ± 0.009 g cm^{-3}.

It is obvious from a comparison of the data shown in Figure 1 that constant partition coefficients are only obtained for Br concentrations greater than 70 to 300 μg Br/g solution for all systems investigated. An exception for this rule is the kainite system, where constant partitioning was never reached in our experiments. However, at low concentrations of Br in the aqueous solution, significantly increasing partition coefficient for decreasing Br contents were observed in all systems investigated.

4. DISCUSSION

Figure 2 clearly indicates that the partition coefficient of Br into halite is independent of the evaporation speed. Because of the direct link of the evaporation rate and the crystallization speed, it is thus not possible to explain different Br contents in primary marine halites by variations in the crystallization speed. It is more likely that different Br contents in primary halites are the result of variations in the Br concentration or the major element composition of the brine.

It is not our aim here to contribute to the theoretical discussion of thermodynamic equilibrium and stoichiometric saturation in solid solution–aqueous solution systems (Thorstensen and Plummer, 1977; Stoessell and Carpenter, 1986; Königsberger and Gamsjäger, 1987, 1990; Glynn and Reardon, 1990a,b; Glynn et al., 1990, 1992; Stoessell, 1992). Some of our experimental results suggest that the partition coefficients were obtained at equilibrium. The precipitates of the evaporation experiments shown in Figure 2 crystallized over the course of some days to several weeks or months and showed a fairly consistent partition coefficient. It is unlikely that all these crystals were produced under the same disequilibrium conditions. Furthermore, one of the aliquots was left sealed in the incubator after the first sampling for more than 18 months (black circle in Fig. 2) to allow the salts to age in contact with the brine. A second measurement of the crystals and the brine showed no alteration of the Br concentration. However, the crystallization behavior and evaporation conditions of the systems investigated were so different, but produced such comparable shapes for the partition coefficients, that it seems unlikely

Table 8. Common-ion two electrolyte parameter values used for the calculations in the investigated systems.

Cation	Cation′	$\theta_{cc'}$	$\psi_{cc'Cl}$	$\psi_{cc'Br}$	$\psi_{cc'OH}$	$\psi_{cc'SO_4}$
Na	K	$-0.0100^{a,b}$	-0.0018^{b}	0.0000^{b}	0.0000^{a}	-0.0100^{a}
Na	H	$0.0360^{a,b}$	-0.0040^{a}	-0.0100^{b}	0.0000^{a}	0.0000^{a}
K	Mg	$0.0000^{a,c}$	-0.0220^{a}	-0.0265^{c}	0.0000^{a}	-0.0480^{a}
K	H	0.0050^{a}	-0.0110^{a}	-0.0200^{b}	0.0000^{a}	0.1970^{a}
Mg	H	0.1000^{a}	-0.0110^{a}	0.0000	0.0000^{a}	0.0000^{a}

Anion	Anion′	$\theta_{aa'}$	$\psi_{aa'Na}$	$\psi_{aa'K}$	$\psi_{aa'Mg}$	$\psi_{aa'H}$
Cl	Br	0.0000^{b}	0.0000^{b}	0.0000^{b}	0.0000	0.0000
Cl	OH	-0.0500^{a}	-0.0060^{a}	-0.0060^{a}	0.0000^{a}	0.0000^{a}
Cl	SO_4	0.0200^{a}	0.0014^{a}	0.0000^{a}	-0.0040^{a}	0.0000^{a}
Br	OH	-0.0600^{b}	-0.0100^{b}	0.0000	0.0000	0.0000
SO_4	OH	-0.0130^{a}	-0.0090^{a}	-0.0500^{a}	0.0000^{a}	0.0000^{a}

[a] Harvie et al. (1984).
[b] Pitzer and Kim (1974).
[c] Balarev et al. (1993).

Table 9. Measured mole fractions and calculated activity coefficients of Br in the solid solution of the systems investigated.[a]

	Halite		Sylvite		Kainite		Bischofite		Carnallite	
Run	$X_{Br} \cdot 10^{-6}$	λ_{Br}	$X_{Br} \cdot 10^{-6}$	λ_{Br}	$X_{Br} \cdot 10^{-6}$	λ_{Br}	$X_{Br} \cdot 10^{-6}$	$\lambda_{Br} \cdot 10^{-6}$	$X_{Br} \cdot 10^{-6}$	$\lambda_{Br} \cdot 10^{-10}$
1	13	0.65	23	2.26	789	0.76	121	117	54	7
2	12	0.70	27	2.17	883	0.94	125	135	63	17
3	15	0.64	25	2.47	904	1.12	182	220	70	19
4	16	1.06	38	2.95	1095	0.97	220	281	79	36
5	18	0.94	37	2.77	906	1.42	756	1040	74	70
6	18	0.97	45	3.32	764	2.28	1245	1729	88	67
7	26	1.15	50	2.99	1024	2.20	1818	2556	129	320
8	24	1.23	55	3.44	1259	1.82	3660	5113	128	346
9	24	1.27	58	3.35	1167	2.12	7231	10,359	124	432
10	29	1.31	75	3.50	968	4.51	10,691	15,815	159	479
11	32	1.31	83	3.43	1082	4.25			155	518
12	30	1.41	95	3.39	1347	7.91			157	735
13	32	1.33	98	3.41	1462	7.41			381	2721
14	37	1.42	114	3.53	1816	11.56			347	3208
15	47	1.40	152	3.57	1945	10.91			365	3555
16	56	1.50	285	3.49	2376	13.51			729	10,739
17	62	1.38	290	3.43	2258	14.24			691	12,441
18	279	1.47	499	3.39	2697	14.64			746	12,606
19	588	1.39	514	3.28	2829	13.74			1741	69,140
20	3000	1.36	697	3.36					1753	74,747
21	2543	1.62	713	3.35					3377	290,027
22	5365	1.51	1034	3.42					3591	274,066
23			1860	3.61					3718	309,636
24			2014	3.33					7488	1,095,302
25			1939	3.43					6773	1,246,264
26			3828	3.42					7154	1,251,065
27			4068	3.34					10,299	2,579,625
28			5971	3.33					10,084	2,856,499
29									10,375	2,872,801

[a] λ_{Br} was calculated applying Eqn. 2; the activities were generated by EQ3/6 by use of the thermodynamic parameters given in Tables 6 to 8. The results are plotted in Figure 3.

that all these experiments were performed at the same disequilibrium conditions. Nevertheless, to remove all doubt, future experiments should also include a reversion of the evaporation experiments with a partial redissolution of the precipitated salts.

As shown by previous investigations (Siemann and Schramm, 2000), the partition coefficient of Br into halite greatly depends on the chemical composition of the brine because it is also a function of the activities of Na and Br in the aqueous solution. To discuss the obtained concentration data shown in Figure 1 thermodynamically, the activity coefficients of the trace component in the solid solution systems investigated were calculated by eqn. 8 of Siemann and Schramm (2000). For the calculation of the activities in the solutions, the computer program EQ3/6 (Wolery et al., 1990) was used. The solubility products and their standard molar Gibbs's energies of formation of the end members of the solid solution systems investigated are listed in Table 6. Furthermore, the single electrolyte solution parameters and the common-ion two-electrolyte parameter values for Pitzer's equation (Pitzer, 1979) are listed in Tables 7 and 8. The results of these calculations are listed in Table 9 and plotted in Figure 3.

Some of the systems such as NaCl-NaBr (e.g., Stoessell and Carpenter, 1986) and KCl-KBr (e.g., Glynn et al., 1990) were discussed theoretically in former articles. Most of the articles model Gibbs's free energy for the whole solid solution system by use of a regular model (Kirgintsev and Trushnikova, 1966), a two-parameter Guggenheim polynomial (Glynn et al., 1990), or other formalisms. The aim of this work is to discuss the thermodynamic behavior only of the extreme trace concentration ends of solid solution systems and not the whole system. As we discussed in a previous article, trace-element partitioning of Br in Cl minerals cannot be modeled satisfyingly by means of usual formalisms for Gibbs's free energy (Siemann and Schramm, 2000).

It is obvious from Figure 3 that the pattern of the activity coefficient of the trace component in the halite (Fig. 3a) and sylvite system (Fig. 3b) are similar but differ significantly from the other three systems investigated. The activity coefficients increase with increasing mole fractions of the trace component in the solid solutions, reaching constant values at X_{Br} of ~4 to 5×10^{-5}. The activity coefficients of the trace component in bischofite and carnallite differ significantly from that. Here, λ_{trace} is more or less constant at low mole fractions. At X_{Br} of $\sim 10^{-3}$, the activity coefficients increase with rising mole fractions. In the kainite system, no region of constant activity coefficients can be observed for the concentrations investigated. The pattern obtained is slightly comparable to the halite and sylvite system showing increasing λ_{Br} with rising X_{Br} for the low-concentration area.

Henry's law for the incorporation of trace elements in solid solutions is met when the activity coefficient is constant at different mole fractions. For halite and sylvite, Henry's law behavior can be observed for higher mole fractions rather than

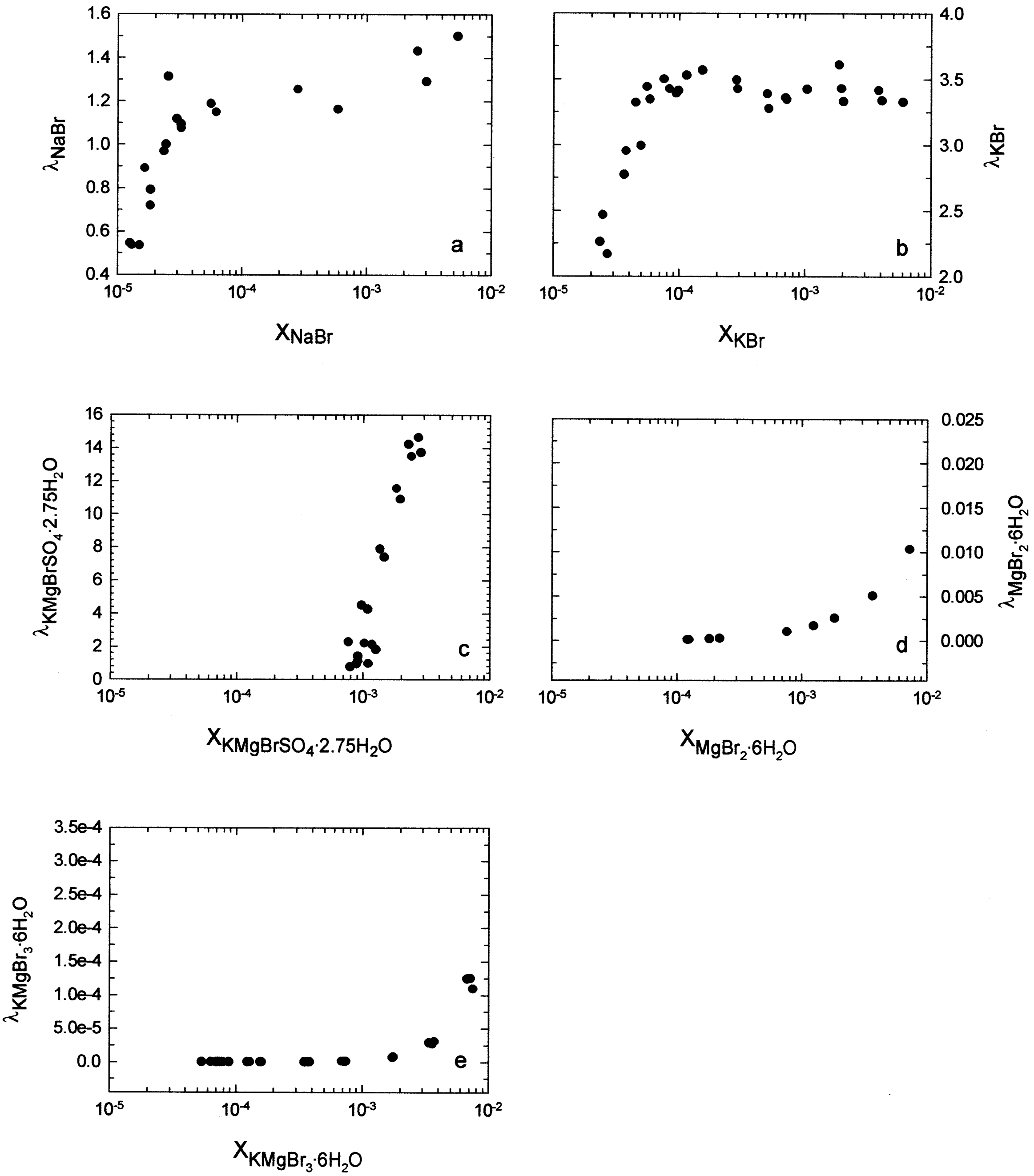

Fig. 3. Measured mole fractions and calculated activity coefficients of Br in solid solution halite (a), sylvite (b), kainite (c), bischofite (d), and carnallite (e). λ_{Br} was calculated applying Eqn. 2; the activities were generated by EQ3/6 by means of the thermodynamic parameters given in Tables 6 to 8. The data are listed in Table 9.

for low concentrations (Figs. 3a,b). In contrast to this, the activity coefficients of the trace component in the bischofite and carnallite system are constant for low mole fractions but do not follow Henry's law behavior with rising concentrations (Figs. 3d,e). It can be assumed that constant λ_{trace}, and thus Henry's law behavior, will be reached in the kainite system for greater than the investigated concentrations of Br in the aqueous and solid solutions, respectively.

To better understand the different Henry's law behavior and the patterns of the activity coefficients in the systems investigated, eqn. 8 of Siemann and Schramm (2000) must be discussed in detail. The formalisms can be rearranged as follows:

$$\lambda_{trace} = A \times B \times C \times D, \qquad (2)$$

with

$$A = \frac{1}{D_{Br}}$$

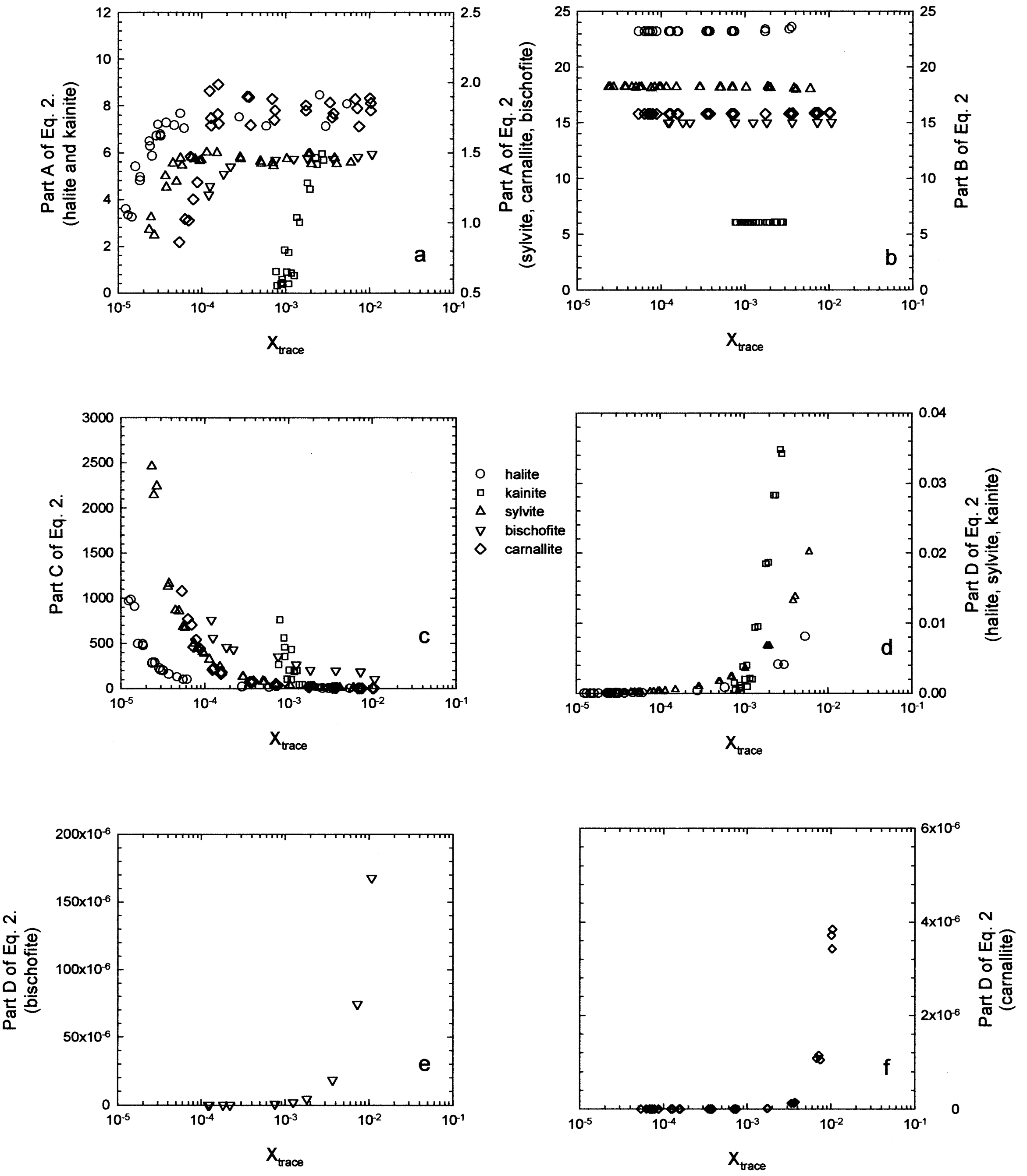

Fig. 4. Courses of the four parts of Eqn. 2 for the systems investigated. (a) Part A of Eqn. 2. (b) Part B of Eqn. 2. (c) Part C of Eqn. 2. (d) Part D of Eqn. 2 for the halite, sylvite and kainite system. (e) Part D of Eqn. 2 for the bischofite. (f) Part D of Eqn. 2 for the carnallite system. See text for details.

$$B = \frac{\sum m_i\, M_i}{\left(X_{trace}\, M_{trace} + X_{major}\, M_{major} + \sum \frac{n_{i\,ne}}{\upsilon_{trace}}\, M_{i\,ne}\right)}$$

$$C = \frac{1}{m_{trace}}$$

$$D = \frac{\prod a_i^{\upsilon_i}}{K_{trace}}$$

where λ_{trace} is the activity coefficient of the trace component, D_{Br} the partition coefficient of Br, m_i the molality of the *i*th solute component in the aqueous solution and M_i its molecular mass, X the mole fraction of the trace and major component in the solid solution, n_i is the number of moles (where "ne" [not exchanged] indicates components in the solid solution that are not exchanged), v_{trace} is the stoichiometric factor of the exchanged components, a is the activity of the trace end-member solid solution components in the aqueous solution, and K_{trace} is

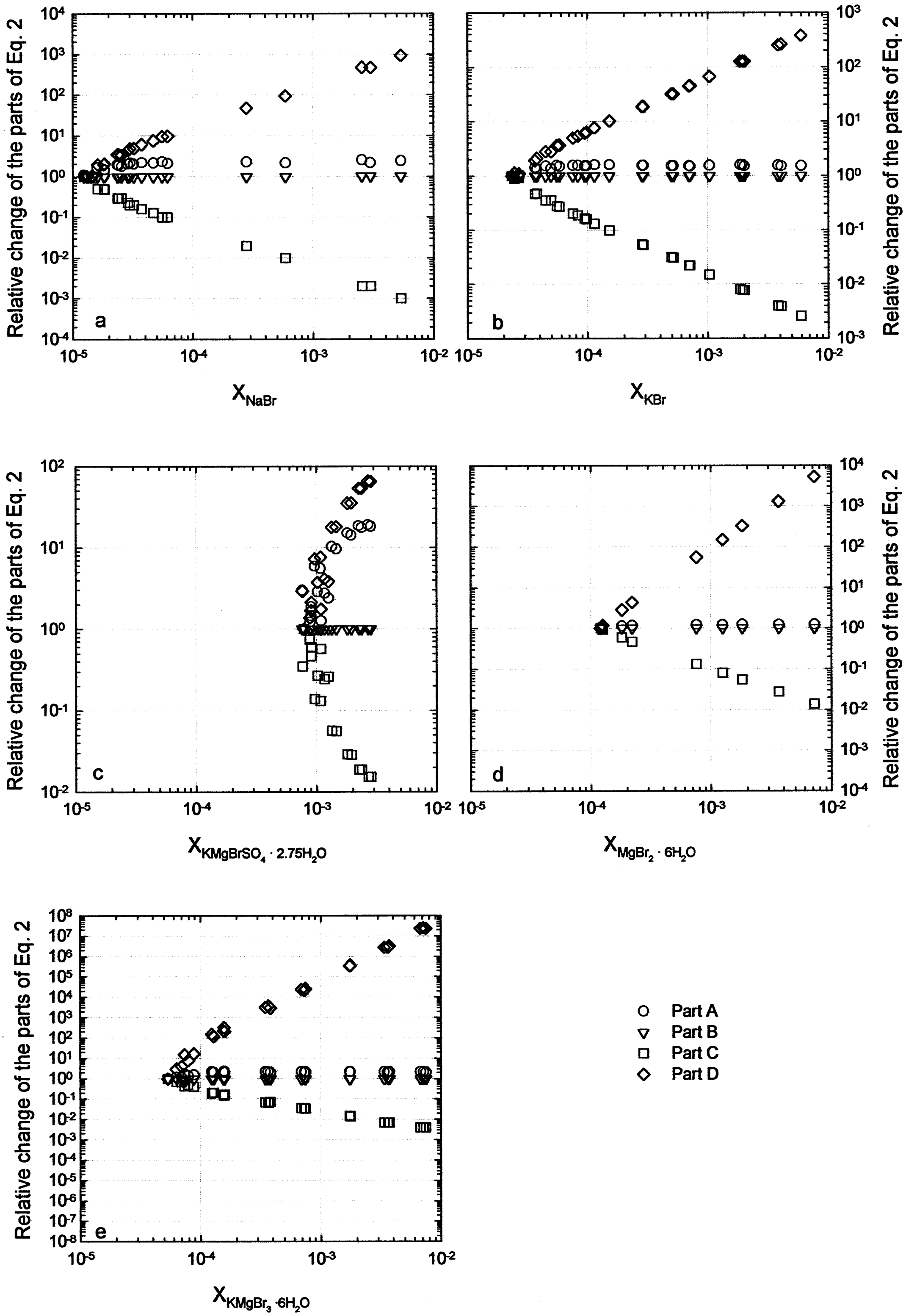

Fig. 5. Change of the four parts of Eqn. 2 relative to the starting value with rising mole fractions of the trace component in the solid solution. The first value was set to 1. Circles represent part A of Eqn. 2, triangles part B, squares part C, and diamonds changes in part D of Eqn. 2. (a) Br in halite. (b) Br in sylvite. (c) Br in kainite. (d) Br in bischofite. (e) Br in carnallite.

the solubility constant of the trace end member of the solid solution (see Siemann and Schramm, 2000, for derivation and details of Eqn. 2.).

The pattern of the single parts of Eqn. 2 as a function of the mole fractions of the trace component in the solid solution is plotted in Figure 4. It is obvious from a comparison of Figure 4 with Figure 3 that the pattern of the activity coefficients of halite, sylvite, and kainite are similar to that of part A (Fig. 4a) of Eqn. 2. On the other hand, the pattern of the activity coefficients of bischofite and carnallite are comparable to that of part D (Figs. 4e,f). The influence of the single parts of Eqn. 2 to the pattern of the activity coefficient in the solid solution greatly depends on the change of their values as a function with the mole fraction of the trace component. This relative change for the systems investigated is plotted in Figure 5. To enable a realistic comparison of the influence, the initial value for all single parts of the equation is set to 1. However, for the systems halite, sylvite, and kainite, the changes of the values of part D are compensated by changes of part C in Eqn. 2. Part B of the equation is constant for the investigated range of concentrations in all systems (Fig. 4b). Thus, the pattern of the activity coefficients in these systems is mostly influenced by changes of the partition coefficient or its reciprocal, respectively (part A of Eqn. 2). As a consequence, the product of the parts C and D of Eqn. 2 is constant. Because B is also constant, the activity coefficient of the trace component in the solid solution for the systems halite, sylvite, and kainite can be easily calculated by the product of the reciprocal of the partition coefficient and a factor:

$$\lambda_{\text{trace}} = \frac{1}{D_{\text{Br}}} \times F \tag{3}$$

where

$$F = B \times C \times D = \text{constant for } \upsilon_{\text{trace}} = 1$$

For the halite system, this factor is 0.195 ± 0.002; for sylvite, 2.35 ± 0.06; and for kainite, 2.45 ± 0.02. As can be derived from Eqn. 2, this factor is unitless.

For the bischofite and carnallite systems, the activity coefficients are mostly characterized by part D of Eqn. 2 because its influence is not fully compensated by changes in part C. The reason for this is that the activity of the trace end-member solid solution component in the aqueous solution is powered by its stoichiometric factor. For halite, sylvite, and kainite, this factor is 1 and thus without any significance. In the bischofite system, the activity of Br in the saturated solution is powered by 2 and in the carnallite system by 3, because these are the stoichiometric factors of the Br component in the chemical formula.

As a consequence, Henry's law behavior and constant activity coefficients of the trace components in the solid solution, respectively, can only be correlated to constant partition coefficients for systems where the stoichiometric factor of the trace component in the crystal equals 1. For higher factors, it is not possible the meet Henry's law at constant partition coefficients because even small changes in the activities of the trace element in the aqueous solution are powered by this factor and reach higher values, as in simple systems.

5. CONCLUSIONS

The experimental studies in the systems investigated show that constant partition coefficients of Br can only be obtained for particular concentration ranges of this trace element in the aqueous solution. Starting at a concentration of ~70 to 200 μg Br/g aqueous solution, the partition coefficient of Br increases with decreasing concentrations. This behavior cannot be explained by kinetic effects related to different evaporation or crystallization rates, as illustrated by Figure 2.

A calculation of the activity coefficients in the systems investigated show that constancy or Henry's law behavior is reached for higher mole fractions of the trace component in the solid solution in halite and sylvite (Figs. 3a,b). For bischofite and carnallite, these constant activity coefficients or Henry's law behavior are restricted to the lower mole fractions. This behavior is caused by the activity of the trace component in the aqueous solution that is powered by its stoichiometric factor in the trace end-member solid solution. For halite, sylvite, and kainite, this factor equals 1 and is 2 for bischofite and 3 for carnallite. However, it is impossible to correlate Henry's law behavior with constant partition coefficients for solid solution systems where the stoichiometric factor of the trace component is greater than 1.

Acknowledgments—We thank M. Schubert and B. Adel for assistance in the laboratory. This manuscript was further improved by the thorough remarks of K. Mengel. We thank Ronald K. Stoessell and an anonymous reviewer for their constructive comments and Lynn M. Walter for editorial assistance.

Associate editor: L. M. Walter

REFERENCES

Balarev C., Christov C., Valyasko V., and Petrenko S. (1993) Thermodynamics of formation of carnallite type double salts. *J. Solution Chem.* **22,** 173–181.

Boeke H. E. (1908) Über das Kystallisationsschema der Chloride, Bromide, Jodide von Natrium, Kalium und Magnesium, sowie über das Vorkommen des Broms und das Fehlen von Jod in den Kalisalzlagerstätten. *Z. Krystallogr. Mineral.* **45,** 346–391.

Bruland K. W. (1983) Trace elements in sea-water. In *Chemical Oceanography*, Vol. 8 (eds. J. P. Riley and R. Chester), pp. 157–221. Academic Press.

Chester R. (2000) *Marine Geochemistry*. Blackwell Science.

Glynn P. D. and Reardon E. J. (1990a) Reply to comment to "Solid-solution aqueous-solution equilibria: Thermodynamic theory and representation" by Erich Königsberger and Heinz Gamsjäger. *Am. J. Sci.*215–225.

Glynn P. D. and Reardon E. J. (1990b) Solid-solution aqueous-solution equilibria: thermodynamic theory and representation. *Am. J. Sci.* **290,** 164–201.

Glynn P. D., Reardon E. J., Plummer L. N., and Busenberg E. (1990) Reaction path equilibrium end-points in solid solution aqueous-solution systems. *Geochim. Cosmochim. Acta* **54,** 267–282.

Glynn P. D., Reardon E. J., Plummer L. N., and Busenberg E. (1992) Reply to Dr. Stoessell's comment on "Reaction path equilibrium end-points in solid solution aqueous-solution systems." *Geochim. Cosmochim. Acta* **56,** 2559–2572.

Harvie C. E., Moeller N., and Weare J. H. (1984) The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25°C. *Geochim. Cosmochim. Acta* **48,** 723–751.

Helgeson H. C., Delany J. M., Nesbitt H. W., and Bird D. K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. *Am. J. Sci.* **278A**, 229 S.

Kirgintsev A. N. and Trushnikova L. N. (1966) Termodynamics of MCl-MBr solid solutions. *Russ. J. Inorganic Chem.* **11,** 1250–1255.

Königsberger E. and Gamsjäger H. (1987) Solid-solute phase equilibria in aqueous solutions I: Solubility canstants and free enthalpy of formation of huntite. *Berichte Bunsengesellsch. Physik. Chem.* **91,** 785–790.

Königsberger E. and Gamsjäger H. (1990) Comment to "Solid-solution aqueous-solution equilibria: Thermodynamic theory and representation" by Pierre D. Glynn and Eric J. Reardon. *Am. J. Sci.* **292,**199–214.

Pitzer K. S. (1979) Theory: Interaction approach. In *Activity Coefficients in Electrolyte Solutions*, Vol. 1 (ed. R. M. Pytcovicz), p. 157. CRC Press.

Pitzer K. S. and Kim J. J. (1974) Thermodynamics of electrolytes IV: Activity and osmotic coefficients for mixed electrolytes. *J. Am. Chem. Soc.* **96,** 5701.

Robie R. A., Hemmingway B. S., and Fisher J. R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascal) pressure and at higher temperatures. Geological Survey Bulletin. 1452, US Government Printing Office, Washington.

Schäfer H., Läubli M., and Döring R. (1996) *Ionenchromatographie*. Metrohm.

Siemann M. G. (1993) A practice orientated way to produce diffraction reference cards using evaporate minerals. *Mater. Sci. Forum* **136,** 27–32.

Siemann M. G. and Schramm M. (2000) Thermodynamic modelling of the Br partition between aqueous solutions and halite. *Geochim. Cosmochim. Acta* **64,** 1681–1693.

Siemann M. G. and Ellendorff B. (2001) The composition of gases in fluid inclusions of Late Permian (Zechstein) marine evaporates in Northern Germany. *Chem. Geol.* **173,** 31–44.

Stoessell R. K. (1992) Comment on "Reaction path equilibrium endpoints in solid solution aqueous-solution systems" by P. D. Glynn, E. J. Reardon, L. N. Plummer and E. Busenberg. *Geochim. Cosmochim. Acta* **56,** 2555–2557.

Stoessell R. K. and Carpenter A. B. (1986) Stoichiometric saturation test of $NaCl_{1-x}Br_x$ and $KCl_{1-x}Br_x$. *Geochim. Cosmochim. Acta* **50,** 1465–1474.

Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific.

Thorstensen D. C. and Plummer L. N. (1977) Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase—Example: The magnesian calcite. *Am. J. Sci.* **277,** 1203–1223.

Wagman D. D., Evans W. H., Parker V. B., Schumm R. H., Halow I., Bailey S. M., Churney K. L., and Nuttall R. L. (1982) The NBS tables of chemical thermodynamic properties. *J. Phys. Chem. Ref. Data.*11.

Weast R. C. (1990) *CRC Handbook of Chemistry and Physics.*CRC Press.

Wolery T. J., Jackson K. J., Bourcier W. L., Bruton C. J., Viani B. E., Knauss G., and Delany J. M. (1990) Current status of the EQ3/6 software package for geochemical modeling. In *Chemical Modeling of Aqueous Systems II*, Vol. 416 (eds. D. C. Melchior and R. L. Bassett), pp. 104–116. American Chemical Society.

Woods T. L. and Garrells R. M. (1987) *Thermodynamic Values at Low Temperature for Natural Inorganic Materials: An Uncritical Summary*. Oxford University Press.

Yamaguchi K., Inoue T., and Nishioka K. (1998) Growth and perfection of KCl crystals grown from aqueous solutions. *J. Cryst. Growth* **183,** 409–416.