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The measurement of sulfate mineral solubilities in the Na-K-Ca-Cl-SO₄-H₂O system at temperatures of 100, 150 and 200°C

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Abstract—At $T > 100^\circ\text{C}$ development of thermodynamic models suffers from missing experimental data, particularly for solubilities of sulfate minerals in mixed solutions. Solubilities in $\text{Na}^+ - \text{K}^+ - \text{Ca}^{2+} - \text{Cl}^- - \text{SO}_4^{2-} / \text{H}_2\text{O}$ subsystems were investigated at 150, 200°C and at selected compositions at 100°C. The apparatus used to examine solid-liquid phase equilibria under hydrothermal conditions has been described.

In the system $\text{NaCl} - \text{CaSO}_4 - \text{H}_2\text{O}$ the missing anhydrite (CaSO_4) solubilities at high NaCl concentrations up to halite saturation have been determined. In the system $\text{Na}_2\text{SO}_4 - \text{CaSO}_4 - \text{H}_2\text{O}$ the observed glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) solubility is higher than that predicted by the high temperature model of Greenberg and Møller (1989), especially at 200°C. At high salt concentrations, solubilities of both anhydrite and glauberite increase with increasing temperature. Stability fields of the minerals syngenite ($\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$) and goergeyite ($\text{K}_2\text{SO}_4 \cdot 5 \text{CaSO}_4 \cdot \text{H}_2\text{O}$) were determined, and a new phase was found at 200°C in the $\text{K}_2\text{SO}_4 - \text{CaSO}_4 - \text{H}_2\text{O}$ system. Chemical and single crystal structure analysis give the formula $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4$. The structure is isostructural with palmierite ($\text{K}_2\text{SO}_4 \cdot \text{PbSO}_4$). The glaserite (“ $3 \text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ”) appears as solid solution in the system $\text{Na}_2\text{SO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$. Its solubility and stoichiometry was determined as a function of solution composition. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

For studies of complex natural processes in brines or evaporitic deposits at low and at high temperatures variable temperature, thermodynamic models are used to simulate conditions which are difficult to reproduce in the laboratory. One such problem is the prediction of the long term safety of heat-generating radioactive wastes (temperatures up to 200°C) isolated by rock salt formations, where the consequences of an accidental intrusion by fluids have to be considered. Modelling of such scenarios requires a thermodynamic model of the six-component oceanic salt system Na-K-Mg-Ca-Cl-SO₄-H₂O. Recently precipitation and dissolution processes of CaSO₄ phases at high temperatures became of interest in the interpretation of geothermal processes in the deep Red Sea (Monnin and Ramboz, 1996) and for hydrothermal deposits of “black smokers” (Graupner et al., 2001). Møller (1988) and Greenberg and Møller (1989) developed a high temperature model (HT model) for the system Na-K-Ca-Cl-SO₄-H₂O for the temperature range 0 to 250°C using Pitzer’s model (Pitzer, 1973, 1991; Grenthe and Puigdomenech, 1997). Voigt (1999) reviewed the application of the Pitzer model to the available experimental data for the oceanic salt system. Above 100°C solubility data are particularly scarce in the sulfate subsystems. Thus, Greenberg and Møller (1989) had to extrapolate and manipulate the temperature dependent functions of some Pitzer parameters and solubility constants > 100 or 150°C. No solubility isotherms are available in the system $\text{Na}_2\text{SO}_4 - \text{CaSO}_4 - \text{H}_2\text{O}$ at $T > 100^\circ\text{C}$ and thus the behaviour of glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) in hydrothermal solutions remained uncertain.

Greenberg and Møller (1989) could not model stable equi-

Table 1. Names and formulas of investigated or mentioned minerals.

Mineral name	Formula
Anhydrite	CaSO_4
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Halite	NaCl
Glauberite	$\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$
Thenardite	Na_2SO_4 (modification V)
Arcanite	K_2SO_4
Syngenite	$\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$
Goergeyite	$\text{K}_2\text{SO}_4 \cdot 5 \text{CaSO}_4 \cdot \text{H}_2\text{O}$
Glaserite	$\text{Na}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$

libria for syngenite and goergeyite in the system $\text{K}_2\text{SO}_4 - \text{CaSO}_4 - \text{H}_2\text{O}$ at temperatures > 100°C indicated by the few high temperature points of Clarke and Partridge (1934). According to their model anhydrite is more stable than both the syngenite or goergeyite. So, the two double salt hydrates do not exist > 100°C according to the calculations. Anhydrite and arcanite are the stable phases, only. Because of the contradiction to the occasional experimental values of Clarke and Partridge (1934), which confirm the existence of the double salt hydrates, Greenberg and Møller (1989) expressed the necessity of additional experimental data at high temperatures. The missing mineral solubilities in systems mentioned above and the unknown glaserite (“ $3 \text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ”) stoichiometry and solubility at $T > 150^\circ\text{C}$ in the subsystem $\text{Na}_2\text{SO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$ motivated us to investigate phase equilibria in these subsystems experimentally. In addition we determined anhydrite solubilities in concentrated NaCl solutions at 100, 150 and 200°C up to saturation of halite, because these data represent an elementary starting point for modelling scenarios in evaporites at high temperatures.

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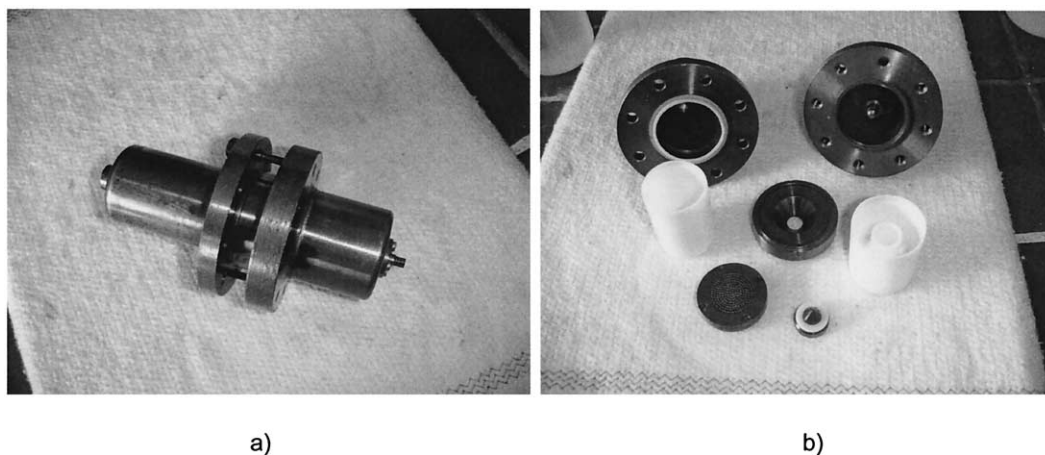


Fig. 1. Autoclave (a) and its components (b), inscription see Fig. 2.

All phases or minerals investigated or mentioned in this study are listed in Table 1.

2. EXPERIMENTAL

2.1. Apparatus

The solubility determinations were performed by means of an apparatus developed earlier (Voigt et al., 1985). The respective solution-solid phase mixtures were placed in Teflon cups situated inside the TiPd0.2 autoclaves (volume of suspension $\sim 20 \text{ cm}^3$) (Figs. 1 and 2).

Four autoclaves were rotated around their own vertical axis with alternating directions in a metal block thermostat at constant temperature (100 ± 0.5 , 150 ± 0.5 or $200 \pm 0.5^\circ\text{C}$) (Fig. 3). After 1 week of equilibration the thermostat was turned upside down (Fig. 3b [10]) and then connected with a special high temperature centrifuge (Fig. 4) for separation of the solid phase from the solution. By means of a square bar (7) the thermal insulation slides (6) of thermostat and centrifuge are turned simultaneously for passing the autoclaves down into a turnable autoclave holder (11). After disconnecting the rods (9) and closing the centrifuge's thermal insulation (6) filtration occurs at 3000 rpm. Thereby the autoclaves turn into a horizontal position and liquid is pressed through the filter plate at ~ 2000 times earth acceleration. The whole procedure takes place at the appropriate equilibrium temperature.

After centrifugation the valves of the autoclaves are closed. The system is allowed to cool down and then opened for sampling of the separated phases.

2.2. Analytical and Techniques

The establishment of solubility equilibria were reached in two ways. In most cases the autoclaves with the starting materials were heated in the block thermostats up to the equilibrium temperature, or, in a few cases, the autoclaves were placed in the preheated block thermostats $\sim 30^\circ\text{C}$ higher than the equilibrium temperature for 1 to 3 h, and then slowly cooled down for equilibration at 100, 150 or 200°C . Because of the time consuming equilibration and analytics a sample composition was prepared in one way only. Altogether, the determined solubilities reached in both ways assemble each other to homogenous solubility branches for the respectively phases are given in Tables 2 to 5.

All salts (NaCl , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Na_2SO_4 , K_2SO_4) used in the experiment were reagent grade (p.a.) from Merck KGaA Darmstadt and were used without further purification.

Chemical compositions of solutions were determined for Ca^{2+} by complexometric titration, 0.05-*m* EDTA (Indicator: Cal-Red) and Na^+ , K^+ and SO_4^{2-} by ion chromatography (Dionex DX100). For most of the samples additional gravimetric analyses for K^+ (as tetraphenylborate) and SO_4^{2-} (as barium sulfate) have been performed. Potentiometric titration with 0.1-mol/L AgNO_3 was used for Cl^- . Analytical

tests of the volumetric and gravimetric methods were carried out to determine the uncertainties for the resulting molalities. Especially the determination of the extreme low Ca^{2+} content was optimized up to a

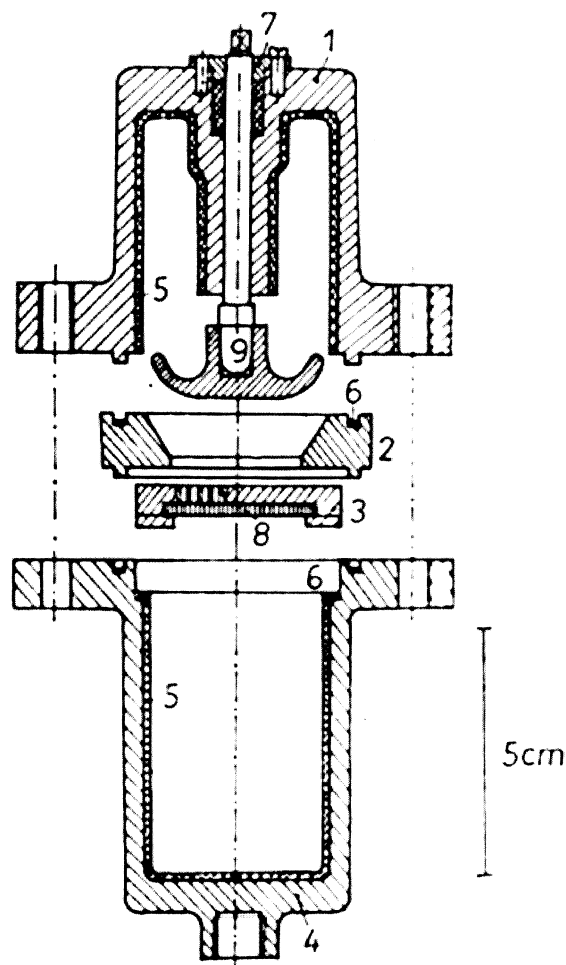


Fig. 2. Cross-section of autoclave components of the autoclave: (1) upper part, (2) spacer, (3) breaker plate, (4) bottom part, (5) Teflon cup: top: liquid phase cup bottom: solid phase cup, (6) seals, (7) Teflon packing, (8) filter, (9) valve.

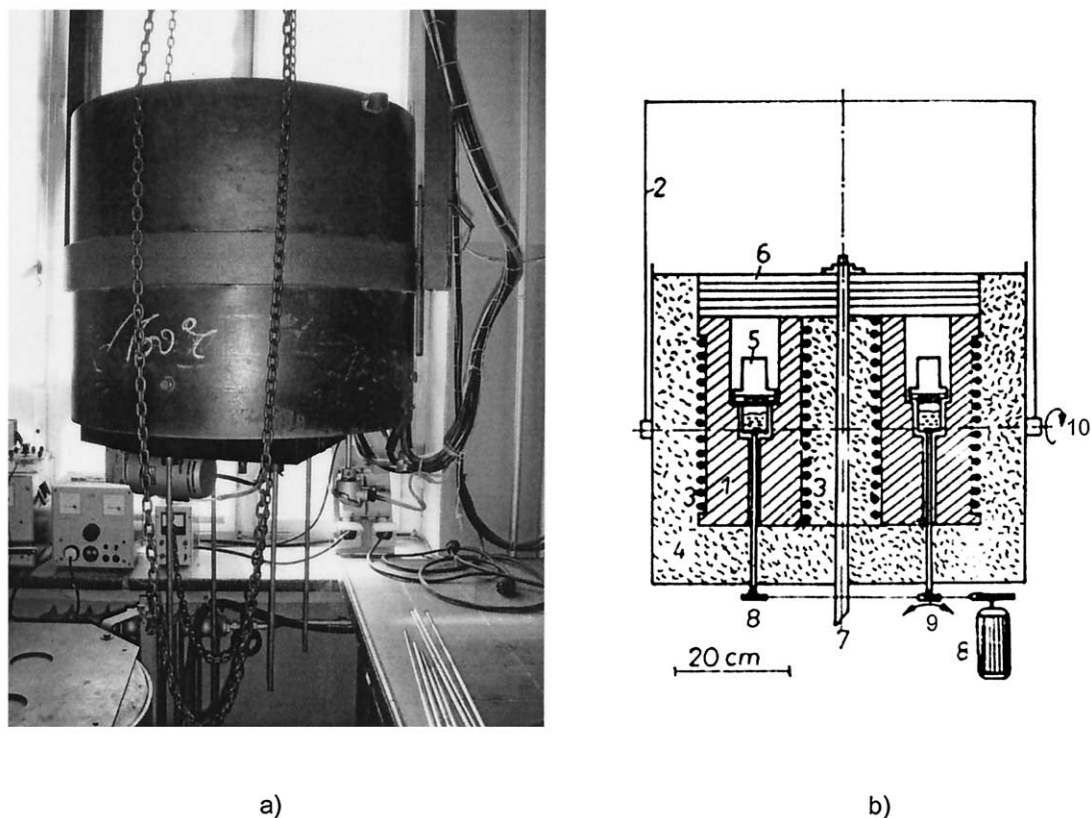


Fig. 3. Thermostat (a) cross-section (b): (1) aluminium block, (2) holder, (3) heating coils, (4) insulating insert, (5) autoclave, (6) thermal insulation slide, (7) square bar, (8) horizontal motor with drive, (9) axis of rotation for autoclave, (10) axis of rotation for block thermostat.

relative uncertainty of $\pm 1\%$. The same uncertainties, $\pm 1\%$, can be given for the gravimetric methods. The potentiometric Cl^- titration is within $\pm 0.2\%$ uncertainty. An uncertainty of 2% was reached for the ion chromatographic determined molalities. SO_4^{2-} ion chromatography was only used for determination of CaSO_4 molalities in the system $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$ to compare with the values determined by Ca^{2+} complexometric titration. For the systems $\text{Na}_2\text{SO}_4\text{-CaSO}_4\text{-H}_2\text{O}$ and $\text{K}_2\text{SO}_4\text{-CaSO}_4\text{-H}_2\text{O}$ the CaSO_4 molalities resulted from Ca^{2+} -titration. Because of the small values of no more than 0.5% referring to the Na_2SO_4 and K_2SO_4 concentrations these molalities were calculated from the gravimetric received total sulfate content. Also, Na^+ and K^+ content were determined by ion chromatography, K^+ additional by gravimetric method for comparison. The values were accepted if deviations for Na_2SO_4 and K_2SO_4 molalities were $< \pm 2\%$ for the different methods (analogous the CaSO_4 molalities in the chloride system). Molalities for the system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ were determined in the same way. The final uncertainties are $\pm 0.2\%$ for NaCl molalities, $\pm 1\%$ for CaSO_4 molalities in the sulfate systems, $\pm 2\%$ in the system $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$, and $\pm 2\%$ for Na_2SO_4 and K_2SO_4 molalities. The last three values represent a mean of gravimetry and ion chromatography uncertainties.

Solid phases were identified by X-ray powder diffraction (D5000 Siemens) and FT-Raman spectroscopy (RFS 100S, Bruker). After establishing a library of mineral spectra FT-Raman spectroscopy represented the most efficient and sensitive identification method. Hydrates were also characterized by DTA/TG. The stoichiometry of the "glaserite" solids in the system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ were determined analogous to the solution compositions.

FT-Raman spectroscopy was also used to determine in-situ the stable Na_2SO_4 phase in aqueous solution depending on temperature. For this experiment 338 mg thenardite and 300 mg H_2O were filled in a gold crucible (volume: 0.45 mL), which was inserted in a TiPd0.2 cylinder

block of $\sim 40 \times 50$ mm diameter. Crucible and metal cylinder were closed with optical glass of 5 mm thickness (hydro thermal cell). This hydro thermal cell, placed into the variable temperature cell (Specac) of the RAMAN spectrometer, was heated up to 215°C in 20°C steps. The spectra were collected in the temperature-holding time of 10 min.

3. RESULTS

3.1. System $\text{NaCl-CaSO}_4\text{-H}_2\text{O}$

Solubilities of anhydrite in sodium chloride solutions up to 6 *m* at 100, 150 and 200°C are available from the literature (Marshall et al., 1964; Block and Waters, 1968; Blount and Dickson, 1969). At 100°C differences between the measured values of Marshall et al. (1964), Block and Waters (1968) and Blount and Dickson (1969) are significant. The values from Marshall et al. (1964) are $\sim 30\%$ higher than those of Blount and Dickson (1969). At 150°C this difference amounts to 24% and the Block and Waters (1968) data are more or less in between. Extrapolations up to NaCl saturation result in quite uncertain anhydrite solubilities at these temperatures. Interestingly, at 200°C the data of the three groups are close but end at $m_{\text{NaCl}} = 6.0$ mol/kg H_2O , whereas NaCl saturation is reached at $m_{\text{NaCl}} = 8.14$ mol/kg H_2O .

Our new data (Table 2, Fig. 5) are in good agreement with the solubilities given by Blount and Dickson (1969) at all three temperatures. The curves intersect at 7.5 mol/kg H_2O . Above this concentration the anhydrite solubility increases with in-

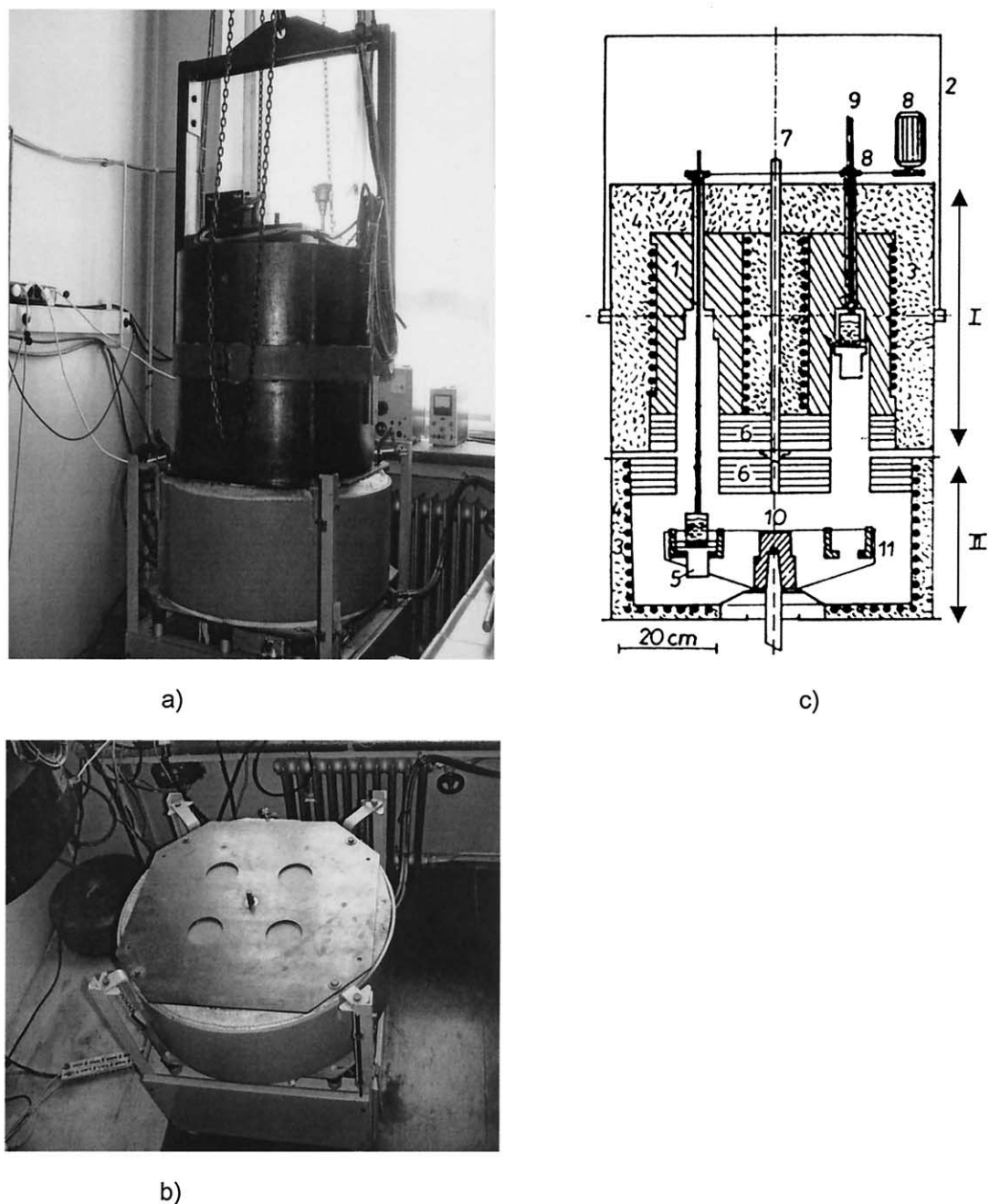


Fig. 4. Thermostat put on centrifuge (a), top view on the high temperature centrifuge (b), cross-section (c) (I) thermostat, (II) centrifuge (1) aluminium block, (2) holder, (3) heating coils, (4) insulating insert, (5) autoclave, (6) thermal insulation slide, (7) square bar, (8) motor with drive, (9) stainless steel rod, (10) rotor with input shaft, (11) turnable autoclave holder.

creasing temperature, whereas below 7.5 mol/kg H_2O the opposite is true. Such changes in the temperature dependence of solubility at high electrolyte concentrations have been reported also for other sparingly soluble salts (Valyashko, 1990).

3.2. System $\text{Na}_2\text{SO}_4\text{-CaSO}_4\text{-H}_2\text{O}$

Solubility data for this system are available from Hill and Will (1934) up to 75°C and at 100°C from Block and Waters

(1968). The stable phases between 100 and 200°C are anhydrite and sodium sulfate as well as the double salt glauberite, $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$. At 180°C sodium sulfate transforms from the thenardite structure to the $\text{Na}_2\text{SO}_4(\text{III})$ type, and at 240°C into the $\text{Na}_2\text{SO}_4(\text{I})$ phase. Above 520°C glauberite decomposes into a solid solution of CaSO_4 in $\text{Na}_2\text{SO}_4(\text{I})$ and anhydrite (Freyer et al., 1997).

In Table 3 and Figure 6 the experimentally determined solubility isotherms at 150 and 200°C are given. The 100°C

Table 2. Anhydrite solubilities in NaCl-CaSO₄-H₂O system at 100, 150 and 200°C.

T (°C)	Starting material (g)			Saturated solution (mol/kg H ₂ O)		
	NaCl	CaSO ₄ · 2H ₂ O	H ₂ O	NaCl	CaSO ₄	
100	3.5086	1.6185	19.6864	2.9849	0.02825	
	3.4600	1.6830	19.6616	2.9454	0.02921	
	4.6556	1.4277	19.7331	3.9719	0.02854	
	4.6652	1.4373	19.7055	4.0168	0.02825	
	5.8452	1.5938	19.6700	5.0527	0.02697	
	5.8448	1.5238	19.6850	5.0461	0.02629	
	7.0075	1.1841	19.7512	6.0241	0.02474	
	7.0254	1.1884	19.7515	6.0578	0.02546	
	2.0198	1.5153	19.6858	1.7831	0.02490	
	2.0090	1.5670	19.7141	1.7386	0.02474	
	6.2055	1.0518	14.7850	6.7269	0.02392	
	6.325	1.0429	14.7884	6.7024	0.02299	
	7.0274	0.9905	14.7958	6.6735	0.02393	
	8.3949	1.0486	17.7851	6.7444	0.02348	
	150	3.5067	2.0306	18.3960	3.2550	0.01973
		3.5066	2.0309	18.3961	3.2674	0.02018
		4.6754	1.0166	19.1970	4.1929	0.02089
		4.6754	1.0826	19.1572	4.1667	0.02015
		5.5756	2.1071	19.5590	4.7637	0.02058
		5.5774	2.1088	19.5587	4.7745	0.02060
6.9807		1.0023	19.7913	5.9659	0.02142	
6.9820		1.0999	19.7703	5.9827	0.02153	
8.0104		1.9100	18.5530	7.3183	0.02141	
8.0047		2.0282	18.3943	7.4536	0.02136	
9.2268		1.1530	19.0945	7.3915	0.02145	
2.1636		2.1251	19.5549	1.8937	0.01469	
2.0239		2.0958	19.5695	1.7832	0.01435	
6.5883		1.4125	14.7070	7.4019	0.02152	
6.6373		1.4160	14.7042	7.3958	0.02162	
7.5407		0.9968	19.7955	6.4069	0.02132	
8.8025		1.0034	19.7902	7.2725	0.02214	
7.7240		1.0316	19.7938	6.2633	0.02117	
7.7241		1.0325	19.7908	6.5609	0.02146	
8.4062		0.9980	19.7970	7.1194	0.02165	
200	8.4056	0.9956	19.7918	7.0896	0.02182	
	2.0734	2.0679	19.5804	1.8596	0.00936	
	2.0636	2.1165	19.5643	1.8650	0.00956	
	6.2056	1.1851	14.7575	7.3640	0.02061	
	6.3081	1.503	14.6885	7.5174	0.02126	
	5.8454	1.6069	19.6652	5.2491	0.01785	
	5.8452	1.6054	19.6641	5.1430	0.01767	
	7.0078	1.2033	19.9984	5.9661	0.01893	
	7.0108	1.2024	19.7507	6.2104	0.01941	
	3.5085	1.6196	19.6615	3.1676	0.01333	
	3.4607	1.6844	19.6498	3.0861	0.01308	
	4.6582	1.4280	19.7021	4.1203	0.01614	
	4.6671	1.4411	19.7027	4.1915	0.01571	
	6.2060	1.0087	14.7945	7.3151	0.02082	
	6.2021	1.0122	17.7924	6.0276	0.01934	
	8.4997	0.9968	17.7955	8.1508	0.02206	
	8.5008	1.0173	17.889	8.1781	0.02223	
	8.5066	0.9973	17.9864	7.9557	0.02208	
	8.5002	0.9981	17.9929	7.9946	0.02213	
	6.5041	1.2023	19.7344	5.5672	0.01849	
6.5005	1.1995	19.7532	5.6086	0.01863		
7.4907	1.0065	19.7950	6.6794	0.02039		
7.5010	1.0062	19.7921	6.6696	0.02063		

data of Block and Waters (1968) were checked for the glauberite branch and are in agreement with the results of the present study.

The solubility of anhydrite decreases with temperature. At 200°C the solubility of glauberite is 2 to 3 times higher than that estimated by the model of Greenberg and Møller (1989)

(HT curve in Fig. 6). An intersection point is observed at 2.3 *m* Na₂SO₄ for the 150 and 200°C glauberite branch which means that above this concentration the solubility of glauberite increases with increasing temperature. The existence of Na₂SO₄(III) was confirmed by means of in-situ Raman spectroscopy. Up to 180°C thenardite (Na₂SO₄[V]) was identi-

Table 3. Solubilities in the system $\text{Na}_2\text{SO}_4\text{-CaSO}_4\text{-H}_2\text{O}$ at 100, 150 and 200°C.

T (°C)	Starting material (g)			Saturated solution (mol/kg H ₂ O)		Solid phase
	Na ₂ SO ₄	CaSO ₄ · 2H ₂ O	H ₂ O	Na ₂ SO ₄	CaSO ₄	
100	6.6861	1.2334	19.7440	1.9711	0.005952	Glauberite
	6.6812	1.2324	19.7455	1.9996	0.005670	Glauberite
	10.5253	0.0106	20.0040	2.9308	0.003589	Glauberite
150	6.6821	1.2259	19.7533	1.9370	0.004112	Glauberite
	6.6821	1.2255	19.7511	2.0089	0.004242	Glauberite
	9.5228	1.2266	19.7762	2.8653	0.003379	Glauberite
	9.5229	1.2270	19.7714	3.0017	0.003577	Glauberite
	4.6930	1.2256	19.7505	1.3020	0.005219	Glauberite
	4.6931	1.2256	19.7430	1.3184	0.005337	Glauberite
	8.1027	1.2268	19.7437	2.3674	0.003828	Glauberite
	8.1024	1.2259	19.7445	2.5290	0.003856	Glauberite
	3.8435	1.2268	19.7449	1.2089	0.005384	Glauberite + anhydrite
	3.8445	1.2263	19.7371	1.2150	0.005302	Glauberite + anhydrite
	5.9701	1.2223	19.7434	1.8230	0.003980	Glauberite
	5.9740	1.2228	19.7415	1.7655	0.004156	Glauberite
	3.1294	1.2249	19.7503	1.0963	0.004588	Anhydrite
	3.1318	1.2259	19.7451	1.1136	0.004701	Anhydrite
	2.4120	1.2215	19.7559	0.8674	0.004112	Anhydrite
	2.4119	1.2215	19.7528	0.8484	0.003757	Anhydrite
	2.7062	1.2284	19.7488	0.9455	0.004233	Anhydrite
	2.7064	1.2270	19.7459	0.9585	0.004186	Anhydrite
	10.0913	1.2245	19.7441	2.9950	0.003437	Glauberite
	10.0912	1.2244	19.7484	2.9964	0.003398	Glauberite
	2.8419	1.2801	19.7367	0.9919	0.004630	Anhydrite
	2.8495	1.2795	19.7420	0.9831	0.004340	Anhydrite
	5.8282	1.2255	19.7518	1.6799	0.004551	Glauberite
	5.8311	1.2279	19.7478	1.7160	0.004722	Glauberite
	2.4237	1.2210	19.7685	0.8680	0.004125	Anhydrite
	2.4258	1.2221	19.7645	0.8578	0.004136	Anhydrite
	11.0541	0.0103	20.0072	3.0230	0.003363	Thenardite
11.0559	0.0103	19.9962	2.9505	0.003280	Thenardite	
1.4231	1.2205	19.7516	0.4824	0.002649	Anhydrite	
1.3478	1.2252	19.7510	0.4662	0.002696	Anhydrite	
8.6601	1.2212	19.7530	2.6109	0.003620	Glauberite	
6.9168	1.2210	19.8075	2.0600	0.003804	Glauberite	
0.8639	1.2212	19.7505	0.3103	0.002119	Anhydrite	
1.9913	1.2222	19.7632	0.7113	0.003441	Anhydrite	
10.5356	0.0073	20.0113	2.9520	0.002682	Thenardite	
10.5302	0.0034	20.0285	2.9810	0.001314	Thenardite	
200	8.2351	3.1049	19.3548	1.9745	0.003556	Glauberite
	8.2351	3.1052	19.3500	1.9834	0.003454	Glauberite
	11.0751	3.1082	19.3490	3.0683	0.004307	Glauberite
	5.8298	1.2239	19.7420	1.7775	0.004099	Glauberite
	5.8292	1.2235	19.7430	1.7691	0.003955	Glauberite
	8.1022	1.2246	19.7458	2.5261	0.004182	Glauberite
	8.1020	1.2246	19.7438	2.6596	0.004182	Glauberite
	3.8410	1.2166	19.7447	1.0852	0.004110	Glauberite
	3.8406	1.2177	19.7475	1.0861	0.003927	Glauberite
	4.6931	1.2205	19.7438	1.3029	0.003916	Glauberite
	4.6947	1.2216	19.7435	1.2010	0.003817	Glauberite
	3.8412	1.2247	19.7401	1.0794	0.003830	Glauberite + anhydrite
	3.8411	1.2235	19.7414	1.0623	0.003730	Glauberite + anhydrite
	8.1044	1.2241	19.7410	2.6452	0.004318	Glauberite
	8.1044	1.2243	19.7426	2.6780	0.004217	Glauberite
	3.8403	1.2261	19.7445	1.0768	0.004034	Glauberite + anhydrite
	3.8418	1.2259	19.7496	1.0549	0.004024	Glauberite + anhydrite
	2.4204	1.2224	19.7385	0.8821	0.003036	Anhydrite
	2.4233	1.2222	19.7470	0.8644	0.003033	Anhydrite
	8.0768	1.2234	19.7433	2.6388	0.004072	Glauberite
	8.0739	1.2253	19.7430	2.6071	0.004063	Glauberite
	2.1385	1.2221	19.7464	0.7619	0.002498	Anhydrite
	2.1370	1.2212	19.7528	0.7817	0.002628	Anhydrite
	2.9882	1.2220	19.7483	1.1040	0.004111	Glauberite + anhydrite
	2.9800	1.2241	19.7449	1.0910	0.003692	Glauberite + anhydrite
	1.4948	1.2716	19.7435	0.5338	0.001791	Anhydrite
	1.5005	1.2705	19.7432	0.5181	0.001774	Anhydrite

Table 3. (Continued)

T (°C)	Starting material (g)			Saturated solution (mol/kg H ₂ O)		Solid phase
	Na ₂ SO ₄	CaSO ₄ · 2H ₂ O	H ₂ O	Na ₂ SO ₄	CaSO ₄	
	5.3306	1.2252	19.7562	1.5339	0.003681	Glauberite
	5.3232	1.2236	19.7502	1.5485	0.003571	Glauberite
	8.1008	1.2252	19.7402	2.6449	0.004168	Glauberite
	8.1014	1.2227	19.7400	2.6749	0.004283	Glauberite
	11.6564	0.0104	20.0012	3.1438	0.004210	Na ₂ SO ₄ (III)
	11.6574	0.0104	20.0061	3.1235	0.003406	Na ₂ SO ₄ (III)
	5.8355	1.2223	19.7455	1.8085	0.003688	Glauberite
	8.6736	1.2245	19.7452	2.8526	0.004140	Glauberite
	11.6549	0.0066	19.9990	3.1431	0.002546	Na ₂ SO ₄ (III)
	11.6587	0.0135	20.0060	3.0860	0.003812	Na ₂ SO ₄ (III)

fied by the continuously monitored spectra with increasing temperature, at 200°C Na₂SO₄(III) was detected as stable phase in aqueous solution. Thus, the transformation of thenardite into Na₂SO₄(III) proceeds between 180 and 200°C.

3.3. System K₂SO₄-CaSO₄-H₂O

The system K₂SO₄-CaSO₄-H₂O was investigated at 150 and 200°C. Experimental data are given in Figure 7 and Table 4. The solubility of goergeyite and syngenite drastically changes

Table 4. Solubilities in the system K₂SO₄-CaSO₄-H₂O at 150 and 200°C.

T (°C)	Starting material (g)			Saturated solution (mol/kg H ₂ O)		Solid phase	
	K ₂ SO ₄	CaSO ₄ · 2H ₂ O	H ₂ O	K ₂ SO ₄	CaSO ₄		
150	2.1469	1.9909	19.6316	1.2310	0.00562	Syngenite + goergeyite	
	4.6063	1.0710	19.7776	0.5520	0.00339	Anhydrite + goergeyite	
	4.5992	1.0727	19.7705	0.5418	0.00343	Anhydrite + goergeyite	
	5.2502	1.0655	19.8888	1.2473	0.00555	Syngenite + (goergeyite)	
	2.2513	1.0669	19.8865	1.2717	0.00547	Syngenite + (goergeyite)	
	2.8377	1.9851	19.6327	0.7142	0.00421	Goergeyite	
	6.6443	1.0719	19.8916	1.6082	0.00469	Syngenite	
	6.6428	1.0705	19.8834	1.6349	0.00465	Syngenite	
	4.2334	1.9868	19.6304	1.1261	0.00509	Goergeyite	
	3.8888	1.9913	19.6423	0.8642	0.00467	Goergeyite	
	3.8875	1.9905	19.6437	0.8782	0.00464	Goergeyite	
	1.3742	1.3105	19.8008	0.3829	0.00258	Anhydrite	
	1.3805	1.2846	19.7802	0.3891	0.00268	Anhydrite	
	7.6347	0.0184	19.9908	1.7204	0.00465	Arcanite	
	7.6313	0.0105	20.0080	1.7303	0.00353	Arcanite	
	200	2.1532	1.9920	19.6294	1.3051	0.00547	Anhydrite
		2.1524	1.9904	19.6322	1.3173	0.00556	Anhydrite
4.6054		1.0706	19.7702	0.6488	0.00256	Goergeyite	
4.6040		1.0756	19.7780	0.6578	0.00247	Goergeyite	
5.2523		1.0661	19.8944	1.5009	0.00629	Goergeyite	
5.2528		1.0661	19.8923	1.4985	0.00635	Goergeyite	
2.8372		1.9878	19.6256	0.8203	0.00336	Anhydrite + (goergeyite)	
2.8382		1.9872	19.6288	0.8173	0.00342	Anhydrite + (goergeyite)	
6.6441		1.0717	19.8856	1.9836	0.00850	Goergeyite	
6.6451		1.0704	19.8928	1.9026	0.00830	Goergeyite	
1.9872		1.9872	19.6259	1.1199	0.00456	Goergeyite	
1.9868		1.9868	19.6278	1.1327	0.00465	Goergeyite	
7.3328		1.1041	19.7090	1.9296	0.008833	Ca-palmierite + (goergeyite)	
7.3356		1.1015	19.7018	1.9801	0.008761	Ca-palmierite + (goergeyite)	
4.2366		1.9853	19.6978	1.1164	0.004837	Goergeyite	
4.2372		1.9878	19.6913	1.1470	0.004794	Goergeyite	
1.3961		2.5334	19.5880	0.4188	0.001709	Anhydrite	
1.3957	2.5420	19.5800	0.4171	0.001775	Anhydrite		
10.0170	0.0272	20.0180	2.0665	0.008091	Arcanite		
10.0176	0.0272	20.0064	2.0107	0.008348	Arcanite		
9.7733	2.3631	19.8565	0.2741	0.001244	Anhydrite		
9.8129	2.3630	19.8520	1.7406	0.007546	Goergeyite		

Table 5. Equilibrium phase composition in the system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ at 150 and 200°C.

T (°C)		Starting material (g)			Saturated solution (mol/kg H ₂ O)		Solid phase and glaserite composition (K ₂ SO ₄ :Na ₂ SO ₄)	
		Na ₂ SO ₄	K ₂ SO ₄	Room temperature solution		Na ₂ SO ₄		K ₂ SO ₄
				Saturated of Na ₂ SO ₄	Saturated of K ₂ SO ₄			
150	b	6.7598–1:1		12.5880	9.5328	1.7970	1.3439	Glaserite 2.37
	a	3.0356	3.7245	12.6075	9.5498	1.9203	1.4105	Glaserite 2.39
	b	8.0004–1:1		12.5880	9.5328	2.1312	1.3053	Glaserite 2.04
	a	3.5931	4.4075	12.6020	9.5320	2.1828	1.3202	Glaserite 2.01
	b	8.0011–2:1		12.6666	9.5377	1.5585	1.4574	Glaserite 2.20
	a	2.3162	5.6838	12.6622	9.5438	1.5618	1.3805	Glaserite 2.54
	b	7.0027–3:1		9.0593	15.0683	0.9690	1.5506	Glaserite 2.83
	a	1.4951	5.5066	9.0770	15.0595	1.0135	1.5792	Glaserite 3.20
	b	8.2786–3:1, 2:1		6.7860	14.9932	0.9737	1.5866	Glaserite 2.77
	b	8.4284–1:2, 1:1		6.3671	15.0578	2.0642	1.3158	Glaserite 2.42
	a	—	7.0005	3.0242	20.0004	0.2317	1.7894	Arcanite
	a	—	6.9843	—	22.6717	0	1.7547	Arcanite
	a	8.5403	—	10.1709	10.8725	3.1263	0.3957	Thenardite
	a	12.6172	—	—	19.7565	3.0950	0.6633	Thenardite
	b	10.0296–1:3		15.0154	9.1911	3.2164	1.1262	Glaserite + thenardite
	b	8.0020–1:1		12.5727	9.6478	2.2326	1.2642	Glaserite 2.25
	b	8.0748–3:1		3.1942	20.6751	0.6457	1.8319	Glaserite 2.96
	b	8.0019–2:1		12.7546	9.5731	1.6599	1.3604	Glaserite 2.50
	a	10.9126	—	—	19.5658	3.1299	0.7142	Thenardite
	a	7.2893	—	29.7656	—	2.9693	0	Thenardite
	a	—	7.0240	4.9848	15.3099	0.5423	1.8586	Arcanite
	a	—	7.1575	21.5133	—	2.1095	1.2306	Glaserite 2.22
	b	8.0300–3:1		3.0529	20.0067	0.5986	1.8354	Glaserite 2.97
	b	8.0588–2:1		11.3539	13.3663	1.3132	1.4762	Glaserite 2.51
	a	—	8.4156	—	20.1688 ^w	0	1.7874	Arcanite
	b	11.0775–1:3		9.5050	14.0544	3.0420	1.1312	Glaserite 1.31
	a	10.9958	—	—	19.9300	3.1734	0.8954	Thenardite
	a	7.8097	3.1969	5.2909	17.0922	2.9017	1.1347	Glaserite 1.36
	a	7.0927	2.9063	13.4338	11.1445	3.2863	1.1587	Glaserite
	a	3.5961	4.4087	13.7624	8.3896	1.9940	1.1465	Glaserite 2.04
	a	7.8069	3.1958	15.2100	8.0382	3.2274	1.1353	Glaserite + thenardite
200	a	10.3198	—	—	19.6134	3.6329	0.7370	Na ₂ SO ₄ (III)
	a	7.2490	—	22.6018	—	3.2178	0	Na ₂ SO ₄ (III)
	a	—	8.0275	21.3205	—	1.5014	1.8696	Glaserite 2.34
	a	—	8.2247	5.0039	15.0104	0.4746	2.2484	Arcanite
	b	9.0894–3:1		3.4057	18.9521	2.3322	1.7356	Glaserite 2.06
	b	9.0034–1:1		11.6608	12.6662	0.7839	2.2227	Glaserite 2.91
	a	10.1660	—	—	18.0561 ^w	3.2696	0	Na ₂ SO ₄ (III)
	b	10.0488–1:3		—	20.0660	2.8625	1.6188	Glaserite 2.60
	b	9.4207–2:1		11.0448	12.9762	1.5489	1.8786	Glaserite 2.91
	b	9.6412–3:1		8.8289	14.9974	1.1721	2.1577	Glaserite 2.52
	a	10.1302	—	3.0700	17.0047	3.5181	0.6004	Na ₂ SO ₄ (III)
	a	—	7.5100	2.5651	17.5100	0.1458	2.0700	Arcanite
	a	—	9.6905	—	20.1521	0	2.1043	Arcanite
	a	—	9.0354	17.5169	3.9616	0.8295	2.2424	Glaserite 2.95
	a	11.0606	1.0517	—	19.4494	3.7252	0.9877	Na ₂ SO ₄ (III)
	a	13.0018	2.2939	—	19.5423	3.9225	1.3861	Na ₂ SO ₄ (III)
	a	—	8.9987	11.1287	10.0665	0.6859	2.3887	Arcanite
	a,b	7.800–1:3 +						
		1.6179	3.9614	10.0359	9.9772	2.9981	1.6206	Glaserite 1.31
	a	12.0053	3.5206	—	19.4490	3.7930	1.3434	Glaserite + Na ₂ SO ₄ (III)
	a	10.2422	3.7834	10.0030	10.0008	3.8028	1.3318	Glaserite + Na ₂ SO ₄ (III)
	ab	9.2268–1:3 +						
	a,b	—	3.8046	12.1200	12.1200	3.7709	1.3359	Glaserite + Na ₂ SO ₄ (III)
	a	7.1474	1.9420	2.7500	19.8652	0.7131	2.2812	Glaserite 2.74

w: water was used instead of room temperature saturated K₂SO₄-solution.

^a Pure K₂SO₄ and pure Na₂SO₄ were used as starting materials.

^b Quenched mixtures with indication of molar ratio K₂SO₄:Na₂SO₄ were used as starting materials.

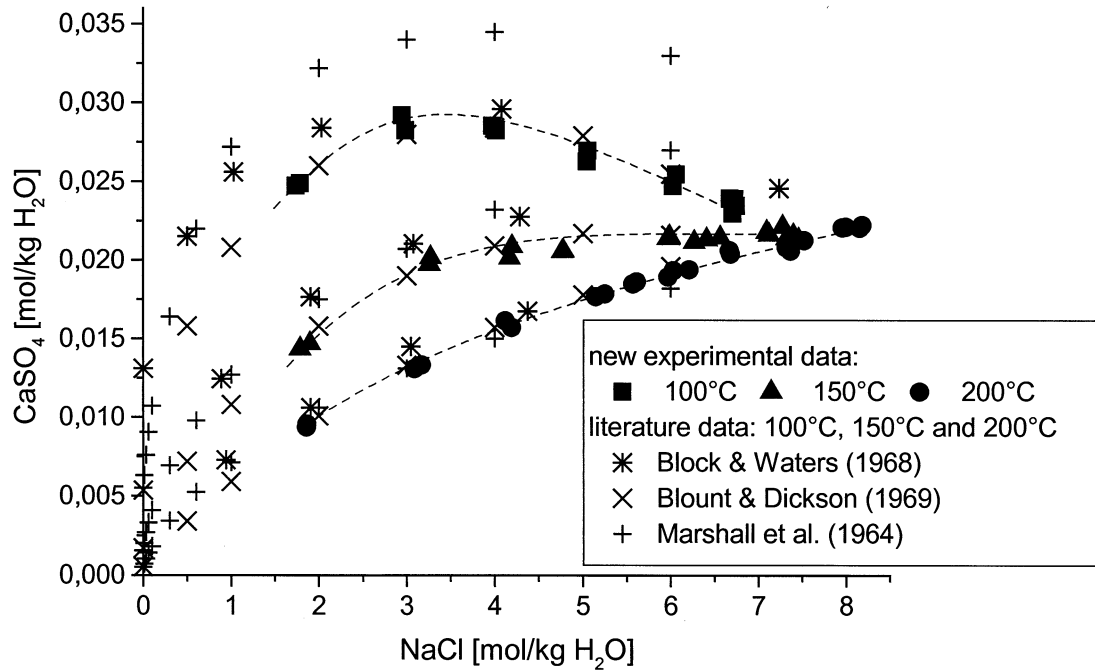


Fig. 5. Anhydrite solubilities in sodium chloride solution at 100, 150 and 200°C.

with both temperature and K_2SO_4 aqueous concentration. The solubility of goergeyite decreases with increasing temperature. Since at the same time the crystallization field of goergeyite is extended and shifted toward higher concentrations of K_2SO_4 , higher solubilities are achieved on this side at increased temperatures. Extrapolation of the 150°C isotherm yields a virtual

crossing-point with the 200°C isotherm at 1.4 mol/kg H_2O K_2SO_4 , where the temperature coefficient of solubility becomes positive.

The solubility of syngenite increases continuously and its stability field becomes smaller. Near 200°C syngenite disappears and a new phase was found. Ion chromatographic anal-

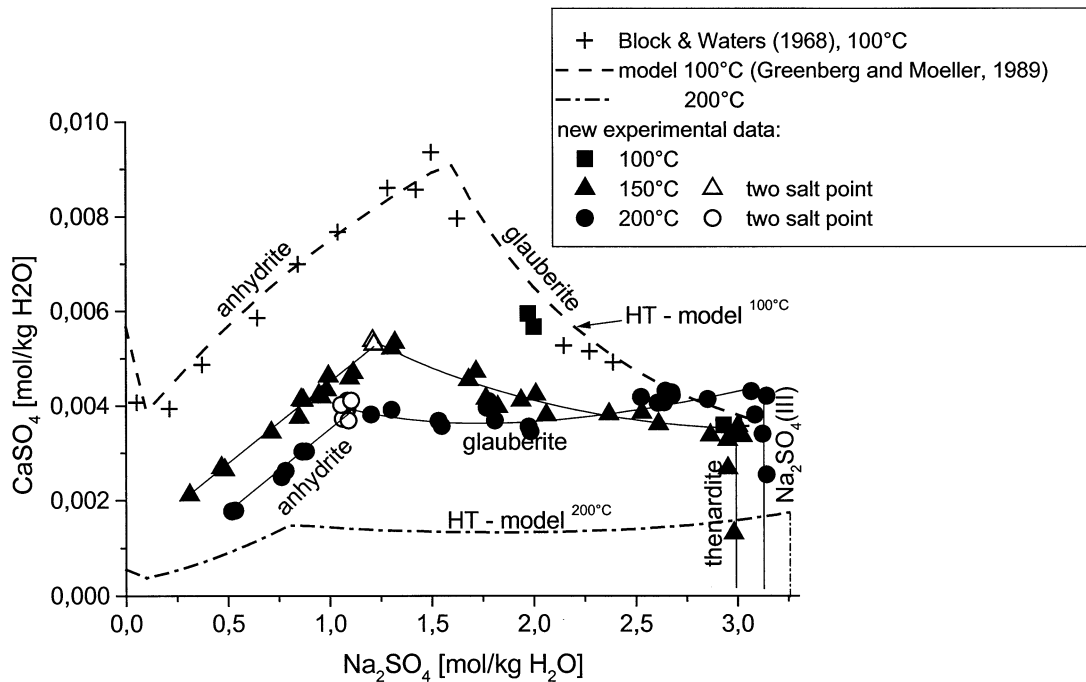


Fig. 6. Solubilities in Na_2SO_4 - $CaSO_4$ - H_2O system at 100, 150 and 200°C.

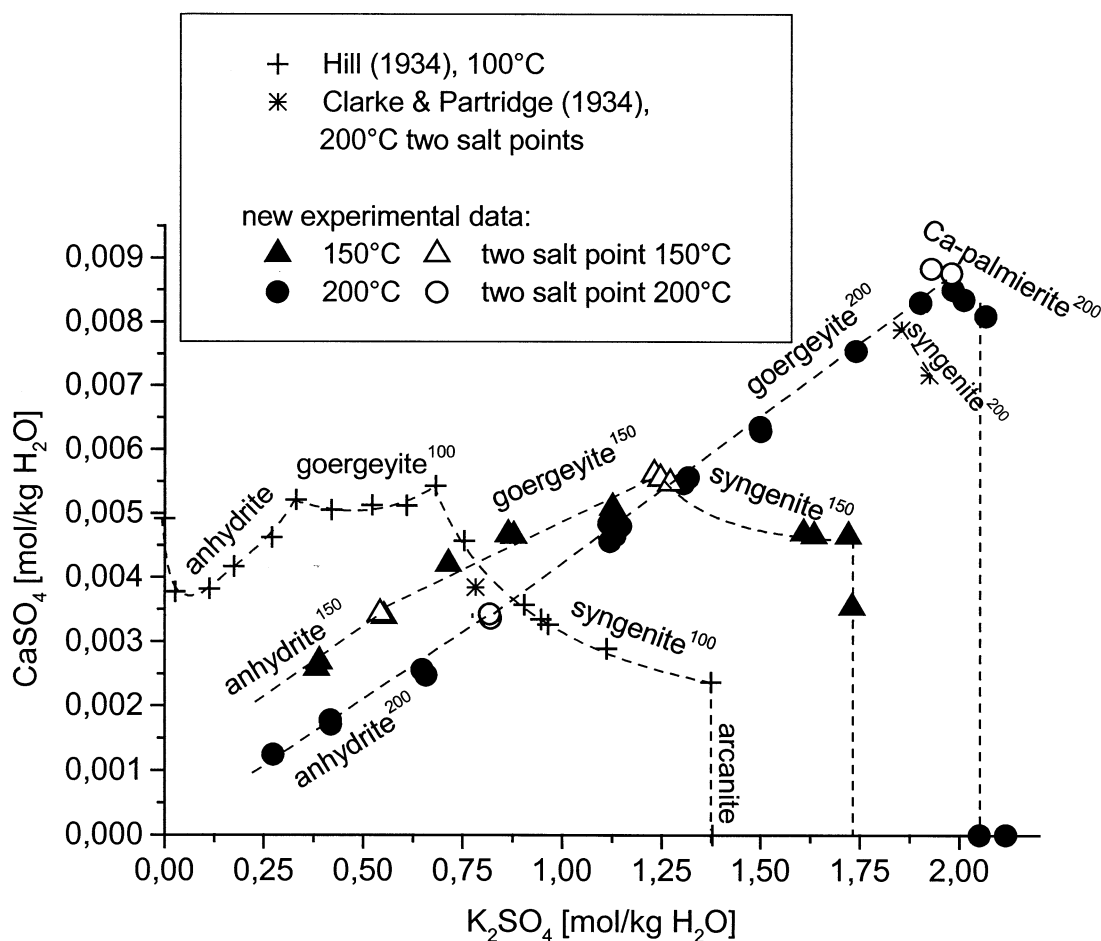


Fig. 7. Solubilities in the system K_2SO_4 - $CaSO_4$ - H_2O at 100, 150 and 200°C.

ysis yielded a K^+/Ca^{2+} ratio of 1:1. From a single crystal structure analysis an unit cell of monoclinic space group $C 2/c$ and $Z=8$ formula units $K_2SO_4 \cdot CaSO_4$ has been derived (Freyer et al., unpublished data). The lattice parameters were determined to be $a=7.510(2)\text{\AA}$, $b=21.856(4)\text{\AA}$, $c=9.237(2)\text{\AA}$ and $\beta = 113.24^\circ$. The new double salt is isostructural with the palmierite ($K_2SO_4 \cdot PbSO_4$) and it can thus be considered as a calcium palmierite. Probably the phase replacement of syngenite by calcium palmierite occurs a few degrees $< 200^\circ\text{C}$, only. Clarke and Partridge (1934) reported the two salt points goergeyite/syngenite and syngenite/arcanite at 200°C , however at lower K_2SO_4 and $CaSO_4$ concentrations. This suggests that the temperature in their experiment was lower, possibly between 180 and 190°C . Consequently, syngenite disappears between 190 and 200°C . At present our data do not allow us precisely to localize the crystallization range of the calcium palmierite. Only experiments at temperatures $>200^\circ\text{C}$ will clarify the situation.

3.4. System Na_2SO_4 - K_2SO_4 - H_2O

Solubilities in the system Na_2SO_4 - K_2SO_4 - H_2O are given by Yanateva et al. (1963) at 100°C and by Itkina and Kokhona (1956) at 150°C . Our data are listed in Table 5 and plotted in

Figure 8. We found $\sim 4\%$ higher solubilities than Itkina and Kokhona (1956) for arcanite and glaserite in the region, rich in K_2SO_4 . On the Na_2SO_4 rich side the data agree well.

Glaserite solubility increases with temperature (Fig. 8), but its stoichiometry varies with temperature and solution composition as can be recognized from Figure 9. Our solid solution compositions at 150°C are quite different from those of Itkina and Kokhona (1956). The latter reported ratios $K_2SO_4/Na_2SO_4 > 3.0$, which are not possible according to the substitution sites available in the crystal structure of glaserite (Okada and Osaka, 1980).

According to the phase diagram of the anhydrous system $Na_2SO_4 - K_2SO_4$ (Eysel, 1973) the K_2SO_4/Na_2SO_4 ratio in the glaserite solid solution varies between 0.8 and 2.8 at 100°C . With increasing temperature more sodium sulfate can be dissolved in the solid phase and the ratio is extended from 0.4 to 2.7 at 200°C . At room temperature the glaserite solid solution possesses a small composition range (ratio between 2.4 and 3.0), only. Natural glaserite minerals show compositions within this small range, mostly near to $3 K_2SO_4 \cdot Na_2SO_4$. So, the phase with a 3:1 ratio is denoted as the "ideal" or "common" glaserite.

The glaserite compositions in the aqueous system deter-

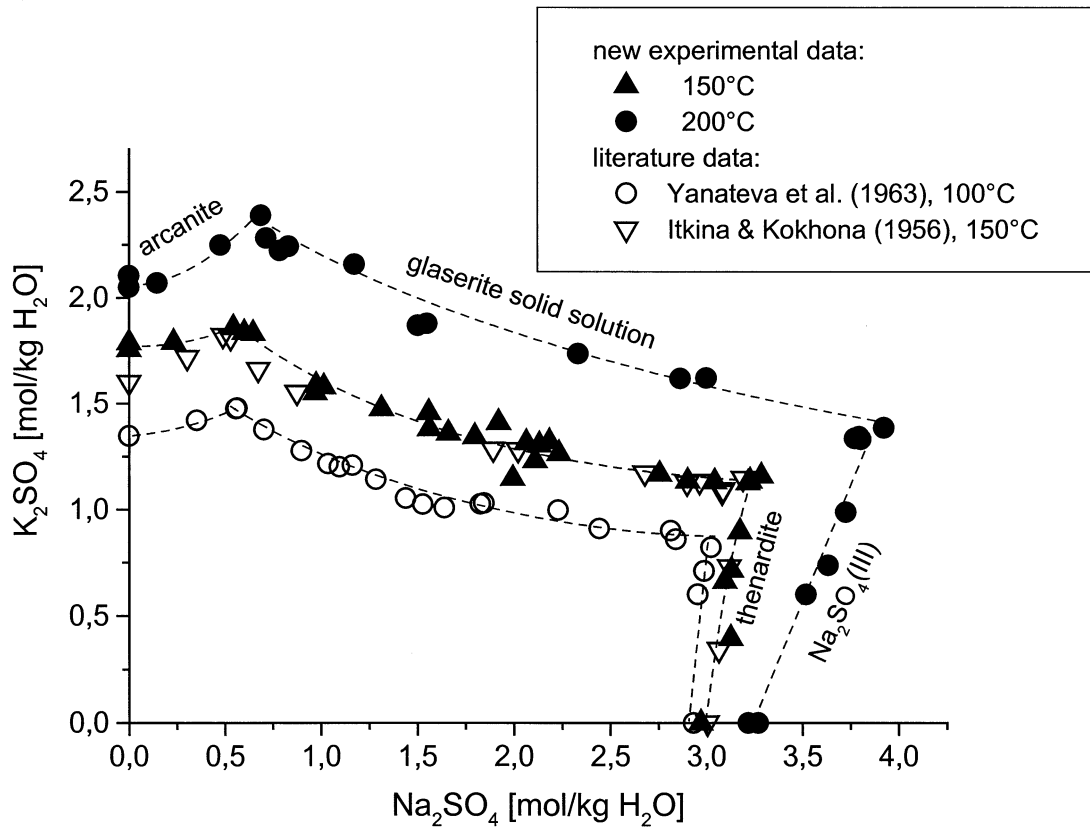


Fig. 8. Solubilities in the system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ at 100, 150 and 200°C.

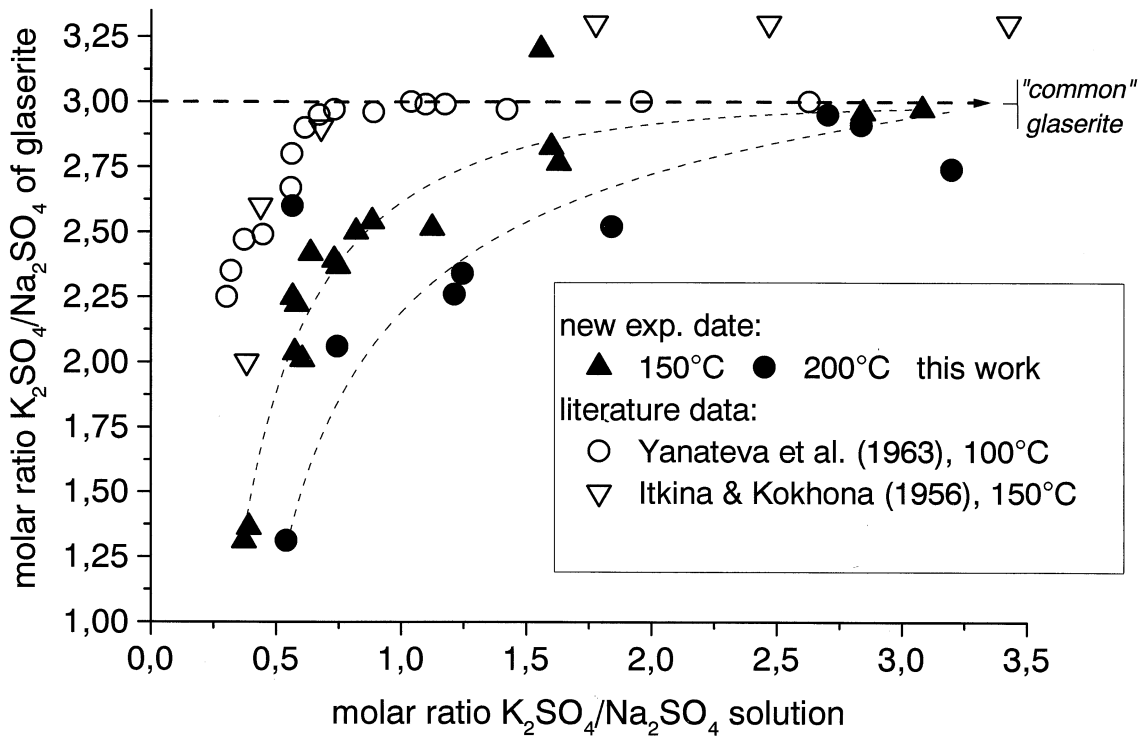


Fig. 9. Glaserite solid solution in dependence on composition of solution at 100, 150 and 200°C.

mined by Yanateva et al. (1963)) at 100°C together with our data reveal clear trends. At a constant aqueous solution ratio of K_2SO_4/Na_2SO_4 the glaserite solid solution becomes richer in Na_2SO_4 with increasing temperature. The range of aqueous solution compositions where glaserite has approximately an ideal 3:1 ratio shrinks drastically above 100°C. In the K_2SO_4 richest aqueous solution the glaserite composition reached nearly the "ideal" value of glaserite.

4. SUMMARY

Sulfate mineral solubilities of the oceanic salts system were investigated in the ternary sulfate subsystems Na_2SO_4 - $CaSO_4$ - H_2O , K_2SO_4 - $CaSO_4$ - H_2O , Na_2SO_4 - K_2SO_4 - H_2O , and in the system $NaCl$ - $CaSO_4$ - H_2O at 150 and 200°C. At 100°C consistency with literature data was checked at selected fluid compositions.

As a result of this work reliable solubility data for glauaberrite are now available up to 200°C. Normally the solubility for anhydrite and glauaberrite decreases with increasing temperature. However, now it can be stated that at very high salt concentrations this dependence is reversed. In the system K_2SO_4 - $CaSO_4$ - H_2O stable fields of syngenite and goergeyite were determined and a new double salt $K_2SO_4 \cdot CaSO_4$, with a palmierite structure was found. Glaserite solubility and stoichiometry were investigated as a function of composition were at 150 and 200°C in the system Na_2SO_4 - K_2SO_4 - H_2O systematically. Solubility data for anhydrite in concentrated sodium chloride solution were completed up to saturation of $NaCl$ at 100, 150 and 200°C.

The new data provide a basis to improve the present high temperature model for the five-component system Na - K - Ca - Cl - SO_4 - H_2O (Greenberg and Møller, 1989) and to develop a new model for the hexary sea water system Na - K - Mg - Ca - Cl - SO_4 - H_2O in combination with the high-temperature data base for the magnesium-containing system Na - K - Mg - Cl - SO_4 - H_2O (Voigt, 1999).

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