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Title	Mineral precipitations and hydrochemical evolution of brines in graduation towers
Authors	Ostwald, Laura-Jane;Banning, Andre
Publication date	2021-04-15
Original Citation	Ostwald, L. J. and Banning, A. (2021) 'Mineral Precipitations and Hydrochemical Evolution of Brines in Graduation Towers', Environmental Processes, 8 (2), pp. 729–746. doi: 10.1007/s40710-021-00511-5
Type of publication	Article (peer-reviewed)
Link to publisher's version	https://link.springer.com/article/10.1007%2Fs40710-021-00511-5 - 10.1007/s40710-021-00511-5
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Download date	2026-11-17 14:08:48
Item downloaded from	https://hdl.handle.net/10468/12336

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Mineral Precipitations and Hydrochemical Evolution of Brines in Graduation Towers

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Abstract

The purpose of this study is to examine hydrochemical changes of saline groundwater and precipitation of mineral phases during evaporative graduation processes. Therefore, concentrated brines and mineral precipitates were sampled at four graduation towers with differing evaporation approaches. Solid phase compositions were qualitatively and quantitatively analysed. Hydrochemistry changes of dissolved ion concentrations during successive evaporation was assessed by comparing natural with concentrated brines. PHREEQC was used to simulate sequence and quantity of mineral precipitates. Finally, a prognosis for expected precipitations of a newly built graduation tower was made using PHREEQC modelling.

The identified mineral phases included calcite, aragonite, gypsum and halite in varying proportions. Concentrations of all investigated ions (except bicarbonate) increase, eventually leading to supersaturation and sequential precipitation of evaporite minerals. Modelled saturation indices show that calcite is the first and halite is one of the last precipitating phases

at all sites. Further calculated precipitates include the carbonates dolomite, siderite and strontianite; manganese oxide and hematite; and the sulphates baryte, celestine and gypsum which precipitate depending on local hydrogeochemistry and graduation conditions. Calculated precipitation quantities reach a maximum of 48.6 g/L of applied natural brine at an evaporation grade of 90%. After 25 years, the total expected mass of precipitates at the new graduation tower is about 34.4 t for a graduation process up to a salt content of 19%, and about 356 t for a permanent evaporation grade of 90%.

Article Highlights

- Except for bicarbonate, concentrations of all ions increase to different degrees.
- Mineral precipitations are composed of calcite, aragonite, gypsum and halite.
- Modelled precipitation sequence: carbonates, sulphates, chlorides.
- Modelled precipitation amounts: max. 48.6 g/L for natural brine at 90% evaporation.
- 25 y precipitation forecast for new graduation tower: max. 356 t at 90% evaporation.

Keywords: graduation tower, saline groundwater, concentrated brine, Münsterland Cretaceous Basin, Germany, evaporite mineralogy

1 Introduction

The saline groundwater of the Münsterland Cretaceous Basin, which has been pumped and used for several centuries, is concentrated in some health resorts by graduation towers, i.e., evaporation (Himstedt et al. 1907; Käß and Käß 2008). This leads to a hydrochemical change in the natural brine and to the precipitation of various mineral phases on the brushwood used as precipitation surface. These precipitates are also called thornstone. In the past, graduation

48 towers were mainly used for salt production. Nowadays, they are mostly used for constitutional
49 open-air inhalation because the increasing concentration of brine by graduation creates a
50 seaside-like climate in its surroundings. Graduation towers are present in several health resorts
51 in Germany, but also in Poland and Austria (GLA NRW 1995; Käß and Käß 2008; GD NRW
52 2016; Kalwasińska et al. 2018). Outside the Münsterland Cretaceous Basin, brines in graduation
53 towers are used for balneological purposes at several locations mainly in central and western
54 Germany, e.g., the edges of the Taunus and Spessart mountain ranges, Hesse (Schäffer and Sass
55 2016; Schäffer et al. 2018). Chruszcz-Lipska et al. (2021) statistically assessed 248 medicinally
56 certified natural waters (partly used in graduation towers) in Polish health resorts and discussed
57 the problem of partly elevated boron concentrations. Halaj (2015) analysed the geothermal
58 potential of waters used in some recreational centres in Poland. Until today, graduation towers
59 represent an important contribution to public health. This is underlined by the new construction
60 of the graduation tower in Bad Sassendorf at the edge of the Münsterland Cretaceous Basin
61 (Bredensteiner 2020), which was completed in 2019.

62 Several investigations have been carried out for the two health resorts Ciechocinek and
63 Inowroclaw in Poland, where aerosols are produced by graduation towers (Nienartowicz et al.
64 2011; Krzyaniak-Sitarz 2012; Burkowska-But et al. 2014; Kalwasińska et al. 2018). These
65 studies dealt with the influence of aerosols on the microbiological air quality, the microbial
66 composition of the concentrated brine and the influence on the soils and flora in the area of the
67 graduation towers. Among other things, they show that aerosols have a positive influence on
68 air quality and can also influence soil composition. A correlation was established between the
69 aerosols of the graduation towers in health resorts and a reduced microbiological contamination
70 in the air. The diversity and number of archaeal and bacterial communities increase due to the
71 graduation process in the brine (Nienartowicz et al. 2011; Krzyaniak-Sitarz 2012; Burkowska-
72 But et al. 2014; Kalwasińska et al. 2018). Graduation towers and their surroundings can also

73 host a rich variety of bryophytes and halophytes due to heterogeneous substrates and a stable
74 gradient of salinity in the landscape (Gugnacka-Fiedor 2011).

75 The thornstone that forms from mineral precipitation on the brushwood must be removed if a
76 graduation tower is operated for a long period of time. Otherwise, the functionality will be
77 impaired and the graduation tower may even collapse. This restoration is time-consuming and
78 expensive, as the encrusted brushwood bundles have to be removed and replaced by new ones.
79 So far, no more effective or cheaper method for removing the precipitates has been developed,
80 although research has already been done on a chemical process for removing thornstone
81 (Forbert 2017).

82 There are currently only few investigations on the composition of mineral precipitates
83 (thornstone) at graduation towers in Germany: a study of gypsum crystals forming at the
84 graduation tower in Bad Kösen in eastern Germany (Engelhardt 2015), and some older
85 references such as Roth (1879). To the authors´ best knowledge, there is no published research
86 available on the evolution and quantity of mineral precipitates in graduation towers, which gave
87 rise to the present study.

88 Since the precipitation of the mineral phases at the graduation towers results from concentration
89 increase in the brines due to evaporation of water, the composition of the solid phases together
90 with the hydrochemical change of the natural brines during a graduation process was examined
91 in this work. Besides, the sequence and the amount of the precipitated minerals for the different
92 evaporation steps were determined. The sequence is expected to be the same as for evaporation
93 of seawater (Herrmann et al. 1973). Furthermore, a prognosis was made for the expected
94 amount of mineral precipitation during the next 25 years for a newly built graduation tower in
95 the spa town Bad Sassendorf.

96

97 **2 Study Area**

98 The four investigated sites are located in different parts of the Münsterland Cretaceous Basin
99 (Fig. 1). This is an asymmetrical syncline structure, which consists of a thick Cretaceous
100 sedimentary succession above the Variscan basement (GLA NRW 1995; AD-HOC-AG
101 Hydrogeologie 2016).

102 Hydrogeologically, the Münsterland Cretaceous Basin can be regarded as a more or less closed
103 groundwater basin in the northwestern part of Germany. This can be subdivided into three parts:
104 the shallow pore aquifer is separated from the lower karst aquifer by the almost impermeable
105 marly Emscher Formation (GLA NRW 1995; AD-HOC-AG Hydrogeologie 2016). The shallow
106 pore aquifer is an isolated sand and gravel layer formed above the Emscher formation. This
107 aquifer consists of Santonian sand layers and sands and gravels of the Quaternary. The
108 underlying Emscher formation was formed from Coniacian to Lower Campanian. There is a
109 local hydraulic connection between the upper and lower aquifer only in the peripheral area of
110 the Münsterland Cretaceous Basin because of the absent Emscher formation. The lower aquifer
111 consists of limestone and marlstone, and was formed in the period from Cenomanian to Lower
112 Coniacian. It crops out along the edges of the Cretaceous Basin. In this area, meteoric water
113 infiltrates through local karst formations to form karst groundwater. It emerges from springs
114 along the Emscher formation boundary (GLA NRW 1995; AD-HOC-AG Hydrogeologie 2016).

115 The deep parts of the Cretaceous Basin are filled with saline water, which emerges at its
116 perimeter. This saline water is diluted by mixing with infiltrated meteoric water (GLA NRW
117 1995; Käß and Käß 2008; AD-HOC-AG Hydrogeologie 2016; Wisotzky et al. 2018).

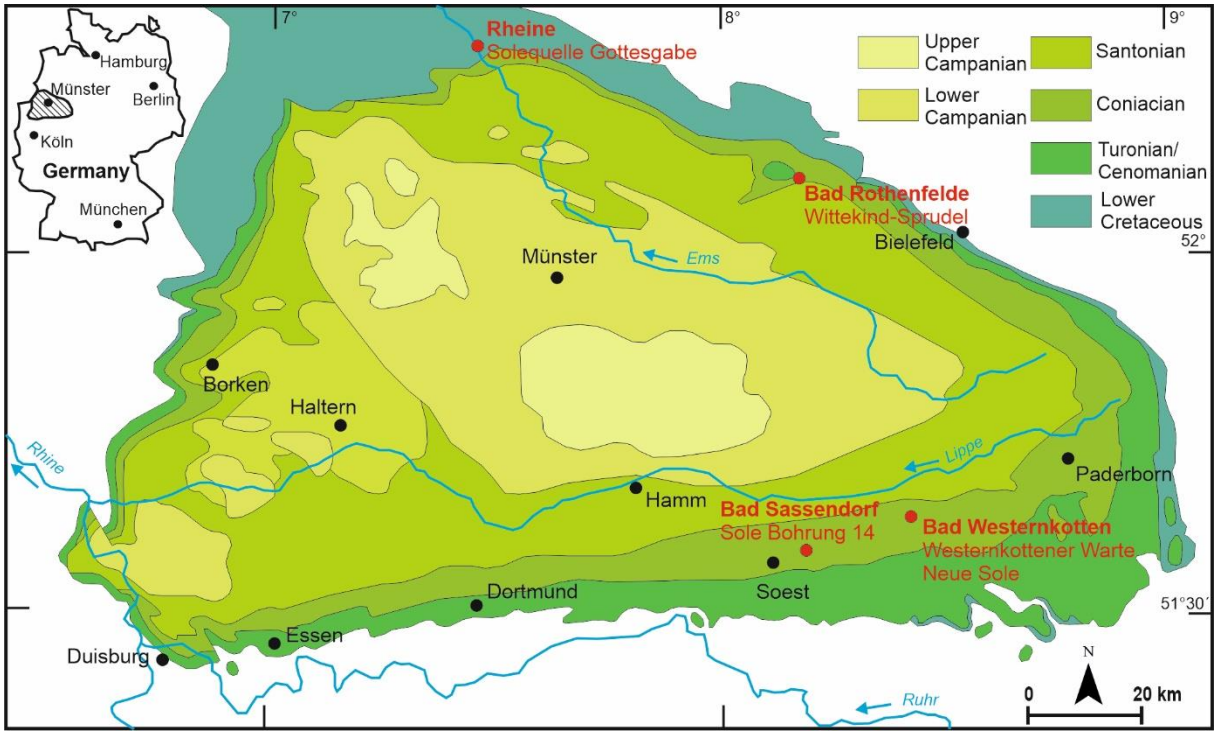


Fig. 1 Location of the study area in Germany (upper left corner) and geological map of the Münsterland Cretaceous Basin with the studied sites and the names of the extracted and used brines on site in graduation towers (red) (modified after Banning et al. 2013)

The origin of the brine of the Münsterland Cretaceous Basin could not yet be clearly identified. It is assumed to result from several processes such as water-rock interaction, migration and mixing of waters of different origin during the geological development (Grobe and Machel 2002).

On the basis of water analyses for the used natural brines (cf. Fig. 1) and the study of Grobe and Machel (2002), it can be seen that all brines have a higher total dissolved solids content than seawater. Nevertheless, these contents vary considerably depending on the location. Rheine has the lowest value with approximately 38500 mg/L and the natural brine used in graduation tower 1 at Bad Westernkotten site has the highest value with almost 82000 mg/L.

133 The share of Na^+ and Cl^- in the total ion concentration is over 90% in each natural brine. Other
134 ions are Ca^{2+}, Mg^{2+} and HCO_3^-. The concentration of HCO_3^- in Bad Rothenfelde is substantially
135 higher than at the other locations. SO_4^{2-} is found in all brines with the exception of Rheine and
136 shows the highest concentration with a value of 1930 mg/L for the Bad Rothenfelde site.
137 Furthermore, the brines have a high content of free dissolved CO_2: 2470 mg/L in the natural
138 brine of Bad Rothenfelde and 1190 mg/L in Bad Sassendorf. The natural brines in Bad
139 Westernkotten have a CO_2 concentration of 1225 mg/L.

140 A high content of free dissolved CO_2 is typical for the brines from the Münsterland Cretaceous
141 Basin (GLA NRW 1995).

142

143 # 3 Materials and Methods

144 ## 3.1 Sampling and Analyses

145 A total of 19 solid phases and 6 concentrated brines were sampled to investigate the
146 precipitation and brines in the graduation towers (Table 1).

147

148 Table 1: Sampled solid phases and concentrated brines for the Bad Rothenfelde, Rheine and
149 Bad Westernkotten sites (✓ sample was taken or × sample was not taken)

	Bad Rothenfelde			Rheine	Bad Westernkotten	
	Section 1	Section 2	Section 3		Graduation tower 1	Graduation tower 2
Concentrated brine	✓	✓	✓	✓	✓	✓
Solid phase						
white	✓	✓	✓	✓	✓	✓
beige	✓	✓	✓	✓	✓	✓
reddish	✓	✓	×	×	✓	✓

greenish	×	✓	✓	×	✓	×

150

151 Physico-chemical parameters (pH, electrical conductivity, redox potential, temperature,
152 dissolved oxygen) and organoleptic characterization were carried out on site during sampling.
153 The measurement of pH, electrical conductivity and temperature were carried out using a WTW
154 340i handheld pH/Cond Meter. A WTW 340i with a Ag/AgCl probe was used to measure
155 oxidation-reduction potential (ORP, subsequently converted to standard hydrogen electrode
156 (SHE) corrected Eh and pe for PHREEQC modelling), and a WTW Oxi197 was used to
157 measure dissolved oxygen concentrations. Samples for cation and anion analyses were
158 subjected to 0.45 µm filtration on site. Concentrated HNO_3 was added to the samples for cation
159 analysis as a stabilising agent. The samples were stored dark and cool until laboratory analysis.

160 Samples were taken from both graduation towers at the Bad Westernkotten site and from the
161 western part of the graduation tower at the location Rheine. In Bad Rothenfelde, brines and
162 solid phases were sampled for each of the three sections of the new graduation tower.

163 The precipitated mineral phases show vertically running colour zones along the brushwood
164 walls (Fig. 2), which served as selection criteria for sampling (Table 1 and Table 2). The
165 coloured zones indicate that the already crystallised phases serve as crystal nucleus upon
166 contact with the supersaturated solution. This nucleation contact leads to overcoming kinetic
167 inhibition, and thus, to precipitation of the corresponding phase (Reznik et al. 2009; Scholz and
168 Kahlert 2018). The concentrated brines were sampled in the lower part of the brushwood walls.
169 Photos of the sampled precipitates were taken on site. These are shown in Fig. 2 for selected
170 solid phases of the graduation tower in Bad Rothenfelde.

171 The sampled precipitates from the graduation towers were pulverised after drying in an agate
172 mortar and analysed by powder X-ray diffraction using PANalytical Empyrean instrumentation.
173 The computer program Match! Version 3.8.3.151 (Putz 2019) with the database COD inorganic

174 compounds only was used for the qualitative evaluation of the diffractograms. The program
175 compares the diffraction pattern of the analysed sample with the reference patterns in the
176 database, whereby the peak intensities and positions are considered. The quantitative analysis
177 was carried out by Rietveld refinement with the program FullProf Version 7.20 implemented
178 in Match! (Putz 2019). The detection limit for X-ray diffraction analysis is different for each
179 mineral and depends, among other things, on the crystal structure and crystallinity. The
180 approximate detection limit is 0.5% to 5% for a total rock analysis of sedimentary rocks
181 (Petschick 2002). Concentrations of anions and cations of the concentrated brines were
182 determined by ion chromatography. For cation analysis, the Dionex DX-500 and for anion
183 analysis, the Dionex ICS-1000 Ion Chromatography System were used. As the ion
184 concentrations were above the load limits of the columns, samples were previously diluted in a
185 ratio of 1:200 to 1:10000. Bicarbonate concentrations were determined by titration with 0.1 M
186 HCl in the laboratory, directly upon returning from the field.



Fig. 2 Top: sampling points for the concentrated brine (white arrow) and for the solid phases (white points). Bottom: (a) white, (b) beige and (c) reddish precipitates of the new graduation tower in Bad Rothenfelde (length 412 m (Käß and Käß 2008) and height 10 m (Elsner 2016)).

3.2 Hydrogeochemical Modelling with PHREEQC

The hydrogeochemical computer program PHREEQC Interactive Version 3.5.0.14000 (Parkhurst and Appelo 2013) with the database pitzer.dat (a database for the specific-ion-

interaction model of Pitzer (Pitzer 1973) as implemented in PHRQPITZ (Plummer et al. 1988) was used to model the processes occurring during a graduation process. Hydrochemical data of the natural brines were applied for the modelling. Bicarbonate concentrations were put in as alkalinity. The pH from the water analysis of Bad Sassendorf was slightly increased from 5.79 to 5.98 for modelling to adjust the concentration of dissolved carbon dioxide and bicarbonate to the values of the analyses. As the extent of analysis was not the same for all sites, the Eh value from Bad Sassendorf was used for the unquantified redox conditions of the locations Bad Westernkotten and Rheine. The respective ORP/Eh values were converted to pe and added to the input file. When modelling with the Pitzer database implemented in PHREEQC, pe of the initial solution was used for each modelling step. In contrast to that, when modelling with phreeqc.dat, the pe value entered in the initial solution is overwritten with a new pe for each evaporation step. Therefore, an assumption for pe was made for the modelling with pitzer.dat based on the pe values modelled with the standard PHREEQC database. Because the ionic strength was either already greater than 1 mol/L in the natural brine or reached this value after the first evaporation steps, the Pitzer database was used for modelling (Parkhurst and Appelo 2013). The mineral phases and ions, which are not included in the Pitzer database, have been added through the supplement of thermodynamic information from the database wateq4f.dat (a database file derived from WATEQ4F, Ball and Nordstrom 1991). The graduation process was simulated by stepwise evaporation of water using the keyword REACTION. Contact with the atmosphere was simulated by equilibrating with atmospheric oxygen and carbon dioxide (keyword EQUILIBRIUM_PHASES). The mineral phases selected for batch reaction modelling (keyword EQUILIBRIUM_PHASES) were chosen based on the dissolved ions found in the natural brines of the respective location, and allowed to precipitate. These were modelled according to the evaporation sequence of seawater as mineral phases of carbonates, sulphates and halite (Herrmann et al. 1973). Furthermore, the precipitation of the minerals indicated in the literature for thornstone (Roth 1879) was modelled. Amounts of precipitating

minerals were read from the output file for the respective evaporation step. The evaporation step of 90% was chosen because halite was detected in the precipitates of the graduation towers and precipitates at this evaporation grade at all locations. Additionally, the evaporation step was selected for a salt content of 18%-19%. In the past, brine was considered as "suitable for boiling" starting from 18%, and was therefore at least concentrated to this salt content (Schulze-Seeger 1988). The salt content was calculated from the modelled sodium content and the modelled density of an evaporation step.

In order to convert the total mass of mineral precipitates to kg/d, the amount of natural brine evaporating per day is required. This is based on a daily evaporation of 25000 L of natural brine for hot days for a graduation tower in Bad Dürkheim, SW Germany, with a length of 330 m and a height of 18 m (Pfenning 2014). Out of this, assumptions were made for the investigated graduation towers considering their dimensions: for the graduation tower at the site Rheine (length approx. 35 m (Käß and Käß 2008) and height approx. 7.50 m (Stockmann and Stockmann 1998)), an evaporation of 1105 L/d; for Bad Rothenfelde (length 412 m (Käß and Käß 2008) and height 10 m (Elsner 2016)), an evaporation of 17340 L/d; for Bad Westernkotten graduation tower 1 (length 120 m and height 12.5 m (Käß and Käß 2008)), an evaporation of 6313 L/d; and for graduation tower 2 (length 58 m and height 13 m (Käß and Käß 2008)), an evaporation of 3173 L/d.

An evaporation of 3072 L/d is assumed for the modelling of the new graduation tower in Bad Sassendorf (length 73 m and height 10 m (Bredensteiner 2020)). In addition, the total amount of mineral precipitation per year and for 25 years is calculated at this location. Since the quantities of the precipitating mineral phases for the forecast are extrapolated to 25 years, the modelling for an annual average temperature of 11 °C (Führer 2020) was carried out for the Bad Sassendorf site.

4 Results and Discussion

4.1 Composition of the Mineral Precipitation

Table 2 shows results of powder X-ray diffraction and the composition of sampled precipitated mineral phases. Solid samples from Rheine consist of the minerals halite and calcite. Precipitates from the locations Bad Westernkotten and Bad Rothenfelde contain the minerals halite, calcite, gypsum and aragonite.

By classifying results according to the colouration of the sampled solid phases (Table 2), it can be seen that the white samples do not contain calcite or aragonite at any site. They are composed of gypsum and halite. No gypsum was found in the reddish samples. These show high calcite contents instead. Consequently, there is a correlation between the increasing intensity of the reddish colour and increasing calcite content. The reddish or brownish colouration of the mineral calcite may be due to the inclusion of organic matter (Martínez-Pillado et al. 2020) or Fe(III) phases (cf. 4.3).

A comparison of the results for the three sections of the graduation tower in Bad Rothenfelde shows that at least one sample for section 1, 2 and 3 contains halite. The amount of gypsum in the samples increases from section 1 to 3. Only one sample of the first section consists of gypsum (100 wt.%). For the second and third section, gypsum is present in 3 samples for each section. The gypsum content in the samples of section 2 is 65 wt.%, 100 wt.% and 32 wt.%, and of section 3, 65 wt.%, 100 wt.% and 100 wt.%. The carbonates calcite and aragonite are detected for sections 1 and 2, but they are not present in the samples of section 3. This trend corresponds to the evaporation sequence of seawater. The carbonates of lower solubility precipitate before the sulphates as evaporation increases. Finally, the highly soluble chlorides precipitate (Herrmann et al. 1973).

Table 2 Results of powder X-ray diffraction (in % by weight) for the white, beige, reddish and greenish samples of the locations Rheine (R), Bad Westernkotten graduation tower 1 (G1) and 2 (G2) and Bad Rothenfelde section 1 (S1), section 2 (S2) and section 3 (S3)

Sample	**Identified mineral phases (% by weight)**			
	Halite	**Calcite**	**Gypsum**	**Aragonite**
White				
Rheine	100	-	-	-
Bad Westernkotten G1	87.0	-	13.0	-
Bad Westernkotten G2	48.8	-	51.2	-
Bad Rothenfelde S1	-	-	100	-
Bad Rothenfelde S2	35.5	-	64.5	-
Bad Rothenfelde S3	34.7	-	65.3	-
Beige				
Rheine	18.0	82.0	-	-
Bad Westernkotten G1	3.9	-	96.1	-
Bad Westernkotten G2	10.9	84.9	4.2	-
Bad Rothenfelde S1	2.8	39.4	-	57.8
Bad Rothenfelde S2	-	-	100	-
Bad Rothenfelde S3	-	-	100	-
Reddish				
Bad Westernkotten G1	8.6	73.3	-	18.1
Bad Westernkotten G2	4.3	95.7	-	-
Bad Rothenfelde S1	12.7	72.1	-	15.2
Bad Rothenfelde S2	5.7	80.2	-	14.1
Greenish				
Bad Westernkotten G1	33.4	66.6	-	-
Bad Rothenfelde S2	8.4	46.8	32.1	12.7
Bad Rothenfelde S3	-	-	100	-

4.2 Composition and Evolution of the Concentrated Brine

The pH values of the sampled concentrated brines were between 7.3 and 7.9. Electrical conductivities for 25 °C showed values of approximately 110 to 251 mS/cm, thus, they are in the typical range (over 100 mS/cm) for brines (Wisotzky et al. 2018). The redox milieu can be described as oxidizing for all samples (Wisotzky et al. 2018).

A comparison between the concentrations of the constituents of the natural brines and the composition of the concentrated brines shows concentration increases for almost all ions. Only the content of the anion bicarbonate is higher in the natural brine than in the concentrated brine. This is illustrated for selected ions in Fig. 3. The rise in concentration results from the evaporation of water during the graduation process. The difference in increase or possibly even decrease of the ion concentration indicates precipitation of these ions as mineral phases. In the case of bicarbonate, it must also be considered that the increased content of free dissolved carbon dioxide in the natural brine (cf. 2) lead to degassing of CO_2 upon contact with the atmosphere. This results in a shift of the carbonate balance and precipitation of carbonates.

The differences in concentration changes are reflected by the factors in Table 3. For this purpose, the respective ion concentrations in the concentrated brine were divided by the ion concentrations in the natural brine. Potassium shows the greatest concentration increase for all sites, and thus, it has the lowest probability of precipitating. The ions sodium, magnesium and chloride also show a significant increase in concentrations with a high factor. The concentrations of calcium and sulphate rise by the smallest factor. Section 1 in Bad Rothenfelde is an exception. Here, the factor of sulphate is slightly higher than that of chloride. Bicarbonate shows decreasing concentrations for all sites. The two graduation towers in Bad Westernkotten and sections 2 and 3 in Bad Rothenfelde have the smallest factor (Table 3).

298 **Table 3** Calculated factors for the concentration change of ions in the natural brines and
299 concentrated brines for the locations Bad Westernkotten graduation tower 1 (G1) and 2 (G2),
300 Rheine (R) and Bad Rothenfelde sections 1 (S1), 2 (S2) and 3 (S3)

Location	**Cations (mg/L)**				**Anions (mg/L)**		
	Na^+	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**SO_4^{2-}**	**Cl^-**	**HCO_3^-**
Bad Westernkotten G1	3.8	6.8	1.9	2.8	2.4	3.1	0.1
Bad Westernkotten G2	3.9	7.1	2.5	3.7	3.5	3.8	0.1
Rheine	6.3	8.0	3.2	6.2	-	6.1	0.4
Bad Rothenfelde S1	2.0	4.2	1.3	2.3	1.9	1.8	0.3
Bad Rothenfelde S2	3.4	4.1	2.0	3.8	2.9	3.1	0.1
Bad Rothenfelde S3	4.1	4.6	2.2	4.6	3.6	4.2	0.1

301

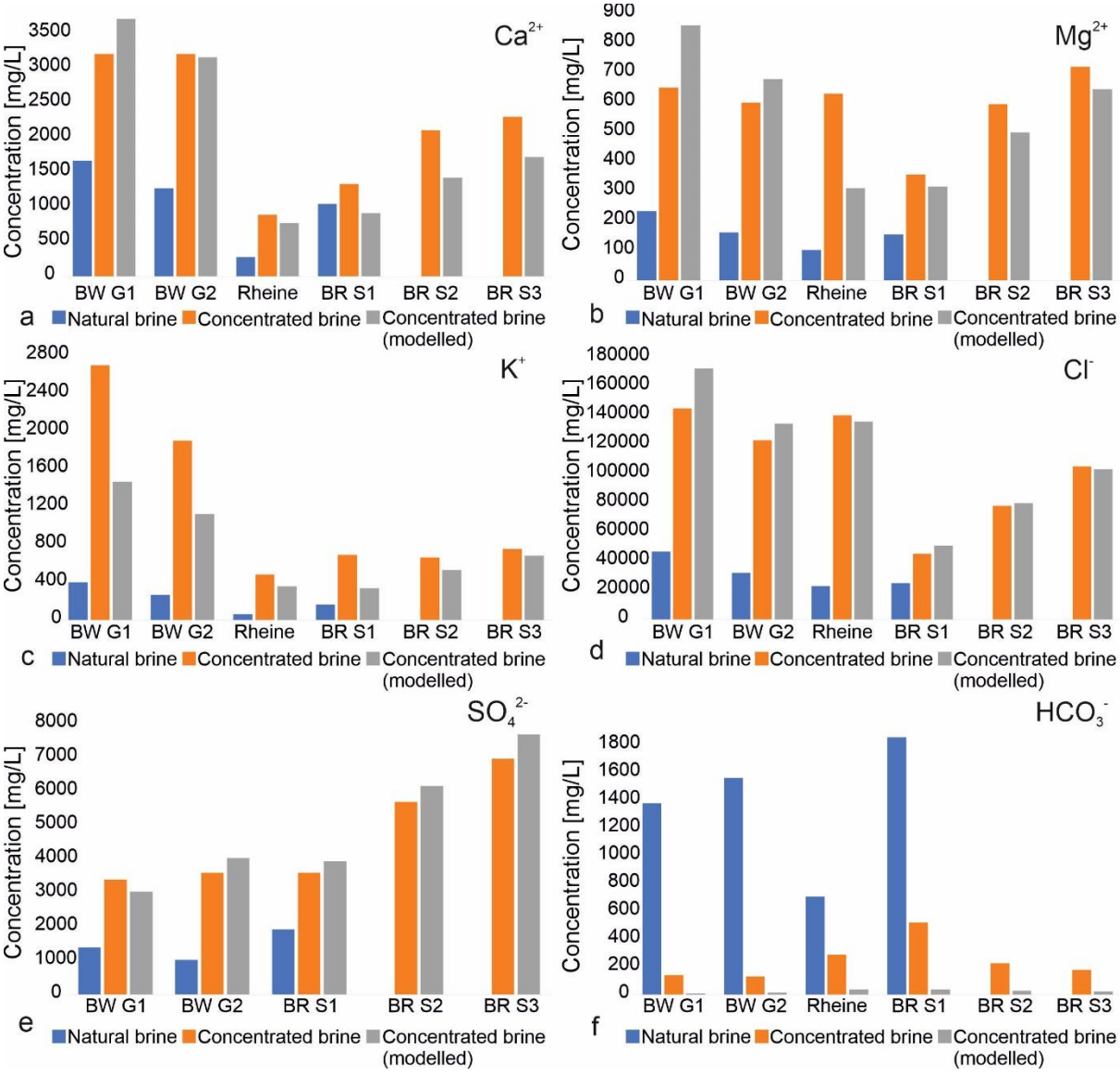
302 For the comparison of laboratory results with modelled ion concentrations (Fig. 3), modelled
303 values were read from PHREEQC modelling output files for a selected sodium ion
304 concentration. The respective ion concentrations were read for the modelling step where the
305 Na^+ concentration best matches the measured Na^+ concentration in the sampled concentrated
306 brines. Therefore, the modelled and analysed Na^+ concentrations coincide.

307 Chloride concentrations are also in a good agreement except for Bad Rothenfelde section 1 and
308 Bad Westernkotten graduation tower 1. There, modelled values are higher. This could also
309 explain the positive error of ion balance (5.8 % and 11.9 %, respectively) observed for these
310 samples. The ion balance is below 5 % for all other sampled brines at the graduation towers:
311 3.9 % for section 2 and –0.7 % for section 3 in Bad Rothenfelde, 2.6 % for the graduation tower
312 2 in Bad Westernkotten and 1.4 % in Rheine.

313 For Ca^{2+}, Mg^{2+}, K^+ and SO_4^{2-}, laboratory results partly show different values compared to the
314 modelled concentrations (Fig. 3). These deviations have no obvious regularity regarding the
315 type of ion or location and have both positive and negative signs. In Fig. 3, it can be seen that

316 bicarbonate concentrations deviate considerably from the modelled values: modelled
317 concentrations are significantly lower for all sites.

318 Modelling atmosphere contact plays an essential role here, because it leads to a significant
319 carbon dioxide degassing already at the beginning of the modelling. This could explain the
320 significantly lower bicarbonate concentrations by modelling. Besides, it should be taken into
321 account that precipitation kinetics were neglected in the modelling, leading the model to assume
322 that chemical equilibrium has already been established. However, a supersaturated solution for
323 a mineral phase can also be obtained over a longer period of time by a slow precipitation
324 reaction (Merkel and Planer-Friedrich 2008). Its inobservance in the model could lead to
325 overestimation of carbonate precipitation. Furthermore, it should be noted that when modelling
326 with PHREEQC, weather-dependent changes (e.g., temperature fluctuations and dilution by
327 rain) are not included.



328

329 **Fig. 3** Concentration change of calcium (**a**), magnesium (**b**), potassium (**c**), chloride (**d**),
330 sulphate (**e**), and bicarbonate (f) in the natural brines and the concentrated brine (own samples
331 and modelled with PHREEQC) for the locations Bad Westernkotten graduation tower 1
332 (BW G1) and 2 (BW G2), Rheine and Bad Rothenfelde section 1 (BR S1), section 2 (BR S2)
333 and section 3 (BR S3)

334

335 **4.3 Saturation State of Mineral Phases and Mineral Precipitation Quantities**

336 In Fig. 4, the courses of the modelled saturation indices (SI) are illustrated with increasing
337 evaporation for a graduation of the natural brine in Bad Rothenfelde and Bad Westernkotten

graduation tower 1. Except for aragonite, all minerals reach an SI-value of 0 at different evaporation rates. Manganese dioxide, hematite and calcite already precipitate at the beginning of the modelling. Precipitating Fe(III) phases may therefore play a role in thornstone colouration, but quantitatively appear to be of lower importance compared to the spa site Bad Nauheim near Frankfurt, for example (Schäffer 2018). After that, the sulphates barite, celestine and gypsum precipitate. The minerals siderite, dolomite and halite precipitate at the end.

Figure 4 reflects the precipitation of the ferrous carbonate siderite for the Bad Westernkotten site. In contrast to that, the ferric oxide hematite precipitates in Bad Rothenfelde. Besides, the sulphate, baryte reaches an SI value of 0 in Bad Rothenfelde, which results from the different extent of analysis data for the different locations: for the sites Rheine and Bad Westernkotten, the mineral phases including Ba, Fe(III) and Mn(III) as stoichiometric constituents were not modelled due to the absence of total iron, manganese and barium values. Therefore, the precipitation of hematite is more probable, because both siderite and hematite were considered in the modelling for the site Bad Rothenfelde. The modelling results of the saturation indices for the Bad Rothenfelde site show the precipitation of the same mineral phases as for Bad Sassendorf. However, iron and manganese are removed from the natural brine in Bad Sassendorf by treating it before it is used in the new graduation tower. Therefore, the mineral phases nsutite and hematite are not likely to precipitate in considerable amounts at the graduation tower in Bad Sassendorf. Modelled SI of the second graduation tower in Bad Westernkotten have a similar course as for the first one. The natural brine used in Rheine has a low Mn(II) and sulphate content. Because of this, the precipitation of sulphates and Mn(II)-containing minerals was not included in the modelling. Instead, the carbonate strontianite is likely to precipitate in Rheine. With the exception of aragonite, the mineral phases detected in the diffractograms (Table 2) were successfully simulated in the modelling approach. The absence of aragonite in modelled precipitates is probably due to its higher solubility in comparison to calcite, leading to preferential precipitation of the less soluble $CaCO_3$

polymorph, and the highly complex interplay of parameters controlling $CaCO_3$ polymorph precipitation (Jones 2017) which cannot be considered in total by the modelling approaches used here.

Overall, the modelled precipitating mineral phases (Fig. 4) and the calculated factors for the hydrochemical evolution during the graduation process (Table 3) are in agreement. Precipitation of calcite already occurs at the beginning of the modelling which is one explanation for the only small increase in Ca^{2+} concentration and the strong decrease in HCO_3^- concentration. The small factor for SO_4^{2-} increase corresponds to the precipitation of the sulphates baryte, celestine and gypsum. The significant increase of Na^+, Mg^{2+} and Cl^- concentrations is caused by the late precipitation of halite and dolomite at high evaporation stages. Observed hydrochemical signatures and evaporite sequences are in general agreement with the evolution of sabkha brines in Tunesia and playa brines in Iran and Afghanistan studied and modelled by Nasri et al. (2015) and Kaseb et al. (2020), respectively, with the exception of dolomite which appears to precipitate substantially earlier in desert environments.

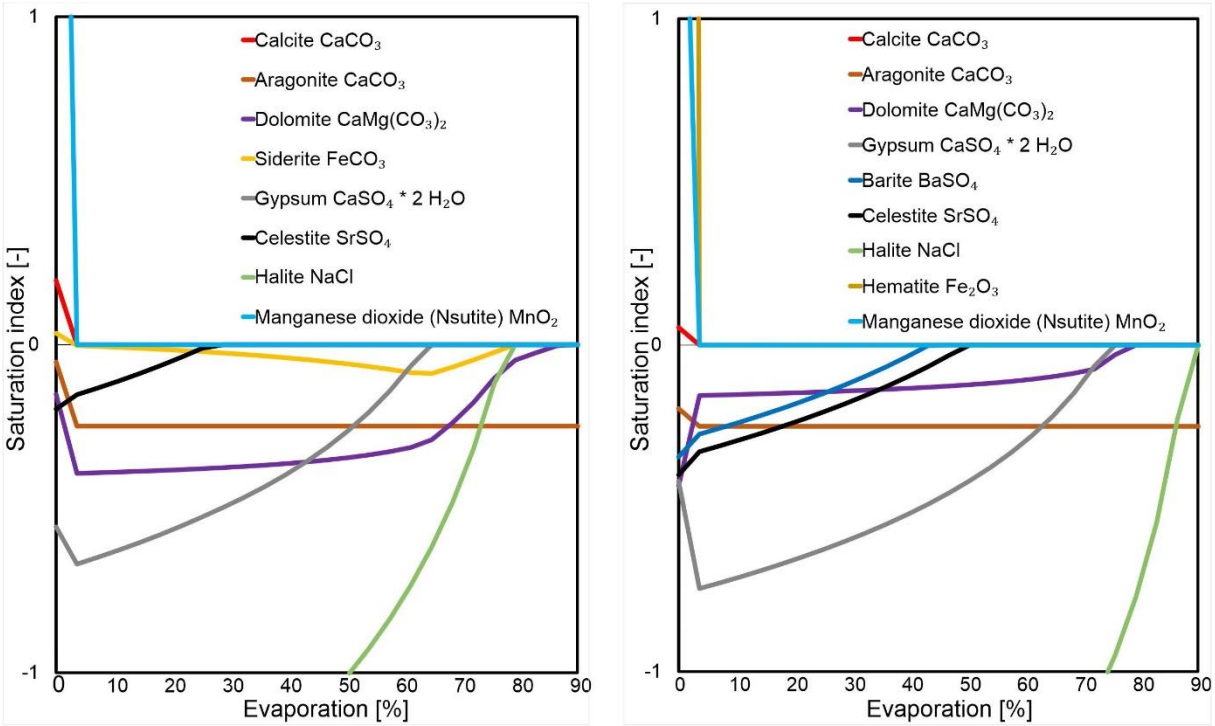


Fig. 4 Saturation indices (modelled with PHREEQC) of the precipitating mineral phases and the mineral aragonite with increasing evaporation for the locations Bad Westernkotten graduation tower 1 (left) and Bad Rothenfelde (right)

The expected amounts of mineral precipitation for the graduation of natural brines in the graduation towers are specified in Table 4. Modelled precipitation quantities are listed for a salinity of 18/19% and 28/29%, respectively. Results for the sums of mineral precipitates at the different sites show substantial differences. The reason for this is the different composition of the applied natural brines, and differences in the graduation processes.

The brine of Bad Rothenfelde has the largest total amount of precipitates (2.14 g/L) and Rheine the smallest total amount (0.56 g/L) for the salinity of 18/19%. In contrast to that, both graduation towers in Bad Westernkotten show values up to 48.6 g/L for total precipitation at a salinity of 28/29%, which consists of approx. 90% halite. Corresponding to the higher bicarbonate concentrations in the natural brines of Bad Rothenfelde and Bad Westernkotten (Fig. 3), carbonates represent the main component of the precipitation quantity for these sites

394 at lower evaporation grades. At higher evaporation, gypsum forms the main part of the
395 precipitates besides halite. The only exception is the low-sulphate natural brine in Rheine.
396 Besides, the ratio of calcite to dolomite shifts within the carbonates for a higher evaporation.
397 This is probably due to higher relative accumulation of Mg^{2+} in concentrated brine as compared
398 to Ca^{2+} (Table 3) which is partly removed from solution by gypsum precipitation at higher
399 evaporation grades.

400 The modelled precipitating mineral quantities for an evaporation of 90% can be regarded as
401 maximum values, since the maximum obtainable salt concentration of 27% for a moderate
402 climate zone mentioned in Kalwasińska et al. (2018) is already exceeded. Nevertheless, halite
403 only reaches saturation starting from an evaporation of 90% for Rheine und Bad Rothenfelde
404 (Fig. 4) and was detected in the sampled precipitates for these two sites (Table 2). Additionally,
405 the modelling neglected the formation of aerosols, which would probably reduce precipitation
406 quantities and might be an aspect of future research.

407 Modelled precipitation amounts for carbonate phases may be questioned, because the deviation
408 between modelled and measured concentrations for bicarbonate is remarkably high (Fig. 3).
409 However, modelling results for carbonate-dominated earlier precipitation stages fit XRD results
410 for samples probably representing such stages very well.

411 The precipitation of Fe(II) and Fe(III) containing minerals such as siderite and hematite depends
412 on the respective iron concentrations which in turn is controlled by pH and pe. The same applies
413 analogously to manganese. As an assumption was made for pe during modelling and the
414 thermodynamic data for the iron and manganese ions were added from another database (cf.
415 3.2), the precipitated quantities of Fe- and Mn-containing mineral phases need to be considered
416 an estimate, but are not likely to play a major role in total precipitate compositions anyway.

417

418 **Table 4** Converted results of the precipitated mineral quantities for the indicated evaporation
419 degrees modelled with PHREEQC

Graduation degree, expressed as…	**Rheine**		**Bad Rothenfelde**		**Bad Westernkotten graduation tower 1**		**Bad Westernkotten graduation tower 2**	
…Evaporation [%]	83	90	79	90	61	90	76	90
…NaCl content in the brine [%]	19	29	18	29	18	28	19	28
Amount of precipitating minerals [g/L]								
Calcite	0.17	0.10	1.32	0.52	1.16	1.12	1.30	1.13
Dolomite	0.38	0.44	0.18	0.93	-	0.04	-	0.16
Siderite	0.01	0.01	-	-	-	2×10^{-3}	5×10^{-3}	9×10^{-3}
Gypsum	-	-	0.59	2.26	-	2.17	0.01	1.42
Barite	-	-	3×10^{-5}	3×10^{-5}	-	-	-	-
Celestite	-	-	0.04	0.05	0.12	0.16	0.12	0.14
Hematite	-	-	0.01	0.01	-	-	-	-
Manganese dioxide (Nsutite)	-	-	6×10^{-4}	6×10^{-4}	5×10^{-4}	5×10^{-4}	5×10^{-4}	5×10^{-4}
Halite	-	2.65	-	6.19	-	45.1	-	18.8
Total precipitates [g/L]	0.56	3.20	2.14	9.96	1.28	48.6	1.44	21.7
Assumed evaporation amount of natural brine [L/d]	1105		17340		6313		3173	
Total precipitates [kg/d]	0.62	3.54	37.1	173	8.08	307	4.57	68.9

420

4.4 Prognosis for the Newly Built Graduation Tower in Bad Sassendorf

A forecast was made for the expected amount of mineral precipitates for the next 25 years for the newly (in 2019) built graduation tower in Bad Sassendorf. Saturation indices of considered mineral phases have a similar course as those for the location Bad Rothenfelde (Fig. 4). The precipitated solid phases and their quantities are listed in Table 5. Because iron and manganese are removed before the natural brine is used in the new graduation tower in Bad Sassendorf, the minerals hematite and nsutite are not likely to precipitate in considerable amounts, and therefore, were not considered in the calculation of the total precipitation quantities and the extrapolation to 25 years. A total amount of mineral precipitates of 1.23 g/L inserted natural brine is obtained for an evaporation of 69%. This total quantity consists of 90% calcite. The total amount of precipitates increases to 37.9 g/L for an increased evaporation of 90% and consists of 93% halite. After one year, a precipitation quantity of 1.4 t can be expected for an evaporation of 69%. This value rises to 34.4 t after 25 years. The precipitation quantities for an evaporation of 69% are projected for 365 days over a year in Table 5. This is based on the assumption that a salinity of 19% is reached after only one day. Afterwards, the quantities are extrapolated for 25 years. The brine can be concentrated in a graduation tower to a maximum salt concentration of 27% within 3 days under good weather conditions (Kalwasińska et al. 2018). This 27% is achieved for the natural brine in Bad Sassendorf at an evaporation rate of 90%. Therefore, the values given for this evaporation can be regarded as the maximum precipitation quantity to be expected (Table 5). Considering the three-day period required for a salt concentration of 27% (evaporation of 90%), the quantities were projected for one year and finally for 25 years.

444 **Table 5** Converted results of the precipitating mineral quantities up to an evaporation of approx.
445 69% and 90%, modelled with PHREEQC for the new graduation tower in Bad Sassendorf

Graduation degree, expressed as…	**Amount of precipitating minerals**					
	[g/L]		**[g/L/yr]**		**[kg/L/25 yr]**	
…Evaporation [%]	69	90	69	90	69	90
…NaCl-content in the brine [%]	19	27	19	27	19	27
Calcite	1.13	0.89	413	108	10.3	2.70
Dolomite	-	0.23	-	28.0	-	0.70
Barite	2×10^{-4}	1×10^{-4}	0.07	0.01	2×10^{-3}	3×10^{-4}
Celestite	0.10	0.15	36.5	18.3	0.91	0.46
Gypsum	-	1.21	-	147	-	3.68
Halite	-	35.4	-	4307	-	108
Total precipitates	1.23	37.9	450	4608	11.21	116
Total precipitates for an evaporation of 3072 L/d natural brine	3.78 kg/d	116 kg/d	1.4 t/yr	14.2 t/yr	34.4 t/25 yr	356 t/25 yr

446

447 ## 5 Conclusions

448 During a graduation process, the evaporation of water leads to concentration of the natural brine
449 and related precipitation of different mineral phases. An analysis of the precipitates showed
450 they are composed of the minerals calcite, aragonite, gypsum and halite. White samples contain
451 gypsum and halite. No gypsum was detected in reddish samples, but high calcite contents were

found. A connection between increasing calcite contents and the intensity of the reddish colouring is discernible.

Hydrochemical brine evolution is assessed by comparing the changes in ion concentrations of the natural brine and the concentrated brine. Only the concentration of bicarbonate decreases with increasing evaporation. The concentration increase of the other ions varies, indicating that some ions are precipitated as mineral phases. Calcium and sulphate show smallest relative accumulation in the concentrated brine. This and the significant bicarbonate decrease is explained, among other things, by the precipitation of carbonates and sulphates. Potassium has the most pronounced concentration increase, it is contained neither in the XRD detected mineral phases nor in the modelled precipitates.

Modelled saturation indices indicate calcite precipitation already at the beginning of the modelling. Sulphates only precipitate at a higher evaporation degree of about 28% and chlorides only reach saturation at an evaporation degree of more than 78%. XRD results for three successive sections at the Bad Rothenfelde graduation site are in good agreement with this order of precipitation.

The precipitating mineral quantities modelled with PHREEQC show that a total precipitation between 0.62 kg/d and 37.1 kg/d occurs at a graduation process up to 18-19% NaCl with the carbonates calcite and dolomite as main components. Precipitation amounts are between 3.54 kg/d and 307 kg/d for a high evaporation rate of 90% and consist mainly of halite.

For the modelled prognosis of the new graduation tower in Bad Sassendorf, a total precipitation amount of about 34.4 t for a graduation process up to 19% salt content is predicted, and about 356 t if a permanent evaporation grade of 90% is considered. The applied modelling approach can provide an estimate of the expected amount and sequence of mineral precipitations depending on the quantity of evaporated water.

Large quantities of precipitating evaporite minerals can impair the functionality of a graduation tower. These deposits have to be removed in time consuming and cost intensive procedures. Therefore, besides contributing to a better understanding of hydrogeochemical and mineralogical processes during brine concentration and thornstone formation, this study showed that the applied modelling approach can be a powerful tool to aid in graduation tower planning and management in spa towns.

Authors' contributions

Conceptualization: Andre Banning, Laura-Jane Ostwald; Methodology: Andre Banning, Laura-Jane Ostwald; Formal analysis and investigation: Laura-Jane Ostwald; Writing - original draft preparation: Laura-Jane Ostwald; Writing - review and editing: Andre Banning; Resources: Andre Banning; Supervision: Andre Banning

Declarations

Funding: this research did not receive any specific funding.

Conflicts of interest/Competing interests: the authors declare that there is no conflict of interest or competing interests

Availability of data and material: on request

Code availability: PHREEQC, publicly available code for hydrogeochemical calculations: https://www.usgs.gov/software/phreeqc-version-3

Acknowledgements

The authors thank the contact persons of the graduation towers: Mr. Vleugels (Rheine), Mr. Meck (Bad Sassendorf), Mr. Köchling and Mr. Kemper (Bad Westernkotten) as well as Mr.

Wilker (Bad Rothenfelde) and the Kurverwaltung Bad Rothenfelde GmbH for enabling the sampling as well as for providing data for the natural brines. Our thanks also go to Ilka Hinzer (RUB) and Nikolaus Richard (RUB) for carrying out hydrochemical analyses and to Hartmut Mammen (RUB) for carrying out powder X-ray diffraction measurements.

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