

The origin of formation waters in the abandoned Konrad iron ore mine (Salzgitter, Germany)

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Abstract: In the abandoned Konrad iron ore mine near Salzgitter, Germany, an underground repository for low-level and intermediate radioactive waste is planned in a Jurassic iron ore body. For the critical examination of the long-term safety of this disposal the elemental composition of formation waters and the sulfur isotope composition of dissolved sulfates in the formation waters were used to discuss their origin. The $\delta^{34}\text{S}$ values of the dissolved sulfate lie between + 21 ‰ and + 40 ‰ (rel. CDT, Canyon Diablo Troilite standard). Bacterial sulfate reduction is shown by the relationship between the absolute sulfate concentration and $\delta^{34}\text{S}$ values of the dissolved sulfate. Further a possible primary $\delta^{34}\text{S}$ value (about + 16 ‰) was obtained using the relationship between the sulfur isotope composition and absolute sulfate concentration. This value agrees with published data on the sulfur isotope composition of sulfate in Jurassic evaporites (e.g., Nielsen, 1979). Due to the high bromine concentration of about 375-825 $\mu\text{g Br/g}$ solution the formation waters cannot have originated by dissolution of marine evaporites. The sulfur isotope and chemical composition show that the studied formation waters are Jurassic sea water trapped in pore spaces during sedimentation.

Key-words: formation water, sulfur isotope composition, bacterial sulfate reduction, dissolution of marine evaporites, bromine concentration.

1. Introduction

The former Konrad iron ore mine is located southeast of Hanover (Fig. 1). Upper Jurassic sediments (Oxfordian and Kimmeridgian) have been exposed during mining operations. These sediments (e.g., coral oolite) deposited in the Gifhorn trough. This trough is a part of the North German Jurassic basin. Diapirism of the neighboring Permian Vechelde and Broistedt salt domes had a dominant influence on the geology of this area (Fig. 2).

An underground repository for low-level and intermediate radioactive waste is to be estab-

lished in the Konrad mine. Knowledge of the origin of the salt solutions occurring in the mine is important to the long-term safety of this repository.

Therefore, the sulfur isotope composition of the dissolved sulfate in the formation waters was investigated. The Na, Cl, and Br concentrations are also very important, since these components hardly change during diagenesis of marine sediments (v. Engelhardt, 1973). In addition, the Br concentration could provide evidence of whether the formation waters represent dissolved marine evaporites or connate waters that were trapped in pore spaces.



Fig. 1. Geographic position of the Konrad mine.

2. Samples and sampling

The sampling technique is important for the study of concentrated salt solutions. The chemi-

cal composition of the analyzed solution must not be altered during sampling. Evaporation and contamination were prevented by using narrow-necked bottles (polyethylene, 1000 cm³) to col-

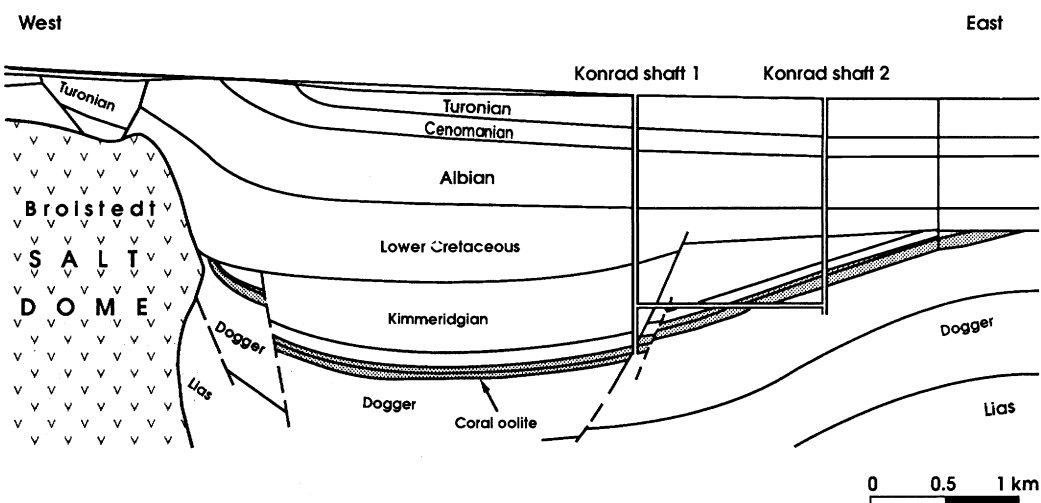


Fig. 2. Geological sketch of the Konrad mine (after Kolbe & Simon, 1969).

Table 1. List of samples.

| sample | depth [m] | temperature [°C] | flow rate [ml/min] | stratigraphic horizon |
|-----------|--------------|---------------------|-----------------------|-----------------------|
| 410 N | 933 | 28.5 | 15 | Dogger/Oxfordian |
| 300 P | 900 | 34.0 | 96 | Middle Oxfordian |
| 300 | 900 | 39.6 | 300000 | Middle Oxfordian |
| Cornbrash | 934 | 35.5 | 120000 | Cornbrash/Dogger |
| 370 A | 805 | 31.0 | 0.6 | Upper Oxfordian |
| 101 S | 689 | - | 0.18 | Middle Oxfordian |
| 110 N | 661 | 32.2 | 42 | Upper Oxfordian |
| 400 A | 774 | 30.0 | 30 | Upper Oxfordian |
| 660 A | 1146 | 40.6 | 150 | Lower Oxfordian |
| 601 | 1206 | 39.0 | 12 | Middle Oxfordian |

lect the solutions (Herrmann, 1980a). The investigated formation waters were taken from older boreholes that were sealed with a packer. If the flow rate was very low, a wooden plug with a hole and an attached hose was used for sampling. The solution drained from the hose.

Ten samples of formation waters were taken in the Konrad mine. Flow rate, temperature, depth, and stratigraphic horizon are listed in Table 1.

3. Analytical methods

The cations were analysed by atomic emission/absorption spectrometry (AES/AAS). The detection of anions with sufficient precision in concentrated solutions like the investigated formation waters require classical analytical methods like titration and gravimetry. The analytical methods for measurement of cations and anions of the formation waters are listed in Table 2.

Sample preparation and analysis of the sulfur isotope distribution was carried out by the authors with a mass spectrometer Finnigan MAT 251 at the Geochemical Institute, University of Göttingen. After precipitation of sulfate with BaCl₂ as BaSO₄ from the formation waters, the procedure followed was identical with that of Harmon *et al.* (1987) and Knipping (1989: 21ff). The isotope ratios (³⁴S/³²S) are reported as δ values in permill (‰) relative to the CDT standard according to the following definition:

$$\delta^{34}\text{S} = \frac{{}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}} - {}^{34}\text{S}/{}^{32}\text{S}_{\text{CDT}}}{{}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}}} \cdot 1000$$

The analytical precision for the δ³⁴S values is ± 0.2 ‰.

Table 2. Analytical methods and relative standard deviation.

| element | method | S _{relative} [%] |
|-----------------|------------|------------------------------|
| Na | AES | ± 1.8 |
| K | AES | ± 2.0 |
| Mg | AAS | ± 2.0 |
| Ca | AAS | ± 2.0 |
| Cl | titration | ± 0.3 |
| SO ₄ | gravimetry | ± 1.7 |
| Br | titration | ± 1.6 |

AAS, atomic absorption spectrometry; AES, atomic emission spectrometry.

4. Analytical results

The elemental composition of the investigated formation waters and the sulfur isotope composition of the dissolved sulfate are given in Table 3. The high Br concentration (375-825 µg Br/g solution) and the high NaCl concentration (13-14 %, mass fraction), calculated from the analyzed Na and Cl values (Table 4), are notable.

The δ³⁴S values of the dissolved sulfate lie between + 21 ‰ and + 40 ‰ (Table 3). The sulfur isotope values of three investigated anhydrite samples of the Konrad mine are + 19.1 ‰, + 17.4 ‰, and + 17.5 ‰. For comparison additional isotope data (δ³⁴S and δ¹⁸O) obtained by the Gesellschaft für Strahlen- und Umweltforschung (GSF 1987) are given in Table 5.

Table 3. Analytical data of the investigated formation waters.

| sample | density [g/cm ³] | Na | K | Mg | Ca | Cl | SO ₄ | Br [μg/g] | δ ³⁴ S [‰] rel. CDT |
|--------------------|---------------------------------|-----|-------------------|------|------|-------------------|-------------------|--------------|--------------------------------------|
| mass fraction in % | | | | | | | | | |
| 410 N | 1.129 | 5.3 | 0.02 ₆ | 0.20 | 0.92 | 10.3 ₄ | 0.04 ₀ | 590 | 30.1 |
| 300 P | 1.127 | 5.3 | 0.02 ₄ | 0.22 | 0.97 | 10.4 ₅ | 0.07 ₇ | 620 | 22.2 |
| 300 | 1.130 | 5.3 | 0.02 ₅ | 0.21 | 0.96 | 10.4 ₆ | 0.05 ₀ | 620 | 26.3 |
| Cornbrash | 1.124 | 5.3 | 0.02 ₅ | 0.22 | 0.96 | 10.3 ₆ | 0.01 ₆ | 620 | 40.0 |
| 370 A | 1.131 | 5.3 | 0.02 ₂ | 0.22 | 0.94 | 10.4 ₅ | 0.09 ₄ | 370 | 21.7 |
| 101 S | 1.118 | 5.2 | 0.01 ₉ | 0.18 | 0.74 | 9.7 ₇ | 0.04 ₃ | 425 | 25.6 |
| 110 N | 1.120 | 5.2 | 0.01 ₇ | 0.17 | 0.70 | 9.6 ₂ | 0.04 ₈ | 375 | 24.5 |
| 400 A | 1.131 | 5.5 | 0.02 ₂ | 0.22 | 1.02 | 10.7 ₈ | 0.06 ₂ | 665 | 24.4 |
| 660 A | 1.142 | 5.6 | 0.02 ₄ | 0.25 | 1.17 | 11.3 ₂ | 0.06 ₂ | 780 | 24.1 |
| 601 | 1.142 | 5.8 | 0.02 ₃ | 0.26 | 1.15 | 11.5 ₅ | 0.06 ₁ | 825 | 22.5 |

CDT, Canyon Diablo Troilite.

5. Discussion

The concentration of components like Na, Cl and Br have been constant in sea water from the Cambrian until today. This is not true for the sulfur isotope composition of the sulfate. Fig. 3 shows the age-curve for the sulfur isotope composition constructed from isotope data by Nielsen (1979). It varies with geological time of formation in a characteristic way. According to this information, three possible interpretations of the investigated δ³⁴S values should be tested to get information on the genesis of formation waters.

1. Dissolution of Lower Triassic evaporites is the origin of the elemental composition of the formation waters. The primary sulfur isotope com-

position of the Lower Triassic, given with up to + 27 ‰ has not been changed (e.g. Nielsen 1979, for mean value see Fig. 3).

2. Dissolution of Zechstein or Middle Triassic evaporites is the origin of the elemental composition of the formation waters. The primary sulfur isotope composition of the dissolved sulfate has been changed by bacterial sulfate reduction.

3. The investigated formation waters represent Upper Jurassic sea water that was trapped in pore spaces of the sediment during genesis of the iron

Table 5. Sulfate, δ³⁴S, and δ¹⁸O values of formation waters (from GSF 1987, Table 33); same exposures as for this work.

| sample | sulfate [mass fraction in %] | δ ³⁴ S [‰] rel. CDT | δ ¹⁸ O [‰] rel. SMOW |
|---------|------------------------------------|--------------------------------------|---------------------------------------|
| 660 A | 0.060 | 22.3 | 15.7 |
| 660 A | 0.061 | 22.7 | 15.7 |
| 660 A | 0.061 | 22.7 | 16.1 |
| 300 | 0.045 | 24.9 | 16.6 |
| 300 | 0.049 | 24.6 | 16.8 |
| 300 | 0.049 | 24.6 | 16.7 |
| 300 | 0.049 | 24.6 | 16.7 |
| 302 A | 0.064 | 21.1 | 15.5 |
| 2402/1 | 0.062 | 22.3 | 15.6 |
| PP 1226 | 0.150 | 19.3 | 14.9 |
| PP 1226 | 0.150 | 19.4 | 14.9 |

CDT, Canyon Diablo Troilite, SMOW, Standard Mean Ocean Water.

Table 4. NaCl, KCl, and MgCl₂ in the investigated formation waters calculated from the elemental composition.

| sample | NaCl | KCl | MgCl ₂ |
|----------------------|------|------------------|-------------------|
| [mass fraction in %] | | | |
| 410 N | 13.4 | 0.0 ₅ | 0.7 ₉ |
| 300 P | 13.6 | 0.0 ₅ | 0.7 ₉ |
| 300 | 13.6 | 0.0 ₅ | 0.8 ₂ |
| Cornbrash | 13.5 | 0.0 ₅ | 0.8 ₇ |
| 370 A | 13.5 | 0.0 ₄ | 0.8 ₄ |
| 101 S | 13.1 | 0.0 ₄ | 0.7 ₁ |
| 110 N | 13.1 | 0.0 ₃ | 0.6 ₈ |
| 400 A | 14.0 | 0.0 ₄ | 0.8 ₈ |
| 660 A | 14.2 | 0.0 ₅ | 0.9 ₈ |
| 601 | 14.6 | 0.0 ₄ | 1.0 ₁ |

ores. The Jurassic sulfur isotope composition $+15 \pm 19 \text{‰}$ (Fig. 3, Nielsen, 1979) has been changed by bacterial sulfate reduction.

Two problems must be discussed:

i) Has the original sulfur isotope composition of the formation waters been changed by bacterial sulfate reduction?

ii) Is dissolution of marine evaporites the origin of the element composition of the investigated solutions?

Bacterial sulfate reduction

Anaerobic bacteria like *Desulfotribrio* get the energy for their metabolism by reducing the sulfate to sulfide. The sulfate consisting of lighter isotopes (^{32}S and ^{16}O) is preferably changed by bacterial sulfate reduction. This causes a relative enrichment of ^{34}S in the remaining sulfate. Thus a correlation of the $\delta^{34}\text{S}$ values with the sulfate

concentration shows bacterial sulfate reduction (Fig. 4). The prerequisite for this process is a closed system with respect to sulfate.

Further evidence for bacterial sulfate reduction is the linear relationship between the $\delta^{34}\text{S}$ and the $\delta^{18}\text{O}$ values of the sulfate due to the influence of bacterial sulfate reduction on oxygen. The theoretical oxygen isotope fractionation should be one quarter of the sulfur isotope fractionation. In natural samples a good correlation between $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ shows a similar fractionation mechanism (Fig. 5). Deviations from the ratio of 1:4 were found as a function of the $\delta^{18}\text{O}$ value of the H_2O used as medium (Krouse, 1987).

Calculations of the initial $\delta^{34}\text{S}$ value of the formation waters

An estimate of the initial $\delta^{34}\text{S}$ value of the formation waters may be obtained by using the re-

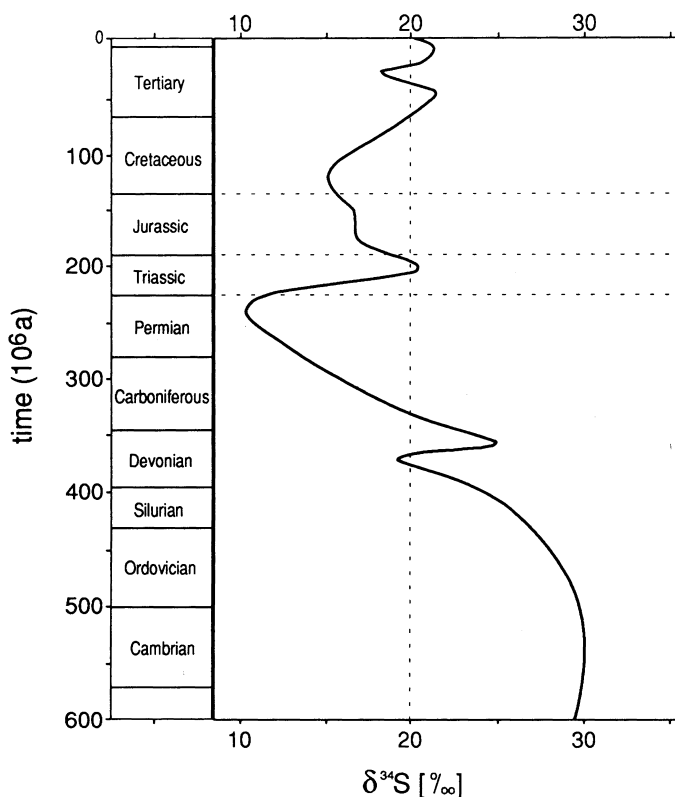


Fig. 3. Mean values of the sulfur isotope composition in sea water from the Cambrian until today (after Nielsen, 1979).

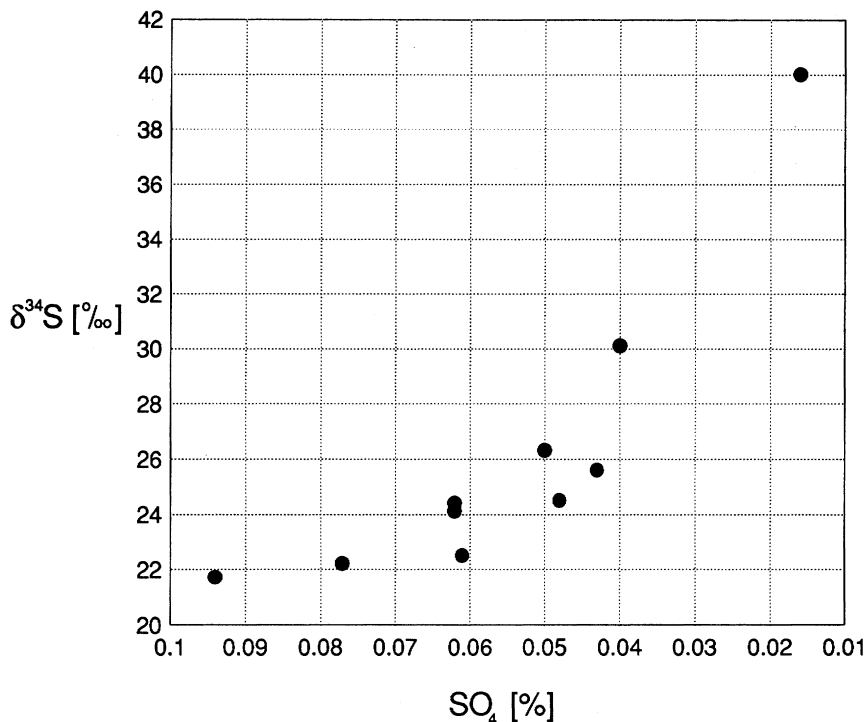


Fig. 4. $\delta^{34}\text{S}$ values versus sulfate concentration of the investigated formation waters. The correlation between increasing $\delta^{34}\text{S}$ values and decreasing sulfate shows bacterial sulfate reduction of the SO_4 content of the formation waters.

lation between the sulfate concentration and the $\delta^{34}\text{S}$ values given above. This relation has to be extrapolated to the original sulfate concentration. The following assumptions are important for this calculation:

1. The fractionation mechanism for all the investigated formation waters has to be the same. This is proven by the small deviation of the individual data points of the $\delta^{34}\text{S}/\delta^{18}\text{O}$ diagram from the line of regression (Fig. 5).
2. The limit of the extrapolation (*i.e.*, the original sulfate concentration) has to be known.

Since the sulfate concentration of sea water is regarded to have been constant from the Upper Triassic onwards (0.27 %, mass fraction), the original sulfur isotope distribution was extrapolated to 0.27 % SO_4 . This gives an original $\delta^{34}\text{S}$ value of about +16 ‰ (Fig. 6). This agrees with published data on the sulfur isotope distribution of Jurassic evaporites (Fig. 3, Nielsen, 1979). Three anhydrite samples of the Konrad mine were investigated to allow a comparison of the $\delta^{34}\text{S}$ values in the salt solutions with those of a

mineral phase. Due to isotope fractionation between crystal and solution during crystallization, the $\delta^{34}\text{S}$ value of the crystal is 1-2 ‰ higher than that of the solution (Michel & Nielsen 1977). Therefore, a $\delta^{34}\text{S}$ value between +17 ‰ and +19 ‰ for sulfate minerals precipitated from solutions like the investigated formation waters are to be expected. So the values found for anhydrites from the Konrad mine (+19.1 ‰, +17.4 ‰, and +17.5 ‰) agree with the theoretical model.

Dissolution of marine evaporites

To test the hypothesis that the chemical composition of the investigated formation waters is due to the dissolution of marine evaporites, the NaCl and Br concentration of the investigated solutions must be considered. The NaCl concentration ranges between 13.1 % (mass fraction) and 14.6 % (Table 4). Compared with Braitsch (1971: 86, Table 8), this value corresponds to a degree of NaCl saturation of evaporated sea water of about 55 %.

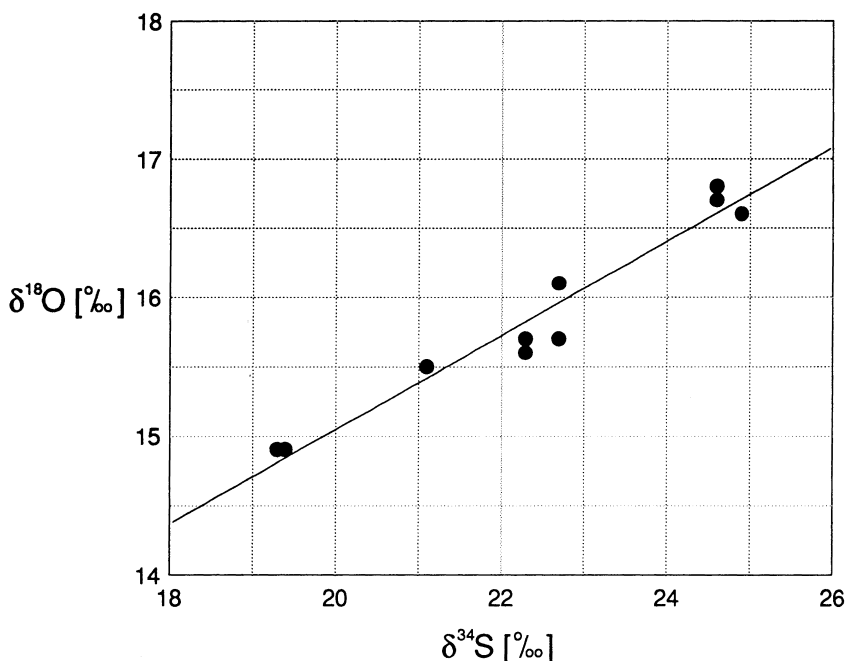


Fig. 5. Correlation of the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of the dissolved sulfate (see Table 5, data from GSF, 1987). The line of regression has a slope of $m = 0.34$. The good agreement between the analyzed formation waters and the line of regression shows a similar fractionation mechanism for the individual formation water samples investigated.

Chloride minerals in marine evaporites incorporate bromine in their structure through ionic substitution. The concentration of bromine in the different minerals depends on the concentration, temperature, and chemical composition of the solution. Pressure is unimportant. The distribution coefficient b ($b = \% \text{ Br}_{\text{crystal}} / \% \text{ Br}_{\text{solution}}$) expresses this dependency (Braitsch, 1971: 131 ff; Braitsch & Herrmann, 1962, 1963; Herrmann, 1972, 1980b; Herrmann *et al.*, 1973).

During initial halite crystallization an evaporating sea water contains $538 \mu\text{g Br/g}$ solution (isothermal, static evaporation; Braitsch, 1971: 138, Table 18; Herrmann, 1977; Fig. 7). The halite crystallizing at this point incorporates $75 \mu\text{g Br/g}$ halite. These theoretical results were proven by investigations of recent sea water (Herrmann, 1972, 1980b; Herrmann *et al.*, 1973). During initial crystallization of carnallite, the solution contains $5080 \mu\text{g Br/g}$ solution (Fig. 7). Crystallizing halite now incorporates $381 \mu\text{g Br/g}$ halite. For the following calculations we use a Br concentration of $381 \mu\text{g Br/g}$ halite.

Different reactions of dissolving evaporites are

possible as genetic models for the investigated formation waters.

Genetic model 1 – Dissolution of halite in the NaCl-H₂O system (25°C)

The solubility of NaCl is 55.5 mol NaCl in $1000 \text{ mol H}_2\text{O}$ ($36 \text{ g NaCl}/100 \text{ g H}_2\text{O}$; D'Ans, 1933). Based on this solubility, the resulting solution contains $98 \mu\text{g Br/g}$ solution (rs1, Table 6). This maximum theoretical Br concentration must be reduced to $54 \mu\text{g Br/g}$ solution, since the formation waters are only saturated to about 55 % NaCl compared with sea water evaporation. This calculation shows that the Br concentration of the formation waters ($375 - 825 \mu\text{g Br/g}$ solution) cannot be obtained by dissolution of halite.

Genetic model 2 – Dissolution of K-Mg evaporites (potash salts)

This is more a theoretical consideration since the amount of K-Mg minerals in an evaporite sequence is very small. The following reactions

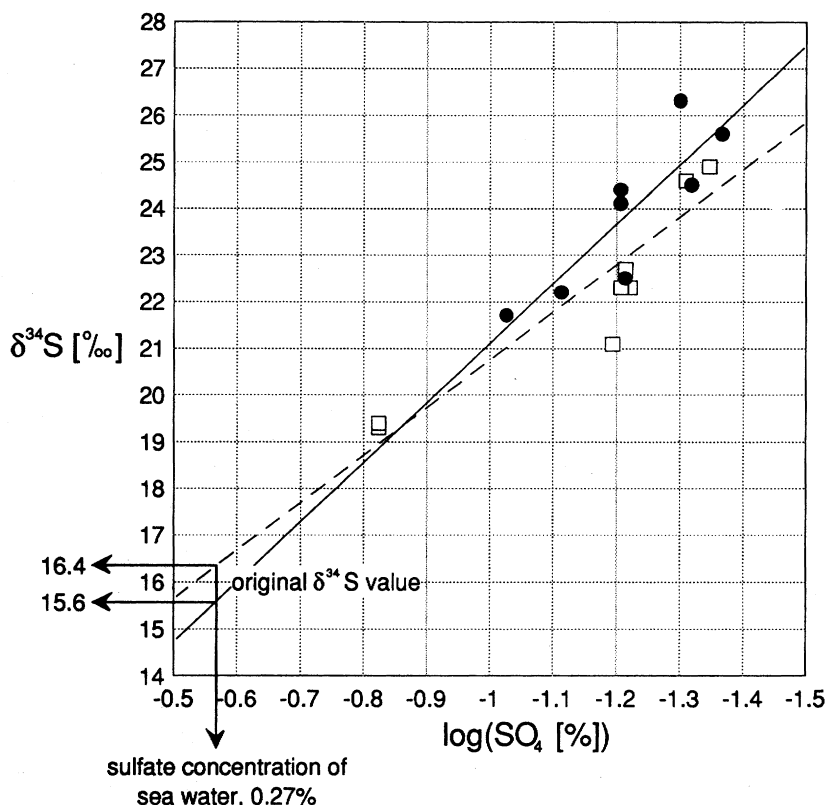
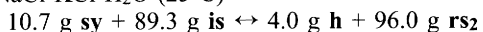


Fig. 6. Calculation of the original $\delta^{34}\text{S}$ value by extrapolation. The data from Table 3 were used without 410N and Cornbrash (possible contamination from drilling water). The end of the line of regression (solid line, filled symbols) matches with the sulfate content of sea water and thus the primary $\delta^{34}\text{S}$ value (+ 15.6 ‰). The same procedure with the data of the GSF, 1987 (Table 5) yields a $\delta^{34}\text{S}$ value of about + 16.4 ‰ (dashed line, open symbols).

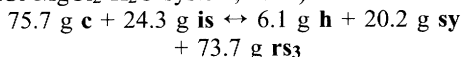
are possible (quantitative calculations according to the stable solution equilibria, Herrmann & Knipping, 1993):

is, infiltrate solution (NaCl saturated); **rs**, resulting solution; **h**, halite; **sy**, sylvine; **c**, carnallite

Dissolution of sylvine (KCl) in the system NaCl-KCl-H₂O (25°C)



Incongruous dissolution of carnallite (NaCl-KCl-MgCl₂-H₂O system, 25°C)



The data necessary for calculation are shown in Table 7. The chemical composition of the resulting solutions (**rs**) is shown in Table 6. Comparison of these results with the chemical composition of the investigated formation waters (Table 4) shows that dissolution of K-Mg eva-

porites cannot explain the composition of the formation waters.

Genetic model 3 – Formation water as concentrated sea water

Comparison of the Br concentration of the formation waters (375-825 µg Br/g solution) with the Br concentration of evaporated sea water shows the correspondence of the formation waters with the range of halite crystallization (Fig. 7), leading to the hypothesis that concentrated sea water is the origin of the formation waters. They must have been diluted later.

The initial composition of the solution should lie in the range of halite crystallization. Herrmann *et al.* (1973) give possible solution compositions. The data obtained from the model cal-

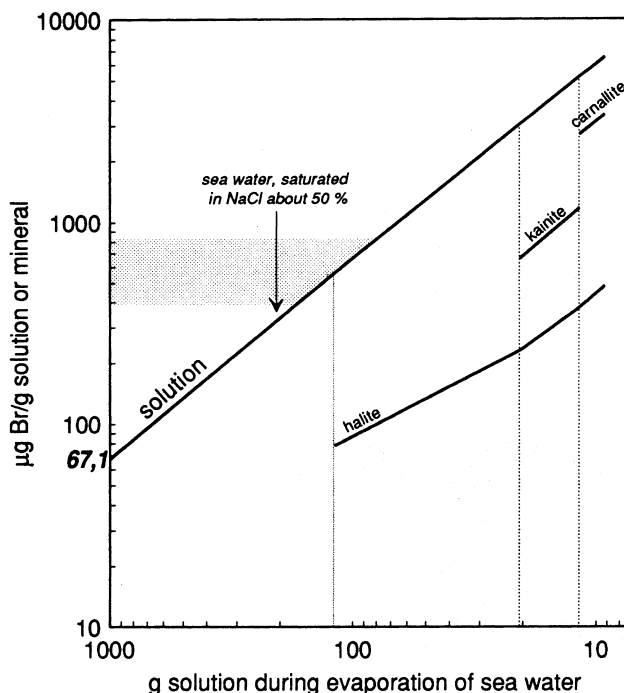


Fig. 7. Behavior of bromine during static, isothermal evaporation of 1000 g sea water at 25°C (after Braitsch, 1971). The shaded area represents the variation of Br in the investigated formation waters.

culations are shown in Table 8. Seven parts of concentrated solution must have been diluted with three parts sea water. Both the NaCl and Br contents of the formation waters can be calculated in this way (13 % NaCl, mass fraction; about 600 µg Br/g solution). The Mg and K contents must have been changed during diagenesis (e.g., v. Engelhardt, 1973). The sulfate content is reduced by bacterial sulfate reduction.

6. Conclusions

The sulfur isotope composition of the dis-

solved sulfate in the formation waters can be interpreted as follows:

- Bacterial sulfate reduction seems to have taken place. Therefore, the sulfur isotope composition must not be used for calculating the relative age of the formation waters without further interpretation.

- A possible primary sulfur isotope value of the sulfate in the range of the Jurassic sulfur isotope distribution was found ($\delta^{34}\text{S}$ = about + 16 ‰). This agrees with the sulfur isotope value of three Jurassic anhydrites of the Konrad mine.

The Br content of the formation waters can be interpreted as follows:

Table 6. Calculated composition of the resulting solutions (rs) for the model calculations 1 and 2 (see text).

| | 2NaCl | | 2KCl | | MgCl ₂ | | Br |
|-----------------|-------------------------------|------|-------------------------------|------|-------------------------------|-------|------|
| | [x/1000 mol H ₂ O] | [%] | [x/1000 mol H ₂ O] | [%] | [x/1000 mol H ₂ O] | [%] | |
| rs ₁ | 55.5 | 26.5 | - | - | - | - | 98.2 |
| rs ₂ | 46.0 | 20.4 | 19.7 | 11.2 | - | - | 447 |
| rs ₃ | 0.98 | 0.41 | 0.28 | 0.14 | 103.7 | 35.21 | 2923 |

Table 7. Distribution coefficient *b* of bromine; range of bromine incorporated in different evaporite minerals and solubility of the main components in different evaporite systems used for the model calculations (see text).

| mineral | system | <i>b</i> | Br [μg/g] | solubility [x/1000 mol H ₂ O] | references |
|----------------|---|----------|--------------|---|---|
| h (halite) | NaCl-H ₂ O point of initial halite crystallization | 0.14 | 75 - 381 | 55.5 mol 2NaCl | Braitsch & Herrmann 1962, 1963; Herrmann 1980b; D'Ans 1933 |
| | NaCl-KCl-MgCl ₂ -H ₂ O point of initial carnallite crystallization | 0.075 | | | |
| sy (sylvine) | KCl-NaCl-H ₂ O | 0.80 | 1200 - 3200 | 46.0 mol 2NaCl 19.7 mol 2KCl | Braitsch & Herrmann 1962, 1963; Herrmann 1980b; D'Ans 1933, Peters 1988 |
| | NaCl-KCl-MgCl ₂ -H ₂ O | 0.73 | | | |
| c (carnallite) | NaCl-KCl-MgCl ₂ -H ₂ O | 0.52 | 1400 - 3400 | | Braitsch 1971; Braitsch & Herrmann 1962, 1963; Herrmann 1980b; D'Ans 1933 |

Table 8. Results of a model calculation to show that the probable origin of the formation waters is concentrated sea water, which was diluted later by normal sea water.

| NaCl | KCl | MgCl ₂ | SO ₄ | Br [μg/g] |
|--|------|-------------------|-----------------|--------------|
| [mass fraction in %] | | | | |
| <i>initial solution, concentrated sea water</i> | | | | |
| 16.6 | 0.92 | 6.19 | 2.99 | 840 |
| <i>normal sea water</i> | | | | |
| 2.6 | 0.08 | 0.39 | 0.27 | 65 |
| <i>resulting hypothetical solution, 7 parts initial solution + 3 parts sea water</i> | | | | |
| 12.9 | 0.70 | 4.67 | 2.28 | 608 |

- Dissolution of rock salt (mainly NaCl) as well as dissolution of potash salts cannot explain the chemical composition of the formation waters.

- The Br content of the formation waters corresponds to the Br content during crystallization of halite from sea water. Therefore, the formation waters must previously have been concentrated up to halite saturation.

Both the results of the sulfur isotope investigations and the interpretation of the Br contents show that the composition of the formation waters cannot be explained by dissolution of Zechstein evaporites.

The investigated formation waters consist of initially concentrated Jurassic sea water, which was trapped in pore spaces during sedimentation. These solutions were diluted later by fresh sea water, and their material composition altered by diagenesis.

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