

# Fluid inclusions in halite from the Middle Triassic salt deposits in northern Switzerland: evidence for seawater chemistry\*

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The chemical composition of individual fluid inclusions in seven halite samples from the lower unit of the Middle Triassic salt deposits of northern Switzerland was determined using the method introduced by Pertichenko [1]. The analyses of primary fluid inclusion in sedimentary halite indicate, that the original basin brines were of the Na-K-Mg-Cl-SO<sub>4</sub> type, and the ion ratios were similar to modern seawater concentrated to the beginning of halite precipitation. However, SO<sub>4</sub> content was significantly lower. The chemical composition of brine inclusions in recrystallized halite varies widely between the Na-K-Mg-Ca-Cl type and the Na-K-Mg-Cl-SO<sub>4</sub> type. Marine origin of the evaporites is supported by the data on sulphate sulphur isotopic composition (+18.73 to +20.34‰). The data evidence of a Na-K-Mg-Cl-SO<sub>4</sub> type of seawater in Triassic salt layers shows the same composition as recent sea water, but with a probably lower SO<sub>4</sub> ion content compared to recent seawater.

## 1. INTRODUCTION

Earlier fulfilled analysis of data on the chemical composition of primary fluid inclusions in primary-bedded halite from many evaporite formations of northern Pangea showed that during the Phanerozoic the chemical composition of marine brines was oscillating significantly between the Na-K-Mg-Ca-Cl type and Na-K-Mg-Cl-SO<sub>4</sub> type [2]. These changes were considered to correspond to the secular variation in seawater chemistry. In addition, the concentration of K, Mg, Ca and SO<sub>4</sub> ions in marine brines underwent important changes influenced by local factors, including rock-water interaction. The role of global and local factors in basin brine change, however, is a topic of dispute [2-5]. The problem of original brine modification during the postsedimentary stages is also poorly known.

In the present paper we discuss these questions based on a study of fluid inclusions in sedimentary and recrystallized halite from the Middle Triassic salt deposits of northern Switzerland. To confirm a marine origin of the deposits the isotopic

composition of sulphate sulphur in the anhydrite was also studied.

The interest in the study of fluid inclusions in halite is caused by two reasons. (1) No similar study has been previously recorded for the Middle Triassic evaporites. (2) The Triassic is a particularly interesting period due to the important changes in the isotopic composition of ocean sulphate.

## 2. GEOLOGICAL SETTING

The salt of the Swiss salt mines along the Rhine river east of Basel is deposited in the Middle Muschelkalk layers (Triassic). These layers east of Basel are a part of the Mesozoic sedimentary cover of the Herzynian Massifs of the Black Forest north of Basel and the Vosges in the north-west. The salt formation of the Muschelkalk salt is widespread in southern Germany and Switzerland and belongs to a relatively small gulf from northern-Germany to southern-France [6-8].

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East of Basel, the Muschelkalk is near the surface and therefore the salt is therefore partially eroded (subrosion), mainly along the faults which belong to the system of the Rheingraben rift valley (Paleogene). The two salt fields Schweizerhalle and Rheinfelden-Riburg are separated by such faults (Fig. 1). Both locations have wells drilled which are in use for solution mining.

The salt layer has a thickness up to 100 m. The salt shows about 20% impurities of anhydrite, clay, and dolomite and is normally recrystallized. Some parts which still contain the original structure.

### 3. PETROGRAPHY OF THE SAMPLES

All the samples were pieces of drilled cores supplied by United Swiss Saltworks in Pratteln. Sampling was confined to the lower unit of the

Rheinfeld-Riburg and Schweizerhalle salt deposits. Figure 1 and Table 1-3 show the location of the studied wells (R-65, R-101, R-103 and S-129) and the core interval.

Primary chevron and hopper structures (outlined by fluid inclusions) of halite were found only in two samples (R-65, 198.2-198.4 m and S-129, 395.7-396.2 m). The first of them is represented by the salt layer of coarse-grained (up to 3 cm) halite. The layer looks light grey and clear, without sufficient impurities. The primary structures occur most commonly in large halite grains (Figure 2a) from which it is difficult to conclude if these structures are relics of chevron or hopper crystals. However, in some grains clear chevron structures may be seen (Figure 2b).

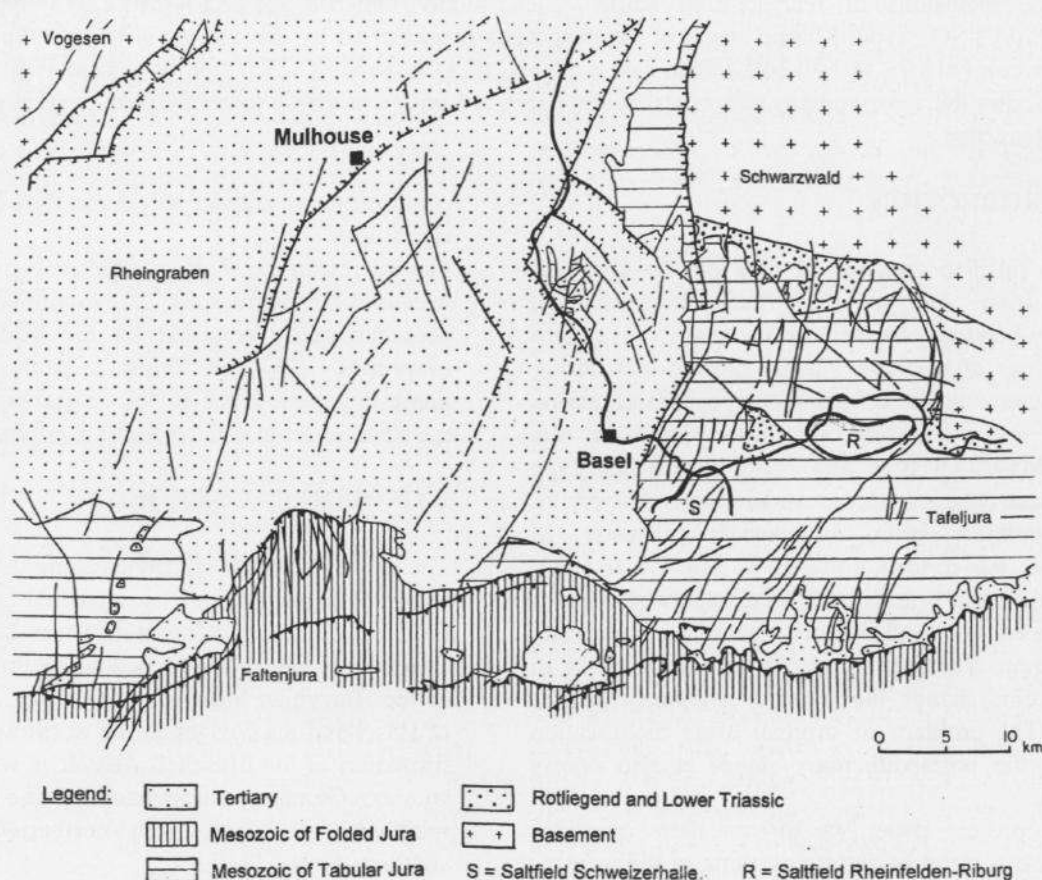


Figure 1. Geological situation of the salt fields east of Basel, Switzerland; S — Salt field Schweizerhalle with salt well S-129; R — Salt field Rheinfelden-Riburg with salt wells R-65, R-101 and R-103.

The size of chevron and hopper forms reaches a few millimetre to 1 cm. and the size of individual inclusions is from a fraction of 1 to 100 micron. Larger inclusions are very rare (Figure 2b). The inclusions are single phase, liquid, have a cubic shape, or close to a cubic shape. In parent halite (in the sample), which occurs in peripheral parts of grains with zonal relics, more rare, but relatively large, fluid inclusions (up to 1 mm across) of irregular shape occur (Figure 2c). Typically, the inclusions contain clots of clay material, anhydrite crystals or gas bubbles. These inclusions seem to have a post-sedimentary origin, because in some of them the fluids were formed under elevated pressure and high gas saturation.

The second sample (S-129, 395.7-396.2 m) is composed of intercalated dark grey and light grey come grained (up to 3 cm.) halite with impurities of clay, dolomite and anhydrite in millimetre thick layers. Chevron and hopper structures of halite were found in large grains in one of the light grey layers of the sample. The crystal structures and the fluid inclusions in the interior or in the transparent peripheral part of the crystals are like those in the cores of well R-65.

The rest of the samples are represented by recrystallized coarse grained and/or coarse crystalline halite with clay, dolomite and anhydrite impurities. One sample (R-101) is represented by breccia in which halite clasts-crystals (up to 3 cm in size) float in clay-dolomite-anhydrite matrix. The grains and crystals of halite are transparent and seem completely recrystallized. Nevertheless, some features of the original sedimentation are still persisting in some of the samples, e.g. the thin cyclic films of anhydrite and the distribution of clay, dolomite and anhydrite within the salt. Many crystals in the samples contain single, relatively large (up to 3 mm) fluid inclusions of irregular shape. Some of these inclusions are connected with tight fractures. Many inclusions contain gas phase; its volume, as a rule, does not exceed 1% of inclusion volume. Elongated anisotropic crystals (anhydrite) and clots of clay and micro-drops of hydrocarbons can be noticed in the inclusions. An often increased pressure and high gas saturation are recorded in these inclusions.

An unusual occurrence of fibers of an uncertain mineral have been found in one clear crystal of halite from the R-103 sample. Many fibers appear to radiate from a point located in the fluid inclusions of irregular shape (Figure 2d). These fibers are similar to those recently described by Belkin and Libelo [9] for Permian bedded salt of the Palo Duro Basin and were determined by the authors as cryptomelane-hollandite originated as a result of diffusion growth process after salt crystallization.

#### 4. ANALYTICAL METHODS

The analysis of individual brine inclusions was done using the ultramicroanalytical method (or method of glass capillaries) by Petrichenko [1]. The method allows us to determine the content of major ions (K, Mg, Ca, and  $\text{SO}_4$ ) in brine inclusions except for Na and Cl. The analytical error of the applied method is ca. 20%. In order to decrease the error of determination several analyses for each major ion in inclusion brine have been carried out. Inclusions close to 100 micron across were used for analyses, although the method permits the analysis of smaller inclusions (down to 40 micron).

The isotopic composition of sulphate sulphur was determined at the laboratory of the Institute of Physics, Maria Curie-Skłodowska University (Lublin, Poland). For the extraction of sulphur dioxide from sulphates the method of Halas and Wolanciewicz [10] was used. The error of the analyses was ranged from  $\pm 0.03$  to  $\pm 0.06\%$  and the data were reported in the  $\delta^{34}\text{S}$  CDT notation. The sulphate specimens for the analyses were represented by nodules and/or thin horizons of anhydrite taken from the large salt samples described above.

#### 5. RESULTS AND DISCUSSIONS

##### 5.1. fluid inclusion composition

The analyses (4 to 5 measurements for each ion) of primary fluid inclusions in primary bedded halite of two samples are presented in table 1. We consider these results as typical to the composition of brines in the evaporite basin during the Triassic. The data indicate that the original brines belonged to the Na-K-Mg-Cl- $\text{SO}_4$  ( $\text{SO}_4$ -rich) type, which is the



chemical type of modern seawater. The correlation with data on modern seawater on evaporation (see table 1, lower line) shows that we have established the brine composition at the initial stages of halite precipitation. However,  $\text{SO}_4$  content was significantly lower.

A very similar chemical composition of solutions has been determined already in the inclusions in sedimentary halite of the Early Triassic basin of Polish Lowland [12] and the Late Triassic Lorraine basin [5]. The data evidence a Na-K-Mg-Cl- $\text{SO}_4$  type of seawater in Triassic and, probably, of a lower  $\text{SO}_4$  content compared to recent seawater. This is in accordance with the results of study of secular variation in seawater chemistry during the Phanerozoic [2]. Nevertheless, we cannot exclude a certain impact of local factors (such as: sulphate reduction, inflow of surface or underground water, run-off of terrigenous material and rock-water interaction) on the brine composition in the basin. The chemical composition of brine inclusions in recrystallized halite of all other samples varies widely between the Na-K-Mg-Ca-Cl type and the Na-K-Mg-Cl- $\text{SO}_4$  type (Table 2).

The ratios of K, Mg and  $\text{SO}_4$  ion in some inclusion brines of the  $\text{SO}_4$ -rich type are close to those in the primary, i.e. sedimentary halite. The information that two types of brines exist in inclusions from recrystallized halite may be used to support indirectly the concept that the on-evaporite-forming brines of the basin were of  $\text{SO}_4$  rich type. We suppose (see also [2]) that the brines of  $\text{SO}_4$ -rich type gradually lose the  $\text{SO}_4$  in burial conditions, ion and gain the Ca ion due to the rockwater interactions. Therefore, brine inclusions in recrystallized halite of such formations may be of any chemical type depending on the timing of their conservation in recrystallized halite and the physico-chemical regime existing during the recrystallization process of salts in an appropriate place. Such interpretation is also supported (for both studied deposits) by the data that the highest pressure and gas saturation of brines were determined in the inclusions with Ca-rich type of brines.

Table 1. Average chemical composition (in g/l) of inclusion brines in sedimentary halite from the Middle Triassic salt deposits, Switzerland

K	Mg	$\text{SO}_4$
Rheinfelden-Riburg deposit, Borehole R-65, 198.2-198.4 m		
6.3 (5) *	11.8 (4)	5.2 (5)
Schweizerhalle deposit, Borehole S-129, 395.7-396.2 m		
9.2 (5)	15.7 (5)	5.6 (5)
Concentrated modern seawater at the beginning of halite precipitation**		
3.9	12.6	17.6

\*In brackets - number of analyses;

\*\*Data after [11]

Table 2. Chemical composition (in g/l) of inclusion brines in recrystallized halite from the Middle Triassic Rheinfelden-Riburg deposit, northern Switzerland

Inclusion No	K	Mg	Ca	$\text{SO}_4$
Borehole R-65, sample 1 (lower unit)				
1	4.0	19.2	10.0	.*
2	8.2	43.0	-	8.6
3	11.5	11.4	3.3	-
Borehole R-65, sample 2 (lower unit)				
1	4.1	13.1	4.5	-
2	5.1	8.2	6.4	-
Borehole R-65, sample 3 (lower unit)				
1	3.1	10.0	58.8	-
2	3.6	32.3	5.6	-
Borehole R-101, 215.6-216.0 m				
1	2.4	42.3	-	-
2	7.2	13.7	-	3.7
Borehole R-103, 191.8-191.9 m				
1	3.1	26.0	-	-
2	5.0	8.9	-	3.6

\* below the detection limit (ca. 1 g/l brine)

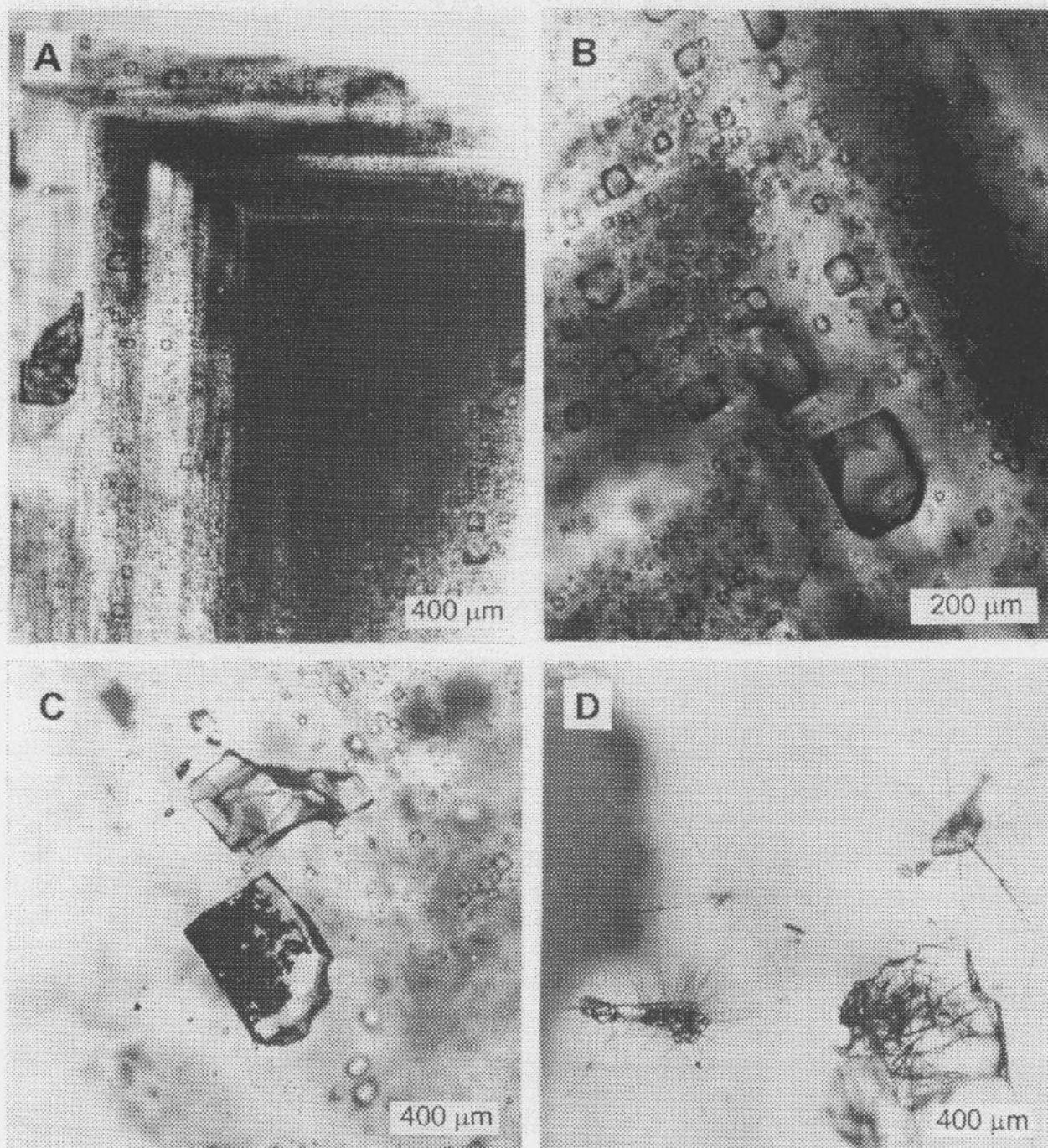


Figure 2. Photographs of characteristic sedimentary structures and fluid inclusions in halite grains from the middle Triassic salt deposits of northern Switzerland; A - A relic of chevron or hopper structure in a grain of halite. Sample R-65, 198.2 – 198.4 m; B - A fragment of a chevron structure with a large fluid inclusion (lower part of the photo). Sample R-53, 198.2 – 198.4 m; C - Large fluid inclusions of irregular shape in the transparent peripheral part of the halite grain. Sample R-65, 198.2 – 198.4 m; D - Large fluid inclusions of irregular shape in recrystallized halite. The fibers of an unknown material appear to radiate from a point located in the two smaller inclusion and penetrate the host mineral. Sample R-103, 191.8 – 191.9 m.



## 5.2. Sulphate sulphur isotopic composition

Sulphate sulphur isotopic composition in 4 studied samples show a narrow scatter of its values (Table 3) which range between +18.73 to +20.34 ‰. They are similar to the data characteristic for marine sulphate of Middle Triassic or Muschelkalk age from throughout Europe and elsewhere ([13] +15 to +22 ‰).

Table 3.

Isotopic composition of sulphate sulphur in anhydrite taken from the samples of the Middle Triassic Rheinfelden-Riburg salt deposit, northern Switzerland

Depth/sample	$\delta^{34}\text{S CDT}(\text{‰})$
Borehole R-65	
198.2-198.4 m	19.64±0.03
Sample 2(lower unit)	19.54±0.03
Borehole R-101	
215.6-216.0 m	18.73±0.06
Borehole R- 103	
191.8-192.9 m	20.34±0.04

## 6. IMPLICATION AND CONCLUSION

Primary chevron and hopper structures outlined by fluid inclusions were found only in two halite samples (from seven studied ones) taken from two Middle Triassic salt deposits of northern Switzerland (Rheinfelden-Riburg and Schweizerhalle). The relatively rare findings of sedimentary forms in halite evidence about significant recrystallization of salts in these deposits.

The analysis of primary fluid inclusions in primary bedded halite of two samples indicates that the original brines belonged to the Na-K-Mg-Cl- type, which is the chemical type of modern seawater. However,  $\text{SO}_4$  content was significantly lower. It is important to stress that a very similar chemical composition of solutions has been reported recently for the early Triassic [12] and late Triassic [5] evaporite basins situated near by this region. The chemical composition of brine inclusions in recrystallized halite varies widely between the Na-K-Mg-Ca-Cl type and Na-K-Mg-Cl- $\text{SO}_4$  type

and this information, as we suppose, supports indirectly the concept of Na-K-Mg-Cl- $\text{SO}_4$  type of the original evaporite-forming basin brines. Some other examples and the background of such interpretation have been published earlier [2]. Marine origin of the evaporites is supported by the data on sulphate sulphur isotopic composition. Its values range between +18.73 to +20.34 ‰.

All these results together permit us to suppose that seawater was the main source of the Middle Triassic basin, but the chemical composition of Middle Triassic ocean differs from the modern water composition by decreased  $\text{SO}_4$  content. The decreased content of  $\text{SO}_4$  ion in the solution of the studied basin may be only partly explained by impact of local factors.

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