

Quantitative analysis of fluid inclusions in evaporites by ion chromatography

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ABSTRACT

Natural salt minerals often contain inclusions of saturated salt solutions with diameters from 1 to > 100 μm . With the quantification of the composition of the fluid inclusions, the origin and metamorphism of the salt rocks can be interpreted. Hence, these data are important concerning the long-term safety of underground repositories in salt rocks [1]. For the extraction of the solutions in fluid inclusions with diameters $\geq 300 \mu\text{m}$, an optical precision instrument was developed. For the simultaneous determination of Cl^- , Br^- , SO_4^{2-} , Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} two ion chromatographic systems with conductivity detection for cations and anions and additional photometric detection for Br^- were used. To prevent column overload, the Cl concentration must be less than 50 $\mu\text{g/ml}$ in the measuring solution. The extracted samples (volumes > 0.1 μl) are diluted with demineralized water by a factor of $1 \cdot 10^4$ (20- μl sample loops). The practical limit of determination for the measured elements is 0.01–0.3 $\mu\text{g/ml}$ in the measuring solutions. By calculation of the anion and cation charge balance (molar equivalence), a relative error of < 5% for the analysis of fluid inclusions was found.

INTRODUCTION

Natural salt rocks (evaporites) always contain saturated aqueous solutions (brines). Often with gases the solutions are stored in cracks, joints and cavernous voids (volumes ranging from ml to > 1000 m^3) and in so-called fluid inclusions (with diameters ranging from 1 to > 100 μm) of salt minerals such as halite (NaCl), sylvite (KCl), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) and others.

In our department, extensive research on salt solutions has been directed at quantifying geochemical processes involved in the formation and metamorphism of marine evaporites and the long-term safety of underground repositories for anthropogenic wastes in evaporites (*e.g.*, ref. 1).

Although the chemical compositions of the solutions found in cracks, joints and caverns are well known, there have been no systematic studies on

the quantitative composition of individual fluid inclusions in the minerals of marine evaporites regarding their origin and metamorphism.

The composition of the saturated solutions in fluid inclusions in salt minerals can be characterized by quaternary and quinary systems for marine evaporites. The chloride type of marine evaporites is characterized by the systems $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ and $\text{NaCl-KCl-MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$ and the sulphate type of marine evaporites by the system $\text{NaCl-KCl-MgCl}_2\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ [2]. Both the major constituents Na, K, Mg, Ca, Cl and SO_4 and the minor components Li and Br have to be determined in order to characterize the composition and interpret the genesis of the fluid inclusions (*e.g.*, refs. 2 and 3).

The composition of salt solutions in fluid inclusions can only be quantified by direct methods. For the extraction of the solutions in fluid inclusions with diameters $\geq 300 \mu\text{m}$, an optical precision instrument was developed [4]. This allowed systematic studies and the consideration of the inclusion

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composition in salt minerals for the quantitative interpretation of evaporite-forming processes. Ion chromatography is necessary for chemical analysis of the extracted solutions because of their usually small volumes of about $0.5 \mu\text{l}$.

EXTRACTION OF FLUID INCLUSIONS AND SAMPLE PREPARATION

In addition to other methods, the direct analysis of individual inclusions is possible by opening the fluid inclusions with a needle or micro-drill followed by extraction of the solutions (*e.g.*, refs. 5–8). The best-developed method for the determination of the major and minor chemical components of individual fluid inclusions (diameters $>250 \mu\text{m}$) in salt minerals was the extraction method optimized by Lazar and Holland [8].

For our studies, a new extraction apparatus was developed [4]. This instrument can be used for extracting aqueous salt solutions from fluid inclusions with diameters $\geq 300 \mu\text{m}$ (for explanation, see Fig. 1). A video system is used for documentation of the

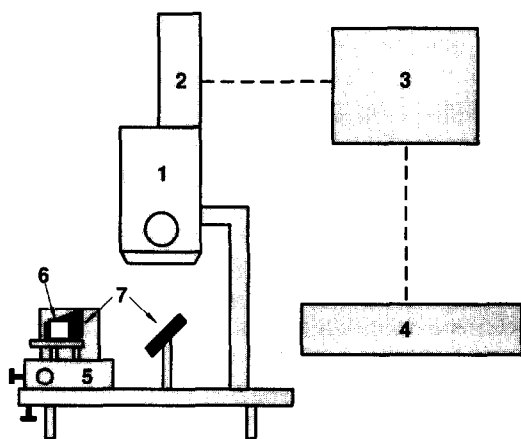


Fig. 1. Schematic diagram of equipment for extracting salt solutions from fluid inclusions $>300 \mu\text{m}$. 1 = Stereo microscope with (2) a colour video camera, (3) monitor, and (4) video recorder. (5) Universal stage attached to the built-on stage of the stereo microscope. The stage in front of the microscope is used for securing the mineral or rock sample containing the inclusions (6) to work with the tungsten-carbide micro-drill and micro-pipette for penetration and extraction of the inclusion. Since the universal stage is in front of the stereo microscope, the image must be projected by two flat mirrors (7) into the optical system of the microscope and the videocamera for observation and monitoring of the work. The mirror system allows a simultaneous view of the sample from two directions.

processes occurring within the inclusion upon penetration, *e.g.*, enlargement of pressurized gas bubbles when the inclusions are opened. Thus, the pressure experienced by a gas bubble in an inclusion can be calculated by measuring its diameter before and after penetration of the inclusion (Boyle–Mariotte law).

After the inclusion has been penetrated with a tungsten micro-drill, a micro-pipette (a capillary tube made of borosilicate glass) is used for extraction of the saturated salt solutions if the inclusions have diameters of $300\text{--}400 \mu\text{m}$; for diameters $>400 \mu\text{m}$ a microlitre syringe is used. The projecting end of the capillary is about 0.01 mm thick. The steel cannula of the microlitre syringe has a diameter of 0.18 mm .

The capillary is inserted in the fluid inclusion and the salt solution is drawn from the inclusion into the glass capillary with a plastic syringe. To prevent water from evaporating during this procedure (causing a change in the concentration of the solution and crystallization of salt), a small volume of oil is first drawn into the empty capillary. After the aqueous solution has been extracted, oil is again drawn into the capillary so that both ends are protected from evaporation.

Depending on the size of the fluid inclusion, $0.1\text{--}1 \mu\text{l}$ of saturated salt solution is extracted with the glass capillary. The volume of this solution is calculated based on the geometry of the liquid column in the capillary. Subsequently the organic (oil) and inorganic (salt solution) phases in the capillary are carefully separated as they are pushed out, to prevent contamination of the columns with organic phases.

The embedding of the inclusion solution in oil is not necessary if a microlitre syringe is used. Hence, there is no risk of contaminating the columns with organic phases. The cannula has to be filled with membrane-filtered demineralized water before extraction. Thus the volume of the solution is directly given by the graduation marks on the syringe. For a detailed description of the extraction procedure, see ref. 3.

The salt solutions are diluted by a factor of about 10^4 with deionized water (see Table I) and frozen in plastic flasks until analysis.

It should be emphasized that all measuring solutions should be membrane filtered and the tools

TABLE I
COMPOSITION OF ANIONS AND CATIONS IN TWO FLUID INCLUSION SAMPLES AFTER DILUTION

See Figs. 3–5; data after ref. 3 and L. E. von Borstel (personal communication). For measuring conditions see Table II.

Parameter	Sample GO-K		Sample WI-5	
	Diluted sample	Extracted solution	Diluted sample	Extracted solution
Volume	1.8 ml	0.16 μ l	2.99 ml	0.31 μ l
Calculated density ^a	–	1.297 g/cm ³	–	1.226 g/cm ³
Dilution factor	11 250.00	–	9354.84	–
Cl [–]	26.4 μ g/g	22.9%	21.1 μ g/g	16.1%
Br [–]	0.38 μ g/g	3353 μ g/g	0.06 μ g/g	486 μ g/g
SO ₄ ^{2–}	0.71 μ g/g	0.62%	2.36 μ g/g	1.8%
Li ⁺	0.022 μ g/g	191 μ g/g	n.d. ^b	–
Na ⁺	0.98 μ g/g	0.85%	12.1 μ g/g	9.2%
K ⁺	0.55 μ g/g	0.48%	1.31 μ g/g	1.0%
Mg ²⁺	8.53 μ g/g	7.4%	0.96 μ g/g	0.73%
Ca ²⁺	0.01 μ g/g	0.009%	n.d. ^b	–
Molar equivalents, anions		0.6584		0.4914
Molar equivalents, cations		0.6583		0.4862
Molar equivalents, relative error referred to the anions		0.01%		0.7%

^a Calculated after ref. 9.

^b Not detected.

should be repeatedly cleaned with hot deionized water before use. This is necessary because of the small volumes of the concentrated solutions. For example the microlitre syringe has to be cleaned about 20 times after use until there are no residues of the extracted solutions.

SET-UP OF THE USED ION CHROMATOGRAPHIC SYSTEM

The anions and cations in the fluid inclusions are determined by ion chromatography with chemical suppression of the background conductivity. We used two 2000iSp systems from Dionex. Fig. 2 shows a scheme of the instrumental set-up and Table II gives a summary of the measurement conditions.

At the beginning of the studies the samples were injected manually, but for flushing and proportionally filling the two 20- μ l sample loops for measurement of anions and cations usually just 1–3 ml of

measuring solution are available (see Table I). Because of these small volumes the arrangement of the chromatographic modules was carefully optimized to minimize the dead volume by shorting the lines as far as possible. The manual injection still gave no reproducibility of the measured values. An acceptable relative standard deviation (R.S.D.) of < 5% could only be achieved by using an automatic sample changer.

A knowledge of the concentrations of Br[–] and Li⁺ is necessary for the interpretation of the data, but the concentrations of the major components are up to 1000 times higher than the concentrations of Br[–] and Li⁺ (see Table I). A decrease in the background conductivity and an increase in the detection limits could be achieved by using the suppressor technique. From experience a Cl[–] concentration of > 50 μ g/ml in the measuring solutions leads to values that are not reproducible. This is an effect of overloading the separation column with Cl[–]. Overloading of the columns causes longer rinsing

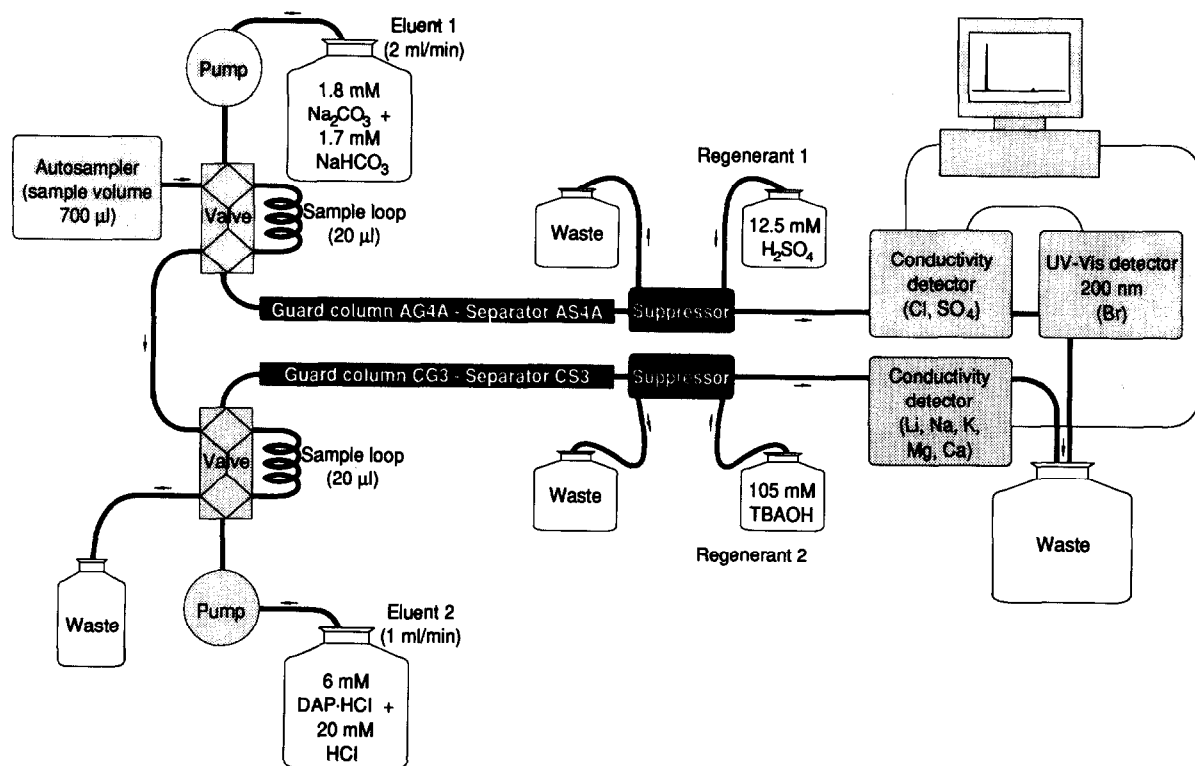


Fig. 2. Scheme of the chromatographic system used for the simultaneous determination of anions and cations in fluid inclusions. For experimental conditions see Table II.

TABLE II

MEASUREMENT CONDITIONS FOR SIMULTANEOUS DETERMINATION OF ANIONS AND CATIONS IN FLUID INCLUSIONS WITH TWO ISOCRATIC DIONEX 2000iSp CHROMATOGRAPHIC SYSTEMS

Cf., Fig. 2. Total injected volume of measuring solution, 700 µl.

Parameter	Anions (Cl ⁻ , Br ⁻ , SO ₄ ²⁻)	Cations (Li ⁺ , Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺)
Guard column	AG4A	CG3
Separation column	AS4A	CS3
Eluent	1.8 mM Na ₂ CO ₃ + 1.7 mM NaHCO ₃	6 mM 2,3-diaminopropionic acid (DAP · HCl) + 20 mM HCl
Flow-rate	2 ml/min	1 ml/min
Pressure	8.3 MPa (1200 p.s.i.)	5.5 MPa (800 p.s.i.)
Sample loop	20 µl	20 µl
Suppressor	AMMS-1	CMMS-1
Regenerant	12.5 mM H ₂ SO ₄	105 mM tetrabutylammonium hydroxide (TBAOH)
Flow-rate	4–5 ml/min	4–5 ml/min
Detection	(a) Conductivity (Cl ⁻ , SO ₄ ²⁻) (b) Photometry, UV detection at 200 nm (Br ⁻)	Conductivity
Background	(a) 19.9 µS (b) Set to 0 automatically	3.4 µS

times. In addition, often the volumes of the extracted solutions are too small to work with different dilution steps because we try to carry out at least two measurements per sample.

The AS4A separation column and the AMMS suppressor are suitable for the determination of the anions Cl^- , Br^- , and SO_4^{2-} . The anions are determined by using two different detection systems, a conductivity detector and a UV detector. Two systems are necessary as the amount of Cl^- is up to 300 times higher than that of Br^- . In addition, the retention times of Cl^- and Br^- are similar. Hence a measurement of the signals for Cl^- and Br^- using conductivity detection alone is not possible when there are large differences in concentration (e.g., ref. 10, p. 320). Br^- is determined by direct UV absorption as Cl^- is significantly less photoactive than Br^- . This means that the Cl^- peak in the UV detector is substantially smaller, and thus the Br^- signal is clearly separated from that of Cl^- (Fig. 3). The conductivity detector is used for measuring Cl^- and SO_4^{2-} (Fig. 4).

The CS3 separation column and the CMMS suppressor are used for determining the cations Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} with a conductivity de-

tector. The monovalent alkali metal ions Li^+ , Na^+ and K^+ and the divalent alkaline earth metal ions Mg^{2+} and Ca^{2+} are determined in a single run (Fig. 5).

For filtration of the TBAOH, the common acetate and nitrate filters were first used, but these materials are not completely resistant to the regenerant. It should be emphasized that the background conductivity of the cation system could be decreased from about 9 to $3.4 \mu\text{S}$ by using nylon filters.

Table III gives an overview of the retention times of anions and cations. For the evaluation of the results a three- to six-point calibration is required. Complete measurement of anions and cations takes about 15 min. A drift correction can be carried out by using the blank and one calibration solution.

When measuring near the detection limit manual reintegration of the peaks is often necessary in order to obtain reliable analytical data. The Windows software used makes possible a convenient and clear optimization of the results. In combination with spreadsheet software a rapid statistical evaluation of the results or, for example, the calculation of the mole equivalents for examination of the quality of the results (*cf.*, Table I) is possible.

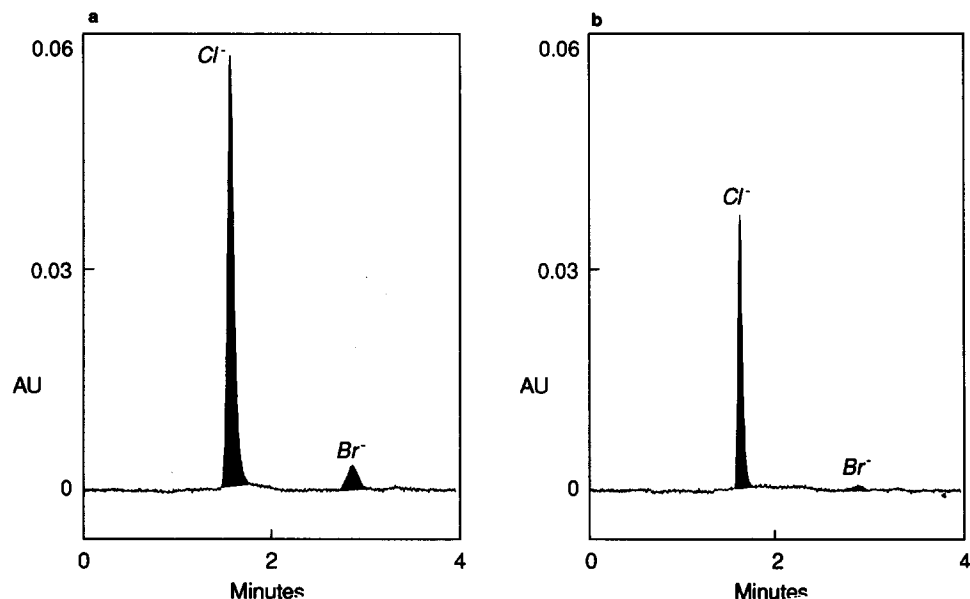


Fig. 3. Determination of Br^- in fluid inclusion samples in natural NaCl crystals with direct UV detection. (a) Sample GO-K; (b) sample WI-5. For concentration data see Table I and for experimental conditions see Table II.

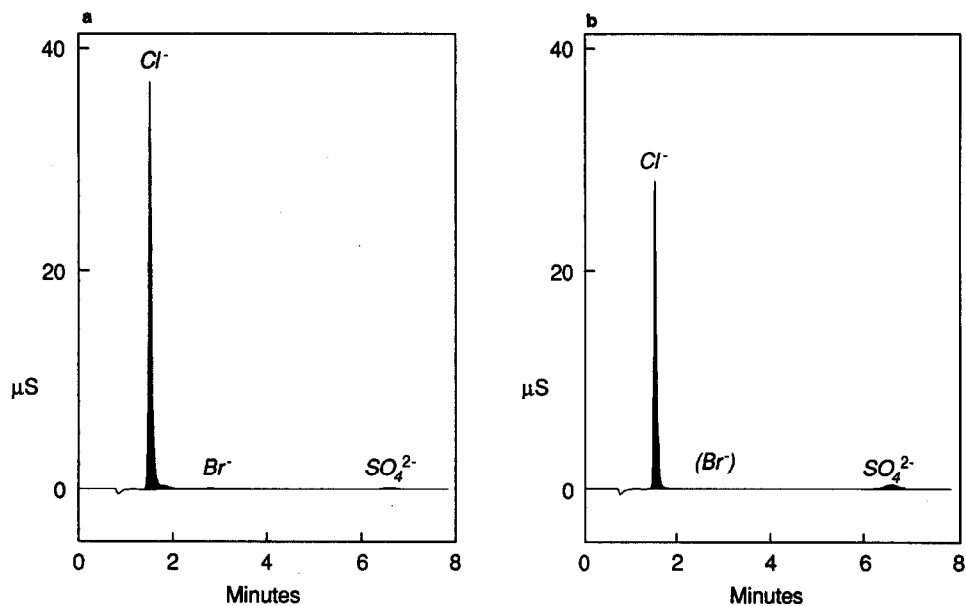


Fig. 4. Determination of anions in fluid inclusion samples in natural NaCl crystals with conductometric detection. (a) Sample GO-K; (b) sample WI-5. For concentration data see Table I and for experimental conditions see Table II.

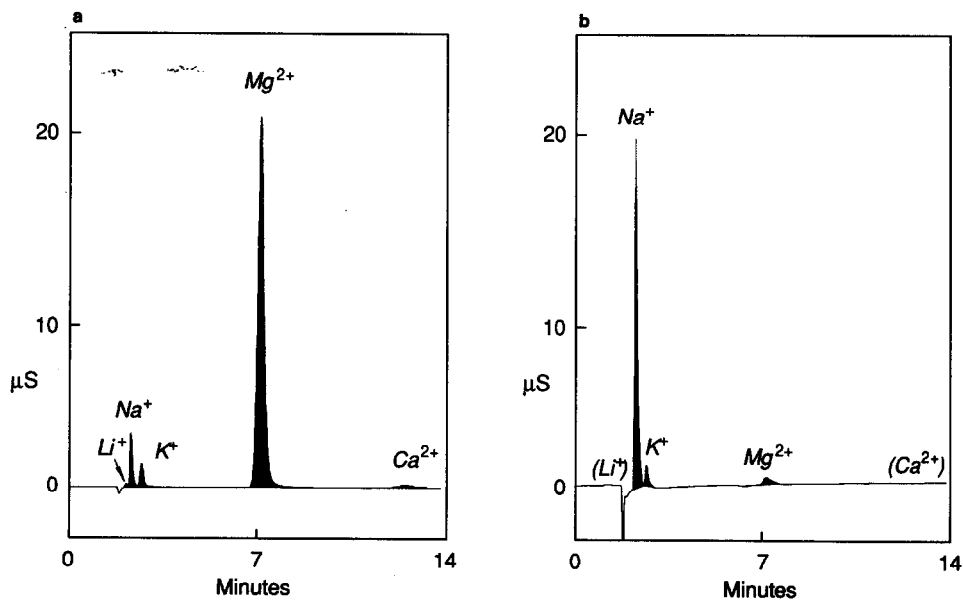


Fig. 5. Determination of cations in fluid inclusion samples in natural NaCl crystals with conductometric detection. (a) Sample GO-K; (b) sample WI-5. For concentration data see Table I and for experimental conditions see Table II.

TABLE III

RETENTION TIMES FOR SIMULTANEOUS DETERMINATION OF ANIONS AND CATIONS IN FLUID INCLUSIONS

For measuring conditions see Table II. Retention times \pm threshold values for peak detection.

Component	Retention time (min)	Component	Retention time (min)
Cl ⁻	1.54 \pm 0.023	Na ⁺	2.29 \pm 0.034
Br ⁻	2.89 \pm 0.043	K ⁺	2.69 \pm 0.040
SO ₄ ²⁻	6.74 \pm 0.169	Mg ²⁺	7.06 \pm 0.177
Li ⁺	2.14 \pm 0.032	Ca ²⁺	12.21 \pm 0.305

Calculation of the analytical data

Table I shows the composition of two typical solutions from fluid inclusions. For calculation of the analytical results in other common units (*e.g.*, g/l or mol per 1000 mol of water), a knowledge of the density of the extracted solutions is necessary. Because of the small volumes this cannot be measured directly. Therefore, the density is calculated based on the volume and quantitative composition of the solution using a computer program [4] based on the method of D'Ans *et al.* [9].

The mean composition of the measuring solutions is Cl⁻ 20, Br⁻ 0.3, SO₄²⁻ 10, Li⁺ 0.1, Na⁺ 10, K⁺ 3, Mg²⁺ 10 and Ca²⁺ 1 μ g/g. A mean error (R.S.D., $n = 30$) of <0.5% was calculated for this composition. The R.S.D. of the complete method including extraction by using a glass capillary and dilution is 10–13%, which is about ten times higher than for extraction of the solutions from the fluid inclusions with a microlitre syringe (*ca.* 1–3%).

The detection limits in one-component solutions are about 0.01–0.04 μ g/g for Br⁻, 0.1 μ g/g for Li⁺, Mg²⁺ and Ca²⁺ and about 0.1–0.3 μ g/g for Cl⁻, SO₄²⁻, Na⁺ and K⁺. It should be emphasized that these are theoretical values. For example the empirical determination limit for Li⁺ depends strongly on the Na⁺ content of the solutions (*cf.*, Fig. 5).

Interpretation of analytical data

The geochemical interpretation of the data involves the formation and origin of the fluid inclusions in the evaporite minerals. Two important questions should be answered: are the inclusions residues of concentrated brines (sea water) from former basins in which the salts were deposited mil-

lion years ago, or do the fluid inclusions contain solutions that are products of mineral reactions and material transports after the evaporite deposition? The mathematical calculations necessary to answer these questions are based on physical chemistry and experimental data of solution equilibria (*e.g.*, refs. 1, 2, 3 and 11).

In conclusion, these investigations, in connection with geological and other geochemical studies [1], enable one to state whether and where a salt rock body suffered metamorphism in the geological past. These results are important contributions to statements about the long-term safety of underground repositories in salt rocks [1].

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