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Chemistry and isotopes of deep geothermal saline fluids in the Upper Rhine Graben: Origin of compounds and water-rock interactions

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Abstract—Deep boreholes (≤2870 m) in the Upper Rhine Graben produce medium-temperature (120–150°C) saline fluids that circulate through the granitic basement and/or the overlying sedimentary rocks. The salinity of these deep fluids, sampled from both the granite and the sedimentary rock, can be explained by a three-step model: (1) evaporation of seawater which produces a primary brine; (2) mixing between a dilute fluid and the primary brine; and (3) dissolution of halite by the later fluid. The thermal waters sampled at shallower depths are the result of mixing of the deep saline fluid and surface water.

Geothermometer calculations indicate that some of the deep fluids did reach high temperatures (up to 220–260°C). During cooling, reactions between fluid and rock took place, but the fluids did not have enough time to reach complete equilibrium with the surrounding rock.

INTRODUCTION

The Rhine Graben has a high geothermal gradient, between 5 and 10°C (average 6.5°C at a regional scale) per 100 m, which was the reason that a few boreholes were drilled specifically for geothermal studies. These holes produce saline fluids that could be sampled at depths surpassing 2000 m in 320 Ma granite or 225–230 Ma triassic sandstones (Buntsandstein).

During mining activities, it was discovered long ago that highly saline fluids circulate in crystalline rock. Such fluids have been studied in the Canadian Shield (FRITZ and FRAPE, 1982; FRAPE et al., 1984; FRAPE and FRITZ, 1987), at Stripa in Sweden (NORDSTROM et al., 1989a,b), in Finland (LAHERMO and LAMPEN, 1987), in the U.K. (EDMUNDS et al., 1984, 1985), in Australia (MCARTHUR et al., 1989), in the Bohemian Massif (PAČES, 1987), and in various places of Eastern Europe, from the Kola Peninsula to the Black Sea, and from the Baltic to the Urals (VOVK, 1987).

All fluids studied as part of the European Hot Dry Rock project at Soultz-sous-Forêts, which were sampled in both the granite and the overlying Buntsandstein sandstones, have identical chemical and isotopic compositions (PAUWELS et al., 1991), indicating a common origin. The aim of this paper is to assemble all available chemical and isotopic data on the deep fluids found in the Upper Rhine Graben, discussing the origin of the dissolved salts as well as the changes in chemical composition over time. We will also discuss the origin of the chemical composition of the thermal waters sampled at shallower depth around Soultz-sous-Forêts.

GEOGRAPHICAL AND GEOLOGICAL SETTING

The ten boreholes and the spring that yielded fluids for this study are located in the Rhine Graben (Fig. 1), which forms part of the West European Rift (VILLEMIN, 1986). The graben extends over a distance of 300 km, between Basel in the south to Mainz in the north, with an average width of about 40 km. Faults with strike lengths of up to several kilometres separate the graben from the Hercynian crystalline massifs (Vosges, Black Forest, and Odenwald) and their overlying sedimentary rocks (rims of the Paris Basin and the Jura Mts.). In some parts of the graben, the succession of Permian to Quaternary sedimentary rocks can be as much as 3 km thick.

Soultz-sous-Forêts, the area chosen for investigations as part of the European Hot Dry Rock project, has been known since the 18th Century for its oil production at Pechelbronn, literally pitch spring. The geothermal gradient here is very high and reaches 10.5°C per 100 m, which could in part be the result of forced convection (CLAUSER, 1987), or of hydraulic discharge (OTTO and TÓTH, 1988). The fluids from three deep boreholes were studied. Holes GPK1 and EPS1 reached depths of 2000 and 2200 m, and produced in the granite fluids with a slight artesian flow at depths of 1820 and 2175 m, and at temperatures of about 137 and 150°C, respectively. Hole 4616 is an old oil well that has a total depth of 1403 m; the producing level here is in Buntsandstein sandstones at a temperature of 116°C.

The Cronenbourg borehole is located around 5 km north of Strasbourg city center. It has a producing level in Buntsandstein at a depth of 2870 m, where the temperature is about 160°C.

The total depth of the Bühl hole in Germany is 2655 m; it produces fluids from Buntsandstein at a temperature of about 115°C.

The Bruchsal holes in Germany were drilled for geothermal exploitation; GB1 was drilled to 1800 m in Buntsandstein, and the GB2 hole stopped at 2540 m depth in Permian rocks. Temperatures measured were 114 and 128°C, respectively.

In a geothermal sense, Soultz-sous-Forêts is the most interesting site. At Cronenbourg and Bruchsal, the geothermal anomaly is less intense and at Bühl the geothermal gradient is the lowest.

In addition to these deep holes, the Pechelbronn area contains several shallower wells that were drilled for thermal spas. They are located to the west of Soultz and farther away from the centre of the geothermal anomaly. The Hélions borehole at Merckwiller produces from Buntsandstein 1100 m deep, and at Morsbronn there are two 600 m deep holes. Morsbronn bas (low) and Morsbronn haut (high). The Roman spring at Niederbronn issues from 215–225 Ma triassic dolomitic limestones (Muschelkalk) rocks.

PETROGRAPHY

The petrography of the granite was described by GENTER (1989) and TRAINEAU et al. (1991), based on cores from the GPK1 and EPS1 holes. The rock is a porphyritic granite with K-feldspar megacrysts, quartz, biotite, hornblende, and plagioclase. Accessory minerals are apatite, titanite, and magnetite. Pervasive alteration has formed secondary chlorite, corrensite, carbonates, epidote, and hydrogarnet. Fluid circulation in the fractures caused the precipitation of white mica, illite and smectite, carbonates, galena and pyrite, iron oxide, and quartz.

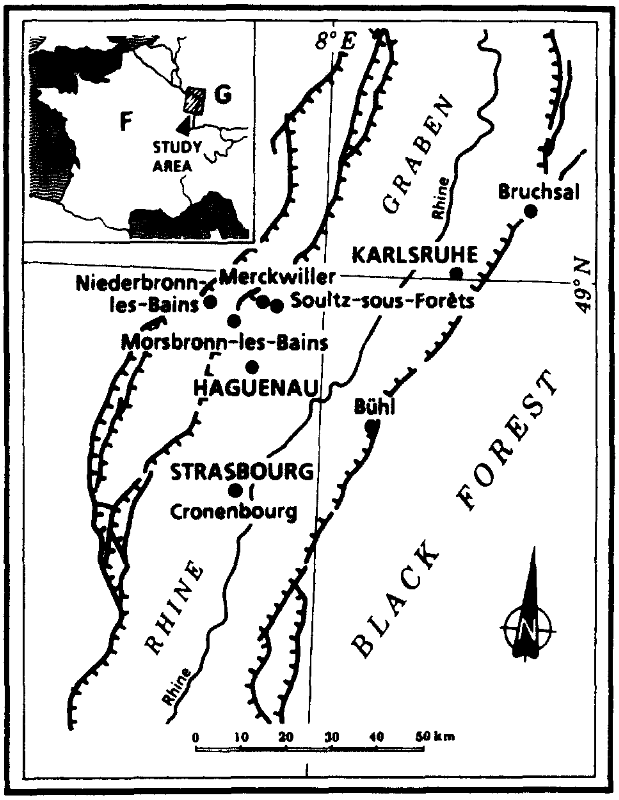

FIG. 1. Location of geothermal boreholes and thermal waters in the Rhine Graben.

Permian rock is poorly-sorted reddish, clay-rich sandstone, with conglomerate horizons containing granite and volcanic-rock pebbles. Permian rock is 10 m thick in hole EPS1 but was not found in hole GPK1.

Triassic Buntsandstein consists of sandstone, siltstone, claystone, polymictic conglomerate, and dolomite. Diagenesis has transformed unit rock in a very irregular fashion, depending on the depth of burial (CLAUER et al., 1986). Hydrothermal infilling of fractures consists of vein quartz, barite, calcite, galena, and pyrite. Its thickness is between 400 and 500 m.

Triassic Muschelkalk consists of dolomitic limestone with clay and evaporite deposits. It is up to 170 m thick.

FLUID SAMPLING AND ORIGIN OF DATA

The fluids, and in some cases the associated gases, collected by our group were sampled between 1986 and early 1991, at the well head or at the spring discharge point. This concerned the GPK1 (KS228), EPS1, 4616, Morsbronn bas, Morsbronn haut, and Hélions wells, and the Niederbronn's spring. In GPK1, three more samples, KD005, KD006, and KD007, were taken with a downhole sampler, respectively, at depths of 1810, 1845, and 1930 m. The fluids of all samples passed through a 0.45 μm filter. A few parameters were determined on site, such as pH, total alkalinity, and GLR (gas/liquid volume ratio discharged during production). The sample fraction reserved for determining cations was acidified to pH = 2 with ultrapure HNO_3. Cadmium acetate was added to the solutions used for sulphur-isotope determinations and water isotopes were determined on a non-filtered fraction. All analyses were made at BRGM, except the sulphur isotope analyses of the Morsbronn and Niederbronn waters, which are from TARDY (1980) and FRITZ (1981).

Chemical analysis of the Cronenbourg fluids was done at the geochemical laboratory of the Centre de Géochimie de la Surface (CNRS) at Strasbourg [FRITZ (1980) and discussed by RICHARD et al., (1993)], and the isotope analyses of the same samples were done at BRGM.

Two fluid samples were collected with a downhole sampler from the Bühl hole by the NL fB team led by Prof. Schellschmidt in Buntsandstein at depths of 2460 and 2535 m. They were then analysed at BRGM.

The chemical data on the Buntsandstein fluids from the two Bruchsal holes were obtained by Matthess and Schenk from the Geology and Paleontology Institute of Kiel University and by Pekdeger from the Institute of Applied Geology of the Free University of Berlin. The isotope results were obtained by Buheitel, Eichingen, and Ertl from Hydroisotop GmbH (Attenkirchen, Germany). All these data were reported by FRITZ et al. (1989).

RESULTS

The fluids from boreholes GPK1 (TDS = 99 g/L), EPS1 (TDS = 101 g/l), and 4616 (TDS = 103 g/l), regardless of whether they come from the granite (GPK1 and EPS1) or the Buntsandstein below Soultz-sous-Forêts, are highly saline and have very similar chemistry and isotope compositions (Tables 1, 2, and 3). The same characteristics are found in the Cronenbourg fluid. Sodium and chloride are the dominant ions, but the fluids are equally enriched in Li, Sr, and some other elements. They also contain large quantities of gas (gas/liquid volume ratio GLR at 25°C has a value of 20%). Samples taken at different depths in GPK1 also gave very similar results, and little chemical variation seems to exist with depth. However, in GPK1 differences were noted between the samples taken with downhole sampler and the one collected at the well head (KS228). They occur in the hydrogen concentration in the gas fraction (Table 2), and the pH and alkalinity (Table 1), and are due to interaction of the saline fluid with the well casing, which provokes a consumption of H^+ ions to liberate hydrogen and iron. Only a few elements, such as sulphate or calcium, show different contents among the various wells. The sodium-chloride fluids of the Bühl well are the most saline (TDS = 207 g/L). The sampling of these fluids did not properly preserve silica in solution, as recommended for geothermal solutions (FOURNIER, 1981), so that the analytical results cannot be used. The Bruchsal fluids (TDS = 120 and 124 g/L) are slightly more mineralized than those of the Soultz-sous-Forêts area.

The thermal-spa wells in the Soultz area, which are much shallower than the geothermal wells, tap in the Trias, fluids that are much less strongly mineralized; e.g., the Merckwiller, Morsbronn, and Niederbronn waters, respectively, have TDS values of 20.5, 5 to 6, and 4.7 g/L.

In the following discussion, these Soultz, Cronenbourg, Bruchsal, and Bühl fluids will be referred to as the deep fluids, whereas other fluids will be termed thermal waters.

DISCUSSION

The Deep Fluids

The fluids sampled in the granite below Soultz are thus very strongly mineralized. The origin of such brines, which are found in crystalline rocks in different parts of the world, is puzzling. Different hypotheses have been advanced, such as a strong contribution from the interaction between water and rock (EDMUNDS et al., 1984, 1985), the dissolution of fluid inclusions (NORDSTROM and OLSSON, 1987; NORDSTROM et al., 1989b), and influx of seawater (MCARTHUR et al., 1989).

Table 1: Chemical composition of the Upper Rhine Graben fluids.

	pH	Alk meq/l	Na g/l	K g/l	Ca g/l	Mg mg/l	Cl g/l	SO4 mg/l	Br mg/l	SiO2 mg/l	B mg/l	F mg/l	Li mg/l	Fe mg/l	Sr mg/l	Ba mg/l	Rb mg/l	Cs mg/l
DEEP FLUIDS																		
Soultz-sous-Forêts																		
GPK1 KS228	5.82	10.6	28.2	3.32	6.73	150	58.5	215	299	97	34.0	3.9	123	232	480	12.3	25.1	15.7
KD005	5.22	4.29	27.2	3.21	6.76	145	57.0	205	291	97	32.0	-	122	53	-	12.0	-	-
KD006	5.02	3.09	28.0	3.28	6.96	152	58.1	220	310	94	33.6	-	126	7.5	-	12.5	28.8	12.0
KD007	5.14	4.18	27.9	3.40	6.93	152	58.5	225	302	93	34.6	-	126	30	-	12.5	-	-
EPS1	-	-	28.3	3.36	7.99	122	59.8	76	234	150	36.0	1.6	199	400	512	8.4	-	-
4616	5.50	14.1	27.8	3.45	8.40	140	60.9	240	280	110	40.3	4.5	148	275	440	10.0	39	13.3
Cronenbourg	-	2.2	31.5	4.03	4.81	126	62.0	480	361	143	37.9	5.5	210	-	405	-	29	12.0
Bühl																		
B2460	-	-	64.0	0.494	11.6	1930	120.3	1586	711	-	29.0	31.8	41.0	41	456	-	0.9	0.6
B2535	-	-	63.9	0.503	11.7	1900	120.5	1525	726	-	31.1	31.0	41.2	36	485	2.3	1.0	0.6
Bruchsal																		
GB1	-	7.70	38.1	2.20	7.74	434	75.2	387	230	41.8	4	0.85	166	78	324	4	1.9	2.2
GB2	-	6.97	36.8	3.22	7.89	403	74.3	243	-	30.7	27.4	0.40	-	69.8	-	-	-	-
THERMAL WATERS																		
Merckwiller/les Hélions	6.20	5.09	5.20	0.564	1.50	111	11.3	675	47.3	37.4	7.0	3.9	29.6	-	67.8	0.69	4.25	-
Morsbronn-les-bains																		
Morsbronn haut	6.34	5.12	1.55	0.175	0.463	31.2	2.77	675	12.3	18.6	-	2.4	8.6	-	16.1	0.078	-	-
Morsbronn bas	6.43	5.10	1.33	0.142	0.318	25.2	2.39	380	9.9	19.2	-	2.2	6.9	-	12.1	0.078	-	-
Niederbronn-les-bains	6.67	5.12	1.26	0.119	0.345	55.0	2.46	80.3	14.7	14.4	-	2.0	6.2	-	1.4	0.162	-	-

In the case of Soultz, all deep fluids have very similar chemical and isotopic compositions, whether they were sampled in granite or sedimentary rock. The large number of faults in the Rhine Graben enable fluids to circulate between different geologic units, which led us to look for a common origin of the fluids found in granite and those sampled in overlying sedimentary rocks.

To construct the hypotheses on the origin of the salinity of the deep fluids of the Upper Rhine Graben, we plotted the data on two series of binary diagrams (Figs. 2 and 3). The difference between the fluids from Soultz, Cronenbourg, or Bruchsal, and those from Bühl cannot be explained by simple mixing in different proportions between a saline fluid and fresh water, as the deuterium content of the water hardly varies with the chloride-ion concentration (Fig. 3b). If mixing had occurred, the two endmembers of the mixture should have had the same δD value, which is unlikely.

The Cl/Br ratio of fluids is a commonly used tool to define the origin of such fluids (e.g., COLLINS, 1967; RITTENHOUSE, 1967; PATTERSON and KINSMAN, 1977; RETTIG et al., 1980; WALTER et al., 1990, and others). A graph of chloride vs. bromide content of the deep fluids (Fig. 2) compares data with the evaporation curve of present-day seawater up to the precipitation of KCl (data compiled by MATRAY, 1988). The diagrams suggest that the salinity of the deep fluids could be simply due to the evaporation of seawater before NaCl precipitated, as the points in the diagrams lie only very slightly below the evaporation curve. However, following this hypothesis, the Bühl fluids would have derived from more intense evaporation, even though such an hypothesis is in contradiction with the deuterium data. In fact, the deuterium content increases during the evaporation of seawater (PIERRE, 1982). This means that the fluids should have a positive δD, and that the Bühl fluids should be richer in deuterium than the ones from Soultz, Cronenbourg, and Bruchsal.

The chemistry and isotope [δD, $\delta^{18}O(H_2O)$] composition

Table 2: Free gas composition and gas/liquid volume ratio (G.L.R.) of the Soultz fluids

	Type	G.L.R. %	CO_2 %	N_2 %	CH_4 %	H_2 %	He %
Soultz-sous-Forêts							
GPK1 KS228	Wellhead	20	46.3	27.3	4.8	20.1	1
KD006	In-situ	-	67.1	27.4	4.2	0.61	-
KD007	In-situ	-	54.3	37	6.1	0.25	-
4616	Wellhead	21.3	46.8	28.2	5.6	18.1	1

Table 3: Isotope composition of the Rhine Graben fluids

	$\delta^{18}O(H_2O)$ ‰	$\delta D(H_2O)$ ‰	$\delta^{18}O(SO_4)$ ‰	$\delta^{34}S(SO_4)$ ‰
DEEP FLUIDS				
Soultz-sous-Forêts				
GPK1 KS228	-3.1	-41.0	8.5	17.1
KD005	-3.2	-42.3	7.8	16.6
KD006	-2.6	-39.8	7.8	17.4
KD007	-2.8	-41.0	8.2	17
EPS1	-2.5	-38.2	7.3	16.2
4616	-2.7	-37	8.1	17
Cronenbourg	-2.2	-40.0	8.1	-
Bühl				
B2460	-1.02	-35.8	13.9	16.7
B2535	-1.31	-35.4	13.9	16.9
Bruchsal GB1	-3.29	-41.4	9.2	16.5
THERMAL WATERS				
Merckwiller/les Hélions	-8.4	-62.5	12.6	17.9
Morsbronn-les-bains				
Morsbronn haut	-8.94	-67.0	14.4	17.9
Morsbronn bas	-10.0	-68.0	11.9	18.5
Niederbronn-les-bains	-9.0	-65.4	11.25	16.6

of the deep fluids in the Upper Rhine Graben cannot be explained by a simple process of evaporation or mixing, and a more complex origin must be sought, for which several options are open. The Cl, Br, or B concentrations in combination with the stable isotope compositions of the deep fluids suggest the following scheme:

1) Formation of a primary brine by advanced evaporation of seawater, which has higher Br/Cl, B/Cl, and δD/Cl ratios than those of seawater (compiled by MATRAY, 1988).
2) Mixing of this primary brine with a dilute fluid must have occurred. The proportions of the mixing must be very similar for all deep fluids studied here in order to explain their very similar deuterium composition. The chemical composition of the resulting mixed fluid is represented by point M in Figs. 2a,b, and 3a, at the intersection between the mixing curve and an almost horizontal line which crosses bromine, boron, or $\delta^{18}O$ contents of the deep fluids.
3) This fluid must then have dissolved NaCl, causing a decrease in the Br/Cl and B/Cl ratios. Figure 2a and b show how the chemical composition shifts from point M almost horizontally to the right. Moreover, the oxygen-isotope composition of the water must have changed as a result of the interaction with rocks (shift to the right from point M on Fig. 3a). In fact, salt deposits are quite common in Keuper (Upper Trias) and Tertiary rocks of the Rhine Graben.

The degree of evaporation of the seawater that formed the primary brine cannot be determined; instead, the straight mixing line on Figs. 2 and 3 was arbitrarily continued in the direction of the point that represents the water composition

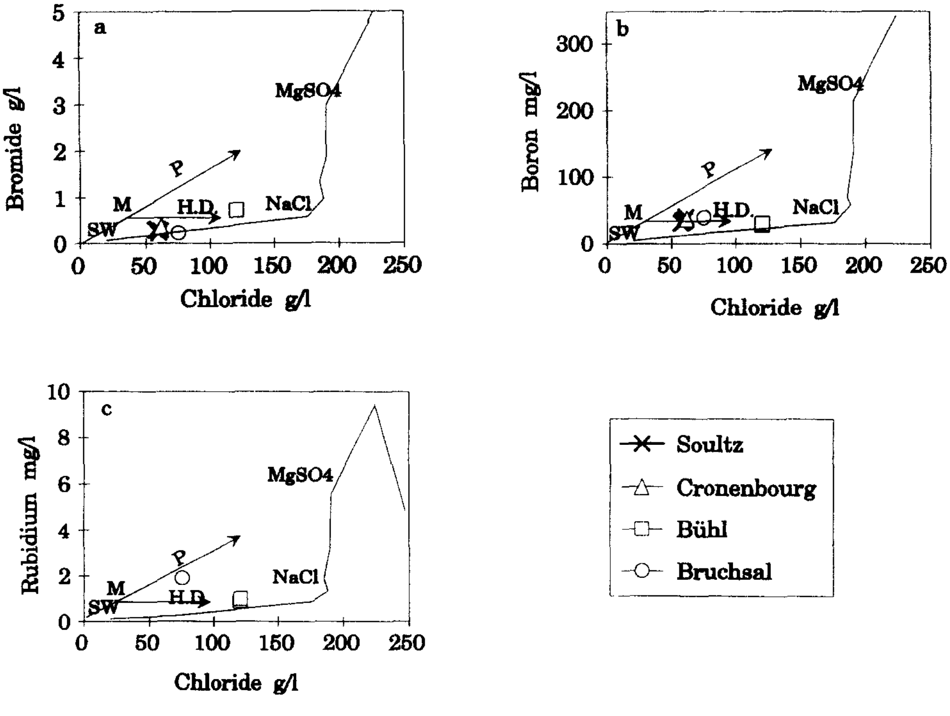

FIG. 2. Bromine, boron, and rubidium concentrations plotted against chloride concentrations of deep fluids from the Rhine Graben. The curve shows the chemical composition during evaporation of seawater (compiled by MATRAY, 1988). SW: seawater; NaCl and $MgSO_4$: start of the precipitation of these phases. P: mixing line between a primary brine and surface water; H.D.: line showing dissolution of halite; M: point on the mixing line depicting composition of deep fluids before halite dissolution.

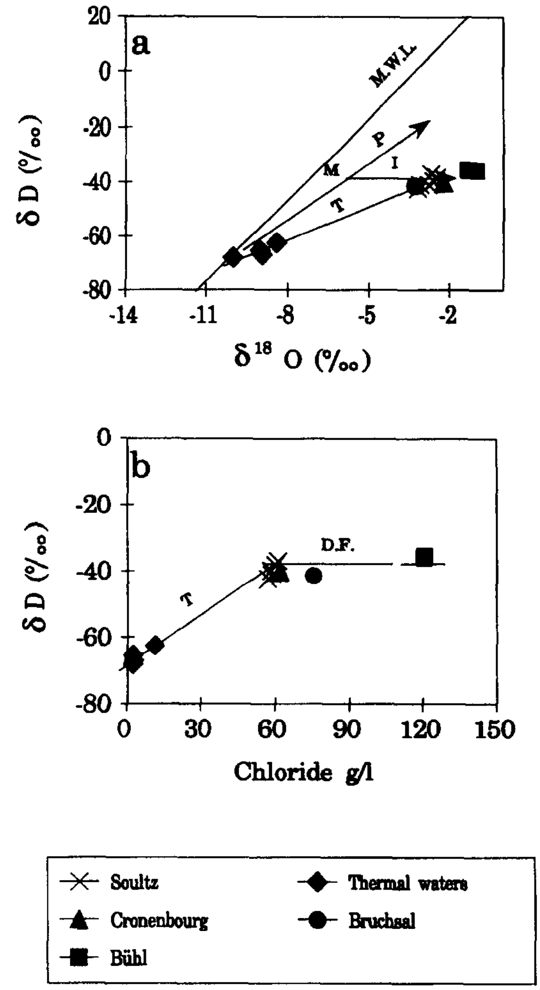

FIG. 3. Isotope composition of the Rhine Graben fluids. M.W.L.: international line for meteoric water; D.F.: line depicting composition of deep saline fluids; T: line indicating mixing between Soultz deep fluid and fresh water to provide thermal waters; I: ^{18}O shift due to interaction with rocks at elevated temperature.

at the start of $MgSO_4$ precipitation. However, the mixing pole might be different, but more geological and chemical data are needed to determine this point more accurately.

Geothermometry

The temperatures of the various deep and thermal fluids were estimated on the basis of chemical and isotopic geothermometers found in the literature. These temperatures are compared with measured values (Fig. 4 and Table 4).

Cation geothermometers

All geothermometers based on cation ratios are empirical. The most commonly used is the Na/K one. The equations (TRUESDELL, 1976; FOURNIER, 1979; ARNORSSON, 1983) have been calibrated in relatively dilute solutions, and therefore give inconsistent results when applied to brines. These geothermometers are based on the theoretical hypothesis of equilibrium between water and the mineral assemblage. Therefore, in saline fluids, a better approximation of temperatures would be obtained from a thermodynamic study as done in recent works by GUIDI et al. (1990) and CHIODINI et al. (1991). Temperature predicting in brines requires a powerful method, particularly to calculate activities. PITZER'S (1973) formulation, which allows calculation of the thermodynamical properties of multicomponent electrolyte solutions up to very high concentrations, could therefore be used. Nevertheless, some geothermometer equations have been tested and even calibrated in saline solutions. KHARAKA and MARINER (1989) investigated the use of several geothermometers to estimate the temperatures of formation waters, including oil-field waters where salinities are generally higher than those found in geothermal waters. They proposed a modified version of the Na/K geothermometer (Table 4) and considered that for saline waters, among the commonly used geothermometers, the Na-K-Ca-Mg one (FOURNIER and POTTER, 1979) provides the best temperature estimate. For the fluids from the Upper Rhine Graben (Fig. 4a,c, and d), the Na-K-Ca geothermometer (FOURNIER and TRUESDELL, 1973) gives temperatures in close agreement with the measured ones for the Bühl waters. For the other fluids, the three geothermometers give much higher temperatures than are actually found. The maximum calculated temperatures are 225°C at Bruchsal, and 250–260°C at Soultz, Cronenbourg, and for the thermal spas. The Na/K geothermometer gives the highest temperature and the Na-K-Ca-Mg one the lowest.

Mg/Li and Na/Li geothermometers (KHARAKA and MARINER, 1989) were specially conceived for waters from sedimentary basins, and a recent study on brines from Gulf of Mexico sedimentary basins confirms that they are the most useful geothermometers in such a setting (LAND and MACPHERSON, 1992). These geothermometers give at Bühl results that agree with the measured temperatures (Fig. 4b and e). At Soultz, Bruchsal, and Cronenbourg, both thermometers give high results, like the other cation thermometers. The Na/Li temperature of the thermal waters is the same as that estimated with the Na/K geothermometer, but the Mg/Li results indicate lower temperatures, similar to those for Na-K-Ca-Mg.

These calculations show that the cation composition of the Bühl fluids is approximately in equilibrium with its environment at the sampling depth. The Soultz, Bruchsal, and Cronenbourg deep fluids, however, are not in equilibrium with the rock at the sampling depth, and the results are independent of the rock type where the samples were taken. They apparently reached equilibrium at very high temperatures (e.g., in a deeper reservoir), which were up to 220–260°C at Soultz and Cronenbourg, and up to 160–230°C at Bruchsal, depending on which cation geothermometer is used.

Each geothermometer shows similar behavior for all the thermal waters. The Na/K, Na-K-Ca, and Na/Li equations yield the highest results which are about the same as the temperatures estimated for the Soultz fluids. These thermal waters are not at equilibrium with the rock at the sampling depth. The magnesium geothermometers (Na-K-Ca-Mg or Mg/Li) provide intermediate temperatures which is not surprising because in a sedimentary environment, relatively rapid exchange reactions of lithium and magnesium with clay minerals justifies the use of the Mg/Li geothermometer, even at low temperatures (KHARAKA and MARINER, 1989).

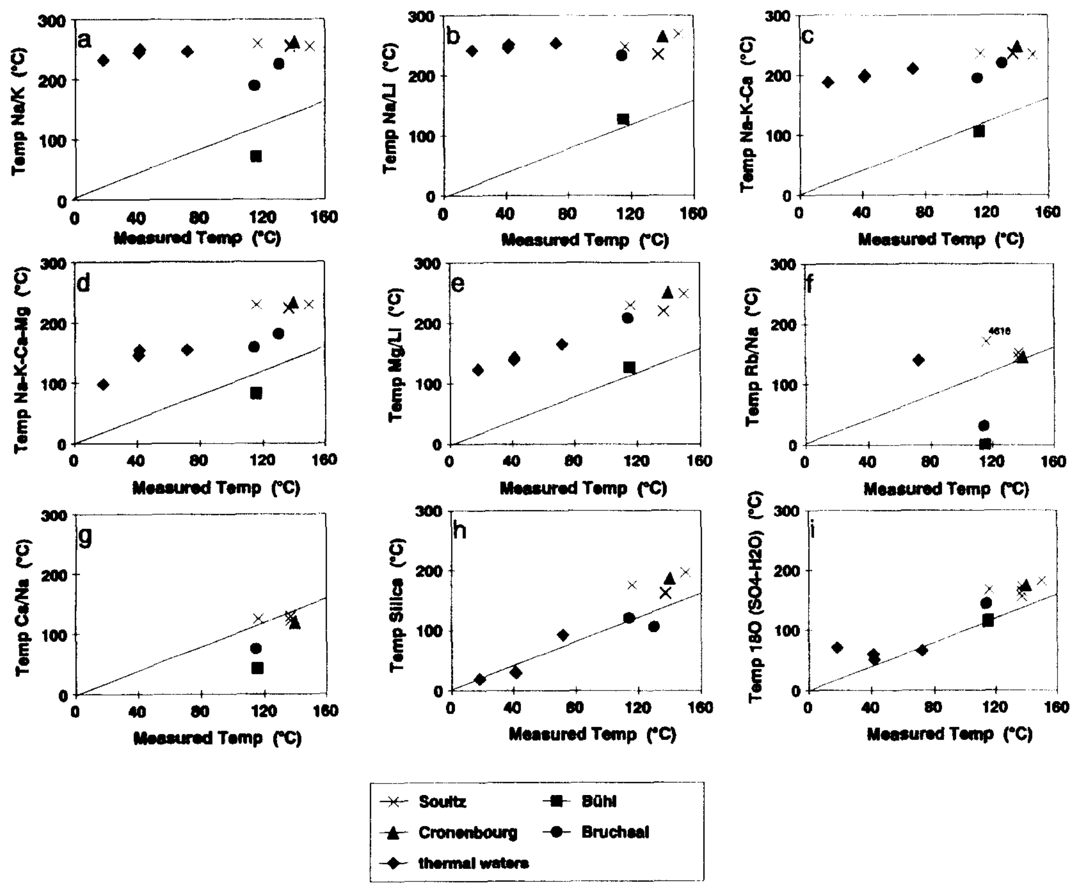

FIG. 4. Graph of calculated temperatures based on chemical and isotope geothermometers vs. measured temperatures of Rhine Graben fluids. Solid line indicates equivalence of measured and calculated temperatures. (a–e) temperatures estimated with cation geothermometers plotted against measured temperatures; (f–g) temperatures estimated from rubidium and caesium concentrations (MICHARD, 1990), plotted against measured temperatures; (h) temperatures estimated from silica concentrations plotted against measured temperatures; (i) temperatures estimated from the isotope geothermometer, plotted against measured temperatures.

Moreover, according to these authors, the Na-K-Ca-Mg geothermometer is known to give good temperature estimates in sedimentary rocks.

Many studies have shown that the behavior of trace elements in fluids and rocks depends on the temperature. For this reason, relations between temperature and (trace element)/(major element) ratios were established from chemical data on fluids circulating in granites (MICHARD, 1990). We then applied the relations between Rb/Na, Cs/Na, and temperature to fluids of the Upper Rhine Graben, where data for caesium and/or rubidium were available. The temperatures of deep fluids in the sedimentary rocks at Bruchsal and Bühl thus calculated are low, particularly the Rb/Na temperatures. However, the GPK1, 4616, and Hélions fluids have Rb/Na and Cs/Na temperatures that are close to the temperature measured in the roof of the granite at Soultz (123°C). The reason that the temperatures thus calculated for Bühl and Bruchsal are so low is because the thermometric relations of the caesium and rubidium used are not applicable to fluids seeking an equilibrium in sedimentary rock. These relations are not yet proven, and no conclusions should be drawn concerning the differences with temperatures obtained with the usual cation geothermometers; it can only be concluded that the results are of the same order of magnitude.

Silica geothermometer

This geothermometer (FOURNIER and ROWE, 1966) is based on the experimental solubility of silica minerals in water, which is expressed by the following reaction:

$$SiO_2(\text{solid}) + 2H_2O \leftrightarrow H_4SiO_4, \qquad (1)$$

where, in a high-temperature geothermal environment the solid silica phase is either quartz or chalcedony.

The solubility product *Ks* of this reaction is given by the equation

$$Ks = \frac{^{a}H_4SiO_4}{^{a}SiO_2(s)\cdot {}^{a^2}H_2O}, \qquad (2)$$

where a is the activity of the indexed species.

In fact, the silica geothermometers assume that the activity coefficients of H_4SiO_4 and water are both equal to unity. This

Table 4: Temperatures of fluids in the Upper Rhine Graben: measured, calculated by assuming equilibrium with quartz or chalcedony and calculated with cation and isotope geothermometers

	Measured Temp	Quartz (a)	Chal (b)	Na/K (c)	Na-K-Ca (d)	Na-K-Ca-Mg (e)	Na/Li (f)	Mg/Li (g)	$^{18}O(SO_4)$ (h)
DEEP FLUIDS									
Soultz-sous-Forêts									
GPK1 KS228	137	162.5	132.0	253.8	235.1	223.3	233.3	219.2	155.6
KD005	137	162.0	131.5	254.1	234.4	223.5	235.3	219.6	163.9
KD006	137	160.5	130.0	253.3	234.2	222.9	235.5	220.1	172.9
KD007	137	160.0	129.5	257.4	236.9	225.2	235.8	220.1	164.0
EPS1	150	196.5	160.5	254.7	233.9	229.6	269.0	248.9	182.4
4616	116	175.0	142.5	259.3	235.9	229.8	247.7	230.0	166.9
Cronenbourg	140	186.5	153.5	262.4	247.4	233.0	264.9	250.9	174.5
Bühl									
B2460	115	-	-	71.6	105.9	82.1	127.1	126.9	117.0
B2535	115	-	-	72.5	106.6	83.4	127.4	127.3	114.0
Bruchsal									
GB1	114	120.5	96.0	189.9	195.2	159.4	233.2	208.4	144.0
GB2	128	105.5	80.5	225.2	219.7	181.1			
THERMAL WATERS									
Merckwiller/les Hélions	72	92.5	67.5	245.6	209.5	155.0	252.7	165.0	65.9
Morsbronn-les-bains									
Morsbronn haut	41.6	60.7*	28.6*	249.7	199.5	154.8	250.8	143.3	51.2
Morsbronn bas	41	61.9*	29.8*	243.6	196.7	146.3	245.4	139.5	59.8
Niederbronn-les-bains	18	51.5*	19.1*	231.9	187.8	98.1	241.6	123.4	70.9

The borehole temperatures were estimated from measurements made during or after drilling.

(a) (b) * : calculated with quartz or Chalcedony geothermometer.

(c) : $t = \frac{1180}{\log(Na/K) + 1.31} - 273$; (d) : Fournier and Truesdell (1973)

(e) : Fournier and Potter (1979); (f) : $t = \frac{1590}{\log(Na/li) + 0.799} - 273$

(g) : $t = \frac{2200}{\log(\sqrt{Mg/Li}) + 5.47} - 273$ (h) : Mizutani and Rafter (1969)

assumption is correct in dilute solutions only, as is true for the relatively dilute fluids of Morsbronn and Niederbronn. However, this assumption should be reconsidered for the more saline fluids (FRITZ et al., 1987). Therefore, water activity and the activity coefficients for H_4SiO_4 of the Soultz, Bruchsal, and Merckwiller fluids were calculated, as was earlier done for the Cronenbourg fluid (ZINS-PAWLAS and FRITZ, 1988). The water activity was calculated with the EQ3/6 software (WOLERY et al., 1990) from the equation (HELGESON et al., 1970)

$$\log(a_{H_2O}) = 0.00782 \cdot vi \cdot mi \cdot \rho i, \quad (3)$$

where vi is the number of ion moles in the formula of the electrolyte i, mi is the molality and ρi is the osmotic coefficient of i.

For modelling the salt effect upon neutral molecules (i.e., H_4SiO_4), an equation can be used that is similar to PITZER (1973) formulation, but is known as SETCHENOW's (1892) equation:

$$\log(\gamma) = D \cdot m, \quad (4)$$

where m is the molality of salt in solution, D is a parameter that varies with temperature and the type of salt in solution and γ is the activity coefficient. Parameter D is calculated at any temperature from the data published by MARSHALL (1980) and CHEN and MARSHALL (1982) (Table 5).

For solutions with several electrolytes, the activity coefficient is calculated by applying the principle of additivity as discussed by MARSHALL and CHEN (1982):

$$\log(\gamma) = \sum_i (Di \cdot mi), \quad (5)$$

where Di and mi correspond to the parameter D and the molality of each electrolyte i.

For each fluid the activity coefficients of H_4SiO_4 and water at different temperatures were calculated; after this we compared the second half of Eqn. 2 with the solubility constants of quartz and chalcedony at various temperatures, and with the pressure in the producing level. Equality indicates an equilibrium temperature of the fluid with either quartz or chalcedony.

The temperatures thus calculated were all higher than those calculated with traditional silica geothermometers, a discrepancy already noted by KHARAKA and MARINER (1989). The higher the salinity, the larger the difference in temperature. If one considers that the Hélions (TDS = 20.5 g/L) and KS228 (TDS = 98.8 g/L) fluids are in equilibrium with quartz, the temperatures calculated by the previous method

Table 5: Parameters in eqn: $D = a + bT = CT^2$ for calculating the activity coefficient of silica (Marshall, 1980; Chen and Marshall, 1982)

Specific salt	a(10)	b(10^4)	c(10^7)
NaCl	1.8754	-4.5052	3.0504
Na_2SO_4	0.5472	2.0844	-8.6803
$MgCl_2$	3.3566	-0.8385	-6.3309
$MgSO_4$	7.5108	-28.74	29.828
KCl	0.28		
LiCl	1.43		
$CaCl_2$	2.8		

are, respectively, 4°C and 30°C higher than those calculated with the geothermometers.

A common problem for application of silica geothermometers is the identification of the mineralogical phase that is in equilibrium with the fluid. ANORSSON (1975) showed that in Iceland, above 180°C, quartz is always in equilibrium with the fluid, whereas below 110°C, it is always chalcedony. Between these two temperatures it is difficult to determine which of the two phases is in equilibrium with the fluid. In granite, MICHARD et al. (1986) noted that the fluids are in equilibrium with quartz or chalcedony between 70 and 140°C. According to KHARAKA et al. (1977), the chalcedony geothermometer should be used for waters in a sedimentary basin where the temperature is below 70°C, and the quartz geothermometer should be used at higher temperatures. For these reasons, the temperatures of the Morsbronn and Niederbronn thermal waters were calculated using the chalcedony geothermometer (Fig. 4h), but for all other fluids, the temperature was calculated assuming equilibrium with quartz according to the method developed previously. For the Soultz, Cronenbourg, and Merckwiller fluids, the calculated temperature (Fig. 4h) is slightly higher than the measured one, but this difference would disappear if chalcedony rather than quartz were chosen. However, in view of the temperatures measured in the producing levels as those calculated from cation geothermometers, it seems more reasonable to consider that their chemical composition tends towards equilibrium with quartz. If the silica would have been the only element of the aqueous phase to be taken into account, it might have been possible to erroneously conclude that the fluid was in equilibrium with chalcedony.

Regardless of the silica phase considered, the silica geothermometers give temperatures that are much closer to the measured temperatures than those provided by the various cation geothermometers. The fluids were cooled and silica was one of the first elements to respond to this change. A faster re-equilibration of silica geothermometers than cation ones is frequent, and for example was already noted by EDMISTON and BENOIT (1984) for many geothermal reservoirs in the Basin and Range tectonic province of the western USA.

Isotope geothermometer

The ^{18}O isotope geothermometer of SO_4-H_2O (MIZUTANI and RAFTER, 1969) when applied to the Bühl fluids, like the Na-K-Ca, Na/Li, or Mg/Li geothermometers, gives a good approximation of measured temperatures. For all other fluids, this geothermometer indicates temperatures that are clearly lower than those obtained by the cation geothermometers (Fig. 4i). Chemical mechanisms must have disturbed this ^{18}O geothermometer. The agreement between the temperatures calculated using this geothermometer and those calculated from the silica geothermometer must be fortuitous because according to the kinetic data of LLOYD (1968) and CHIBA and SAKAÏ (1985), several years would be required to reach an isotopic equilibrium between H_2O and SO_4, for the relevant temperature and pH conditions of the fluids.

For the deep Soultz, Cronenbourg, and Bruchsal fluids, which reached temperatures of up to 250°C according to the cation geothermometers, a linear relationship is observed between the ^{18}O composition of sulphates and the inverse of the sulphate concentration (Fig. 5). This relationship supports the hypothesis that sulphates were supplied by dissolution, and the Y axis intercept thus indicates the isotope composition of the dissolving mineral (+8.6‰). Assuming isotopic equilibrium of the deep fluids at the temperature given by the Na/K geothermometer and using the isotopic geothermometer formula and the $\delta^{18}O$ values of H_2O, we recalculated the isotope composition that the sulphates must have had in a hot deep reservoir: the result falls between +3.4 and +3.7‰. These figures indicate that between 75 and 90% of the sulphate content of the deep fluids derives from the dissolution of sulfate minerals during the cooling. Because sulphate mineral (anhydrite, gypsum) solubilities increase as temperature decreases, the disturbance of the ^{18}O isotope geothermometer of SO_4-H_2O in deep fluids probably was caused by the dissolution of sulphate minerals which have precipitated during earlier hydrothermal circulation. For the thermal waters, the relation between $^{18}O(SO_4)$ and the inverse of sulphate concentration cannot be observed and several processes may have played a role, e.g., mixing, dissolution, and precipitation with

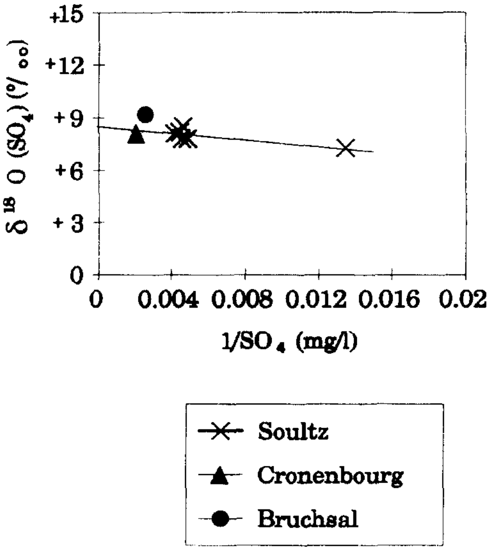

FIG. 5. The $\delta^{18}O$ values of dissolved sulphates from the deep saline fluids plotted against the inverse sulphate concentration.

fractionation. These processes explain why temperatures calculated with the isotope and the Na/K and Na/Li geothermometers differ.

Consequences of the Geothermometer Results on the Use of Such Geothermometers and on Understanding of the Reservoir

The deep saline fluids of Soultz, Cronenbourg, and Bruchsal apparently reached high temperatures (up to 260°C), which indicate that they originated in a hot and deep reservoir. The geothermometer calculations for the thermal waters indicate equally high initial temperatures. During cooling, the chemical composition of most of these fluids did not have the time to re-equilibrate. Furthermore, it was found that these deep fluids occur in areas where the geothermal gradient is highest. In the case of Soultz, OTTO and TÓTH (1988) showed that the geothermal-gradient anomaly is partly related to forced convection.

The Bühl fluids, however, show no imprint of very high temperatures; the hole has the lowest geothermal gradient and should thus lie outside an area with deep groundwater flow.

The cooling of the fluids did not lead to a complete chemical re-equilibration of the fluids with their environment. The silica geothermometer re-equilibrates the quickest, followed by the Mg/Li and Na-K-Ca-Mg ones, and finally by the rather inert Na/K, Na/Li, and Na-K-Ca ones. The ^{18}O composition from dissolved SO_4 was subjected to several disturbances (dissolution, precipitation) that caused temperatures calculated from the ^{18}O of SO_4-H_2O geothermometer to be lower than those estimated from the cations.

The results from the Bühl fluids show that the Na-K-Ca, Mg/Li, Na/Li, and ^{18}O of SO_4-H_2O geothermometers give good results in this type of sedimentary environment.

The Thermal Waters

The thermal waters sampled around Soultz-sous-Forêts are more dilute than the deep fluids. Moreover, they have different chemistry and isotope compositions.

The deuterium- and oxygen-isotope compositions of these waters show a very strong meteoric component (Fig. 3a), but most cation geothermometer results indicate that all fluids reached the same high temperatures as the Soultz fluids. This duality can be explained by mixing of fresh surface water and a deep, very saline fluid. During such mixing, if no time is available to reach a new equilibrium with the surrounding rock, the Na/K or Na/Li ratios would remain unchanged and the fluid memorizes the equilibrium temperature of the most concentrated fluid. The concentrations of potassium, sodium, and bromine for the Soultz fluids and the thermal waters vary linearly with chloride content (Fig. 6). However, the concentrations of other elements such as fluorides, magnesium, and sulphates, cannot be explained by a simple binary mixing mechanism and other phenomena, such as dissolution of minerals and re-equilibration of the fluids, must have occurred.

The chloride/δD diagram (Fig. 3b) confirms this mixing between a deep saline fluid and fresh water. This figure indicates also that the deep Soultz fluid is one of the mixing endmembers because it lies at the intersection between the mixing line (T) and the horizontal line (D.F.) representing the composition of the deep fluids. The mixing itself was favoured by the existence of the dense Rhine Graben fault network.

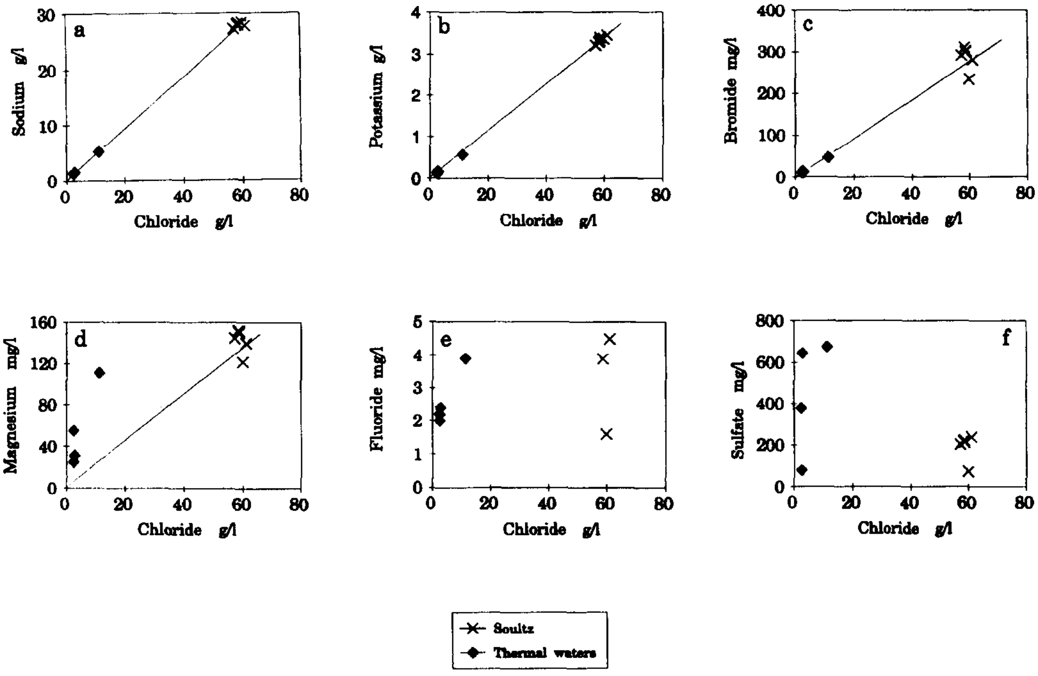

FIG. 6. Chemical composition of the thermal waters and deep Soultz fluids.

Evolution of the Fluids During Their Circulation in the Rhine Graben

The concentrations of several elements (e.g., silica, sulphates . . .) show that chemical reactions between the fluids and the surrounding rock occurred during the cooling of the deep saline fluids or their mixing with fresh water. For that reason, we studied the degree of saturation of the fluids for several minerals (Fig. 7). The saturation index of each mineral was then calculated, i.e., the ratio between the ion activity product (IAP) and the solubility constant (*KT*) of the mineral at the sampling pressure and temperature. The activity of the various species was then calculated according to PITZER's (1973) formula in those cases where the necessary parameters were available.

The results of the ^{18}O of SO_4-H_2O geothermometer and the concentration variations in sulphate ions observed in closely spaced wells, like those drilled at Soultz, made us particularly interested in sulphate minerals.

Excluding the fluids of Bühl, which seem to be almost in equilibrium with gypsum (Fig. 7b), the deep fluids appear to be close to equilibrium with anhydrite (Fig. 7a). This mineral was observed in Buntsandstein and as an alteration phase in granite around Soultz (GENTER and TRAINEAU, 1992). The sulphate-ion concentration of the fluids thus reaches a fairly rapid equilibrium after cooling, which means that the fluid would have dissolved anhydrite during its rise, explaining the results obtained with the ^{18}O of SO_4-H_2O geothermometer.

The thermal waters, even though enriched in sulphate ions when compared with a simple mixture of deep and dilute fluids, are neither in equilibrium with gypsum nor with anhydrite. This means that the anhydrite found in sedimentary rocks must dissolve.

The thermal waters are in equilibrium with barite (Fig. 7c). While cooling, the solubility of barite decreases and it can precipitate. This process can explain the disturbance of the ^{18}O isotope geothermometer of SO_4-H_2O on the thermal waters. Data of the deep fluids are more scattered. Traces of this mineral were observed in granite in borehole EPS1. Its $\delta^{34}S$ determined on seven samples (+13.6 to +18‰) showed that only a small fraction of this barite can have precipitated from the studied fluids ($\delta^{34}S$ between +16.2 and +17.4‰), as sulphur-isotope fractionation relative to SO_4 for barite is 4.5‰ at 150°C (KUSAKABE and ROBINSON, 1977). Most of the barite must then have precipitated during earlier hydrothermal circulation.

The variations in fluoride concentrations are quite large: this ion seems quickly affected by cooling and is not preserved during the subsequent mixing. Our tests of the degree of saturation of the fluid for fluorite (Fig. 7d) showed that even though most of the thermal waters are close to equilibrium for this mineral the other fluids scatter widely from the saturation level. In any case, no fluorite was detected during the petrographic work on granite and Buntsandstein samples.

The degree of saturation of the fluids for carbonate minerals cannot be directly calculated, as many of the basic data are missing, like gas/liquid ratio, pH, or the composition of the gaseous phase that is associated with the fluid. Furthermore, during the rise of these fluids to the surface, the pH is strongly modified because of oxidation of the well casing. Petrographic observations showed the presence of calcite in the granite and Buntsandstein and of dolomite in the granite. We thus consider the following reaction:

$$2CaCO_3 + Mg^{2+} \leftrightarrow CaMg(CO_3)_2 + Ca^{2+}. \qquad (6)$$

If the solution is in equilibrium with both calcite and dolomite phases, the following equation can be checked:

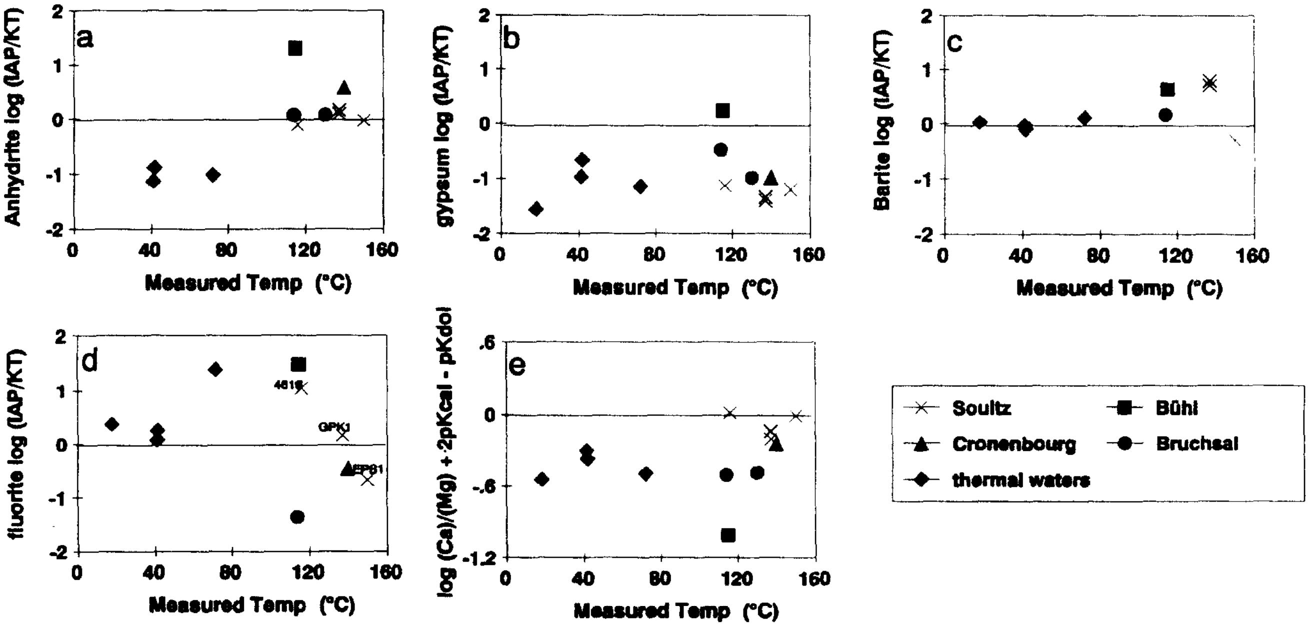

FIG. 7. Saturation index of the Rhine Graben fluids for the following minerals: (a) anhydrite; (b) gypsum; (c) barite; (d) fluorite. Horizontal line indicates saturation, so that data points that plot above the line are oversaturated and those that plot below are undersaturated. diagram (e) shows the reaction: 2 calcite + Mg^{2+} ↔ dolomite + Ca^{2+}

$$\frac{(Ca^{2+})}{(Mg^{2+})} = \frac{Kcal^2}{Kdol}, \qquad (7)$$

where *K*cal and *K*dol are the equilibrium constants of calcite and dolomite.

The results are plotted on Fig. 7e. From this diagram, it is not possible to predict if solutions are at equilibrium with the two mineral phases, for which two independent tests with calcite and dolomite would be necessary. Nevertheless, it appears that the thermal waters and the Bühl and Bruchsal fluids are very far from equilibrium with the calcite-dolomite assemblage (Fig. 7e), but some chemical modifications of the Soultz and Cronenbourg fluids during their rise appear from the figure. Because calcite samples in GPK1 are not in isotopic equilibrium with the fluid (FOUILLAC and GENTER, 1991) and because solubility of carbonate minerals increases with decreasing temperature, the Soultz and Cronenbourg deep fluids should have a tendency to dissolve carbonate minerals during cooling until an equilibrium is reached.

According to borehole location, the concentrations of the trace alkaline elements rubidium and caesium show strong variations. The Bühl and Bruchsal deep fluids are very depleted in trace alkalines in comparison with the other deep fluids. The plot of rubidium vs. chloride (Fig. 2c) is similar to that for bromine or boron. The Soultz and Cronenbourg fluids are not considered in this diagram because of their high rubidium contents. The rubidium content of Bühl waters can be explained in the same way as for boron and bromine, which is by mixing of dilute water and a primary brine, followed by the dissolution of halite. The other deep fluids would have acquired higher rubidium contents during interaction with the geological environment. Rubidium supply to Bruchsal fluid is shown to only a little extent. Previously, we saw that temperatures of the Soultz and Cronenbourg fluids calculated from cesium and rubidium contents agree with the temperature measured in the roof of the granite in GPK1 (123°C). However, the thermometric Rb/Na and Cs/Na relationships were calculated from the composition of fluids circulating in the granite. The high trace alkaline contents in the Buntsandstein from the 4616 and Cronenbourg wells would thus have been picked up by the deep saline fluid during its circulation through the underlying granite.

CONCLUSIONS

The deep saline fluids in the Rhine Graben show common chemical and isotopic characteristics, whether these fluids are sampled in the granite or the overlying Buntsandstein. According to the chloride, bromide, boron, or deuterium contents in the fluid, a common origin can be explained with the help of the following scheme: (1) formation of a primary brine by advanced evaporation of seawater; (2) mixing of surface water and the primary brine; (3) dissolution of halite by the resulting fluid.

These deep fluids have circulated through very deep levels in the Rhine Graben, where they could reach very high temperatures (up to 220–260°C). They are found in areas where the geothermal gradient is highest, which in the Soultz-sous-Forêts area is known to be due to hydraulic discharge.

The chemistry and isotope (δD, $\delta^{18}O$) data of the thermal waters found in the area around Soultz can be explained by the fact that the deep saline fluid sampled in the deep holes at Soultz is mixed with dilute near surface waters.

Interaction between rock and the fluids also occurred during cooling. Some chemical elements are more sensitive to cooling than others; for instance, the silica geothermometer gives a relatively good estimate of the actual fluid temperature at the sampling depth. At the other end of the scale, the Na/K and Na/Li geothermometers are those that preserve the best memory of the original equilibrium temperature reached earlier.

The ^{18}O isotope geothermometer of SO_4-H_2O was disturbed by different chemical reactions. The deep brines seem to have dissolved sulphate minerals, whereas precipitation of barite from thermal waters is deduced.

The concentration of certain trace elements suggests that the fluids have circulated through the granite, even though the brines were originally evolved from evaporated seawater.

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