Main geochemical characteristics of the deep geothermal brine at Vendenheim (Alsace, France) with constraints on temperature and fluid circulation

Bernard Sanjuan, Gabrielle Negrel, Morgan Le Lous, Ewan Poulmarch, Frédérick Gal, Pierre-Clément Damy

HAL Id: hal-02335810

https://hal.science/hal-02335810

Submitted on 28 Oct 2019

Main geochemical characteristics of the deep geothermal brine at Vendenheim (Alsace, France) with constraints on temperature and fluid circulation

Bernard Sanjuan[1], Gabrielle Négrel[2], Morgan Le Lous[3], Ewan Poulmarch[3], Frédérick Gal[1], Pierre-Clément Damy[3]

[1]BRGM - 3, Av. Claude Guillemin - BP6009 - 45060 ORLEANS Cedex 2, France

[2]Compagnie Française de Géothermie (CFG) - 3, Av. Claude Guillemin – BP46429 - 45064 ORLEANS Cedex 2, France

[3]FONROCHE Géothermie - 2 B, Avenue de l'Energie - 67800 BISCHHEIM, France

b.sanjuan@brgm.fr

Keywords: geochemical data, brine, geothermal well, geothermometers, temperature, water circulation, Rhine Graben, Vendenheim

ABSTRACT

The first analytical results relative to the native geothermal brine discharged from the two deep wells drilled at Vendenheim, in the Rhine Graben, in Alsace (France), obtained within the framework of the Vendenheim FONROCHE geothermal project and the H2020 European DEEP-EGS project, suggest the geochemical composition of this brine is very similar to that of the fluid which was discharged from the neighboring Cronenbourg deep well, in the past. It is also close to that of the brines discharged from the other deep wells located in more northern areas of the Rhine Graben, such as Soultz-sous-Forêts, Rittershoffen, in France, and Landau, Insheim, in Germany. This Na-Cl brine has a TDS value around 100 g/l and a pH value close to 5, before cooling and degassing. Except for the calcium and strontium concentration values, which are much lower than those in the Soultz-sous-Forêts, Rittershoffen, Landau and Insheim brines, the other concentration values of major and trace species are comparable. Given the similarity of the geochemical composition of all these waters, their origin is probably similar but also multiple, because it results from processes of mixing between primary brines formed by advanced evaporation of seawater (probably until the stage of halite precipitation) and meteoric freshwaters, plus contributions from halite dissolution following successive marine transgression-regression cycles from the Triassic to Oligocene. As for the other deep brines, the main solute cation geothermometers give estimations of reservoir temperature close to $225 \pm 25°C$ for the Vendenheim native brine. This estimation probably corresponds to the temperature of equilibrium at which this brine acquires its chemical composition by interaction with the reservoir rocks. The mineralogical assemblage in equilibrium with the brine at this temperature was described in previous studies. The concordant estimations of reservoir temperature, using thermometric relationships such Na-Li and Mg/Li, especially developed for oil-field and sedimentary basin brines, and existing thermal gradients from 40 to 60°C/km, suggest that the deep brines discharged from the granite basement could probably originate from Triassic sedimentary formations (Buntsandstein, for example) located at great depth (≥ 4 km), in the centre of the Rhine Graben, in which they acquire their high salinity and chemical composition at temperatures close to $225 \pm 25°C$. This assumption seems to be also supported by their Li, B and Sr isotopic signatures. These hot brines would then migrate through a complex, but still poorly defined system of deep faults (probably NE-SW but also NW-SE faults), from the sedimentary centre of the Rhine Graben to the granite-fractured basement and the Graben's NW borders.

1. INTRODUCTION

In France, within the framework of the "Energetic Transition" law, several projects or exploration works are engaged in the Upper Rhine Graben (URG), especially for the development of geothermal energy for electricity or heating production, or cogeneration (both electricity and heating production), from the exploitation of deep fluids within the top of the basement. This type of reservoirs constitutes fractured dominated systems. If the deep temperatures are adequate for such projects (> 160°C), the permeability of these systems is not always appropriate to have sufficient productivity and injectivity indices in the exploitation wells. The hydraulic behaviour of the fracture networks and their connections are poorly known and their knowledge constitutes an important way to better target the exploration works. An improvement of the permeability and connectivity of these systems is often necessary for their geothermal exploitation and EGS (Enhanced Geothermal Systems) technologies must be used.

In all the known URG deep geothermal sites (Soultz-sous-Forêts, Rittershoffen, Cronenbourg, in France, and Landau, Insheim, in Germany; from 2580 to 5000 m; Fig. 1), the fluids are Na-Cl brines, with TDS values ranging from 99 to 107 g/l and pH values close to 5 (Sanjuan *et al.*, 2016a). Fluid geochemistry is similar, in spite of some small local discrepancies, and mainly results from a multiple origin with mixing between primary brine formed by advanced evaporation of seawater (probably until the stage of halite precipitation) and dilute meteoric water, plus contributions from halite dissolution following successive marine transgression-regression cycles from the Triassic to the Oligocene. Chemical, isotopic and gas geothermometers, as well as geochemical modelling calculations suggest these brines are in full equilibrium with a specific mineralogical assemblage of the reservoir rocks at a temperature value close to $225 \pm 25°C$ (Sanjuan *et al.*, 2016a). This temperature value is slightly higher than those measured on site until now in the bottom-holes (200-205°C). Given the high salinities of these brines, their similar geochemical compositions, their Li, B and Sr isotopic signatures and the geothermometric results, they would be in full chemical equilibrium with sedimentary rocks (carbonate, clastic) rather than crystalline rocks (Sanjuan *et al.*, 2016a).

The geothermal site of Vendenheim is located in the NE of France, about 10 km NE of Strasbourg, in France, at the URG western rim (Fig. 1). This Vendenheim FONROCHE project started in 2017, with the aim to exploit heat from EGS reservoir for power and heat production, by developing a deep heat exchanger in fractured crystalline basement and improving the connectivity of the existing fracture network. Therefore, two deep deviated wells (VDH-GT1 and VDH-GT2), deep of about 5 km TVD, had to be drilled down to the crystalline basement. The drilling of VDH-GT2 is presently finished, and that of VDH-GT1, for which the works had to be resumed, is finishing.

Despite the low fluid discharge of the first production tests carried out on these wells, some fluid samples have been collected for geochemical analyses, from both wells between March 6 and 8, 2018, January and February 2019 (for VDH-GT1), and between May 9 and 10, 2019 (about 30 h, for VDH-GT2), within the framework of the Vendenheim FONROCHE and the H2020 European DEEP-EGS projects. The analytical results are presented in this paper and discussed relative to the existing geochemical data of the other URG deep wells.
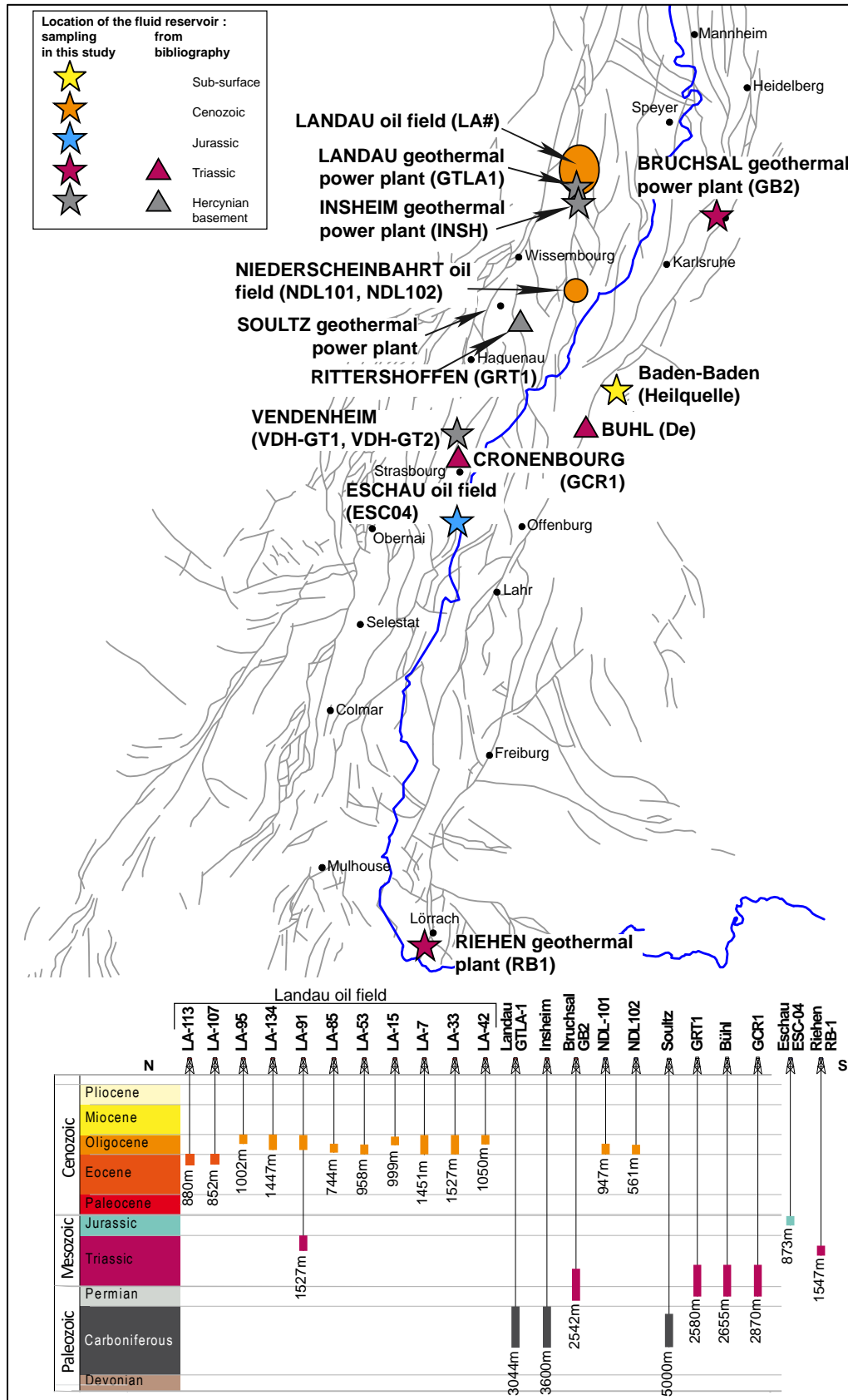

Figure 1: Location of the main deep geothermal sites in the Upper Rhine Graben (URG) and stratigraphic position of the reservoirs (extracted from Sanjuan *et al.*, 2016a).

2. GEOLOGICAL SETTING

The Rhine Graben is part of an intra-continental rift that resulted from the collision of the European and African plates during the Palaeogene and which crosses Western Europe from the North Sea to the Mediterranean. The Graben itself, with an average width of 35 km and extending approximately 300 km from Frankfurt (Germany) in the north to Basel (Switzerland) in the south, is located in the upper-middle Rhine river basin (Fig. 1). It forms a complex evaporite setting in which the rifting process played a major role by a) providing the physical space for sedimentation, b) creating a series of intermediate basins, and c) facilitating a network of faults along the active rift margins that promoted fluid circulation and controlled water exchanges with other basins and/or the open sea.

Globally, the Graben's Palaeozoic crystalline basement, underlying a Mesozoic to Cenozoic sedimentary cover as much as 4-5 km thick in its asymmetrical centre, comprises massive granite. In the Vendenheim site, the crystalline basement has been crossed by the well VDH-GT1 along 756 m, between the range of 4600 to 5408 m MD (Measured Depth). It is mainly constituted of a granitoid rock, which has been classified in the granodiorite family, given the abundance of the three main minerals analyzed by XRD method (quartz, plagioclase and alkaline feldspars) in the cuttings. However, this classification is preliminary and must be confirmed by additional analyses in laboratory. The granitoid rock crossed by the well VDH-GT1 is not homogeneous and several areas, which present variable degrees of alteration and fracturation can be observed. The main minerals observed using XRD method in the cutting analyses from the altered areas were illite, chlorite/biotite, anhydrite, silica/quartz, and carbonates. These observations are in concordance with the previous ones mentioned in the literature. As indicated by Aquilina *et al.* (1997), the amount of alteration (biotite and plagioclase dissolution, and illite, quartz and carbonate precipitation) is locally intense, with open fractures being partially filled by quartz.

The overlying sedimentary sequences, which are relatively well known from several oil- and mineral-exploration studies and from the drilling of numerous oil wells (Le Masne and Lambert, 1993), consist of Cenozoic evaporites and claystone underlain by Mesozoic limestone and sandstone. Intervals of relatively high permeability within the sedimentary succession make up the major aquifers, of which the most important is the Triassic Buntsandstein composed of continental conglomerate to siltstone with interbeds of claystone and dolomite (Aquilina *et al.*, 1997). Unfortunately, few geochemical data are available concerning the water levels crossed by the deep wells, temperature and water salinity being commonly the only measured parameters.

The general tectonic structure of the Rhine Graben is represented by a series of N10°E-striking faults (Fig. 1), despite the area's complex tectonic history indicating the existence of old sutures or faults with other strike directions (NE-SW or NW-SE, for example; Dezayes *et al.*, 2015). In its southern part, the Graben is limited by a system of faults placing the Hercynian massifs and Triassic deposits into contact with the Palaeogene fill, whilst in the north, a complex system of structures brings the basin into contact with Triassic, Jurassic and Permian material. The sedimentary deposits of the rift sequence are asymmetrical, with the deeper parts located in the southwestern and northeastern parts of the Graben, and the Palaeogene fill lying directly on the Jurassic basement.

3. FLUID SAMPLING

Collection and conditioning of all the water samples followed the classical procedures recommended for each of the chemical and isotopic analyses to be performed, as described by Sanjuan *et al.* (2016a). Collection of the fluid samples in the field was accompanied by appropriate on-site measurements such as fluid temperature, conductivity, pH redox potential, alkalinity and H_2S detection. The temperature, conductivity, pH and Redox potential measurements were performed on the raw fluid samples, whereas alkalinity was analysed on fluid samples filtered at 0.45 µm. Absolute uncertainty concerning the pH measurements was 0.05 pH units and relative uncertainty concerning the other parameters varied from 5% to 10%, depending on the parameter and the range of measured values.

Some fluid samples have been collected for geochemical analyses in order to reconstruct a geochemical composition representative of the deep geothermal fluids. Between March 5 and 9, 2018, during the period of VDH-GT1 clearing and warm up, several parameters such as temperature, conductivity, pH, TDS, density, Cl and Ca concentrations were monitored by FONROCHE Géothermie and the Compagnie Française de Géothermie (CFG) in the fluid discharged from the weir-box (WB). These parameters became relatively stable at the end of this period. Two fluid samples (VDH-GT1A and VDH-GT1B) were collected from the weir box on March 8, 2018, by CFG and FONROCHE Géothermie for geochemical analyses in the BRGM laboratories. The corresponding on-site measurements are reported in Table 1.

Fluid sample	Sampling point	Sampling date	T$_{measurements}$ °C	cond. (25°C) mS/cm	pH	Eh$_{measured}$ mV	Dissolved O$_2$ %	mg/l	Alk. meq/l	Comments
VDH-GT1A - Well warm up period - Air-lift	Weir-box	08/03/2018	38	130	7.40	0			9.52	Selected for geochemical analyses in the BRGM laboratories
VDH-GT1B - Well warm up period - Air-lift	Weir-box	08/03/2018	34	120	7.50				7.52	Selected for geochemical analyses in the BRGM laboratories
VDH-GT1 - Drill pipe depth: 2494 m - 37% CO$_2$	Weir-box (shaker)	16/02/2019 13:35	20	130	5.81					
VDH-GT1 - Drill pipe depth: 2494 m - 50% CO$_2$	Weir-box (shaker)	16/02/2019 13:35	20	135	5.41					Selected for geochemical analyses in the BRGM laboratories
VDH-GT1 - Drill pipe depth: 4536 m	Weir-box (shaker)	17/02/2019 15:00	20	86	6.24					
VDH-GT1 - Drill pipe depth: 4670 m	Weir-box (shaker)	17/02/2019 05:54	20	96	5.80					
VDH-GT1 - Drill pipe depth: 4670 m - 31% CO$_2$	Weir-box (shaker)	17/02/2019 06:28	20	101	5.82					Selected for geochemical analyses in the BRGM laboratories
VDH-GT2 - WB1 - Artesian just after Air-lift	Weir-box	10/05/2019 08:30	85	89	6.60					
		10/05/2019 12:45	25	105	7.46	175	53	4.33		
VDH-GT2 - WB2 - Air-lift	Weir-box	10/05/2019 15:30	59	101	7.17					Selected for geochemical analyses in the BRGM laboratories
		10/05/2019 15:55	35	105	7.48	-65	67	4.60	3.50	
		10/05/2019 16:00	91		6.60					
VDH-GT2 - MS1 - Air-lift	Mini-separator	10/05/2019 19:00	19	105	7.69	-48	48	4.39		
VDH-GT2 - MS2 - Air-lift	Mini-separator	10/05/2019 19:45	30	104	6.88	-17	90	7.12		
VDH-GT2 - MS3 - Air-lift	Mini-separator	10/05/2019 23:00	24	106	7.01	-56	85	7.02	3.91	Selected for geochemical analyses in the BRGM laboratories

Table 1: Water sampling and on-site measurements in the fluids discharged from the Vendenheim geothermal wells.

Other water samples from VDH-GT1 were collected and stored by FONROCHE Géothermie in February 2019, but were not specifically conditioned. Some on-site measurements were done by BRGM and CFG on these water samples in May 2019 and are reported in Table 1. Among these five raw samples, only two ones were conditioned for geochemical analyses in the BRGM laboratory (see Table 1).

In May 2019, just after a period of acid injection with a significant volume of fluid and during a production test using air-lift, only two water samples were collected by CFG, BRGM and FONROCHE Géothermie, from the well VDH-GT2, at the weir-box (WB) and using a portable mini-separator (MS) acquired by CFG, connected to the production line between the wellhead and the weir-box. The corresponding water samples were conditioned for geochemical analyses in the BRGM laboratories (see Table 1). Associated and additional on-site measurements were carried out and are also reported in Table 1.

No gas sample could be collected from the wells.

4. ANALYTICAL METHODS AND RESULTS

All the chemical analyses for both major and trace elements in the collected water samples were done in the BRGM laboratories using standard water analysis techniques such as Ion Chromatography, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Flame Emission Spectrophotometry, TIC analysis and Colorimetry. The chemical analysis results, for which the analytical precision is better than $\pm 5\%$ for the major elements and $\pm 10\%$ for the trace elements, are given in Tables 2 and 3.

The isotopic analyses of the water samples (δD and $\delta^{18}O$ of the water, $\delta^{18}O$ and $\delta^{34}S$ of the dissolved sulphate, $\delta^{13}C$ of the dissolved carbonate, plus the $^{87}Sr/^{86}Sr$ ratio, $\delta^{11}B$ and $\delta^{7}Li$) were also performed in the BRGM laboratories, using Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS), Thermo Ionization Mass Spectrometry (TIMS) and Neptune Multi Collector ICP-MS, respectively. More details relative to the BRGM analytical procedures are given in Millot *et al.* (2011). The absolute uncertainty for the δD and $\delta^{18}O$ analyses of the water samples is $\pm 0.8‰$ and $\pm 0.1‰$, respectively. The absolute uncertainty for the $\delta^{18}O$ and $\delta^{34}S$ analyses of the dissolved sulphate is $\pm 0.1‰$ and $\pm 0.3‰$, respectively, whilst for the $\delta^{13}C$ analyses of the dissolved bicarbonates, it is $\pm 0.1‰$. The external reproducibility of the $\delta^{7}Li$ and $\delta^{11}B$ analyses is estimated at around $\pm 0.5‰$ and $\pm 0.3‰$, respectively, and the in-run precision of the $^{87}Sr/^{86}Sr$ ratio was generally better than $\pm 10 \times 10^{-6}$ ($2\sigma_m$). All the isotope analytical results are given in Table 4.

Fluid sample	Sampling point	Sampling date	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	HCO3 mg/l	SO4 mg/l	NO3 mg/l	NO2 mg/l	SiO2 mg/l	TDS mg/l	Cl/Br weight	I.B. %	F mg/l	Br mg/l	B mg/l	Sr mg/l	Li mg/l
VDH-GT1A - Well warm up period - Air-lift	Weir-box	08/03/2018	28640	3881	3634	65.5	62032	581	627	< 0.5		138	100	238	-12.89	10.3	261	38.6	202	162
VDH-GT1B - Well warm up period - Air-lift	Weir-box	08/03/2018	26230	3555	3328	60.0	56812	459	574	< 0.5	0.15	127	92	238	-14.70	9.4	239	35.4	185	149
VDH-GT1 - Drill pipe depth: 2494 m - 50% CO2	Weir-box (shaker)	16/02/2019 13:35	34000	2410	2010	65.9	59000	431	398	< 10		59.7	99	355	-0.84	< 2	166	28.2	127	121
VDH-GT1 - Drill pipe depth: 4670 m - 31% CO2	Weir-box (shaker)	17/02/2019 06:28	21600	4100	1990	46.5	41500	317	339	< 10		101	70	314	-1.84	< 2	132	15.8	99	72
VDH-GT2 - WB2 - Air-lift	Weir-box	10/05/2019 15:55	23656	4164	2783	121	45600	188	334	< 10		210	78	272	0.40	11.6	168	25.7	135	110
VDH-GT2 - MS3 - Air-lift	Mini-separator	10/05/2019 23:00	22945	3971	2817	123	45900	191	313	< 10		198	77	259	-2.81	11.1	177	26.4	141	115

Table 2: Chemical analyses (major and some trace species) of the water samples collected from the Vendenheim geothermal wells.

Fluid sample	Sampling date	PO4 mg/l	HS mg/l	NH4 mg/l	Ba mg/l	Mn mg/l	Fe mg/l	Rb mg/l	Cs mg/l	Ge µg/l	Al µg/l	As µg/l	Be µg/l	Ti µg/l	Pb µg/l	Zn µg/l	Ni µg/l	Cu µg/l	Ag µg/l	Co µg/l	Cr µg/l	Cd µg/l	Sb µg/l	Hg µg/l	W µg/l	Pd µg/l	Nd µg/l	U µg/l	Th µg/l
VDH-GT1A - Well warm up period - Air-lift	08/03/2018			14.8	15.7	6.82	23.9	13.5								1870													
VDH-GT1B - Well warm up period - Air-lift	08/03/2018	< 0.5		28.1	13.5	14.4	0.30	21.9	12.4	8.03	11.4	956		1.58		1713	27.4	164	0.54		4.5	17.0	1.71	< 15	283		20.5	0.10	< 0.5
VDH-GT1 - Drill pipe depth: 2494 m - 50% CO2	16/02/2019 13:35	< 0.05		0.42	8.4	9.4	8.23	13.5	11.7	0.81	2.41	2.64	< 0.5	0.92		1260	18.5	2.65	0.16	54.6	0.7	0.7	2.41	< 15	0.25	< 0.5	14.8	0.07	< 0.5
VDH-GT1 - Drill pipe depth: 4670 m - 31% CO2	17/02/2019 06:28	0.10		21.1	7.3	12.7	57.1	9.5	6.4	4.89	66.9	811	< 0.5	26.1		320	30.5	6.50	0.55	5.67	1.6	0.6	2.23	< 15	9.36	< 0.5	48.9	0.12	< 0.5
VDH-GT2 - WB2 - Air-lift	10/05/2019 15:55	< 1	107	13.0	14.9	< 0.02	15.5	11.9	17.5	< 5	5050	0.16	< 1	3.39		1211	3.60	4.68	0.48	1.55	< 1	3.1	9.34	< 15	10.5	110	21.1	< 0.1	< 0.5
VDH-GT2 - MS3 - Air-lift	10/05/2019 23:00	< 1	107	12.8	14.3	< 0.02	15.5	11.9	17.8	< 5	5487	0.31	< 1	2.92		1936	50.1	4.62	0.65	2.61	1.3	4.7	10.9	< 15	12.3	107	15.4	< 0.1	< 0.5

Table 3: Chemical analyses (other trace species) of the water samples collected from the Vendenheim geothermal wells.

Fluid sample	Sampling point	Sampling date	δD vs SMOW ‰	δ18O vs SMOW ‰	δ18O_SO4 vs SMOW ‰	δ34S_SO4 vs CDT ‰	δ13C vs VPDB ‰	δ7Li ‰	±2σm	δ11B ‰	±2σm	87Sr/86Sr	±2σm
VDH-GT1B - Well warm up period - Air-lift	Weir-box	08/03/2018	-39.6	-1.9			3.3	2.50	0.5	2.80	0.08	0.711735	0.000006
VDH-GT1 - Drill pipe depth: 2494 m - 50% CO2	Weir-box (shaker)	16/02/2019 13:35	-34.4	-1.8				1.21	0.1	2.51	0.05	0.712746	0.000006
VDH-GT1 - Drill pipe depth: 4670 m - 31% CO2	Weir-box (shaker)	17/02/2019 06:28	-41.7	-3.0				0.19	0.2	2.54	0.11	0.711771	0.000006
VDH-GT2 - WB2 - Air-lift	Weir-box	10/05/2019 15:55	-39.5	-2.7	6.8	12.4	-5.7	-2.57	0.5	2.40	0.05	0.712329	0.000006
VDH-GT2 - MS3 - Air-lift	Mini-separator	10/05/2019 23:00	-41.5	-2.6	6.4	12.4	-4.8	0.79	0.1	2.33	0.04	0.712315	0.000007

Table 4: Isotope analyses of the water samples collected from the Vendenheim geothermal wells.

5. DISCUSSION

5.1 Reconstruction of the geochemical composition of the Vendenheim deep native geothermal brine

All the analytical results obtained during this study (Tab. 1, 2, 3 and 4) require to be confirmed relative to their representativeness of the chemical composition of the deep geothermal fluid, because the fluid production, in most of the cases, was not sufficient to fully clean the wells and completely reject the external waters injected in these wells, during preliminary operations. Before carrying out other production tests in the future, the binary diagrams of Figure 2 involving the concentrations of dissolved Na, K, Cl and Br, and the diagrams of Figure 3 involving the concentrations of Br, B, Sr, Li, Rb, Cs and Ba suggest that the chemical composition of the VDH-GT1A water sample collected in March 2018 is the most representative one for the Vendenheim deep native geothermal brine.

The diagrams of Figure 2 also indicate that the brine discharged from the well VDH-GT2 is constituted of about 65-70% of deep native geothermal brine and 30-35% of external waters (Na-K-Cl brine free of Br). These external waters are a mixing of the fluids which have been injected into the well during the different operations carried out before the production test (fluid acidizing, for example). These binary diagrams allow to estimate the concentrations of dissolved Na ($\approx$ 15 g/l), K ($\approx$ 4.3 g/l) and Cl ($\approx$ 20 g/l) of this Na-K-Cl mixing of external waters, which has as effect to dilute the native geothermal brine (TDS from 100 to 77 g/l). It clearly appears that the relatively significant volume of fluids injected in VDH-GT2 during the operations carried out before the production test has not been totally discharged from this well, given the low value of produced fluid.
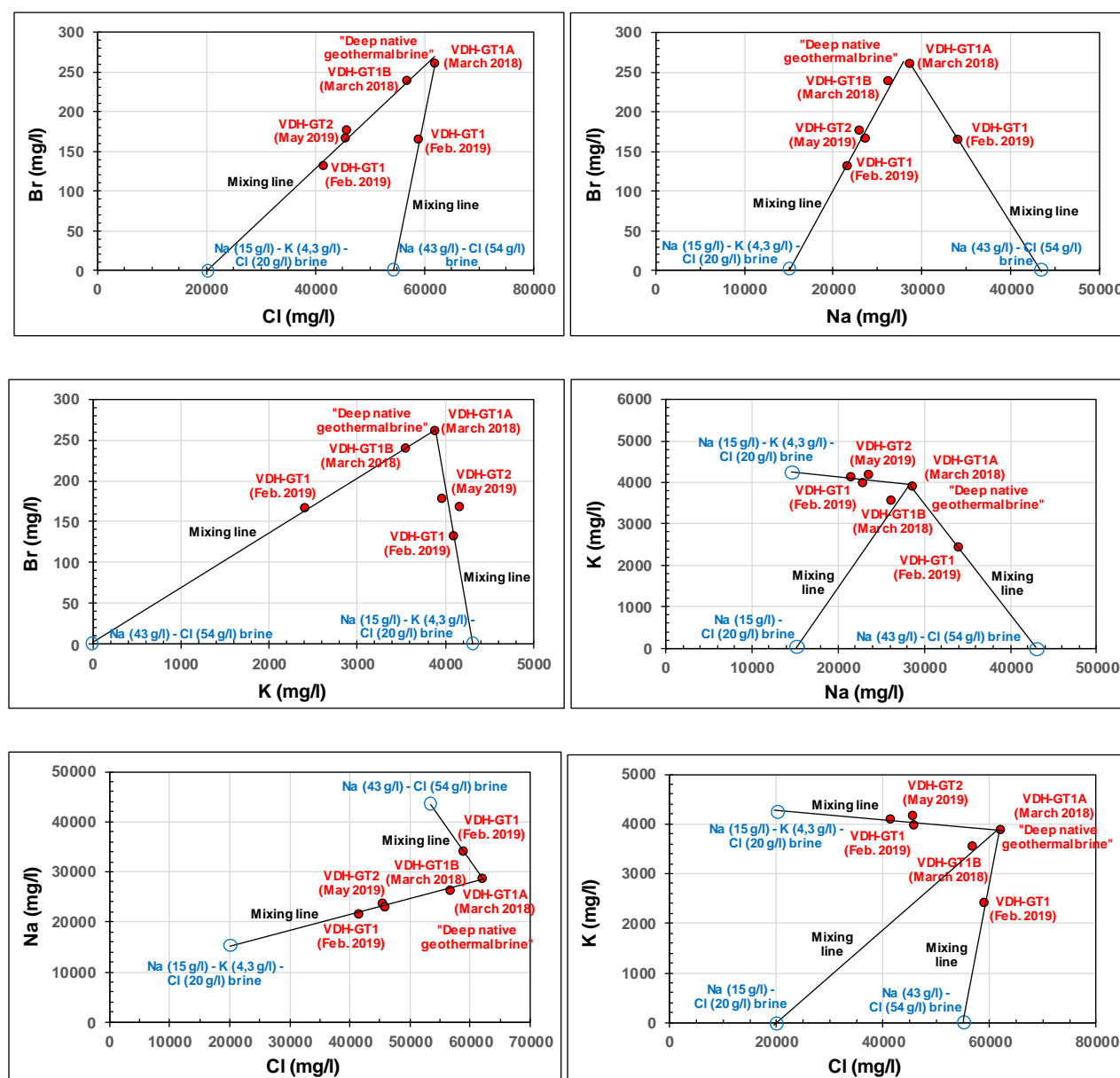

Figure 2: Binary diagrams involving Na, K, Cl and Br concentrations for the water samples collected from the wells VDH-GT1 and VDH-GT2.

5

The diagrams of Figure 3, involving Br, B, Sr, Li, Rb, Cs and Ba concentrations, confirm the percentages of mixing and also suggest that the external waters are constituted of Na-K-Cl brine free of Br, B, Sr, Li, Rb, Cs and Ba.
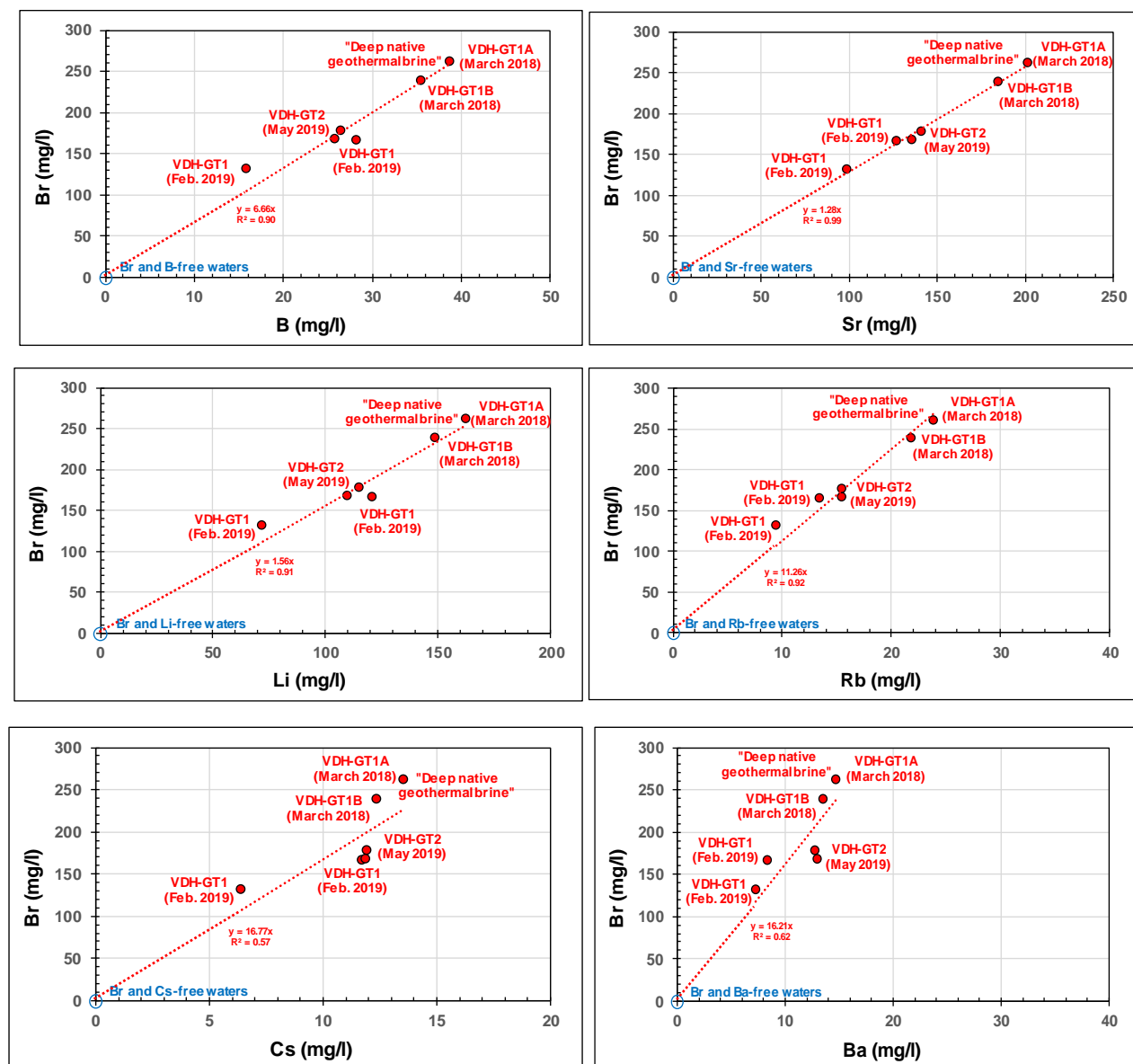

Figure 3: Binary diagrams involving Br, B, Sr, Li, Rb, Cs and Ba concentrations for the water samples collected from the wells VDH-GT1 and VDH-GT2.

In addition, the diagrams of Figures 2 and 3 show that one of the VDH-GT1 samples collected in February 2019 (annoted drill pipe depth: 4670 m) is also a mixing between 50% of deep native geothermal brine and 50% of the same external waters (Na-K-Cl brine free of Br, B, Sr, Li, Rb, Cs and Ba). The other VDH-GT1 sample collected in February 2019 (annoted drill pipe depth: 2494 m) is constituted of about 64% of deep native geothermal brine and 36% of external waters, whose the chemical composition (Na-Cl brine free of K, Br, B, Sr, Li, Rb, Cs and Ba) is different from the previous external waters. From the diagrams of Figure 1, we can also estimate the concentrations of dissolved Na ($\approx$ 43 g/l) and Cl ($\approx$ 54 g/l) of these external waters. Finally, the VDH-GT1B sample collected in March 2018 would be a mixing between 91.6% of deep native geothermal brine and 8.4% of external waters (Na-Cl brine free of K, Br, B, Sr, Li, Rb, Cs and Ba, with Na and Cl concentrations of 15 and 20 g/l, respectively). Its chemical composition is close to that of the VDH-GT1A sample also collected in March 2018. So, as the chemical composition of the VDH-GT1A sample is considered as the most representative one for the Vendenheim deep native geothermal brine, it will be used for the comparisons with the other URG deep brines.

When compared with the chemical compositions of other URG deep geothermal brines (Sanjuan *et al.*, 2016a), and especially with that of the Cronenbourg neighboring well, the analytical results obtained for the VDH-GT1A brine sample collected in March 2018 indicate similar data (Tab. 5). Indeed, except for the calcium and strontium concentration values, which are much lower than those in the Soultz-sous-Forêts, Rittershoffen, Landau and Insheim brines (Fig. 4), the other concentration values of major and trace species are comparable. This Na-Cl brine has a TDS close to 100 g/l. The alkalinity value (and especially, for dissolved bicarbonate) seems to be too high compared with the other values, and could not be representative of the deep native brine, because the well cleaning and fluid production were not sufficient. The probable presence of other dissolved compounds could be responsible of the increasing alkalinity value.

The δ^{13}C value determined for the VDH-GT1B brine sample collected in March 2018 (3.3 ‰) is very different from the values analysed in the waters sampled from VDH-GT2 in May 2019 (-5.7 and -4.8 ‰, respectively; Tab. 6), and from the values observed in the waters discharged from Landau (12.6 ‰), Insheim (12.2 ‰) and Soultz (13.4 ‰), but it approaches the value determined in the Bruchsal brine (5.5 ‰; Sanjuan *et al.*, 2016a). Presently, its representivness is very questionable (possible contamination due to partial contribution of drilling and re-injection fluids?).

Parameters	Unit	GTLA-1 Landau Well-head 09/08/2011	GTLA-1 Landau Well-head 20/06/2013	INSH Insheim Well-head 20/06/2013	GPK-2 Soultz Well-head 19/06/2013	GRT-1 Rittershoffen Well-head 10/01/2013	CRON Cronenbourg Well-head 1980	VDH-GT1 Vendenheim Well-head March 2018
T$_{measurements}$	°C	25	26	46	37	51		38
pH		5.15	4.96	5.23	4.98	6.27	6.70	7.40 (5.40)
Na	mg/l	28200	29600	29900	28140	28451	31500	28640
K	mg/l	4000	3795	3816	3195	3789	4030	3881
Ca	mg/l	7700	7391	7254	7225	7200	4810	3634
Mg	mg/l	76	85	99	131	138	126	66
Cl	mg/l	64200	64500	64900	58559	59900	62000	62032
NO$_3$	mg/l	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Alk. $_{meas. on site}$	mg/l HCO$_3$	176	124	150	168	187	134	581
SiO$_2$	mg/l	159	158	167	201	146	143	138
Cl/Br	poids	293	326	351	271	239	172	238
TDS	g/l	106	106	107	99	101	104	99
Br	mg/l	219	198	185	216	251	361	261
B	mg/l	39.0		41.1	40.8	45.9	37.9	38.6
NH$_4$	mg/l	37.2		44.0	25.7	26.8		30.7
Li	mg/l	179	182	168	173	190	210	162
Sr	mg/l	430		456	455	498	405	202
Ba	µg/l	11500		8270	5070	17638		14780
Mn	µg/l	26100		25160	16900	15565		15730
Fe	µg/l	21700		25064	25500	48671		6820
As	µg/l	11600		11620	9310	6314		7800
Rb	µg/l	27600		27200	25700	30159	29000	23890
Cs	µg/l	19300		14530	14900	16800	12000	13530
Ge	µg/l	59.8		70.4	47.1	30.1		26.5
Zn	µg/l	6300		5894	2168			1870

Table 5: Chemical data for the Vendenheim deep native geothermal brine (considered as the most representative one) compared with data of other URG deep native waters (Sanjuan *et al.*, 2016a).
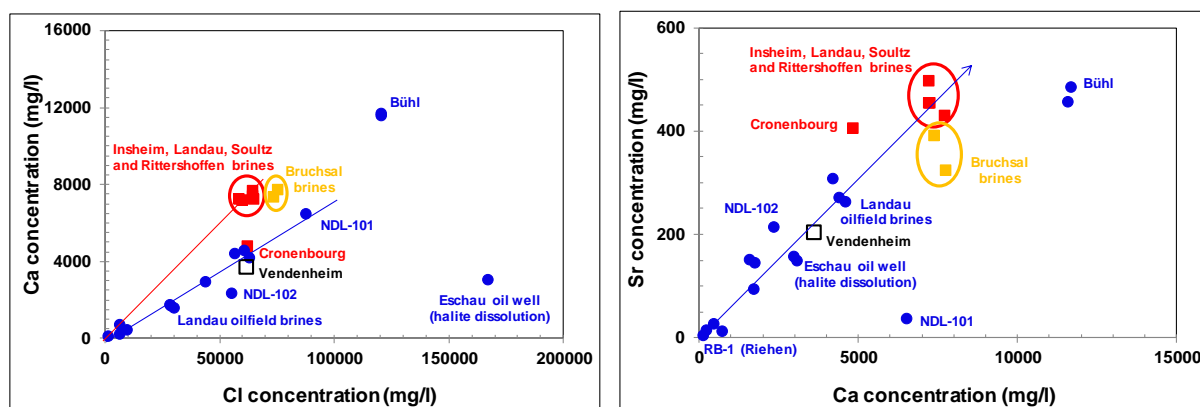

Figure 4: Binary diagrams Ca-Cl and Sr-Ca for the most representative deep brine of the Vendenheim wells.

As for the other URG deep Na-Cl geothermal brines, the pH of the Vendenheim geothermal brine is close to 5 in the deep reservoir, before fluid cooling and degassing. The fluids collected from VDH-GT1 shakers, in February 2019, indicate measured pH values between 5.4 and 5.8 (Tab. 1), differently to the fluids collected during periods of fluid production using air-lift, which indicate higher pH values between 6.6 and 7.7 (after probable CO$_2$ degassing).

5.2 Water origin

Given the similarity of the geochemical composition of all the UGR deep waters, their origin is probably similar but also multiple, because it results from processes of mixing between primary brines formed by advanced evaporation of seawater (probably until the stage of halite precipitation) and meteoric freshwaters, plus contributions from halite dissolution following successive marine transgression-regression cycles from the Triassic to Oligocene (Sanjuan *et al.*, 2016a).

The concentrations of the conservative species of the VDH-GT1A brine sample collected in March 2018, such as Cl and Br, and the weight Cl/Br ratio of about 238, slightly lower than that for seawater (290), close to that for Rittershoffen brine (239) and ranging between those of the Cronenbourg brine (172) and the other URG brines (271-351; Fig. 5) confirm this complex origin. For this type of fluid, where Na is by far the predominant cation and indicates very high concentrations, Na can also be considered as a conservative element (in this case, the Na contribution from the water-rock interaction processes is negligible). Figure 5 also seems to indicate that the process of mixing between primary brines formed by advanced evaporation of seawater (probably until the stage of halite precipitation) and meteoric freshwaters is the dominant process for these deep native brines. The δD and $\delta^{18}O$ values of the VDH-GT1B sample (Fig. 6; Tab. 4) confirm this dominant process.
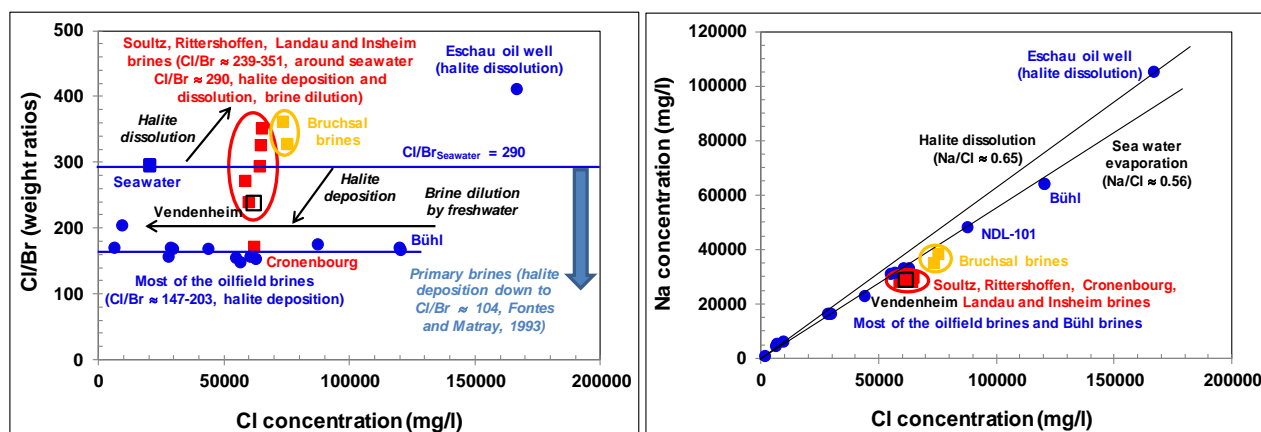

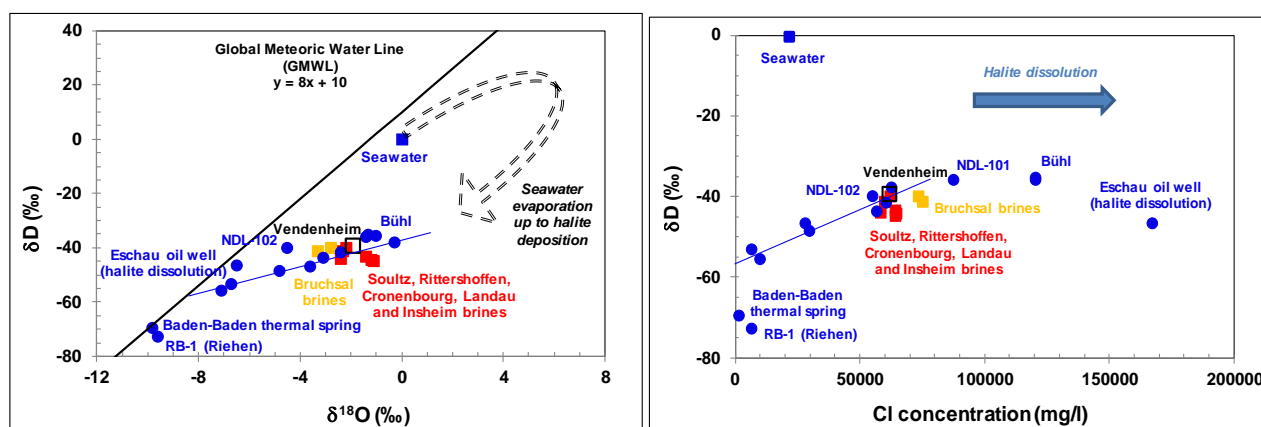**Figure 5: Binary diagrams Cl/Br-Cl and Na-Cl for the most representative deep brine of the Vendenheim wells.**

Figure 6: Binary diagrams δD-$\delta^{18}O$ and δD-Cl for the most representative deep brine of the Vendenheim wells.

5.3 Solute geothermometry and water-rock interaction processes

As for the other deep brines (Sanjuan *et al.*, 2016a), the main solute cation and isotope geothermometers give estimations of reservoir temperature close to 225 ± 25°C for the Vendenheim native geothermal brine (Tab. 6). This estimation probably corresponds to the temperature of equilibrium at which this brine acquires its chemical composition by interaction with the reservoir rocks. The mineralogical assemblage in equilibrium with the brine at this temperature was described in Sanjuan *et al.* (2016a) and would be mainly constituted of albite, K-feldspar, quartz, calcite, dolomite, CaSO$_4$:0.5H$_2$O (β), barite, fluorite, pyrite, Mg-illite, and smectite or montmorillonite. This temperature estimated using geothermometers is slightly higher than that measured at the bottom-hole in the Vendenheim and Soultz-sous-Forêts sites (Sanjuan *et al.*, 2016a), close to 200-210°C. Nevertheless, this temperature discrepancy could be explained if we assume that the native geothermal brine comes from a slightly deeper reservoir (about 5500 m) and is somewhat cooled during its ascent at a depth of 5000 m. For example, at Soultz-sous-Forêts, temperatures close to 160-165°C were measured in the brines collected at depths of 3500 m in the wells GPK-1 and GPK-2, whereas the temperature of the GPK-2 brine measured at 5000 m was close to 205°C.

Well	Locality	Water sampling	T_{Qz} °C	$T_{Na\text{-}K}$ (1) °C	$T_{Na\text{-}K}$ (2) °C	$T_{Na\text{-}K\text{-}Ca}$ β=1/3 °C	$T_{Na\text{-}K\text{-}Ca\text{-}Mg}$ °C	$T_{K\text{-}Mg}$ °C	$T_{Na\text{-}Li}$ °C	$T_{Mg\text{-}Li}$ °C	$T_{Na\text{-}Rb}$ °C	$T_{Na\text{-}Cs}$ °C	$T_{K\text{-}Sr}$ °C	$T_{18O(H2O\text{-}SO4)}$ (1) °C	$T_{18O(H2O\text{-}SO4)}$ (2) °C	$T_{18O(H2O\text{-}CaSO4)}$ °C	Estimated T_{deep} °C
GTLA-1	Landau	Well head	165	237	248	246	241	235	261	256	222	260	214	207	205	228	225 ± 25
INSH	Insheim	Well head	168	224	238	241	235	226	252	245	219	244	209	212	211	234	225 ± 25
GPK-2	Soultz-sous-Forêts	Well head	180	211	227	232	223	211	259	240	219	248	197	225	225	248	225 ± 25
GRT-1	Rittershoffen	Well head	160	230	242	243	233	218	265	243	225	253	205	218	217	240	225 ± 25
CRON	Cronenbourg	Well head	158	225	238	247	232	223	265	251	219	233	216	179	174	197	225 ± 25
VDH-GT1	Vendenheim	Well head	156	232	244	253	245	237	252	255	215	243	239	204	201	224	225 ± 25
GBRU-1	Bruchsal	Well head	124	185	206	220	191	191	236	215	206	230	200	182	177	200	190 ± 25
BUHL	Bühl	Well head		25	65	106	82	97	127	127	90	112	102	122	113	135	110 ± 25

T_{Qz} : Fournier (1977)

$T_{Na\text{-}K}$ (1) : Michard (1979); $T_{Na\text{-}K}$ (2): Fournier (1979)

$T_{Na\text{-}K\text{-}Ca}$: Fournier and Truesdell (1973)

$T_{Na\text{-}K\text{-}Ca\text{-}Mg}$: Fournier and Potter (1979)

$T_{K\text{-}Mg}$: Giggenbach (1988)

$T_{Mg\text{-}Li}$: Kharaka and Mariner (1989)

$T_{Na\text{-}Li}$: Kharaka *et al.* (1982)

$T_{Na\text{-}Rb}$, $T_{Na\text{-}Cs}$, $T_{K\text{-}Sr}$: Sanjuan *et al.* (2016b)

$T_{18O(H2O\text{-}SO4)}$ (1): Lloyd(1968); $T_{18O(H2O\text{-}SO4)}$ (2): Mizutani and Rafter (1969)

$T_{18O(H2O\text{-}CaSO4)}$: Boschetti *et al.* (2011)

Table 6: Reservoir temperature estimated using chemical and isotopic geothermometers for the Vendenheim deep native geothermal brine compared with those estimated for other URG deep native geothermal brines.

Note that, as for the other URG brines, the temperature given by the silica (quartz) geothermometer (156°C) is underestimated because the dissolved silica probably precipitates both during the ascent of the deep geothermal fluid to the surface and during the subsequent cooling. Moreover, as the activity of dissolved silica significantly differs from silica concentration in concentrated solutions (Azaroual et al., 1997a, b), the temperatures estimated using quartz geothermometer are always lower than the measured values for high salinity waters. For example, calculated temperatures are about 18°C and 35°C lower than the correct values in the 3- and 6-molal NaCl solutions at 100°C (Kharaka and Mariner, 1989) and these discrepancies increase at higher temperatures (Azaroual et al., 1997b). The high pressures have also an effect on the quartz solubility, but much lower than fluid salinity (Kharaka and Mariner, 1989). We can underline that the silica concentrations determined for the water samples collected from VDH-GT2 in May 2019, mixed with external waters depleted in dissolved silica, are slightly higher (198-210 mg/l) and give temperature estimations close to 180°C.

Note that the Na-Rb, Na-Cs, and K-Sr thermometric relationships developed by Sanjuan *et al.* (2016b) for the URG deep native geothermal brines give concordant estimations of reservoir temperature for the Vendenheim native geothermal brine (Tab. 6).

Figure 7 illustrates the variations of the Na/Li ratios, which decrease with increasing temperatures. The estimations of good concordant temperatures, using Na/Li and Mg/Li geothermometric relationships, especially developed for oil-field and sedimentary basin brines (Kharaka *et al.*, 1982 and Kharaka and Mariner, 1989, respectively), suggest that the native geothermal brines are in chemical equilibrium at 225 ± 25°C with sedimentary rocks rather than granite. As for the other URG deep native geothermal brines, the Li isotopic signature of the VDH-GT1 brine sample collected in March 2018 (Tab. 4) are also in agreement with this assumption, if we estimate the δ^7Li value of the rocks (< -4‰), using the Li isotope fractionation equation given by Millot *et al.* (2010), at 225°C. The $\delta^{11}B$ values determined for all the water samples collected from VDH-GT1 and VDH-GT2 are similar (from 2.33 to 2.80 ‰; Tab. 4) and are within the range of the values found for the other URG deep native geothermal brines (from 1.78 to 3.32 ‰; Sanjuan *et al.*, 2016a). These authors had concluded that the Li and B isotopic signatures were in good agreement with a fluid signature mainly derived from high-temperature (225 ± 25°C) water/rock interaction involving sedimentary (carbonate and clastic) rocks, with the fluid essentially resulting from a seawater-derived brine end-member diluted by meteoric water.
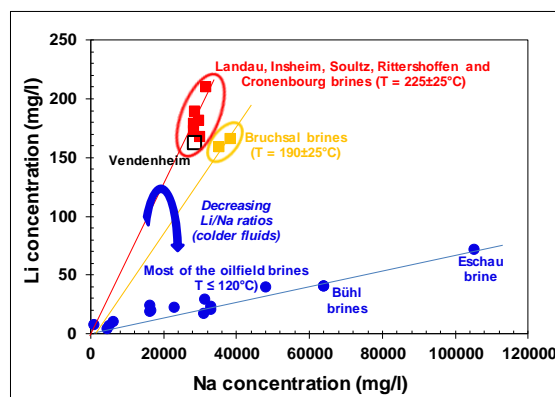

Figure 7: Binary diagram Li-Na for the most representative deep brine of the Vendenheim wells.

In addition, the Sr isotopic signatures of the VDH-GT1 deep brine samples (Tab. 4) are very close to those of the other URG deep native geothermal brines, especially to that of the Cronenbourg geothermal brine ($^{87}Sr/^{86}Sr$ = 0.7118), which is in direct contact with clastic rocks, such as the Buntsandstein sandstones. The Sr isotopic signatures of the VDH-GT2 brine samples are slightly higher (Tab. 4). As shown in Figure 4, the concentrations of dissolved Ca and Sr of the Vendenheim deep native geothermal brine are proportionally lower than those of the other URG hot geothermal brines (similar Ca/Sr ratios), but these lower concentrations have little impact on the reservoir temperature estimated using the Na-K-Ca and K-Sr geothermometers (Tab. 6).

Figure 8 clearly indicates the influence of temperature on the concentrations of dissolved SiO_2, K, Mn, Rb, Cs, which increase with increasing temperature. Similar trends are observed for trace elements such as As, Ba, and Zn. By contrast, the concentration of dissolved Mg and SO_4 decrease with increasing temperature.
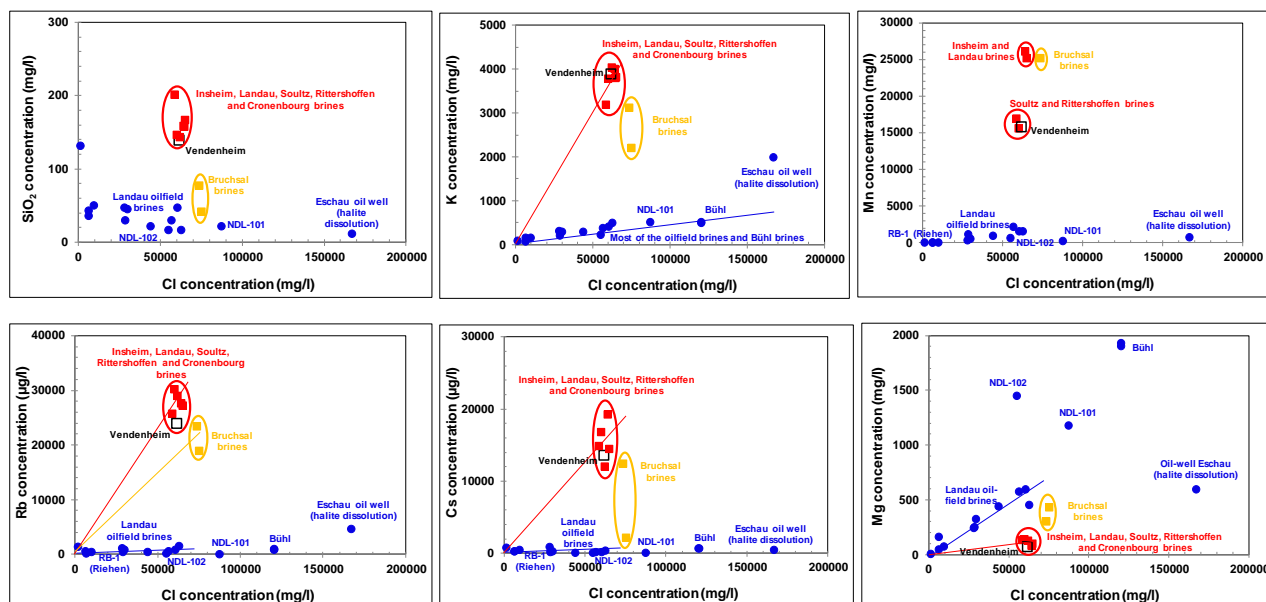
Figure 8: Binary diagrams SiO₂-Cl, K-Cl, Mn-Cl, Rb-Cl, Cs-Cl, and Mg-Cl for the most representative deep brine of the Vendenheim wells.

5.4 Geochemical constraints on the deep fluid circulation

According to all these results, as for the other URG deep brines discharged from the granite basement (Sanjuan *et al.*, 2016a), the Vendenheim native geothermal brine, near the Cronenbourg well, could probably originate from Triassic sedimentary formations (Buntsandstein, for example), located at great depth (≥ 4 km), in the centre of the Rhine Graben, in which it acquires its high salinity and chemical composition at a temperature close to $225 \pm 25°C$ (Fig. 9). Indeed, thermal gradient values ranging from 40 to 60°C in the Graben center have been reported by Vernoux and Lambert (1993). This hot brine would then migrate through a complex, but still poorly defined system of deep faults (probably NE-SW but also NW-SE faults), from the sedimentary centre of the Rhine Graben to the granite-fractured basement and the Graben's NW borders.
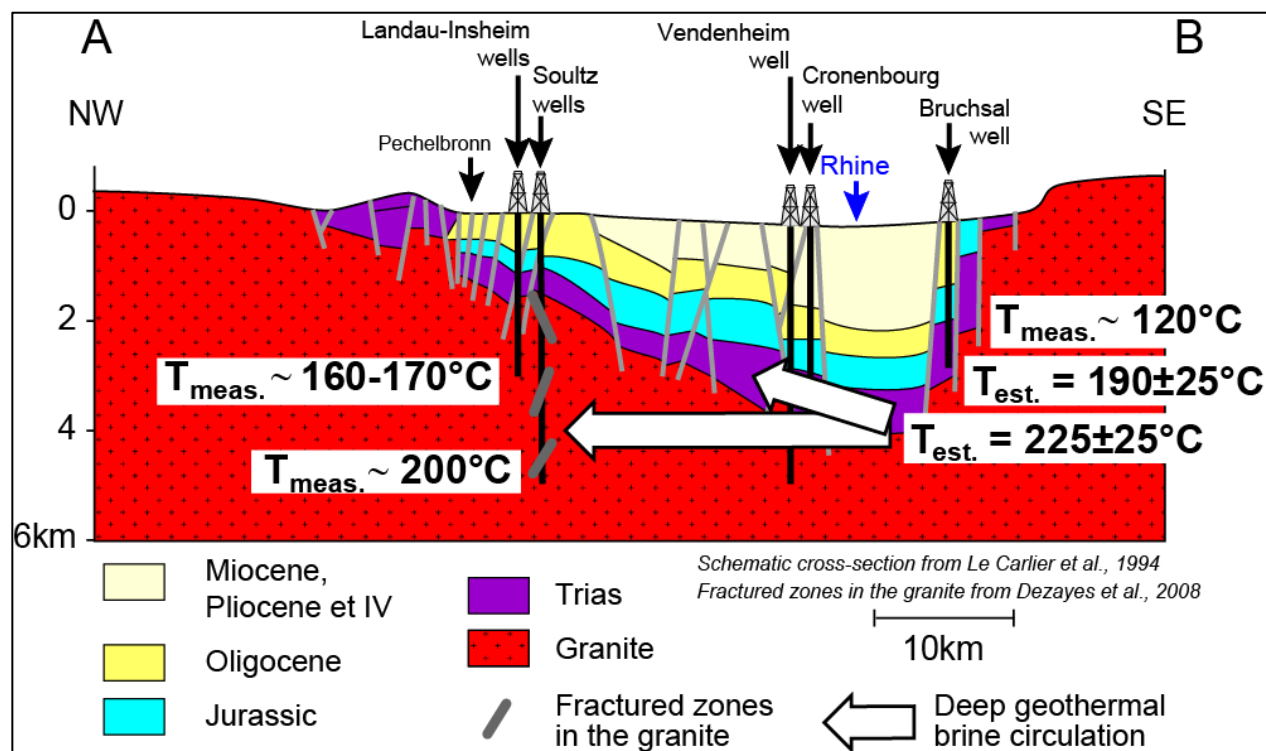

Figure 9: Schematic NW-SE cross-section of the Upper Rhine Graben in which several deep wells (Bruchsal - Cronenbourg, near Vendenheim - Landau - Insheim - Soultz) drilled to depths between 2450 and 5000 m have been reported (from Le Carlier *et al.*, 1994; Dezayes and Genter, 2008; Sanjuan *et al.*, 2010; 2016a).

6. CONCLUSION

This paper is the first one to present the main geochemical characteristics of the brine samples collected from the deep wells VDH-GT1 and VDH-GT2 (about 5 km) of the Vendenheim site, located in Alsace, France, which penetrate the granite basement below the sedimentary cover. All the analytical results obtained during this study require to be confirmed relative to their representativeness of the chemical composition of the deep native geothermal fluid, because the fluid production, in most of the cases, was not sufficient to fully clean the wells and completely reject the external waters injected in these wells, during the preliminary operations. However, it appears that the VDH-GT1 brine sample collected in March 2018 seems to be the most representative of the Vendenheim deep native geothermal brine and consequently, it was used as reference for the comparisons with the other URG deep brines, in this study.

When compared with the other URG deep native geothermal brines, the geochemical composition of the Vendenheim brine is very similar to that of the fluid which was discharged from the neighboring Cronenbourg deep well, in the past. It is also close to that of the brines discharged from the other deep wells located in more northern areas of the Rhine Graben, such as Soultz-sous-Forêts, Rittershoffen, in France, and Landau, Insheim, in Germany. Except for the calcium and strontium concentration values, which are much lower than those analysed in these last brines, the other concentration values of major and trace species are comparable.

As the other URG deep native geothermal brines, this Na-Cl brine has a TDS value around 100 g/l and its pH value is probably close to 5, before cooling and degassing. Its Cl, Na and Br concentrations, and its δD and δ^{18}O values, suggest a multiple origin with a mixing between primary brines formed by advanced evaporation of seawater (probably until the stage of halite precipitation) and dilute meteoric waters, along with contributions of halite dissolution following successive marine transgression-regression cycles from the Triassic to the Oligocene. Given the slight discrepancies (TDS and Cl concentration values, Cl/Br ratios, etc.) that exist between the URG brines, it may be that they derive from different reservoirs.

Chemical and isotopic geothermometers give concordant reservoir temperatures close to $225 \pm 25°$C for all these geothermal brines, even though the maximum deep on-site temperature measured so far has been 200-210°C. This estimation probably corresponds to the temperature of equilibrium at which this brine acquires its chemical composition by interaction with the reservoir rocks. The mineralogical assemblage in equilibrium with the brine at this temperature would be mainly constituted of albite, K-feldspar, quartz, calcite, dolomite, $CaSO_4$:0.5H_2O (β), barite, fluorite, pyrite, Mg-illite, and smectite or montmorillonite. All these hot brines are very enriched in K, Ca, SiO_2, Li, Rb, Cs, As, Sr, Ba, Mn, and in metals such as Zn, are depleted mainly in Mg, SO_4. The high salinities of the geothermal brines collected from the granite basement, their similar chemical composition, their Li, B and Sr isotopic signatures and the geothermometer results, especially obtained using the Na-Li and Mg-Li thermometric relationships developed for oil-field and sedimentary basin hot brines, suggest that they all reacted with sedimentary rocks at temperatures close to $225 \pm 25°$C, rather than with granite.

Given these constraints, the main brine reservoirs could be situated further east, towards the centre of the graben where the Triassic Buntsandstein is deepest and hottest. Given the thermal gradient values ranging from 40 to 60°C/km determined in at least eight deep wells in this area, it would be possible for the Buntsandstein to reach temperatures close to $225 \pm 250°$C at depths of ≥ 4 km. From the centre of the Upper Rhine Graben, the geothermal brines would then migrate through a complex, but still poorly defined, system of deep faults to the granite basement at the graben's NW borders (Soultz, Rittershoffen, Landau, Insheim). The different TDS and Cl/Br values of the brines suggest the existence of several geothermal reservoirs with comparable temperatures along the centre of this graben.

In spite of the low number of "unaltered" water samples collected from the Vendenheim wells (common mixing with external fluids injected into the wells, during preliminary operations), interesting data and information could be collected about the geochemical characteristics of the native geothermal brine and some constraints on its location, the temperature and nature of the reservoir rocks with which its interacts, and its deep circulation. In order to have more water and gas samples representative of the Vendenheim native deep geothermal fluids, it will necessary to continue the fluid sampling in the future, after significant volumes of fluids discharged from the wells.

REFERENCES

Aquilina, L., Pauwels, H., Genter, A., Fouillac, Ch.: Water-rock interaction processes in the Triassic sandstone and the granitic basement of the Rhine Graben: geochemical investigation of a geothermal reservoir. *Geochim. Cosmochim. Acta*, **61**, (1997), 4281-4295.

Azaroual, M., Fouillac, Ch., Matray, J.-M.: Solubility of silica polymorphs in electrolyte solutions - I. Activity coefficient of aqueous silica from 25° to 250°C, Pitzer's parameterization. *Chem. Geol.*, **140**, (1997a), 155-165.

Azaroual, M., Fouillac, Ch., Matray, J.-M.: Solubility of silica polymorphs in electrolyte solutions - II. Activity of aqueous silica and solid silica polymorphs in deep solutions from the sedimentary Paris Basin. *Chem. Geol.*, **140**, (1997b), 167-179.

Boschetti T.: Oxygen isotope equilibrium in sulfate-water systems: A revision of geothermometric applications in low-enthalpy systems. *Journal of Geochemical Exploration*, **124**, (2013), 92-100.

Dezayes, Ch., Genter, A.: Large-scale fracture zone network based on Soultz borehole data. *Proceedings EHDRA Scientific Meeting, Soultz-sous-Forêts, September 24-25, 2008,* 12 p.

Dezayes, Ch., Lerouge, C., Sanjuan, B., Ramboz, C., Brach, M.: Toward a better understanding of the fluid circulation in the Rhine Graben for a better geothermal exploration of the deep basin. *Proceedings World Geothermal Congress 2015, Melbourne, Australia, 19-25 April 2015*, 12 p.

Flehoc, Ch., Girard, J.-P.: Analyses isotopiques δD et δ^{18}O des saumures par équilibration eau-gaz. *Final report BRGM/RP-52164-FR*, (2002), 72 p.

Fontes ,J.-Ch., Matray, J.-M.: Geochemistry and origin of formation brines of the Paris Basin, France. 1. Brines associated with Triassic salts. *Chem. Geol.,* **109**, (1993), 149-175.

Fouillac, Ch., Michard, G.: Sodium/lithium ratio in water applied to geothermometry of geothermal reservoirs. *Geothermics*, **10**, (1981) 55-70.

Fournier, R.O.: Chemical geothermometers and mixing models for geothermal systems. *Geothermics*, **5**, (1977), 41-50.

Fournier, R.O.: A revised equation for the Na/K geothermometer. *Geoth. Res. Council Trans.*, **3**, (1979), 221-224.

Fournier, R.O., Potter, R.W.: Magnesium correction to the Na-K-Ca chemical geothermometer. *Geochim. Cosmochim. Acta*, **43**, (1979), 1543-1550.

Fournier, R.O., Rowe, J.J.: Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells. *Amer. J. of Sci.*, **264**, (1966), 685-697.

Fournier, R.O., Truesdell, A.H.: An empirical Na-K-Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta*, **37**, (1973), 1255-1275.

Giggenbach, W.F.: Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim. Cosmochim. Acta*, **52**, (1988), 2749-2765.

Kharaka, Y.K., Mariner, R.H.: Chemical geothermometers and their application to formation waters from sedimentary basins. *In: Naeser, N.D., McCulloch, T.H. (Eds), Thermal history of sedimentary basins: methods and case histories. Springer-Verlag, New York*, (1989), 99-117.

Kharaka, Y.K., Lico, M.S., Law, L.M.: Chemical geothermometers applied to formation waters, Gulf of Mexico and California Basins (abstract). *Am. Ass. Petrol. Geol. Bull.*, **66**, (1982), 588.

Le Carlier, C., Royer, J.-J., Flores, E.-L.: Convective heat transfer at Soultz-sous-Forêts geothermal site: implications for oil potential. *First Break*, **12**, (1994), 553-560.

Lloyd, R.M.: Oxygen isotope behavior in the sulfate-water system. *J. Geophys. Res.*, **73**, (1968), 6099-6110.

Michard, G.: Géothermomètres chimiques. *Bull. BRGM*, Section III, **2**, (1979), 183-189.

Michard, G.: Behaviour of major elements and some trace elements (Li, Rb, Cs, Fe, Mn, W, F) in deep hot waters from granitic areas. *Chem. Geol.*, **89**, (1990), 117-134.

Millot, R., Scaillet, B., Sanjuan, B.: Lithium isotopes in island arc geothermal systems: Guadeloupe, Martinique (French West Indies) and experimental approach. *Geochim. Cosmochim. Acta*, **74**, (2010), 1852-1871.

Millot, R., Guerrot, C., Innocent, Ch., Négrel, Ph., Sanjuan, B.: Chemical, multi-isotopic (Li-B-Sr-U-H-O) and thermal characterization of Triassic formation waters from the Paris Basin. *Chem. Geol.*, **283**, (2011), 226-241.

Mizutani, Y., Rafter, T.A.: Oxygen isotopic composition of sulphates. 3. Oxygen isotopic fractionation in the bisulfate ion-water system. *New Zealand J. of Sci.*, **12**, (1969), 54-59.

Pauwels, H., Fouillac, C., Fouillac, A.-M.: Chemistry and isotopes of deep geothermal saline fluids in the Upper Rhine Graben: origin of compounds and water-rock interactions. *Geochim. Cosmochim. Acta*, **57**, (1993), 2737-2749.

Sanjuan, B., Millot, R., Dezayes, Ch., Brach, M.: Main characteristics of the deep geothermal brine (5 km) at Soultz-sous-Forêts (France) determined using geochemical and tracer test data. *C.R. Geoscience*, **342**, (2010), 546-559.

Sanjuan, B., Millot, R., Innocent, Ch., Dezayes, Ch., Scheiber, J., and Brach, M.: Main geochemical characteristics of geothermal brines collected from the granite basement in the Upper Rhine Graben and constraints on their deep temperature and circulation. *Chemical Geology*, **428**, (2016a), 27-47.

Sanjuan, B., Millot, R., and Dezayes, Ch.: Three new auxiliary chemical geothermometers for hot brines from geothermal reservoirs. *Goldschmidt 2016 Conference Abstract, June 26 - July 1, Yokohama, Japan*, (2016b), 1 p.

Vernoux, J.-F., Lambert, M.: Aquifères profonds d'Alsace. Constitution d'une base de données à usage géothermique. *Final report SGN/IRG ARG 93 T37*, (1993), 41 p.