

Fluid transfers at a basement/cover interface Part II. Large-scale introduction of chlorine into the basement by Mesozoic basinal brines

M.C. Boiron^{a,*}, M. Cathelineau^a, D.A. Banks^b, S. Buschaert^{a,c}, S. Fourcade^d,
Y. Coulibaly^a, J.L. Michelot^e, A. Boyce^f

^a*CREGU-UMR CNRS G2R 7566, BP 23, 54501 Vandoeuvre-les-Nancy Cedex, France*

^b*School of Earth Sciences, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK*

^c*ANDRA, Parc de la Croix Blanche, 92298 Chatenay-Malabry, France*

^d*Géosciences Rennes UMR CNRS 6118, Université de Rennes 1, 35042 Rennes Cedex, France*

^e*UMR-CNRS-UPS Orsay Terre, Laboratoire d'hydrologie et de Géochimie isotopique,*

Université de Paris Sud, Bat 504, 91405 Orsay, France

^f*Scottish Universities Research and Reactor Centre, East Kilbride,*

Glasgow G75 0QF, Scotland, UK

Received 12 July 2001; accepted 22 July 2002

Abstract

Significant fracture and porosity sealing characterizes the sedimentary cover-basement interface in the northwestern margin of the Aquitaine Basin (France). Dolomite and calcite (and sometimes fluorite, barite and quartz) constitute most of the fracture fillings. They contain primary inclusions of brines having chlorinities in the range of 3.3 to 5.5 mol Cl/kg solution, with total homogenization temperatures in between 65 and 130 °C for quartz and slightly lower for dolomite, barite, fluorite and calcite. Crush-leach analyses indicate that brines are characterized by Na/K ratios of 5 to 40, Na/Li ratios of 20 to 530, and Cl/Br ratios of 200 to 1000, which are rather typical of deep basinal brines. The fluid $\delta^{18}\text{O}$ signature is estimated to be $\approx 6.6 \pm 1.8\text{‰}$ SMOW for a crystallization temperature of $100 \pm 20\text{ °C}$ and the δD value is $-30 \pm 10\text{‰}$ SMOW.

The fluid source for the fracture filling mineral is interpreted as a deep sedimentary brine expelled during a period of maximum subsidence in the Aquitaine Basin, which migrated along the sediment cover/basement, a zone characterized interface which is characterized by high permeabilities below the Toarcian shales. The sealing is likely to be linked to the mixing of the brines with dilute, ascending hot waters. These dilute waters infiltrated from emerged zones, convected and heated at depth, reaching temperatures of 100 °C (up to 150 °C on the basis of cation geothermometry).

Extensional activity, of probable Cretaceous age, related to the Gascogne Gulf rifting could be considered as the most likely cause of a significant fluid migration event at the basement/cover interface all along the margins of the French Massif Central. These processes are large scale as shown by the similarities of mineral sequences, fluid types and general features of most of the F–Ba–Pb–Zn deposits located at the basement–sedimentary cover interface.

* Corresponding author. Tel.: +33-3-83-68-47-30; fax: +33-3-83-68-47-01.

E-mail address: Marie-Christine.Boiron@g2r.uhp-nancy.fr (M.C. Boiron).

The mass transfer of Cl linked to this stage is significant and accounts for the early introduction of large amounts of chlorine in the granitoid microporosity. This probably explains the significant chlorine concentrations of the present-day fluids recovered in the granitoid aquifer.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Deep groundwater; Fluid chemistry; Chlorine; Unconformity; Crystalline basement

1. Introduction

Some basement groundwaters have significant chloride contents, the origin of which is still unclear because these waters are more or less equilibrated with their host rocks and have lost their original isotopic and chemical features (Frape and Fritz, 1987). Nordström et al. (1989) consider two sources for chlorine in crystalline rocks: (i) allochthonous sources external to the host rock: in a significant number of cases, brines were recognized as sedimentary in origin (Nurmi et al., 1988; Munz et al., 1995), (ii) autochthonous source such as release of chlorine through water–rock interactions and hydrolysis of silicate minerals (Edmunds et al., 1984; Kamineni et al., 1992), or leakage of secondary fluid inclusions trapped in primary minerals. The last process was, however, demonstrated to be unrealistic on the basis of mass balance calculations (Savoye et al., 1998).

Present-day deep groundwaters of some French Hercynian granites in western Europe, such as the Vendée granites (Chardon uranium mine, Beaucaire et al., 1999) and the Vienne granites (Matray et al., 1997), have significant but much lower chloride concentrations (only $10 \text{ g l}^{-1} \text{ Cl}$) than brines from stable cratons (Canadian shield brines, for instance). Such chlorinate-rich fluids were found during the recent exploration of basement rocks by 17 continuously cored boreholes, 200 to 1000 m deep, by the Agence Nationale pour la gestion des Déchets Radioactifs (ANDRA = French Nuclear Waste Management) in the Vienne granites. The latter are located beneath a Mesozoic sedimentary cover (150 m of limestones and detrital series from Hettangian up to Malm) over an area of $\approx 125 \text{ km}^2$ located between the Armorican massif and the “Massif Central” in France, the so-called “Poitou High”. In the case of plutonites located below a sedimentary cover, such as the Vienne gran-

itoids, present-day saline waters could be interpreted as the result of several processes: (i) penetration of seawater during periods of transgression, (ii) penetration of seawater or evolved seawater during diagenesis of the sedimentary cover, or (iii) penetration of allochthonous brines not related strictly to the overlying sediments: in that case, it could be a diagenetic brine formed in an other part of the basin, a brine produced from seawater evaporation or from evaporite dissolution in a more or less remote area (Yardley et al., 2000). During their migration, brines may be affected by subsequent processes such as mixing with other kinds of water, such as recharge waters which can quickly percolate downwards through fractures or locally ascent from convection cells. This is typically the case in the Rhine graben, where both present-day fluids and inclusion fluids found in fractures fillings are the witnesses of brines resident in Trias formations and of recharge meteoric waters involved in deep convective systems (Pauwels et al., 1993; Dubois et al., 1996). In the Vienne granitoids, preliminary mineralogical and fluid inclusion studies of fracture minerals (carbonates) have shown that these minerals crystallized from a brine at rather low temperatures, brines which experienced mixing process during a period younger than the deposition of the overlying infra-Toarcian sedimentary series (Cathelineau et al., 1999).

The aim of this work was: (i) to determine the origin and nature of brines percolating through the basement and responsible of the fracture sealing, (ii) to evaluate their role in the transfer of elements from the basins towards the basement, and (iii) to search for the origin of chlorine in present-day waters. This was carried out through a study of a selected set of representative samples, previously studied (when possible) by means of petrography and microthermometry, with sizes large enough to permit the analysis of significant quantities of fluid

inclusions by mean of crush and leach techniques and the determination of δD values of inclusion fluids.

Work was focused on the Poitou basement under the sedimentary cover (Charroux–Civray area). In order to evaluate the extension of the process in northern Limousin, several occurrences of the same specific paragenetic sequence filling the fractures, known to have formed from brines, were also sampled within the basement at various distances from the unconformity with the Mesozoic series.

2. Geological setting and mineral sequences of the studied veins

The Charroux–Civray area is located at the northwestern border of the French Massif Central and northwestern border of Aquitaine (see Fig. 1, in Fourcade et al., 2002), below a 150-m-thick sedimentary cover composed of marine Lias and Dogger formations. The basement is dominated by plutonic

rocks from the “Tonalitic Lineament” of the Limousin (Peiffer, 1986; Shaw et al., 1993) and contains multiple intrusions of medium K calc–alkaline tonalites and granodiorites dated around $350\text{--}360 \pm 5$ Ma (U–Pb zircons; Bertrand et al., 2001). The latter were later intruded by peraluminous intrusions (Capdevila, 1997; Cuney et al., 1999). Investigated samples (vein material) from this area were taken from 17 continuously cored, 200–1000-m-deep boreholes drilled by ANDRA. Exceptional and unweathered drilled material from Hercynian plutonites (tonalites and granodiorites) from the Vienne site has shown that the crystalline basement contains rather dense sets of fractures. By means of paragenetic and fluid inclusions in veins and host-rock minerals, the existence of at least three stages of fluid flow was demonstrated, each stage characteristic of extremely distinct P – T conditions and geodynamic contexts (Cathelineau et al., 1999; Fourcade et al., 2002). (i) Hercynian veins (stage I) were produced during thermal heating and fluid circulation linked to the emplacement of the pera-

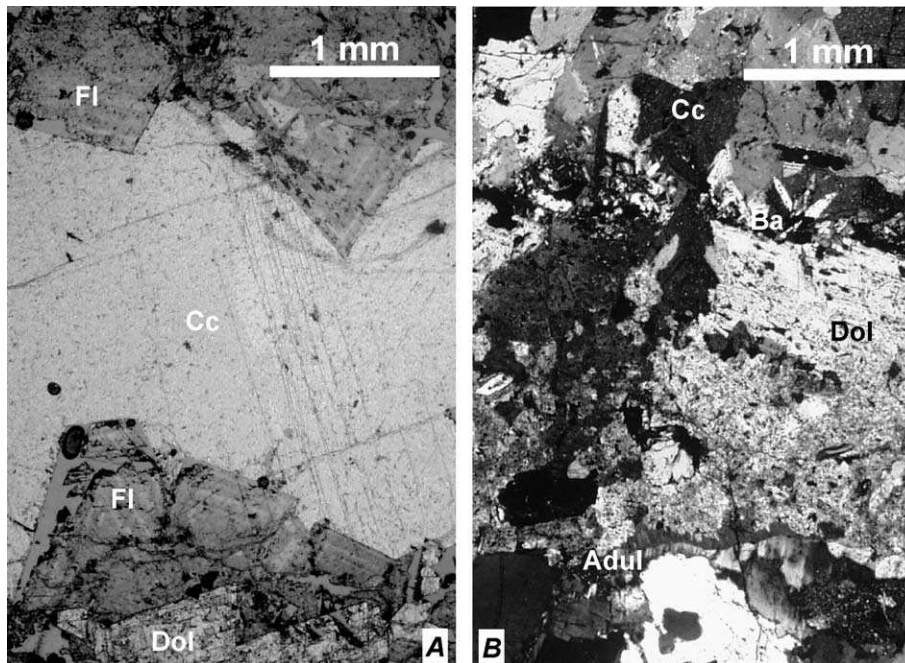


Fig. 1. Photomicrographs of typical vein fillings. (A) Dolomite (Dol)–Fluorite (Fl) and Calcite (Cc) mineral assemblage [sample CIV 107–1016 (253.73–254 m)]. (B) Adularia (Adul)–Dolomite (Dol)–Barite (Ba)–late calcite (Cc) vein filling [sample CIV 107–1018 (293.46–293.79 m)].

luminous intrusions and ultimately, by a late retro-grade alteration (locally pervasive) of plutonic rocks, coeval with the final basement uplift and cooling. A small amount of sealed fractures are related to these stages and consist of quartz–hematite, quartz–chlorite–phengite or illite veins with a small amount of carbonates (Freiberger et al., 2001). The basement was uplifted and the top of the granites was weathered during a Triassic period of emersion. (ii) Abundant fractures, corresponding to several sets striking NW–SE (for the most abundant ones) and NE–SW, filled by dolomite and calcite are found in the plutonic rocks (stage II). (iii) Stage III is characterized by late calcite ($\pm$ kaolinite) fillings crystallized at low temperatures.

Stage II veins which constitute more than 75% of the sealed fractures are the object of the present study (Fig. 1). Dolomite represents the main fracture filling mineral, calcite being much less abundant. Both carbonates have a rather low Fe content (<0.15 mol%) and are close to the two carbonate end-members (pure dolomite and calcite). Most of stage II veins show that without any exception, carbonates crystallize in a specific order within a mineral sequence: hematite–adularia/quartz/dolomite ($\pm$ fluorite and barite $\pm$ Cu, Zn, Fe sulphides)/calcite (Fig. 1). Below 400-m depth, halite crystals were observed by SEM on fragments of fractures and adjacent wall rocks. The typical association of the minor minerals—fluorite, barite, traces of Pb–Zn sulphides—is the most striking index which allows to conclude that stage II fluid circulation was predominantly responsible for the fracture sealing. Its impact is recognized down to 800 m underneath the basement/cover interface and in all studied drill cores (17 drill holes over 200 km²). As this assemblage is also observed in the lower part of the sedimentary cover either as joints or pore fillings in all series below the Toarcian shales (i.e., in Hettangian/Sinemurian limestones and sandstones), it indicates an age younger than Hettangian (Cathelineau et al., 1999).

Stage II mineral assemblages and their location are typical of most F–Ba deposits from the “Poitou High” (Lougnon et al., 1974) and from the northern (Chaillac; Ziserman, 1980) and southeastern parts (Albigeois area, Munoz et al., 1999) of the French Massif Central. Thus, complementary vein material was sampled in outcropping granites: fluorite veinlets in the La Marche peraluminous granites in the north-

ern Limousin basement (Bernardan–Cote Moreau area), and dolomite veins from the Margnac–Peny area in the peraluminous granite of St Sylvestre (see Fig. 1; Fourcade et al., 2002 for location). At Cote Moreau, fluorite occurs as yellow euhedral crystals of millimetre size, deposited on a thin hematite-bearing quartz comb. At Peny, centimetre-sized monocrystals of pink dolomite are observed in fracture fillings, without any other minerals.

In addition, the Chaillac fluorite–barite veins (located at the unconformity on the northern edge of the Limousin area; Ziserman, 1980) were also considered as formed under similar conditions (see below). In Chaillac, the main stage of fluorite deposition produced a yellow to brown amber fluorite followed by grey fluorite, barite and pyrite.

3. Fluid characteristics

3.1. Analytical techniques

Among the population of veins infillings identified as produced during the brines circulation event on the basis of morphology and mineral parageneses (Vienne granitoids), a few samples were selected for microthermometric, Raman, crush-leach and D/H studies of fluid inclusions, as well as representative samples from northern Limousin area (Table 1).

Such samples, very typical and big enough to allow combined analyses (in most cases), are rare especially quartz. To confirm that these samples pertain to the group of brines-derived minerals isotopically defined in Fourcade et al. (2002), they were also analyzed for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (Table 2) with the methodologies described in this companion paper.

3.1.1. Microthermometry and Raman analyses

Microthermometric studies of the fluid inclusions were performed on wafers using a Chaixmeca heating–freezing stage (Poty et al., 1976). The stage was calibrated with melting-point standards at $T > 25^\circ\text{C}$ and with natural and synthetic fluid inclusions at $T < 0^\circ\text{C}$. The rate of heating was monitored in order to obtain an accuracy of $\pm 0.2^\circ\text{C}$ during freezing, $\pm 1^\circ\text{C}$ when heating above 25°C . For microthermometric data, abbreviations are used as follows: T_c : temperature of ice—first melting; T_m ice/hy: final

Table 1

Samples investigated in the microthermometric study, with host rock type and predominant alteration type

Drilling number	Sample number	Depth (m)	Host rock	Mineral succession
<i>Vienne</i>				
CIV 102	CIV 00667	206.5	Quartz tonalite	adularia– dolomite –barite–pyrite
CIV 102	CIV 671	227.02/227.18	Tonalite	calcite
CIV 107	CIV 1016	253.7/254	Quartz monzodiorite	fluorite –pyrite–chalcopyrite
CIV 107	CIV 1019	347.02/347.7	Microdiorite	quartz –pyrite– dolomite
CHA 106	CHA 1052	491.8/491.9	Monzogranite	quartz
CHA 106	CIV 1068	585.7/586.04	Fracture dolerite-polyphased	dolomite –barite
CHA 108	CHA 2421	243.10/243.2	Quartz monzodiorite	fluorite –pyrite–barite–chalcopyrite
CHA 212	CHA 5646	607.2/607.6	Tonalite	adularia– dolomite –barite
CHA 212	CHA 8594	728.5/728.65	Tonalite	dolomite– barite –chalcopyrite–pyrite
CHA 212	CHA 8602	892.3/892.5	Tonalite	adularia– dolomite –pyrite
CHA 212	CHA 8606	800.00	Tonalite	dolomite –barite–pyrite
CHA 212	CHA 8598	855.5/855.8	Fine-grained granite	dolomite –pyrite–barite–galena–calcite
CHA 312	CHA 8805	115.25	Sedimentary cover	quartz in cavity
<i>North Western Massif Central</i>				
Chaillac	C1		Detrital series—Hettangian	Yellow to brown fluorite –barite ± pyrite
	C2		Detrital series—Hettangian	Yellow to brown fluorite –barite ± pyrite
	C4		Detrital series—Hettangian	Yellow to brown fluorite –barite ± pyrite
Cote Moreau	P284L110		Peraluminous granite	quartz–(hematite)–yellow fluorite
Peny	1051 E17b		Peraluminous granite	Pink dolomite in fracture

The mineral studied for fluid inclusion is indicated in bold.

Table 2

Ranges, mode in parenthesis and number of measurements (*n*) of microthermometric data

Location	Mineral	Sample number	T_m ice (°C)	T_h (°C)	δD ($\delta^{18}O/\delta^{13}C$)
Vienne	Quartz	CIV 1019	– 14, – 27.6 (– 22); <i>n</i> = 23	75, 130 (90/110); <i>n</i> = 8	– 46
	Quartz	CHA 1052	– 9, – 11.7; <i>n</i> = 6	n.d.	
	Quartz	CHA 8805	– 12.2, – 22.6; <i>n</i> = 5	101, 120 (100/110); <i>n</i> = 5	
	Dolomite	CIV 00667	n.d.	n.d.	(26.4/– 9.7)
	Dolomite	CIV 1068	– 24.9, – 26.3 (– 25.5); <i>n</i> = 5	88.5, 95.2 (90); <i>n</i> = 6	
	Dolomite	CIV 1019 B	– 21, – 26.7 (– 25.7); <i>n</i> = 9	90.6, 113.5 (110); <i>n</i> = 9	– 19 (27.3/– 8.8)
	Dolomite	CHA 5646	n.d.	n.d.	– 40 (28.7/– 13.4)
	Dolomite	CHA 8598	n.d.	n.d.	– 21 (25.9/– 10.7)
	Dolomite	CHA 8602	n.d.	n.d.	(26.4/– 10.0)
	Dolomite	CHA 8606	n.d.	n.d.	– 28 (26.6/– 9.9)
	Fluorite	CIV 1016	– 15, – 18 (– 16); <i>n</i> = 4	87, 102.7 (90); <i>n</i> = 4	
	Fluorite	CHA 2421	– 14.5, – 22.6; <i>n</i> = 4	86.5, 95.1 (90); <i>n</i> = 13	
	Calcite	CIV 671	– 11.9, – 25.1 (– 19.5); <i>n</i> = 8	64, 102 (70; 100); <i>n</i> = 9	– 28 (23.8/– 10.9)
	Barite	CHA 8594	– 6, – 16.8; <i>n</i> = 11	84, 116 (110); <i>n</i> = 6	
<i>North Western Massif Central</i>					
Chaillac	Fluorite	C1	– 3.8, – 9.8; <i>n</i> = 6	78, 120 (110); <i>n</i> = 6	
		C2	– 7.3, – 19.4; <i>n</i> = 12	90, 116 (110); <i>n</i> = 11	
		C4	– 18.1, – 19.4; <i>n</i> = 7	95, 120 (105); <i>n</i> = 7	
Cote Moreau	Fluorite	P284L110	– 18.4, – 18.7; <i>n</i> = 6	95, 100 (100); <i>n</i> = 5	
Peny	Dolomite	1051 E17b	– 19.7, – 30.2; <i>n</i> = 5	109, 133 (110/130); <i>n</i> = 6	(27.8/– 7.5)

δD values measured on fluid inclusions contained in quartz and carbonates are given together with (in parenthesis) the O and C isotopic compositions which identify them as minerals crystallised from the brines (see text for explanations).

n.d.: Not determined.

melting temperature of ice or an undefined hydrate; T_h (L–V): total homogenization temperature (L+V to liquid or L+V to vapour). Chlorinity was analyzed in individual fluid inclusions in quartz by Raman spectroscopy, using a DILOR LABRAM Raman spectrometer at CREGU, Nancy following the methodology described in Dubessy et al. (2002). However, as the method could not be applied to fluid inclusions in carbonates, due to fluorescence, and fluids are dominated by sodium chloride (Na represents more than 80% of the cationic charge; see results below), chlorinity was also estimated in such instances using microthermometric data and the equation from Bodnar (1993) for the H_2O –NaCl system.

3.1.2. Crush-leach analyses

Bulk crush-leach analysis was performed on samples of quartz, calcite, dolomite, barite and fluorite. Samples were prepared and cleaned using the methods of Banks et al. (2000). The amount of sample crushed was typically between 0.5 and 1 g. Analysis of anions Cl, Br, I, F and SO_4 was performed by ion chromatography on double distilled water leaches. Na and K were determined on the same solutions by flame emission spectroscopy (FES). Ca was not analyzed in series of leachates because most minerals are Ca carriers. Therefore, calcium was estimated from laser-induced breakdown spectroscopy (LIBS, Fabre et al., 1999). The major cations and anions in the fluid inclusions have been calculated in mmol/kg of solution and are discussed in the text in terms of molar ratios.

3.1.3. D/H ratios of fluid inclusions

δD of fluid inclusions was measured directly on FI populations, using standard procedures as described by Fallick et al. (1987) in the Scottish Universities Research and Reactor Centre (SURRC). The uncertainties on hydrogen isotope ratio are 2‰.

3.2. Microthermometry and Raman results

Similar data were obtained from the analyzed minerals from the Vienne site and the deposits of the northwestern Massif Central. The fluid does not contain any detectable CO_2 (undetected by Raman). Within the zoned quartz crystals, primary fluid inclusions are distributed along the growth zones. They are

generally small ($\leq 10 \mu m$) and irregular. Dolomite, fluorite and calcite contain two-phase aqueous inclusions of variable size (up to 20 μm), generally flat and irregular in shape. We stress the point that fluid inclusion planes (FIP) in the host rocks (Vienne plutonites) never contain this type of high-salinity fluids. This could indicate that no FIP developed in quartz in the host granitoids during the stage of brine circulation either because this event was not accompanied by fracturing, or because the temperature was too low for quartz healing.

Microthermometry and Raman microprobe investigations show the existence of a single dominant fluid type (H_2O –NaCl–KCl– $CaCl_2 \pm MgCl_2$) in all primary fluid inclusions from all the minerals of the infilling sequence. The first melting temperature, as low as $-50^\circ C$, is diagnostic of the presence of $CaCl_2$ (and possibly $MgCl_2$; Crawford, 1981) in addition to NaCl. Two-phase fluid inclusions were found in all the minerals of the infilling sequence and show a range of final melting temperatures of a solid from $-12^\circ C$ (and some values up to $-6^\circ C$ for the Vienne barite, and $-3.8^\circ C$ for the Chaillac fluorite) to $-27.6^\circ C$ (ice $\pm$ hydrohalite melting) (Table 2). Most meltings observed in dolomite and quartz fluid inclusions are between -16 and $-27^\circ C$ but cannot be determined unequivocally as corresponding to the melting of ice or hydrohalite, even with the support of Raman spectroscopy. For this reason, the chlorinity of the inclusions has been determined by Raman spectroscopy using the calibration curves from Dubessy et al. (2002). This could only be done on quartz because, for other minerals, fluorescence made the measurements impossible. For inclusions showing a melting of a solid around $-27^\circ C$ (sample CIV 1019), the measured chlorinity is around 5.2 mol/kg solution, i.e., slightly lower than the maximal estimate expected below halite saturation (5.6 mol/kg solution). As the Na–Ca content is dominated by Na ($Na/Ca = 4 \pm 1$, $Na/K > 5.5$; see data below), a maximal estimate of the chlorinity was obtained by considering the microthermometric measurements and the H_2O –NaCl system. In spite of a probable slight overestimation, chlorinities are considered to range from 3.3 to 5.5 mol/kg solution.

Homogenization temperatures are between 75 and $130^\circ C$ for quartz and slightly lower for dolomite (90 – $115^\circ C$), barite (85 – $115^\circ C$), fluorite (85 – 100

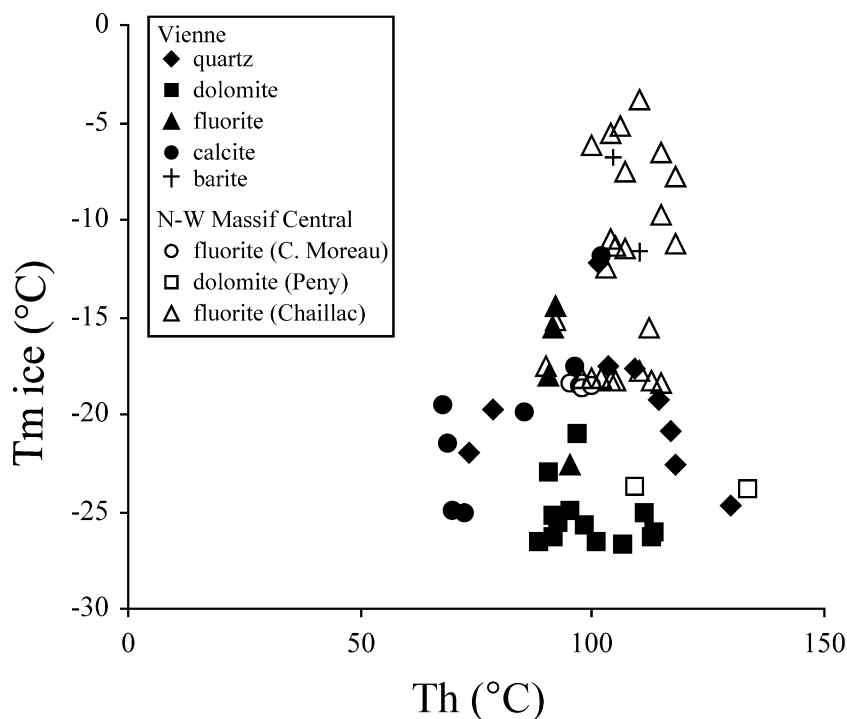


Fig. 2. T_m ice vs. T_h diagram of aqueous fluid inclusions.

°C) and calcite (65–100 °C) (Fig. 2 and Table 2). Because inclusions homogenize into the liquid state, the minimum fluid pressure prevailing during this stage (estimated using the method of the fluid vapour pressure at the homogenization temperature in the H_2O –NaCl system) can be as low as 10–20 bars. The lack of evidence for boiling, however, suggests that pressure was higher but probably did not exceed a few hundred bars (see Discussion).

3.3. Fluid chemistry

The reconstructed fluid chemistry calculated from crush-leach analyses and using the average salinity deduced from microthermometry and Raman spectroscopy is reported in Table 3. Average salinities are evidently lower than the maximum estimates for inclusions showing the lowest T_m ice but are likely more realistic for the bulk population of inclusions analyzed by the crush-leach technique. The maximum salinity of these brines is around 5.5 mol Cl/kg solution, close to the halite saturation. Microthermo-

metric data show that fluid inclusions display a significant range in salinity (3.3 to 5.5 mol Cl/kg solution), from near halite saturation down to lower salinities more typical of brackish waters.

The dominant anion in the fluids analyzed is Cl, and there is a significant amount of SO_4 in some samples (quartz, dolomite). Major cations are Na and K. The presence of Ca, deduced from the microthermometric measurements, is confirmed by the LIBS data. The major cation ratios are the followings: Na/K ratios of 5.5 to 40 and Na/Li ratios of 20 to 600 (Fig. 3). Na/Ca ratios are estimated to be around 3 to 5 from LIBS measurements. Mg is probably also present as the brines precipitate predominantly dolomite, but at a content which was not compatible with its determination by LIBS (therefore, at a content much lower than Ca).

Na/K and Na/Li ratios indicate that the brines studied have similar compositions as those of sedimentary brines, especially two groups of data reported in the literature: the hottest brines (114–121 °C) from the Mississippi salt dome basin (Na/K from 11 to 20,

Table 3

Reconstructed composition (in mmol/kg solution) of fluid inclusions from crush-leach analyses

Location	Sample	Mineral	Na	K	Li	Cl	Br	F	SO ₄	I
Vienne	CIV 01019C	Quartz	1383	144	47	3068	14	185	234	0.0012
	CHA 1052	Quartz	2014	74	30	1989	3	6	146	
	CHA 8805	Quartz	3267	136	169	3931	2			
	CIV 00667	Dolomite	1678	158	5	2688	5	76	441	
	CHA 1068	Dolomite	2332	61	5	3857	4	27	24	0.0006
	CIV 01019A	Dolomite	1782	322	27	2988	15	79	3224	
	CIV 01019B	Dolomite	1565	102	4	3897	17			0.0014
	CHA 5646	Dolomite	1583	79	3	3408	16	42	1354	
	CHA 8602	Dolomite	2275	59	4	3534	8		104	
	CIV 1016	Fluorite	1941	134	4	3316	5		3	
	CHA 02421	Fluorite	1897	126	6	3926	4			
	CIV 00671	Calcite	2180	70	7	3911	8	10		0.0037
	CHA 8594	Barite	1399	269	13	3424	14			0.0056
<i>North Western Massif Central</i>										
Chaillac	C1	Fluorite	1353	100		1738	3		19	
	C2	Fluorite	2141	105		3495	21		18	
	C3	Fluorite	2637	97		3446	9		47	
	C4	Fluorite	2512	73		3684	10		3	
Cote Moreau	P284L110	Fluorite	1656	537	33	2512	2		423	
Peny	1051 E17a	Dolomite	2368	82	4	3810	12	27	31	
	1051 E17b	Dolomite	1358	73	2	3642	22	8	89	

Na/Li from 223 to 356, Kharaka et al., 1987), and a part of the brines reported for Mississippi oil fields (Carpenter et al., 1974). The Na/Li ratios are remark-

ably consistent with those expected at temperatures from 100 to 150 °C, using the Fournier (1979) and Fouillac and Michard (1981) geothermometers

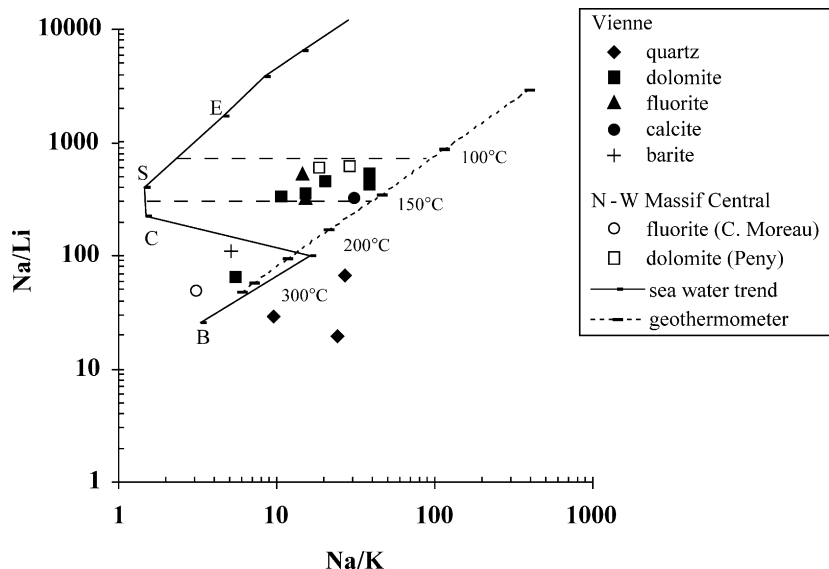


Fig. 3. Na/K–Na/Li ratios of fluids determined from crush-leach analyses. Full line=seawater evaporation trend from Fontes and Matray (1993). B: bischofite, C: carnallite, S: sylvite, E: epsomite. Dotted line: temperature estimation deduced from the geothermometric cation relationships (Verma and Santoyo, 1997).

revised by Verma and Santoyo (1997). The Na/K ratio plots between the geothermometric curve and the seawater trend. The evolution in the Na/K ratio, from that expected after halite saturation towards that predicted for fluids equilibrated at 100–150 °C with crystalline rocks, could indicate either a progressive chemical change due to water–rock (plutonic rocks) interactions, or a Na/K ratio typical of the brine (see Discussion). Some data are quite distinct and especially enriched in Li, yielding low Na/Li ratios.

In the Na vs. Cl and K vs. Cl diagrams (Fig. 4A and B), data plot below and at the left side of the seawater evaporation curve, respectively. The large range of chlorinities could be representative of the following. (i) A series of fluids sampled during the progressive evaporation of a brine having passed gypsum saturation and in the way of reaching halite saturation (primary origin of the brine with no subsequent changes). There are, however, several contradictions with such a model, especially the fact that

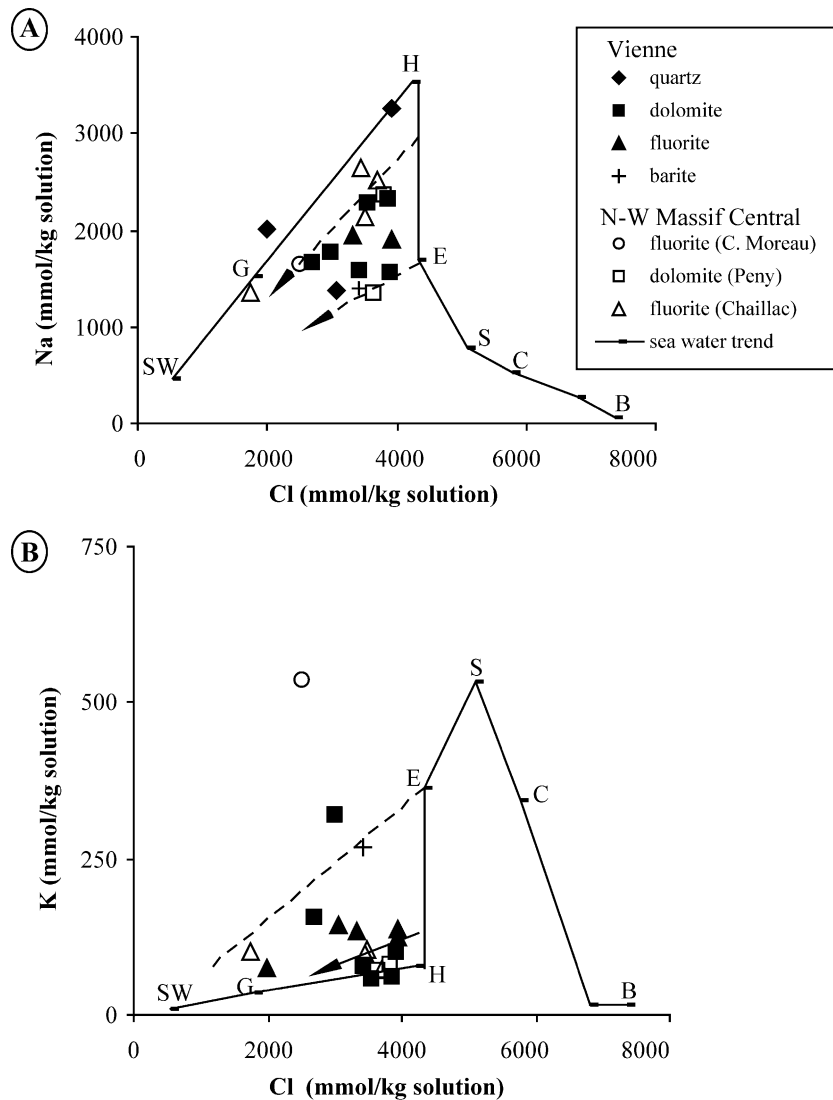


Fig. 4. Na vs. Cl (A) and K vs. Cl (B) diagrams of the composition of the fluids determined from crush-leach analyses. Full line = seawater evaporation trend from Fontes and Matray (1993). SW: seawater, G: gypsum, H: halite, E: epsomite, S: sylvite, C: carnallite, B: bischofite.

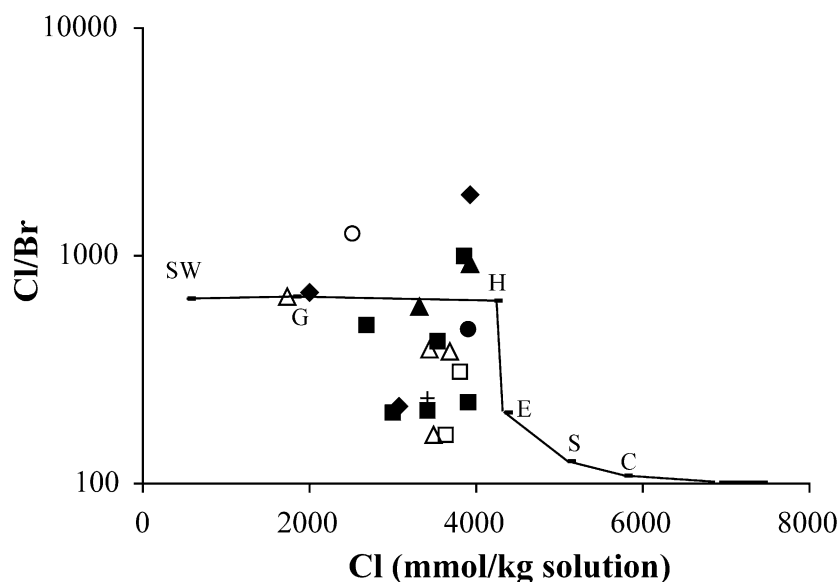


Fig. 5. Cl/Br vs. Cl diagram of the composition of the fluids determined from crush-leach analyses. Full line = seawater evaporation trend from Fontes and Matray (1993). SW: seawater, G: gypsum, H: halite, E: epsomite, S: sylvite, C: carnallite.

seawater evaporation cannot produce such a range of Cl/Br ratios when halite saturation is not reached (see paragraph below), and that Na content is too low for a given chlorinity compared to that expected by the first

part of the seawater curve (increasing Na content up to the halite saturation). (ii) A mixing between a brine having passed halite saturation (evolved brines), therefore with potentially a large range of Na/K, and

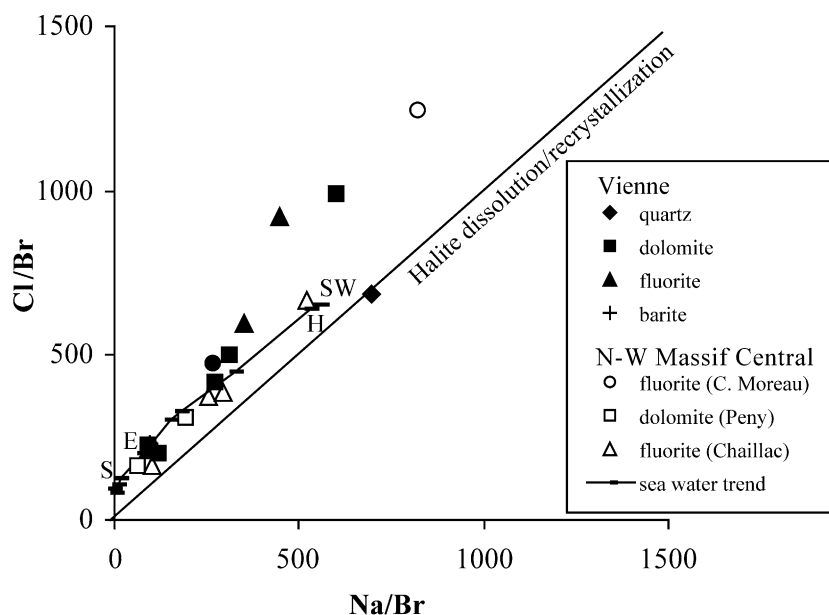


Fig. 6. Na/Br vs. Cl/Br diagram of the composition of the fluids determined from crush-leach analyses. Full line = seawater evaporation trend from Fontes and Matray (1993). SW: seawater, H: halite, E: epsomite, S: sylvite.

Cl/Br ratios at nearly constant chlorinity (4300 mmol/kg solution) and a fluid of low salinity. Dilution is, therefore, the most likely process, as shown by the dashed lines from Fig. 4A. The degree of mixing with fluids having a salinity lower or equal to seawater is estimated using a Cl vs. Br diagram, following method of Connolly et al. (1990) to range from 20% to 70%.

The halogens Cl, Br and, to a lesser degree, I can be used to distinguish sources of fluid (Bohlke and Irwin, 1992) because they display a conservative behaviour in solution and are relatively unaffected by fluid–rock interactions (Banks et al., 1991). Br contents range between 2 and 22 mmol/kg solution and I between 0.0006 and 0.0056 mmol/kg solution. Br/Cl (log Br/Cl from -2.2 to -3) and I/Cl ratios (log I/Cl from -5.8 to -6.8) are typical of deep basinal brines. In the Cl/Br vs. Cl diagram (Fig. 5), the composition of the brines lies mainly below the sea-

water evaporation curve (Fontes and Matray, 1993) with Cl/Br typical of brines which reached saturation with respect to halite. The lower Cl content is interpreted to be due to the dilution of the primary brine as discussed above. The Cl/Br vs. Na/Br plot (Fig. 6), shows that most data plot around the seawater trend and are significantly distinct from that determined by simple halite dissolution (ratio 1:1). In addition, most Na/Br and Cl/Br values (Fig. 6) are lower than those of seawater, as are most inclusions found in evaporite halite (Horita et al., 1991; Kesler et al., 1996). The I contents are rather low and typical of fluids originating from seawater evaporation and noticeably lower than the I content of brines derived from halite dissolution or of oil field brines which are enriched in I due to its release from organic matter.

In conclusion, the present data suggest that the stage II fluids studied are primary brines expelled from evaporites, brines that subsequently underwent

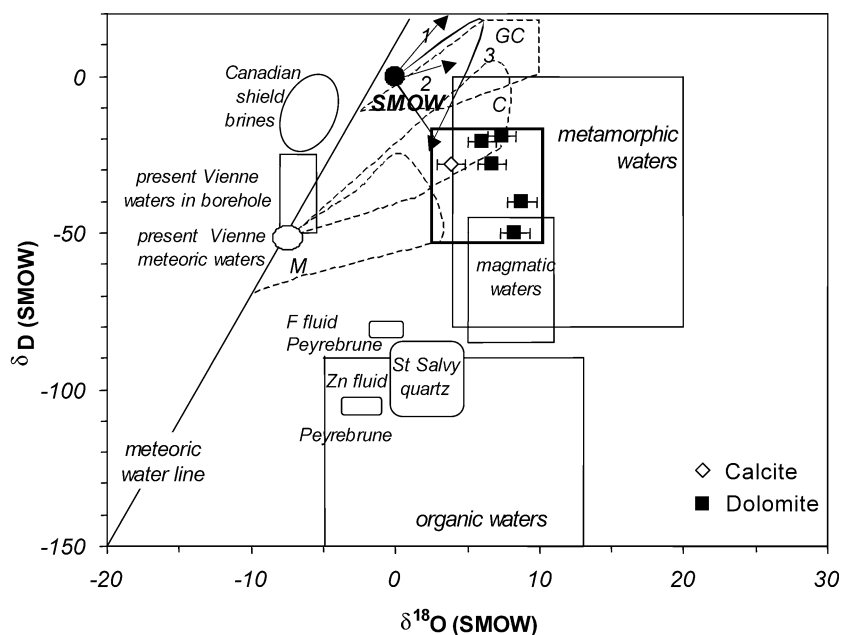


Fig. 7. δD and $\delta^{18}O$ values of fluids (symbols) associated with fractures infillings of the Charroux–Civray site and with mineralised sites at Poitou (northwestern edge of the French Massif Central). Also represented are the compositional fields of some representative fluids (organic waters from Sheppard and Charef, 1986, Basinal fluids from Sheppard, 1984, 1986; GC = Gulf Coast; C = California; M = Michigan) as well as a typical seawater evaporation trends [after Knauth and Beeunas, 1986; Pierre, 1989, initial evaporation under humid conditions (curve no. 1) under arid conditions (no. 2), evaporation curve (no. 3) from Pierre et al., 1984], present-day waters sampled in Vienne boreholes from Michelot (1999), Zn-mineralised sites of Peyrebrune [southeastern edge of the Aquitaine Basin (after Munoz et al., 1995, 1999)], and Canadian shield brines from Frapé and Fritz (1987).

dilution processes in the zones where the minerals crystallized.

3.4. Stable isotopic compositions

Measured fluid inclusion δD values range between -19‰ and -50‰ (Table 2) and discriminate the Poitou and northern Limousin mineralizing fluids from those associated with similar mineralization events at the southeastern edge of the Aquitaine Basin (Fig. 7). For a mean temperature of $100\text{ }^{\circ}\text{C}$, the $\delta^{18}\text{O}$

of the fluid supposed to have been in equilibrium with carbonates is found to be $6.7 \pm 2.0\text{‰}$ (1σ 28) (see companion paper, Fourcade et al., 2002), a value comparable to that obtained with the same method of calculation on the set of samples selected for δD analysis: $6.6 \pm 1.8\text{‰}$ (1σ 5) and to that obtained from coexisting quartz: 6.4‰ and 7.8‰ (Fourcade et al., 2002). Note that we excluded quartz sample CIV 1019 from that calculation because this sample is geometrically associated with an older quartz in the same host fracture and we suspect that the mechanical

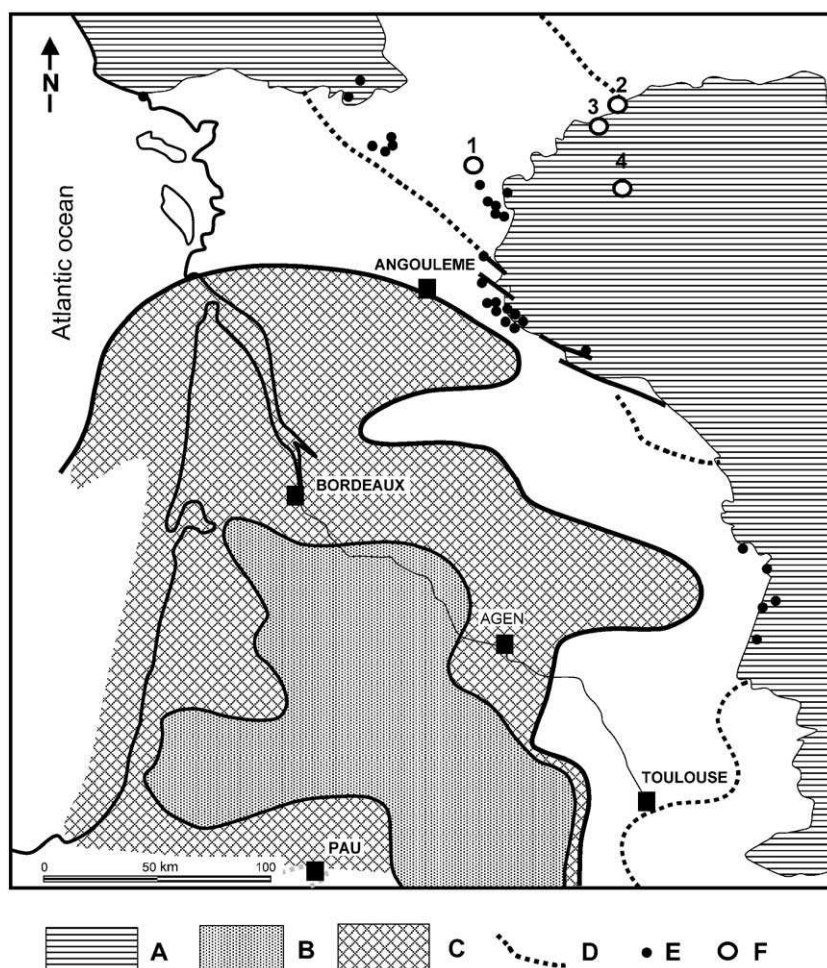


Fig. 8. Simplified geological map of the Aquitaine Basin, with location of the boundary of the presence of halite, gypsum in Lower Lias series (Hettangian) from Curnelle and Dubois (1986), and main occurrences of Pb–Zn–F–Ba occurrences located in Lias or the Hercynian basement. A: basement; B: limit of anhydrite; C: limit of halite; D: present limit after erosion; E: F–Ba (Pb–Zn) deposits; F: Studied sites, 1—Charroux–Civray, 2—Chaillac, 3—Cote-Moreau, 4—Peny.

extraction could have produced a composite sample ($\delta^{18}\text{O}$ of the older quartz may be as low as $+5.1\text{‰}$, Fourcade et al., 2002).

Thus, in a $\delta\text{D}/\delta^{18}\text{O}$ diagram, our brines plot in a sector in which compositions of metamorphic, diagenetic fluids and present-day basinal brines overlap (Fig. 7). On the basis of both the $\delta^{18}\text{O}$ and the δD values, these fluids cannot be pristine marine waters. Such isotopic signatures may be those of fluids derived from deep and relatively high-temperature environments (metamorphic fluids, see Fig. 8), but such a source is difficult to conceive in the geodynamic context at the time of mineral precipitation and with the geometry of the fluid flow (see below). Neither they correspond to fluids (of any primary origin) equilibrated at low temperatures ($100\text{--}150\text{ °C}$) with the basement lithologies (such as the local granitoids themselves) under low fluid/rock ratios because such fluids would have had much lower oxygen isotopic values (i.e., $\delta^{18}\text{O}$ in the range of -3‰ to -8‰ if equilibrated with a granitic feldspar with a $\delta^{18}\text{O}$ value of 8‰). They cannot represent seawater, isotopically modified by evaporation, because δD values are too low for the estimated $\delta^{18}\text{O}$ range (see the evaporation trends in Fig. 7). Unfortunately, we do not have access to the direct isotopic signatures of both O and H in fluid samples, that of O being estimated indirectly from that of whole quartz sample with large temperature (then fractionation) uncertainties. Consequently, we cannot evaluate the possible existence of a correlation between $\delta^{18}\text{O}$ and δD values, which could be helpful in order to discriminate equilibration vs. evaporation vs. mixing processes (generally characterized by different slopes in the $\delta\text{D}/\delta^{18}\text{O}$ diagram). Like many examples of basinal brines, the isotopic compositions of the highly saline fluids are likely the result of several processes, including evaporation and mixing (e.g., Knauth and Beeunas, 1986), combined with the interaction of the fluids with ^{18}O -enriched sediments at temperatures of 100 to 150 °C (e.g., Taylor, 1987; Kyser and Kerrich, 1990 and references therein). It is noteworthy that the homogeneously low $\delta^{13}\text{C}$ values of brines carbonates exclude marine limestones (including the thin carbonate series locally overlying the “Poitou High”) as the recharge source of brines carbon. Such values were acquired by reworking a stock of ancient “metamorphic” carbonate already present in the

granitoids (see Fourcade et al., 2002, companion paper). This indicates that the preferential travelling medium for the brines was the basement rocks themselves and likely its most permeable upper levels located underneath the sedimentary cover (variably altered granitoids and their thin siliclastic cover).

4. Discussion

4.1. Salt source

The solutions are primary brines, resulting from the evaporation of seawater, which evolved chemically during their interaction with the Hercynian basement and the siliclastic infra-Liassic formations. The neighbouring Aquitaine Basin is the most obvious large-scale reservoir of evaporated fluids due to the presence of thick evaporite sequences. Like the Paris Basin, the Aquitaine Basin contains two levels of marine salts (Fig. 8): (i) the first one is located at the base of the sedimentary pile which formed during an initial phase of rifting (275 to 205 Ma , late Triassic), i.e., the so-called “Salifère inférieur” (Curnelle, 1983); (ii) the second one is present in the infra-Toarcian sequence, more precisely within the Hettangian series which occurs in the Charroux–Civray area (some of the studied drillings crosscut such levels). There, the evaporitic horizons are characterized by anhydrite nodules, precipitated in the supratidal zone, and by breccias with cavities resulting from salt or sulfate dissolution. The Hettangian rhythmic evaporite sequence, which is overlain by Sinemurian platform carbonates (Curnelle, 1983), may be thick ($\approx 900\text{ m}$) in some parts of the basin (SW part of the Aquitaine Basin). The primary brines present in the area studied were thus probably derived from these Hettangian evaporitic series, which have a wide extension at the base of the Aquitaine Basin including its northern part.

4.2. Style of fluid migration

The high fluid temperatures obtained indicate that the fluid flow took place in the infra-Toarcian palaeo-aquifer, at greater depths than today (present depth is 100 to 900 m). Because the estimated minimum amount of denudation ranges between 500 and 1000

m, this locates the depth of circulation at more than 600 and up to 1900 m. The homogeneity of the mineralogical sequence, laterally over tens of kilometres and vertically over more than 800 m below the unconformity, indicates mineral precipitation during a major fluid event that did not reiterate. In this respect, the lack of mutual crosscutting relationships among the fracture infillings is very significant. The similarities between fracture minerals in the Vienne granitoids and those from most F–Ba–Pb–Zn mineralized faults all around the Aquitaine Basin, especially the Poitou area (Fig. 8), argue for a brines circulation extending over large distances, similar to that described in most Mississippi Valley-type deposits (Viets and Leach, 1990). From this feature, we infer that the migration of fluids was controlled by two driving forces as follows.

(i) Subhorizontal migration along the unconformity, in relation with pressure–temperature gradients. Thus, the easiest way brines issued from deeper parts in the Aquitaine Basin could have reached the upper part of the series (the “Poitou High”), travelling at the basement/basin boundary during the expulsion associated with the maximum burial (Figs. 8 and 9).

The lack of mineralized fractures above the Toarcian could indicate that the fluid migration did not occur through the shales which constitute a thick and rather low permeability formation over a huge area (cap rock). Sandstones and conglomerates from the infra-Toarcian formations acted as aquifers, as well as the first hundreds of metres of the basement which underwent superficial decompression (generalized opening of preexisting joints) and alteration during emersion.

(ii) Downward penetration of brines in fractured zones in relation with faults, a process which favoured fluid mixing. It is worth noting that zones characterized by sizeable Pb–Zn–Ba–F deposits are frequently associated with horsts and major faults in the basement [mineralized Alloué–Ambernac fault, SE of the Charroux–Civray area; Pb deposit in Melle, located on a horst of granite (Lougnon et al., 1974); F–Ba Chaillac deposit related to a deep subvertical fault zone (Ziserman, 1980)]. Similar processes have also been described for base metal-mineralizing brines in Cornwall (Gleeson et al., 2001) and in Pb–Zn deposits in the Variscides of Belgium (Heijlen et al., 2001).

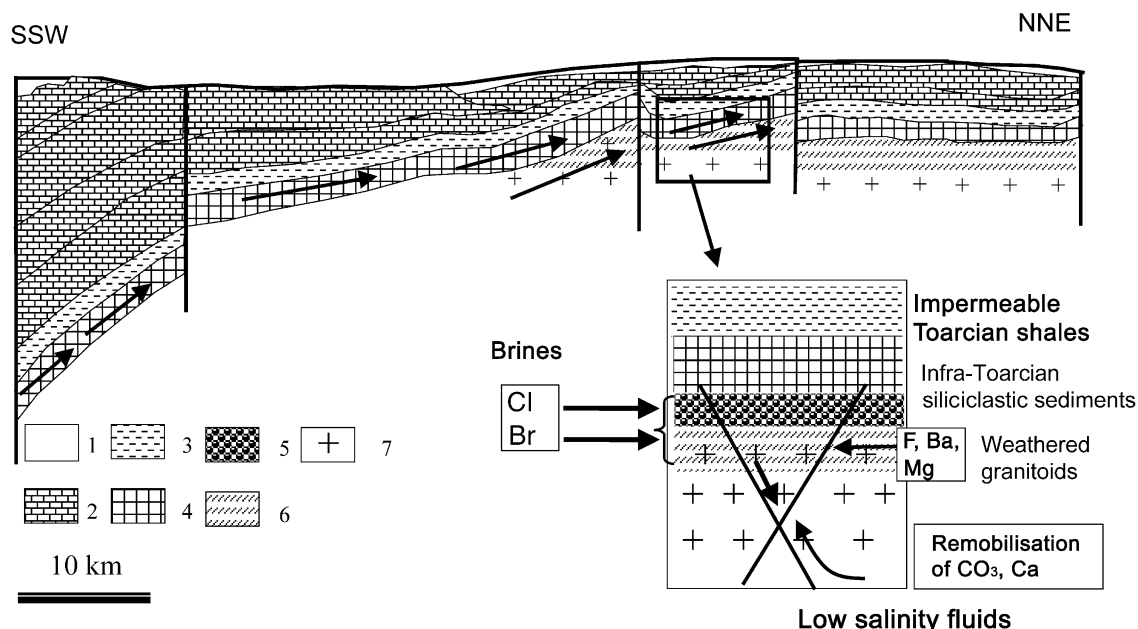


Fig. 9. Schematic model of the hydrothermal circulations within the Charroux–Civray plutonic complex at the unconformity surface. 1—Tertiary cover; 2—Mesozoic limestones; 3—Impermeable shales, Toarcian formation; 4—Basal siliciclastic series and dolomites, Infra Lias; 5—Basal siliciclastic series; 6—Weathered basement (palaeosurface with supergene oxidised facies); 7—Granitoids (hercynian basement).

The relatively high temperature of the mineral deposition, at such a rather shallow level, and the subisothermal character of the mixing event suggest that the recharge diluting fluids were distinct of those generally expected from a shallow-seated granite aquifer, and had probably a temperature close to that of the brines. This implies that the general flow pattern which was a lateral migration of brines at the basement–sedimentary cover interface was locally interfering with ascending low-salinity hot fluids involved in convective cells focused on horst fault systems. Such a situation is typically exemplified in the Rhine graben since the Oligocene (Person and Garven, 1992; Pauwels et al., 1993). There, the fluid movements are long lived (15 Ma) and result in the filling of open fractures with similar mineral assemblages (quartz, barite, carbonate) (Komninou and Yardley, 1997) like in the Vienne granitoids.

4.3. Dating brine migration

The age of brines circulation is not precisely known. The “post-rift” period, which lasted until Upper Jurassic, is dominated by thermal subsidence (Brunet, 1983). The maximum compaction in that part of the basin may have occurred during or slightly after the Barremian (Middle Cretaceous; Brunet, 1983). Over a long period, the evolution of the Aquitaine Basin can be explained in terms of crustal stretching and lithospheric thinning. The optimum epochs for fluid circulation were likely the extension periods, when the geothermal gradient was high. In the absence of absolute dating of the fractures, we speculate that this fluid flow could have occurred during either of the following.

(a) The Lias–Dogger: Indirect dating of the maximal age of the process was given by K–Ar ages obtained on the finest fractions of clays sampled within fractures of the Vienne granitoids, fractures that have experienced the brines episode (ages are younger than 160–170 Ma, Cathelineau et al., submitted for publication); the most significant extensional episode occurred at the Lias–Dogger transition, around 180 Ma ago (Bonhomme, 1982; Curnelle and Dubois, 1986). Coeval with this extension, a significant hydrothermal event is recorded at several sites in the southern Massif Central (Leveque et al., 1988; Lancelot and Vella, 1989; Respault et al., 1991). This

hypothesis is faced to a serious restriction. Indeed, during this period, the thickness of the sedimentary rocks around the “Poitou High” was no more than 200–300 m, and the temperature at the level of the unconformity could not have exceeded a few tens of degrees (30–40 °C at maximum). In such a context, long-distance migration of fluids, in complete thermal disequilibrium (ca. 100 °C), at the basin–basement boundary, i.e., in a cold aquifer, without significant cooling, is difficult to conceive. In addition, active faults at the time of fluid migration were not likely formed or reactivated during Jurassic, a period characterized by little tectonic activity (F. Guillocheau, personal communication).

(b) The Oxfordian–Kimmeridgian (ca. 145 Ma) or (c) the Barremian–Aptian intervals (ca. 110 Ma), which also coincide with new rifting episodes (Brunet, 1983), especially the Gascogne Gulf rifting, and major geodynamic events at the crustal scale (lithospheric flexure, F. Guillocheau, personal communication). A K–Ar date of 112 Ma was obtained on one sample of adularia extracted from a fracture infilling in the Vienne granitoids (Cheilletz et al., 1997). Although the thickness of the sedimentary sequence at that time is debated in the Poitou High, more than 6 km of sediments were deposited in the SW Aquitaine Basin at that time. This situation was also very favourable for the release of hot fluids (≈ 180 °C with a thermal gradient of 30 °C/km). Reactivation and formation of basement fractures are likely during this stage of extensional tectonics as no significant deformation is known during the Jurassic). Faulting and abnormal thermal gradients could also explain the specific location of F–Ba–(Pb–Zn) deposits around basement faults and horsts, and the ascending movements of hot recharge fluids.

4.4. Fluid mixing and fracture sealing

The extreme efficiency of the sealing process can be attributed to the following.

(i) A major interaction between brines and the shallow part of the granitoids weathered during emersion, with a redistribution of the stock of ancient carbonates disseminated in the plutonites (Fourcade et al., 2002, companion paper) and the local extraction of Ba and F from weathered feldspars and biotite ($\pm$ amphibole), respectively. Actually, the fact that

carbonates in the host granites were somewhat remobilized argues that the small-scale permeability was not negligible at the time scale of the sealing event. It also indicates that part of the material filling the fractures in granitoids had a local provenance.

(ii) An efficient mechanism of mineral precipitation. The mixing of two fluids having different salinities (a dilute and a saline end-member) is likely the key factor that promoted precipitation of the dolomite/fluorite ($\pm$ sulphide) association as modelled by Azaroual and Fouillac (1999) in the Paris Basin. According to these authors, mixing of brines with only 10% of dilute water is able to explain a significant amount of mineral precipitation and reproduces the mineral crystallization sequence observed in the studied case. Dilute recharge waters have probably been significantly heated at depth through interaction with deeper rocks to produce temperatures similar to that of brines.

Most of the fluid flow was accommodated by faults and macroscopic (cm-wide, dm-to-m-long) fractures and not by microfractures. Because no brines were significantly trapped as fluid inclusions in the host rocks (no healing of quartz microcracks), this indicates either that: (i) the conditions allowing an efficient trapping of fluids in rock-forming minerals (quartz) were not matched; or/and possibly (ii) the intrinsic permeability of basement rocks in the volumes located between drains was rather small.

4.5. Consequence of the paleofluid migration event on the present-day water chemistry

In the Vienne granitoids, 75% of the present-day sealed fractures can be considered as fractures that were opened (or reopened if formed earlier during Hercynian stages) and (re-)sealed during the Mesozoic event. The chemical consequence of brine migration was the introduction of F, Ba, Cl into the basement and also of a stock of chlorine in the rocks microporosity, preserved as brines inclusions in the minerals and halite crystals in the microporosity as a result of evaporation during sampling. This has three main consequences concerning the hydrological behaviour of fractured granitoid rocks. (i) The discovery of saline (up to 10 g salt/kg solution; Matray et al., 1997) present-day groundwaters at depth in the

Vienne granitic rocks (>400 m below the unconformity) may be explained by a contribution of the Mesozoic brines (up to 300 g salt/kg solution) still preserved in the plutonic rocks to the chemical budget of this present-day deep aquifer. This explanation is an alternative to that proposed by Casanova et al. (2001), who invoked the preservation of marine water within the granitoids since the Mesozoic. (ii) The preservation of some of the Mesozoic stock of chlorine within the basement demonstrates that some rock volumes were preserved from washing effects by the recharge meteoric waters and had, for long periods of time, a limited connection with more transmissive faults and shallower aquifers around the unconformity. (iii) Parts of these relatively close systems were, nevertheless, accessible to remobilization. Indeed, in the conductive faults, the present-day maximum salinity (around 10 g salt/kg) is at least 30 times lower than that of the brines, which implies a large dilution. The rather complex hydrological behaviour of that fractured basement rocks is consistent with results presented in the companion paper (Fourcade et al., 2002), which called for a limited, but recurrent, reworking through time of a still more ancient (Hercynian) stock of soluble material, i.e., basement trace carbonate. Concerning the stock of chlorine, however, we do not know whether the diluting waters penetrated the basement continuously since the Cretaceous, or during specific stages.

5. Conclusions

The pattern of palaeofluid circulations during the major sealing Mesozoic event in the northern part of the Aquitaine Basin is twofold with (i) a major system of laterally migrating brines at the granite–sedimentary cover interface, where both the sandstones and the upper part of the (granitic) basement had a high permeability (a property acquired for the basement through weathering during the emersion period); (ii) local convective cells (rooted at least at 800-m depth) involving low-salinity fluids (presumably surface-derived) as well as brines, and centred on horst fault systems. This picture is inferred from a series of similar fracture sealings found down to 800 m below the cover/basement interface (maximal depth reached by drillings), which indicates that the

brines likely penetrated downwards at least to this depth, into the basement, through dense sets of connected macrofractures. Mixing of the brines with the low-salinity fluids likely infiltrated from emerged zones and heated up at depth to temperatures of 100–110 °C (150 °C on the basis of cation geothermometry) was mostly responsible for the efficient sealing process.

Extensional movements, probably Cretaceous in age, related to the Gascogne Gulf rifting could be considered at the cause of the most significant fluid migration at the basement/cover interface and presently observed all along the margins of the French Massif Central, where erosion led this interface to crop out. This conclusion is strongly suggested by the similarity of paragenetic sequences, fluid chemistry and geometrical characteristics of all the Pb–Zn (F–Ba) deposits known at the western Massif Central margin (from the Atlantic coast in Sables d'Olonne down to the Albigeois area). We consider these discrete or major mineral deposition sites are witnesses of a major fluid dynamic event at the scale of the Aquitaine Basin, the age of which has to be precisely determined.

Unraveling the origin of chloride in aquifers as well as the evolution of its concentration are important clues in understanding the behaviour of fluids in fractured basement rocks. In the present example, possibly representative of many basement rocks located beneath a sedimentary cover, the past fluid circulation revealed by studying the fracture infillings enlightens some past behaviour of the rocks system as well as explains some of the present-day chemistry of deep-seated aquifers. More precisely, the brines circulation was found to be efficient in reducing the present-day basement porosity at depths larger than 400 m below the basement/cover interface. The present data also show that the microporosity of some rock volumes may be somewhat connected to the network of conductive fractures, while some other parts may be relatively isolated and retain soluble material since periods of time which are of the order of tens of Ma. These conclusions are of interest concerning the monitoring of fracture networks in the hot dry rock projects (for instance, the injection tests in the Soultz granites, Rhine graben), or the prediction of water chemistry in deep low-permeability aquifers from basement rocks, such as those

investigated for deep waste-disposal geological laboratories.

Acknowledgements

This work has been initiated within the framework of contracts commissioned by the Agence Nationale pour la gestion des Déchets Radioactifs (ANDRA = French Nuclear Waste Management) and within the framework of the group “Cristallisations dans les fractures” led by J.F. Aranyosy and M. Cuney at CREGU. This study was then supported by the GdR FORPRO—Action 98-III (paper FORPRO no. 2001/11 A), a National Research Program between CNRS and ANDRA. ANDRA is acknowledged for the facilities and permission of sampling the drill cores. S. Buschaert benefits a grant from ANDRA for his PhD. The authors thank Philippe Muchez, Robert Moritz and Eric Oelkers for helpful comments of the manuscript. L.M. Walter is acknowledged for editorial handling. Mr. Grandgirard is thanked for providing the representative samples of the Chaillac fluorites. [MB]

References

- Azaroual, M., Fouillac, C., 1999. Thermodynamic modelling of modern basinal brines from the Paris Basin: implication for MVT ore genesis. Stanley, C.J., et al. (Ed.), *Mineral Deposits, Process to Processing*, vol. 2. Balkema, Rotterdam, pp. 809–812.
- Banks, D.A., Davies, G.R., Yardley, B.W.D., McCaig, A.M., Grant, N.T., 1991. The chemistry of brines from an Alpine thrust system in the Central Pyrenees: an application of fluid inclusion analysis to the study of fluid behaviour in orogenesis. *Geochim. Cosmochim. Acta* 55, 1021–1030.
- Banks, D.A., Giuliani, G., Yardley, B.W.D., Cheilletz, A., 2000. Emerald mineralisation in Colombia: fluid chemistry and the role of brine mixing. *Miner. Depos.* 35, 699–713.
- Beaucaire, C., Gassama, N., Tressone, N., Louvat, D., 1999. Saline groundwaters in the Hercynian granites (Chardon Mine, France): geochemical evidence of the salinity origin. *Appl. Geochem.* 14, 67–84.
- Bertrand, J.M., Leterrier, J., Cuney, M., Brouand, M., Stussi, J.M., Delaperrière, E., Virlogeux, D., 2001. Géochronologie U–Pb sur zircon de granitoides du Confolentais, du massif de Charroux–Civray (seuil du Poitou) et de Vendée. *Geol. Fr.* 1–2, 167–189.
- Bodnar, R.J., 1993. Revised equation and table for determining the freezing point depression of H₂O–NaCl solutions. *Geochim. Cosmochim. Acta* 57, 683–684.

- Bohlke, J.K., Irwin, J.J., 1992. Laser microprobe analyses of noble gas isotopes and halogens in fluid inclusions: analyses of micro-standards and synthetic inclusions in quartz. *Geochim. Cosmochim. Acta* 56, 187–201.
- Bonhomme, M.G., 1982. Age triasique et jurassique des argiles associées aux minéralisations filoniennes et des phénomènes diagénétiques tardifs en Europe de l'Ouest — Contexte géodynamique et implications génétiques. *C. R. Acad. Sci.* 294, 521–524.
- Brunet, M.F., 1983. La subsidence du bassin d'Aquitaine au Mésozoïque et au Cénozoïque. *C. R. Acad. Sci.* 297, 599–602.
- Capdevila, R., 1997. Les suites plutoniques métallumineuses recoupées par les forages Andra de la Vienne: caractérisation, mode de mise en place et discussion du contexte géodynamique. *J. Sci. ANDRA*, Poitiers, 7.
- Carpenter, A.B., Trout, M.L., Pickett, E.E., 1974. Preliminary report on the origin and chemical evolution of lead- and zinc-rich oil field brines in central Mississippi. *Econ. Geol.* 69, 1191–1206.
- Casanova, J., Negrel, P., Kloppmann, W., Aranyosy, J.F., 2001. Origin of deep saline groundwaters in the Vienne granitic rocks (France): constraints inferred from boron and strontium isotopes. *Geofluids* 1, 91–102.
- Cathelineau, M., Cuney, M., Boiron, M.C., Coulibaly, Y., Ayt Ougoudal, M., 1999. Paléopercolations et paléointeractions fluides/roches dans les plutonites de Charroux–Civray—Etude du Massif de Charroux–Civray. *Actes des Journées Scientifiques CNRS/ANDRA*. EDP Sciences, Les Ulis, France, pp. 159–179.
- Cathelineau, M., Fourcade, S., Clauer, N., Buschaert, S., Rousset, D., Boiron, M.C., Meunier, A., Javoy, M., Nitjchoua, R., 2002. Multistage paleofluid percolations in granites: a stable isotope and K–Ar study of fracture illite from Vienne plutonites (N.W. of the French Massif Central). *Clay Miner. Geochim. Cosmochim. Acta* (submitted for publication).
- Cheilletz, A., Cuney, M., Coulibaly, Y., Brouand, M., Cathelineau, M., Stussi, J.M., 1997. L'adularisation à l'interface socle/couverture dans la région de Charroux–Civray. *J. Sci. ANDRA*, Poitiers, 16.
- Connolly, C.A., Walther, L.M., Baadsgaard, H., Longstaffe, F.J., 1990. Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary basin: I. Chemistry. *Appl. Geochem.* 5, 375–395.
- Crawford, M.L., 1981. Phase equilibria in aqueous fluid inclusions. In: Hollister, L.S., Crawford, M.L. (Eds.), *MAC Short Course on Fluid Inclusions*. Mineral. Assoc. Can., pp. 75–100.
- Cuney, M., Brouand, M., Stussi, J.M., Gagny, C., 1999. Le massif de Charroux–Civray (Vienne): un exemple caractéristique des premières manifestations plutoniques de la chaîne hercynienne—Etude du Massif de Charroux–Civray. *Actes des Journées Scientifiques CNRS/ANDRA*. EDP Sciences, Les Ulis, France, pp. 63–104.
- Curnelle, R., 1983. Evolution structuro-sédimentaire du Trias et de l'infra-lias d'Aquitaine. *Bull. Cent. Rech. Explor. Prod. Elf-Aquitaine* 7-1, 69–99.
- Curnelle, R., Dubois, P., 1986. Evolution mésozoïque des grands bassins sédimentaires français, bassin de Paris, d'Aquitaine et du Sud–Est. *Bull. Soc. Géol. Fr.* 8, 529–546.
- Dubessy, J., Lhomme, T., Boiron, M.C., Rull, F., 2002. Determination of chlorinity in aqueous fluids using Raman spectroscopy of the stretching band of water at room temperature: application to fluid inclusions. *Appl. Spectrosc.* 56, 99–106.
- Dubois, M., Ayt Ougoudal, M., Meere, P., Royer, J.J., Boiron, M.C., Cathelineau, M., 1996. Temperature of paleo-to modern self-sealing within a continental rift basin: the fluid inclusion data (Soultz sous Forêts, Rhine graben, France). *Eur. J. Mineral.* 8, 1065–1080.
- Edmunds, W.M., Andrews, J.N., Burgess, W.G., Kay, R.L.F., Lee, D.J., 1984. The evolution of saline and thermal groundwaters in the Carnmenellis granite. *Mineral. Mag.* 48, 407–424.
- Fabre, C., Boiron, M.C., Dubessy, J., Moissette, A., 1999. Determination of ions in individual fluid inclusions by laser ablation optical emission spectroscopy: development and applications to natural fluid inclusions. *J. Anal. At. Spectrom.* 14, 913–922.
- Fallick, A.E., Jocelyn, J., Hamilton, P.J., 1987. Oxygen and hydrogen stable isotope systematics in Brazilian agates. In: Rodriguez Clemente, E. (Ed.), *Geochemistry of the Earth Surface and Processes of Mineral Formation*. Institute de Geologica (CSIC), Madrid, pp. 99–117.
- Fontes, J.C., Matray, J.M., 1993. Geochemistry and origin of formation brines from Paris Basin, France: 1. Brines associated with Triassic salts. *Chem. Geol.* 109, 149–175.
- Fouillac, C., Michard, G., 1981. Sodium/lithium ratio in water applied to geothermometry of geothermal reservoirs. *Geothermics* 10, 55–70.
- Fourcade, S., Michelot, J.L., Buschaert, S., Cathelineau, M., Freiberger, R., Coulibaly, Y., Aranyosy, J.F., 2002. Fluids transfers at the basement/cover interface: Part I. Subsurface recycling of trace carbonate from granitoid basement rocks (France). *Chem. Geol.*, vol. 192, pp. 99–119.
- Fournier, R.O., 1979. A revised equation for Na/K geothermometer. *Geotherm. Res. Counc. Trans.* 3, 221–224.
- Frape, S.K., Fritz, P., 1987. Geochemical trends from groundwaters from the Canadian Shield. In: Fritz, P., Frape, S.K. (Eds.), *Saline Waters and Gases in Crystalline RocksSpec. Pap. - Geological Association of Canada*, vol. 33, pp. 19–38.
- Freiberger, R., Boiron, M.C., Cathelineau, M., Cuney, M., Buschaert, S., 2001. Retrograde *P–T* evolution and high temperature–low pressure fluid circulation in relation to late Hercynian intrusions: a mineralogical and fluid inclusion study of the Charroux–Civray plutonic complex (NW Massif Central, France). *Geofluids* 1–4, 241–257.
- Gleeson, S., Wilkinson, J.J., Stuart, F.M., Banks, D.A., 2001. The origin and evolution of base metal mineralising brines and hydrothermal fluids, South Cornwall, UK. *Geochim. Cosmochim. Acta* 65, 2067–2079.
- Heijlen, W., Muchez, P., Banks, D.A., 2001. Origin and evolution of high-salinity, Zn–Pb mineralising fluids in the Variscides of Belgium. *Miner. Depos.* 36, 165–176.
- Horita, J., Friedman, T.J., Lazar, B., Holland, H.R., 1991. The composition of Permian seawater. *Geochim. Cosmochim. Acta* 55, 417–432.
- Kaminen, D.C., Gascoyne, M., Melnyk, T.W., Frape, S.K., Blomqvist, R., 1992. Cl and Br in mafic and ultramafic rocks: significance for the origin of salinity in groundwater. In: Kharaka, Y.K.,

- Maest, A.S. (Eds.), Water–Rock Interaction. Proceedings of the 7th International Symposium on Water–Rock Interaction, Park City, Utah, vol. 1. Balkema, Rotterdam, pp. 801–804.
- Kesler, S.E., Martini, A.M., Appold, M.S., Walter, L.M., Huston, T.J., Furman, F.C., 1996. Na–Cl–Br systematics of fluid inclusions from Mississippi Valley-type deposits, Appalachian Basin: constraints on solute origin and migration paths. *Geochim. Cosmochim. Acta* 60, 225–233.
- Kharaka, Y.K., Maest, A.E., Carothers, W.W., Law, L.M., Lamothe, P.J., Fries, T.L., 1987. Geochemistry of metal-rich brines from central Mississippi Salt Dome Basin, USA. *Appl. Geochem.* 2, 543–561.
- Knauth, L.P., Beeunas, M.A., 1986. Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters. *Geochim. Cosmochim. Acta* 50, 419–433.
- Kominou, A., Yardley, B.W.D., 1997. Fluid–rock interactions in the Rhine graben: a thermodynamic model of the hydrothermal alteration observed in deep drilling. *Geochim. Cosmochim. Acta* 61, 515–531.
- Kyser, T.K., Kerrich, R., 1990. Geochemistry of fluids in tectonically active crustal regions. In: Nesbitt, B.E. (Ed.), *Short Course on Fluids in Tectonically Active Regimes of the Continental Crust*. Mineralogical Association of Canada, vol. 18, pp. 133–230. Vancouver.
- Lancelot, J., Vella, V., 1989. Datation U–Pb liasique de la pechblende de Rabajac-Mise en évidence d’une préconcentration uranifère permienne dans le bassin de Lodève (Hérault). *Bull. Soc. Géol. Fr.* 8, 309–315.
- Leveque, M.H., Lancelot, J.R., George, E., 1988. The Bertholène uranium deposit-mineralogical characteristics and U–Pb dating of primary U mineralisation and its subsequent remobilization: consequences for the evolution of the U-deposits of the Massif Central, France. *Chem. Geol.* 69, 147–163.
- Loungnon, J., Duthou, J.L., Lasserre, M., 1974. Les gisements plombo-zincifères du seuil du Poitou et de sa bordure Limousine. *Bull. BRGM* 2 (5), 453–476.
- Matray, J.M., Kloppmann, W., Beaucaire, C., Michelot, J.L., 1997. Hydrogéochimie des eaux du socle granitique et des aquifères sédimentaires du Sud de la Vienne: reconnaissance préliminaire. *J. Sci. ANDRA, Poitiers*, p. 30 (abstract VH.9).
- Michelot, J.L., 1999. Les eaux du système granitique de la Vienne: reconnaissance hydrogéochimique et isotopique. *Etude du Massif de Charroux–Civray* Actes des Journées Scientifiques ANDRA. EDP Sciences, Les Ullis, France, pp. 181–199.
- Munoz, M., Boyce, A.J., Courjault-Rade, P., Fallick, A.E., Tollon, F., 1995. Multi-stage fluid incursion in the Palaeozoic basement-hosted Saint-Salvy ore deposit (NW Montagne Noire, southern France). *Int. J. Rock Mech. Min. Sci. Geomech. Abstr.* 32 (5), 202A.
- Munoz, M., Boyce, A.J., Courjault-Rade, P., Fallick, A.E., Tollon, F., 1999. Continental basinal origin of ore fluids from southwestern Massif Central fluorite veins (Albigeois, France): evidence from fluid inclusion and stable isotope analyses. *Appl. Geochem.* 14, 447–458.
- Munz, I.A., Yardley, B.W.D., Banks, D.A., Wayne, D., 1995. Deep penetration of sedimentary fluids in basement rocks from southern Norway: evidence from hydrocarbon and brine inclusions in quartz rocks. *Geochim. Cosmochim. Acta* 59, 239–254.
- Nordström, D.K., Olsson, T., Carlsson, L., Fritz, P., 1989. Groundwater chemistry and water–rock interactions at Stripa. *Geochim. Cosmochim. Acta* 53, 1727–1740.
- Nurmi, P.A., Kukkonen, I.T., Lahermo, P.W., 1988. Geochemistry and origin of saline groundwaters in the Fennoscandian Shield. *Appl. Geochem.* 3, 185–203.
- Pauwels, H., Fouillac, C., Fouillac, A.M., 1993. Chemistry and isotopes of deep geothermal saline fluids in the upper Rhine Graben: origin of compounds and water–rock interactions. *Geochim. Cosmochim. Acta* 57, 2737–2749.
- Peiffer, M.-T., 1986. La signification de la ligne tonalitique du Limousin. Son implication dans la structuration varisque du Massif Central français. *C. R. Acad. Sci. Paris* 303-II, 305–310.
- Person, M., Garven, G., 1992. Hydrologic constraints on petroleum generation within continental rift basins: theory and application to the Rhine graben. *Am. Assoc. Pet. Geol. Bull.* 76, 468–488.
- Pierre, C., 1989. Sedimentation and diagenesis in restricted marine basins. In: Fritz, P., Fontes, J.C. (Eds.), *Handbook of Environmental Isotope Geochemistry: 3. The Marine Environment*. Elsevier, Amsterdam, pp. 257–315.
- Pierre, C., Ortlieb, L., Person, A., 1984. Supratidal evaporitic dolomite at Ojo de Liebre lagoon: mineralogical and isotopic arguments for primary crystallization. *J. Sediment. Petrol.* 54, 1049–1061.
- Poty, B., Leroy, J., Jachimovicz, L., 1976. Un nouvel appareil pour la mesure des températures sous le microscope: l’installation de la microthermométrie Chaixmeca. *Bull. Soc. Fr. Minéral. Cristallogr.* 99, 182–186.
- Respault, J.P., Cathelineau, M., Lancelot, J.R., 1991. Multistage evolution of the Pierres Plantées uranium ore deposit (Margeride, France): evidence from mineralogy and U–Pb systematics. *Eur. J. Mineral.* 3, 85–103.
- Savoye, S., Aranyossy, J.F., Beaucaire, C., Cathelineau, M., Louvat, D., Michelot, J.L., 1998. Fluid inclusions in granites and their relationships with present-day groundwater chemistry. *Eur. J. Mineral.* 10, 1215–1226.
- Shaw, A., Downes, H., Thirlwall, M.F., 1993. The quartz diorites of Limousin: elemental and isotopic evidence for Devonian–Carboniferous subduction in the Hercynian belt of the French Massif Central. *Chem. Geol.* 107, 1–18.
- Sheppard, S.M.F., 1984. Stable isotopes studies of formation waters and associated Pb–Zn hydrothermal ore deposits. *Thermal Phenomena in Sedimentary Basins*. Ed. Technip, pp. 301–317.
- Sheppard, S.M.F., 1986. Characterization and isotopic variations in natural waters. In: Valley, J.W., Taylor Jr., H.P., O’Neil, J. (Eds.), *Stable Isotopes in High Temperature Geological Processes*. Mineral. Soc. Am. Rev. Mineral., vol. 16. Washington, D.C., pp. 165–183.
- Sheppard, S.M.F., Charef, A., 1986. Eau organique: caractérisation isotopique et évidence de son rôle dans le gisement Pb–Zn de Fedj-el-Adoum, Tunisie. *C. R. Acad. Sci.* 302-II, 1189–1192. Paris.
- Taylor, B.E., 1987. Stable isotope geochemistry of ore-forming fluids. In: Kyser, T.K. (Ed.), *Short Course in Stable Isotope*

- Geochemistry of Low Temperature Fluids. Mineralogical Association of Canada, vol. 13, pp. 337–345. Saskatoon.
- Verma, S., Santoyo, E., 1997. New improved equations for Na/K, Na/Li and SiO₂ geothermometers by outlier detection and rejection. *J. Volcanol. Geotherm. Res.* 79, 9–23.
- Viets, J.G., Leach, D.L., 1990. Genetic implications of regional and temporal trends in ore fluid geochemistry of Mississippi Valley-type deposits in the Ozark region. *Econ. Geol.* 85, 842–861.
- Yardley, B.W.D., Banks, D.A., Barnicoat, A.C., 2000. The chemistry of crustal brines: tracking their origins. In: Porter, T.M. (Ed.), *Hydrothermal Iron Oxide Copper Gold and Related Deposits, a Global Perspective*. Australian Mineral Foundation, pp. 61–70.
- Ziserman, A., 1980. Le gisement de Chaillac (Indre): la barytine des Redoutières, la fluorine du Rossignol. Association d'un gîte stratiforme de couverture et d'un gîte filonien du socle. 26° CGI, Gisements français, Fascicule E3. BRGM, Orleans, France, 46 pp.