

GEOCHEMISTRY OF TRACE ELEMENTS IN SPRING WATERS OF THE LOURDES AREA (FRANCE)

Dariusz DOBRZYŃSKI¹ & Davide ROSSI²

¹ Department of Hydrogeochemistry and Groundwater Dynamics, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 Warsaw, Poland; e-mail: d.r.dobrzynski@uw.edu.pl

² Department of Pharmaceutical and Pharmacological Sciences, University of Padova, Via M. Marzolo 1, 35121 Padova, Italy; e-mail: davide.rossi.bazh@gmail.com

Dobrzyński, D. & Rossi, D., 2017. Geochemistry of trace elements in spring waters of the Lourdes area (France). *Annales Societatis Geologorum Poloniae*, 87: 00–00.

Abstract: Geochemical studies on the waters of four springs, including the Massabielle (MS) Spring, were carried out at Lourdes (France) following a long, rainless and warm period, with the aim of at least documenting the groundwater chemistry that was affected by the current meteoric input. The existence of anecdotal reports about anomalously elevated concentrations of trace constituents in the water of the MS Spring in the absence of any detailed studies inspired these first geochemical investigations of trace elements in the spring waters at Lourdes.

The main common features of waters from the four springs studied in Lourdes are low total dissolved solids (255–318 mg/L), a slightly alkaline pH (7.50–7.68), oxidizing conditions ($E_H = 458\text{--}472$ mV), similar temperatures (11.3–13.1 °C), and their Ca-HCO₃ hydrochemical type, all of which are typical characteristics for an active zone within a hydrogeological system that is developed in carbonate-dominated bedrock. The spring waters, which represent an active turnover zone in the hydrogeological system, are only in partial chemical equilibrium with the minerals of the aquifer rocks.

The enrichment of the MS Spring water with numerous elements (Li, Na, Cs, Ba, S, F, Br, REE, B, Sb and Bi), when compared with other springs studied and with the bedrock geochemistry, probably is caused by contributions from fluids (originating from the Pyrenees basement and/or from Triassic saliferous deposits) in the formation of the hydrogeochemical content of the zone under investigation.

The germanium concentration in all of the waters studied was significantly lower than the concentrations typically found in fresh groundwater in the active zone; accordingly, the hypothesis concerning an anomalously high concentration of this element in the MS Spring water was invalidated.

The preliminary geochemical research presented is part of an interdisciplinary geochemical-biological-tensiometric study of the spring waters at Lourdes.

Key words: Groundwater geochemistry, trace elements, spring water, Lourdes springs, France.

Manuscript received 26 January 2017, accepted 9 August 2017

INTRODUCTION

Carbonate rocks, mostly of Jurassic and Cretaceous origin, occur abundantly at the northern edge of the Pyrenees to form many carbonate massifs and aquifers. These include the Saint-Pé Massif (e.g., Le Pochat *et al.*, 1975), in which the most recognizable and globally known spring is that in the MS Cave, used by the Marian Shrine at Lourdes (Hautes-Pyrénées Department, France). This spring, since the disclosure of it in 1858, has raised much interest. Chemical studies of its water are rare, incomplete and not available in scientific publications, although the healing properties of this water sometimes have been linked to its chemical composition. However, the earliest basic quantitative analysis was carried out in 1858 by Édouard Filhol (Fourcade, 1862), who confirmed that this is fresh water, typical for ar-

eas with carbonate bedrock and different from the therapeutic mineral and thermal waters present at adjacent localities in the Hautes-Pyrénées. Later studies also have excluded the increased level of radioactivity in the aforementioned water (Bertrin, 1915; Le Bec, 1949). Hypotheses suggesting that the healing properties of water from the MS Cave are due to an increased level of rare components, such as germanium or hydrogen gas, are unverified.

Water from the spring in the MS Cave (henceforth referred to as the MS Spring) is used intensively by pilgrims and visitors for drinking and bathing. It discharges the groundwater resource retained in the fissured karst carbonate aquifer, which is dependent on present-day infiltration and susceptible to potential contamination. In 1985–1986, a

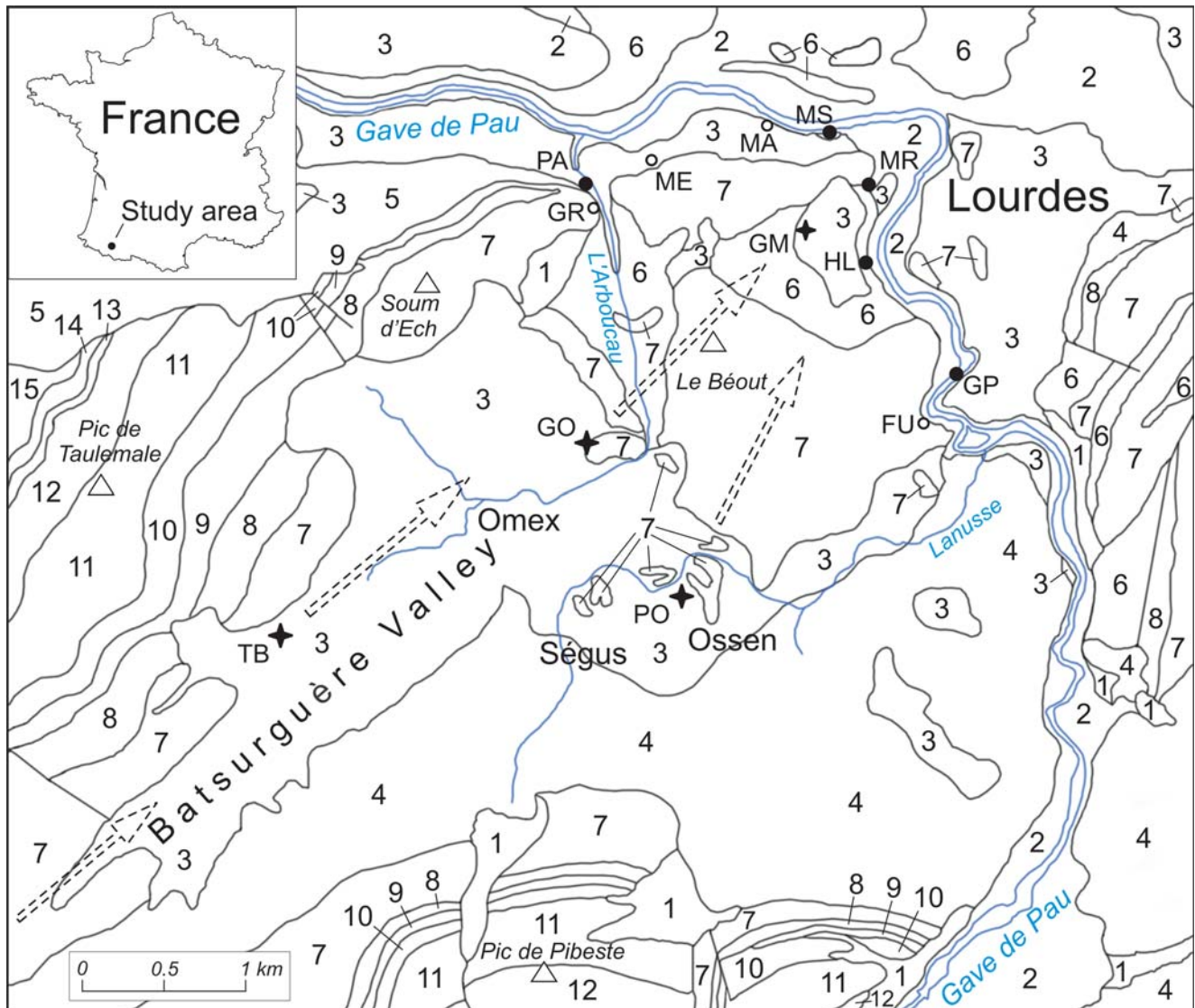


Fig. 1. Geological sketch map of study area (after Casteras *et al.*, 1970) with location of water sampling sites. Explanations. Solid black circles – sampling sites: MS – Massabielle Spring, HL – Hount des Lavasses Spring, MR – Merlasses Spring, PA – Pont de l’Arboucau Spring, GP – Gave de Pau River. Open circles – springs monitored by Astruc *et al.* (1986), unsampled in November 2015 because of drying: GR – Grotte du Roy, ME – Ménigou, MA – Margaret, FU – Fontaine d’Us. Fontorbe Spring, located near Agos-Vidalos, is beyond the southern range of the map. Stars – sinkholes where tracers were injected in 1985 and 1986 (Astruc *et al.*, 1986): PO – Perte du Ruisseau d’Ossen; GM – Gouffre de Millas; GO – Gouffre d’Omex; TB – Trou du Boustut. Sinkhole “Perte de Sauba du Ruisseau de Latée” is situated in the uppermost part of the Batsurguère Valley (off the map), SW of Trou du Boustut. Arrows – general directions of groundwater flow documented by tracing tests in 1985–86. Arabic numbers – generalized geological materials: 1 – debris, superficial and solifluction deposits, 2 – alluvial deposits (undivided), 3 – moraine deposits (undivided), 4 – flysch (Santonian and Campanian), 5 – flysch (Cenomanian), 6 – schistose marls and black marls (late Aptian and Albian), 7 – sub-reef limestones (late Aptian), 8 – marls (middle Aptian), 9 – limestones (Valanginian and Barremian), 10 – dolomites and dolomitic limestones (Tithonian), 11 – black limestones (Kimmeridgian), 12 – black dolomites (Callovian–Oxfordian), 13 – limestones (Callovian and late Early Jurassic), 14 – marls and limestones (middle and late Early Jurassic), 15 – limestones, breccias and dolomites (early Early Jurassic).

series of hydrogeological tracer tests was carried out (Astruc *et al.*, 1986) in the area of the Batsurguère Valley and the Le Béout Massif (WSW of Lourdes) in order to evaluate the groundwater flow velocity and vulnerability to pollution, as well as assess the alimentation area of the MS Spring. Artificial tracers were monitored in springs, including the MS Spring, situated on the northern and eastern peripheries of the carbonate Le Béout Massif. The above-

mentioned studies (Astruc *et al.* 1986) only covered the determination of tracers in spring waters.

The quality of water from the MS Spring (untreated) and water from the taps (after treatment), which is commonly used by pilgrims for drinking, is monitored, respectively yearly and weekly, by the Agence Régionale de Santé (ARS) in terms of parameters in line with sanitary regulations.

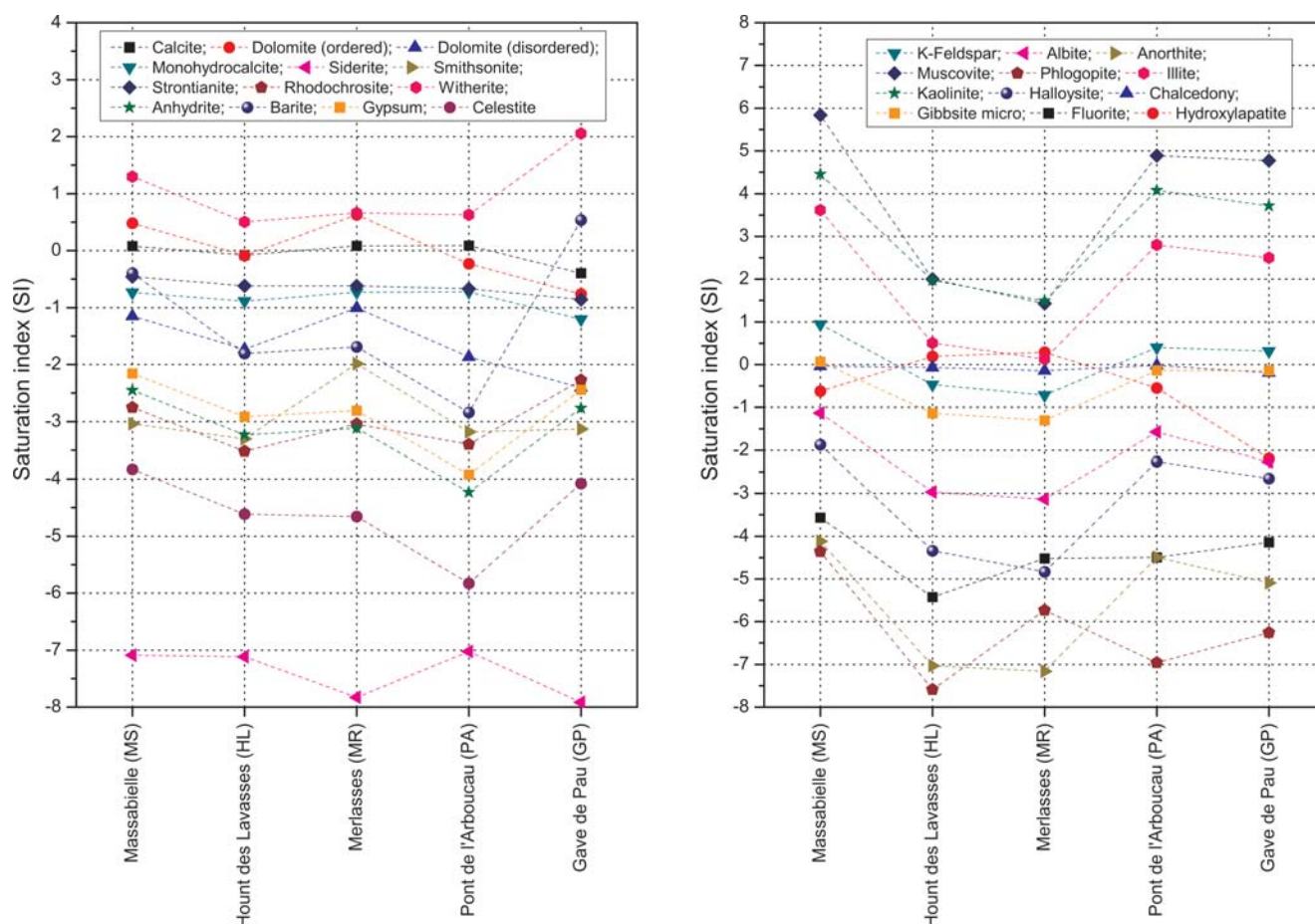


Fig. 2. Saturation state of waters with respect to selected carbonates, sulphates, aluminosilicates and other mineral phases. Saturation indices for annite (varying between -21.4 and -25.1) outside the figure.

The lack of hydrogeochemical research prompted the authors to investigate the water from the MS Spring and other springs present in the area. Reconnaissance and preliminary geochemical studies on spring waters in the area of the Le Béout Massif and the Batsurguère Valley, near Lourdes, were carried out in November 2015.

The aim of the paper is to present and discuss spring water geochemistry in relation to geological and environmental conditions, with a focus on the pattern of trace elements. This topic has not been previously investigated. The preliminary hydrogeochemical studies presented here are part of a broader geochemical-biological-physical investigation into spring waters in the Le Béout-Batsurguère area involving an integrated analytical approach.

GEOLOGICAL AND HYDROGEOLOGICAL OUTLINE

The town of Lourdes is located on the Gave de Pau River (GP), in the foothills of the Pyrenees. Altitudes in the study area range from about 420 m a.s.l. (mean elevation of Lourdes) to 791 m a.s.l. (Le Béout Mt.) and 1,348 m a.s.l. (Pibeste Mt.). From a geological viewpoint, the study area is located in the North Pyrenean Zone (Choukroune, 1992). The area of the Batsurguère Valley, including Le Béout Mt.,

is composed mainly of Lower Cretaceous (Aptian, Albian) sub-reef limestones, black marls, schistose marls and Upper Cretaceous (Campanian, Santonian) flysch (Fig. 1), underlain by Jurassic rocks (mostly limestones and dolomites). The Cretaceous and Jurassic rocks form a synclinal structure, the central part of which is covered by moraine deposits of the Riss and Würm glaciations (Casteras *et al.*, 1970).

The whole area is seismically active, especially the terrains south and east of Lourdes (e.g., Dubos *et al.*, 2004; Souriau *et al.*, 2007; Sylvander *et al.*, 2008; Lacan and Ortuño, 2012), which are located near the North Pyrenean Fault and concomitant dislocations, such as the Bigorre-Adour Fault.

The main aquifer rocks in the Batsurguère hydrogeological system are Cretaceous and Jurassic carbonate rocks, separated by semipermeable lower Aptian marine deposits. Generally, groundwater flows along the axis of the Batsurguère Syncline (i.e., WSW to ENE), then discharges into the GP and its tributaries, such as the l'Arboucau and Lanusse episodic streams (Astruc *et al.*, 1986). The MS Spring is located in a shallow cave at the base of a small hill, positioned on the left bank of the GP. In this section, the river flows west along a steep morphological escarpment, which is a fragment of the 50-km-long active fault scarp of the Lourdes Fault (between Lourdes and Arette), as identified by Alasset and Meghraoui (2005). The first hydrogeological

observation of the MS Spring area recognized this spring as being typical for geological settings in this part of the Pyrenees (Richard, 1879).

Field tests using artificial tracers (sodium iodide, rhodamine, fluorescein) were carried out in 1985 and 1986 (Astruc *et al.*, 1986) with injections into five karst sinkholes (ponors) in the Batsurguère Valley and the Le Béout Massif (Gouffre de Millas, Perte du Ruisseau d'Ossen, Gouffre d'Omex, Trou du Boustut and Perte de Sauba du Ruisseau de Latée; Fig. 1). The expected tracers were monitored in seven springs (MS, Margaret, Menigou, Grotte du Roy, Hount des Lavasses (HL), Fontaine d'Us, Fontorbe; Fig. 1) located in the presumed zone of groundwater discharge along the Gave de Pau Valley. During all tests, a significant and quick recovery of tracers was noted only in the MS and the HL Springs (Astruc *et al.*, 1986). Analytically uncertain concentrations of rhodamine and sodium iodide were detected in the waters of the Margaret and Fontaine d'Us Springs, respectively.

The MS and HL Springs are different in nature, having been found to be vulnerable to potential contamination and recharged by modern water, which infiltrates south-west of the Lourdes town area in the Batsurguère Valley, i.e., in the Batsurguère Syncline from a geological viewpoint (Astruc *et al.*, 1986). The MS Spring is a small spring of the fissure-and-contact type, while older literature sources (Diday, 1873; Mazoyer, 1895) report the flow rate value of the MS Spring as 4.2–5.1 m³/h. The first detailed daily measurements, carried out during the period from December 1984 to April 1986, showed a yield that varied between 1.1 and 4.5 m³/h, with the highest values from January to March. In both the MS and HL Springs, the lowest flow rate was documented during the hydrological summer half-year, especially in the period June–October (Astruc *et al.*, 1986).

Water from the MS Spring is used in its entirety by the Marian Shrine. The karst HL Spring is located in the eastern foothills of the Le Béout Massif, tens of metres from the GP, and represents the main karst outflow in the Batsurguère Valley hydrogeological system. It has a huge flow rate, varying between 100 and 1,000 L/s (360–3,600 m³/h) (Astruc *et al.*, 1986). The water from HL is only used for fish farming and is discharged into the GP.

Tracer tests by Astruc *et al.* (1986) were carried out in the first half of February 1985 and January–March 1986 at the times of high spring discharge. During tests, recharge amounts from swallow holes were found to be approximately 0.5–1.0 L/s (Gouffre de Millas), 4 L/s (Gouffre d'Omex), 20 L/s (Perte du Ruisseau d'Ossen), 1.5 L/s (Trou du Boustut), and 1 L/s (Perte de Sauba du Ruisseau de Latée). The flow rate for the MS Spring was about 2.5–3.0 m³/h and for the HL Spring 720–1,800 m³/h. On the basis of tracer recovery, it was estimated that the MS Spring discharges only about 5% of the groundwater, which turns over in the system, whereas the rest of the water mostly discharges in the HL outflow. The mean effective velocity of the groundwater flow in the Batsurguère hydrogeological system was very high and varied from 54 to 170 m/h. Considering the input-output transit distance, the injected tracers appeared at the outflow points (MS and HL Springs) within one to four days (Astruc *et al.*, 1986).

METHODS

The studies of the chemical composition of groundwater, sampled from the MS and other springs in the area of the Le Béout Massif, were planned after a dry period and before the start of the autumn rainfall in order to minimize the influence of current infiltration on groundwater chemistry. Field work and studies were carried out after a dry and very warm summer and an early autumn, at the beginning of November 2015. The primary objective of the research was the MS Spring. The field reconnaissance revealed that the majority of springs monitored in 1985–1986 had dried up at the beginning of November 2015. Thus, it was only possible to sample water in four springs (Fig. 1), namely, MS, HL, Merlasses (MR) and Pont de l'Arboucau (PA); the two last-mentioned springs were not examined by the Bureau de Recherches Géologiques et Minières (BRGM) in 1985–1986. Water from the GP (above Lourdes, near the dried spring of Fontaine d'Us) was also sampled.

The MR Spring, now located in the basement of a hotel, initiates the MR stream, which is channelized under Avenue Mgr. Schoepfer and the area of the shrine into the tributaries of the GP. The PA Spring is located on the edge of the Gave de Pau Valley, on the west side of the Marian Shrine and at the mouth of the l'Arboucau Creek (Fig. 1).

The chemical composition of water from the MS Spring and from the GP is examined periodically by French state agencies. Waters from the other three springs studied (HL, MR, PA) are not monitored.

The physico-chemical analyses of water carried out by the authors in 2015 comprised field and laboratory measurements and determinations (pH, E_H, T, EC, H₂S, O₂, bicarbonates, sulphates, chlorides, nitrate (V), nitrate (III), fluorides, phosphates, main cations and trace elements). The last two of these were analysed by ICP-MS, while the anions were analysed spectrophotometrically or volumetrically. Water samples for cation and metal determinations were filtered in the field through nylon membrane filters with a pore size of 0.45 µm (Whatman) and preserved by means of ultra-pure HNO₃ (Merck).

Geochemical modelling of the water was performed using the PHREEQC programme, Version 3.3 (Parkhurst and Appelo, 2013), along with the *lnl* thermodynamic database. The average chemical composition of the Earth's continental crust followed Rudnick and Gao (2003), while that of shales followed Li (2000) and that of carbonates followed Hem (1985).

CHEMICAL COMPOSITION OF THE WATERS

The results of the physico-chemical analyses are reported in Appendix 1. The waters studied are mineralized to a very low extent (total dissolved solids varying between 170 and 318 mg/L). The prevailing chemical character of the spring waters analysed is of the calcium-bicarbonate type, whereas the GP water is of the calcium-bicarbonate-sulphate type. The waters are slightly alkaline (pH = 7.5–7.8) and at a low temperature (T = 10.8–13.1 °C), while representing oxidative conditions (E_H = 456–472 mV).

Table 1

Chemical composition of the Massabielle water and spring waters in the Batsurguère Valley

Parameter [unit]	Massabielle (MS) Spring			Parameter [unit]	Massabielle (MS) Spring		
	This study (Nov.2015)	ARS ¹	ADES ²		This study (Nov.2015)	ARS ¹	ADES ²
EC ³ [μ S/cm]	438	311–348	259 (13–413) [64]	K [mg/L]	0.43	0.34–0.50	0.37 (0.10–0.76) [13]
pH [-]	7.64	7.47–7.81	7.51 (6.80–8.25) [74]	NH ₄ [mg/L]	na	<0.05	<0.05 [60]
T [°C]	13.1	11.0–16.2	9.9 (7.7–16.2) [43]	As [μ g/L]	<0.5	<2	<2 [12]
HCO ₃ [mg/L]	198.8	173–195	153 (90.3–255) [18]	B [μ g/L]	10	<20	<20 [12]
SO ₄ [mg/L]	31	8.4–18.9	15.1 (2.25–54.3) [18]	Cd [μ g/L]	0.13	<1	<1 [12]
Cl [mg/L]	12.0	4.2–8.1	2.15 (1.34–3.03) [18]	Fe [μ g/L]	46	<10	<10 [19]
F [mg/L]	0.09	<0.01–0.15	(<0.01–0.15) [18]	Mn [μ g/L]	1.12	<5	<10 [18]
NO ₃ [mg/L]	7.53	2.03–3.74	1.34 (0.01–3.56) [60]	Ni [μ g/L]	<0.2	<5	<5 [12]
NO ₂ [mg/L]	0.007	<0.02	<0.02 [60]	Sb [μ g/L]	0.16	<2	<2 [12]
PO ₄ [mg/L]	0.24	0.09	<0.05 [18]	Se [μ g/L]	<0.5	<2	<2 [12]
Ca [mg/L]	58.08	55–61.2	51.3 (27.2–79.4) [18]	SiO ₂ [mg/L]	5.51	4.5–5.75	4.62 (1.95–7.93) [18]
Mg [mg/L]	5.62	2.4–5.6	2.92 (0.8–6.0) [18]	TOC ⁴ [mg/L C]	na	0.4–0.96	0.55 (0.37–0.85) [12]
Na [mg/L]	3.72	3.47–6.4	1.71 (0.90–3.22) [18]	So ₂ ⁵ [%]	na	70–106	98 (87–121) [8]

¹ – studies carried out by ARS, Tarbes, between January 2007 and March 2015 [N = 10] (A. Casterot, unpubl. data, 2016); ² – studies carried out by BRGM in groundwater from intakes (at springs) at Omex, Ossen, and Ségus villages (monitoring points: 10527X0037, 10527X0049, 10528X0021, 10528X0044, 10528X0045, 10528X0046, 10528X0136, 10528X0152) available at the ADES (“Accès aux Données sur les Eaux Souterraines”) data bank (www.ades.eaufrance.fr) [28.08.2016], with arithmetic mean, range and amount of samples, given respectively; ³ – electrical conductivity (specific conductance); ⁴ – total organic carbon; ⁵ – oxygen saturation; na – not analysed.

The waters studied, including the MS Spring, had not been analysed previously with regard to such a wide range of minor and trace elements. The very low total amount of dissolved solids in the waters is combined with very low concentrations of trace elements. The following elements were not detected (below the indicated detection limits) in all water samples tested: <10 μ g/L – Ti; <1 μ g/L – Sc; <0.5 μ g/L – Se; <0.2 μ g/L – V, Ni, Pd; <0.1 μ g/L – Hg; <0.05 μ g/L – Be, Ru, Au, Ga, Ge, Te; <0.02 μ g/L – Hf, Ta; <0.01 μ g/L – Re, Rh, In, Tl.

In November 2015, the MS Spring exhibited a composition similar to that documented in 2007–2015 by the ARS (Table 1). Higher mineralization (in Table 1, expressed as electrical conductivity) results from the higher concentration of bicarbonates, sulphates, calcium and nitrates (V) in the water during November 2015, caused by sampling after a long dry and very warm period.

The area of the Batsurguère Valley (geologically, the Batsurguère Syncline) was indicated as an alimentation area for the MS and HL Springs (Astruc *et al.*, 1986). Groundwater in the Batsurguère Valley is monitored by the BRGM in a few intakes (at springs), used for the local drinking water supply, and data are available at the ADES website (www.ades.eaufrance.fr). The lower mineralization and lower concentration levels of the main solutes (HCO₃, Cl, Mg and Na) in spring waters from the Batsurguère Valley, compared with MS water (Table 1), undoubtedly result from much shorter water transit times. Springs monitored in the Batsurguère Valley discharge the groundwater from the mountainous frame of the valley (Pibeste – 1,348 m a.s.l., Taulemale – 1,113 m a.s.l., Soum d’Ech – 913 m a.s.l., Le

Béout – 791 m a.s.l.), whereas the springs studied in the Lourdes area (e.g., MS) discharge groundwater from the longer and probably deeper turnover in the hydrogeological system.

The main physico-chemical parameters of water from the GP were monitored up- and downstream in the town of Lourdes. The analysis of 6 November 2015 showed the typical water composition of the river (sampled upstream in Lourdes) at the beginning of November and as revealed in recent years (Table 2).

SATURATION STATE OF THE SPRING WATERS

The main bedrock present in the hydrogeological system, discharged by the springs studied, is limestone, associated with various marls and black flysch rocks. Saturation indexes, which show the equilibrium state of water with respect to a given mineral, were calculated using the PHREEQC program (Parkhurst and Appelo, 2013).

Saturation state analysis takes into account the typical and most likely mineral phases, as data are lacking on the mineral composition of the aquifer bedrock in the Batsurguère Syncline. The spring waters studied exhibit a saturation state that is typical for fresh groundwater occurring in a zone with a short turnover time. The waters are undersaturated with respect to sulphate mineral phases and most of the carbonate phases (Fig. 2). Saturation is reached only with respect to calcite. The saturation state with respect to dolomite depends on the degree of ordering: saturation with

respect to ordered dolomite varies from undersaturation in the PA water, through saturation in the HL water, to supersaturation in the MS and MR waters; all waters are undersaturated with respect to disordered dolomite. Saturation for trace-element-containing pure end-members in the sulphate and carbonate phases is included (Fig. 2) in order to illustrate the behaviour of Fe, Zn, Sr, Mn, and Ba substitutions in the common mineral phases, i.e., in calcite, dolomite and gypsum/anhydrite. Despite the significant exchange of CO₂ between groundwater and the vadose zone, which occur in the flow regimes of karst systems (e.g. Bakalowicz, 1994), the spring waters studied show similar values for carbon dioxide partial pressure (Table 1) and saturation with respect to calcite (Fig. 2).

With regard to the Al- and/or Si-bearing phases, the spring waters are undersaturated with respect to Na/Ca-feldspars and biotites, in equilibrium with chalcedony, and supersaturated with respect to muscovite and clay minerals (e.g., illite, kaolinite; Fig. 2). Halloysite, which has a higher solubility than that of kaolinite, shows undersaturation in all of the waters. The MS and PA waters are saturated with respect to microcrystalline gibbsite, whereas the HL and MR waters show undersaturation. The higher saturation indexes for aluminosilicates in the MS and PA waters, compared to the HL and MR waters, directly result from higher aluminium and silicon concentrations in the former two springs (Appendix 1). The GP shows a similar pattern of saturation indexes with regard to spring waters, despite having half as much mineralization.

As most of the main minerals that form the bedrock in the studied area are unstable in terms of the actual hydrogeochemical conditions, they could transform and release chemical elements into the groundwater. In conclusion, regarding saturation states, the chemical composition of the spring waters seems to be a result of irreversible water-aluminosilicate reactions and carbonate chemistry controlled by calcite.

ELEMENT RATIOS

Ratios between selected elements are helpful tools in hydrogeological and hydrogeochemical discussions. The Br/Cl ratio is a sensitive factor, which is used, e.g., to decipher the origin of chloride in groundwater or the effects of groundwater mixing. The Br/Cl ratio in groundwater varies widely, depending on the source of chloride and/or bromide mineralization, such as seawater, halite/sylvite dissolution, brines, soil processes and anthropogenic sources. Usually, chlorides and bromides behave inertly in fresh groundwater, so that the Br/Cl ratios remain unchanged, while the water component with another Br/Cl signature does not enter into the system. Generally, the higher the chloride concentration in groundwater, the lower the Br/Cl molar ratio.

The Br/Cl (mM/M) ratio in seawater, which is defined as being between 1.52 and 1.57 (mostly 1.54; Morris and Riley, 1966; Herczeg and Edmunds, 2000; Steele *et al.*, 2010), is usually considered a reference point in such discussions. Summarizing the numerous cases studied (Davis *et al.*, 1998), groundwater (with Cl below 5 mg/L) usually

Table 2

General chemical characteristics of the Gave de Pau River water

	Gave de Pau River, upstream Lourde		Gave de Pau River, downstream Lourdes
	This study (6 Nov. 2015)	NAÏADES ¹	NAÏADES ¹
EC [μ S/cm]	223	179 (153–238) [13]	191 (154–252) [12]
pH [-]	7.46	7.71 (7.05–8.40) [13]	7.88 (7.28–8.40) [12]
T [°C]	10.8	8.4 (7.6–11.6) [13]	9.5 (8.0–11.9) [12]
NO ₃ [mg/L]	7.08	(1.27–1.66) [2]	na
NO ₂ [mg/L]	0.016	(0.01–0.017) [2]	na
PO ₄ [mg/L]	0.13	(0.023–0.06) [2]	na
NH ₄ [mg/L]	na	(0.021–0.036) [2]	na
TOC [mg/L C]	na	(0.81–0.927) [2]	na
SO ₂ [%]	na	95 (60–115) [11]	94 (58–112) [10]

¹ – analyses of Gave de Pau water from beginning of November in years 2002–2013, after NAÏADES data bank (www.naiades.eaufrance.fr) [22.08.2016], with arithmetic mean, range and amount of samples, given respectively; na – not analysed

has a Br/Cl (mM/M) ratio between 2.8 and 5.6, connate water has a ratio of 1.1–2.2, sewage commonly has a ratio between 0.75 and 1.5, and groundwater that was affected by the dissolution of halite has a ratio of below 0.45. However, in subsurface brines, the mean of the Br/Cl (mM/M) ratio could range very widely, from 0.08 to 7.65, despite chloride concentration varying between 63 mg/L and 340 g/L (Davis *et al.*, 1998). In this study, the spring waters, despite low chloride concentrations (7.7–12.0 mg/L), show low Br/Cl (mM/M) ratios of 0.63–1.37 (Appendix 1).

The chloride concentration revealed in the waters studied may be generally attributable to atmospheric and lithogenic contributions. The chemistry of atmospheric wet deposition is monitored by the Iraty and Peyrusse Vieille Stations (part of the EMEP/MERA network; <http://ce.mines-douai.fr/pages/observatoire-mera>), while the chemistry of bulk deposition is controlled at the Ance and Losse Stations (part of the RENECOFOR/CATAENAT network; www.onf.fr/renecofor), whose sites are the closest to the area being investigated. Moreover, the chemical composition of wet deposition was also monitored in 2011–2012 in the Ursuya Massif (Jaunat *et al.*, 2013).

Weighted mean chloride concentrations in wet deposition at the Iraty (1,300 m a.s.l.; at a straight-line distance of 74 km W of Lourdes) and Peyrusse Vieille (236 m a.s.l.; a straight-line distance of 63 km N of Lourdes) Stations (0.76 and 1.50 mg/L for 1990–2008 and 1998–2008, respectively) and calculated on the basis of data available from the European Monitoring and Evaluation Programme (EMEP; <http://ebas.nilu.no>) are very similar to those previously published (Iraty: 0.73 (\pm 0.2) mg/L; Peyrusse Vieille: 1.50 (\pm 0.5) mg/L; after Sicard *et al.*, 2007).

The annual mean weighted chloride concentration in bulk deposition for 1993–2015 at the Ance (400 m a.s.l.; 50 km W of Lourdes) and Losse (150 m a.s.l.; 113 km N of Lourdes)

Stations is 1.75 (± 0.41) and 2.09 (± 0.43) mg/L, respectively, calculated using archival RENECOFOR data (M. Nicolas, unpubl. data, 2016).

The weighted mean chloride concentration in wet deposition from the Ursuya Mountain (rain gauge sampler at 570 m a.s.l.; 108 km W of Lourdes) was 4.67 (± 3.61) mg/L (Jaunat *et al.*, 2013). As the mountain is situated only 25 km from the Atlantic shoreline, the relatively high chloride concentration depends on the chemistry of atmospheric deposition, because this area is strongly and directly influenced by ocean salt.

Considering the region of Lourdes, the level of chloride in bulk deposition (1.75 mg/L), according to the Ance Station, was adopted as a reference value for this area. In order to compare the chloride concentration in the groundwater investigated with that of the recharge water, the reference concentration of chloride in effective rainfall was estimated using an enrichment factor (EF) of 2.3 (after Jaunat *et al.*, 2013). The enrichment factor is defined as a proportion of the annual height of precipitation to effective infiltration, both expressed in mm. The concentration of the *i*-th element in the infiltration can be estimated from the formula, $C_{i_infiltration} = EF \times C_{i_precipitation}$, where $C_{i_infiltration}$ and $C_{i_precipitation}$ are concentrations of *i*-th element in the infiltration and in the total precipitation, respectively. Taking the EF value of 2.3, the approximate chloride concentration in recharge water in the studied area is 4.03 (± 0.94) mg/L.

Fresh groundwater from various regions with chloride contents similar to the spring waters studied exhibit Br/Cl (mM/M) ratios of 1.80–3.26 (Davis *et al.*, 1998). For the purpose of comparison, the Br/Cl (mM/M) ratio in potable groundwater aquifers of the UK varies between 1.15 and 2.29 (Edmunds, 1996). In uncontaminated HCO₃-Ca karst spring waters (TDS 362–458 mg/L, Cl 0.7–1.2 mmol/L, temperature 14.5–16.0 °C) of the La Clape Massif (Eastern Pyrenees), Khaska *et al.* (2013) found a Br/Cl (mM/M) ratio of 1.55 to 1.62 [$N = 4$], i.e., very close to the value for seawater (1.54). Chlorides and bromides in groundwater of the La Clape Massif are the result of being located very close to the Mediterranean Sea and Triassic salt formations.

Fluids from various types of bedrock in the Central Pyrenees are characterized by a Br/Cl (mM/M) ratio that usually is considerably higher than that of seawater, varying between 0.33 and 10.78 (mean 4.12, median 3.26, $N = 36$) (McCaig *et al.*, 2000). In the thermal mineral waters of Bagnères-de-Bigorre, located near Lourdes, the Br/Cl (mM/M) ratio varies between 1.46 and 4.32 (mean 2.83; $N = 15$; after data presented by Nartet and Soule, 1985).

In all of the waters studied, the Br/Cl ratio is lower than the mean marine ratio (1.54). The Br/Cl ratio in the MS water is 1.37, while it is between 0.63 and 0.75 in the other springs (HL, MR, PA), and 0.49 in the GP (Appendix 1).

The Br/Cl ratio in precipitation often deviates from the value for sea salt, both in plus and minus terms. This could be caused by different factors, such as distance from the sea coast or altitude. For instance, in the Montpellier-Nîmes area (Southern France), the monthly mean Br/Cl ratio in bulk precipitation varies between 0.70 and 6.04 (Ladouche *et al.*, 2009).

The Br/Cl ratio in the spring waters investigated is lower than the mean seawater value. This phenomenon

could be caused by the following factors: (1) recharging by precipitation is relatively depleted in bromides; (2) groundwater enrichment with chlorides originates from other sources, such as anthropogenic sources; or (3) bromide depletion during the infiltration of water throughout the soil cover. The lack of research on Br/Cl in atmospheric deposition in the study area does not allow direct comparison with the chemistry of the spring waters. The alimentation zone of the springs studied, i.e., the Batsurguère Valley, with its mountainous framework, generally is subjected to small anthropogenic stress. The high-altitude parts of the area (i.e., Pibeste Range, Soum d'Aserole, Pic de Taulemale) are protected by the Massif du Pibeste-Aoulhet Nature Reserve, while the central part, the valley, is used for agriculture and rural settlements. The lack of sewerage systems in the villages, scattered breeding of livestock (cattle, goats, sheep) and the use of natural fertilizers (manure, slurry) could pose a threat to the quality of both groundwater and surface water. Although the adsorption of bromides dissolved in infiltrating waters by soil matter is also possible, in the absence of evidence, this must remain as a hypothesis only. The relative bromide depletion in groundwater, with respect to precipitation, could also be linked to selective bromide removal by vegetation during infiltration (Edmunds, 1996). In conclusion, regarding the actual state of recognition, the lowered Br/Cl ratio in the spring waters studied seems to be caused mainly by anthropogenic chlorides.

The low Br/Cl ratio in the GP (lower than that of the springs) could be the result of both anthropogenic contamination in the upper parts of the catchment and an "altitude effect". The decrease in the Br/Cl ratio in precipitation, when moving with altitude, probably is caused by fractionation between chloride and bromide during atmospheric transport and raindrop condensation. In the atmosphere, chlorides occur in higher concentrations than bromide and mostly form larger atmospheric aerosol particles than do bromides (Winchester and Duce, 1967). This relationship favours raindrop nucleation and relatively easier chloride removal with precipitation, as well as the consequent decline in the Br/Cl ratio in precipitation with respect to the original proportion in atmospheric vapour (Ladouche *et al.*, 2009).

Even though the discharge water of the springs studied is from the same hydrogeological system, the MS water shows relative enrichment in both bromides and chlorides (Fig. 3).

Other springs (HL, MR, PA) each show an individual Br-Cl pattern, indicating that their chemistry may be partly formed under different conditions, compared to the MS Spring. Assuming the existence of environmental contamination, which would introduce an additional chloride influx into the hydrogeological system, it is possible to assume that a particular source only enriches the MS water with bromides and chlorides. The MS Spring discharges from the Urganian limestones next to dislocation (the Lourdes Fault) that separates the aforementioned limestones from the low-permeability Upper Cretaceous flysch rocks (Astruc *et al.*, 1986). In a previous report (Astruc *et al.*, 1986), it was hypothesized that the MS water is a mixture of water components with various transit flow paths, turnover times

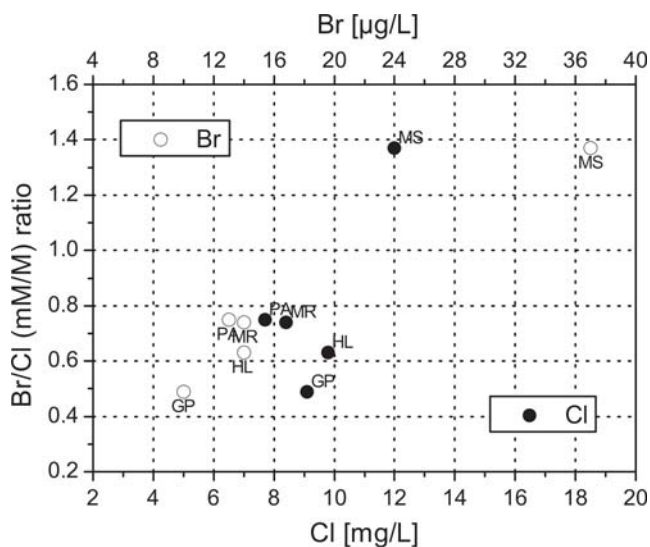


Fig. 3. The Br/Cl (mM/M) ratio versus Cl and Br concentrations in waters studied. Acronyms of water samples as given in Appendix 1.

and depths, i.e., from shallower waters with the shortest turnover time in the carbonate aquifer to deeper waters with longer turnover times in the Batsurguère Syncline, and ascends towards the surface along the tectonic dislocation until it meets a lithological barrier. The existence of a seismically active fault (known as the Lourdes Fault) in this area was documented by Alasset and Meghraoui (2005). Meanwhile, the migration of mineral water from deeper parts of the lithosphere along the dislocation mentioned above seems to be a logical explanation for the Br-Cl enrichment observed in the MS water.

It was possible to quantify other ratios, which are sometimes helpful for deciphering groundwater chemistry, such as B/Cl, Li/B, and Cs/Rb, in the MS water (Appendix 1), although boron and caesium were not detected in all of the waters studied.

In the MS water, the B/Cl [mM/M] ratio is 2.73 (Appendix 1), which places it between the mean B/Cl ratio of sea water (B/Cl = 0.76; after data presented by Steele *et al.*, 2010) and the median value for precipitation in the Dax Station, west of Lourdes (B/Cl: 5.19; after data presented by Millot *et al.*, 2010). The B/Cl ratio in brines from fluid inclusions in quartz veins in the Central Pyrenees varied between 2.54 and 3.91 (mean 3.27; N = 8; Banks *et al.*, 1991). The Li/B [mM/M] ratio in the MS water (202.5; Appendix 1) is higher than the Li/B ratio in precipitation from the Dax Station (median ratio: 67.5; after data presented by Millot *et al.*, 2010) and the mean Li/B ratio for sea water (62.3; after data presented by Steele *et al.*, 2010). The Cs/Rb [mM/M] ratio in the MS water (160.8) is distinctly higher than in other waters (≤ 26.2 ; Appendix 1), as well as higher than in sea water (1.64; after the data presented by Steele *et al.*, 2010) and in the average global chemical compositions of fresh groundwater from the supergene zone (89.9; after data presented by Shvartsev, 2008). The ratios presented show that the MS water is distinctly enriched with Br, Li and Cs, compared to the other waters studied.

TRACE ELEMENTS IN THE SPRING WATERS

With the aim of identifying the elements that most significantly enrich the groundwater studied, as well as determining the effects of bedrock composition, the concentration of each element in the spring waters was referred to the silicon solute content and to the relevant ratios in the bedrock. The Batsurguère Syncline is mainly built of carbonate rocks and various shales. Owing to the lack of data on the chemical composition of the bedrock in the study area, the mean composition of the Earth's upper crust (Rudnick and Gao, 2003) and of crustal shales (Li, 2000) and carbonates (Hem, 1985) was used for such normalization. Silicon was selected as a reference element, because of its common occurrence and participation in numerous mineral-water reactions. Various chemical elements could be released into solutions, owing to the decay and transformation of silicate minerals in weathered zones, as well as in carbonate-dominated bedrocks. The relative enrichment in individual elements from the Earth's upper crust and from crustal shales and carbonates, as calculated in the manner indicated, are shown in Figures 4, 5 and 6, respectively.

All spring waters are relatively enriched in Li, Na, Mg, Ca, Sr, U, Mo, Cu, Ag, Zn, Sb, S, F, Cl and Br with respect to the mean composition of the Earth's upper crust and are impoverished in Rb, Y, Zr, Mn and Fe (Fig. 4). Potassium, caesium, barium and lead show different tendencies in individual springs. The MS Spring contains the only water enriched in caesium and barium with respect to the composition of the upper crust. Water from the PA Spring shows a relative reduction in potassium, whereas water from the MR Spring shows a relative reduction in lead. Ratio patterns, relative to the composition of the Earth's shales (Fig. 5), were found to be very similar to those for the composition of the upper crust (Fig. 4). The only difference is that water from the PA Spring also shows a relative reduction in terms of lithium. Different patterns and ratio values, with respect to the mean composition of carbonates (Fig. 6), result from their chemical composition, including a low mean silicon content in carbonates (34 ppm Si; Hem, 1985). The highest ratio values, with respect to carbonates, are found in chlorides, sodium and bromium.

Delivering the chemical elements from glacial deposits, filling the central part of the Batsurguère Valley, and flysch shales to groundwater in a karst environment should also be considered. The moraines probably contain material of crystalline rocks from the central part of the Pyrenees. The PA Spring, which discharges water from a fully carbonate aquifer, is relatively depleted in Li, K, Rb, Mg, Sr, Y, Mo, Sb, and S (Figs 4–6) with respect to other springs, which are partly alimanted by waters infiltrated through glacial deposits and/or shales.

The MS water has a composition similar to that of other springs studied in terms of physico-chemical parameters (T, pH, E_H) and most of the main solutes (HCO_3 , Cl, K, Ca and Mg; Appendix 1). Comparing absolute concentrations, the MS water contains higher concentrations of many elements (Li, Na, Cs, Ba, REE, Th, Zr, Cr, Mn, Cd, B, Sb, Bi, F and Br) than other spring waters (Appendix 1). The small en-

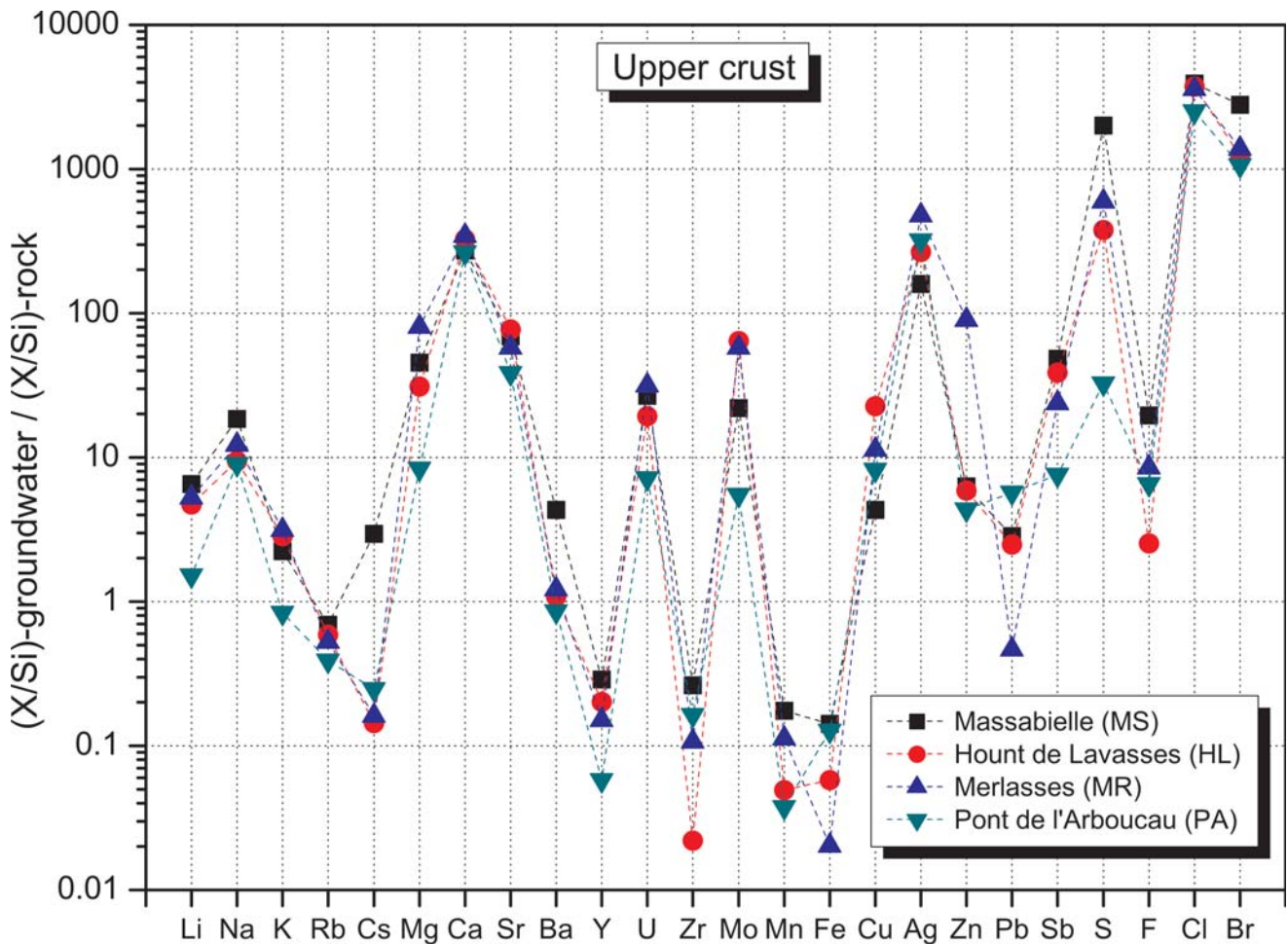


Fig. 4. The X-element/Si ratio in groundwater normalised with respect to mean composition of Earth's upper crust (after Rudnick and Gao, 2003).

richment of the MS water in REE is noticeable. However, the concentrations of REE in MS water are only slightly higher than the detection limits. Any discussion on REEs and their profile requires repeating the tests using much more sensitive methods. In terms of relative enrichment (Figs 4–6), it can be concluded that the MS water is the most enriched (at least) with Li, Na, Cs, Ba, S, F and Br. That said, a comparison with other elements, e.g., REE, B, Sb and Bi, is difficult because they were not detected in all of the waters studied (Appendix 1); notwithstanding, the MS water probably is relatively enriched with these elements as well. Enrichment of the MS water with Br, Li and Cs was further confirmed by the above-mentioned element molar ratios.

The measurable enrichment of the MS water with various elements indicates the possibility of limited participation involving the component that originated from deep saline waters, which may migrate along the active Lourdes Fault, as identified by Alasset and Meghraoui (2005). The rise of saline fluids from the basement through the dislocation zones in the Pyrenean overthrust was documented by McCaig (1988), including the proposed action of a seismic pumping mechanism. Toutain *et al.* (1997) demonstrated that earthquakes in the Pyrenees favour the upward migra-

tion of deep saline fluids along tectonic dislocations to the surface, before mixing with shallower fresh groundwater.

The geochemical anomaly of elements in fresh groundwater may be associated with the effects of saline fluids from the Pyrenees basement and/or brines from the Triassic saliferous deposits. Distinguishing between the influences of these two sources could be complicated because of the possible reaction between deep fluids and Triassic salts during upward migration to the surface (Khaska *et al.*, 2015). Increased concentrations of Cs, Rb, Sr, B, Li and Cl in shallow fresh groundwater were recognized as the effects of saline fluids by Khaska *et al.* (2015) and Toutain *et al.* (1997). The impact of the dissolution salts (mainly anhydrite and halite) from the Triassic strata on the thermal waters of Bagnères-de-Bigorre has been documented (Levet *et al.*, 2002).

The noticeable enrichment of water from the MS Spring with numerous elements (demonstrated for Li, Na, Cs, Ba, S, F and Br; presumably also for REE, B, Sb and Bi) requires further detailed geochemical research. At the actual stage of recognition, the anomalous geochemical pattern in the MS water appears to be due to the probably subtle, but traceable action of highly mineralized fluids. This hypothesis is proposed as a plausible explanation.

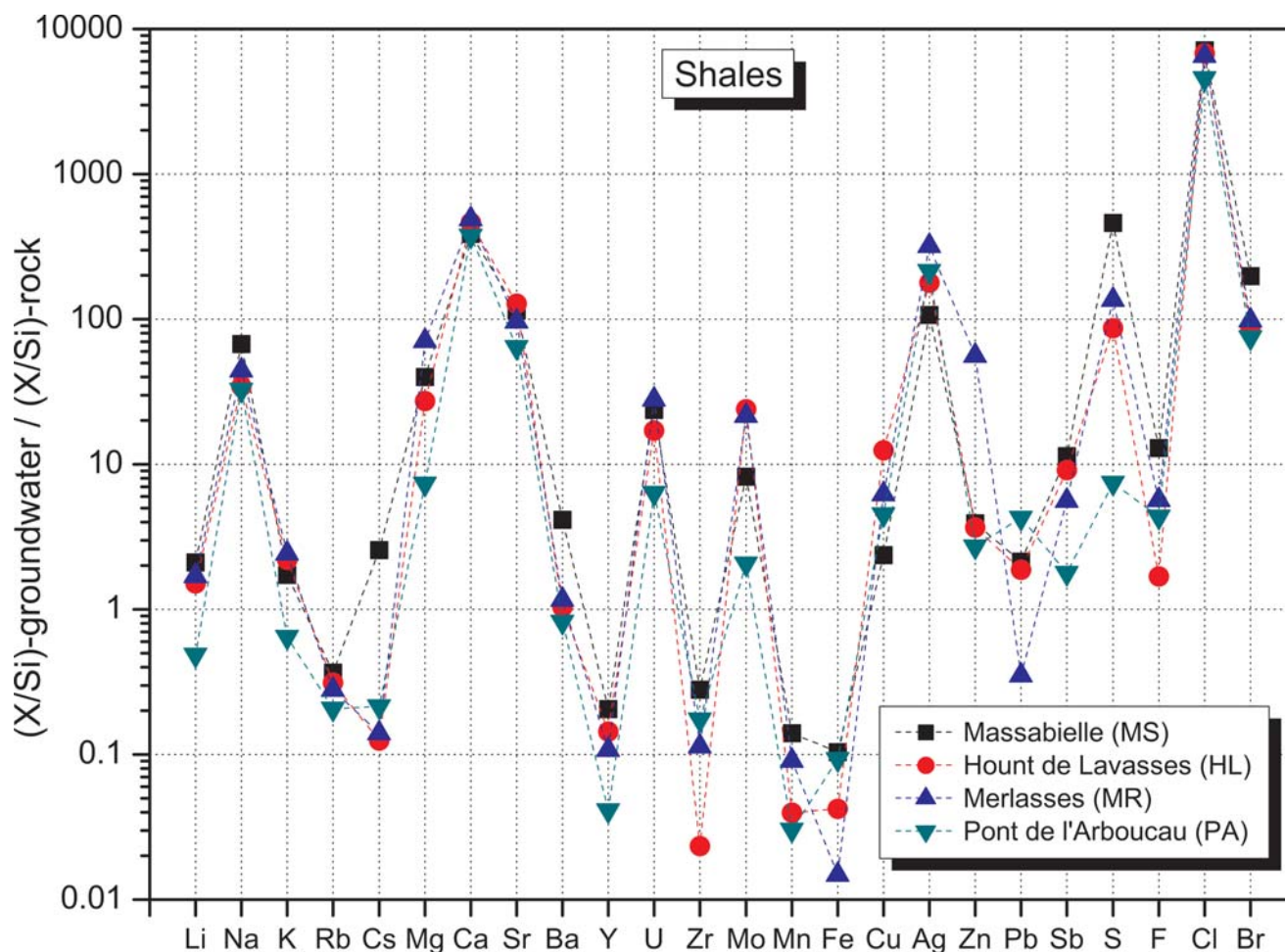


Fig. 5. The X-element/Si ratio in groundwater normalised with respect to mean composition of shales in Earth's crust (after Li, 2000).

ALLEGED ENRICHMENT OF WATER WITH GERMANIUM

From the beginning, i.e., since the disclosure of it in 1858, water from the MS Spring has aroused a great deal of interest and excitement. The presence of components or factors, which are responsible for actual or putative healing properties of the water, has been hypothesized. Soon after the disclosure of the spring, it was suggested that the healing properties of the MS water were caused by the fact that its composition was similar to medicinal and mineral waters associated with the popular health resorts located in the vicinity, such as Bagnères-de-Bigorre, Gazost and Cauterets. Chemical analysis of the MS water, as performed by Édouard Filhol, was unable to verify this suggestion (Fourcade, 1862). In the years that followed, other explanations were put forward, such as the role of the putatively high radioactivity of the MS water. Studies carried out by Albert Nodon (in 1915) and Adolphe Lepape (in 1938) failed to confirm the elevated radioactivity (Bertrin, 1915; Le Bec, 1949). Le Bec (1949) also cites other explanations proposed in the first half of the 20th century, such as strong enrichment in oxygen, or the presence of ozone, penicillin and bacteriophages; none of these claims has been corroborated by tests.

Similar ideas continue to appear in the context of water

from the MS Spring. Indeed, popular science publications and health-oriented websites have published claims that the healing properties of the MS water are due to the presence of an anomalously high concentration of particular constituents, such as germanium or hydrogen gas, which are otherwise beneficial for health.

Germanium dissolved in water was proposed as an active and beneficial substance, following successful tests involving Ge-rich Dunaris mineral water (Eifel, Germany) in the treatment of cancer (Goldstein 1927, 1932). Kazuhiko Asai (1981), the Japanese chemist, who espoused the beneficial role of germanium in human health, after analysing germanium in healing waters from well-known sites around the world, claimed that the amount of germanium in Lourdes water was far greater than that found in other waters. This opinion, while not supported by any quantitative data on the germanium concentration in Lourdes water, began to take on a life of its own, restated by other authors, e.g., Loren (1987), and Wallach and Lan (1994).

Our research carried out in 2015 showed that all of the waters tested, including the MS water, contain very low concentrations of germanium (below 0.05 µg/L of Ge), which does not verify the claim that Lourdes water is rich in germanium. Germanium concentrations in the Lourdes spring waters studied are found to be lower than the typical

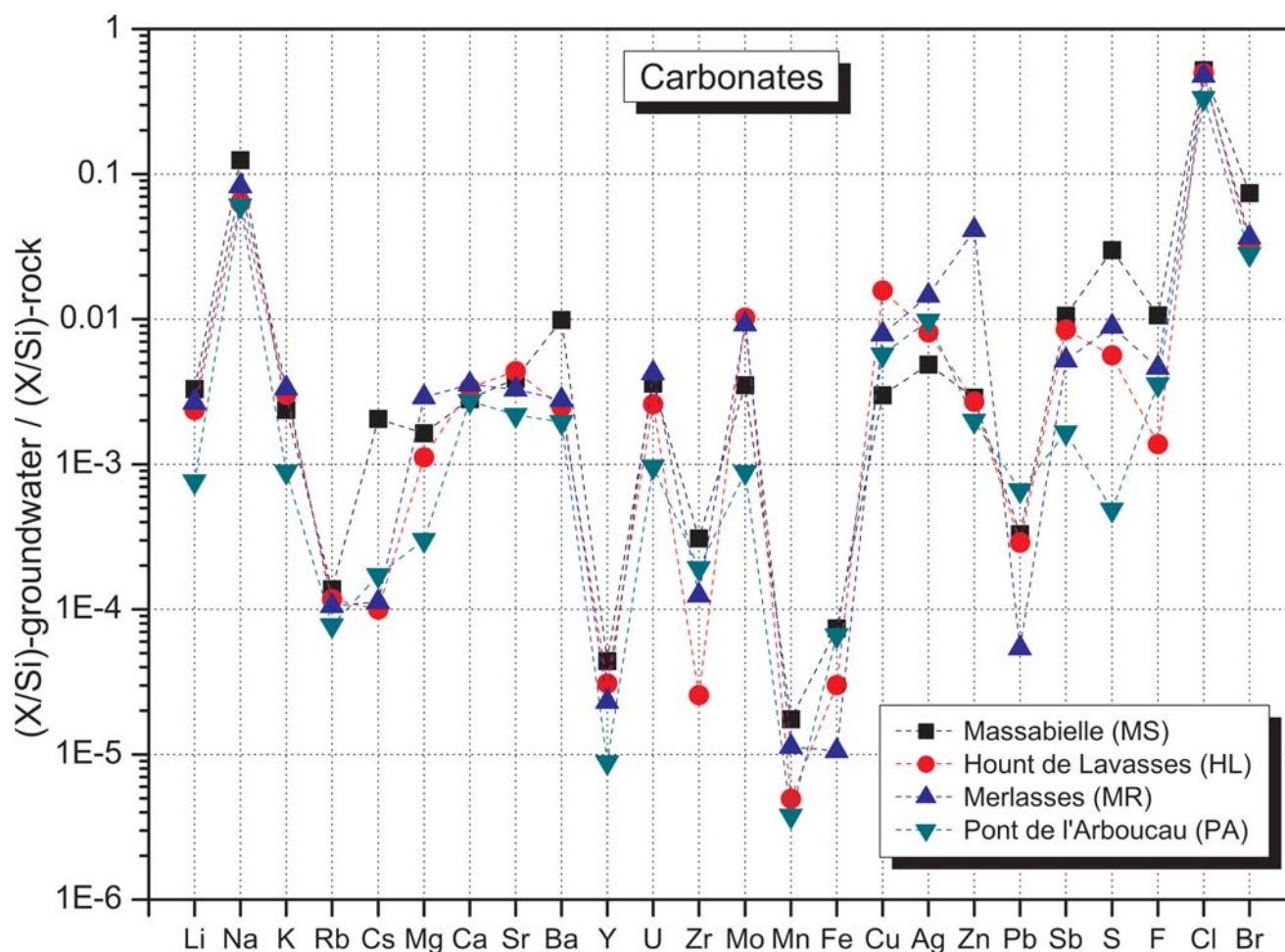


Fig. 6. The X-element/Si ratio in groundwater normalised with respect to mean composition of carbonate deposits (after Hem, 1985).

range proposed for the Earth's fresh groundwater (0.1–1 $\mu\text{g/L}$ of Ge; Shvartsev, 2008), which means that the “high germanium” explanation can join the ranks of the other claims that were previously dismissed.

Increased concentrations of germanium, in the order of several tens of $\mu\text{g/L}$, are usually found in thermal and/or alkaline groundwater, which occurs in active volcanic zones and/or in crystalline bedrocks that incorporate reactive silicate minerals. While the highest documented germanium concentrations reach up to 300 $\mu\text{g/L}$, even in thermal waters, Ge rarely exceeds 50 $\mu\text{g/L}$. The available analytical data on germanium in groundwater in this part of the Pyrenees are still very limited and relate to thermal curative waters. Increased Ge concentrations were found in the thermal waters of the spa at Bagnères-de-Luchon (between 2.69 to 15.18 $\mu\text{g/L}$ of Ge; mean: 9.35 $\mu\text{g/L}$; N = 16; Criaud *et al.*, 1984) and in two thermal springs at Barèges and Barzun, near Barèges (2.95 and 3.4 $\mu\text{g/L}$ of Ge, respectively; Nartet and Soule, 1985).

CONCLUSIONS

The spring waters studied represent an active turnover zone in a hydrogeological system and are in partial chemical

equilibrium with the aquifer rocks. The groundwater is only equilibrated with respect to calcite and dolomite.

This first research investigation into such a wide range of trace and minor elements in the waters studied, including the MS water, revealed an anomalous geochemical pattern in the latter spring. The MS water is enriched in numerous elements (Li, Na, Cs, Ba, S, F, Br, REE, B, Sb and Bi).

At the actual recognition stage, this anomalous geochemistry in the MS water could be explained by contributions from highly mineralized fluids, originating in the Pyrenees basement and/or in Triassic saliferous deposits, which migrate along the active Lourdes Fault.

Further geochemical studies of the waters, covering trace elements by means of more sensitive analytical methods and also stable (O, H, Li, B and Br) isotopes, and of the aquifer bedrock in the hydrogeological system of the Batsurguère Valley, are needed for complete documentation, as well as the elucidation of various aspects, such as the contributions of saline fluids and atmospheric deposition to the MS water and the scale of anthropogenic impacts on the spring waters.

The hypothesis of an anomalously high germanium concentration in the MS water is definitely invalidated. Germanium concentrations in all of the waters studied are significantly lower than in the average fresh groundwater.

Geochemical studies should be performed to verify the claim that there is a putatively increased content of hydrogen gas in the MS water.

Acknowledgements

Alessandro de Franciscis (President of the Bureau des Constatations Médicales, Lourdes), the authorities of the Sanctuary of Our Lady of Lourdes, and Nicolas Brouwet, Bishop of Tarbes and Lourdes, are gratefully thanked for supporting our research and granting us permission to study the MS water directly at the outflow site. The following persons are acknowledged for their help and providing archival data or difficult-to-access publications: Manuel Nicolas (RENECOFOR Network, Office National des Forêts, Fontainebleau) for archival chemical data on chlorides in precipitation at the Ance and Losse Stations; Annie Casterot (Agence Régionale de Santé, Tarbes) for sanitary analyses of water from the MS Spring; and Pascale Leroy-Castillo (Archives of the Sanctuary, Lourdes) for old publications. Our friends from Lourdes, Marie Josée Pomes Boudasso and Jean Omnès, are cordially thanked for their great help during the field work and in gathering materials. The authors are indebted to two anonymous reviewers for their very helpful comments and suggestions, and to Frank Simpson for linguistic correction and comments which allowed them to improve the manuscript.

REFERENCES

- Alasset, P.-J. & Meghraoui, M., 2005. Active faulting in the western Pyrenees (France): Paleoseismic evidence for late Holocene ruptures. *Tectonophysics*, 409: 39–54.
- Asai, K., 1981. *Miracle Cure. Organic Germanium*. Kodansha, New York, 240 pp.
- Astruc, G., Paris, J. P., Roche, J. & Vernet, R., 1986. *Etude hydrogéologique de la région de Lourdes (1985-1986)*. BRGM, Report no. 86 SGN 355 MPY. <http://infoterre.brgm.fr/rapports/86-SGN-355-MPY.pdf> [19.07.2015]
- Bakalowicz, M., 1994. Water geochemistry: Water quality and dynamics. In: Gilbert, J., Danielopol, D. L. & Stanford, J. A. (eds), *Groundwater Ecology*. Academic Press, San Diego, pp. 97–127.
- 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. *Geochimica et Cosmochimica Acta*, 55: 1021–1030.
- Bertrin, G., 1915. *Histoire critique des événements de Lourdes apparitions*. Lourdes-Paris, 592 pp.
- Casteras, M., Villanova, M. & Godechot, Y., 1970. *Carte Géologique détaillée de la France, 1:50 000, feuille Lourdes (1052)*. Bureau de Recherches Géologiques et Minières, Orléans.
- Choukroune, P., 1992. Tectonic evolution of the Pyrenees. *Annual Review of Earth and Planetary Sciences*, 20: 143–158.
- Criaud, A., Vuataz, F. D. & Garcia, D., 1984. *Etude géochimique et géothermique des eaux sulfureuses sodiques de Luchon, Pyrénées*. BRGM, Rapport 84 SGN 384 IRG. <http://infoterre.brgm.fr/rapports/84-SGN-384-IRG.pdf> [11.08.2016]
- Davis, S. N., Whittemore, D. O. & Fabryka-Martin, J., 1998. Uses of chloride/bromide ratios in studies of potable water. *Ground Water*, 36: 338–350.
- Diday, P., 1873. *Examen médical des miracles de Lourdes*. Masson, Paris, 97 pp.
- Dubos, N., Sylvander, M., Souriau, A., Ponsolles, C., Chevrot, S., Fels, J.-F. & Benahmed, S., 2004. Analysis of the 2002 May earthquake sequence in the central Pyrenees, consequences for the evaluation of the seismic risk at Lourdes, France. *Geophysical Journal International*, 156: 527–540.
- Edmunds, W. M., 1996. Bromide geochemistry in British groundwaters. *Mineralogical Magazine*, 60: 275–284.
- Fourcade, M. J. G. A., 1862. *L'apparition à la grotte de Lourdes en 1858*. Fougat, Tarbes, 106 pp.
- Goldstein, F., 1927. Über den Einfluss des Wassers aus dem Kreise Daun in der Eifel auf den Krebs. *Journal of Cancer Research and Clinical Oncology*, 25(1): 71–77.
- Goldstein, F., 1932. *Der Krebs. Seine Verhütung und Heilung nach den Grundsätzen moderner Säftelehre*. Hummel Verlag, Leipzig, 71 pp.
- Hem, J., 1985. Study and interpretation of the chemical characteristics of natural water. *U.S. Geological Survey, Water Supply Paper*, 2254, 264 pp.
- Herczeg, A. L. & Edmunds, W. M., 2000. Inorganic ions as tracers. In: Cook, P. G. & Herczeg, A. L. (eds), *Environmental Tracers in Subsurface Hydrology*. Springer, US, Boston, pp. 31–77.
- Jaunat, J., Celle-Jeanton, H., Huneau, F., Dupuy, A. & Le Coustumer, P., 2013. Characterisation of the input signal to aquifers in the French Basque Country: Emphasis on parameters influencing the chemical and isotopic composition of recharge waters. *Journal of Hydrology*, 496: 57–70.
- Khaska, M., Le Gal La Salle, C., Lancelot, J., ASTER team, Mohamad, A., Verdoux, P., Noret, A. & Simler, R., 2013. Origin of groundwater salinity (current seawater vs. saline deep water) in a coastal karst aquifer based on Sr and Cl isotopes. Case study of the La Clape massif (southern France). *Applied Geochemistry*, 37: 212–227.
- Khaska, M., Le Gal La Salle, C., Videau, G., Flinois, J.-S., Frape, S., ASTER team & Verdoux, P., 2015. Deep water circulation at the northern Pyrenean thrust: Implication of high temperature water-rock interaction process on the mineralization of major spring water in an overthrust area. *Chemical Geology*, 419: 114–131.
- Lacan, P. & Ortuño, M., 2012. Active Tectonics of the Pyrenees: A review. *Journal of Iberian Geology*, 38: 9–30.
- Ladouche, B., Aquilina, L. & Dörfliker, N., 2009. Chemical and isotopic investigation of rainwater in Southern France (1996–2002): Potential use as input signal for karst functioning investigation. *Journal of Hydrology*, 367: 150–164.
- Le Bec, E., 1949. *Raisons médicales de croire au miracle*. 8ed. Bonne Presse, Paris, 208 pp.
- Le Pochat, G., Paris, J. P., Ternet, Y., Albinet, M., Chamayou, J., Maget, P., Moussie, B. & Roche, J., 1975. *Action concertée Adour, ressources en eaux souterraines*. BRGM, Report no. 75 SGN 018 AQI. <http://infoterre.brgm.fr/rapports/75-SGN-018-AQI.pdf> [24.07.2015]
- Levet, S., Toutain, J. P., Munoz, M., Berger, G., Négrel, P., Jendrzewski, N., Agrinier, P. & Sortino, F., 2002. Geochemistry of the Bagnères-de-Bigorre thermal waters from the North Pyrenean Zone (France). *Geofluids*, 2: 25–40.
- Li, Y. H., 2000. *A Compendium of Geochemistry: from Solar Nebula to the Human Brain*. Princeton University Press, Princeton, 475 pp.
- Loren, K., 1987. *The Report on Germanium*. Life Extension Educational Service, 82 pp.
- Mazoyer, P., 1895. *Lourdes et Bétharram*. Lethielleux, Paris, 312 pp.
- McCaig, A. M., 1988. Deep fluid circulation in fault zones. *Geology*, 16: 867–870.
- McCaig, A. M., Tritlla, J. & Banks, D. A., 2000. Fluid mixing and

- recycling during Pyrenean thrusting: Evidence from fluid inclusion halogen ratios. *Geochimica et Cosmochimica Acta*, 64: 3395–3412.
- Millot, R., Petelet-Giraud, E., Guerrot, C. & Négrel, P., 2010. Multi-isotopic composition ($\delta^7\text{Li}$ – $\delta^{11}\text{B}$ – δD – $\delta^{18}\text{O}$) of rainwaters in France. Origin and spatio-temporal characterization. *Applied Geochemistry*, 25: 1510–1524.
- Morris, A. W. & Riley, J. P., 1966. The bromide/chlorinity and sulphate/chlorinity ratio in sea water. *Deep Sea Research and Oceanographic Abstracts*, 13: 699–705.
- Nartet, M. & Soule J.C., 1985. *Departement des Hautes-Pyrenees. Stations thermales et sources thermo-minerales*. BRGM Raport 85-SGN-596-MPY. <http://infoterre.brgm.fr/rapports/85-SGN-596-MPY.pdf> [11.08.2016]
- Parkhurst, D. L. & Appelo, C. A. J., 2013. *Description of input and examples for PHREEQC version 3 - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p. <http://pubs.usgs.gov/tm/06/a43> [29.05.2013]
- Richard, P., 1879. La Fontaine de la Grotte. *Annales de Notre-Dame de Lourdes*, 12(5): 29–34.
- Rudnick, R. L. & Gao, S., 2003. Composition of the Continental Crust. In: Holland, H. D. & Turekian, K. K. (eds), *Treatise on Geochemistry*. Vol. 3. (Rudnick R. L. (ed.)). *The Crust*. 1 ed. Elsevier, Amsterdam, pp. 1–64.
- Shvartsev, S. L., 2008. Geochemistry of fresh groundwater in the main landscape zones of the Earth. *Geochemistry International*, 46: 1285–1398.
- Sicard, P., Coddeville, P., Sauvage, S. & Galloo, J.-C., 2007. Trends in chemical composition of wet-only precipitation at rural French monitoring stations over the 1990-2003 period. *Water, Air, & Soil Pollution: Focus*, 7: 49–58.
- Souriau, A., Roullé, A. & Ponsolles, C., 2007. Site effects in the city of Lourdes, France, from H/V Measurements: Implications for seismic-risk evaluation. *Bulletin of the Seismological Society of America*, 97: 2118–2136.
- Steele, J. H., Turekian, K. K. & Thorpe, S. A. (eds), 2010. *Marine Chemistry and Geochemistry. A Derivative of Encyclopedia of Ocean Sciences*, 2nd Ed. Elsevier, Amsterdam, 631 pp.
- Sylvander, M., Souriau, A., Rigo, A., Tocheport, A., Toutain, J.-P., Ponsolles, C. & Benahmed, S., 2008. The 2006 November, $M_L=5.0$ earthquake near Lourdes (France). *Geophysical Journal International*, 175: 649–664.
- Toutain, J. P., Munoz, M., Poitrasson, F. & Lienard, A. C., 1997. Springwater chloride ion anomaly prior to a $M_L = 5.2$ Pyrenean earthquake. *Earth and Planetary Science Letters*, 149: 113–119.
- Wallach, J. D. & Lan, M., 1994. *Rare Earths: Forbidden Cures*. Double Happiness Publishing, Bonita, California, 496 pp.
- Winchester, J. W. & Duce, R. A., 1967. The global distribution of iodine, bromine and chlorine in marine aerosols. *The Science of Nature (Naturwissenschaften)*, 54: 110–113.

Appendix 1 Chemical composition of waters studied

Concentrations in $\mu\text{g/L}$, unless otherwise indicated

	Massabielle (MS) Spring	Hount des Lavasses (HL) Spring	Merlasses (MR) Spring	Pont de l'Arboucau (PA) Spring	Gave de Pau (GP) River
Date	5.11.2015	4.11.2015	4.11.2015	4.11.2015	6.11.2015
pH	7.64	7.50	7.64	7.68	7.77
T [°C]	13.1	11.3	12.3	12.2	10.8
E _H , corrected [mV]	472	459	459	458	456
EC [$\mu\text{S/cm}$]	438	484	514	435	223
TDS [mg/L]	317.5	284.4	297.2	254.7	169.7
Ionic strength ¹ [mmol/L]	5.638	4.966	5.265	4.419	2.974
logPCO ₂ ¹	-2.442	-2.327	-2.425	-2.513	-2.887
PCC ²	HCO ₃ -Ca	HCO ₃ -Ca	HCO ₃ -Ca	HCO ₃ -Ca	HCO ₃ -SO ₄ -Ca
O ₂ [mg/L]	7.53	9.65	8.75	10	11.3
H ₂ S [mg/L]	0.02	<0.01	<0.01	<0.01	0.02
NO ₃ [mg/L]	7.53	7.97	6.64	2.21	7.08
NO ₂ [mg/L]	0.007	0.010	0.003	0.002	0.016
PO ₄ [mg/L]	0.24	0.77	0.54	0.22	0.13
HCO ₃ [mg/L]	198.8	196.1	208.8	185.1	95.9
SO ₄ [mg/L]	31	5	7	<1	26
Cl [mg/L]	12.0	9.8	8.4	7.7	9.1
F [mg/L]	0.09	0.01	0.03	0.03	0.06
Br	37	14	14	13	10
Li	1.3	0.8	0.8	0.3	0.8
Na [mg/L]	3.72	1.63	1.87	1.80	1.08
K [mg/L]	0.43	0.47	0.46	0.16	0.36
Rb	0.48	0.35	0.28	0.27	0.49
Cs	0.12	<0.01	<0.01	0.01	0.02
Mg [mg/L]	5.62	3.28	7.59	1.03	1.49

Appendix 1 continued

	Massabielle (MS) Spring	Hount des Lavasses (HL) Spring	Merlasses (MR) Spring	Pont de l'Arboucau (PA) Spring	Gave de Pau (GP) River
Date	5.11.2015	4.11.2015	4.11.2015	4.11.2015	6.11.2015
Ca [mg/L]	58.08	59.40	55.87	56.00	28.50
Sr	182.52	174.89	116.81	101.81	100.59
Ba	22.47	4.83	4.82	4.44	167.50
Y	0.05	0.03	0.02	0.01	0.01
La	0.06	0.02	<0.01	0.02	<0.01
Ce	0.05	<0.01	<0.01	0.05	0.01
Pr	0.03	<0.01	<0.01	<0.01	<0.01
Nd	0.03	0.02	0.03	<0.01	<0.01
Sm	0.02	<0.02	<0.02	<0.02	<0.02
Eu	0.02	<0.01	<0.01	<0.01	<0.01
Gd	0.02	0.01	<0.01	0.01	<0.01
Tb	0.03	<0.01	<0.01	<0.01	<0.01
Dy	0.02	<0.01	<0.01	<0.01	<0.01
Ho	0.01	<0.01	<0.01	<0.01	<0.01
Er	0.02	<0.01	<0.01	<0.01	<0.01
Tm	0.02	<0.01	<0.01	<0.01	<0.01
Yb	0.02	<0.01	<0.01	0.01	<0.01
Lu	0.02	<0.01	<0.01	<0.01	<0.01
Th	0.09	<0.05	<0.05	<0.05	<0.05
U	0.60	0.37	0.54	0.16	0.99
Zr	0.42	0.03	0.13	0.26	0.27
Nb	0.01	<0.01	<0.01	<0.01	<0.01
Cr	0.8	<0.5	<0.5	0.5	<0.5
Mo	0.2	0.5	0.4	<0.1	0.5
W	<0.02	<0.02	<0.02	<0.02	0.13
Mn	1.12	0.27	0.55	0.24	4.78
Fe	46	16	<10	41	15
Co	0.02	<0.02	<0.02	<0.02	<0.02
Pt	<0.01	<0.01	0.03	0.05	<0.01
Cu	1.0	4.5	2.0	1.9	2.1
Ag	0.07	0.10	0.16	0.14	0.31
Zn	3.5	2.8	38.0	2.4	4.2
Cd	0.13	<0.05	<0.05	<0.05	0.06
B	10	<5	<5	<5	<5
Al	13	<1	<1	8	8
Si	2576	2205	1963	2565	1613
Sn	0.08	<0.05	<0.05	0.07	<0.05
Pb	0.4	0.3	<0.1	0.8	4.4
As	<0.5	<0.5	<0.5	<0.5	2.9
Sb	0.16	0.11	0.06	<0.05	0.13
Bi	0.07	<0.05	<0.05	<0.05	<0.05
Br/Cl [mM/M] ratio	1.37	0.63	0.74	0.75	0.49
B/Cl [mM/M] ratio	2.73	<1.67	<1.95	<2.13	<1.80
Li/B [mM/M] ratio	202.5	>249	>249	>94	>249
Cs/Rb [mM/M] ratio	160.8	<18.4	<23.0	23.8	26.2

¹ – calculated by PHREEQC programme; ² – prevailing chemical character (hydrochemical type). Molar (mM/M) ratios in sea water are: Br/Cl = 1.54; B/Cl = 0.76; Li/B = 62.3; Cs/Rb = 1.64; all calculated after mean concentrations given by Steele *et al.* (2010).