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Identification of different groundwater flowpaths within volcanic aquifers using natural tracers for the evaluation of the influence of lava flows morphology (Argnat basin, Chaîne des Puys, France)

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SUMMARY

Hydrochemical and stable isotopic (^{2}H, ^{18}O) data were used to characterize the groundwater flow and major chemical features within a complex fractured volcanic aquifer system, the Argnat basin, which is located in the Chaîne des Puys (French Massif Central).

From 10 sampling points, the study of the transfer into the saturated zone from upstream to downstream, given the geological context and topography, allows to estimate the role of supply from high and low altitudes to the recharge processes. This work shows the existence of different types of supply between pahoehoe and a'a flows. Therefore, the morphology of volcanic flows impacts the chemical and isotopic signatures of groundwater, enhancing or reducing the influence of the unsaturated zone on the pathways of infiltrated water. Pahoehoe flows imply horizontal water flows of low discharge at the top of the lava whereas a'a flows seems to be much more heterogeneous and locally able to promote the existence of perched water bodies and further vertical circulations. Taking into account these two types of behaviour, a conceptual scheme of the functioning of this heterogeneous environment is proposed, which will help towards a sustainable management of volcanic aquifers in relation with the European Union Groundwater Directive (2006/118/CE) (2006).

1. Introduction

The hydrogeology of volcanic aquifers is a vital topic for water resources management in many locations around the world (Stieltjes, 1988; Cruz and Silva, 2001; Cruz and Franca, 2006; Custodio, 2007; Demlie et al., 2008; D'Ozouville et al., 2008) and especially in developing countries such as Mexico (Carrillo-Rivera et al., 2007), Ethiopia (Demlie et al., 2008), and India (Kulkarni et al., 2000). Volcanic terrains have been revealed to be non negligible valuable sources of fresh water of good quality (Custodio, 2007; Josnin et al., 2007). Therefore, the management of volcanic aquifers is and will be an important stake in the future and implies first of all the knowledge of their hydrodynamic behaviour and secondly the consideration of their vulnerability facing the anthropogenic pressure.

The hydrological particularities of the Chaîne des Puys region were recognized as early as the late 1800s. These volcanic formations have been regarded as valuable sources of fresh water since the first half of the 20th century (Michel, 1957; Livet et al., 2006). Around a dozen of aquifers associated with lava flows are used for the domestic water supply or for the bottled mineral water industry (Josnin et al., 2007). Several studies (Aubignat, 1973; Belkessa, 1977; Barbaud, 1983; Fournier, 1983; Bouchet, 1987; Belin et al., 1988; Gaubi, 1990; Joux, 2002; Bertrand et al., 2007a,b; Loock et al., 2008) were undertaken, using geological, hydrochemical and geophysical tools, in order to understand the functioning of the volcanic aquifers of the Chaîne des Puys. Gaubi (1990) pointed out peculiarly the heterogeneity of the chemical contents in wells drilled in the Chaîne des Puys. Heterogeneity characterises also volcanic flow structures (a'a or pahoehoe) in which packed clinkers or massive rocks constrain the infiltration

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of water i.e. the supply of both unsaturated and saturated zones. Natural tracers allow to identify these flowpaths and to estimate how lava flows structures, in a given environmental and hydrological context, can influence the quantity and the quality of the groundwater. Such an approach will provide precious information that can help in the definition of safeguard zones around volcanic springs, wells or galleries. This aims to meet regulation standards coming from the implementation of the European Union Water Framework Directive (2000/60/CE) (2000) and of its groundwater "daughter directive" (2006/118/CE) (2006).

In this purpose, a combination of hydrodynamical data, major ions and stable isotopes (δD, $\delta^{18}O$) were used: (1) to identify the recharge areas, (2) to investigate the environmental and geological factors which influence the chemical composition of groundwater, and (3) to propose a conceptual model of the functioning of the Argnat basin a'a and pahohoe flows.

2. Regional geology and hydrogeological setting

The Argnat basin is located in the Chaîne des Puys which is formed by a North–South alignment of Upper Pleistocene and Holocene volcanoes running in the northern part of the French Massif Central.

From a geological point of view (Fig. 1), the studied area is composed of volcanic materials that overlie the fractured granitic and gneissic basement called "Plateau des Dômes" and the sedimentary basin of the "Limagne" mainly composed of marls. Regional volcanism is mainly characterized by monogenic strombolian volcanoes due to the activation of hercynian fractures of the plutonic horst of the "Plateau des Dômes" (Camus, 1975), and basaltic and trachybasaltic flows that settled in paleothalwegs at the end of the volcanic activity (Boivin et al., 2004; Livet et al., 2006). Basaltic and trachybasaltic flows present both a'a and pahoehoe structures (Macdonald, 1953) in the Chaîne des Puys. A'a lava flows, which are the most common, are constituted by vesicular scoria located at the top and at the bottom surrounding a central massive part vertically fissured during the cooling of the lava flow (thermal contraction). Pahoehoe lava flows are essentially massive and frequently present prisms (Kiernan et al., 2003).

The Argnat Basin comprises five lava flows aged between 38,000 and 75,000 years, that corresponds to the strombolian volcanic activity in this area (Boivin et al., 2004). They superimposed in a deep and narrow thalweg on the plutonic basement. At the lowest end of the thalweg, after the Limagne fault, two lava flows (Blanzat on the northern part and Grosliers on the southern part) reached the sedimentary terrains of the Limage where the plane topography permitted these lavas to spread a bit. In this area, volcanic flows are now thrown into relief. Drillings performed near Féligonde (Fig. 1) by Belin et al. (1988), geological mapping by Boivin et al. (2004) and field observartions done by Loock et al. (2008) and Celle-Jeanton et al. (2008) permitted to precise their morphologies types, dimensions and chronological history from the oldest to the youngest. These lava flows are the Grosliers pahoehoe lava flow (40–60 m thick), the Blanzat a'a flow (10–20 m thick), the Féligonde a'a flow (5–15 m thick). Additionally, field observations showed that the Mas d'Argnat a'a flow is 30 m thick above Argnat gallery and that the Egaule a'a flow is 10 m thick above the Egaule outlet. From a chemical point of view, the Argnat volcanic rocks are of alkali basalt and potassic trachybasalt (Camus, 1975; Boivin et al., 2004) and composed mainly of olivine, potassic and plagioclase feldspaths (Table 1).

The understanding of the morphology and location of lava flows has an important influence on water circulations within volcanic aquifers. Basaltic lava has traditionally been classified as either pahoehoe or a'a (Macdonald, 1953) based on surface morphology. A'a lava flows (such as Féligonde or Blanzat flows) have a rough surface composed by clinkers whereas pahoehoe lava flows (such as Grosliers flow) are characterized by a smooth surface without clinkers. According to Hon et al. (1994) and Self et al. (1998), these morphological differences are related to the setting features of

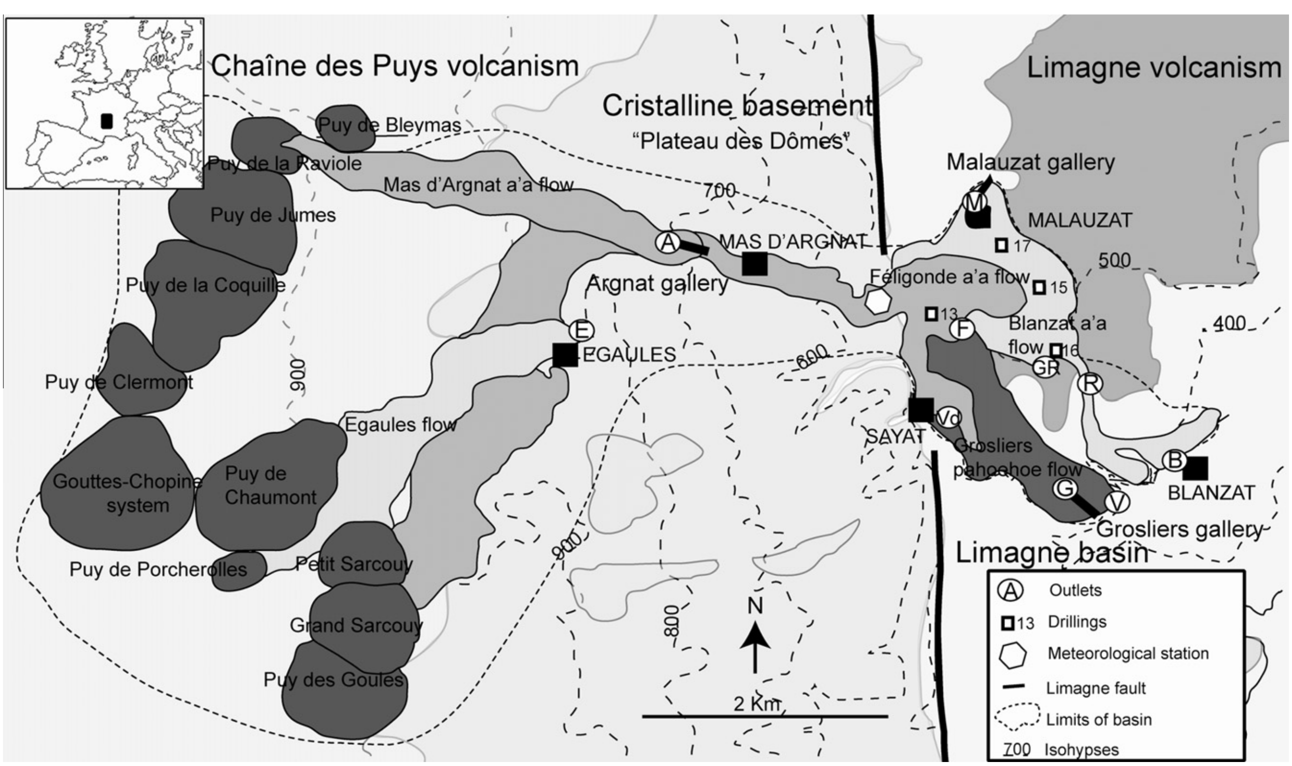

Fig. 1. Geological settings of the Argnat basin and localisation of the studied outlets. V: Vergnes, B: Blanzat, A: Argnat, E: Egaule, R: Reilhat catchment, Vd: Vernède, F: Féligonde, M: Malauzat, GR: Grande source de Reilhat, G: Grosliers.

Table 1
Chemical composition (main oxides and virtual mineral phases according to the IUGS nomenclature in % of weight) of two lava flows located in the Argnat basin (from Camus, 1975 and Boivin, unpublished data).

Chemical composition (%)	Grosliers lava flow (basalt)	Féligonde lava flow (trachybasalt)
SiO_2	45.35	50.52
MgO	8.30	3.81
CaO	10.35	7.86
Na_2O	2.80	3.96
K_2O	1.05	2.70
P_2O_5	0.40	0.83
Normative mineral phases (% weight)	**Grosliers lava flow (basalt)**	**Féligonde lava flow (trachybasalt)**
Orthose	9.1	10.64
Albite	20.38	17.53
Anorthite	22.7	21.86
Forstérite	8.63	6.68
Diopside	19.66	21.69

each lava type: a'a flows move heavily as a single mass with clinkers forming on their surface; pahoehoe flows consist of multiple, overlapping flow lobes, sheets and toes. These placing differences can also be found in the internal structure of lava flows. As a consequence, a'a flows can be described as a massive fractured material mixed with more or less large scoria masses. Such a structure, from a hydrogeological point of view, is considered to present great heterogeneities regarding the porosity and the permeability values but it can constitute an efficient sink for rains. Pahoehoe flows present a massive, poorly fractured feature (Fig. 2), and thus are not supposed to be valuable aquifer structures. However, recent studies, for example in the Deccan Volcanic Province (Walker et al., 1999; Bondre et al., 2004; Druraiswami et al., 2008 and references therein), Columbia River Basalt province (MacDonald, 1972; Keszthelyi et al., 2001), Iceland or Kerguelen Plateau by Keszthelyi and Thordarson (2000) have precised the detailed morphology of pahoehoe flows and their internal arrangements. These structures, called "rubbly pahoehoe flows", present a basal zone with smooth, glassy and often displaying joints, a central zone often jointed, and a crustal part characterized by a variably preserved, vesicular upper crust and a discontinuous layer of flow-top breccias. These features can locally be observed on the Grosliers lava flow (Fig. 3) which allows groundwater circulations.

Environmental settings highlight the fact that strombolian cones and lava flows located up to Féligonde are mainly occupied by coniferous and deciduous forest. Near and downward Féligonde, these lava flows are mainly featured by human occupation such as villages (Sayat, Malauzat, Blanzat), vineyards (on the Grosliers and the Blanzat lava flows) and corn fields (on the Blanzat lava flow). Plutonic terrains are mainly featured by meadows used for rearing. Few roads connect cities. On the Chaîne des Puys area, salt is currently spread on roadway during winter in order to favour the snow melt (Livet, 2001; Joux, 2002).

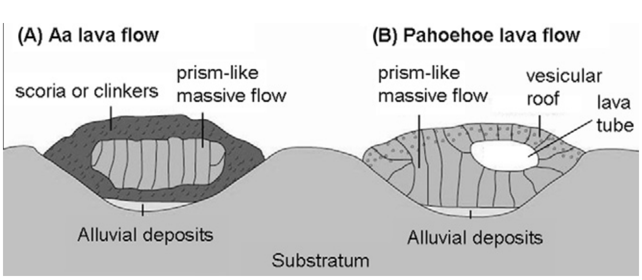

Fig. 2. Pahoehoe and a'a flows morphologies (from Loock, 2008).

From a hydrological point of view, heterogeneities in the recharge processes should be pointed out. The Argnat Basin is a small area of 26.1 km^2 characterized by a high variability in the altitude, from 1159 m (Puy de la Coquille) to 380 m (Blanzat) with a mean altitude of 811 m. These physical characteristics lead to an important heterogeneity in the meteorological parameters (precipitation, temperature) that directly affects the recharge. Three pathways have been described for infiltrated waters (Barbaud, 1983; Joux, 2002; Livet et al., 2006). Precipitation can infiltrate into strombolian cones, composed of clinkers, cinders and lapilli, which present at their base a thin saturated zone (compared with the height of such edifices). This latter recharges the aquifer in the lava flow located downstream, even though such flows are often many kilometers long (Martin-Del Pozzo et al., 2002; Hildenbrand et al., 2005). The recharge can also happen directly on lava flow through scoria, prisms or inflation fissures (Barbaud, 1983; Kiernan et al., 2003; Celle-Jeanton et al., 2008). At last, surface streams circulating over the plutonic impermeable substratum (Hottin et al., 1989; Joux, 2002) may infiltrate into the volcanic aquifer at the contact between basement and the volcanic flows. Thus, water flows downstream in the basal scoria zone or in the spoiled zone near the volcanic flow/basement interface.

Meteorological datasets (Temperature, Precipitation) of Sayat, (45°50′18″N, 3°02′42″E, $z = 550$ m, Météo-France reference: 63417001) Volvic (45°52′30″N, 3°03′00″E, $z = 472$ m, Météo-France reference: 63470001) and Fontaine du Berger (45°47′54″N, 2°59′30″E, $z = 971$ m, Météo-France reference: 63263005) located in the Chaîne des Puys, allow estimating the infiltration amount ($h_{\text{annual precipitation}} - h_{\text{annual actual evapotranspiration}}$; see Eq. (1)) for each 100 m altitude range). Evapotranspiration was evaluated by using Thornwaite's method (1954). This led to a calculated annual basin discharge of about 300 l s^{-1}over the period 1994–2007 (Bertrand, 2009).

3. Methodology

3.1. Sampling

Sampling was carried out during the December 2005/June 2007 period. Ten outlets (Fig. 1) were sampled at least on a monthly basis, the first week of each month: seven springs emerging at the front of the volcanic flows and three horizontal galleries (Argnat, Grosliers and Malauzat) that were drilled during the first half of the 20th century for drinking water supply. Nowadays, only the Argnat and Grosliers galleries are still used for water supply purposes. Rainwater was also sampled on a weekly basis at Sayat meteorological station (Fig. 1) in order to determine the input signal. The can in which rainwater was stored was buried and recovered by an isolated case to avoid evaporation processes. Each week, the rainwater was sampled, the can was rinsed with demineralised water, dried and then buried again.

Moreover, a weekly-scale sampling of the saturated and unsaturated zone of the Grosliers pahoehoe flow was organised. Such an approach is constrained by the accessibility to the sampling site. Concerning the Grosliers flow, the unsaturated zone was sampled through the Grosliers gallery (Fig. 1), where infiltration occurs and it can be observed through little fractures.

On the Blanzat lava flow, as there is no direct access to the unsaturated zone, we used water wells analysis carried out by Gaubi (1990) during the reconnaissance drillings (Belin et al., 1988) of the A89 highway. These data allowed to obtain indirect information about the unsaturated compartment of an a'a flow. Considering the low organic and inorganic carbon contents into Argnat basin water (Barbaud, 1983; Joux, 2002), samples were directly stored in double caps polyethylene bottles for chemical

Fig. 3. Field observations of Grosliers pahoehoe and Blanzat a'a flows. Under the soil a thin layer of scoria is sometimes observable in the grosliers lava. Blanzat flow looks very heterogeneous (scoria masses, lava tunnel) over a 3 m thick outcrop.

analyses and into glass bottles with air tight seals to prevent atmospheric exchange before isotopic characterisation.

3.2. Analyses

Electrical conductivity, temperature and pH measurements as well as bicarbonates concentration determination by acidic titration (with a solution of a 0.02 M of H_2SO_4) were performed directly after the sampling, in the field.

Concentrations of ionic species for the December 2005/June 2007 period were determined at the "Observatoire de Physique du Globe of Clermont-Ferrand" (France) by ion chromatography, using a DIONEX DX320 chromatograph with detection limits of 0.05 μeq l^{-1} for Cl^-, 0.1 μeq l^{-1} for NO_3^-, 0.6 μeq l^{-1} for SO_4^{2-}, 0.06 μeq l^{-1} for Na^+, 0.04 μeq l^{-1} for NH_4^+, 0.3 μeq l^{-1} for K^+, 0.1 μeq l^{-1} for Mg^{2+} and Ca^{2+}. The uncertainty of the DX320 chromatograph is 5%. In order to assess the validity of the sampling device, blanks were determined for the analyzed elements. The highest value were 1.0 μeq l^{-1} for sodium and 0.7 μeq l^{-1} for calcium, the other elements were not detected. The charge balance between anions and cations $(\sum[\text{Anions}] - \sum[\text{Cations}])/(\sum[\text{Anions}] + \sum[\text{Cations}])$; concentrations in μeq l^{-1}) was assessed and analyses were accepted for deviations of less than 5%.

The isotopic composition of rainwater and groundwater for the April 2006/April 2007 period were measured by mass spectrometry at the "Observatoire de Physique du Globe of Clermont-Ferrand" (France). 42 precipitation events ($1 < h < 68$ mm) were analyzed, corresponding to a total height of 954 mm. During this period, 963 mm of precipitation dropped at the Sayat meteorological station, therefore the collected dataset is considered as representative of a complete hydrological year. Preparation of samples was conducted according to the techniques detailed by Epstein and Mayeda (1953) for $\delta^{18}O$ and by Bigeleisen et al. (1952) for δ^2H. The results are expressed in ‰ versus VSMOW (Vienna Standard Mean Ocean Water). The uncertainties are respectively of ±0.2‰ for $\delta^{18}O$ and ±2‰ for δ^2H.

4. Results

4.1. Origin of groundwater

Stable isotopic measurements permit the quantitative determination of the origin and flow paths of groundwater on a regional scale (Fontes, 1980; Rose et al., 1996; Mazor, 2004), and more particularly when examining fracture flow hydrology, since these systems are difficult to treat using conventional models. On Fig. 4 are plotted the mean isotopic composition of each sampled points (δ^2H, $\delta^{18}O$), the Argnat Meteoric Water Line (AMWL: $\delta^2H = 7.9\ \delta^{18}O + 7.3$) defined using isotopic data (December 2005–June 2005) analyzed at Sayat meteorological station, the Massif Central Meteoric Water Line (MCMWL: $\delta^2H = 8\ \delta^{18}O + 13.1$; Fouillac et al., 1991) and the World Meteoric Water Line ($\delta^2H = 8\ \delta^{18}O + 10$; Craig, 1961). In order to present results in the clearest way as possible, and because temporal isotopic variations for each sampling point are quite smooth (Table 2), annual averages are used in the following part of the paper.

All the groundwater samples fall between the AMWL and the MCMWL (Fig. 4). This feature, firstly, confirms the meteoric origin of groundwater. Secondly, positions of groundwater samples are consistent with the inter-annual and spatial variability of isotopic signatures trend in precipitations, especially in mountainous areas. Indeed, above these terrains, topographic reliefs strongly influence precipitation by lifting atmospheric moisture and by facilitating precipitation at the windward slope (mainly west one in the Chaîne des Puys). The converse is true on the leeward side, generally leading to less precipitation amounts. From an isotopic point of view, on the leeward side, a small amount of precipitation can be isotopically altered by subcloud evaporation and moisture exchange, resulting in isotopically heavier precipitation in comparison with that drops on the whole mountain (Liebminger et al.,

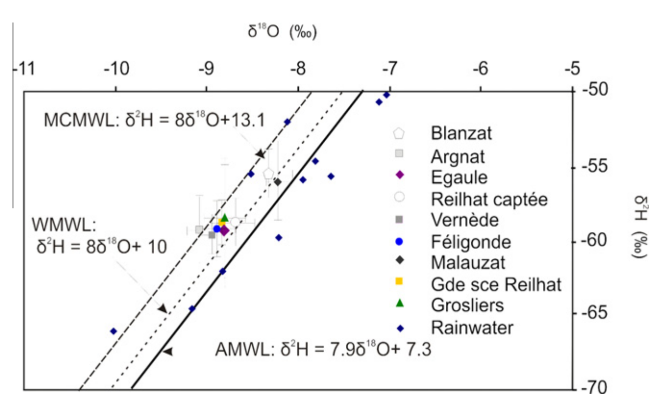

Fig. 4. Argnat meteoric water line (AMWL) and annual mean isotopic signature for the 10 saturated zone sampling locations listed in Table 2. World Meteoric Water Line (WMWL, Craig, 1961) and Massif Central Meteoric Water Line (MCMWL, Fouillac et al., 1991) are also reported.

Table 2
Altitude, $\delta^{18}O$, $\delta^{2}H$ (mean and standard deviation), discharge and recharge altitude of studied springs (SZ and UZ correspond to is saturated zone and unsaturated zone, respectively). Recharge altitude was calculated using the local altitudinal gradient of −0.28 ‰ calculated by Barbaud (1983).

	Z (m)	X	Y	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	Recharge area altitude (m)	Mean annual discharge ($l\,s^{-1}$) (number of measurements)
Egaule (n = 13)	800	45°50′10″N	03′00′20″E	−8.8 ± 0.2	−59 ± 5	990 ± 80	n.d.
Argnat (n = 13)	700	45°50′39″N	03′03′57″E	−9.1 ± 0.2	−59 ± 2	1090 ± 60	117 ± 9 (n = 17)
Féligonde (n = 13)	510	45°50′12″N	03′03′06″E	−8.9 ± 0.2	−59 ± 2	1020 ± 80	0.19 ± 0.16 (n = 17)
Reilhat G.S. (n = 13)	500	45°50′07″N	03′03′42″E	−8.8 ± 0.2	−59 ± 2	1000 ± 60	10[a]
Malauzat (n = 13)	497	45°50′35″N	03′03′05″E	−8.2 ± 0.1	−56 ± 3	780 ± 50	20[a]
Reilhat catch. (n = 12)	490	45°50′05″N	03′03′52″E	−8.7 ± 0.2	−59 ± 2	950 ± 70	20[a]
Vernède (n = 13)	480	45°49′50″N	03′02′54″E	−8.9 ± 0.1	−60 ± 1	1040 ± 50	0.35 ± 0.01 (n = 18)
Grosliers SZ (n = 79)	420	45°49′20″N	03′03′57″E	−8.8 ± 0.2	−58 ± 4	980 ± 100	9.0 ± 0.9 (n = 79)
Vergnes (n = 13)	410	45°49′32″N	03′04′06″E	−8.9 ± 0.3	−59 ± 2	1020 ± 100	30[a]
Blanzat (n = 13)	385	45°49′35″N	03′04′29″E	−8.3 ± 0.3	−56 ± 2	820 ± 100	0.78 ± 0.18 (n = 12)
Grosliers UZ (n = 79)	420	45°49′20″N	03′03′57″E	−8.1 ± 0.3	n.d.	740 ± 100	1.0 E−05 ± 9.4E−07 (n = 79)
Precipitation Sayat (n = 42)	550	45°50′18″N	3°02′42″E	−6.9 ± 2.6	−47 ± 20		
Effective infiltration on the basin mean altitude	811			−8.3 ± 1.0	n.d.		

[a] Estimation on the field.

2006; Guan et al., 2009). This is consistent with the observed AMWL falling on the right to the regional meteoric water line (MCMWL).

Assuming the absence of physical evaporation once rain has reached the ground (Barbaud, 1983; Dafny et al., 2006), and using both the mean isotopic signal of rainwater sampled at Sayat meteorological station (−6.9 ‰ $\delta^{18}O$; −47.1 $\delta^{2}H$ at z = 550 m) and the local altitudinal gradient (−0.28 $\delta^{18}O$/100 m) defined by Barbaud (1983) in the eastern part of the Chaîne des Puys at the hydrological year scale, the isotopic signature of the effective infiltration at z = 811 m (mean altitude of Argnat basin) was estimated. The first step was to calculate effective infiltration on a monthly time scale. The second step was to weight the monthly mean isotopic composition of rainwater by the effective infiltration amount. Thus, the value of the mean annual isotopic signature of infiltration was estimated to be close to −8.3 ‰ $\delta^{18}O$. Then, using both the latter value and the altitudinal gradient of −0.28 $\delta^{18}O$/100 m, the recharge altitudes of each outlet can be calculated (Table 2). The recharge area of the Argnat basin is defined between 780 and 1090 m, which corresponds to the highest areas of the basin, mainly occupied by strombolian scoria cones. Based on the estimation of the effective rainfall amount for each altitude range of the basin (Bertrand, 2009), it is possible to estimate the contribution of the high-altitude infiltration. The highest parts ([900–1000 m], [1000–1100 m] and [1100–1159 m]) correspond to the strombolian cones area of the basin (9.8 km^2 i.e. 38.3% of the total basin surface). The calculation of annual infiltration for this surface led to an annual discharge estimation of 152 $l\,s^{-1}$, i.e. 50% of the total discharge basin. Hence, this is consistent with the fact that the infiltration which occurs through strombolian edifices appears to be the major component of the recharge in the Argnat volcanic hydrosystem.

4.2. Chemical variations along the flowpaths

After entering the saturated zone, water flows downstream into the basal scoria zone or the spoiled zone near the volcanic flow/basement contact. The evolution of the chemical composition of water along this flowpath has been measured in order to precise the circulation conditions of groundwater and the hydrodynamic context of the lava flows within the Argnat basin. Statistics presented on Table 3 shows a limited temporal variability of chemical parameters during our observation period, and major chemical trends along groundwater flowpaths can be viewed through the annual mean values. Additionally, knowing the mean annual chemical rain composition and using an enrichment factor of 2.64, equal to the ratio between the calculated effective rain and total rain amount (Eq. (1), Appelo and Postma, 1994), background concentrations of the effective infiltration were calculated (Eq. (2)) by Bertrand (2009) for each chemical parameter (Table 3):

$$\epsilon = \frac{h_{\mathrm{precip}}}{h_{\mathrm{precip}} - h_{\mathrm{evapotransp}}} \tag{1}$$

$$[\mathrm{X}]_{\mathrm{infiltration}} = \epsilon[\mathrm{X}]_{\mathrm{precip}} \tag{2}$$

where ϵ is the enrichment factor, h_{precip} the annual heigh of precipitation, $h_{evapotranp}$ the actual annual evapotranspiration, $[X]_{infiltration}$ and $[X]_{precip}$, respectively the concentration of the element X in the infiltration and in the total precipitation.

Infiltration water shows a low mean concentration for all the major ions (between 0.8 $mg\,l^{-1}$ for Mg^{2+} and 8.2 $mg\,l^{-1}$ for HCO_3^-) and presents a mean pH of 5.5.

Groundwater presents an Electrical Conductivity ranging from 134 to 420 µS/cm, with a mean value of 273 $\mu S\,cm^{-1}$. For most waters the pH is close to the neutrality with values ranging from 6.3 to 8.3 (mean value of 7.1). Concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and HCO_3^- observed along the flow line are consistent with the development of alteration processes which may affect volcanic aquifers in lightly acidic water: The increase of the water residence time causes an increase in the content of these elements (Cruz and Franca, 2006). In addition, alteration can also be enhanced when water slows down in the system (Freeze and Cherry, 1979). Stumm and Morgan (1981) described the alteration occurring into crystalline aquifers by the following equation:

$$\begin{aligned} &\mathrm{Plagioclase} + \mathrm{FeldspathK} + \mathrm{Olivine} + \mathrm{Pyroxène} + CO_2 + H_2O \\ &\quad \rightarrow [\mathrm{Al{-}Si}]\mathrm{Minerals} + H_4SiO_4 + HCO_3^- \\ &\qquad + Ca^{2+}/Mg^{2+}/Na^{+}/K^{+} \end{aligned} \tag{3}$$

During this process, cations and balancing bicarbonate ions are released into the water and new alumino-silicates such as kaolinite and smectite are formed (Garrels, 1967; Bertrand, 2009).

Chloride, sulfate and nitrate, considering the types of the aquifer rocks and their main chemical composition (Camus, 1975; Table 1), can not be provided by such an alteration process. They are therefore considered being elements provided by either rainwater or anthropogenic inputs. They can be provided by rainwater dissolving anthropogenic dusts and gas (including Cl^-, SO_4^{2-}, NO_3^-) or sea aerosols (including Cl^- and SO_4^{2-}) during the cloud life (Bertrand et al., 2007b, 2008; Celle-Jeanton et al., 2009). Considering the environmental conditions, Na^{+} and K^{+} can be also associated with Cl^- because they are constituents of the sea salt

Table 3
Precipitations, effective infiltration (calculated values, see Eqs. (1) and (2) and groundwater chemical data statistics: main variables (pH, temperature, electrical conductivity) and major ions composition.

		T °C	E.C. ($\mu S\ cm^{-1}$)	pH	SiO_2 ($mg\ l^{-1}$)	HCO_3^- ($mg\ l^{-1}$)	Cl^- ($mg\ l^{-1}$)	NO_3^- ($mg\ l^{-1}$)	SO_4^{2-} ($mg\ l^{-1}$)	Na^+ ($mg\ l^{-1}$)	K^+ ($mg\ l^{-1}$)	Mg^{2+} ($mg\ l^{-1}$)	Ca^{2+} ($mg\ l^{-1}$)
Effective infiltration	Mean					8.1	2.7	4.1	2.7	1.4	1.4	0.8	6.0
Sayat meteorological station (n = 70)	Mean	n.d.	26	5.9	n.d.	3.6	2.1	3.2	1.5	1.1	1.1	0.3	2.6
	Std dev.	n.d.	22	0.6	n.d.	2.5	2.8	5.0	1.4	1.6	1.7	0.4	2.4
	Min	n.d.	5	4.1	n.d.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Median	n.d.	19	5.8	n.d.	3.1	1.2	1.8	1.2	0.6	0.6	0.3	2.0
	Max	n.d.	114	7.3	n.d.	11.0	19.2	36.4	7.6	11.2	13.0	2.6	11.7
Grosliers UZ (n = 79)	Mean	n.d.	205	7.4	46	112.2	4.1	3.7	4.9	15.3	6.8	9.1	13.6
	Std dev.	n.d.	24	0.2	4	20.8	0.2	0.2	0.2	1.3	0.6	1.8	2.8
	Min	n.d.	175	7.1	34	85.4	3.8	3.3	4.4	13.3	5.8	6.8	9.8
	Median	n.d.	196	7.4	46	102.5	4.1	3.7	4.9	14.9	6.7	8.4	12.9
	Max	n.d.	256	8.0	57	158.6	4.7	4.2	5.3	18.7	8.1	13.6	20.4
Grosliers SZ (n = 79)	Mean	10.3	258	7.2	36	83.5	21.5	12.5	12.0	14.6	8.0	11.2	16.3
	Std dev.	0.0	7	0.4	3	4.2	1.4	0.6	0.5	0.4	0.4	0.6	1.2
	Min	10.3	244	6.6	28	75.6	19.0	11.2	11.1	13.7	7.3	9.6	13.3
	Median	10.3	258	7.0	36	83.0	21.5	12.4	12.0	14.6	7.9	11.1	16.3
	Max	10.3	273	7.9	45	93.9	25.1	13.9	13.5	15.7	9.4	12.3	18.5
Egaule (n = 19)	Mean	8.7	135	6.9	22	50.2	8.5	4.5	8.2	6.0	2.2	4.9	12.9
	Std dev.	0.3	11	0.3	3	6.8	1.3	1.0	0.9	0.4	0.3	0.6	2.0
	Min	7.9	117	6.5	16	41.5	6.3	3.2	6.7	5.3	1.7	4.2	10.3
	Median	8.8	133	6.9	23	48.8	8.3	4.3	8.4	6.0	2.2	4.8	12.4
	Max	9.0	159	7.6	29	61.0	11.4	7.1	9.7	7.1	2.7	6.2	16.9
Argnat (n = 19)	Mean	8.6	210	6.7	36	80.6	14.1	6.8	8.2	13.0	6.9	9.2	13.2
	Std dev.	0.1	2	0.2	2	3.7	0.4	0.3	0.4	0.4	0.3	0.4	1.3
	Min	8.3	205	6.5	31	73.2	13.4	5.7	7.6	12.5	6.5	8.5	11.4
	Median	8.6	210	6.7	37	80.5	14.2	6.8	8.2	12.9	7.0	9.2	13.2
	Max	8.6	213	7.3	39	90.3	14.8	7.2	9.1	14.2	7.5	10.1	16.3
Féligonde (n = 19)	Mean	9.9	238	7.3	34	78.6	20.7	11.0	10.0	14.9	7.3	9.8	15.0
	Std dev.	0.5	11	0.3	4	6.7	2.9	1.6	0.3	0.9	0.3	0.8	1.8
	Min	8.9	221	6.9	26	68.3	17.2	8.8	9.2	13.7	6.7	8.6	12.5

	Median	9.9	238	7.2	34	79.3	19.7	10.5	10.1	14.8	7.3	9.8	14.7
	Max	11.5	263	7.8	41	92.7	28.5	13.6	10.5	16.9	8.0	10.8	17.7
Malauzat ($n = 19$)	Mean	10.2	421	7.2	45	101.5	49.1	31.7	16.8	22.0	13.0	17.2	29.1
	Std dev.	0.3	14	0.4	5	9.4	3.9	3.4	0.8	1.7	1.9	1.4	2.9
	Min	9.7	401	6.7	35	80.5	42.8	25.7	15.1	20.2	10.7	15.1	25.4
	Median	10.1	420	7.1	45	102.5	48.9	30.6	16.7	21.6	13.2	16.8	28.7
	Max	10.8	459	8.0	54	109.8	56.5	39.4	18.1	25.1	17.2	19.4	33.4
Reilhat catch. ($n = 18$)	Mean	10.7	309	7.3	36	89.8	21.9	31.1	13.3	15.8	8.3	13.7	20.7
	Std dev.	0.6	18	0.4	2	10.2	1.8	5.7	0.9	0.8	0.4	1.5	3.1
	Min	9.3	272	6.9	31	73.2	19.8	19.1	11.6	14.7	7.4	11.4	16.2
	Median	10.8	314	7.1	36	91.5	21.2	30.5	13.4	15.7	8.3	13.9	21.0
	Max	11.6	333	8.3	39	108.6	25.9	42.4	15.2	17.2	9.0	16.4	26.6
Vernède ($n = 19$)	Mean	9.6	232	6.9	36	75.8	20.9	9.5	9.6	15.0	7.1	9.6	14.5
	Std dev.	0.2	8	0.2	4	4.7	2.7	0.9	0.3	0.7	0.5	0.6	1.5
	Min	9.1	221	6.3	30	68.3	17.3	8.3	9.2	13.7	6.4	8.7	12.1
	Median	9.5	229	6.9	35	73.2	20.3	9.2	9.5	15.0	7.0	9.5	14.5
	Max	9.9	255	7.3	48	86.6	28.3	11.1	10.3	16.7	8.2	10.9	17.2
Vergnes ($n = 19$)	Mean	10.0	244	7.3	35	85.5	19.8	10.3	10.3	14.1	7.5	10.8	15.6
	Std dev.	0.2	5	0.3	3	5.4	1.0	0.4	0.4	0.4	0.4	0.7	1.7
	Min	9.6	239	6.8	29	78.1	18.4	9.5	9.3	12.9	7.0	9.7	13.0
	Median	10.0	244	7.2	35	85.4	19.7	10.3	10.3	14.2	7.4	10.5	15.1
	Max	10.3	253	8.1	42	97.6	21.9	10.9	11.2	14.7	8.2	12.3	18.6
Blanzat ($n = 19$)	Mean	11.7	404	7.1	37	150.8	25.8	28.3	19.7	20.1	8.7	18.5	32.6
	Std dev.	0.6	20	0.2	3	7.6	1.8	3.1	1.2	1.5	0.5	1.4	2.6
	Min	10.0	365	6.7	28	134.2	22.8	23.1	17.7	17.9	8.0	16.0	28.0
	Median	11.8	410	7.0	36	150.1	26.3	29.1	19.8	20.0	8.6	18.3	32.3
	Max	12.5	424	7.4	42	165.9	28.6	33.9	21.9	24.0	9.5	20.8	37.1
Reilhat G.S. ($n = 15$)	Mean	10.1	264	6.9	33	82.5	21.7	18.3	11.2	15.0	8.0	11.1	16.9
	Std dev.	0.0	6	0.2	5	7.7	2.0	1.2	0.5	1.6	1.5	1.1	2.0
	Min	10.1	251	6.7	21	70.8	19.3	16.1	10.5	10.0	7.1	7.8	11.2
	Median	10.1	263	6.9	34	83.0	21.2	18.4	11.0	15.2	7.7	11.2	17.4
	Max	10.2	276	7.7	40	95.2	25.9	20.4	12.2	16.7	13.2	12.5	19.2

aerosols (KCl, NaCl) or of the salt widely spread on roads into the Chaîne des Puys during winter (Joux, 2002). In this context, concentrations of both these elements must be considered with care. Downgradient evolution of these elements implies further supplies along the flowpath, where anthropogenic activities are more developed. Sendler (1981) and Barbier (2005) indicate that higher nitrate content into basalt aquifer than into effective rainwater (calculated levels for the Argnat basin are reported in Table 3) can originate from natural biogenic activity in the uppermost soil. Higher concentrations of nitrate at specific locations are more likely to indicate massive biogenic contamination from cattle pasture fields or sewage from human origin. Moreover, crop fertilization and manure spraying increase the concentration of NO_3^- as well as this one of SO_4^{2-} (Appelo and Postma, 1994).

In the context of the Argnat basin, low-altitude rainfall can also reach the saturated zone through two processes. The first one is infiltration of run-off circulating over plutonic basement in the area upper than the Limagne fault. From the fault, lava flows are thrown into relief inversion due to erosion process that occurred after their setting, therefore there is no water streaming which can reach the saturated zones of lava flows. The second process is direct infiltration on the volcanic flows through fractures and clinkers.

Fig. 5 shows two kinds of evolution of the chemical content of groundwater along the flow path. The chemical signature of waters circulating downward into the Grosliers pahoehoe lava flow (Grosliers, Vergnes, Féligonde, Vernède outlets) indicates grouped values. In contrast, samples from the Blanzat lava flow (Blanzat, Reilhat, Malauzat, Grande Source de Reilhat) present a markedly increase in all the concentrations downward the flow line.

Run-off is able to provide anthropogenic elements through the infiltration processes at the contact between plutonic basement and lava flow in the area located upper the Limagne fault. The chemical content of all these outlets, sampled lower than the Limagne fault, are modified by these supplies. As a consequence, the specific evolution of the chemical composition of the two groups can be attributed to a different infiltration process on the a'a or pahoehoe lava flows, through the unsaturated zone.

In order to characterize the pahoehoe lava flow, the Grosliers unsaturated and saturated zones have been sampled on a weekly scale. The two reservoirs show similar hydrodynamic behaviour with a clear seasonal variation (Fig. 6).

The unsaturated zone is characterized by low Cl^-, NO_3^-, SO_4^{2-} concentrations, closed to the rainwater's ones and that remain constant in time, showing then no additional anthropogenic source for these elements. Taking into account the potential double origin of Na^+ and K^+, we should focus on Ca^{2+} and Mg^{2+} to discuss alteration processes. Their concentrations vary seasonally between 6.8 and 13.6 mg l^{-1} for Mg^{2+} and 9.8 and 20.4 mg l^{-1} for Ca^{2+}. This feature is related to the seasonality of soil respiration that controls the CO_2 dissolution into water and then favours alteration processes during the warm season. This leads to higher dissolved cations contents,

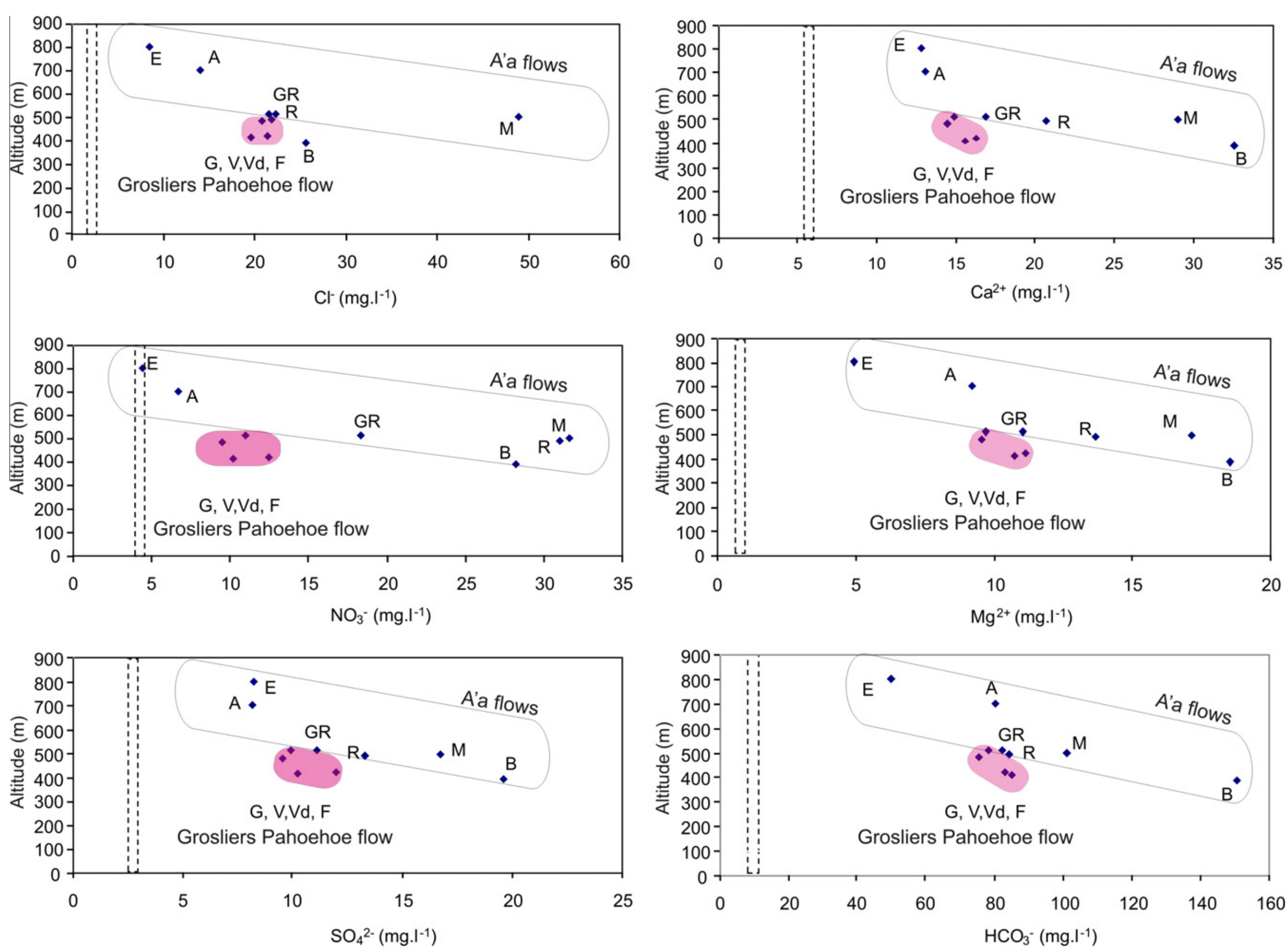

Fig. 5. Downstream chemical evolution. V: Vergnes, B: Blanzat, A: Argnat, E: Egaule, R: Reilhat catchment, Vd: Vernède, F: Féligonde, M: Malauzat, GR: Grande source de Reilhat, G: Grosliers. Vertical bars indicate the calculated mean chemical content of efficient infiltration. *Y* axis shows the emergence altitude.

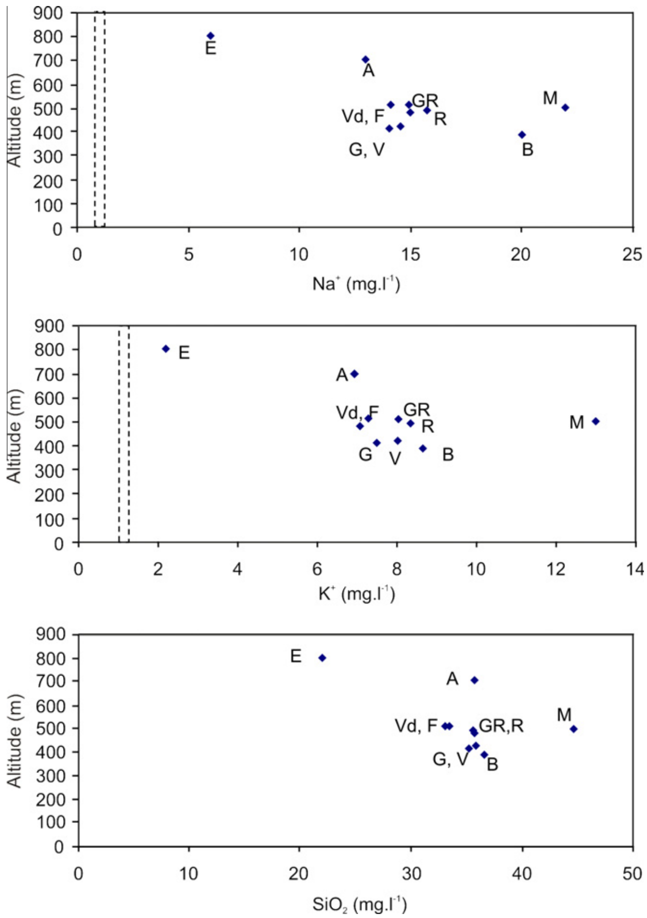

Fig. 5 (*continued*)

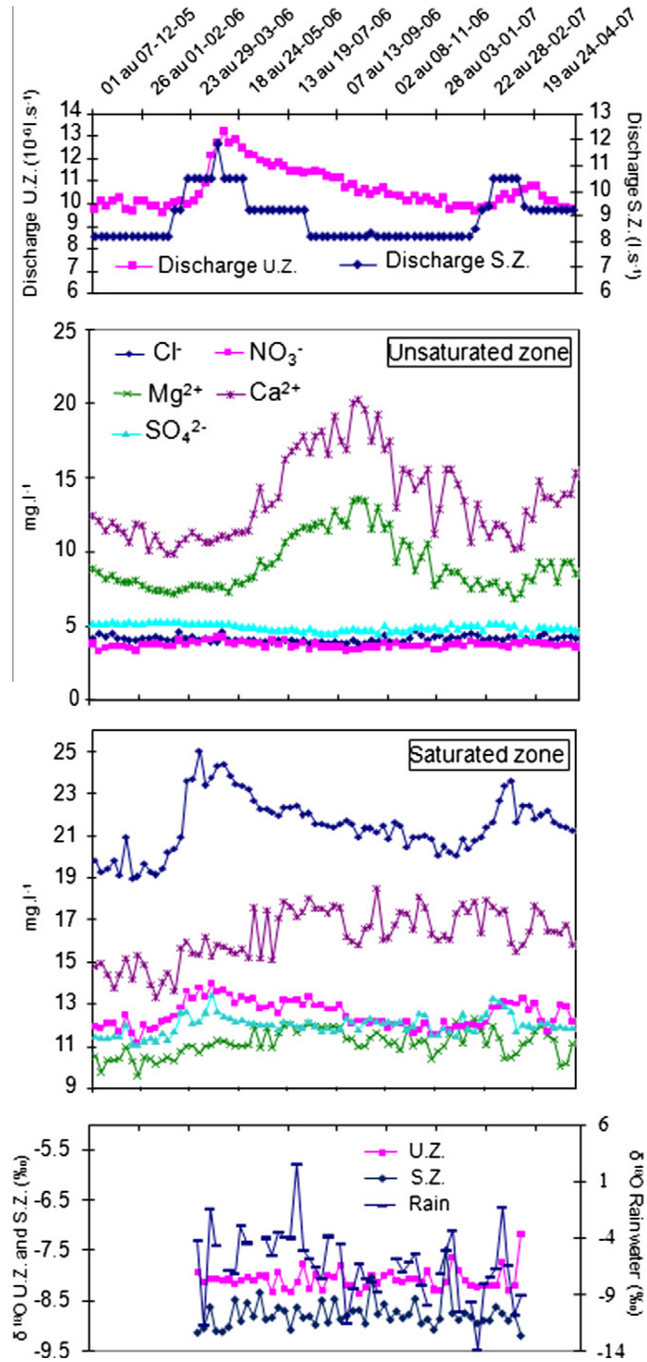

Fig. 6. Temporal variations of discharge, Cl^-, NO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, electrical conductivity, ^{18}O into the saturated (SZ) and unsaturated (UZ) zones of Grosliers gallery and ^{18}O of Sayat rainwater. Note that a factor 10^6 exists between UZ discharge and SZ discharge.

especially during summer (Reich and Potter, 1995; Lohila et al., 2007; Bertrand, 2009). This temporal variation testifies of a superficial circulation closed to the soil fraction on the lava flow instead of direct vertical supplies. This is consistent with the temporal stability of $\delta^{18}O$, with a mean of -8.1 ± 0.2 $\delta^{18}O$‰ and the calculated mean recharge altitude of 750 m that corresponds to an area located 3 km far from the unsaturated zone sampling device, then implying horizontal circulations. The saturated zone of the Grosliers lava flow is characterized by higher and variable Cl^-, NO_3^-, SO_4^{2-} concentrations (varying respectively into [15–25 mg l^{-1}] [8.9–16.3 mg l^{-1}] and [8.6–13.5 mg l^{-1}] ranges) compared to the unsaturated zone (Fig. 6). On the contrary, elements provided by alteration processes present similar or slightly lower concentration compared to the unsaturated zone ([Mg^{2+}] ranges from 8.2 to 17.7 mg l^{-1} and [Ca^{2+}] ranges from 13.3 to 19.7 mg l^{-1}); these concentrations are more stable in time. This behaviour excludes a significant impact of infiltration water through the unsaturated zone of the pahoehoe Grosliers flow. Additionally, the $\delta^{18}O$ of the unsaturated and the saturated zones are significatively different all along the sampling period, which testifies of mainly parallel flow patterns.

Then, the Grosliers saturated zone appears to be only supplied by strombolian cones and run-off over plutonic.

Concerning the a'a lava flow, we used data gathered from Gaubi (1990) and reported on Table 4. $\delta^{18}O$ of the groundwater ranges from -7.2 (W17) to -8.9 $\delta^{18}O$‰ (W15); that is consistent with the existence of local vertical supplies through the unsaturated zone in some areas of the Blanzat a'a flow. A hypothetical contribution of water coming from volcanic terrains of the Limagne can be rejected because boreholes are located over the Limagne volcanic flow. Ca^{2+} and Mg^{2+} range respectively from 18.0 mg l^{-1} (W16) to 44.0 mg l^{-1} (W13) and from 19.4 mg l^{-1} (W16) to 30.4 mg l^{-1} (W17). Higher concentrations could be attributed to longer water–rock interactions and/or stronger alterability of porous scoria due to the larger specific surface of this material. Anthropogenic elements tend to also show heterogeneous concentrations: [Cl^-] and [NO_3^-] respectively range from 8.2 mg l^{-1} (W17) to 25.0 mg l^{-1} (W16) and from 1.2 mg l^{-1} (W13) to 26.7 mg l^{-1} (W16) which could be due to the influence of various land occupation features on the a'a Blanzat flow.

Table 4
Chemical and isotopic data from Gaubi (1990).

Well	z	$\delta^{18}O$ (‰)	pH	E.C. (μS/cm)	HCO_3^- (mg l^{-1})	Cl^- (mg l^{-1})	NO_3^- (mg l^{-1})	SO_4^{2-} (mg l^{-1})	Na^+ (mg l^{-1})	K^+ (mg l^{-1})	Mg^{2+} (mg l^{-1})	Ca^{2+} (mg l^{-1})
W13	507.69	−8.19	7.4	508	280.7	18.73	1.24	12.05	30.35	7.038	20.66	44.09
W15	495.04	−8.89	7.45	419	195.3	22.57	6.82	14.89	29.2	5.474	21.87	22.04
W16	485.05	−8.64	7.6	412	159.3	24.97	26.66	13.83	29.2	11.34	19.44	18.04
W17	496.06	−7.21	7.75	460	261.8	8.165	11.78	9.927	17.24	2.737	30.38	32.06

5. Discussion

5.1. Role of the unsaturated zone within lava flows

Chemical and isotopic heterogeneities observed between unsaturated and saturated zone of the Grosliers pahoehoe flow provide the illustration of the strong anisotropy in lithologic material properties in a single lava flow. Because of the massive structure of the pahoehoe lava flow of Grosliers, infiltration water's supply through the unsaturated zone seems to be very limited. However, small parallel horizontal circulations can occur in the upper zone of the lava where a porous crust is developed into "rubbly pahoehoe lava flows". In contrast, local vertical supply into the Blanzat a'a flow implies the presence of more extensive perched aquifers in the vertical axis within the unsaturated zone, which can locally enhance the low-altitude rainfall recharge and then entail a great modification of the geochemical conditions of the saturated zone. The water from perched aquifers is assumed to vertically recharge the basal aquifer through fissures. This additional supply can be provided by a succession of accumulated allochthonous colluvial deposits on the very first lava flow that was transformed by the heat flux coming from the overriding lava flows during the volcanic building process. The result is an extensive patchwork of permeable–impermeable layers in which water accumulates (Aubignat, 1973; Lecoq, 1987; Nascimento Prada et al., 2005; D'Ozouville et al., 2008). This implies inter-flow perched aquifers located at the top or the bottom of each lava flow and linked by some vertical fractures. This scheme was often involved in numerous volcanic areas such as the Golan heights in Israel (Dafny et al., 2006), Reunion Island (Join and Coudray, 1993; Violette et al., 1997; Join et al., 2005), Mayotte Island in the Comoros archipelago (Stieltjes, 1988), Madeira Island (Nascimento Prada et al., 2005) Galapagos Islands (D'Ozouville et al., 2008) and was also described by Aubignat (1973) in the Volvic basin located 3 km north from the Argnat basin. However,

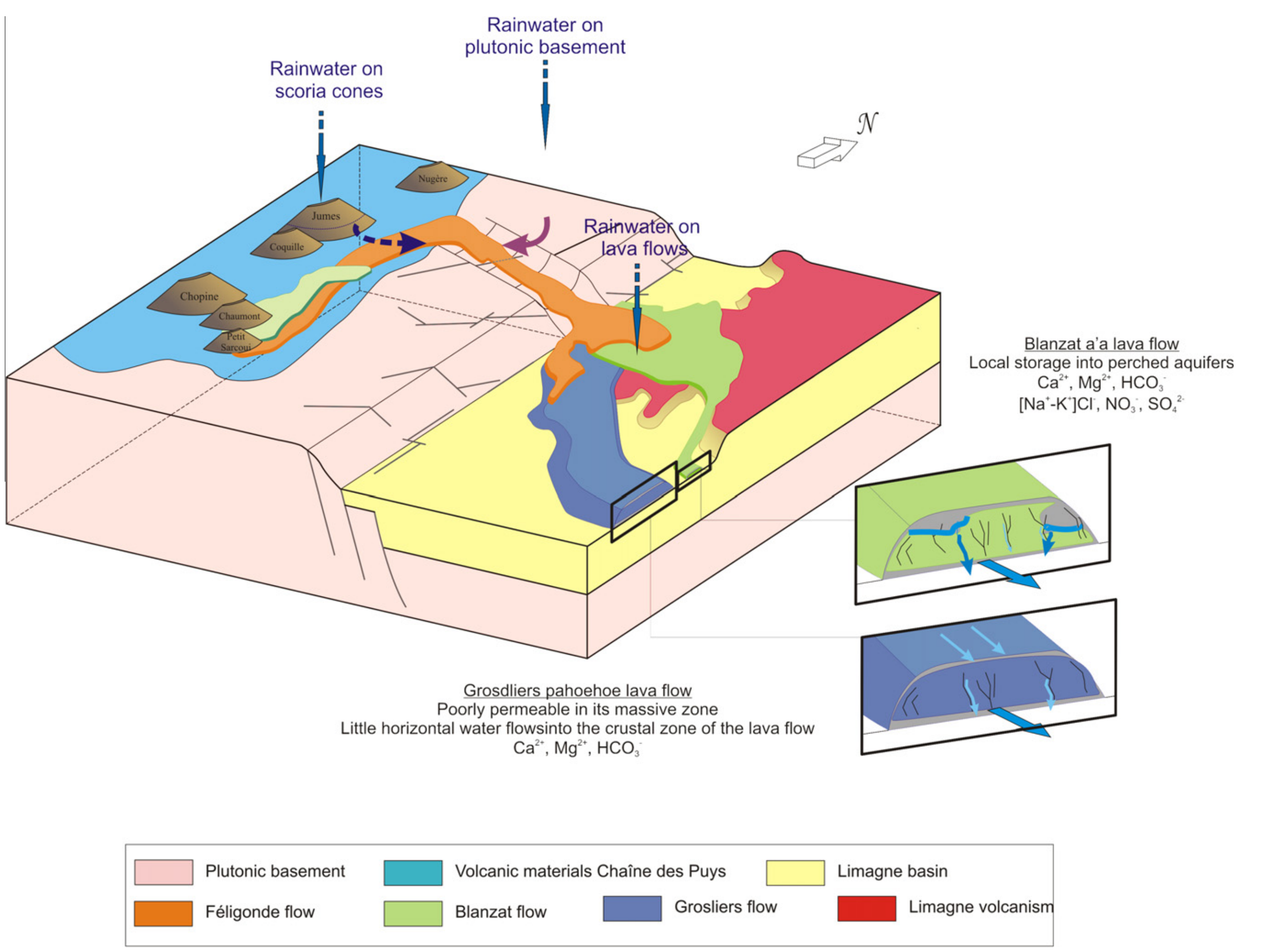

Fig. 7. Conceptual scheme of the Argnat basin functioning.

regarding the geological settings of the a'a Blanzat flow, which took place in a single time, the most probable model would rather imply an endogen permeability contrast into the a'a lava due to its placing features, involving the mixing of scoria masses with a fractured massive matrix, which was observed on the field (Fig. 3). These scoria masses can punctually contain and provide local water if they are hydraulically linked with the surface. Locally, the absence of these scoria masses may allow a higher contribution of a more-distant source of water like into the W15 well. In this case, this system could be called "intra-flow perched aquifer".

Thus, our observations provide new examples of complex hydraulic connectivity into lava materials. However, these results show that overlying of different lava flows of different ages are not obligatory to observe either parallel flows or inter-flow patterns: these kinds of groundwater pathways can be met into a single lava flow due to its own lithologic heterogeneity.

5.2. Conceptual model of the Argnat basin functioning

By compiling all the evidences based on hydrochemistry, isotopes, and lava flow morphologies, a conceptual scheme of the Argnat basin functioning can be proposed (Fig. 7).

The Argnat system is predominantly supplied by precipitation on scoria cones that ensures a great discharge and an overall good water quality. Two types of supply can be identified and are able to modify the water quality:

- Participation of plutonic slopes run-off that affects all the outlets and provides allochthonous elements such as NO_3^-, SO_4^{2-} and Cl^- (associated with Na^+ and K^+).
- Direct infiltration on lava flows depending of the type of lava flow. Major differences can be observed between typically a'a and pahoehoe lava flows.

The internal structure of these rocks influences the hydrodynamic and thus the flowpaths of water into the system, which controls the acquisition of dissolved species (HCO_3^-, Ca^{2+}, Mg^{2+}, K^+, Na^+). The Grosliers pahoehoe flow is almost impervious whereas the Blanzat a'a flow locally permits important infiltration water amount, which modifies the water chemistry due to anthropogenic influence and the residence of water in the upper part of the lava flow. A conceptual model implying the existence of little perched water bodies into a'a flows is consistent with our observations.

Furthermore, from a socio-economic point of view, the effective management of this system has to protect strombolian cones to ensure the infiltration water quality and amount. In the Chaîne des Puys, these areas are protected because they are included in a Regional Park «Parc Naturel Régional des Volcans d'Auvergne», which avoid all industrial and urban projects in the volcanoes area. From a qualitative point of view, areas at a lower altitude need to be peculiarly protected: drainage of run-off waters could notably limit the pollution fluxes to aquifers. The development of a land management scheme able to take into account the anthropogenic impact on low altitude infiltration waters, particularly on Blanzat a'a flow has also to be considered.

6. Conclusions

This study has demonstrated the wide spatial variations in the hydrochemistry and the variability of environmental isotopic compositions of groundwater in the fractured volcanic aquifers of the Argnat catchment. This distribution illustrates the different flow systems and highlights the complexity of water flowpaths into such a system. The water supply from strombolian edifices ensures an important water discharge with a good quality. However, although run-off and low altitude infiltration are not a major way of supply of water to the aquifers, they considerably modify the saturated zone chemistry because of the local anthropogenic pressure. This study shows the great difference between the hydrogeological behaviour of pahoehoe lava flows and a'a lava flows. It appears that although pahoehoe lava flows are not especially recognized as valuable aquifers, they play an interesting role in the water transfer due to the relatively high permeability of their basal zone, and seem to be naturally protected thanks to their massive central zone. A'a lava flows are of a special interest because they allow larger infiltration amount and are assumed to provide massive groundwater discharge. However, the infiltration through the unsaturated zone can bring anthropogenic elements that may alter the quality of groundwater. Cities, industries and agriculture developments can be considerably promoted in these areas but authorities in charge of the land planning will have to keep in consideration the great vulnerability of these terrains to avoid future conflicts of interests over the water resources.

These results allow to propose a conceptual model of the volcanic hydrosystem that will be useful for their management. They will help to respect the regulations of the water directives of the European Union (2000/60/CE [2000], 2006/118/CE [2006]), including the objective to meet a "good chemical status of groundwater bodies" by 2015, the objective on pollutions trends, and to prevent or limit input of pollutants to groundwater.

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