



# Structure and hydrogeochemical functioning of a sparkling natural mineral water system from a multidisciplinary approach: a case study from southern France

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Structure and hydrogeochemical functioning of a sparkling natural mineral  
water system determined using a multidisciplinary approach: a case study  
from southern France

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ABSTRACT

Natural mineral waters (NMW), often used to produce bottled water, are of high socio-economic interest and need appropriate management to ensure the sustainability of the resource. A complex sparkling NMW system at La Salvetat, southern France, was investigated using a multidisciplinary approach. Geological and geophysical investigations, pumping test analyses, time-series signal processing, hydrogeochemical and isotopic data (both stable and radiogenic), and numerical modelling provided complementary information on the geometry, hydrodynamic characteristics and functioning of this mineral system. The conceptual model consists of a compartmentalized reservoir characterized by two subvertical, parallel deeply-rooted hydraulically independent permeable structures that are fed by deep CO<sub>2</sub>-rich crustal fluids. The non-mineralized shallow aquifer system corresponds to a fissured layer within the weathered zone that is recharged by leakage from the overlying saprolite. This surficial aquifer responds rapidly to recharge (40-80 days), whereas the deep system's response to recharge is much longer (up to 120 days). This research demonstrates the need for multidisciplinary

approaches and modelling (quantity, hydrochemistry) for understanding complex NMW systems. This knowledge is already being applied by the bottling company that manages the resource at La Salvetat, and would be useful for conceptualizing other NMW sites.

Keywords: thermal conditions, CO<sub>2</sub>, fractured rock, natural mineral water, France

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## 1. INTRODUCTION

Sparkling natural mineral waters, and more generally natural mineral waters (NMW), often used to produce bottled water, are of socio-economic interest. In order to sustain these resources, appropriate management is needed that is well informed by local hydrogeological understanding.

Hydrothermal systems comprise the following three main geological components: water, heat and permeability (Clemente and Villadolid-Abrigo 1993; Lachassagne et al. 2009). Sparkling natural mineral water systems comprise water, CO<sub>2</sub> and permeability so water and gas can flow and rise to the land’s surface. Geogenic CO<sub>2</sub> may originate from three sources: metamorphism of carbonate rocks in the Earth (Kerrick and Caldeira 1998), transformation of organic matter during oil, gas and coal formation (Battani et al. 2000), or degassing of the mantle (Shipton et al. 2005). Consequently, in most cases, CO<sub>2</sub> is of deep origin. In crystalline rocks, deep fractures create the required permeability to bring the CO<sub>2</sub> to the surface, often as springs. At a relatively shallow depth (tens to hundreds of meters), these structures also constitute the drilling targets for safely abstracting the NMW. Therefore, the identification of the

51 geometry, hydrodynamic properties, extent(both laterally and with depth), and thickness of such  
52 permeable structures are the key factors for correctly understanding, tapping, managing, and  
53 protecting the mineral water system.

54 In crystalline rocks, the hydrodynamic properties of shallow (0-100 m) aquifers, and their  
55 relationships with weathering processes are now well characterized, with comprehensive  
56 conceptual models (Dewandel et al. 2006; Dewandel et al. 2011; Lachassagne et al. 2011).  
57 Deeper, nuclear waste storage projects have achieved very precise characterization of the (low  
58 permeability) fractured network of crystalline rocks, but in areas specifically chosen to avoid  
59 deep fracturing (Gustafson et al. 2009; Morosini and Rhen 2000). Thus, it appears that the  
60 precise characterization of deep permeable structures is very rare, and often based on  
61 conjecture and/or uncertain assumptions. This research is devoted to characterizing such  
62 complex NMW structures.

63 Another objective of the research was to show that such complex natural mineral water  
64 systems require multidisciplinary approaches, combining several techniques, in order to propose  
65 an appropriate precise, realistic and robust conceptual model to tackle this complexity. The  
66 approach used combines geological, geophysical, hydrodynamic and times series analysis,  
67 hydrogeochemical and isotopic data, and a comprehensive numerical model in order to  
68 characterize and simulate the permeable reservoir of a NMW system in crystalline rocks. This  
69 approach is applied to the La Salvetat sparkling natural mineral water system in southern France  
70 which is bottled. The knowledge about the structure and functioning of this mineral water system  
71 is of high interest for the bottling company for the development, sustainable management and  
72 protection of its spring. Developing a realistic conceptualization for a well characterized site is  
73 also of broad interest in order to inspire conceptualizations of other NMW sites.

## 74 2. STUDY AREA

The sparkling water spring at La Salvetat (Hérault region, southern France) has been known at least since the Middle Ages, particularly by the Santiago de Compostella pilgrims who rested and bathed at the Rieumajou spring. The spring has been operated for NMW bottling by the Danone group (Evian Volvic World Sources, Danone Waters France) since the early 1990s, and is now, together with forestry and traditional mountain agriculture, one of the key drivers of the local economy and employment. This NMW spring emerges in a bedrock region composed primarily of metamorphic rocks without obvious visible tectonic structures at the surface. The field is located south of the Raviège hydropower lake dam within the large south eastern France CO<sub>2</sub> region (an area where numerous carbonate-rich springs occur), which is part of the larger CO<sub>2</sub> Alpine foreland (Blavoux and Dazy 1990). The reservoir is currently exploited by six wells (B1, R1, R2, R3, R5 and R6, **Erreur ! Source du renvoi introuvable.**). Observation boreholes (R4 inoperative well, P1, P3, MLC2, ML3, Pz1 to 7) are used for reservoir monitoring. Recently, five new cored 200 m-long exploration boreholes were drilled (HF1 to HF5). The data from numerous older wells, now closed, are also available.

The local climate is predominantly Mediterranean with a strong mountainous (“Cévenole”) influence. During the 1993-2008 period, the mean annual rainfall was 1,444 mm with a mean annual potential evapotranspiration of 806 mm. A reservoir model (Ladouche et al., BRGM, unpublished data, 2013), calibrated using the daily time series of shallow aquifer water table fluctuations (water supply Port well) and runoff (at the 48 km<sup>2</sup> Agout River crystalline watershed scale), provides estimates of effective rainfall (920 mm/yr), recharge to the shallow aquifer (169 mm/yr) and runoff (751 mm/yr).

### 3. METHODOLOGY

The multidisciplinary approach, implemented to characterize the permeable reservoir of La Salvetat NMW field, comprised four stages. The first involved a detailed geological study (lithology, weathering, sequence stratigraphy, structural geology, fissure and

fracture identification) and a field hydrogeological study. The geological approach combined a pole-dipole geophysical survey (14 mostly north-south profiles with an investigation depth of about 120 m totaling about 16.5 km performed in 2011 - Figure 1), and geological field investigation, involving a comprehensive survey of the outcrops and their comparison to local lithotypes to complement the 1:50000 scale BRGM geological map (Demange et al. 1995). The geological field investigation also comprised the geological reinterpretation of all available cores (11 boreholes), cuttings (3 boreholes), and existing geological logs for those boreholes where the cuttings and cores were no longer available, along with macroscopic and microscopic (thin section) analysis. In the studied area (Fig. 1), due to the weathering, the outcrops are small in size (less than a few square meters), and mostly restricted to granite veins that appear to be less weathered than the nearby geological formations. There the fracturing is mostly linked to weathering processes.

The field hydrogeological approach was primarily focused on characterizing the springs (fresh water and NMW), particularly during the La Ravière lake's low water-level period. To characterize the hydrodynamic properties of the aquifer, pumping tests and interference tests between production wells were analyzed. The interpretation of pumping tests in crystalline aquifers is a difficult task, as groundwater flow can be fractionalized (Black 1994), ie. controlled by the hydraulic conductivity of fractures, fracture density and orientation, their relationship with the low-hydraulic-conductivity blocks or matrix (Maréchal et al. 2004), and the geometry of the faults or intrusive bodies acting as permeable or impervious structures (Dewandel et al. 2011). To reveal the various aspects of the hydrogeological properties of such a complex hydrogeological system, and particularly the geometry of fractured zones tapped by NMW pumping wells, careful attention was paid to diagnosing the test responses prior to modelling with an analytical solution. Diagnoses were based on the analysis of derivative drawdown curves on log-log plots, which allows flow-regime identification (Ehlig-Economides 1988; Renard et al. 2009). According to the results of the diagnosis, suitable analytical models for partitioned

1965) or leaky aquifers (Hantush 1960) were used in order to calculate the hydrodynamic and geometric parameters of the aquifer.

The hydrogeological processes were characterised using a signal processing method applied to the rainfall, piezometric level and fluid electrical conductivity time series. The functions used (autocorrelation and cross-correlation) and their corresponding mathematical expressions have been described by several authors (Mangin 1984). An analysis methodology was also developed in this study to extract recharge information from the measured signal, disturbed, amongst others factors, by pumping, thereby providing quantitative information on the recharge rate and the dynamics of its transfer function. Piezometric and electrical conductivity variations (O: system output) were explained by considering the input variables likely to influence the system. This involved describing a Multiple Input Single Output (MISO) system (Kothyari and Singh 1999). The calculations were performed using the Tempo software with a one-day time step (Pinault et al. 2001).

Water chemistry and isotopic tracing (stable isotopes of water, strontium) were used in order to constrain the hydrochemical mechanisms and to understand the origin of the mineral waters system. The pH, temperature and electrical conductivity were measured onsite on raw water samples. Samples for cation, trace metallic element and Sr isotope determination were filtered through 0.45  $\mu\text{m}$  Millipore membrane filters and acidified (with ultrapure  $\text{HNO}_3$  to  $\text{pH} < 2$ ). Anions were determined by ion chromatography; cations and trace elements by ICP-MS. The measurement uncertainties for major and trace elements are 5 and 10%, respectively. Oxygen ( $^{18}\text{O}$ ) and hydrogen (D) isotope measurements were done with a standardized method, using a Finnigan MAT 252 mass spectrometer with a precision of  $\pm 0.1\text{‰}$  vs SMOW for  $\delta^{18}\text{O}$  and  $\pm 0.8\text{‰}$  for  $\delta\text{D}$ . The  $^{18}\text{O}/^{16}\text{O}$  ratio is reported as  $\delta$  deviation (per mil) of this ratio in the sample from that of the V-SMOW standard. Isotopic compositions are reported in the usual  $\delta$ -scale in  $\text{‰}$ . Analysis of the  $\delta^{13}\text{C}$  composition of the  $\text{CO}_2$  was done by mass spectrometry with a precision of 0.1  $\text{‰}$ . The  $^{13}\text{C}/^{12}\text{C}$  ratio is expressed in per mil notation relative to standard V-PDB. In addition, strontium

isotope analyses on the main rocks and mineral phases were performed to better understand water-rock interactions. The objective was to define the isotopic signatures for strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) in the main rocks comprising the La Salvetat reservoir in order to interpret the origin and variations in the isotopic strontium ratio in the sparkling NMW field. Chemical purification of Sr (~3  $\mu\text{g}$ ) was done using an ion-exchange column (Sr-Spec) before mass analysis according to a method adapted from (Pin and Bassin 1992), with total blank <1 ng for the entire chemical procedure. After chemical separation, around 150 ng of Sr was loaded onto a tungsten filament with a tantalum activator and analysed with a Finnigan MAT 262 multi-collector mass spectrometer. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized to  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194. An average internal precision of  $\pm 10 \times 10^{-6}$  (2 $\sigma$ ) was obtained and the reproducibility of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measurements was tested by repeated analyses of the NBS987 standard, for which a mean value of  $0.710230 \pm 18 \times 10^{-6}$  (2 $\sigma$ , n=12) was obtained.

To determine the theoretical isotopic signature of water interacting with a given rock, a theoretical dissolution model must be used (Bullen et al. 1997). Such a dissolution model has been developed (Negrel et al. 2001) assuming that most of the Sr released by weathering comes from the following three main minerals: plagioclase, K-feldspar and biotite. Model parameters are: (i) Sr content in the main mineral phases (plagioclase, K-feldspar and biotite), (ii) their isotopic Sr composition ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), (iii) the proportion of each of these minerals in the studied rock and, (iv) the weatherability of each of these minerals (Petelet Giraud et al. 2003). The total rock sample and separate minerals were analysed for Rb and Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio. The separation of K-feldspars, plagioclases and biotite was performed by particle-size (on the 50-400  $\mu\text{m}$  fraction), densimetric (K-feldspars, plagioclases and part of biotite) and magnetic separation (rest of biotite). The nature of the plagioclases was analysed by electronic microprobing: they can be classified as oligoclase (An<sub>90-70</sub>Ab<sub>10-30</sub>) and andesine (An<sub>30-50</sub>Ab<sub>70-50</sub>). Calcite separation in the Cipolin marble sample (R6 149.1) was performed by rock



stripping (thin sections and hand samples) using a microgrinder. The results of these dissolution models were then compared to the water samples from the wells to explain their origin.

Finally a hydrodynamic and reactive hydrogeochemical numerical model was developed to dynamically simulate the functioning of the NMW system. It was used to integrate all the information provided by the multidisciplinary study, and to validate the conceptual model. The modelling method selected is the networked reservoir and chemical reactor methodology (Collon et al. 2002). It is based on the main assumption that piezometric levels and chemical concentrations are uniform within each reservoir. The system modelled is then described by a set of ordinary coupled differential equations translating water storage and chemical elements in each of the variable volume reactors. The water-rock interactions were taken into account by introducing aqueous phase chemical kinetics for certain reactive chemical elements. The relevance of the model to reflect the system studied lies in the choice of the number of reservoirs, the way they are connected, the laws chosen to describe the water and matter exchanged amongst the reservoirs, and the choice of the reactive chemical elements and the related chemical kinetics.

## 4. RESULTS

### 4.1. GEOLOGICAL STRUCTURE OF THE MINERAL WATER SYSTEM

The detailed geological approach confirmed the overall high quality of the 1:50000 geological mapping (Demange et al. 1995) in the Rieumajou spring area. The main lithotypes were observed in the field and their distributions were well contoured, at least at the scale of the map. The bedrock in La Salvetat area is mostly composed of intensely folded and foliated metamorphic rocks derived from a sedimentary sequence overlying a more ancient granitic substratum. In the mineral spring area, this series exposes, from South to North, a conformable succession, from bottom (South) to top (North) (**Erreur ! Source du renvoi**

**introuvable**): (i) the Larnorthogneiss derived from a Cadomian granite metamorphosed during the Hercynian orogeny, and weathered prior to being covered by sediments and prior to being further metamorphosed; (ii) a Cambrian sedimentary sequence lying unconformably on the metamorphosed granite, and consisting of four main geological formations:

1) a 50 to 100 m thick schist-quartzite Puech-Plô grey gneiss composed of ancient, coalescent and detritic deltas aligned perpendicularly at contact between the ancient basement and the paleo sedimentary series;

2) a 20 to 30 m thick quartzo-feldspathic Murat gneiss, a metamorphosed volcanic-sedimentary formation (conglomerates, leptynites) infilling the lowest points between the paleo deltas;

3) a more than 100 m thick Nagesparagneiss rich in calcic levels: plagioclase-rich gneiss, gneiss with calcic silicates and Cipolin marbles. This series is a prograding-retrograding platform which, in top part is mostly carbonated. It shows a typical klupfelian carbonated deposit profile which provides a distal deeper facies, probably located at the south towards a coastal proximal located at the north with the following geological facies: clay-rich siltites, carved aggrading alternations from a subsiding bay, coastal prograding alternations, tidal dunes, beach, and intertidal stromatolites. The analysis of the sedimentary signal shows that this carbonated platform series is transgressive on the Puech-Plô and the Larn Gneiss formations. In several wells, this series is duplicated with first (near the surface) the inverted series, and then the normal one. Moreover, the resulting inversion line (and also the series) is folded.

4) Late hercynian granite and pegmatite intrusive veins (tourmaline leucocratic granite and pegmatite).

The foliation is mostly N050 to 090°E (Figure 2). The units dip at 70 to 80° South to North; consequently, these geological formations are considered to be deeply rooted and are still crosscut in the boreholes at depths greater than 200 m.

The main outcome of the detailed geological mapping concerned the granite veins. The authors of the 1:50000 geological map inferred that these veins resulted from the partial melting of the other lithological units during metamorphism, and consequently, that they are conformable (same dip) with the main foliation of the lithological units and effectively are sills “invading” the other lithological units. However, the field survey clearly showed that the granite is much younger and occurs as subvertical, N110 to N160°E oriented veins that are meters to tens of meters thick and tens to hundreds of meters long. These veins are not conformable with the other rocks as they cross-cut all the other lithologies (Figure 2).

These formations are deeply weathered with an up to 30 m thick cover of unconsolidated saprolite. Differential weathering has resulted in higher relief granite veins (with several outcrops), whereas the Nages formation rocks outcrop only very locally. As a consequence, in the spring area, the outcrops are quite poor and do not allow performing a detailed structural analysis. As far as faults can be identified on cores, the drillings crosscut several fracture zones which mostly seem to be dilational (no compressive tectoglyphs). Several fractures comprise breccias that in places are cemented with calcite and/or silica and can show signs of hydrothermal activity. It was possible to characterize the orientation and dip of 15 open or mineralized fractures observed on the cores. These fractures were oriented, using the foliation measured in the well as a geometric reference. The following main results were obtained: fracture orientation in the wells is mostly N100-110°E (n = 9), and then N130-140°E (n = 3), and N020-030°E (n = 3).

Electrical profiles (survey lines shown in Fig. 1) clearly reveal the depth of the weathering profile. Typically, the electrical resistivity is below 1000  $\Omega \cdot m$  within the first 50 m below ground surface (Figure 3). There is a sharp resistivity contrast at approximately 50 m, where the resistivity

increases to more than 5000  $\Omega\cdot\text{m}$ , which can be followed within most of the Nages formation in Fig. 3 (M profile from X = 160 to 550 m and C profile from X = 120 to 340 m, and X = 600 to 840 m). In these profiles, the thickest granite and pegmatite veins appear as more resistant (higher electrical resistivity) bodies within the low resistivity weathering profile (X = 480 m on the M profile). However, apart from this result about some granite veins, the electrical profiles do not provide unambiguous information about the lithology, notably below the weathering profile. The electrical profiles also reveal enhanced weathering (or past hydrothermalism) along some lithological contacts, particularly the southern Puech-Piô/Murat and Nages contact (subvertical, about 150 m wide - locally much wider - 50 to 70  $\Omega\cdot\text{m}$  structure that can be followed on most of the North-South electrical profiles; Fig. 3 - M profile from X = 90 to 155 m and C profile from X = 60 m to 120 m). The most interesting results from the geophysical survey are the deep (more than 100 to 120 m) subvertical conductive structures (locally down to about 10  $\Omega\cdot\text{m}$ , but more frequently between 150 and 200  $\Omega\cdot\text{m}$ ; Fig. 3 - M profile from X = 550 m and C profile from X = 340 to 480 m). These structures are 30 to more than 50 m wide, are oriented N100-110°E, and coincide with the fractured zones in wells producing NMW (see the dotted blue curves on Figure 2). One of these structures, the southern one, identified on five North-South electrical profiles, seems to link the R4 area (West) at least to HF4 and B1 wells (East). The second structure, the northern one, only identified on two profiles due to the presence of the lake (which limited the geophysical measurements), links the area of R5 (West) with the HF2 area (East). These structures (HF2, HF4 boreholes) and some other conductive anomalies (HF1, HF3, HF5 boreholes) were targeted during the last drilling campaign, and only the HF2 and HF4 boreholes successfully tapped permeable NMW bearing fracture zones in the “southern” and “northern” structures.

#### 4.2. PRELIMINARY HYDRODYNAMIC APPROACH

The synthesis of blowing discharge measurements performed during down-hole-hammer drilling shows that the fissured zone of the Puech-Piô formation is much less productive than the Nagesformation, with mean discharges 3 to 4 times lower. The productivity of the Nages formation is nearly nil within the saprolite (first 20 to 30 meters below ground surface) and is relatively higher within the underlying 30 - 40 m thick fissured zone. Productivity is nil within the deeper unweathered rock, except where the borehole crosscuts a deep NMW bearing fracture.

Piezometric measurements available from the wells tapping the NMW bearing fractures show two East-West slight piezometric depressions corresponding to the two structures identified from geological and geophysical data (Figure 1). These depressions appear to be related to the natural flow within the mineral aquifer and to the pumping in the wells. The first piezometric depression extends from R4 to R1 (pumping in R1, R2, R3). The second one corresponds to R5 and R6 pumping. Most of the formerly flowing or still-existing NMW springs appear to be located at the intersection between the two East-West structures and the topographical low points (**Erreur ! Source du renvoi introuvable.** and **Erreur ! Source du renvoi introuvable.**). One main location is West of each structure, at their lowest topographical point. The second one is a small North-South valley in the vicinity of R1 and R2 wells where the main NMW spring was located. There is no significant NMW outflow in the HF4-B1 area, which is interpreted as a consequence of the low permeability of the geological cover in this valley, as piezometric levels in the mineral aquifer in that area are aboveground level. Consequently, from these data, it can be inferred that the natural mineral water may have flowed naturally (i) upwards and then westward from the B1 area toward the main NMW spring (between R1 and R2) and then to R4, and (ii) from R5 (or even from HF2) to the springs located east of R6.

#### 4.3. HYDRODYNAMIC PARAMETERS AND AQUIFER STRUCTURE FROM PUMPING TESTS

Data from 30 pumping tests, a few hours to several months in duration, and performed on ten of the Rieumajou area wells were interpreted to establish interferences between the wells,

and to evaluate the geometry of the permeable formations and their hydrodynamic parameters. Except well R5, in which the screened part mainly crosscuts a granite vein, all others are sited within the Nages gneiss. The tests were performed between 1990 and 2011 at the time of well drilling. During the pumping tests, water level changes in nearby wells and piezometers were also observed.

One example of a 10-day pumping test performed on well R4 in 2010 is presented (**Erreur ! Source du renvoi introuvable.**). R4 is 63.3 m deep and screened between 46.2 and 57.0 m into the NMW bearing fractures. The derivative curve is complex, but illustrates various typical flow regimes (**Erreur ! Source du renvoi introuvable.**):

- from the beginning of the test to 20 minutes duration describes the wellbore storage effect,
- from 20 to 50 minutes, the flat trend of the derivative curve is typical of infinite radial flow from which aquifer transmissivity can be calculated ( $T=5.4 \times 10^{-4} \text{ m}^2/\text{s}$ ),
- from 50 to 400 minutes, the derivative curve tends to a  $\frac{1}{2}$  slope, and the drawdown reaches two parallel no-flow boundaries,
- from 400 to about 6,000 minutes, the derivative curve follows a unit slope typical of bounded aquifers (at least two additional no-flow boundaries),
- finally, from 6,000 minutes to the end of the test, drawdown tends to stabilize, and the decrease of the derivative suggests leakage from shallow aquifers. Such a leakage effect was only observed in this well.

This diagnostic shows that R4 is located in a bounded aquifer, the boundaries of which are close to the well (between 50 and 400 minutes). In addition, the aquifer is connected to another aquifer (most probably the shallow aquifer) by leakage: consequently, this well is not exploited, as pumping might induce shallow aquifer water inflow. This test was interpreted using a rectangular aquifer model with seepage (Hantush 1960) with four orthogonal no-flow

boundaries, wellbore storage effect and well skin(**Erreur ! Source du renvoi introuvable.** - black curves). The evaluated aquifer surface is  $0.09 \text{ km}^2$  (about 400 m length by 200 m wide).

Test diagnosis and modelling were carried out to interpret the 29 other pumping tests, the main results of which are summarized in **Erreur ! Source du renvoi introuvable.** and Table 1. In summary, the interference tests clearly demonstrate that the site is partitioned into two approximately East-West direction compartments: a northern one (R5 and R6) and a southern one (R1-R2-R3-R4-P3-DAC). This result is supported by most of the test diagnoses. It is also highly consistent with the geophysical and piezometric data. Diagnostic and pumping test modelling also provide information about the aquifer geometry. The southern compartment is characterized by a permeable (fractured) zone, about  $0.1 \text{ km}^2$  area (200x400 m approximately) and oriented in a near East-West direction ( $N105^\circ E$ ). Its eastern limit, however, is not well constrained. Its transmissivity is about  $3 \times 10^{-4} \text{ m}^2/\text{s}$  and is relatively constant from one well to another. Its storativity is about  $5 \times 10^{-4}$ . The northern compartment is also elongated in a near East-West direction and is probably smaller than the southern one; however, pumping tests were not long enough to reach all the boundaries. Transmissivity is similar to that of the southern compartment, but storativity is less,  $2 \times 10^{-5}$ .

Two of the pumping tests, at B1 and HF4, could not demonstrate any interference despite seeming to belong, geometrically and geologically, to the eastern continuation of the southern compartment. Nevertheless, interferences show that the two wells belong to the same fractured system ("B1" compartment). HF4 yielded a high transmissivity ( $8 \times 10^{-3} \text{ m}^2/\text{s}$ ) corresponding to a zone a few meters wide. The geometry of compartment B1 is not well constrained, but from pumping tests, two parallel no-flow boundaries are reached relatively late after the start of the pumping (3 000 min). This leads to the interpretation of an apparently (depending on assumption on S) very large fractured zone (about 800 m wide); the orientation of this fractured zone was not constrained by the modelling of the pumping tests, but it was by the

geophysical data. As discussed below (section '*Multiple input single output*'), the piezometric time series analysis confirms that the HF4-B1 compartment is the eastern prolongation of the R4-R1 compartment.

Several pumping tests show evidence of partial penetration (Table 1), suggesting that the fractured zone extends much deeper than the bottom of the wells, which generally do not exceed 100 to 120 m depth.

#### 4.4. HYDROGEOLOGICAL FUNCTIONING OF THE SYSTEM FROM TIME SERIES ANALYSIS

##### 4.4.1. PRELIMINARY DESCRIPTION OF HYDROLOGICAL TIME SERIES

Flow rate variations in the pumping wells (**Erreur ! Source du renvoi introuvable.**b) generally follow the same pattern, i.e., because of the constraints dictated by NMW production, flow rates are all increased or lowered synchronously. Very few periods exist in which differential flow rate variation is available.

Piezometry trends measured at R5 in the northern compartment show a correlation with lake water level, which, according to dam management records, is low during the winter energy production season and high in summer during the tourist season. For R6, time series are too short to provide a basis for conclusion. The head in the aquifer is thus affected by the surface hydraulic head imposed by the lake surface. At daily time scale, piezometric fluctuations at R5 are impacted by pumping but it is not possible to identify whether this is only due to pumping at R5 or also at neighbouring wells. The very short-term piezometric fluctuations are due to the high quadratic (non-linear) head losses in the R5 well visible in 2004 and 2008-2009 when pumping rates are variable. Piezometric variability therefore appears to be essentially controlled by pumping rates and by variations in the lake water level, while piezometric variations linked to rainfall (recharge) appear to be negligible on short- and mid-time frames (several days to several weeks).



Piezometric trends in wells located to the South (R1, R2 and R3) do not appear to be influenced by water level variations in the La Raviègelake. Piezometric trends at R1 and R2 are very comparable, which confirms the existence of a hydraulic link between the two wells. Piezometric time series for R3 also show similar trends to those measured at R1 and R2. The piezometric variations appear to be controlled by pumping rate variations. Here again, these piezometric variations are primarily linked to high quadratic head losses. In a similar way to R5, piezometric variations induced by recharge are hidden in the short- (several days) and mid-timeframes (several weeks) by variations induced by pumping.

For several years after being put into operation (see R5, R6 and B1 because R1, R2, R3 data were not recorded for the first years of service), all wells show an initial decrease in electrical conductivity (EC) over a period spanning several years (**Erreur ! Source du renvoi introuvable.**). EC then becomes relatively stable and shows variations with a shorter wavelength. Annual fluctuations in EC at R5 are in the range of 100  $\mu\text{S}/\text{cm}$ ; the annual amplitude appears to be relatively synchronous with lake level variations: maximum EC levels correspond to high water levels in the lake. Short-term pumping variations do not cause a significant variation in the EC of pumped water. The gradual increase in pumping rates at R5 in 2009 (from 1 to 1.8  $\text{m}^3/\text{h}$ ), and again in 2010 (up to approximately 1.9  $\text{m}^3/\text{h}$ ), seems to cause a decrease in EC, as it did when the well was put into production (with R6 being put into production in 2009, overall pumping in this compartment reached nearly 4  $\text{m}^3/\text{h}$  as of 2010). In the other wells (R1, R2, R3 and B1), the EC does not appear to be controlled by lake water level fluctuations. Long-term oscillations observed in B1, R1 and R2 are explained below.

#### 4.4.2. CROSS CORRELATION ANALYSIS

Cross-correlation analysis involved three input variables: rainfall (P), lake water level ( $H_{\text{Lake}}$ ) and the aggregate flow rates at wells ( $Q_x + Q_y$ ). Output included piezometry (H-well) or water mineralisation - EC, which is primarily controlled by  $\text{HCO}_3$  and calcium content (**Erreur ! Source**

du renvoi introuvable.a, b and c). Rainfall-piezometry cross-correlograms (**Erreur ! Source du renvoi introuvable.**a) are very noisy and show very low cross-correlation coefficients ( $<0.1$ ) indicating that the rainfall signal is highly filtered/dampened by the system. Maximum correlation is observed for offsets ranging from 80-120 days. The shape of rainfall-piezometry cross-correlograms provides an approximation of recharge impulse response; it is indicative of hydraulic transfer within a weakly diffusive system. The end of the recharge impulse response occurs at an offset of approximately 250 days. The memory effect (inertia) of the hydrosystem cannot be assessed using the piezometric time series autocorrelograms as the wells' piezometry is over-affected by other influences. Correlation of piezometry and EC with lake water levels is high for wells R5 and R6. Maximum lake - piezometry correlation in R5 is 0.6 for an offset of 0 days (**Erreur ! Source du renvoi introuvable.**b) (fast pressure transfer). Lake level - EC correlation in R5 is not as high with a maximum of 0.13 for an offset ranging from 15 to 30 days: EC increases when the lake level increases. For the other wells (R1, R2 and R3), no correlation is observed between piezometry and lake level (diagrams not shown). Likewise, the EC of water pumped from these wells is not correlated with fluctuations in the La Ravière lake level.

Logically, the correlation between pumping rate and measured piezometry is negative (**Erreur ! Source du renvoi introuvable.**b) due, among other factors, to the large quadratic well head losses. The cross-correlogram between the pumping rate (QR5) and EC in R5 (**Erreur ! Source du renvoi introuvable.**c) shows an inverse correlation.

#### 4.4.3. MULTIPLE INPUT SINGLE OUTPUT

The qualitative description of piezometric trends, water EC monitoring and cross-correlation analysis indicate that the variations linked to rainfall recharge are low-amplitude compared to other factors (La Ravière Lake levels for R5 and R6 and/or pumping rate). A multiple input single output (MISO) deconvolution analysis was therefore undertaken to highlight and better characterize the recharge mode.

In this model (see the example for well R1 - **Erreur ! Source du renvoi introuvable.**), the aim was to reproduce the output (piezometry) from three inputs: (1) recharge, (2) R1 well discharge rate, and (3) aggregate discharge rate other than from well R1 ( $\Sigma Q = QB1 + QR2 + QR3$ ); QB1 being added in order to check the hypothesis that the B1 eastern compartment is the prolongation of the R4-R1 compartment. Calculation of piezometric impulse response was capped at a value of 256 days, corresponding to an approximate duration of recharge impulse response in pressure transfer (**Erreur ! Source du renvoi introuvable.**a). The model reproduces satisfactorily the piezometric trends observed at well R1 with a Nash criterion (Nash and Sutcliffe 1970) equal to 0.79 (**Erreur ! Source du renvoi introuvable.**a) with the relative contributions of the various components shown in **Erreur ! Source du renvoi introuvable.**c, d and e. Average contributions for R1 and those calculated for the other wells using the MISO method are summarized in

Table 2. In R1, the variation linked to recharge reaches 4.6 m, compared to nearly 9.5 m for pumping in R1, and nearly 14.4 m for aggregate discharge ( $\Sigma Q$ ). Consequently, it is this last variable that mainly controls the long term changes in piezometry. The sensitivity analysis performed on QB1 demonstrates the hydraulic connection of the R4-R1 and HF4-B1 compartments, and thus confirms the geophysical and geological interpretation.

On the basis of the MISO deconvolution results (Figures 8c, d and e), information related to the recharge process was extracted for each of the wells investigated. The cross-correlation analysis between rainfall and extracted recharge signal (water level (H) series deconvoluted from pumping effects using the MISO approach) is presented in **Erreur ! Source du renvoi introuvable.** The piezometric response to the recharge process is fast in the fissured horizon (Port well), with a maximum pressure transfer response of approximately 40-80 days after a recharge event (Figure 9a). The deep system's response to recharge is much longer for well B1 (about 120 days) and wells R1 and R2 (around 100 days). The shape of the impulse response is indicative of pressure transfer within a weakly diffusive system that can be attributed to: (i) the

low permeability saprolite, (ii) the Nagesstratiformfissured zone, and (iii) the very low permeability of the underlying unfractured bedrock for the NMW wells. The response gap between B1 and R1/R2 (around 20 days) appears to be consistent considering the local geological structure: the B1 aquifer structure may be “confined” by the overlying impervious granite vein, and the water-bearing structure at the origin of the Rieumajou spring located between R1 and R2 may enhance the relationship between the deep fractures and the fissured horizon in surface. The responses of wells R3 and R5 are bimodal (**Erreur ! Source du renvoi introuvable.**b) with first a fast response and then a delayed response similar to the one observed on the other wells (B1, R1, R2) and a slightly faster response. The responses suggest that these wells are better connected (pressure transfer) to the subsurface formations.

The MISO approach was also used to describe mineralisation trends (EC) in water. It can be used to track the deep component of the system, as  $\text{HCO}_3$  content is linked to  $\text{CO}_2$  of deep origin. An example of a deconvolution result is given for well R1 (**Erreur ! Source du renvoi introuvable.**b). As described previously, three inputs were considered: (1) pumping time series for well R1 (QR1), (2) aggregate discharge rate at the other wells ( $\Sigma Q = Q_{B1} + Q_{R2} + Q_{R3}$ ), and (3) recharge time series corresponding to the recharge time series previously deconvoluted from piezometric data. Calculation of mineralisation impulse response was assumed at a maximum value of 512 days, as the duration of mass transfer is intuitively longer than that of pressure transfer (256 days). The mineralisation trend at borehole R1 is reproduced satisfactorily with the MISO approach (Figure 8b, Nash = 0.75). Increased pumping rates (compared to mean pumping rate) cause a decrease in mineralisation. Variations in pumping rates in R1 generate changes in mineralisation ( $\Delta$ ) in the range of  $-20 \mu\text{S}/\text{cm}$  at large temporal scale (Figure 8d). Increases in other pumping rates ( $\Sigma Q$ ) also result in decreased mineralisation (**Erreur ! Source du renvoi introuvable.**e). This cumulative pumping ( $\Sigma Q$ ) plays a significant role in mineralisation trends, which once again confirms that wells R1, R2, R3 and B1 are

hydraulically connected and, additionally, are connected to the same deep, CO<sub>2</sub>-rich water reservoir. Recharge induces an increase in mineralisation with a long-term cumulative effect(**Erreur ! Source du renvoi introuvable.c**): the succession of several wet cycles in 1994, 1995 and 1996 (1668 mm, 1637 mm and 2412 mm rainfall,respectively) generates a greater mineralisation delta ( $\Delta = +60 \mu\text{S/cm}$ ) than dry cycles in 2001 (932 mm) and 2005 (1145 mm), ( $\Delta < +10 \mu\text{S/cm}$  a year). These results indicate that intensive recharge events do not result in a dilution of the mineral waterby surface water. Instead, recharge events result in an increase in water mineralization because of increased pressure on the deeper parts of the system. This behaviour relative to recharge is similar to the one revealed for lake level increase.

#### 4.5. WATER-ROCK INTERACTION FROM HYDROCHEMISTRY AND ISOTOPE ANALYSIS

From the hydrogeochemical viewpoint (Table 3), the reservoir waters are characterised by acalciumbicarbonatefacies(300 to 1200 mg/l of HCO<sub>3</sub>) typical of the “deep component” and by significant silica content (50 to 90 mg/l). The NMWtherefore representsa fairly specific facies with typical basement water-rock interaction markers. The traditional indicators of high temperature water-rock interaction (Milot and Négrel, 2007) are low in concentration (low sodium content [ $<7 \text{ mg/l}$ ], and very low lithium [ $<0.1 \text{ mg/l}$ ] and boron [ $<0.15 \text{ mg/l}$ ] contents). The NMW has a low chloride content (a few mg/l), this element being characteristic of the shallow componentand mainly due to rainfall.

The carbon isotopic signature of  $\delta^{13}\text{C}$  from the gaseous CO<sub>2</sub> ( $\delta^{13}\text{C}$  ranges from  $-5.6\text{‰}$  to  $-7.8\text{‰}$ ) clearly demonstrates its mantle origin according to Deines(1970) andBlavoux et al. (1982). In the  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$ graph(**Erreur ! Source du renvoi introuvable.**), the water samples are located between the global meteoric water line (Craig 1961), which globally represents Atlantic origin rainfall, and the local meteoric water line determined for the Hérault region(Ladouche et al. 2009), affected by air masses from the Mediterranean. The graph does not highlight isotopic exchange phenomena, such as exchange with gaseous CO<sub>2</sub> or with rock

silicates at high temperature. The waters sampled in the shallow aquifer that were recharged at about 700 m a.s.l. are slightly more enriched in heavy isotopes compared to the NMW from the wells, which suggests recharge at a slightly higher elevation:  $800 \pm 50$  m a.s.l. with a  $-0.3 \text{ ‰}/100$  m gradient (Ladouche et al. 2009), but that is nevertheless compatible with a local recharge. A paleoclimatic effect does not have to be factored in to explain the depleted isotopic signatures from wells B1 and HF4. Tritium data are explained as a result of mixing between old tritium-free water (deep sparkling water) and recent water (post 1952) with an exponential flow model (Malozewski and Zuber 1982), in which the distribution function of the transit time of water in the shallow aquifer is exponential. Tritium content in well F1 (1991) and in well R3 (1997 and 2010) may be explained by a mixture of 80% old water (prior to early 1950s) and 20% recent water, resulting in a mean transit time of more than 50 years.

The dominant aquifer lithology is Nages gneiss which is cross-cut by subvertical granite intrusions (**Erreur ! Source du renvoi introuvable.**). To conduct strontium isotope analysis, three rock samples from the Nages formation were selected from cores taken in well R6 and three granite samples from well R5 cores and a nearby outcrop of a granite vein (**Erreur ! Source du renvoi introuvable.**). The results of water-rock interaction modelling for the granites and Nages gneiss (Table 4) show that, for the R6 sample (76 m depth), the absence of K-feldspar minerals in the model results in a  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.71064 in the water at equilibrium, very close to the plagioclase value (0.710379). For the other R6 sample (96.9 m depth), the absence of plagioclase results in a higher computed value (0.71975) of the  $^{87}\text{Sr}/^{87}\text{Sr}$  ratio in the water at the equilibrium with the rock. The theoretical dissolution model was not applied to the R6 sample (149.1 m depth—Cipolin marble) as the model is not applicable to carbonate rocks. The analyses were performed on the whole rock (Cipolin) as well as on the calcite that is present in light and dark layers. This Cipolin has the lowest Sr isotopic composition of all the rocks measured in the La Salvetat system. The isotopic composition of the calcite (0.708567), which

constitutes 69% of the light grey rock, has an isotopic signature that is fairly similar to that of the total rock. The residual calcite (calcite not yet dissolved) in dark beds is somewhat more radiogenic (0.709179).

The Srisotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) signature in water sampled from the wells ranges between 0.708956 and 0.709121 (Table 3). Compared to theoretical values calculated above for waters in equilibrium with the various rock types, the results clearly show that pumped waters have Srisotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) signatures comparable to those measured in the Cipolin (R6, 149.1 m). The well waters are much less radiogenic than the waters calculated to be in equilibrium with the intrusive granites and spotted gneiss (R6, 96.9). The calcium bicarbonate facies of sparkling mineral waters is therefore acquired on contact with the Cipolins of the Nages formation.

## 5. NUMERICAL MODELLING

### 5.1. MODEL ARCHITECTURE

A model was developed for the South compartment exploited by wells R3, R2, R1, HF4 and B1. The compartment was modelled with two superimposed aquifer levels: a shallow reservoir and five deeper reservoirs, one for each production well (**Erreur ! Source du renvoi introuvable.**). The physical laws describing the various flows exchanged within this network of six reservoirs were selected on the basis of the conclusions of the multidisciplinary study. Thus, taking the piezometric data and location of the springs into account, it was ascertained that flow between the five reservoirs representing the deep aquifer is directed from the area around borehole HF4 towards the others (respectively towards the east (B1) and the west (F1, R2, R3...)) and reproduces the NMW discharge measured before exploitation began on the site. Horizontal flow generated by the head difference between the reservoirs is described in the model by a Darcy-type law. Vertical flow from the shallow reservoir towards the deep reservoirs is assumed proportional to the head difference in order to reproduce the leakage phenomenon

revealed by some hydraulic tests. Lastly, analysis has shown that, before the site was exploited, natural springs and shallow groundwater could be highly mineralised locally due to inflow of deep NMW into the shallow aquifers. To reproduce this mineralization, the deep reservoirs were forced to empty into the shallow reservoir according to a decreasing exponential (emptying time 5 to 10 days depending on the reservoir) which terminates below a certain piezometric threshold.

A “soil” module in the model calculates the partitioning of rainwater into evapotranspiration, runoff, and infiltration according to the Thornthwaite classical model. Runoff flows towards the La Ravière Lake outside the modelled system. Infiltration comprises two components, with given chemical composition. The first component has a “shallow” type geochemical signature and is imposed as input to the shallow reservoir. The chemical composition of water is not calculated by the model but rather is a boundary condition, constant over time. In order to reproduce the observed inflow of NMW in the shallow aquifer (reservoir), this boundary condition was spatialized. Consequently, the chemical composition of water in the shallow reservoir could vary from one reservoir to the other. Thus, a composition C1 (Figure 11) is imposed for transfers from the shallow reservoir feeding R1, R2 and R3 reservoirs, and a more mineralised composition C2 is imposed as input for feeding B1 and HF4. This conceptualization allows for reproduction of a higher chemical inertia of B1 and HF4 wells as compared to R1, R2 and R3. The second component feeding the deep reservoirs is the deep geochemical signature C3. All these imposed compositions are chosen among available results of surface or deep water analyses. These two components are imposed at the reservoir input with a time lag relative to the rainfall that generated them. This is used to introduce inertia into the model on the basis of a maximum lag of 80 to 130 days as highlighted by time series analysis.

The chemical composition of the water in each of the five reservoirs is calculated by the model according to a mixing process due to flow exchange between the reservoirs. Water-rock geochemical reactions are also taken into account where necessary. The chemical heterogeneous reactions that produce or consume calcium, carbon and silica in aqueous phase



aredescribed by first-order kinetic laws. The other chemical elements are considered non-reactive.

The model was numerically transposed using Matlab and Simulink© software with a one-day time step. The physical parameters of the model were determined according to the results of the multidisciplinary study. In this way, the dimensions of the five deep reservoirs are such that they form a deeply-rooted, lens-shaped structure 50 m wide and 600 m long. As defined by the model, these reservoirs are unconfined. An effective porosity of 1%, a classical value in the shallow weathered-fractured zone of crystalline rocks (Marechal et al. 2006; Maréchal et al. 2004), leads, at an equivalent water head, to a body of water of the same order of magnitude as that stored in the natural confined aquifer (storage coefficient estimated at  $5 \times 10^{-4}$ ) including wells R3, R2, R1, HF4 and B1. The reservoir time constants are fitted so that, without pumping, flow is within an order of magnitude of the estimated discharge of natural springs before production, mainly to the west (R3) and to a much lower extent to the east (B1). In order to estimate the other model parameters, time series of production discharge, daily piezometric data and weekly chemical analyses are available on a 10 to 22 years period. A long transient period was needed for initialization because, owing to the inertia of the hydrogeological system, the observed system is never in a stationary regime. The area of the upper reservoir's catchment zone was determined during fitting, at  $0.6 \text{ km}^2$ . This value is in agreement with the  $^{18}\text{O}$  data and the physical geography of the site, and corresponds to 3/4 of the surface catchment area. Lastly, to most accurately reflect the concentrations of chemical species observed in the water from the different wells, the chemical reactivity of calcium, carbon and silica were considered. For the other chemical elements considered by the model, the perfect tracer hypothesis is acceptable (i.e. the chemical species are considered un-reactive).

## 5.2. SIMULATION

The calculated water levels were compared to the piezometric levels measured (corrected for quadratic head loss) over the calibration period (1991-2012) after initialisation. The results obtained at wells R1 and R2, which benefit from the longest observation period, are given for illustration purposes in **Erreur ! Source du renvoi introuvable.** The high amplitude fluctuations observed (and simulated) over the period 1994-1998 are linked to high precipitation periods. The year 1996 is an atypical year with 2,412 mm of precipitation, while the annual mean is 1,370 mm over the period 1987-2011. The model also reproduces satisfactorily long-term concentration dynamics (**Erreur ! Source du renvoi introuvable.**). The annual fluctuations are consistent with the observations. In particular, the model correctly forecasts increased concentrations following a series of rainy years (**Erreur ! Source du renvoi introuvable.**). However, in the short-term, the model lacks inertia and does not sufficiently absorb fluctuations compared to reality.

Once fitted, the numerical model was used to explore how the system functions and to verify the consistency of the conceptual model with the entire set of observations. For instance, in its natural state (without pumping), the discharge from the reservoirs approximates 60 m<sup>3</sup>/day for R1 and R2, and 10 m<sup>3</sup>/day for B1. These values match the estimated discharge from natural springs before exploitation in each area. In its natural state, the shallow reservoir mainly feeds the deep reservoir HF4 (which receives 45% of flow from the shallow reservoir), followed by R1 and R2 (20% each). These flow differences induce pressure differentials between the deep reservoirs, which induce flow from HF4 towards B1 (to the east) and from HF4 to R1 (to the west), and from R2 towards R3. Modelling therefore allows one to rule out that sector B1-HF4 may not be hydraulically connected to the western part of the aquifer. From the geochemical standpoint, 50% of flow feeding reservoirs B1 and R1 correspond to highly mineralised water (deep geochemical signature), versus 30% in HF4 and R2.

## 6. DISCUSSION

The absence of connectivity between the North and South compartments (piezometry, interference between wells), and their contrasting hydrodynamic functioning demonstrate the existence of two permeable bodies oriented E-W (N100-110°E) (**Erreur ! Source du renvoi introuvable.**a and b). This orientation is consistent with the major extensional structures related to the alpine orogeny, which resulted from the Miocene opening of the western Mediterranean. Furthermore, signal treatment and modelling demonstrated the continuity of the southern compartment towards the East until at least B1 well. These hydraulic data agree with the geological structure deduced from the geophysics and calibrated against the geological data from the wells and the basic data such as topography, location of NMW springs, and piezometry. The geology alone, however, was not clear enough to be demonstrative. Based on these findings, it appears that the granite veins do not explain the permeability of the La Salvetat mineral aquifer. Water mineralisation is primarily acquired at depth on contact with the Cipolin marbles which must, consequently, be deeply rooted, while the granites form fairly thin local veins, which are not deeply rooted. Analysis of pumping and interference tests between production wells, in addition to the structure (two distinct permeable bodies) and the characterization of their hydrodynamic parameters, highlights the existence of three major hydraulic boundary conditions.

First, the presence of a leakage effect for several wells, correlated with the existence of a discontinuous aquifer in the stratiform fissured layer, shows that it is drained *per descensum* by leakage into the deep fractures intersected by the wells. In this type of crystalline rock, this aquifer corresponds to the middle part of the weathering profile formed by a fissured layer in the Nages gneiss, itself supplied through leakage from overlying weathered products (saprolite). The relationship between the deep aquifer tapped by the wells and this aquifer is confirmed by the hydrochemistry and, above all, by the numerical model, which requires this type of vertical exchange to correctly reproduce piezometric trends and the water chemical composition.

Second, no-flow boundary conditions show that the deep fractures drain a spatially closed aquifer with a width (North-South) of about 50 to 200 m (pumping tests, geophysics) and a

length of about 600 meters (West to East, from R4 at least to B1) which is realistic considering the pumping test and modelling data. Well data (discrete water bearing structures separated by impermeable formations) show that within this subvertical fractured strip, only a small part of the volume (about one percent in volume) is fractured and permeable.

Third, the partial penetration of the wells is confirmed by modelling which requires at least a depth of 600 meters for each reservoir to account for the high inertia of the mineral system, most of the pumped water flowing upward from this great depth. This suggests that each permeable structure is very deeply rooted with a fissured zone along main faults. Both these two faults appear to be tension joints. Data currently available do not provide a basis for determining whether other joints exist further North or South. In addition, the available geophysics does not suggest it. Nevertheless, new drillings are scheduled at the eastern tip of the southern structure (East of B1) in order to check its potential eastern continuation.

Another similar structure in the Nages gneiss gives rise to a mineral spring (Font Rouge), 6 km west of the investigation site with a similar hydrochemical composition. It is the only such spring within a radius of about 50 km around La Salvetat. Thus, such permeable structures are not common. They cannot be identified only by simple means (lineament analysis, for instance). Such fractures are mostly revealed by NMW outflow where they cross-cut a topographical low. Other similar fractures not cross-cutting a topographical low probably exist, but they are not identifiable at the surface by a NMW spring.

Signal processing on piezometric and geochemical data logically shows the existence of two types of groundwater flow: (i) a "fast" recharge corresponding to local flow path (40-80 days), within the non-mineralized shallow aquifer of the fissured layer, and (ii) the increase of the NMW component hydraulic head (80-130 days) itself resulting in an increase in mineralisation. High water levels in the shallow aquifer (related to rainfall or to lake level variations) give rise to an increase in the mineral component. The inertia of the system is such that several successive wet years induce a continuous increase in this mineral component. Modelling also shows that R3

(and particularly R4) is apparently not directly supplied by the deep permeable structure, but results from mixing between overflow from mineral water coming from the East (B1, HF4, R1, R2) and ancient waters (without tritium) from the shallow fissured aquifer. Additional modelling of the northern compartment (R6, R5, HF2) scheduled for the second phase of the project will undoubtedly fine-tune this conceptual model, particularly the possible relationships between the two systems through the fissured layer, and the recharge evaluation.

This investigation showed the importance of characterising initial flow conditions (and geochemistry) before the system went into production in order to understand how these hydrothermal systems function. In fact, these elements were essential for reliably fitting the hydrodynamic model. Such a characterization should systematically be performed in detail prior to beginning to pump in a NMW system. The study also illustrates the need for suitable analytical models for modelling pumping tests where it is necessary to consider, among other parameters, the anisotropy in hydraulic conductivity of a faulted zone, and the partial penetration of wells within such a faulted aquifer. This could be particularly helpful for better characterization of the B1 compartment to improve the system geometry, and also to better constrain the depth of the fracture or, at least, if it is very deep, to assess it. In fact, it is probable that at B1 the far no-flow boundaries appear very late after the start of the pumping because of such a very strong anisotropy of the pumped fractured zone, and also as a consequence of the very deep root of the fractured zone.

## 7. CONCLUSION

A detailed characterization of a complex NMW system at La Salvetat (France) was made possible through the use of a combination of techniques. Two neighbouring fractured zones in the Nages gneiss constitute the main pathways for deep CO<sub>2</sub> and NMW to rise to the land's surface. Geological investigations, pumping test analysis, time series signal processing, hydrogeochemical and isotopes approaches, and numerical modelling provided complementary

information on the geometry and hydrodynamic characteristics of the permeable structure, and on the functioning of this mineral system. This applied research investigation demonstrates the need of multidisciplinary approaches and modelling (quantity, quality) as a tool for understanding complex NMW systems. Only through a combination of evidences, each obtained from one discipline, which on its own did not lend sufficient insight, was it possible to build a representative conceptual model. This model then allowed determining, with an acceptable degree of certainty, the geometry of the permeable structure at the origin of the mineral system, whereas most classical studies, mainly based only on a structural geology approach, do not generally exhibit this degree of reliability and are merely speculative. The multidisciplinary approach also allowed a more thorough understanding of the hydrodynamic and hydrogeochemical functioning of the system, from a rather great depth (a few hundred meters) to the surface. This knowledge about the structure and functioning of such a sparkling NMW system is of interest as it may provide a conceptual model that could be used at other NMW sites. The knowledge of the system is also of high interest for the bottling company that is already applying it for the sustainable management of the spring, to program additional hydrogeological surveys aimed at increasing the available resource, and to implement protection policies on its watershed. It also opens up perspectives for a complete spatialized deterministic 3-D modelling of such complex hydrosystems.

## 8. ACKNOWLEDGMENTS

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## Tables

Table 1: Summary of pumping test results

PW	Geol	No. of Tests	OW	Diagnostic feature	Analytical model	T or T1 (m <sup>2</sup> /s)	S	Distance to boundary (m)	T2 (m <sup>2</sup> /s)
R1	N	3	R2, DAC, P1	Partitioned aquifer, PP	Hantush (1961); Nind (1965)	2.3 x 10 <sup>-4</sup>	5.1 x 10 <sup>-4</sup>	180	4.5 x 10 <sup>-4</sup>
R2	N	2	R1, DAC,	Partitioned aquifer	Nind (1965)	2.3 x 10 <sup>-4</sup>	5.2 x 10 <sup>-4</sup>	180	4.7 x 10 <sup>-4</sup>



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R3	N	2	R1, R2	Partitioned aquifer	Nind (1965)	$2.4 \times 10^{-4}$	$5.7 \times 10^{-4}$	300	$2.6 \times 10^{-5}$
R4	N	3	MLC2, ML3, P3	Bounded aquifer with leakage	4 orthogonal no-flow boundaries + leakage	$5.4 \times 10^{-4}$	$5.0 \times 10^{-4}$	100, 100, 140, 260	-
R5	G	2	R6*	Partitioned aquifer (PP)	Hantush (1961); Nind (1965)	$5.0 \times 10^{-4}$	$4.0 \times 10^{-5}$	Not evaluated	-
R6	N	10	R5*	Partitioned aquifer	Nind (1965)	$1.8 \times 10^{-4}$	$1.3 \times 10^{-5}$	450	$9.3 \times 10^{-4}$
DAC	N	1	R1, R2	Homogeneous aquifer	Theis (1935)	$1.4 \times 10^{-4}$	$3.9 \times 10^{-4}$	-	-
P3	N	1	R3, R4	Bounded aquifer	4 orthogonal no-flow boundaries	$5.0 \times 10^{-4}$	$8.3 \times 10^{-4}$	70, 70, 70, 70	-
B1	N	4	-	Channelized flow	2 parallel no-flow boundaries	$9.0 \times 10^{-5}$	-	400, 400	-
HF4	N	2	B1	Channelized flow	2 parallel no-flow boundaries	$8.7 \times 10^{-3}$	$4.0 \times 10^{-4}$	30, 30	-

812 PW pumping well; OW observation well; T – transmissivity (in case of partitioned aquifer: T1 - transmissivity of the  
813 local aquifer where the PW is drilled and T2 – transmissivity of the aquifer beyond the boundary); S – storativity.  
814 Geology: N – Nages and G – granite; PP: Partial penetration;\*no reaction of other wells

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819 Table 2: Relative contributions of hydrological time series to the water level in five production wells

Mean Relative Contributions					
Well	Depth of well screening (m)	Recharge (%) [maximum amplitude]	Discharge at the well (%) [maximum amplitude]	Discharge of the other wells (%) [maximum amplitude]	Raviège Lake level(%) [maximum amplitude]
R1	60-87	13% [4.6 m]	37% [9.5 m]	50% [14.4 m]	No contribution
B1	111-121	39% [3.1 m]	61% [4.9 m]	-	No contribution
R2	45-101	12% [2.2 m]	44% [5 m]	54% [8.4 m]	No contribution
R3	41.9-44	8% [1.8 m]	87% [5.5 m]	5% [1.6 m]	No contribution
R5	73-130	8% [1 m]	42% [6 m]	-	50% [7 m]

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Table 3 : Major cations and anions (Na, K, Mg, Ca, Cl, HCO<sub>3</sub>, SO<sub>4</sub>, and SiO<sub>2</sub> in mg/L), trace elements (Li, B, Sr, Fe, Mn and Ba in µg/L), stable isotopes of the water molecule (δ<sup>2</sup>H and δ<sup>18</sup>O), tritium, stable isotopes (δ<sup>13</sup>C) of the dissolved CO<sub>2</sub> and <sup>87</sup>Sr/<sup>86</sup>Sr ratios

Well		B1	R5	R3	R6	R1	R2	HF4
Date (dd/mm/yy)		10/09/10	10/09/10	10/09/10	10/09/10	10/09/10	10/09/10	14/09/11
pH		5.8	6.2	6.4	6.2	6.1	5.9	5.81
EC	µS/cm	1645	884	477	588	1076	816	1460
Temp	°C	14.7	14.0	15.1	14.1	14.0	14.3	13.0
SiO <sub>2</sub>	mg/l	81.0	91.3	61.5	80.4	74.9	71.5	96.8
Na <sup>+</sup>	mg/l	6.6	4.8	4.5	3.4	5.3	4.4	7.1
K <sup>+</sup>	mg/l	2.9	2.0	2.3	1.5	2.4	2.3	2.9
Ca <sup>2+</sup>	mg/l	374	176	137	112	222	162	373
Mg <sup>2+</sup>	mg/l	15.6	9.5	7.0	4.8	10.5	7.5	15.4
Cl <sup>-</sup>	mg/l	3.7	4.2	4.1	4.2	4.5	5.1	3.4
HCO <sup>3-</sup>	mg/l	1186	561	289	358	681	544	1192
SO <sub>4</sub> <sup>2-</sup>	mg/l	9.0	20.3	9.0	7.4	43.6	7.9	8.5
NO <sub>3</sub> <sup>-</sup>	mg/l	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
NH <sub>4</sub> <sup>+</sup>	mg/l	0.14	0.07	<0.05	<0.05	0.05	0.19	
F <sup>-</sup>	mg/l	0.3	0.4	0.3	0.4	0.3	0.4	0.3
Fe(tot)	µg/l	14500	8430	5230	5790	11400	7660	48024
Mn(tot)	µg/l	1581	581	458	455	843	568	1722
Ba	µg/l	12.47	11.35	7.58	8.19	7.33	7.27	50.1
B <sup>-</sup>	µg/l	59.4	24	32.1	16.2	36.1	39.6	10.4
Li <sup>+</sup>	µg/l	28.3	21.5	16.9	13.1	21.2	16.9	21.9
Sr <sup>2+</sup>	µg/l	1910	914	780	601	1210	868	1718
<sup>87</sup> Sr/ <sup>86</sup> Sr		0.708985	0.709048	0.709121	0.708963	0.709018	0.709024	0.708956
2σ for <sup>87</sup> Sr/ <sup>86</sup> Sr(m)		0.000008	0.000008	0.000009	0.000008	0.000007	0.000008	0.000009
δD	‰	-46.0	-44.5	-45.3	-45.3	-45.2	-45.1	-48
δ <sup>18</sup> O	‰	-7.3	-7.1	-7.2	-7.1	-7.2	-7.2	-7.5
<sup>3</sup> H	UT	2	2	<1	2	3	2	3

2σ for <sup>3</sup> H(m)		1	1		1	1	1	1
d <sup>13</sup> C (CO <sub>2g</sub> )	‰	-5.6	-6.7	-7.8	-7.8	-6.6	-6.4	

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833 Table 3(continued)

		P3	MLC1	R4	HF1	HF2	HF3	HF5
		08/09/10	08/09/10	13/09/10	13/12/11	27/12/11	15/09/11	13/12/11
pH		6.77	6.89	6.64	7.20	6.50	7.23	7.80
EC	μS/cm	232	132	718	126	863		179
Temp	°C				14.0		11.7	14.0
SiO <sub>2</sub>	mg/l	10.4	13.9	35.6	19.5	39.0	15.4	10.2
Na <sup>+</sup>	mg/l	4.7	3.8	4.7	4.9	8.7	3.7	3.4
K <sup>+</sup>	mg/l	1.0	1.0	1.7	2.8	2.5	0.8	1.5
Ca <sup>2+</sup>	mg/l	40	22	182	38	203	26	30
Mg <sup>2+</sup>	mg/l	2.4	1.5	6.7	3.2	11.6	1.5	2.5
Cl <sup>-</sup>	mg/l	18.5	7.5	7.9	3.0	3.0	4.0	6.5
HCO <sub>3</sub> <sup>-</sup>	mg/l	107	76	542	79	686	82	106
SO <sub>4</sub> <sup>2-</sup>	mg/l	3.5	3.0	9.5	5.5	5.5	2.0	2.5
NO <sub>3</sub> <sup>-</sup>	mg/l	14.5	1.6	0.4	0.40	3.6	1.6	5.30
NH <sub>4</sub> <sup>+</sup>	mg/l					<0.02		
F <sup>-</sup>	mg/l				<0.1		<0.1	<0.1
Fe(tot)	μg/l	1.5	4	194		0.60	24	
Mn(tot)	μg/l	0.3	0.5	180	374	0.10	13.5	18
Ba	μg/l	7	7.5	14	12.5	17	4.1	6.5
B-	μg/l	<20	30	<20	<20		3.0	<20
Li <sup>+</sup>	μg/l	1.5	1.5	21.0	5.5	29.0	1.7	3.5
Sr <sup>2+</sup>	μg/l	301	157	1201	397	1370	307	286
<sup>87</sup> Sr/ <sup>86</sup> Sr		0.708933	0.709473	0.708840			0.709012	
2σ for <sup>87</sup> Sr/ <sup>86</sup> Sr (m)		0.000009	0.000009	0.000009			0.000009	
δD	‰	-45.2	-42.9	-44.5			-46.5	
δ <sup>18</sup> O	‰	-7.2	-6.9	-7.0			-7.2	
<sup>3</sup> H	UT	3	3	2				
2σ for <sup>3</sup> H(m)		1	1	1				

834  $\sigma$ : standard deviation

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838 **Table 4:** Strontium (Sr) and rubidium (Rb) data on rock samples

Formation	Sample (depth)	Mineral	Rb (ppm)	Rb* (ppm)	Sr (ppm)	Sr* (ppm)	<sup>87</sup> Sr/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr W-model
Granite	Granite 8 (outcrop)	TR	271	-	76	-	0.755219	0.76116
		P+Q	135	271	46	92	0.748866	
		K-F	532	-	104	-	0.773991	
		B	609	-	10	-	1.390815	
Granite	R5 (102.8 m)	TR	373	-	48	-	0.799635	0.80615
		P+Q	219	547	34	84	0.784069	
		K-F	530	-	76	-	0.793338	
		B	1807	-	10	-	2.805149	
Granite (pegmatite)	R5 (117.4 m)	TR	451	-	28	-	0.897886	0.88075
		P+Q	273	414	20	30	0.872317	
		K-F	959	-	45	-	0.959064	
Nages gneiss	R6 (76 m)	TR	94	-	471	-	0.712446	0.71064
		P+Q	21	54	886	2816	0.710379	
		K-F	264	-	160	-	0.729277	
Nages gneiss	R6 (96.9 m)	TR	157	-	241	-	0.717688	0.71975
		K-F	222	-	592	-	0.713817	
		B	206	-	193	-	0.72217	
		C	117	-	168	-	0.71759	
Cipolin marble	R6 (149.1 m)	TR	34	-	1937	-	0.708719	-
		C1	14	-	2283	-	0.708567	
		C2	89	-	1834	-	0.709179	

839 TR: total rock sample; P+Q: plagioclase + quartz; K-F: K-feldspar ; B: biotite; C: calcite; C1: light calcite; C2: dark  
840 calcite.

841 Rb\* and Sr\* contents are corrected from the quartz proportion of the sample.

842 <sup>87</sup>Sr/<sup>86</sup>Sr W-model means the <sup>87</sup>Sr/<sup>86</sup>Sr of water in theoretical equilibrium with the rock

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