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Acquisition of water chemistry in a mobile fissured basement massif: its role in the hydrogeological knowledge of the La Clapière landslide (Mercantour massif, southern Alps, France)

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Abstract

Groundwater flowpaths of the La Clapière landslide are studied by chemical and isotopic water analysis and modeling of the landslide springs. In our case, it appears that sulfate can be taken as a chemical tracer of the different flowpaths. On the gneissic slope of La Clapière, geochemical modeling explains sulfate concentrations from 0 to 130 mg/l by dissolution of sulfurous minerals present in the gneisses. Such a variability of the concentrations measured in the springs is due to different infiltration paths: direct paths through the basement ($[SO_4^{2-}] = 10$–60 mg/l or indirect path through superficial deposits like screes or fluvio-glacial terrains which cover the basement ($[SO_4^{2-}] = 60$–130 mg/l). The high concentrations (600–800 mg/l) cannot be explained by thermodynamic geochemical simulations, and they reveal Triassic gypsum dissolution hidden under the studied slope. So, two main flowpaths are differentiated in the La Clapière landslide: (1) flow through low permeable Triassic deposits pinched under the foot of the landslide, (2) flow through a more permeable fissured basement with different flow paths; and, consequently, with different transit times due to the anisotropic nature of the top and the central part of the landslide. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Landslide; Metamorphic rock; Water chemistry; Sulfate; Oxygen; Thermodynamic modeling

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1. Introduction

The La Clapière landslide mobilizes a huge volume (55×10^6 m^3) of a metamorphic slope in the Mercantour massif (Follacci et al., 1988). A good correlation exists between precipitation and landslide velocity variations (Follacci, 1987, 1999), expressed by 30–40 mm/day movements during snowmelt flood periods and 5–10 mm/day during low water periods. Groundwater drainage in such a landslide cannot be easily studied by usual hydrogeological methods (Antoine et al., 1994). This is due to the anisotropy of the reservoir where piezometric measurements are not representative. In all cases, boreholes in such a moving media do not persist through time and so it is impossible to follow infiltration effects. For these reasons we develop an original approach based on the interpretation of chemical variations of groundwaters infiltrating in an area including the landslide. The problem in the La Clapière site is to know if water content fits with water flows in two or

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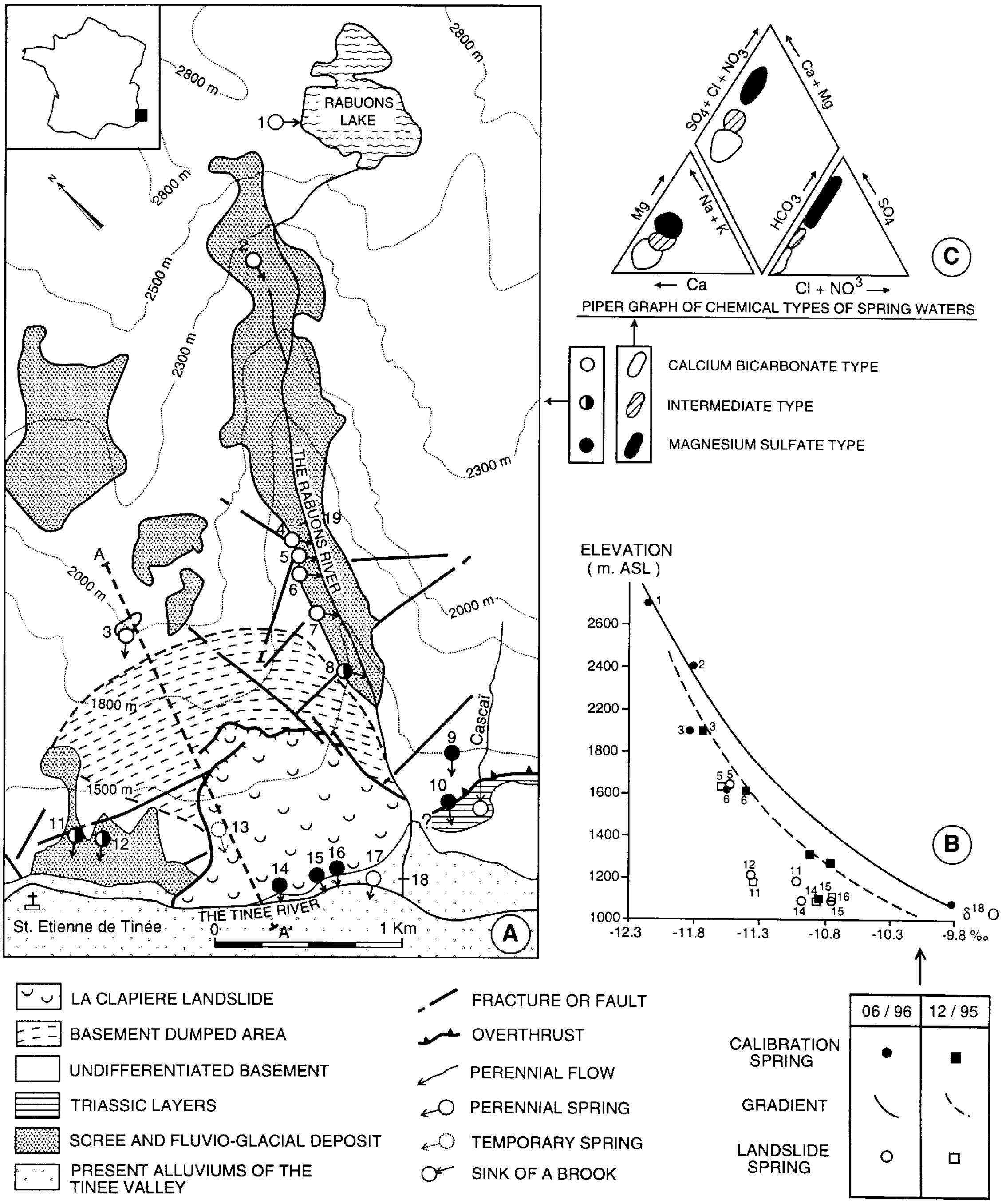

Fig. 1. Hydrogeology of the La Clapière versant: (A) Hydrogeological map; (B) Isotopical gradient [black squares: calibration springs in December 1995 (low-water) $\delta^{18}O = -2.10\ \ln(\text{elevation}) + 4.18$ with $r = 0.989$; black circles: calibration springs in June 1996 (snowmelt) $\delta^{18}O = -2.92\ \ln(\text{elevation}) + 10.69$ with $r = 0.988$. Recharge elevation is plotted for calibration springs. white squares: springs sampled in December 1995 (low-water); white circles: springs sampled in June 1996 (snowmelt). Outlet elevation is plotted for the studied springs. (C) Piper diagram.

three well-defined areas of the reservoir (landslide, decompressed area, stable area) or if there are a lot of possible poles according to the infiltration transit (e.g. one chemical output per mineralogical facies). In the first case, chemistry leads directly to the determination of different drainage zones in the reservoir. In the second case, the complexity of the drainage cannot be studied and only variability is associated with differences in transit times. The methodology developed here consists in the comparison of hydrogeological and water chemistry field data with computed data issued from simulations of water–rock interactions.

2. Geographical and geological setting

The La Clapière landslide is located on the left bank of the NW–SE-flowing Tinée river, near the town of Saint-Etienne-de-Tinée (Alpes-Maritimes Prefecture, France; Fig. 1A). It is bordered on its southeastern side by a major tributary, the Rabuons brook, which flows from a lake located at an elevation of 2500 m. Nearby mountain peaks have elevations commonly exceeding 3000 m. From the summits down to the Tinée valley (Fig. 2), the whole slope is occupied by two-mica gneisses of the Variscan Argentera-Mercantour massif (Bogdanoff and Ploquin, 1980). The foliation of the gneisses strikes N140°E on average, and dips northeastwards with values comprised between 55 and 90°. Fracturation of the slope includes three families of faults: N10–30°E, N90°E and N110–140°E. To the south-east of the Rabuons brook side, the gneisses tectonically lie upon overturned Triassic sedimentary strata forming a tight syncline with outer sandstone layers and inner gypsum and *cargneules* (cellular tectonized dolomites) layers (Faure-Muret, 1947; Ivaldi et al., 1991). The thrust plane separating the gneisses from the Triassic strata is exposed in the Cascaï brook valley. It strikes N140°E and dips about 80°NE. Scree and fluvio-glacial deposits locally cover the gneisses, especially in the upper reaches of the Rabuons brook.

The base of the La Clapière landslide is located at an elevation of 1100 m and is 1 km wide. The toe progressively overthrusts the Quaternary alluvial deposits of the Tinée river. The top of the landslide stands at elevation 1600 m. It consists of a 120-m

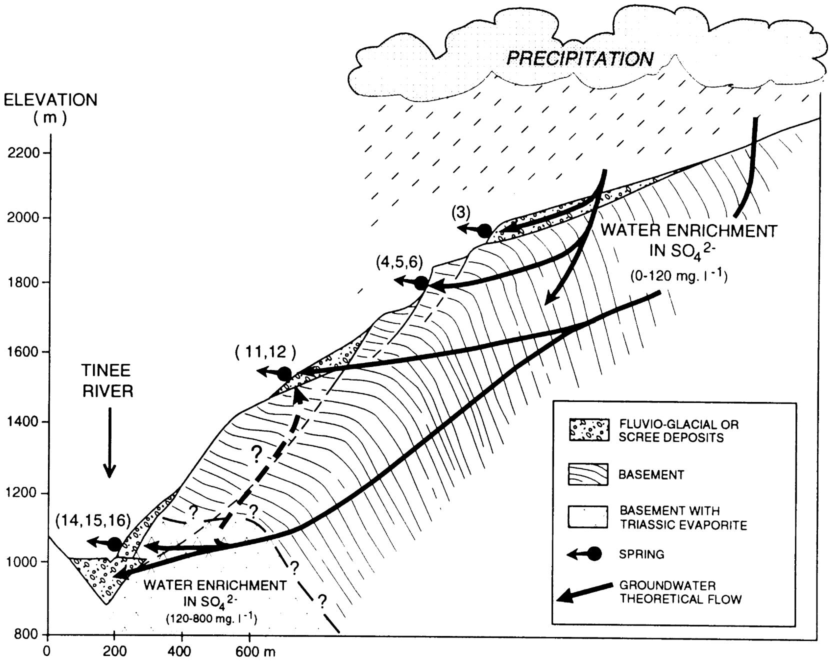

Fig. 2. Schematic hydrogeological cross-section of the La Clapière slope showing location of the different water–rock interactions (the cross-section line appears in Fig. 1).

high, 800-m wide scarp. Due to internal cracks, scarps, tilted terraces and numerous rock-fall accumulations (screes), the surface of the landslide is quite irregular. The head and flanks of the landslide are rimmed by a 200-m wide transitional zone which makes the transition between the stable slope areas and the landslide itself. This transitional zone shows several evidence of incipient instability: trees having curved trunks, extension cracks, toppled blocks.

3. Hydrogeological setting

The foot of the landslide is drained by a group of perennial springs with a total discharge estimated at 0.5 l/s (Fig. 1A; springs 14–16). On the upper part of the landslide, several temporary springs flow on the top of massive gneisses free from rock cover of the intermediate area (spring 13). Outside of the landslide, spring outlets are observed on the edge of the transitional dumped zone. Some of these springs outflow directly from the basement on along different faults directions (springs 6 and 7) or in the weathered superficial formations (spring 5). The other springs outflow indirectly through the fluvio-glacial and scree deposits (springs 4, 8, 11 and 12). The mean discharge of a single spring reaches about 0.2 l/s and the total discharge of these lateral outflows is about 5 l/s. Very locally on the overthrusting basement/Triassic in the Cascaï talweg, flows of 4–5 l/s were measured (springs 9 and 10), outlining the importance of this N140°E direction with regard to drainage. All these springs drain the basement aquifer which is the most important one in the La Clapière slope.

Some springs only drain screes at the top of the slope (springs 2 and 3) or fluvio-glacial deposits at the foot of the slope (spring 17). These deposits which are drained by perennial springs can so be considered as superficial perched aquifers on the basement.

The existence of perennial and temporary springs is due to the very discontinuous Mediterranean precipitation, to the lack of infiltration during frost periods in winter, followed by massive snowmelt; and also to the size and hydraulic conductivity of the different aquifers: several temporary springs drain very local areas, whereas springs of the foot of the landslide drain larger areas with a low permeability.

In order to take into account any significant variations in such an Alpine mountainous area (Razafindrakoto, 1988; Fig. 1B), we used the following methodology to determine the average recharge altitude of the landslide springs:

- two samplings, performed during a low-water period (December 1995), and during a snowmelt flood period (June 1996);
- a selection of local calibration springs located between 1100 and 2500 m, whose recharge elevation is known: black squares for low-water and black circles for snowmelt in Fig. 1B.

All these calibration springs cannot be situated on the framework of Fig. 1A, because several have been sampled upstream St-Etienne-de-Tinée (Ublan—altitude 1320 m, Rio de Claï—altitude 1280 m), others downstream the valley (Bourguet—altitude 1100 m). But they are all situated on the same side of the Tinée valley.

- Two isotopic gradients $\delta^{18}\mathrm{O} = f(\mathrm{elevation})$ are calculated at the scale of the La Clapière slope, using $^{18}\mathrm{O}$ content and recharge altitude of the springs (Compagnon, 1996; Compagnon et al., 1997): a low-water and a snowmelt gradient can be calculated thanks to these calibration springs. Nevertheless, taking into account springs with a local recharge area to define the gradients could exhibit some influence of seasonal effect, smoothed out in larger springs, with a longer residence time of water. As in other Mediterranean and Alpine areas (Mudry et al., 1994; Guglielmi et al., 1998), these gradients fit a semi-logarithmic relation better than a linear one: the actual evaporation rate of these sites modulates the infiltration coefficient versus altitude, according to a semi-logarithmic fitting (Blavoux et al., 1992)

$$-\delta^{18}\mathrm{O} = -2.10\ \ln(\mathrm{elevation}) + 4.18 \text{ with } r = 0.989 \text{ in December 1995,}$$

$$-\delta^{18}\mathrm{O} = -2.92\ \ln(\mathrm{elevation}) + 10.69 \text{ with } r = 0.988 \text{ in June 1996.}$$

- The samples from the landslide springs, plotted with their ^{18}O content and their outlet altitude (white squares for low-water and white circles for snowmelt in Fig. 1B), are situated under these gradients. Thanks to the intercept of a vertical straight line, parallel to the altitude axis with the gradient, their recharge area can be determined.

The lateral springs of the landslide have an infiltration area which ranges in elevation from 1600 to 1800 m. This corresponds to the transitional area surrounding the landslide. The recharge area of waters outflowing from the foot of the landslide have an average altitude ranging from 1570 ± 150 m at the end of the low water period to 1780 ± 150 m during the snowmelt flood period. So the area of water infiltration for all the springs outflowing from the basement aquifer is approximately the same, larger and higher than the landslide area, and variable according to the seasons. This aquifer corresponds to the slipping, the transitional dumped zone and depending on the seasons to a part of the basement.

4. Methodology

Acquisition of water chemistry is the result of mass transfers between interstitial fluids and rock-forming minerals. These mass transfers depend on several parameters involved in weathering processes (temperature, pH and redox conditions, chemical concentration of weathering solutions, mineralogical composition), but also the residence time of water in contact with the minerals. This period depends in turn on hydraulic parameters which are the infiltration rate, the porosity and the permeability.

At the La Clapière slope, we performed a double approach which is based on the one hand on a chemical analysis of spring waters and, on the other hand, on modeling different interface water–rock exchanges observed on the field. In the basement aquifer, water follows different pathways to the landslide area. Chemical analysis of waters originating in springs outflowing from this aquifer has been performed during different periods of the year. We define a typology of different existing water-types depending on in situ hydrological conditions. This typology is compared with a parametrical study on a geochemical model (Made et al., 1990).

Sampling of spring waters was performed between March and June 1996 (Compagnon, 1996). They were repeated two or three times a week when infiltration in the hillslope corresponded to snowmelt floods. The concentrations in HCO_3^- were measured by acid titration on the field (few hours after sampling) with a 1% accuracy. All the other analyses were performed at the laboratory of hydrogeology of the Department of Geosciences, University of Franche-Comté. The concentrations in K^+, Na^+, Ca^{2+} and Mg^{2+} were measured by atomic absorption spectrometry. Accuracy is ±0.05 mg/l. The concentrations in SO_4^{2-}, Cl^- and NO_3^- were measured by high-pressure ionic chromatography. Accuracy is ±0.02 mg/l.

The thermodynamic geochemical model KINDIS (Made et al., 1990) has been used to simulate the acquisition of water composition according to different water–rock interactions. This model describes the interactions between minerals and aqueous solutions taking into account the irreversible dissolution of reactants and the reversible precipitation of secondary products. Evolution of the chemical composition of the solution and the distribution of elements between simple and complex ions are also determined. KINDIS calculates, by incrementation, the quantity of destroyed or formed phases per kilogram of solution, according to the reaction rate which corresponds to the mass of dissolved rock per kilogram of weathering solution. This reaction rate is in fact a rock–water ratio: in an open system, a low rock–water ratio characterizes media with a significant solution renewal with more or less short residence time. A high rock–water ratio corresponds to a poorly drained medium where the renewal of the solution is low where the residence time is long (Destrigneville et al., 1991; Del Néro, 1992; Guy et al., 1992).

Based on the hydrogeological evolution of aqueous solutions obtained from the analysis of water samples, we separate the final output into a sum of intermediate inputs. Every intermediate step (of concentration) corresponds to a precise interface which is localized on the site, and for which we model the influence on the chemistry of infiltration waters.

5. Results: physical and chemical typology of springs

Based on their chemical compositions, waters

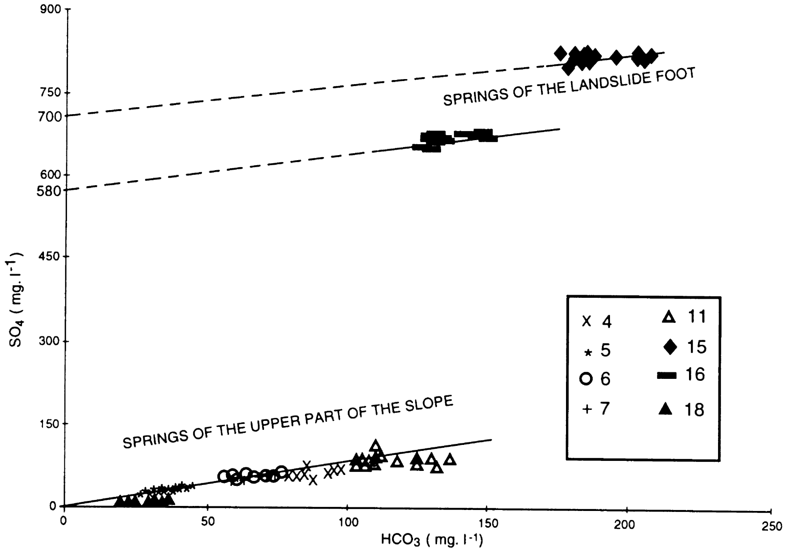

Fig. 3. Plot of the La Clapière springs on a SO_4^{2-} versus HCO_3^- diagram.

flowing out of the landslide foot can be clearly distinguished from other waters flowing out of the La Clapière slope. There is a clear increase in SO_4^{2-} concentration at the landslide foot (800 mg/l on average), which is 10–40 times higher than that on the landslide top (50 mg/l on average). If we plot the chemical types previously defined on the Piper diagram on the hydrogeological map, three chemical water types appear (Compagnon, 1996; Compagnon et al., 1997):

- calcium bicarbonate-rich waters, including springs of the stable part at the top of the La Clapière slope (Fig. 1C, springs 4–7);
- magnesium sulfate-rich waters which correspond to the springs at the landslide foot. The springs located along the thrust fault separating the gneisses from the Triassic rocks also belong to this group (Fig. 1C, springs 9, 10, 14–16);
- chemically intermediate waters between both previous types characterize springs situated on the central part of the slope between the foot and the top of the La Clapière slope (Fig. 1C, springs 11 and 12).

The location of sulfate incorporation can be done precisely on a $SO_4^{2-} = f(HCO_3^-)$ scattergram where we have replaced all the waters sampled in the La Clapière slope springs (Fig. 3). These waters cluster in two groups which fit regression straight lines with the same positive slope, but with a different intercept:

- the straight line corresponding to the springs of the top and the middle of the slope ($r = 0.71$; $n = 161$) which intersects the origin;
- the straight lines corresponding to the springs of the landslide foot ($r = 0.96$; $n = 38$) whose intercept ranges from 580 to 700 mg/l.

The identical slope of the lines demonstrates that a part of the sulfate in the waters sampled is acquired by waters as they are enriched in HCO_3^-. Such an enrichment in HCO_3^- is usual for infiltrations in the unsaturated zone of a massif (Bakalowicz, 1979). So the maximum concentrations that can be incorporated by La Clapière waters infiltrating the unsaturated zone are 90–130 mg/l for sulfates and 100–150 mg/l for bicarbonates. The different intercepts of the lines demonstrate an SO_4^{2-} origin independent from that of HCO_3^-, therefore independent from the infiltration zone of the reservoir. So, sulfate concentrations must be acquired more deeply in the reservoir.

This is the case only for the landslide foot springs. The 580 and 700 mg/l intercepts of the lines correspond to deeper flows within the saturated zone of the slope.

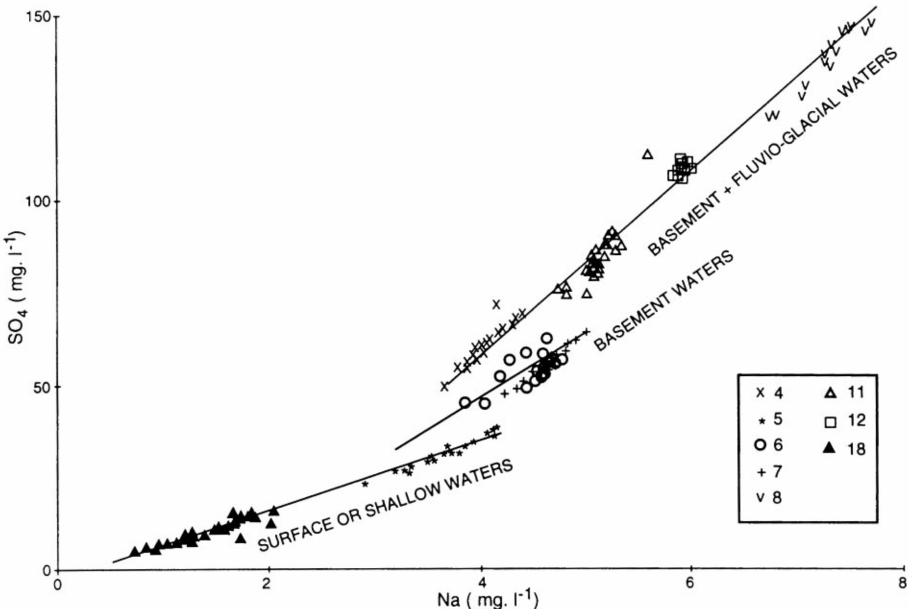

Fig. 4. Plot of the La Clapière springs on a SO_4^{2-} versus Na^+ diagram.

Infiltration in the unsaturated zone of the La Clapière slope can be decomposed on a SO_4^{2-}–Na^+ scattergram (Fig. 4). Springs draining screes or undecompressed basement (springs 5 and 18) which correspond to surface waters or waters circulating in shallow, well oxygenated horizons fit the low mineralized waters line ($r = 0.99$; $n = 66$). In this case the sulfate concentrations range between 0 and 20 mg/l. Waters circulating in the basement (springs 6 and 7) are more mineralized ($r = 0.98$; $n = 92$) with sulfate concentrations ranging between 20 and 60 mg/l. Waters originating in the basement relayed by the fluvio-glacial deposits (springs 4, 8, 11 and 12) are more mineralized, with a significant enrichment in SO_4^{2-} ions ranging between 50 and 130 mg/l ($r = 0.98$; $n = 78$).

Thus, sulfates of the La Clapière slope springs are partly acquired in the unsaturated zones of the hillslope and partly in the basal saturated zone. At the landslide foot, the concentrations increase to 600–800 mg/l. This value is significantly higher than the maximum 90–150 mg/l value acquired in the unsaturated zone. The problem of the sulfate origin is posed for all the springs of the La Clapière slope. Which SO_4^{2-} concentrations measured in the different springs can be obtained by a simple interaction with metamorphic rocks? What is the part of the fluvio-glacial effect in the quantity of dissolved sulfates? In order to answer these questions, we have modeled the incorporation processes of sulfates at the main water–rock interfaces previously defined.

6. Interpretation: results of water–rock interaction modeling with results of chemical analysis

6.1. Initial conditions

The minerals which are taken into account in the modeling are quartz, plagioclase (An40), muscovite, biotite and accessory minerals which are potassic feldspar, calcite, chlorite and pyrite. Two chemical compositions of the initial water are used: a snowmelt-type water and a water which has already flown on fluvio-glacial deposits (Fig. 5A). The system is open to the gases (the atmosphere is considered as an infinite reserve of gases). The partial pressure of CO_2 is that of the atmosphere, that is 3.14×10^{-4} atm. The partial pressure of O_2 is fixed to a value of 10^{-30} atm, quite lower than that in the atmosphere (about 0.21 atm), in order to take into account the

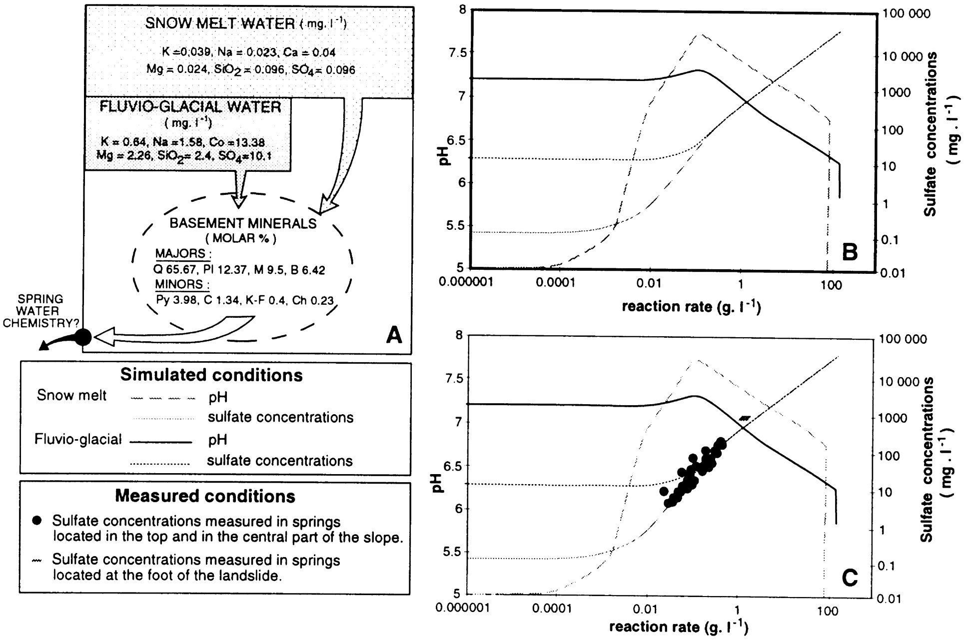

Fig. 5. Simulation of water–rock interactions: (A) initial conditions; (B) simulating pH and sulfate versus reaction rate diagram; (C) plot of measured data on the simulating pH and sulfate versus reaction rate diagram. Grey bars correspond to sulfate concentration of about 800 mg/l and pH higher than 7.5, black circles correspond to sulfate concentrations of about 1–130 mg/l and pH ranging from 6 to 7.

fact that the redox equilibrium cannot be attained in natural solutions (Michard, 1989). The 10^{-30} atm partial pressure of oxygen and pH determine the initial redox potential of the solution at 560 mV for a snowmelt water and at 437 mV for a fluvio-glacial type water (oxidizing medium). During the modeling, secondary phases allowed to precipitate are siderite and gibbsite. Calcite is the only primary mineral allowed to precipitate when it reaches saturation. The other minerals have too slow precipitation kinetics to precipitate at these temperatures. Simulations are performed in an open medium.

6.2. Results

Theoretical curves of sulfate incorporation according to the weathering rate of the gneisses by snowmelt waters which are infiltrated directly or through a fluvio-glacial surficial layer display the same general shape (Fig. 5B):

- for reaction rates lower than 0.11 g/l, a very progressive increase of the sulfate concentrations correlated to a pH increase;
- for reaction rates comprised between 0.11 and 77 g/l, a linear increase of sulfate concentrations corresponds to a decrease of the pH;
- for reaction rates higher than 77 g/l, a stabilization of the sulfate concentration corresponds to a steady-state pyrite dissolution.

During the simulation, sulfate concentrations are only controlled by oxidizing dissolution of pyrite which is the only primary mineral of the rock to release sulfates in solution. The more oxygen there is in the medium, the less stable is the pyrite, like under surface weathering conditions (Deutsch, 1997). Only the pH range comprised between 5 and 8 was plotted because it fits to the pH measured on the field (Fig. 5B). The increase of pH is due to silicate minerals dissolution (plagioclases) which incorporates the protons of the solution and those brought by pyrite dissolution. Then, when these minerals are saturated with respect to the solution, the pH decreases by input of protons coming from the pyrite dissolution, until reaching values below 6 at the end of the simulation.

This kind of diagram (Fig. 5B) also indirectly demonstrates the field conditions under which water percolates: (1) at the beginning of the modeling (reaction rate of about 0.11 g/l), there is formation of iron and aluminum oxides and hydroxides which characterize low concentrated and well drained media; (2) at the end of simulation (reaction rate upper than 70 g/l), there is formation of carbonate mineral (calcite). Precipitation of this mineral is possible only in more concentrated water and poorly drained media.

The sulfate concentrations measured in different spring waters are plotted on the simulated curves of sulfate (Fig. 5C).

The springs of the foot of the landslide (Fig. 5C) are clearly remote from the theoretical curves. Solutions with the same order of magnitude of sulfate concentrations have pH lower than 7.3 for snowmelt waters and than 7 for fluvio-glacial waters. So, sulfate concentrations of these springs cannot only be explained by pyrites dissolution in the basement rocks and require existence of evaporitic terrains in the massif.

Springs of the top and the central part of the slope (Fig. 5C) fit with the theoretical curves in a low reaction rate (about 0.03–0.3 g/l of dissolved rock) area. Sulfate concentrations analyzed in the springs fit well with modeled sulfate concentrations explained by dissolution of pyrites contained in the basement rocks which reach 17–126 mg/l. The low reaction rates, much less than 1 g/l, also mean that all these terrains appear well drained. This observation fits well with the nature of the top and the central part of the slope composed of fractured and weathered basement with superficial screes and fluvio-glacial formations

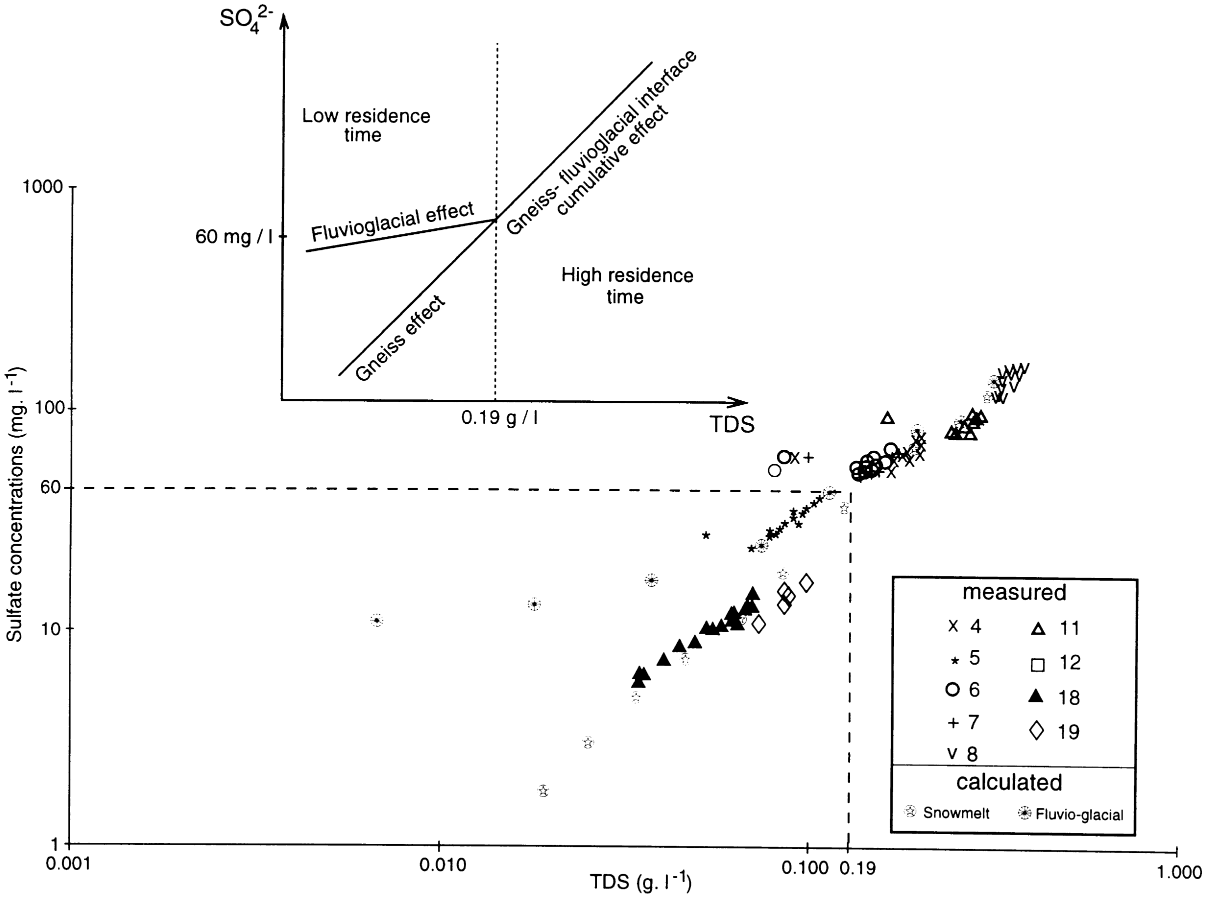

Fig. 6. Comparison of measured and simulated sulfate concentrations versus TDS values for the springs of the upper part of the slope.

with a heterogeneous granulometry, which all are well aired and rather permeable. The variability of sulfate concentrations can be explained on a SO_4^{2-}–TDS (Total Dissolved Solid) scattergram, where the measured TDS is compared to the one calculated from the reaction rate (Fig. 6). A TDS lower than 0.19 g/l corresponds to low reaction rates, therefore a short residence time. It is the case for running waters of springs 18 and 19, and water flows in well aired areas of springs 5. Sulfate concentrations of springs 18 and 19 are only explained by dissolution of the basement in contact with snowmelt type waters, while those of spring 5 originate in basement dissolution by a fluvio-glacial type water. TDS value higher than 0.19 g/l correspond to significant reaction rates, then to longer residence times. It is the case for waters of springs 4, 6, 7, 8, 11 and 12 originating in the basement overlaid by fluvio-glacial. In these springs, acquisition of sulfate concentrations higher than 60 mg/l is mainly regulated by flowpaths, and, consequently by residence time of water in the terrains. Indeed, for a TDS value higher than 0.19 g/l, SO_4^{2-} concentrations acquired by a snowmelt type water or by a fluvio-glacial type water are similar (Fig. 6). In conclusion, drainage of infiltration waters through the unweathered or weathered basement accounts for low sulfate concentrations (<20 mg/l). Over 20 and up to 130 mg/l, the drainage of the slope is controlled by basement-fluvio-glacial interfaces. These interfaces increase the residence time of waters in the slope. This is in turn induces a significant modification of mineralization and pH of water.

7. Conclusion

Comparison of field data with the results of simulations carried out with exposed basement rock composition enables to constrain hydrogeological hypotheses.

On the basement slope of La Clapière, geochemical modeling explains sulfate concentration of waters from 0 to 130 mg/l by dissolution of sulfurous minerals which exist in the basement. The high concentrations (600–800 mg/l) cannot be explained by results from simulations. The method then strongly suggests existence of non-exposed rocks hidden under the studied slope (Fig. 2). In the local geological context, these rocks can only be Triassic gypsum which could correspond to the extension of Cascaï fault under the La Clapière slope.

Also, simulation of water infiltration directly in the basement does not explain the variability of 0–130 mg/l sulfate concentration at springs. The role of superficial formations which cover the basement is displayed under two main aspects. Firstly, these near-surface interfaces, with a different permeability than the basement, increase the transit time of infiltrated waters; and secondly, during water residence in these formations, their concentration is modified. In a basement area such as La Clapière, where residence time of waters in contact with the rock is short (TDS <0.3 g/l), hydrochemical influence of these superficial deposits explains up to 70% of water chemistry at the spring.

A geochemical approach combined with the hydrogeological one shows two main origins of water flowpaths in the La Clapière landslide. At the base of the landslide, groundwaters flow through Triassic deposits pinched along N140°E faults located on the eastern border of La Tinée lineament. At the top and central parts of the landslide, groundwaters directly flow through the fissured basement with different flowpaths depending on the presence of Quaternary deposits, and, consequently slightly different transit times. These differences in the landslide drainage can be correlated with the different mechanical behaviors: high sliding speeds of the top and the medium and slow speeds of the base of the landslide (Follacci, 1999).

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