

Interactive comment on “Variability of the groundwater sulfate concentration in fractured rock slopes: a tool to identify active unstable areas” by S. Binet et al.

S. Binet et al.

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Received and published: 29 October 2009

Thank you for your comments. You will find here, for each point, a remind of your questions following by my answers. (text “” is a citation from the corrected manuscript)

- The basis of this work relating groundwater geochemistry to rock movements has been discussed before even by the same authors (see references within the text). Therefore it is not new concept that is presented in this study.

This is a new concept, previous paper links deformation with porosity and permeability changes. The chapter was rewritten: “To overcome these difficulties hydrogeologists

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had transfer specific hydrogeochemical methods from karstic hydrology (Mudry, 1990) to the unstable fractured areas (Vengeon, 1998; Guglielmi et al., 2000; Tullen, 2002) in aims to characterized the groundwater flows. The results highlight, the gravitational deformations induce a motion of the entire rocky slope, a propagation of discontinuities in the rock material (Barla and Chirietti, 1996; Agliardi et al., 2001), can generate additional cracks (Scavia, 1995), that lead to a porosity and permeability changes creating a new water pressure distribution (Binet et al. 2007c). Thus, in theory this hydro-mechanical deformation phenomenon may generate additional reactive surface areas, which in turn can change the chemical weathering rate and the groundwater chemistry. The aim of the present study is to characterize a chemical changes of major ions of water flowing through gravitational active faults compared to inactive ones in a similar geological context."

- For the more ambitious goal of this work it is hard for me to see that even on the local scale of the work done for many years in the mentioned sites the geochemical analysis of water can give a major advantage in monitoring landslide or rock movement or predictive tool.

Ok In the abstract, the new sentence is : "This result opens interesting perspective for the follow-up of sliding or friction dynamic in landslides or in (a)seismic faults.".

The chapter 5.2 was rewritten to be more concrete with this question: "By performing sampling very close to the potential unstable area, it is possible to deduce if the sampled zone is moving or not. If a potentially unstable slope is monitored, water chemistry is like a syn-deformation signal that can be use to recorded fracture the growing or the sliding evolution. With time, the fracture growing can lead to a catastrophic rupture (Scavia, 1995) and water chemistry can be a help to the prediction of this catastrophic rupture."

- On paragraph 2 page 5423 - I don't see the correlation between the sulfate concentration and landslide motion. This is the only place where sulfate concentration is related

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to movement and it is not clear or fully explainable.

This chapter was rewritten 3.3 was divided in 2 sub-paragraphs

“1- dependent on stable/unstable zones 2- dependent on landslide motion The S15 spring is characterized by a particularly high SO₄ concentration. The long observation period of the S15 spring (Fig. 4) shows that the sulfate changes with time. If we focus on the recession stages (black squares in Figure 4) where no dilution process occurring from rainwater or snow melting infiltration, the sulfates relates to the landslide acceleration (strong accelerations are grey shaded in Figure 4). Thus in 4/1996, a 8.5 mmol/L concentration (see S15(0) in Table 3;) after an high acceleration is observed. It decreases then to 7.9 in the low movement period during until 12/1996. Similarly in 1999, after a relatively long low movement period (concentration at 6.2 mmol/L in S15 (1 and 2) in May 1999), the concentrations increase to 7 in December 1999. An short increase-decrease-increase of the concentrations from 6.8 to 8.8 to 6 to 6.5 mmol/L is also observed in 2000. The 02/2001 acceleration of the landslide is correlated with 7.4 sulfate concentration (S15(4)). Then an overall decrease from 2002 (see S15(7, 8 and 9). Theses movements correlate qualitatively and positively to the landslide acceleration. Note that the S15(5) analysis is an example of a no null nitrate value. The water is influenced by fresh water intrusion. The analysis is excluded to our interpretation.”

- When inverse modeling is considered in page 5426 a set of negative concentration of compounds are provided in tables 2 and 3 please relate and explain.

New legend for Table 2: “Table 2: Spatial variability of water quality recorded on the six major springs from the two studies valleys. S5 refers to the spring of the La clapière (Tinée) site. Calculated values of the saturation index and inversed values of the amount of dissolved minerals (positive values means dissolution, negative values means precipitation).”

- On page 5428 when O₂ saturation is discussed values in table 3 are more than order of magnitude larger than limit of saturation - no explanation is given.

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Our choice was to use O₂ like a mineral and to evaluate which amount of O₂ is used to dissociate the pyrite. "Following the pyrite oxidation equation (1), 3.75 oxygen atoms are needed to oxidise two sulphur atom to sulfate. O₂ saturated water at 5° C (Saturation [O₂]_{aq} = 0.4 mmol/L) may thus produce a maximum of 0.21 mmol/L sulfate from pyrite in a closed system. Most of the inversed O₂ values presented in the Table 2 exceed this theoretical value by a factor of one or two. This means that the system is open for oxygen. Some surface oxygen supposedly diffuses into the groundwater, thus contributing to enhance the dissolved oxygen content needed for the oxidation of pyrite." Legende table 2 and 3 was detailed

- The explanation for table 2 that relates to exchange and recharge of O₂ from the atmosphere is not in accordance with the later explanation of CO₂ concentration which is claimed to be low due to no contact with the atmosphere.

The chapter 4.3.2 was rewritten: "pCO₂ values at the spring outlet (Table 2 and 3) range between -3.32 and -2.7 and are superior to the atmospheric pCO₂ pressure (pCO₂ = 10-3.5 atm.). In the given system of open fractures, we consider that the system is opened to the atmosphere. This means that CO₂ (together with oxygen) diffuses continuously to the groundwater providing the necessary acid for the neutralization of the base generated through the dissolution of the gneiss minerals. This generates the alkalinity (i.e. the HCO₃⁻ concentration) measured at the spring outlet. The Inversed modeling indicates that low CO₂ exchanges with the atmosphere occurred. Realized a model without CO₂(g), to simulate a closed system do not modify the calculated solutions presented in Table 2. The soil alkalinity input (0.1 mmol/L) is sufficient to explain the bicarbonates evolution with the pH increase, but errors range one the alkalinity measurements (+- 0.1) do not enable to exclude possible CO₂ exchanges with the atmosphere."

SpeciënAc comments:

- Abstract (p. 5417): line 8-10 please rephrase sentence ("Potentially. as

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observed") - not clear.

New sentences: "This suggests that the increase of dissolved sulfate relates to oxidative dissolution of Pyrite". Line 19 "(a)" please explain: New sentences: "This result opens interesting perspective for the follow-up of sliding dynamic and and for the monitoring of fracture growth in landslides or in (a)seismic faults.

- Line 20 – prediction (in general) and specifically of catastrophic ruptures not discussed in the manuscript. Ok deleted

Introduction: Line 3 (p. 5418) suggest to replace "durably" with "in turn" ok

- Line 5-7 please rephrase sentence - not clear. "Because of the variability of crack openings, the transfer times of individual water molecules differ strongly in these fractured areas, dependent on the chosen flow path."

Paragraph beginning in line 8 not completely clear why heterogeneity makes it especially difficult to monitor movement in physical tools also what about remote sensing? This sentence speak about groundwater flows: "The heterogeneity of the fractured rocks and their perpetual displacements makes it difficult to monitor groundwater through installations of automated devices"

- Line 20 suggests to change the sentence to read: "2001).It can generate additional cracks (Scavia, 1995), leading to a porosity" Done

Page 5419 line 1 monitored should be monitoring Done

- Line 20 prediction capabilities are not discussed should not be claimed here or anywhere in the text

Ok all reference to prediction capacity was deleted, expected in chapter 5 "With time, the fracture growing can lead to a catastrophic rupture (Scavia, 1995) and water chemistry can be a help to the prediction of this catastrophic rupture."

- M&M Line 8 page 5419 suggest to change "forms " to shape or control * Done (shape)

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- Line 10 should read cubic meter Done
- Line 14 m.a.s.l. should be deňđned iňđrst time you use it. Done, meters above sea level (m.a.s.l.)
- Line 17 how many “centimeters” in 2001 are we talking few 10>/50>/100>? about 1 to 10 cm
- Line 20 to 22 please rephrase sentence - not clear. Water flows through the cracks, until 100 meter under the ground surface where the water reaches the saturated zone, increases the pore pressure and thus participates to the landslide triggering (Cappa et al., 2004).
- Line 10 p. 5420 why the jump from iňđg.1 to iňđg 4? (Where are iňđgs. 2 &3?) Figure 4 is became Figure 2, and Fig.2 is became Fig.3...
- Line 15 should read analyzed Done
- Line 26 please replace an by a Done
- Line 2 p.5421 Fig 1b I couldn't iňđnd 35 marks of the springs. Corrected: On the Orco valley, 22 springs were analyzed in June 2004
- Line3 and everywhere else in the manuscript waters should read water Done
- Line 12 should read “a seven years survey” Done
- Results Lines 14-15 please rephrase sentence - not clear. New sentences: “The water (four samples) from soil has a 580 - 650 mV/H₂ redox values and the bicarbonate concentration is 0,1 mmol/L +- 0,01. the calculated log of the CO₂ pressures, ranges from -1.7 to -1.9. Average values are presented in the Table 2”.
- Line 20 please begin the sentence with “The water collected” (delete Instead) Done
- Line 1 p. 5423 please begin the sentence with “ Fig . 2” Done
- Line 6 ratios should be ratio Done Line 7 please delete the second“ratio” Done

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- Line 14 should read higher than or equal to higher than
- Line 14 should read low movement period until 1/1996. Done
- Line 26 please change to a “A short increase“ Two short increases of the concentrations from 6.8 to 8.8 and to 6 to 6.5 mmol/L is also observed in 2000
- Modeling: Line 6 p. 5424 and everywhere in the text please refer to gneiss rock and not just gneiss. Done everywhere.
- Paragraph begin in line 11 pH of 4.5 can't be explained by CO₂ maybe explainable by Eq. 1 and production of sulfuric acid. According to reviewers 1: “The soil water is considered representing the initial chemical composition of the flowing groundwater (Guglielmi et al., 2002). The mean bicarbonate concentrations of the four samples is 0.1 mmol /L +- 0.1 (analysis Soil in Table 2) , the pH is 5.5 +- 0.5.
- Line 16-20 please rephrase sentences - not clear.: Ok. The soil water represents the initial chemical composition of the flowing groundwater (Guglielmi et al., 2002). Once infiltrated in the deeper fractures, the organic matter is considered entirely degraded and/or outfiltered and not further being supplied. This modeling hypothesis is supported from the oxygenated conditions found in all springs water (Table 2, Eh data)
- Line 22 should read This open air system Done
- Lines 1-4 p. 5425 there is not agreement with table 1 for example anorthite requires 2 H⁺ , albite 4 and Kmica 1 according to table 1. Corrected
- Lines 11-12 please rephrase sentence - not clear. The increase in pH will also lead to a decrease of the pCO₂ through transformation of dissolved CO₂ into HCO₃⁻. This mechanism, associated with Ca from the dissolution of primary minerals, may lead to calcite precipitation
- Lines 13-15 sentence is redundant please delete. For me, it is an important statement to argue that precipitation take place if SI is > to 0,5 and not 0 as usual.

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- Line 18 a should be replaced with an Done
- Line 20 p. 5426 Ph should be pH Done
- Line 25 should read 0.1 mmol/L of pyrite or from 0.2 mmol/L o Done
- Discussion Line 7 p. 5430 please rephrase sentence - not clear. Thus mix process between water from the landslide and a sulfate rich water can be reasonably discard.
- Table 2 and 3 SI should be defined New legend: “Calculated values of the saturation index (SI)” Fig 1 no legend is given for 1D Corrected “D/ schematic geological cross section through the “La Clapière” landslide, and localization of the monitored springs”.
- Fig 2 legend back symbols should be black Done

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Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 6, 5415, 2009.

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