

Interactive comment on “Hydrogeology and hydrogeochemistry of an alkaline volcanic area: the NE Mt. Meru slope (East African Rift – Northern Tanzania)” by G. Ghiglieri et al.

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Dear Referee

we have answered to your suggestions (you can also have a look to the attached new revised paper):

1R: 1- pag. 8259. At the end of the page the authors should add uncertainties for 18O, D, and 3H; A: We agree and we have added the uncertainties for 18O and D, whereas for 3H values it already was reported in table 3. 2R: 1âĀĤ Point 2.2, pg. 8258, line 23. See reference to “cone group complex Nvm”. What does Nvm means? I have not

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been able to read it anywhere else in the manuscript. It is mentioned in Fig.1. Maybe it should be mentioned. A: Thanks for the suggestion, we have specified where the Nvm means is reported in the text. 2R: 2. Point 2.2, pg.8258, line 24. “groundwater is characterized by a multidirectional flow”. Is this “multidirectional flow” controlled by the cone morphology of the volcano slope, or to large-scale geological heterogeneities, as geological contacts, faults, gravitational processes that alter the underground geological structure, . . .? Please, provide a detailed opinion. A: Thanks for the suggestion, now we have stressed this point in the text also quoting the previous paper (Ghiglieri et al., 2010). 2R: 3. Point 3.1, pg. 8260, line 20–24. The fluoride content is described in this paragraph. I would suggest to add a histogram showing the number of samples per range of fluoride content, i.e., every 5 mg/L. Looking at Table 1, it looks like most of the samples are below 0.3–0.4 meq/L, and that those large values only correspond to very few samples. Since, later on in the paper, fluoride content is related to two major hydrogeological environments, I suggest differentiating them using a stacked vertical bar chart. Moreover, I see no problem on using meq/L in Table 1, and mg/L in the text, since meq/L unit are useful for plotting hydrochemical relationships, and mg/L are more understandable units for readers. A: Thanks for the suggestion, we have added the stacked vertical bar chart in the text.

2R: 4. Point 3.1., pg. 8261, line 5–8. Those lines provide an early conclusion of the paper. As a reader, when I reached this statement I thought: how? I suggest the authors to add something as: “as we will show later on, the presence of bicarbonate and sodium ions . . .” or similar. A: We agree and we have added a phrase according to referee two suggestion.

2R: 5. Point 3.3, pg. 8262, lines 13–28. There are several questions regarding the discussion of isotopic data. Those are. The most common GWML is given by $dD=10 + 8d^{18}O$, however the authors use a similar one ($dD= 10.793 + 8.130d^{18}O$) in Fig 6. Could they provide the reference for such a line? A: We agree that the values in the equation of GMWL line were different from those reported by Craig, (1961)

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now we have changed the equation adopted by Craig. Why waters show dilution by infiltrated rain water? Do isotopes show this? How? In line 22, the authors claim that “some groundwater samples (which ones?) show higher 18O and 2H content, and this is thought to reflect stronger influence of evaporation . . .”. Later on, line 26, they state that “those samples (are those the same ones as in line 18?) plot below the LMWL, indicating the importance of evaporation. . . . Well. Data do not show a trend of samples that move along an evaporation line of appropriate slope that support some evidence. Just a few samples have a smaller $\delta^{18}\text{O}$ excess than the rest of the other ones. Moreover, if those were evaporated samples, the original water would show depleted isotopic content, i.e, $\delta^{18}\text{O} < -6\text{‰}$, so from waters recharge at great altitude. Does this make sense? Could we expect evaporation from waters recharged in the volcano summit? Please, contrast this to support, or neglect, potential evaporation processes. A: We have answered to these observations with new comments in the text The LMWL equation been plotted from a previous reference. Why do not estimate a LMWL from your own data? I think however that samples that could represent isotopic processes should not be included. How your LMWL compare with that of Dettman et al 2005? A: Unfortunately we have only a few sample representative of water which surely did not experienced isotopic processes. About Figure 6, please add a legend. I guess that colours may refer to the geological map in Figure 1, but it should be clearly stated. A: Thanks, we have added the legend.

1R: 2- pag 8262, line 14. The statement “ The majority of groundwater....., and readily diluted by the infiltration of rainwater” as it stands has no mean. I suggest to compute the best 18O-D linear fitting and to compare the slope of the best fitting line for groundwater with that of the LMWL. After this the authors may assess to what extent secondary processes, including evaporation, evapo-transpiration, and water-rock interaction, affect the isotope ratios of shallow groundwater; 1R: 3- pag 8262, line 17. In the statement “some groundwater samples do show a higher 18O and D content (Table 3)”.....” the authors should explain which of these waters show higher 18O and D. Furthermore the authors explain this phenomena trough evaporation and “leaching

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from the rock to the groundwater”. I suggest to add something more about the leaching process in order to better explain its relevance. 1R: 4- pag. 8262, lines 21-22. The authors declare that at higher altitude stable isotopic content is moderately depleted. The statement is unclear: depleted to what? Do they observe more negative isotopic values with increasing altitude? A: Thanks a lot; we have followed the referee’s advice and added the answer in a new comments in the text

1R: 5- pag. 8264, line12 and line. The positive correlation between bicarbonate content and metals can also be properly estimated by the Pearson coefficient. 2R: 6. Point 4.1, pg. 8264, line 11. Correlation shown in Fig 9 seems obvious as it compares the major anions with respect to the sum of the major cations. So a perfect correlation must appear! Nevertheless, it could be interesting comparing the relationship of alkalinity (mainly as HCO_3 , I guess) with $\text{Ca}+\text{Mg}$, and separately, with $\text{Na}+\text{K}$, to point out potential geochemical differences of the cation origin. A: We agree that the perfect correlation is greatly influenced by the sum of major cations. Now we have compared the relationships separately.

2R: 7. Point 4.2, pg. 8264, lines 20. Even though I also use the plot in Fig. 10 to look for exchange processes, I have always wondered if the $\frac{\text{Ca}+\text{Mg}}{\text{HCO}_3+\text{SO}_4}$ axis value is meaningful when we deal with igneous rocks, and $\text{Ca} + \text{Mg}$ derive from hydrolysis of feldspars and plagioclases. The plot obviously works for groundwater data in sedimentary formations; however...it is not obvious to me that it will be adequate for igneous environments. May the authors go through my doubt (in case I was right)? 1R: 6- pag. 8264, lines 22-23. The statement about Fig. 10 is unclear. I believe that the significance of $\text{Na}+\text{K}+\text{Cl} + \text{F}$ and $\text{Ca}^{2+}+\text{Mg}^{2+}-\text{HCO}_3-\text{SO}_4$ relatively to the ionic exchange have to be explained.

A: We agree with both reviewers remarks, nevertheless we noted that this graphical approach is common to some several papers (namely those we have quoted below) in evaluating the ionic exchange also in metamorphic and igneous setting (Subramani et al., 2010; Rajmohan and Elango, 2004; Jalali, 2004). Igneous rocks are able to

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interact with groundwater depending on their porosity and on the amount of mineral phases capable of ionic exchange and/or dissolution. The plot of figure 11 highlight the gain or the lost of cations taking in account the weathering of study area and the related mineral phases their solubility and / or cation exchange capacity. Particularly If cation exchange is a meaningful process, the plot should exhibit a negative slop. We acknowledge that we did not specify which mineral phases (responsible for the releasing of the plotted ions) are involved in ionic exchange or dissolution. In any case, the geology reported in the text is exhaustive enough. Glass from volcanic ash, lahar with both clay and zeolite all contain the considered ions. Moreover calcium precipitation/dissolution is testified by widespread calcrete. Also magadi crust (see mineral phase of this concretion in table –) is widespread in the area.

1R: 7- pag. 8265, lines 22-23. Can the authors really support the idea of a negative correlation between calcium and fluoride? This correlation seems obvious considering that: 1) It is known that, when the exchangeable ions have different valences, the selectivity of a zeolite for cations of higher valence increases with dilution (Pabalan & Bertetti, 2001). Consequently, in low concentrated waters (the highest ionic strength recorded attains 0.055 - Fig. 14) the zeolites can act as a “trap” for the Ca²⁺ ion; 2) Calcrete and CaCO₃ concretion are widespread in the area. Those two factors of Ca-abatement reduces the possibility for nucleation of Ca-bearing phases, obviously including fluorite and fluorapatite in supergenic environment;

1R: 8- In Table 1 please add altitude. A: Thanks, we added it.

1R: 9- In Table 3 one decimal place for 18O and no decimal place for D. A: Thanks, we have provided.

2R: 8. Comments to Figures: General comment: please, include a full legend in ALL plots! Figure 2 (pg. 8276). This ternary plots are somehow a simplification of the usual Piper-Hill diagram; nevertheless, the authors plot sodium and potassium separately as they are the major ions. It sounds good. However, could they state

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in the text? Why do not put (Ca+Mg) in the third component? There are some equal signs (=) in the legend that are difficult to understand.

2R:Fig 3 and so on, claim that legend is as in Fig. 3. It should be Fig. 2, however ... include a full legend in ALL plots!

A: Good suggestion! Now we have included legends in all graphs and modified the ternary diagram.

2R:Fig 8. I would suggest moving the right vertical axis (that of fluoride) to the top of the graph, and have a real Fluoride–Altitude plot in this figure. In that way, you can substitute the label with the fluoride concentration by the sample code. A: We agree and the plot now has been corrected.

2R:Fig. 12. Will it be possible to draw the equilibrium line Ca–F in this graph? It will be helpful to indicate fluorite saturation, and support some of your discussion.

A: We agree that the graph is not a cogent piece of supporting for our considerations. We decided to eliminate it, also in consideration that the reported values are relative to waters coming from phonolite aquifers where only glass and feldspars are involved in dissolution. In any case we think that the occurrence of mineral phases acting as Ca-scavengers reduce the possibility of fluorite precipitation

Please also note the supplement to this comment:

<http://www.hydrol-earth-syst-sci-discuss.net/8/C5428/2011/hessd-8-C5428-2011-supplement.pdf>

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 8, 8255, 2011.

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