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Comment on hess-2021-611

Anonymous Referee #2

Referee comment on "$\delta^{13}C$, CO_2□/□^3He and ^3He□/□^4He ratios reveal the presence of mantle gas in the CO_2-rich groundwaters of the Ardennes massif (Spa, Belgium)" by Agathe Defourny et al., Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2021-611-RC2, 2022

Review of “CO2/3He ratios reveal the presence of mantle gas in the CO2-rich groundwaters of the Ardenne massif (Spa, Belgium)” by Defourny et al. submitted to Hydrology and Earth System Sciences

This paper by Defourny et al. reported new data of hydrochemical, δ13C, and 3He/4He for water and gas samples from the Ardenne Massif (Belgium) and presented a model to establish a link between the CO2-rich groundwater and the magma source beneath the Eifel volcanic field in Germany. As pointed out by Referee #1, the authors should be careful to propose a mantle plume origin for the gases. In addition, the influence of He-CO2 fractionation and carbon isotope fractionation should be evaluated in the discussion part. Overall, the manuscript is well written, and I support the publication of this work after minor revision based on the comments below.

General points.

1. In the title, the authors seem to only emphasize CO2/3He ratios as evidence for the presence of mantle gases (e.g., CO2 and He). However, in the main text, the authors also mentioned δ13C and 3He/4He evidence; especially 3He/4He is more direct in tracing the release of mantle He and CO2 (commonly interpreted as the carrier gas for He). Therefore, I suggest an appropriate revision of the title based on the integrated lines of evidence presented in this study.

2. It may be better to show some data (e.g., the δ13C and 3He/4He values) in the abstract to make it easier for the readers to get some detailed information.

3. Overall, the results section should be appropriately shortened by simply reporting the

data and not going too much into data interpretation. Some sentences or paragraphs (e.g., Lines 130-135 and 138-143) in the Results can be moved to the discussion part. In addition, the titles of sub-sections 4.1, 4.2, and 4.3 are commonly used in the discussion of a paper.

4. In the discussion part, it should be noted that CO2 and He have different solubilities in melts and water, and CO2/3He ratios are easy to be fractionated from their original values due to magma degassing, hydrothermal degassing, or calcite precipitation (see details in Ray et al., 2009, Chemical Geology). Additionally, the influence of carbon isotope fractionation should also be evaluated for the δ13C data.

Other points.

Line 41. The reference citation style should be corrected as that will appear in the final printed version. Similar problems are also found in other places of the main text (e.g., Lines 74-75, 80, 109, and 142-143).

Line 87. Better to replace traces with trace, which is more frequently used in literature. Same problem in Line 91.

Line 118. Typo. It should be CGS samples.

Line 122. PlG or PGd? Table 1 and Figure 4 show that the sample with Cl content of 58.2 mg/L is PGd.

Line 143. A reference is needed for the δ13C value of the atmosphere.

Line 163. Usually, the corrected 3He/4He ratios should also be reported for the samples considering contamination by air-derived helium. The correction method was proposed by Craig et al. (1978) and summarized in detail by Hilton (1996, Chemical Geology).

Line 166. A 4He/20Ne ratio of 0.318 is recommended for the atmosphere, according to Sano and Wakita (1985, JGR).

Lines 170-179. The proportions of air, mantle and crust can be calculated following Sano and Wakita (1985, JGR) equations, which are more commonly used for helium inventory calculation.

Line 173. R/Ra=8 is recommended for the MORB mantle source (Graham, 2002, RiMG).

Line 185-187. It would be interesting to show air-corrected 3He/4He ratios (or mantle He proportions) versus distance to the Eifel volcanic fields, including Eifel, Spa, and Bru data, which would allow constraining of the mantle-derived CO_2 and He transport from magma source beneath Eifel to the discharging sites in Spa and Bru. Usually, increasing crustal contamination with the increasing transport distance is expected for the source-to-surface migration of mantle fluids.

Line 190. The authors should be careful about the conclusion of a mantle plume origin for the CO_2 and He. For the mantle plume settings (e.g., Iceland and Yellowstone), the 3He/4He ratios of geothermal fluids usually exceed the upper mantle value (8 Ra) a lot.

Line 217. I wonder whether the δ13C data of the Eifel samples were also measured from DIC, as those reported in this study. Such comparison should be based on the evaluation of carbon isotope fractionation between the gas and water phase samples.

Figure 4. The sample symbols overlap with some sample names (e.g., Art). Also, “PGd” overlaps with the axis title Ca+Mg and the axis value in the right lower corner.