Response to the comments of reviewers

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"Rock alteration at the post-Variscan nonconformity: implications for Carboniferous-Permian surface weathering versus burial diagenesis and paleoclimate evaluation"

Dear Reviewers and Editor,

we would like to express our sincerest appreciation to the reviewers who provided a very constructive feedback, which helped to significantly enhance the quality of our manuscript. Below please find a point-by-point response to the general and specific comments of Prof. Dr. Reinhard Gaupp (reviewer #1). The response is provided in blue color whereas replaced and new text in the manuscript is indicated by *italic blue* font.

For Prof. Dr. Reinhard Gaupp (reviewer #1) a point-by-point response is as following:

a) Chapter 5.4. Climate: The timing of Permian deglaciation cycles fixed into the climate curve of Roscher & Schneider 2006 is not a reliable base to evaluate the ages of the observed nonconformities (see Fig.12). This pretends the possibility to estimate the lengths of exposure to atmospheric influence and erosion.

Thanks for this valuable comment, this was also my supervisor's Prof. Dr. Matthias Hinderer concern, we tried to carefully express our assumption with "**Possibly**, that this humid interval can be correlated with the deglaciation event Ⅳ between 290-287 Ma". Nevertheless, we agree that this expression together with Fig. 12 might pretend the possibility to estimate the length of exposure. Consequently, we removed Fig. 12 and the relevant content.

b) The term "hydrothermal" is not clearly constrained in this article. Unfortunately, this is often the case in the present papers. What evidence is given to define the fluid as "hydrothermal"? We should know the geothermal situation at the time of influx or mineralization and evaluate the deltaT to the observable mineralization or fluid inclusion data. Otherwise, it is "possibly or likely hydrothermal".

We agree that the term "hydrothermal" is weakly defined. As we do not have specific temperature information, the term "hydrothermal" in the manuscript has been adopted where it had been used in the manuscript.

c) Mesozoic sedimentary cover of the investigated sequence: 600 to 1500m given in Line130; the minimum value of 600m is not justified by evidence within the preserved stratigraphy, and also by thermal consideration (>130°C in the Odenwald top basement)

Thanks for your comments, the lower limit thickness "600 m" has been deleted and relevant content has been adopted in the manuscript.

d) Kaolinite in lithologies like the basalt. Table S1 does not include the mineralogy of the Rotliegend sediments. Can we exclude that kaolinite is a subrecent surface related weathering effect from petrography (present Telodiagenesis)? With an assumed maximum Mesozoic burial of the post-Variscan nonconformity of ca. 1500m, the illitisation of the small kaolinite contents would have occurred. This illitization of kaolinite (K-metasomatism?) would be supported by the assumed hydrothermal processes. Fig.2I shows adularia and kaolinite (replacing the adularia?)

Yes, we can exclude that kaolinite is a subrecent surface related weathering effect. The XRD results indicate the existence of Kaolinite, with the petrologic features observed under the ESEM-EDS, the Kaolinite includes two morphologies, namely, vermiform (fig. 2H) and booklet form (fig. 2I). Both are euhedral and formed due to diagenesis. From these, the vermiform kaolinite is favored as the in situ formation of kaolinite as a result of a dissolution-precipitation mechanism (Chen et al., 2001; Erkoyun & Kadir, 2011). The euhedral booklet form is in turn favored for the autogenic diagenesis, e.g. Bauluz et al. (2008). The kaolinite formed by chemical weathering is usually more anhedral (Bauluz et al., 2008; Varajao et al., 2001), therefore, the effect of telodiagenesis in this case can be excluded. **(line 410-414)**

And with the mineral assemblages, a temperature of nearby 200 ℃ is settled (Stimac et al., 2015) , This roughly coincides with temperatures from thermochronological apatite fission track studies in the surrounding basement of the Odenwald which indicate heating up to more than 130 °C before 80 to 105 Ma and homogenization temperatures from fluid inclusions in hydrothermal veins with up to ca. 290 °C (Burisch et al., 2017; Wagner et al., 1990). **(line 491-493)**

Thanks for your comments, the relevant content has been added and adopted in the manuscript.

e) A very interesting aspect of the study is the interpretation of K-Metasomatism. An increase in K in clastic deposits downsection in wells is observed frequently, with diverse attempts to get a grip on the sources and mechanisms. Metasomatism presumes the export from one volume to import in another volume of rock. In this study the increase of alkali elements is quantified for the gabbroic diorite and the basaltic andesite. Why should an export of potassium from the overlaying Rotliegend arkosic sediments be impossible? The Neogene to Quaternary weathering and erosion effect on the investigated section is only poorly touched.

Previous studies indicate the ratio among K and Rb can be a useful indicator of diagenetic fluids as these two elements are easily extracted by diagenetic fluids. Generally, these two elements are in consistent with each other if the diagenetic fluids are form the same source (Brueckner & Snyder, 1985; Elliott & Haynes, 2002). If the diagenetic fluids are geothermal or hydrothermal fluids, the K, Rb and Cs will correlate (Melzer & Wunder, 2001; Palmer & Edmond, 1989). In our case, based on the K-Cs-Rb plot (Fig.9C), the K, Cs and Rb in the sediments, basaltic andesite and gabbroic diorite all have a positive correlation with each other. Especially in the basaltic andesite and gabbroic diorite, the relationship is nearly linear. Overall, the ratios between Cs-Rb, Cs-K and Rb-K from basaltic andesite and gabbroic diorite are parallel, which means the three elements of basaltic andesite and gabbroic diorite should come from the same source. If the K came from the overlying sediments, the relation between K-Rb among the sediments, basaltic andesite and gabbroic diorite should be parallel or nearly parallel too, but all the relations of Cs-Rb, Cs-K and Rb-K from the sedimentary rock deviate from the data from the basaltic andesite and gabbroic diorite, which means that all the three elements in the basaltic andesite and gabbroic diorite do not come from the overlying sediments, at least not from the Rotliegend sediments.

After having systemically analyzing the Permian Rotliegend sediments in the Sprendlinger Horst, Molenaar et al. (2015) proposed that the sediments in this area formed a “closed diagenesis system”, “despite the highest permeability of all locations, the solute has not been exported from the system.” This in fact corresponds well with the results in this case. Therefore, we think that the enrichment of the K in the basaltic andesite and gabbroic diorite do not originate from the overlying Permian Rotliegend sediments. **(line 365-369)**

And about the influence of Neogene to Quaternary weathering and erosion, since the Oligocene, the Sprendlinger Horst has been exhumed in relation to the adjacent northern Upper Rhine Graben and the Hanau Basin. A second pulse of exhumation is evident for the middle Quaternary (Lang 2007). **(line 497-501)**

3. Technical corrections

a) Line 118: Barruelian, compare Nelson & Lucas 2021: The Cantabrian and Barruelian substages…; in Fossil Record 7. New Mexico Museum of Natural History and Science Bulletin 82._ please adjust to their suggestions (?)

Based on the literature, which point out the “Barruelian substage” is not an appropriate item, but it seems the literature does not give a specific item to substitute “Barruelian substage”. Here I replaced the “Barruelian substage” as “Stephanian A” as it was used as regional term before the “Barruelian substage” was proposed.

b) Fig 11: "retrograde" trend is not explained beyond his figure caption. Please omit or explain. Retrograde is a term in metamorphic petrology; does it apply here for K+ trends, metasomatism??

For the word “retrograde” was firstly used by Panahi et al. (2000) to describe this process. But it seems this is not a universal word now, thus “retrograde” has been replaced by “K-metasomatism”.

c) Line 445: we do not need subhumid climatic conditions to promote eventual flood events that create alluvial massflows. This occurs even in very arid conditions (Jahrtausend-Ereignisse).

Thanks for your correction, the sentence has been deleted.

Other revise:

1. Line 56: “please state clear when climate turned back”.

   After revision: Relevant content has added in line 54-55: From Lopingian, the climate turned back to semiarid conditions (Roscher and Schneider, 2006).

2. Line 108: “until or since”.

   After revision: in line 102: “until” has changed to “since”.

3. Line 108: “were connected initially?”

After revision: “when the basins have had connected initially” has been deleted.

4. Line 105, 112 and 123: (Schäferorgname, 2011).

   After revision:The name of the author has corrected to “(Schäfer, 2011)” in line 104, 110 and 665.

5. Line 121 (of the Gondwana ice cap).

   After revision: “of the Gondwana ice cap” has added in line 119.

6. Line 135.

   After revision: a space has added before the reference in line 134.

7. Line 161: “carefully”.

   After revision: “carefully” has changed to “careful” in line 159.

8. Line 162: “bragg-brentano goniometer”.

   After revision: “bragg-brentano goniometer” has changed to “Bragg-Brentano-Goniometer” in line 160.

9. Line 188: “fracture”.

   After revision: “fracture” has changed to “fractures” in line 187.

10. Line 188: “reducing”.

    After revision: “reducing” has changed to “reducing downwards” in line 187.

11. Line 202: “acore”.

    After revision: “acore” has revised as “a core” in line 202.

12. Figure 2 has been adjusted.

    After revision: fig.2C ---->fig.2B, the old fig. 2B is deleted, new fig.2C is the recrystallization of quartz coupled with calcite, and relvent content is also adopted (the figure caption, and line 492-493).

13. Line 278 “Mclennan (1993)”.

After revision: “Mclennan (1993)” has corrected as “McLenn (1993)” in line 280, and also in the reference (line 621).

14. Caption of figure 8 : Should the CIA value in Fig8B diagram (y-axis) read CIA corr Value?

Thank for your comments, and it is not necessary, the Y-axis is a constant scale.

15. Line 365 “removed”.

Yes, the enrichment degree of K, Rb and Cs are too high, it will affect the scaling of all other elements within one plot.

16. Line 415 “as it discussed”.

After revision: “as it discussed” has revised as “as it is discussed” in line 442.

17. Line 422 “to a seasonal an alternating”.

After revision: “to a seasonal an alternating” has revised as “to a seasonal and alternating” in line 449.

18. Line 454 “non-conformity”.

All the “non-conformity” have revised as “nonconformity”.

19. Line 480 “diageneses”.

After revision: the “diageneses” has revised as “diagenesis” in line 506.

And the language has also been polished.

For Prof. Dr. Henrik Friis (reviewer #2) a point-by-point response is as following:

Point 1. “In this study there is an increase in K2O compared to the protolith which seems to be well identified in both cases, and the authors have decided for “no loss” during weathering by choosing the K-value of the protolith for the CIA diagram (the equation used for K_2O_{corr} does not add any information as it can simply be reduced to K_2O_{corr}=K). Without a reliable estimate for K-loss during weathering, an important aspect of the study is lost.”

Thank you very much for the very thoughtful and constructive comments, in chapter 5.1, some detail information for the equation (5) and (6) to calculate the K_2O_{corr} are missing. The original equations are:

$$K_2O_{corr} = \frac{\mathbf{m}*A+\mathbf{m}*\mathrm{CN}}{1-\mathbf{m}} \tag{5}$$

where

$$\mathbf{m} = \frac{\mathrm{K}}{\mathrm{A+CN+K}} \tag{6}$$

and the K, A and CN values for **m** calculation are from the protolith sample.

A and CN in equation (5) refer to the molecular weight of Al_2O_3 and (CaO^*+Na_2O) content in the **weathering zone**, A, CN and K in equation (6) come from the protolith zone. The revised form is as following:

$$K_2O_{corr} = \frac{\mathbf{m}*A_w+\mathbf{m}*CN_w}{1-\mathbf{m}} \tag{5}$$

A_w and CN_w refer to the Al_2O_3 and (CaO^*+Na_2O) content in the weathering zone, where

$$\mathbf{m} = \frac{\mathrm{K}}{\mathrm{A+CN+K}} \tag{6}$$

and the K, A and CN values for the calculation of **m** are from the protolith sample.

K will surely be lost during the chemical weathering process, and the principle of these two equations is that, during the chemical weathering process, the extraction ratio of K, Ca and Na are fixed for a specific rock type (the ratio is corresponding to the ratio of “weatherable” minerals) (Nesbitt & Young, 1984). That is also the reason why the original weathering trend of the upper continental crust always is parallel to the A-CN join in the A-CN-K diagram. **(line 301-305)**

Point 2. “Similarly, Ca-loss cannot be well established when calcite and dolomite are present. At least the evaluation of the Ca-content should be made in the light of the presence of carbonates rather than apatite. The chois in this study has been to assume that Ca must be lower than Na."

Indeed, due to the overprint of diagenesis, the τ value cannot be applied to evaluate Ca behavior during weathering stage. The CIA and PIA indices for chemical weathering are calculated based on weathering of silicate minerals. Therefore the CaO content should represent Ca in the silicate minerals only (Mclennan, 1993; Nesbitt & Young, 1982, 1989a). In practice, the presence of Ca in phosphates (apatite) and carbonates (calcite and dolomite) needs correction of CaO (Fedo et al., 1995; Mclennan, 1993). The CaO in the phosphate should be firstly corrected with P_2O_5 if it is available, after this, the CaO should be further corrected for carbonates.

As we investigated the thin sections by ESEM, we tested the geochemical composition of the minerals by EDX, (we did not explain in the manuscript before, and thanks for your comments, we have added this information in our manuscript **(line 189 and 197)**). In both basaltic andesite and gabbroic diorite, the dominating "weatherable mineral" is plagioclase. In the basaltic andesite part, the plagioclase mostly belongs to albite ($Na_{0.92}Ca_{0.08}Al_{1.08}Si_{2.92}O_8$), i.e. the content of Ca is much lower than the Na. In the gabbroic diorite, the plagioclase includes oligoclase ($Na_{0.89}Ca_{0.11}Al_{1.11}Si_{2.89}O_8$) and labradorite ($Na_{0.43}Ca_{0.57}Al_{1.57}Si_{2.43}O_8$). In the albite and oligoclase the Ca content is also lower than the Na. In the labradorite the ratio between Ca and Na is nearly 1. That is why we applied the method for CaO correction as proposed by Mclennan (1993) to minimize error of the chemical weathering indices. The results of the CIA and PIA are corresponding well with the mineralogic and petrologic characteristics. **(line 275-279)**

Point 3. "How did diagenesis influence the content of Na and Ca – the other key elements in relation to evaluation of weathering intensity?"

For the basaltic andesite part: based on the A-CN-K diagram, the predominant first secondary mineral formed by chemical weathering in the topmost part of the basaltic andesite (13.9 m) should be kaolinite, after the overprint of the diagenesis, the kaolinite was transferred into I/S, theoretically, during this process, both Na and Ca were enriched, but the τ values of Na and Ca in this part are -0.99 and -0.93, respectively, which indicates the extra Na and Ca input to the topmost part is negligible. Hence, CIA and PIA calculations are little affected. According to the A-CN-K diagram, the first secondary mineral formed by chemical weathering in lower part of the basaltic andesite (14.3-19.3 m) should be smectite, which was converted to illite during diagenesis. Theoretically, herewith Ca and Na were depleted, and this will increase the CIA and PIA values. And in this part, due to the low content of the first secondary minerals formed under lower chemical weathering degree, the depletion of Ca and Na content should also be limited during the transformation of smectite to illite, therefore, the CIA and PIA values here for weathering intensity evaluation is acceptable.

For Gabbroic diorite: similar to the basaltic andesite, the predominated first secondary minerals formed by weathering is smectite according to the A-CN-K. During overprint of diagenesis, the smectite was transformed into I/S in the topmost part (20.6- 21.5 m), in the lower part (22.5-28.5 m) all smectite was transformed into illite. Hence, Ca and Na should be depleted and the CIA and PIA increased. In the topmost part, this influence should be maximal, with the decreasing content of the secondary minerals towards the lower part, this influence will also decrease.

Thanks for your comments, we have adopted this part in our manuscript. **(line 397, line 415-431)**

Point 4. Was K lost during weathering and just more than fully replied during diagenetic transfer - or was it partly consumed by the illitic interlayers in the smectite – or simply not released from primary minerals in the protolith?

Based on the A-CN-K diagram, the minerals formed by weathering in both basaltic andesite and gabbroic diorite should predominated be smectite and kaolinite (in the topmost part of the basaltic andesite) (Nesbitt & Young, 1989b) , There might have existed some illite, but based on the τ value characteristics calculated with the corrected K_2O, we must assume that K from feldspar was partly depleted in both basaltic andesite and gabbroic diorite during weathering process and a small quantity of K may kept by the illitic interlayers within the system. Based on the corrected K content (relevant result has added in Table S5), the τ value plots for both basaltic andesite and gabbroic diorite are as follow (fig.1):

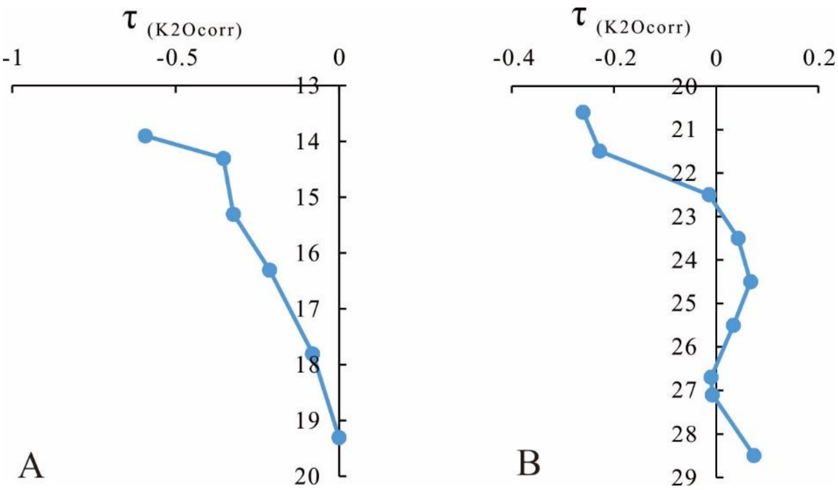

Fig. 1 τ value plots for corrected K_2O, (A) basaltic andesite; (B) gabbroic diorite.

The enriched K in later diagenesis was consumed by the smectite and transferred into illite and illitic interlayers in the smectite.

Thanks for your comments, we have clarified and reinforced this in the manuscript. **(line 352-356)**

Point 5. Was Na and possibly some Ca consumed by smectite formation and only released as respond to the diagenetic illitization (transfer of K)? Or were they already lost by leaching during weathering?

The release of the Ca^{2+} and Na^{+} can be divided into two separate stages:

As we mentioned in **point 3**, the first stage is during transformation of "weatherable minerals" such as plagioclase, hornblende and pyroxene to smectite, where Ca^{2+} and Na^{+} will be transferred to form smectite (Eq. 2, Eq. 3, Eq. 7). Based on the A-CN-K diagram, smectite should be the "first secondary mineral". Based on chemical equation of feldspar transform to smectite. the primary Ca^{2+} and Na^{+} was partly depleted during the weathering stage in both lithologies.

The second stage was during late diagenesis with the transformation of smectite to illite or I/S. Hereby, primary Ca^{2+} and Na^{+} contents were further depleted (Eq. 10)

The relevant contents have revised in our manuscript. **(line 485-488, together with the content mentioned in point 3)**

Other modification:

Figure 14 is further modified.

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