

Response to the comments of reviewer #2

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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 comments of Prof. Dr. Henrik Friis (reviewer #2). The response is provided in **blue color** whereas replaced and new text in the manuscript is indicated by *italic blue* font.

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 K₂O_{corr} does not add any information as it can simply be reduced to K₂O_{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 K₂O_{corr} are missing. The original equations are:

$$K_2O_{corr} = \frac{m \cdot A + m \cdot CN}{1 - m} \quad (5)$$

where

$$m = \frac{K}{A + CN + K} \quad (6)$$

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 Al₂O₃ and (CaO*+Na₂O) content in the **weathering zone**, A, CN and K in equation (6) come from the protolith zone. The revised form is as following:

$$K_2O_{corr} = \frac{m \cdot A_w + m \cdot CN_w}{1 - m} \quad (5)$$

A_w and CN_w refer to the Al₂O₃ and (CaO*+Na₂O) content in the weathering zone, where

$$m = \frac{K}{A + CN + K} \quad (6)$$

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 choice 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 (Fedot 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):

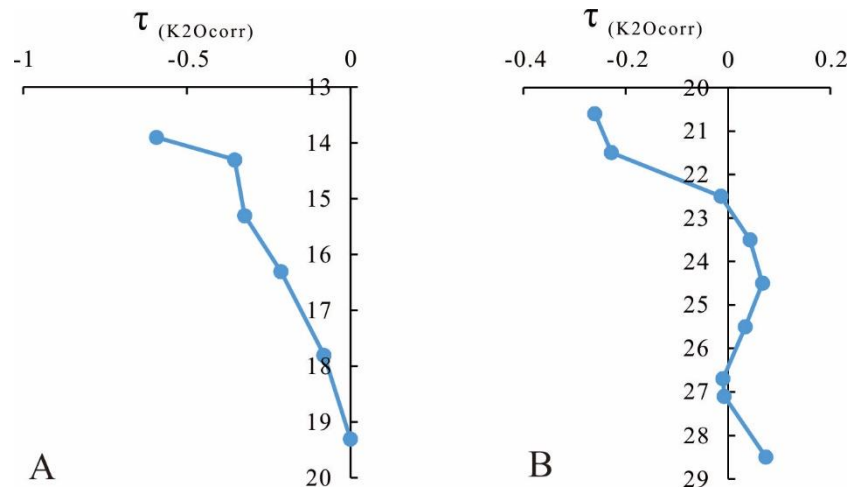


Fig. 1 τ value plots for corrected K_2O , (A) basaltic andesite; (B) gabbroic diorite.

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)

References

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