ELSEVIER

Contents lists available at ScienceDirect

Earth and Planetary Science Letters



journal homepage: www.elsevier.com/locate/epsl

Reply to comment by Zhao et al. on "Hydrothermal events in the Linzizong Group: Implications for Paleogene exhumation and paleoaltimetry of the southern Tibetan Plateau"



Wentao Huang^{a,*}, Peter C. Lippert^b, Peter W. Reiners^c, Jay Quade^d, Paul Kapp^d, Morgan Ganerød^e, Zhaojie Guo^f, Douwe J.J. van Hinsbergen^g

^a State Key Laboratory of Tibetan Plateau Earth System, Environment and Resources (TPESER), Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100101, China

^c Department of Geography, Earth, and Environmental Sciences, University of Northern British Columbia, Prince George, BC V2N429, Canada

^d Department of Geosciences, University of Arizona, Tucson, AZ, 85721, USA

^e Centre for Geodynamics, Geological Survey of Norway, Leiv Eirikssons vei 39, 7491 Trondheim, Norway

^f Key Laboratory of Orogenic Belts and Crustal Evolution, Ministry of Education, School of Earth and Space Sciences, Peking University, Beijing, China

^g Department of Earth Sciences, Utrecht University, Princetonlaan 8a, 3584 CB Utrecht, the Netherlands

ARTICLE INFO

Article history: Received 15 October 2022 Accepted 22 December 2022 Available online xxxx Editor: A. Webb

Keywords: hydrothermal alteration Linzizong Group southern Tibet

ABSTRACT

In their comment on our publication about the discovery of two hydrothermal events in the Linzizong Group (Huang et al., 2022), Zhao et al. question the reliability of our thermochronologic data and the existence of hydrothermal events experienced by these rocks. They argue that their field and microscopic observations, as well as paleomagnetic studies, indicate that the lower Linzizong volcanic rocks preserve primary igneous textures and paleomagnetic signals. In this reply, we address these issues raised by Zhao et al., provide more field evidence, and conduct additional analyses that show that their assertions are not supported. We emphasize that hydrothermal events related to magmatism and deformation have systematically induced resetting of thermochronologic, stable isotopic, and paleomagnetic records of the lower Linzizong Group in the Linzhou basin of southern Tibet.

© 2022 Elsevier B.V. All rights reserved.

1. Introduction

The well-exposed Linzizong volcanic-sedimentary sequence in the Linzhou basin of the Gangdese arc comprises the Dianzhong (~69-58 Ma, E₁d), Nianbo (58-52 Ma, E₂n), and Pana (52-47 Ma, E₂p) formations separated by two unconformities. It is located in the footwall of the north-dipping Gulu-Hamu thrust, and has been a primary target for investigating the surface uplift and latitude drift history of southern Tibet (e.g., Dupont-Nivet et al., 2010; Ingalls et al., 2018). In Huang et al. (2022), we conducted zircon U-Pb, whole rock ⁴⁰Ar/³⁹Ar, zircon U-Th/He (ZHe), and apatite U-Th-Sm/He (AHe) dating of the Linzizong Group, dikes (~52 Ma) intruded into the E₁d and E₂n, and the Qianggeren granite (~52 Ma) in the hanging wall of the Gulu-Hamu thrust. Both inverse and

DOI of original article: https://doi.org/10.1016/j.epsl.2022.117390. DOI of comment: https://doi.org/10.1016/j.epsl.2022.117972. forward modeling of the thermochronologic data reveals that the Linzizong Group experienced two episodes of hydrothermal events. Combined with field observations, we attributed the ${\sim}54\text{-}50$ Ma thermal event, which heated the E_1d and E_2n to $300^{\circ}C$, to the eruption of massive E₂p ignimbrite, intrusion of dikes and concomitant hydrothermal fluid flow. We suggest that the second \sim 42-27 Ma thermal event, reheating the Linzizong Group to 130-170°C, was induced by the Gulu-Hamu thrust activity and associated faulting-pumped hydrothermal fluid flow. We argue that the older thermal event caused by magmatic activity is part of the regional conductive cooling of the Gangdese arc after a high-flux magmatic event that peaked at \sim 52 Ma. Post-magmatic conductive cooling can explain the 50-45 Ma zircon fission track and ZHe dates. It implies that erosional exhumation of the Gangdese arc was of low magnitude and rate and that a low relief proto-plateau was established in the southern Lhasa terrane during Eocene time. We also suggest a limited exhumation of \sim 3 km for the Linzizong Group based on cooling after the \sim 42-27 Ma thermal event. Moreover, the hydrothermal events provide a reasonable explanation for

^b Department of Geology and Geophysics, University of Utah, Salt Lake City, UT, 84112, USA

^{*} Corresponding author. *E-mail address:* whuang@itpcas.ac.cn (W. Huang).

the calcite recrystallization and δ^{18} O and Δ_{47} alteration in carbonates from the Linzizong Group.

2. Field and petrographic evidence for the hydrothermal events

Our field observations show that volcaniclastic sandstones intercalated with tuff layers from the upper E₂p and the ignimbrites above the bottom of E₂p are fresh, whereas the remaining strata below are variably hydrothermally altered (Fig. 2 in Huang et al. (2022)). The hydrothermal alteration aureole is characterized by precipitation of reddish pigmentary hematite and/or yellowish goethite or other secondary iron oxides, on rock surfaces, along microfractures, and within the interiors of the rocks (Fig. 1). Replacement of silicate minerals (e.g., biotite, feldspar) by sericite, calcite and rutile is prevalent in volcanic rocks (Huang et al., 2015). The strongest alteration is observed in strata adjacent to the dikes and two unconformities, indicating that the alteration was controlled by the distance from dikes and fluid flow channel. The upper E₁d lavas, which are below the unconformity between E₂n and E₁d and were intruded by dikes extensively and are strongly to completely altered (Figs. 1d-f). The distribution of the alteration aureole along joints or fractures in the volcanic rocks further confirms that fluid flow has played a role in the alteration (Figs. 1g, h). The lower E_1d lavas and volcanic breccias lie above the angular unconformity between the Linzizong Group and Cretaceous redbeds. Most of these rocks are moderately to strongly altered, and alteration is weak for very few lavas (Figs. 1i-o).

In their comment, Zhao et al. argue that the lack of metamorphism and preservation of original sedimentary and volcanic structures and mineralogy of the red mudstones from the bottom E_2n and volcanic rocks from the E_1d preclude hydrothermal events. Firstly, hornfels (baked siltstones) can be found in the contact metamorphic zone of dike (Fig. 1a). The formation of other types of metamorphic minerals and rocks requires elevated temperature/pressure at sufficient time. When the E₁d and E₂n rocks were heated to 300°C during the older hydrothermal event, these strata were at shallow crustal levels (<3 km) and the timescale of heating was relatively short. Secondly, the red mudstones from the bottom of the E₂n were relatively impermeable to hydrothermal fluid circulation, so it is not surprising that they preserve the original sedimentary structure and mineralogy (Fig. 1b). In contrast, the permeable conglomerate layers interbedded with the mudstone clearly show signs of hydrothermal alteration indicated by their yellowish color (Fig. 1a in Zhao et al. and Fig. 1b in this reply). Thirdly, the structure of strongly to completely altered E₁d lavas has been modified (Figs. 1d-g). Preservation of volcanic structure and texture in some slightly to moderately altered lavas does not exclude hydrothermal alteration. Zhao et al. agree on the alteration of the upper E₁d volcanic rocks, but argue that such an alteration occurred during the late-stage of volcanism. For the lower E_1d lavas, they and Yi et al. (2021) exaggerate the observation of slightly altered (not fresh) lavas and mistakenly interpret the widespread hydrothermally altered yellowish lavas as being weathered. However, neither alteration in the late-stage of volcanism nor weathering could induce such extensive, intensive, and infiltrative replacement of minerals within the rocks. They also could not explain the thermal disturbance of the Linzizong rocks shown by the reset thermochronologic ages (Huang et al., 2022).

3. High fidelity of our $^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$ and U-Th/He thermochronologic results

The whole rock ⁴⁰Ar/³⁹Ar results of both volcanic samples SH25 from the E_{2n} (Huang et al., 2022) and SH01 from E_1d (Huang et al., 2015) show high degrees of disturbance with high scatter: this reminds us that they must be interpreted with caution. A >10 Myr time lag between these ages and the zircon U-Pb ages of the same samples suggests that the 40 Ar/ 39 Ar ages do not represent the formation age, but a later thermal resetting age. In contrast, the whole rock ⁴⁰Ar/³⁹Ar ages of two volcanic samples from the overlying E₂p are consistent with their zircon U-Pb ages, suggesting the absence of such a thermal event (Huang et al., 2015). Moreover, these reset whole rock 40 Ar/ 39 Ar ages of the E₂n and E₁d samples are similar to the 40 Ar/ 39 Ar ages and zircon U-Pb ages of dikes intruded into the E_2n and E_1d and volcanic rocks from the E₂p, which strongly suggests that this thermal event was due to dike intrusion and E₂p ignimbrite eruption. The reliability of our whole rock 40 Ar/ 39 Ar ages of the E₂n and E₁d samples is also confirmed by the ZHe dates of 37 grains: the ZHe ages of the E₂n and E₁d volcanic and sedimentary samples are reset and have a maximum age of \sim 52 Ma (Figs. 4 and 7 in Huang et al. (2022)). Therefore, the scatter of the whole rock ⁴⁰Ar/³⁹Ar results itself is the result of a later thermal disturbance. We reported these ages to characterize the thermal disturbance via comparison between individual samples, as well as between geochronologic methods (i.e., whole rock 40 Ar/ 39 Ar, plagioclase 40 Ar/ 39 Ar, and zircon U-Pb and ZHe). For these reasons, the whole rock 40 Ar/ 39 Ar results serve our purpose well and are of high fidelity. As to the question about the comparable whole rock and single plagioclase ⁴⁰Ar/³⁹Ar ages of sample LZ9931 from the E₁d, the apparent ages of the whole rock sample during degassing vary from 58-70 Ma and no plateau age could be calculated as stated by Zhou et al. (2004). Such whole rock ages are thus unreliable and cannot be used to compare with the plagioclase age.

In our publication, we reported zircon U-Pb and dates from multi-thermochronometers (whole rock 40 Ar/ 39 Ar, ZHe, and AHe) and combined them with the published geochronologic results to determine the thermal history. Every selected zircon grain fulfills

Fig. 1. Field observations of the Nianbo (E₂n) and Diazhong (E₁d) formations from the Linzizong Group in the Linzhou basin and results of susceptibility versus temperature measurements. The division of the Linzizong Group in the Linzhou basin presented in Zhao et al. follows Yi et al. (2021), in which the mudstone and conglomerate layers from bottom of E₂n that unconformably overlie E₁d lavas in our and most geologists' division (e.g., Zhu et al., 2015; Huang et al., 2022) was termed as member III of the E1d (Fig. 1a in Zhao et al. and Fig. 1 in Yi et al. (2021)). (a) Siltstones from the upper Nianbo Formation were intruded by a dike with hornfels formed along the contact metamorphic zone, (b) Conglomerates interbedded with red mudstones from the bottom of the Nianbo Formation. The impermeable mudstones show no sign of alteration, but the permeable yellowish conglomerates are clearly affected by hydrothermal alteration. (c) The lower sedimentary strata of the Nianbo Formation unconformably overlie the lavas of the upper Dianzhong Formation. Aureoles of the hydrothermal alteration of the lavas are characterized by its reddish, yellowish, and purplish color. (d-e) Dikes intruded the Nianbo and Dianzhong formations, the adjacent Dianzhong lavas were completely altered. (f-h) Moderately to completely altered lavas from the upper Dianzhong Formation. Distributions of calcite veins within the dike and alteration zone along the joints and fractures of the lavas strongly suggest the existence of hydrothermal fluid flow. (i-l) Altered lavas and volcanic breccias from top of the lower Dianzhong Formation. The volcanic breccias layer is ~30 m thick. Baked and chilled margins can be observed between the clasts and matrix. The petrology of clasts is identical to the underlying lavas, indicating that fragments of consolidated lavas were emplaced by later magma. These volcanic breccias were mistakenly identified as conglomerates, and thus were the focus of a paleomagnetic conglomerate test by Yi et al. (2021). (m-o) Altered lavas from the lower Dianzhong Formation. Slightly altered lavas are rarely observed, whereas most lavas are strongly hydrothermally altered. (p) Low-field multicycle susceptibility versus temperature curves of three moderately to strongly altered E1d lava samples from Huang et al. (2015). The defined Curie temperatures of 550-560°C of the three samples correspond to Ti-poor titanomagnetite. Slow increase in susceptibility upon heating to 300°C and following graduate decrease until 500°C form a maghemite bump (Bilardello, 2020); Ti-rich titanomagnetite is not identified from these results. The experiments were performed on bulk material in air using Kappabridge KLY3-CS at Fort Hoofddijk Palaeomagnetic Laboratory, Utrecht University, Netherlands. Successive heating and cooling steps of 20, 350, 250, 450, 300, 700, and 20°C were used. Red and blue curves represent heating and cooling steps, respectively. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)



typical standards for ZHe dating. Most single grain ZHe ages of the Linzizong samples show positive correlations with their concentration of effective uranium (eU). Such a variation and trend in the same sample was caused by accumulation of radiation damage over time in grains with different U-Th concentrations. We binned samples from distinct stratigraphic levels into several groups and applied forward modeling to retrieve the best-fit t-T paths, in which every single ZHe date was considered to evaluate to the modeled ZHe-eU envelopes of a designed t-T path. Our forward modeling thus avoided the use of mean values of variable ZHe dates from the same sample as such in inverse modeling. Therefore, the question from Zhao et al. that we dated too few zircon grains in each sample is not tenable and ignores the forward modeling of the positive ZHe-eU correlations. The cooling curves restored by Zhao et al. after arbitrarily ignoring our thermochronologic results show that the Linzizong Group cooled rapidly after eruption, which is typical for volcanic rocks. Their estimated cooling rates are unreasonable because the error bar of each zircon U-Pb date far exceeds the cooling time of the magma.

4. Stable isotopic and paleomagnetic evidence of hydrothermal alteration

Microscopic petrography has documented extensive calcite recrystallization in the lacustrine and pedogenic carbonate samples from the E₂n and E₂p. The extremely low δ^{18} O values (-9% to -22%, VPDB, Vienna Peedee belemnite) of most carbonate samples were interpreted to have been reset (Ingalls et al., 2018; Quade et al., 2020). Moreover, T(Δ_{47}) values determined from clumped isotopic analysis of most E₂n carbonate rocks vary from 41 to 105°C, indicating that the primary clumped isotopic compositions are not retained and that the E₂n was heated above the clumped isotope closure temperatures of 100-150°C. This is also consistent with the vitrinite reflectance result of >135°C from a E₂n shale sample (Ingalls et al., 2018). The elevated temperatures cannot be solely explained by burial heating. Therefore, widespread calcite recrystallization and δ^{18} O and Δ_{47} reset support the hydrothermal fluid alteration of the E₂n carbonates.

Our previous paleomagnetic and rock magnetic studies show that the E_1d lavas, which yield an abnormally low latitude ($\sim 6^{\circ}N$) of the Gangdese arc in the early Paleocene, were hydrothermally chemically remagnetized (Huang et al., 2015). Yi et al. (2021) challenged this interpretation by using a positive conglomerate test of cobbles of a 'conglomerate layer' in the lower E1d. However, previous field investigations of the Linzizong Group did not document any sedimentary layers in the E_1d (e.g., Zhu et al., 2015). Our own revisiting of the section confirms that this layer comprises volcanic breccias, not 'conglomerates'. The clasts have the same lithology as the underlying lavas and chilled/baked margins are commonly observed (Fig. 1i-l). Volcanic clasts within volcanic breccias may or may not record a consistent paleomagnetic direction, depending on the emplacement temperature of the clasts (e.g., Chadwick, 1971). Moreover, the compact clasts are different from the loss matrix in lithology (Fig. 1j-l), the matrix can easily be chemically remagnetized but not the clasts. We thus conclude that the conglomerate test of Yi et al. (2021) is meaningless. Our multicycle susceptibility versus temperature experiments show a rapid decrease in susceptibility between 300 and 500°C (Fig. 1p): this does not represent Ti-rich titanomagnetite, but rather the transformation of (titano)maghemite to hematite (Bilardello, 2020). We argue that the absence of magmatic Ti-rich titanomagnetite and presence of authigenic (titano)maghemite provide support that the E₁d volcanic rocks were hydrothermally altered.

5. Summary

Paleocene exhumation, paleoaltimetry and paleolatitude history of the Gangdese arc in southern Tibet is crucial for investigating growth of the Tibetan plateau. Discrepancies exist, however, on how to interpret the reported thermochronolgic, stable isotopic, and paleomagnetic results. Our recent geochronologic and thermochronologic studies on the Linzizong Group of the Gangdese arc in the Linzhou basin provide a new perspective to reevaluate these data and reconcile previous interpretations (Huang et al., 2022). Our conclusions are, however, challenged by Zhao et al. In this reply, we show that the comments from Zhao et al. on our work are based on their incorrect interpretation of the field and petrographic observations, and incomplete understanding of thermochronology and stable isotope paleoaltimetry. Their positive paleomagnetic conglomerate test, a key to argue for preservation of primary remanence in the E1d, was mistakenly conducted on volcanic breccias. We reject their assertions and emphasize that investigations of exhumation, paleoelevation, and paleolatitude history of southern Tibet, and other tectonically and magmatically active areas, should carefully consider the effects of hydrothermal events.

CRediT authorship contribution statement

Wentao Huang: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Writing – original draft. Peter C. Lippert: Conceptualization, Writing – review & editing. Peter W. Reiners: Conceptualization, Methodology, Writing – review & editing. Jay Quade: Formal analysis, Investigation, Methodology, Writing – review & editing. Paul Kapp: Writing – review & editing. Morgan Ganerød: Investigation. Zhaojie Guo: Resources. Douwe J.J. van Hinsbergen: Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

W.H. acknowledges the support from the Second Tibetan Plateau Scientific Expedition and Research Program (STEP, grant No. 2019QZKK0708) on this work.

References

- Bilardello, D., 2020. Practical magnetism II: humps and a bump, the maghemite song. Educ. IRM Q. 30, 1–16.
- Chadwick, R.A., 1971. Paleomagnetic criteria for volcanic breccia emplacement. Geol. Soc. Am. Bull. 82, 2285–2294.
- Dupont-Nivet, G., Lippert, P.C., van Hinsbergen, D.J.J., Meijers, M.J.M., Kapp, P., 2010. Palaeolatitude and age of the Indo-Asia collision: palaeomagnetic constraints. Geophys. J. Int. 182, 1189–1198.
- Huang, W., Dupont-Nivet, G., Lippert, P.C., van Hinsbergen, D.J.J., Dekkers, M.J., Waldrip, R., Ganerød, M., Li, X., Guo, Z., Kapp, P., 2015. What was the Paleogene latitude of the Lhasa terrane? A reassessment of the geochronology and paleomagnetism of Linzizong volcanic rocks (Linzhou Basin, Tibet). Tectonics 34, 594–622.
- Huang, W., Lippert, P.C., Reiners, P.W., Quade, J., Kapp, P., Ganerod, M., Guo, Z., van Hinsbergen, D.J.J., 2022. Hydrothermal events in the Linzizong Group: implications for Paleogene exhumation and paleoaltimetry of the southern Tibetan Plateau. Earth Planet. Sci. Lett. 583, 117390.

- Ingalls, M., Rowley, D., Olack, G., Currie, B., Li, S., Schmidt, J., Tremblay, M., Polissar, P., Shuster, D.L., Lin, D., 2018. Paleocene to Pliocene low-latitude, high-elevation basins of southern Tibet: implications for tectonic models of India-Asia collision, Cenozoic climate, and geochemical weathering. GSA Bull. 130, 307–330.
- Quade, J., Leary, R., Dettinger, M.P., Orme, D.A., Krupa, A., DeCelles, P.G., Kano, A., Kato, H., Waldrip, R., Huang, W., Kapp, P., 2020. Resetting Southern Tibet: the serious challenge of obtaining primary records of paleoaltimetry. Glob. Planet. Change 191, 103194.
- Yi, Z., Wang, T., Meert, J.G., Zhao, Q., Liu, Y., 2021. An initial collision of India and Asia in the equatorial humid belt. Geophys. Res. Lett. 48, e2021GL093408.
- Zhou, S., Mo, X., Dong, G., Zhao, Z., Qiu, R., Guo, T., Wang, L., 2004. ⁴⁰Ar/³⁹Ar geochronology of Cenozoic Linzizong volcanic rocks from Linzhou Basin, Tibet, China, and their geological implications. Chin. Sci. Bull. 49, 2095–2103.
- Zhu, D.-C., Wang, Q., Zhao, Z.-D., Chung, S.-L., Cawood, P.A., Niu, Y., Liu, S.-A., Wu, F.-Y., Mo, X.-X., 2015. Magmatic record of India-Asia collision. Sci. Rep. 5, 14289.