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Discussion

Comment on "Kawahara, H., Yoshida, H., Yamamoto, K., Katsuta, N., Nishimoto, S., Umemura, A., Kuma, R., 2022. Hydrothermal formation of Fe-oxide bands in zebra rocks from northern Western Australia. Chemical Geology 590 (2022), 120699"

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ABSTRACT

This comment questions an hypothesis for formation of the ornamental stone "zebra rock" from Ediacaran red shales of northwestern Australia as hydrothermal alteration zones. The hypothesis is falsified by absence of Eu anomalies in REE arrays, lack of associated carbonate, low degree of chemical weathering, associated soluble gypsum, strata concordance in narrow bands, low thermal stability of magnetization, modest diagenetic alteration, and patterns unlike liesegang banding. Rather than Cambrian hydrothermal veins, zebra rocks were gleyed paleosols with redox banding, from acid sulfate weathering at low temperature during the Ediacaran.

Zebra rock is a green-red-banded ornamental siltstone from the Ediacaran Ranford Formation sold in rock shops around Kununurra, Western Australia. Kawahara et al. (2022) propose that zebra rock formed "in an acidic hydrothermal system, and that pH buffering of Fe^{2+}-bearing acidic fluid, in a neutralization reaction with primary carbonate minerals, induced rhythmic Fe precipitation." A hydrothermal model may work for other banded textures in coarse grained, crystalline, fractured, carbonate rocks, with sulfide minerals (Wallace and Hood, 2018), but hydrothermal model fails for Western Australian zebra rock non-calcareous siltstones for the following eight reasons.

1. Europium enrichment in rare earth element arrays is characteristic of hydrothermally altered siltstone (Sugahara et al., 2010) and basalt (Shikazono et al., 2008), yet no such anomalies are found in YREE patterns of two samples of zebra rock siltstone, or of unbanded siltstone immediately above and below those samples (all within a single 10 cm thick Wajing bed of Retallack, 2021). YREE patterns of Western Australian zebra rock are very close to post-Archean Australian Shale (Nance and Taylor, 1976), and thus clastic rather than chemical sediments or ores.
2. Zebra rock includes no carbonate needed for the model of Kawahara et al. (2022), nor is it interbedded with limestone or dolostone dolomite, as revealed by chemical and petrographic data (Wajing bed of Retallack, 2021). Western Australian zebra rock has no grains larger than sand, is unfractured, and lacks sparry textures of carbonate zebra banding (Wallace and Hood, 2018). The molar ratio CaO + MgO/Al_2O_3 of 14 specimens of zebra rock and other shales of the Ranford Formation averages 0.0025 ± 0.0024 (one standard deviation: Retallack, 2021), so these shales were neither calcareous nor dolomitic.
3. Alumina/bases molar ratios of zebra rock are high (30 ± 4), and Ba/Sr ratios low (0.15 ± 0.09), and little changed with depth within beds of zebra rock (Wajing bed Retallack, 2021), unlike leached hydrothermal clays (Shikazono et al., 2008). Nor is there chemical, nor petrographic evidence of hydrothermal K-feldspathization, albitization, biotitization, or chloritization (Lottermoser, 1992).
4. Zebra rock is associated with gypsum desert roses (Retallack, 2021). These sand crystals cut across bedding of parent material, and are at a fixed depth below the leached upper surface of paleosols (Retallack, 2021). How did highly soluble gypsum formed between episodes of sedimentation withstand hydrothermal dissolution?
5. Zebra rock is found in thin (5–15 cm) bands traceable laterally for up to 90 m within single quarries, and forming several distinct horizons in the Ediacaran Ranford Formation over 45 km

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of strike (Loughnan and Roberts, 1990). Detailed section measuring (Retallack, 2021), shows that it is not a single unconformity paleosol, contrary to Trainer (1931). Even in single commercially sold slabs like those studied by Kawahara et al. (2022), zebra rock inclined bands pass downward and upward conformably into horizontally bedded unbanded red siltstones. Zebra rock bands do not cut across regional bedding. The inclined oxide bands are silty not colloidal, contrary to Mattievich et al. (2003). Nor do they show grainsize variation like cross bedding, as proposed by Larcombe (1927). Zebra rocks of Western Australia are dominantly silt sized grains (48–81% by volume), like overlying and underlying parts of the same bed (Retallack, 2021). Zebra rock has no massive sulfides, no hydrofracturing, and no gossans common in hydrothermal alteration (Shikazono et al., 2008). Nor is there any known connection of zebra rock with dikes or flows of Cambrian flood basalts in the region (Retallack, 2021).

6. Lack of metamorphism and hydrothermal alteration and burial temperatures less than 300 °C are indicated by low thermal stability of remnant magnetization of zebra rock (Abrajevitch et al., 2018).
7. Weaver index of clays in zebra rock indicate burial depths no more than 3.3 km, compatible with mapped overburden in the region (Loughnan and Roberts, 1990; Retallack, 2021). This depth of burial would give temperatures no more than 90-270º C inferred by Zotov et al. (1998), for dickite in zebra rock (Loughnan and Roberts, 1990; Kawahara et al., 2022). These are normal burial temperatures for that burial depth without hydrothermal activity (Abrajevitch et al., 2018). No high temperature minerals were found to explain abiotic reduction of ferric oxide by alteration to amphibolite facies metamorphism (Klein, 2005; Hagemann et al., 2016). Microbial reduction of iron is much faster than abiotic reduction at low to moderate burial temperatures (Melton et al., 2014).
8. Zebra rock is not liesegang banding as asserted by Hobson (1930) and Kawahara et al. (2022), because zebra rock does not have concentric curves, nor asymmetric concentration gradients within each band (Sadek et al., 2010). Zebra rock red banding is best matched by symmetrical, to slightly asymmetrical, redox banding of gleyed soils (Retallack, 2021).

Zebra rock is a striking ornamental stone popular among tourists to Kununurra, northeastern Western Australia. Evidence so far suggests that it represents acid sulfate weathering at low temperature during the Ediacaran (Loughnan and Roberts, 1990; Retallack, 2021), but the hydrothermal hypothesis of Kawahara et al. (2022) fails eight critical observations listed above.

Declaration of Competing Interest

Gregory J. Retallack has no competing financial or patent interest in publication of this comment of a published paper in *Chemical Geology*.

Data availability

Data will be made available on request.

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References

Abrajevitch, A., Pillans, B.J., Roberts, A.P., Kodama, K., 2018. Magnetic properties and paleomagnetism of Zebra Rock, Western Australia: Chemical remanence acquisition in hematite pigment and Ediacaran geomagnetic field behavior. Geochem. Geophys. Geosyst. 19, 732–748.
Hagemann, S.G., Angerer, T., Duuring, P., Rosière, C.A., Silva, R.F., Lobato, L., Hensler, A.S., Walde, D.H.G., 2016. BIF-hosted iron mineral system: a review. Ore Geol. Rev. 76, 317–359.
Hobson, R.A., 1930. Zebra rock from Kimberley. J. Roy. Soc. West. Australia 16, 57–70.
Kawahara, H., Yoshida, H., Yamamoto, K., Katsuta, N., Nishimoto, S., Umemura, A., Kuma, R., 2022. Hydrothermal formation of Fe-oxide bands in zebra rocks from northern Western Australia. Chem. Geol. 590, 120699.
Klein, C., 2005. Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, metamorphism, geochemistry, and origins. Am. Mineral. 90, 1473–1499.
Larcombe, C.O.G., 1927. Some rocks from four miles east of Argyle Station, Ord River, King district, Kimberley division. In: Ann. Progr. Rep. Geol. Surv. Western Australia for 1926. pp. 23–24.
Lottermoser, B.G., 1992. Rare earth elements and hydrothermal ore formation processes. Ore Geol. Rev. 7, 25–41.
Loughnan, F.C., Roberts, F.I., 1990. Composition and origin of the 'zebra rock' from the East Kimberley region of Western Australia. Austral. J. Earth Sci. 37, 201–205.
Mattievich, E., Chadwick, J., Cashion, J.D., Boas, J.F., Clark, M.J., Mackie, R.D., 2003. Macroscopic ferronematic liquid crystals determine the structure of Kimberley Zebra Rock. In: Conf. Handbk Ann. Condensed Matter Physics Meet. Wagga Wagga, 27, pp. 1–3.
Melton, E.D., Swanner, E.D., Behrens, S., Schmidt, C., Kappler, A., 2014. The interplay of microbially mediated and abiotic reactions in the biogeochemical Fe cycle. Nat. Rev. Microbiol. 12, 797–808.
Nance, W.B., Taylor, S.R., 1976. Rare earth element patterns and crustal evolution—I. Australian post-Archean sedimentary rocks. Geochim. Cosmochim. Acta 40, 1539–1551.
Retallack, G.J., 2021. Zebra rock and other Ediacaran paleosols from Western Australia. Austral. J. Earth Sci. 68, 532–556.
Sadek, S., Rabih, S., Lagzi, I., 2010. Liesegang patterns in nature: a diverse scenery across the sciences. In: Precipitation Patterns in Reaction-Diffusion Systems, 661, pp. 1–43.
Shikazono, N., Ogawa, Y., Utada, M., Ishiyama, D., Mizuta, T., Ishikawa, N., Kubota, Y., 2008. Geochemical behavior of rare earth elements in hydrothermally altered rocks of the Kuroko mining area, Japan. J. Geochem. Explor. 98, 65–79.
Sugahara, H., Sugitani, K., Mimura, K., Yamashita, F., Yamamoto, K., 2010. A systematic rare-earth elements and yttrium study of Archean cherts at the Mount Goldsworthy greenstone belt in the Pilbara Craton: implications for the origin of microfossil-bearing black cherts. Precambrian Res. 177, 73–87.
Trainer, D.W., 1931. Zebra rock. Am. Mineral. 16, 221–225.
Wallace, M.W., Hood, A.S., 2018. Zebra textures in carbonate rocks: fractures produced by the force of crystallization during mineral replacement. Sediment. Geol. 368, 58–67.
Zotov, A., Mukhamet-Galeev, A., Schott, J., 1998. An experimental study of kaolinite and dickite relative stability at 150–300 C and the thermodynamic properties of dickite. Am. Mineral. 83, 516–524.