

■ Comment on “Formation of abnormally high density H₂S fluid in sedimentary basins” by Liu *et al.*, 2025

H. Cui^{1*} 



<https://doi.org/10.7185/geochemlet.2528>

■ Comment

Received 14 April 2025 | Accepted 22 July 2025 | Published 26 August 2025

Liu *et al.* (2025) recently reported high density H₂S in fluid inclusions from the Ediacaran Doushantuo Formation, South China. Based on this novel finding, they proposed: (i) widespread Mississippi Valley-Type (MVT) lead-zinc ore deposits within the Doushantuo Formation, (ii) a “calcite purification model” to explain the presence of H₂S-rich fluid inclusions, and (iii) a hydrothermal origin for methane-derived authigenic calcite (MDAC) nodules.

While the results presented in this study are intriguing and potentially significant, the proposed conceptual model appears inconsistent with several key geological observations. This comment is intended to encourage further discussion and clarification of the issues outlined below.

MVT Lead-Zinc Ore Deposits. The authors interpret the presence of H₂S-rich fluid inclusions and MDAC nodules in the context of extensive MVT lead-zinc ore deposits within the Doushantuo Formation (Liu *et al.*, 2025). However, despite decades of intensive investigation (Ader *et al.*, 2009; Li *et al.*, 2010; Jiang *et al.*, 2011; Macouin *et al.*, 2012; Cui *et al.*, 2016, 2017, 2022; Shi *et al.*, 2022), no enrichment of lead-zinc minerals—such as galena, sphalerite, pyrite, or chalcopyrite—has been documented at the studied Yangjiaping, Zhongling, Caojunba, and Nanbeizhan sections. In the absence of direct geological evidence for lead-zinc mineralisation at these locations, the claim of widespread MVT lead-zinc ore deposits is perhaps misleading.

Calcite Purification Model. The authors propose a “calcite purification model” to explain the association between MDAC and H₂S-rich fluid inclusions. In this model, the progressive precipitation of authigenic calcite consumes the alkalinity generated by thermogenic sulfate reduction (TSR), thereby driving diagenetic fluids increasingly enriched, and eventually saturated, in H₂S (Liu *et al.*, 2025).

It is important to note that the process described above is not self-sustaining. H₂S-rich fluids are stable only under highly acidic conditions, which would promote rapid dissolution of calcite, rather than being continuously enriched by calcite precipitation. In other words, the formation of authigenic calcite cannot progressively enrich diagenetic fluids in H₂S, as a pH equilibrium would eventually be reached due to the concurrent dissolution of carbonates—including both MDAC and the dolomite host rock in the case of Doushantuo—in such acidic conditions. Therefore, to form large scale MVT deposits, the source of sulfide must be external; otherwise, internal generation of

sulfide (*e.g.*, TSR) within the host carbonates would be neutralised by carbonate dissolution, which buffers acidity.

Additionally, the authors’ calcite purification model also appears inconsistent with published petrographic observations. In this model, authigenic calcite precipitates prior to quartz mineralisation during nodule growth, with quartz forming in the centre of the nodules (see Fig. 4 in Liu *et al.*, 2025). However, previous studies have shown that the MDAC nodules in the upper Doushantuo Formation are typically lined by a thin quartz rim, with quartz crystals growing centripetally inward (Cui *et al.*, 2016, 2017; Shi *et al.*, 2022), suggesting that quartz likely formed before or concurrently with MDAC. Similar petrographic patterns have also been observed elsewhere (see Xiao *et al.*, 2010; Wang *et al.*, 2020). We suggest that any conceptual model for these authigenic features should align with the existing petrographic observations.

Complex Diagenetic and Burial Histories. The homogenisation temperatures of fluid inclusions measured by Liu *et al.* (2025) are not totally unexpected, as similar or even higher values have been reported using various methods (Table 1). Notably, a burial temperature of ~241 °C has been estimated for the South China region (Wang *et al.*, 2017). While each geothermometer carries its own assumptions and uncertainties, the collective implication is clear: the Ediacaran strata in South China have undergone a complex history of diagenesis and deep burial.

Disentangling the influence of each individual process during deposition, diagenesis, and deep burial remains a challenging, yet critical, task when evaluating the veracity and significance of these sedimentary fabrics. On the one hand, the meticulous work of Liu *et al.* (2025) offers valuable new data and interpretations, and is therefore truly commendable; on the other hand, perhaps more work is warranted to fully understand these enigmatic textures and geochemical signatures.

■ Acknowledgements

The author gratefully acknowledges support from Kansas State University and thanks editor Raúl Fonseca (Ruhr University Bochum) and the two anonymous reviewers for their efficient handling of this comment. Appreciation is also extended to Liu *et al.* (2025) for their willingness and openness in engaging in this scientific discussion.

Editor: Raúl Fonseca

1. Department of Geology, Kansas State University, Manhattan, KS 66506, USA

* Corresponding author (email: huancui@ksu.edu)

Table 1 Published temperature estimates for the Ediacaran Doushantuo (DST) Formation based on various analytical approaches. Sources are listed in chronological order: 1) Bristow *et al.* (2011); 2) Loyd *et al.* (2015); 3) Wang *et al.* (2017); 4) Zhou *et al.* (2017); 5) Shi *et al.* (2023); 6) Liu *et al.* (2025). MDAC, methane-derived authigenic calcite.

Methods	Published temperatures	Samples and position	Sources
Clumped isotope temperature	86–156 °C	Dolomite veins* in basal DST	#1
Clumped isotope temperature	129–189 °C	White calcite spar in basal DST	#1
Clumped isotope temperature	275–476 °C	Black MDAC* in basal DST	#1
Clumped isotope temperature	34–164 °C	Carbonate matrix in upper DST	#2
Raman spectroscopy	~200–300 °C	Carbonaceous materials in basal DST	#3
Geothermal calculation	~241 °C	DST	#3
Homogenisation temperatures of fluid inclusions	160–220 °C	Quartz cements in basal DST	#4
Clumped isotope temperature	182–212 °C	MDAC in basal DST	#5
Homogenisation temperatures of fluid inclusions	138–160 °C	Calcite cements in upper DST	#6
Homogenisation temperatures of fluid inclusions	113–158 °C	Quartz cements in upper DST	#6

* See also Cui *et al.* (2024) for a critical reassessment of dolomite veins and MDAC cements within cap dolostones of the basal Doushantuo Formation.

Additional Information



© 2025 The Authors. This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0

License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at <https://www.geochemicalperspectivesletters.org/copyright-and-permissions>.

Cite this letter as: Cui, H. (2025) Comment on “Formation of abnormally high density H₂S fluid in sedimentary basins” by Liu *et al.*, 2025. *Geochem. Persp. Let.* 36, 18–19. <https://doi.org/10.7185/geochemlet.2528>

References

- ADDER, M., MACQUIN, M., TRINDADE, R.I.F., HADRIEN, M.-H., YANG, Z., SUN, Z., BESSE, J. (2009) A multilayered water column in the Ediacaran Yangtze platform? Insights from carbonate and organic matter paired $\delta^{13}\text{C}$. *Earth and Planetary Science Letters* 288, 213–227. <https://doi.org/10.1016/j.epsl.2009.09.024>
- BRISTOW, T.F., BONIFACE, M., DERKOWSKI, A., EILER, J.M., GROTZINGER, J.P. (2011) A hydrothermal origin for isotopically anomalous cap dolostone cements from south China. *Nature* 474, 68–71. <https://doi.org/10.1038/nature10096>
- CUI, H., XIAO, S., ZHOU, C., PENG, Y., KAUFMAN, A.J., PLUMMER, R.E. (2016) Phosphogenesis associated with the Shuram Excursion: Petrographic and geochemical observations from the Ediacaran Doushantuo Formation of South China. *Sedimentary Geology* 341, 134–146. <https://doi.org/10.1016/j.sedgeo.2016.05.008>
- CUI, H., KAUFMAN, A.J., XIAO, S., ZHOU, C., LIU, X.-M. (2017) Was the Ediacaran Shuram Excursion a globally synchronized early diagenetic event? Insights from methane-derived authigenic carbonates in the uppermost Doushantuo Formation, South China. *Chemical Geology* 450, 59–80. <https://doi.org/10.1016/j.chemgeo.2016.12.010>
- CUI, H., KAUFMAN, A.J., XIAO, S., ZHOU, C., ZHU, M., CAO, M., LOYD, S., CROCKFORD, P., LIU, X.-M., GODERIS, S., WANG, W., GUAN, C. (2022) Dynamic interplay of biogeochemical C, S, and Ba cycles in response to the Shuram oxygenation event. *Journal of the Geological Society* 179, jgs2021-081. <https://doi.org/10.1144/jgs2021-081>
- CUI, H., KITAJIMA, K., ORLAND, I.J., BAELE, J.-M., DENNY, A., SPICUZZA, M.J., FOURNELLE, J.H., GODERIS, S., DE WINTER, N.J., VALLEY, J.W. (2024) Questioning the role of methane in the wake of a snowball Earth: Insights from isotopically anomalous cap dolostone cements with a complex diagenetic history. *Geochimica et Cosmochimica Acta* 364, 195–210. <https://doi.org/10.1016/j.gca.2023.11.002>
- JIANG, G., SHI, X., ZHANG, S., WANG, Y., XIAO, S. (2011) Stratigraphy and paleogeography of the Ediacaran Doushantuo Formation (ca. 635–551 Ma) in South China. *Gondwana Research* 19, 831–849. <https://doi.org/10.1016/j.gr.2011.01.006>
- LI, C., LOVE, G.D., LYONS, T.W., FIKE, D.A., SESSIONS, A.L., CHU, X. (2010) A Stratified Redox Model for the Ediacaran Ocean. *Science* 328, 80–83. <https://doi.org/10.1126/science.1182369>
- LIU, Y., WANG, X., SONG, Y., SHI, H., CHOU, I.-M., ZHOU, C. (2025) Formation of abnormally high density H₂S fluid in sedimentary basins. *Geochemical Perspectives Letters* 34, 43–49. <https://doi.org/10.7185/geochemlet.2512>
- LOYD, S.J., CORSETTI, F.A., EAGLE, R.A., HAGADORN, J.W., SHEN, Y., ZHANG, X., BONIFACE, M., TRIPATI, A.K. (2015) Evolution of Neoproterozoic Wonoka–Shuram Anomaly-aged carbonates: Evidence from clumped isotope paleothermometry. *Precambrian Research* 264, 179–191. <https://doi.org/10.1016/j.precamres.2015.04.010>
- MACQUIN, M., ADER, M., MOREAU, M.-G., POITOU, C., YANG, Z., SUN, Z. (2012) Deciphering the impact of diagenesis overprint on negative $\delta^{13}\text{C}$ excursions using rock magnetism: Case study of Ediacaran carbonates, Yangjiaping section, South China. *Earth and Planetary Science Letters* 351–352, 281–294. <https://doi.org/10.1016/j.epsl.2012.06.057>
- SHI, H., OUYANG, Q., ZHOU, C., XIAO, S., CHEN, Z., GUAN, C. (2022) Integrated study of the Doushantuo Formation in northwestern Hunan Province: Implications for Ediacaran chemostratigraphy and biostratigraphy in South China. *Precambrian Research* 377, 106699. <https://doi.org/10.1016/j.precamres.2022.106699>
- SHI, H., SUN, Y., OUYANG, Q., GUAN, C., WANG, W., CHEN, Z., ZHOU, C. (2023) U-Pb age of highly ^{13}C -depleted calcite from the basal Ediacaran cap carbonate in Yichang, Hubei Province. *Journal of Stratigraphy* 47, 1–16 (in Chinese with an English abstract). <https://doi.org/10.19839/j.cnki.dcxz.2023.0005>
- WANG, Z., WANG, J., KOUKETSU, Y., BODNAR, R.J., GILL, B.C., XIAO, S. (2017) Raman geothermometry of carbonaceous material in the basal Ediacaran Doushantuo cap dolostone: The thermal history of extremely negative $\delta^{13}\text{C}$ signatures in the aftermath of the terminal Cryogenian snowball Earth glaciation. *Precambrian Research* 298, 174–186. <https://doi.org/10.1016/j.precamres.2017.06.013>
- WANG, Z., CHEN, C., WANG, J., SUESS, E., CHEN, X., MA, X., WANG, G., XIAO, S. (2020) Wide but not ubiquitous distribution of glendonite in the Doushantuo Formation, South China: Implications for Ediacaran climate. *Precambrian Research* 338, 105586. <https://doi.org/10.1016/j.precamres.2019.105586>
- XIAO, S., SCHIFFBAUER, J.D., MCFADDEN, K.A., HUNTER, J. (2010) Petrographic and SIMS pyrite sulfur isotope analyses of Ediacaran chert nodules: Implications for microbial processes in pyrite rim formation, silicification, and exceptional fossil preservation. *Earth and Planetary Science Letters* 297, 481–495. <https://doi.org/10.1016/j.epsl.2010.07.001>
- ZHOU, G., LUO, T., ZHOU, M., XING, L., GAN, T. (2017) A ubiquitous hydrothermal episode recorded in the sheet-crack cements of a Marinoan cap dolostone of South China: Implication for the origin of the extremely ^{13}C -depleted calcite cement. *Journal of Asian Earth Sciences* 134, 63–71. <https://doi.org/10.1016/j.jseas.2016.11.007>