

## Highly metalliferous carbonaceous shale and Early Cambrian seawater: COMMENT and REPLY

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Lehmann et al. (2007) reported trace, rare earth element (REE), and Mo-isotope data from the Ni-Mo sulfide layer and host black shale of the Lower Cambrian Niutitang Formation in southern China. They argue that the metals in the sulfidic rocks originated purely from Early Cambrian seawater. Here we would like to point out that the underpinning assumption of their model (i.e., the stratigraphic correlation of a variety of geochemically anomalous sedimentary beds) is debatable. Furthermore, their geochemical and isotopic evidence is far from conclusive.

### STRATIGRAPHY

Lehmann et al. claim that “the metal-rich sulfidic sediments are stratigraphically equivalent to a spectrum of sediments, including sapropelic alginite, ..., large stratified barite and phosphorite deposits” (p. 403). It has been well established in numerous studies that these deposits do not occur at the same stratigraphic level. The major phosphorite and barite deposits in the lower Cambrian black shale sequence occur far below the Ni-Mo sulfide layer (Zhu et al., 2003). In contrast to a single “euxinic basin” as suggested by Lehmann et al., recent geochemical studies suggest that the depositional environment from the phosphorite and barite deposits to the Ni-Mo sulfide layer changed from oxic/dysoxic to anoxic/euxinic (e.g., Goldberg et al., 2007).

The reference by Lehmann et al. to the footwall of the rocks in question as being “Late Proterozoic dolomite of the Doushantuo Formation” (p. 403) is incorrect. The underlying sedimentary rocks are those of the Dengying Formation dolomite, which is more than 50 m.y. younger than the Doushantuo Formation.

### TRACE AND RARE EARTH ELEMENT EVIDENCE

Lehmann et al. claim that the seawater-like trace element patterns (their Fig. 2) provide strong support for their seawater hypothesis for the Ni-Mo sulfide formation. However, modern seafloor hydrothermal sediments (Cave et al., 2003; Pašava et al., 2004; Dias and Barriga, 2006; Pašava et al., 2007) show similar patterns as those from the Niutitang Formation. Consequently, a hydrothermal contribution to the geochemical signature of the mineralized black shales cannot be excluded. In addition, the pronounced positive Y anomaly, cited by Lehmann et al. as representative of Early Cambrian seawater, has also been observed in many seafloor massive sulfide deposits (Bau and Dulski, 1999) and thus it is not conclusive.

### ISOTOPIC EVIDENCE

Lehmann et al.’s interpretations of the Mo-isotopic data are problematic. They assumed that the small scatter of the  $\delta^{98/95}\text{Mo}$  values ( $-1.24\% \pm 0.10\%$ ) for the Ni-Mo sulfides record that of the Early Cambrian seawater. If this is the case, then some of the shale samples have significantly heavier Mo than the proposed seawater value. This is not known in the current oceans where seawater and euxinic sediments have

the heaviest Mo isotope signature. Here we present an alternative interpretation for the Mo data. We suggest that the large scatter in  $\delta^{98/95}\text{Mo}$  values ( $-1.82\%$  to  $-0.40\%$ ) for the shale samples may represent a heavier authigenic euxinic-sourced Mo (seawater Mo isotopes) mixed with a lighter Mo source of terrigenous materials in the shales (Poulson et al., 2006), whereas the Ni-Mo sulfides are not derived from euxinic seawater but from a third component (hydrothermal fluids). In examining the Mo content and Mo isotope data of the shale samples, it seems that those with heavier Mo isotopic compositions also show higher Mo contents, which can be readily explained by two end-member mixing, although more data are needed to confirm a good correlation between them. The Ni-Mo sulfides and two shale samples with high-Mo content ( $>150$  ppm) (see Table DR2 in the GSA Data Repository 2007097 of Lehmann et al., 2007) plot away from the trend for the low-Mo shale samples, but show uniform  $\delta^{98/95}\text{Mo}$  values, suggesting a dominant additional Mo source with a unique Mo isotope ratio most likely from seafloor hydrothermal solutions. This is consistent with Mo-isotopic data from sediment-hosted modern hydrothermal systems that display high Mo concentration and uniform Mo-isotopic compositions ( $\delta^{98/95}\text{Mo} = -1.5\%$ ) (McManus et al., 2002).

In light of the above comments, the model of an exclusive seawater origin of the metal anomalies in the Niutitang Formation shales is still questionable, and a hydrothermal component to the mineralizing fluid mix remains a viable alternative.

### ACKNOWLEDGMENTS

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### REFERENCES CITED

- Bau, M., and Dulski, P., 1999, Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: Implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater: *Chemical Geology*, v. 155, p. 77–90, doi: 10.1016/S0009-2541(98)00142-9.
- Cave, R.R., Ravizza, G.E., German, C.R., Thomson, J., and Nesbitt, R.W., 2003, Deposition of osmium and other platinum-group elements beneath the ultramafic-hosted Rainbow hydrothermal plume: *Earth and Planetary Science Letters*, v. 210, p. 65–79, doi: 10.1016/S0012-821X(03)00135-3.
- Dias, A.S., and Barriga, F.J.A.S., 2006, Mineralogy and geochemistry of hydrothermal sediments from the serpentinite-hosted Saldanha hydrothermal field (36°34'N; 33°26'W) at MAR: *Marine Geology*, v. 225, p. 157–175, doi: 10.1016/j.margeo.2005.07.013.
- Goldberg, T., Strauss, H., Guo, Q., and Liu, C., 2007, Reconstructing marine redox conditions for the Early Cambrian Yangtze Platform: Evidence from biogenic sulphur and organic carbon isotopes: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 254, no. 1–2, p. 175–193, doi: 10.1016/j.palaeo.2007.03.015.
- Lehmann, B., Naegler, T.F., Holland, H.D., Wille, M., Mao, J., Pan, J., Ma, D., and Dulski, P., 2007, Highly metalliferous carbonaceous shale and Early Cambrian seawater: *Geology*, v. 35, p. 403–406, doi: 10.1130/G23543A.1.
- McManus, J., Naegler, T.F., Siebert, C., Wheat, C.G., and Hammond, D.E., 2002, Oceanic molybdenum isotope fractionation: Diagenesis and hydrothermal ridge-flank alteration: *Geochemistry, Geophysics, Geosystems*, v. 3, no. 12, 1078, doi: 10.1029/2002GC000356.
- Pašava, J., Vymazalová, A., Petersen, S., and Herzig, P., 2004, PGE distribution in massive sulfides from the PACMANUS hydrothermal field, eastern Manus basin, Papua New Guinea: Implications for PGE enrichment in some ancient volcanogenic massive sulfide deposits: *Mineralium Deposita*, v. 39, p. 784–792, doi: 10.1007/s00126-004-0442-z.
- Pašava, J., Vymazalová, A., and Petersen, S., 2007, PGE fractionation in seafloor hydrothermal systems: Examples from mafic- and ultramafic-hosted hydrothermal fields at the slow-spreading Mid-Atlantic Ridge: *Mineralium Deposita*, v. 42, p. 423–431, doi: 10.1007/s00126-006-0122-2.
- Poulson, R.L., Siebert, C., McManus, J., and Berelson, W.M., 2006, Authigenic molybdenum isotope signatures in marine sediments: *Geology*, v. 34, p. 617–620, doi: 10.1130/G22485A.1.

Zhu, M., Zhang, J., Steiner, M., Yang, A., and Li, G., 2003, Sinian-Cambrian stratigraphic framework for shallow- to deep-water environments of the Yangtze Platform: An integrated approach: *Progress in Natural Science*, v. 13, p. 951–960, doi: 10.1080/10020070312331344710.

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**INTRODUCTION**

Jiang et al. (2007) question our interpretation of the Early Cambrian sulfide- and carbon-rich polymetallic marker bed in southern China as being of seawater origin. We believe their arguments are either irrelevant to our model (stratigraphy) or are misinterpretations of our and others' data (rare earth element [REE] and Mo isotope data).

**STRATIGRAPHY**

The polymetallic marker bed occurs within the lowermost few meters of the up to 100-m-thick black shale sequence of the Early Cambrian Niutitang Formation. The sedimentary sequence between the Late Proterozoic dolomite of the Dengying Formation and the polymetallic marker bed has a thickness of 7.4 m at the Ganziping (Sancha-Daping) section and up to 3.0 m at the Huangjiawan mine, west of Zunyi (Mao et al., 2002), the site of most of our samples. In the Huangjiawan area, the sulfide marker bed is underlain by uranium-rich phosphorite with lenses of dolomite, and organic carbon-rich claystone with phosphatic nodules and vanadium enrichment (Mao et al., 2002). The lowermost part of the Niutitang Formation also hosts stratiform barite mineralization, massive phosphorite and manganese carbonate beds, and up to a few tens of meters of "stone coal" beds (i.e., combustible shale) (Coveney et al., 1994). Jiang et al. argue that these highly variable lithologies do not occur at the same stratigraphic level. This may be correct from a microstratigraphic point of view, but this rock sequence is definitely within the lowermost few meters of the Niutitang Formation and probably reflects highly variable environmental conditions. We did not propose that these rocks all represent a euxinic environment; we contend only that the several-cm-thick Mo-Ni enriched sulfide marker bed reflects a strongly euxinic environment.

We admit that the Late Proterozoic dolomite basement on which the black shale sequence of the Niutitang Formations rests unconformably is indeed part of the Dengying Formation, not of the Doushantuo Formation. However, this has no bearing on our seawater model for the Early Cambrian polymetallic marker bed of the Niutitang Formation.

**TRACE AND RARE EARTH ELEMENT PATTERNS**

Jiang et al. state that modern seafloor hydrothermal sediments show similar element patterns "as those from the Niutitang Formation." Much of the Niutitang Formation is an average black shale sequence and has nothing in common with seafloor hydrothermal sediments. Perhaps Jiang et al. imply a possible similarity with the sulfide marker bed. This is incorrect. The marker bed is enriched in Mo, Ni, and As at the percent level, whereas recent hydrothermal seafloor sediments and their ancient analogs

(i.e., massive sulfide deposits), are enriched in Cu, Zn,  $\pm$  Pb at the percent level, and contain very little Mo and Ni (see Lehmann et al., 2003).

The polymetallic marker bed displays a pronounced positive Y anomaly that is typical of aqueous environments and suggests that the source of the REEs of the sulfide bed was dominated by aqueous REE complexes. This is of interest because clastic sedimentary rocks, including the black shales above the polymetallic marker bed, have a chondritic, unfractionated REE pattern with Y/Ho ratios of  $\sim$ 28 (by weight). Jiang et al. claim that the pronounced positive Y anomaly has also been observed in many seafloor massive sulfide deposits and refer to Bau and Dulski (1999). This paper reports on two hydrothermal systems at the Mid-Atlantic Ridge. The precipitates there have chondritic (black and white smokers) and sub-chondritic (anhydrite) Y/Ho ratios. The samples of the fluid phase have chondritic ratios.

**Mo ISOTOPE DATA**

Jiang et al. question our conclusion that the  $\delta^{98/95}\text{Mo}$  values ( $-1.24\text{‰} \pm 0.10\text{‰}$ ) for the Ni-Mo sulfides record the composition of Early Cambrian seawater. They propose a three-component mixing model of a heavier, authigenic euxinic-sourced Mo (seawater Mo) mixed with lighter Mo from terrigenous materials in the shales, and a hydrothermal source.

However, the marker bed has a chemical composition very close to that of a chemical sediment derived from seawater, not from hydrothermal solutions. This is our strongest evidence for a seawater origin of the Mo, and hence is strong evidence for the isotopic composition of Mo in seawater at the time of deposition. There is, indeed, some scatter in the isotopic composition of the low-Mo shales (not the sulfide marker bed), and we cannot exclude more than one source for the Mo in these samples. The identification of the source of this scatter will need more study, which is in progress. Nevertheless, a hydrothermal contribution to the marker bed with a lighter Mo isotopic composition, as proposed by Jiang et al., requires a coeval seawater composition heavier than the marker bed in a mixed sourced interpretation. Consequently, black shales higher in the stratigraphy should evolve to heavier Mo isotope values as the hydrothermal influence decreases. This is not observed. On the contrary, the youngest black shales are identical to the marker bed, thus supporting an overall seawater origin of the Mo.

**CONCLUSIONS**

Jiang et al. prefer to see a hydrothermal component in the metal-rich marker bed, but fail to explain its specific chemical signature with extreme enrichment of the element suite of Mo-Ni-Se-Re-Os-As-Hg-Sb in terms of metal source, hydrothermal metal mobility, and metal deposition.

**REFERENCES CITED**

Bau, M., and Dulski, P., 1999, Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: Implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater: *Chemical Geology*, v. 155, p. 77–90, doi: 10.1016/S0009-2541(98)00142-9.

Coveney, R.M. Jr., Grauch, R.I., and Murowchick, J.B., 1994, The geologic setting of precious metal-bearing Ni-Mo ore beds: *Society of Economic Geologists Newsletter*, v. 18, p. 1, 6–11.

Jiang, S.Y., Zhai, K.D., Li, L., Ling, H.F., and Zhu, M.Y., 2007, Highly metalliferous carbonaceous shale and Early Cambrian seawater: *Comment: Geology*, v.35, doi: 10.1130/G24437C.1.

Lehmann, B., Mao, J., Li, S., Zhang, G., and Zeng, M., 2003, Re-Os dating of polymetallic Ni-Mo-PGE-Au mineralization in Lower Cambrian black shales of south China and its geological significance—A reply: *Economic Geology and the Bulletin of the Society of Economic Geologists*, v. 98, p. 663–665.

Lehmann, B., Naegler, T.F., Holland, H.D., Wille, M., Mao, J., Pan, J., Ma, D., and Dulski, P., 2007, Highly metalliferous carbonaceous shale and Early Cambrian seawater: *Geology*, v. 35, p. 403–406, doi: 10.1130/G23543A.1.

Mao, J., Lehmann, B., Du, A., Zhang, G., Ma, D., Wang, Y., Zeng, M., and Kerrich, R., 2002, Re-Os dating of polymetallic Ni-Mo-PGE-Au mineralization in Lower Cambrian black shales of South China and its geological significance: *Economic Geology and the Bulletin of the Society of Economic Geologists*, v. 97, p. 1051–1061.