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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).


REFERENCES CITED


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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 clays 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, and 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 ~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 δ180Mo values (~1.24% ± 0.10‰) 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 heavier 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