

Highly metalliferous carbonaceous shale and Early Cambrian seawater

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ABSTRACT

We report evidence for the seawater origin of an extremely metal-enriched sulfide- and organic carbon-rich marker bed in a transgressive Early Cambrian black shale sequence along the passive margin of the Yangtze platform. The element concentration pattern in this marker bed suggests that it formed in a sediment-starved, stratified basin with a euxinic water column below an oxic surface layer. Biological activity was high in the surface layer, which was resupplied by communication with oxic oceans. The extremely low terrigenous input and the sulfate-reducing environment in the deeper part of the basin led to exceptionally high metal enrichments by factors of $\sim 10^7$ with respect to modern seawater. The composition of the sulfidic rocks reflects the composition of the Early Cambrian oceans. The molybdenum isotope ratio suggests that during this time $<35\%$ of marine Mo was deposited in oxic sediments, and that suboxic-anoxic marine environments were more widespread during the Early Cambrian than today.

Keywords: Cambrian, black shale, anoxic environments, molybdenum isotopes, China.

INTRODUCTION

Black shales of Early Cambrian age (Niutitang Formation and stratigraphic equivalents; Zhu et al., 2004) are exposed throughout south-eastern China. Their composition is similar to that of average Phanerozoic black shales (Pan et al., 2004; Vine and Tourtelot, 1970). However, a few meters above their transgressive contact with the underlying Late Proterozoic dolomite of the Doushantuo Formation, they locally host a very unusual polymetallic sulfide-rich and organic-rich marker bed, which contains Ni and Mo in the percent range, and platinum group element + Au concentrations of ~ 1 g/t (Fan et al., 1984; Chen et al., 1990; Coveney et al., 1994). This unit is typically a few centimeters thick, has a total organic carbon content of ~ 10 wt%, and contains ~ 20 wt% sulfide sulfur. Its exceptional metal grades have been ascribed to hydrothermal seafloor venting (Lott et al., 1999; Steiner et al., 2001; Jiang et al., 2006). We propose that the metals were derived from Early Cambrian seawater and that the oceans at that time were more reducing than today.

The sulfidic bed occurs sporadically in a narrow NE-striking belt >1600 km in length. The individual patchy exposures are <10 km wide. Paleogeographic reconstructions suggest that the polymetallic sulfide-rich

rocks were deposited in small, sediment-starved euxinic basins along the passive margin of the drowned Yangtze carbonate platform, which was then facing westward, to the open ocean (McKerrow et al., 1992; Steiner et al., 2001). The metal-rich sulfidic sediments are stratigraphically equivalent to a spectrum of sediments, including sapropelic alginite (combustible shale with >30 wt% organic carbon), large stratified barite and phosphorite deposits, and vanadiferous and uranium-rich shale (Fig. 1) (Chen et al., 1990; Wang and Li, 1991; Coveney et al., 1994).

The sulfide-rich rocks occur in two main fabrics: flattened, polymictic millimeter-size pebbles and/or clasts of sulfides in a siliceous-carbonaceous matrix, and distinctly microlaminated sulfide sediment. The sulfide component consists largely of a MoSC phase (Kao et al., 2001) with the approximate composition $(\text{Mo, Fe, Ni})(\text{S, As})_2\text{C}_7$, and pyrite that is rich in Ni and As. Diagenetic cracks in these rocks are filled with pyrite, millerite (NiS), and gersdorffite (NiAsS). Sulfide nodules and/or clasts and laminated sulfide sediments contain abundant pseudomorphosed, micrometer-sized globular aggregates, which are best preserved in a phosphatic matrix (Steiner et al., 2001). Bitumen occurs both interstitially and as clasts.

The isotopic composition of sulfur in the sulfide nodules ranges from $\delta^{34}\text{S}$ values of $+30\text{‰}$ to -30‰ (Canyon Diablo troilite). This large range at the micrometer scale is probably due to bacterial sulfate reduction under fluctuating open-system to sulfate-limiting conditions (Murowchick et al., 1994). The sulfide layer has a Re-Os age of 541 ± 16 Ma and an initial

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$^{187}\text{Os}/^{188}\text{Os}$ of 0.78 ± 0.19 (Mao et al., 2002). This value is equal to the $^{187}\text{Os}/^{188}\text{Os}$ ratio of ~ 0.80 of the shale host rock (Jiang et al., 2003), and is within the range of Cenozoic seawater (Sharma et al., 1997).

METAL DISTRIBUTION PATTERNS

The distribution of many of the metals in the sulfide-rich and carbon-rich layer is remarkably similar to that of seawater (Fig. 2). A broad suite of redox- and particle-reactive elements is enriched by a factor of $\sim 10^7$ with respect to present-day seawater. These elements include

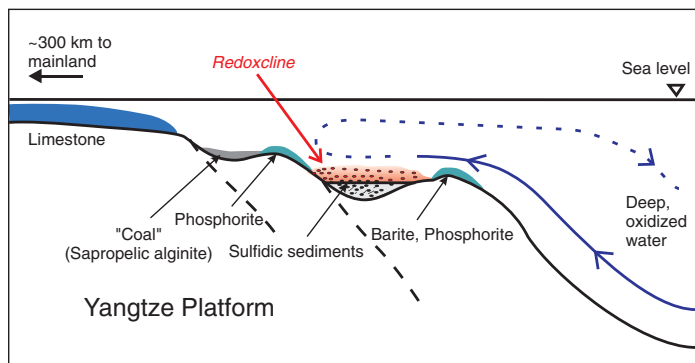


Figure 1. Proposed paleogeography of Early Cambrian Yangtze platform. Synsedimentary polymetallic sulfidic sediments were deposited in local sediment-starved, euxinic basins on then westward-facing passive continental margin (Northern Hemisphere), where widespread phosphorite deposition suggests upwelling of oxic ocean water.

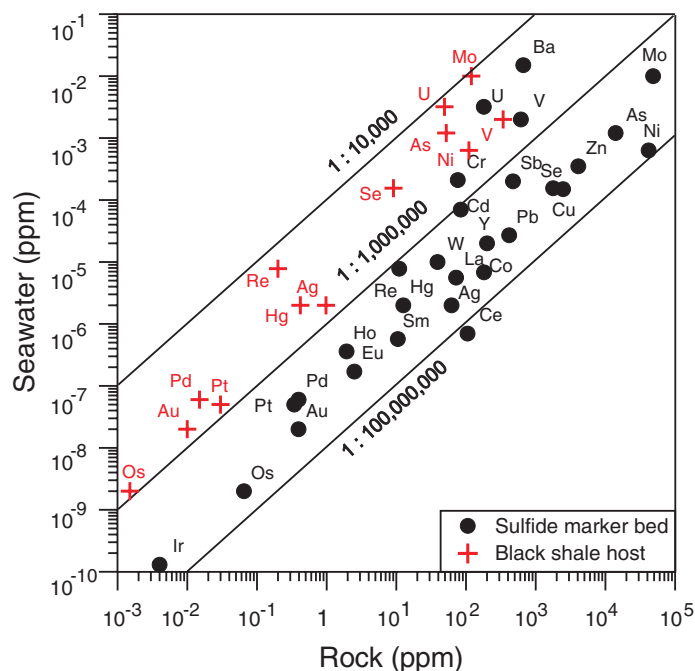


Figure 2. Average concentration of elements in sulfide marker bed and black shale host sequence compared to their concentration in present-day seawater. Large suite of redox- and particle-reactive elements in sulfide rock is enriched by factor of $\sim 3 \times 10^7$. Apparent excessive Ce enrichment is due to pronounced negative Ce anomaly in present-day seawater. Os is common Os, i.e., corrected for radiogenic Os from Re decay. Black shale host sequence displays enrichment in redox-sensitive elements at factor of 10^4 to 10^6 compared to seawater, typical of many ancient and modern anoxic sediments (Holland, 1979).

Mo, As, Ni, Zn, Cu, Se, Sb, W, Pb, Ag, Hg, Co, Y, and rare earth elements (REEs), Pd, Pt, Au, Ru, Os, and Ir. Some metals that are redox-sensitive but not chalcophile (V, Cr, U) are somewhat less enriched in the sulfide marker bed. However, vanadium and chromium concentrations as high as 1 wt% are observed in variably pyritic shale that occurs laterally to the polymetallic sulfide bed.

The REE pattern shows a pronounced positive Y anomaly ($\text{Y}/\text{Ho} = 56 \pm 3$; similar to that in present-day seawater; Bau, 1996). Ce anomalies are weak or absent, and there is a slight positive Gd anomaly (Fig. 3). Y-Ho fractionation is typical of aqueous environments and suggests that the source of the REEs of the sulfide bed was dominated by aqueous REE complexes (Bau, 1996). The black shale stratigraphically above the sulfidic unit has an unfractionated REE pattern with Y/Ho ratio of ~ 28 , typical of igneous and clastic sedimentary rocks, and does not display the weak positive Gd anomaly that is typical of seawater.

METAL DEPOSITION MODEL

Metal enrichment from seawater by a factor of $\geq 10^7$ has been documented in hydrogenous deep-sea sediments (Hein et al., 2000), but has not been reported in black shales. The possibility of such extreme degrees of metal enrichment in shallow, sediment-starved continental-margin settings such as that in Figure 1 can be tested by a rough calculation for a 5000-m-wide euxinic basin. Biological activity is taken to be intense in the oxic surface waters, which are continuously replenished by upwelling oxic deep waters. The mean rate, v , of the upwelling water passing across the basin is 1000 m/yr, i.e., similar to that on the continental slopes off Peru and California (Holland, 1984).

An oxic layer of thickness h , here 100 m, overlies the euxinic water column in the basin. Organic and sulfidic particles rain out and/or precipitate and are reprocessed by sulfate-reducing microbes, as in the Black Sea or in the Cariaco Basin on the Venezuela shelf (Dyrssen, 1999; Emerson and Huested, 1991; Piper and Dean, 2002). We assume that the upwelling seawater contains, as today, 10 ppb Mo, 0.5 ppb Ni, 0.05 ppt Pt, and 0.02 ppt Au (Nozaki, 1997).

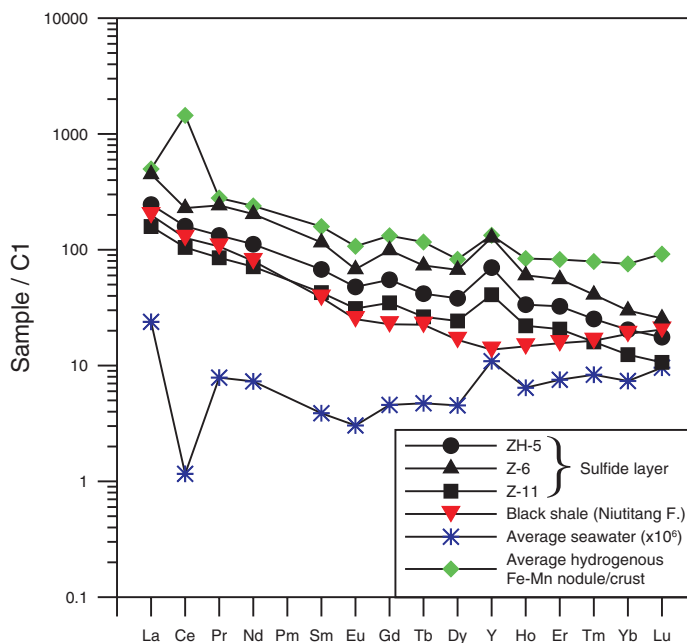


Figure 3. Rare earth element distribution patterns for three representative samples from sulfide layer, average black shale of Niutitang Formation, present-day seawater (Nozaki, 1997), and hydrogenous Pacific Fe-Mn crusts (Hein et al., 2000).

The volume, V , of seawater that passes annually across 1 m of the edge of the euxinic basin is

$$V = h \times v \times 1 \text{ m}^3/\text{yr} = h \times v \times 10^6 \text{ cm}^3/\text{yr}. \quad (1)$$

The quantity of a trace element, M_w , with a concentration c_m (g/g) in seawater (density $\sim 1 \text{ g/cm}^3$) that passes annually across the 1 m section of the euxinic basin is therefore

$$M_w = h \times v \times c_m \times 10^6 \text{ g/yr}. \quad (2)$$

If all of the quantity M_w is removed into the sediments of the euxinic basin, the amount m_w of the trace element that is added annually to 1 cm^2 of the basin is

$$m_w = \left(\frac{h \times v \times c_m}{W} \right) \times 10^6 \text{ g/cm}^2 \text{ yr}, \quad (3)$$

where W is the width of the basin in centimeters. For this basin, m_w is 20 $\mu\text{g Mo/cm}^2\text{yr}$, 1 $\mu\text{g Ni/cm}^2\text{yr}$, 0.1 $\text{ng Pt/cm}^2\text{yr}$, and 0.04 $\text{ng Au/cm}^2\text{yr}$. These are maximum values of the depositional rates. The actual values may, however, have been similar, since the extraction efficiency of these metals can be $>90\%$ in modern anoxic basins (Emerson and Husted, 1991).

These estimated deposition rates are surprisingly similar to those found in modern euxinic basins. The Mo and Ni depositional rates of the Cariaco Basin are as high as 4 $\mu\text{g Mo/cm}^2\text{yr}$ and 0.8 $\mu\text{g Ni/cm}^2\text{yr}$ (Piper and Dean, 2002), and the molybdenum accumulation rate in the seasonally anoxic Saanich Inlet, British Columbia, is 8 $\mu\text{g Mo/cm}^2\text{yr}$ (Zheng et al., 2000). At a Mo input of 20 $\mu\text{g/cm}^2\text{yr}$, ~ 50 k.y. are required to accumulate a 5 cm thickness of sulfidic sediments containing 5 wt% Mo (see GSA Data Repository Table DR1¹). The metal content of the Yangtze platform sulfidic sediments is several hundred times greater than that of sediments in modern euxinic environments. The difference requires that the rate of sedimentation of the Yangtze sulfidic sediments was several hundred times slower than that of modern euxinic sediments. The basins that contain the Yangtze sulfidic sediments were apparently sediment starved.

MOLYBDENUM ISOTOPE COMPOSITION

We have analyzed the isotope composition of molybdenum in five samples containing $>10,000$ ppm Mo from the sulfide marker bed at the Huangjiawan mine in Guizhou. As shown in Figure 4, their $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ value relative to modern ocean water (MOMO = mean ocean molybdenum; Siebert et al., 2003) is $-1.24\% \pm 0.10\%$ (2σ). Five of eight samples of the black shale host sequence stratigraphically near the sulfide layer but as much as 350 km from the Huangjiawan mine were found to have similar Mo isotope values, even though their Mo concentration was lower by up to three orders of magnitude (Fig. 4). The $\delta^{98/95}\text{Mo}$ values of the other three black shale samples scatter well outside the analytical uncertainty.

Quantitative scavenging of Mo preserves the isotopic signature of seawater, as has been demonstrated for some Black Sea sediments (Barling et al., 2001; Arnold et al., 2004). The very small scatter of the $\delta^{98/95}\text{Mo}$ values in the samples from the sulfide layer therefore suggests that the $\delta^{98/95}\text{Mo}$ value of seawater at that time was $-1.24\% \pm 0.10\%$. Complete Mo removal from solution requires sufficiently high H_2S concentrations in the bottom water to activate the geochemical switch, at which particle-reactive MoS_4^{2-} dominates over inert MoO_4^{2-} in seawater. The critical $\text{H}_2\text{S}_{\text{aq}}$ concentration is $\sim 10^{-5}$ M (Erickson and Helz, 2000). A bottom-water H_2S abundance below this H_2S level allows Mo isotope fractionation between MoO_4^{2-} and MoS_4^{2-} , resulting in anoxic sediments with variable

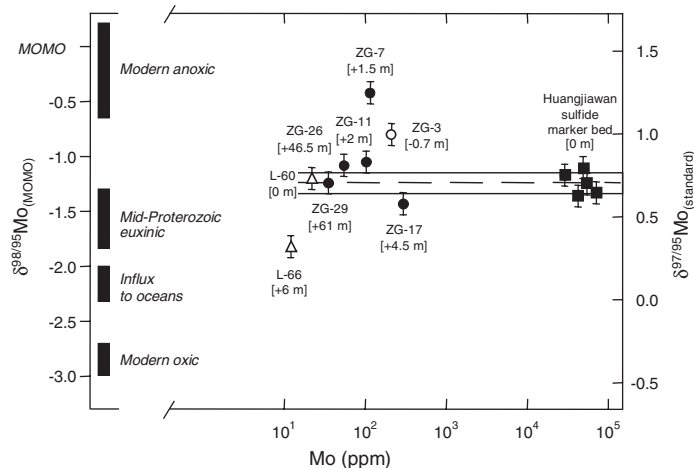


Figure 4. Mo isotopic composition vs. Mo concentration of five samples from Early Cambrian sulfide marker bed (Huangjiawan mine, filled squares; Mao et al., 2002) and eight samples from black shale host sequence. Six of black shale samples are of stratigraphically higher (filled circles) and lower (open circles) positions from Ganzipeng, ~ 350 km NE of Huangjiawan; Pan et al., 2004), where same marker bed is present. Two black shale samples are from Yuanling, ~ 300 km ENE of Huangjiawan (Zhu et al., 2004), where marker bed is not developed (open triangles). Numbers in brackets refer to stratigraphic position relative to sulfide marker bed. Error bars refer to 2σ external standard reproducibility. $\delta^{97/95}\text{Mo}_{\text{(standard)}}$ refers to notation of Arnold et al. (2004). MOMO—mean ocean molybdenum (Siebert et al., 2003). Black bars—Mo isotopic composition ranges of modern anoxic sediments (Black Sea, Cariaco basin) and Middle Proterozoic euxinic sediments (Arnold et al., 2004), influx of Mo to oceans, and modern oxic chemical sediments (Barling et al., 2001; Siebert et al., 2003).

Mo isotopic composition (Näglér et al., 2005). Such low H_2S levels may explain the scatter in the $\delta^{98/95}\text{Mo}$ values of the low-Mo black shales. Other processes, including remobilization of Mo during diagenesis and mild metamorphism, may also have contributed to the scatter (Kendall et al., 2006).

The isotopic composition of Mo in seawater reflects the relative proportion of anoxic and oxic sedimentation in the oceans, since there is a significant Mo isotope fractionation between oxic chemical sediments and ocean water (Siebert et al., 2003). The magnitude of the oxic Mo sink is still uncertain, because the importance of suboxic continental margin sediments as sinks for Mo has not yet been defined. If the effect of these sediments is unimportant, the relative magnitude of oxic and anoxic Mo sedimentation can be calculated as outlined by Arnold et al. (2004). The observed $\delta^{98/95}\text{Mo}$ of the Early Cambrian sulfide-rich samples indicates that the ocean Mo sinks were 35% oxic and 65% anoxic ($\pm 5\%$, based on 2σ analytical uncertainties). This distribution is similar to that in the Middle Proterozoic oceans (Arnold et al., 2004), but quite different from that in the modern oceans, where the model suggests that $70\% \pm 5\%$ of Mo sedimentation is oxic (Siebert et al., 2003). Inclusion of likely suboxic Mo scavenging in the model reduces the estimated amount of oxic Mo sedimentation in the modern oceans to $\sim 45\%$ (see Siebert et al., 2006). Little is known about the effect of suboxic sedimentation in the Cambrian oceans. However, its inclusion would decrease the estimated percentage of oxic Mo sedimentation. The oxic sink in the Early Cambrian oceans was therefore probably $<35\%$, i.e., significantly smaller than in the modern oceans.

CONCLUSIONS

The polymetallic marker bed on the Yangtze platform provides a rare snapshot of Early Cambrian seawater. Element correlations, i.e., lack of major interelement fractionation relative to seawater, for a broad range of chalcophile and redox-sensitive as well as particle-reactive elements,

¹GSA Data Repository item 2007097, Tables DR1 and DR2, chemical and Mo isotope data, is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

and the fact that Mo isotope composition does not vary significantly with Mo abundance, argue for quantitative scavenging of many metals from seawater. We propose that the extreme metal enrichment, unreported so far in marginal marine settings, is due to a paleogeographic situation, where coastal upwelling supported high productivity and where the surface oxic layer above small sediment-starved euxinic basins was continuously resupplied by communication with oxic seawater. Very low terrigenous input during the initial stages of the transgressive black shale event on the drowned Yangtze platform allowed for dominantly hydrogenous sedimentation in the stratified basins (sulfide generated in the deeper basin and metals supplied from above). The Mo isotope data and a lack of Ce anomalies in the sulfidic sediments suggest that anoxic depositional environments were more prevalent in the Early Cambrian oceans than today.

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