Investigation of Metal Associations in the Metal-Rich Black Shales of the Niutitang Formation in the Context of the Cambrian Explosion

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A transition from oxygen-deficient to oxygenated oceans triggered the evolution of complex multicellular life at the Precambrian-Cambrian boundary, 542 million years ago. At this time, both the evolution of metazoan radiation and the genesis of subeconomic Ni, Mo, Rare Earth Elements (REE) and Platinum Group Element (PGE) deposits were triggered in shallow water environments, on the Yangtze platform in China. A thin accumulation of Ni, Mo, Au, Ag, Se, Cr, V, Zn, U and PGEs and other metals including REE is developed within the Lower Cambrian Niutitang formation, and can be traced along the same stratigraphic horizon over distances of several hundreds of kilometers. This is one of the most enigmatic examples of a sediment-hosted base and precious metal deposit showing an association of ore-grade metals with organic matter (OM). The genesis of this and other such strata-bound deposits is poorly understood.

The Niutitang Formation is composed of stratiform cherts, nodular and bedded phosphorites, and black shales in its lowermost part below the Ni-Mo sulfide horizon, and organic carbon-rich black shales above the mineralized layer. The formation of phosphorite concretions commonly occurs within the first meters of sediments below the water-sediment interface during suboxic diagenesis of organic-rich deposits. Concentrations in REE measured in phosphate concretions were reported to be commonly 50-100 times greater than shale-normalized values. In addition, adsorption and complexation of metals by OM under highly reducing conditions has been previously observed in the water column and sediments.

The present study aims to investigate in details the spatial distribution of Ni, Mo, Au, Ag, Se, Cr, V, Zn, U and PGEs in this rare ore layer, providing further insights into the genesis of this metal accumulation. Preliminary organic analyses (rock eval pyrolysis) performed on 30 samples from the mineralized layer and surrounding black shales revealed very low amounts of pyrolizable compounds, limiting the use of traditional OM characterization techniques (i.e. biomarkers). Therefore, combined techniques such as microbeam XRF mapping and scanning electron microscopy (SEM) were used to investigate specific microscale distributions of phosphorite nodules, metals and organic-rich matrix. Analyses of the mineralized horizon revealed the presence of fine-scale segregations of metals. Various layers were detected in these samples, showing segregation of different metals at sub-mm scale. Some layers show fine laminations of phosphorite, Ni, As, Mo, and S. Other layers present brecciated textures of black shales with disrupted OM lenses, fragmented phosphorites and a high abundance of Ni, As, and S-rich clasts. Phosphorite nodules are surrounded by high concentrations of specific elements (i.e., As) accumulating on the edge of the nodules while V, Zn and Cu appear to be associated with the organic-rich matrix, which in some cases appeared to contain “tar-ball” fragments itself.

This fine-scale study of metals, organic-rich matrix and phosphorite nodules allows a greater understanding of metal associations in this unique, highly anoxic and sulfidic sedimentary system, in the context of the Cambrian bioradiation of metazoans.