6 Oral Presentations

6.1 <u>Ai, Jiayi.</u> Tracing the redox evolution of the palaeo-ocean through the Late Neoproterozoic in South China: insights from trace elemental proxies

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Earth experienced major changes during the late Neoproterozoic (Cryogenian and Ediacaran) to early Cambrian transition. Notably, these include continental rearrangement following the break-up of the Neoproterozoic supercontinent Rodinia, multiple occurrences of extreme glacial conditions as well as major perturbations in the chemical composition of the atmosphere–ocean system, which may have led to the radiation of multicellular life on Earth (Lenton et al., 2014). The well-developed sedimentary successions of South China offer the opportunity to study the redox evolution of the palaeo-ocean through geological time, which will shed light on the interactions between these major geo-bio events and the enrichment mechanism of organic matter preserved in post-glacial black shales.

Some of the trace elements can show variations in enrichments and solubility as a function of redox status of the depositional environment. These redox-sensitive trace metals, such as Mo, U and V, tend to be more soluble under oxidizing conditions and less soluble under reducing conditions, resulting in strongly authigenic enrichments in euxinic environments and exhibiting weaker covariation with TOC than in suboxic environments. To estimate the authigenic enrichment of a given element, a practical way is to normalise it to aluminium (Al), which is commonly overwhelmingly of detrital origin and usually immobile during diagenesis (Algeo & Maynard, 2004). Our data shows that Mo/Al, V/Al and U/Al in the study area roughly mirrors the variation of Mo, V and U.

Slope black shales of the interglacial Datangpo Formation and the post-glacial Doushantuo Formation show enrichment of Mo and V to different extents (Figure 1). There is strong enrichment in the black shales of the uppermost member (Member VI) of the Doushantuo Formation, with Mo ranging from 24.3-172 ppm (average = 53.4 ppm). The Mo enrichment in some samples exceeds the average of Phanerozoic euxinic shales (~100 ppm) and the average Mo/TOC ratio of ~25. Algeo & Lyons (2006) demonstrated that the Mo/TOC ratio of sediments in modern euxinic settings is positively correlated with the concentration of dissolved Mo in the water column, which scales with the local and/or global extent of euxinia. V enrichments of ~1350 ppm in Member VI are also comparable with the values of several thousand ppm observed in Phanerozoic anoxic shales. The concentration of U in Member VI ranges from 2.5–28.6 ppm (average = 18.6 ppm), which are similar to the highest value of 30 ppm observed in modern anoxic basins. Additionally, the value of the U/AI ratio in Member VI ranges from 0.49-9.0 (average = 3.7) (Figure 1e), which is comparable with the U/AI of the Black Sea. The strong enrichments of Mo, V and U in the black shales developed at the end of the Ediacaran period thus indicate euxinic sedimentary conditions as a result of the elevated intensity of sulphate reduction under higher sulphate flux and productivity, supporting the Late Neoproterozoic oxygenation event just prior to the Cambrian Explosion. This is consistent with the last significant negative carbon isotope excursion records (Jiang et al., 2007).



Figure 1: Trace-metal abundances (Mo, Mo/AI, V, V/AI, U, U/AI) and TOC from the Sturtian-age Tillite to Late Ediacaran strata. (QZM-Qianzimen; DTP-Datangpo; NT-Nantuo; DST-Doushantuo; DY-Dengying).

The concentrations of Mo, U and V show a significant shift at the boundary between Marinoan-age Nantuo tillites and the overlying black shales of the Ediacaran Doushantuo Formation, but decreased shortly thereafter (Figure 1). This suggests that the continental Mo and V fluxes were elevated for only short periods during the most rapid stages of glacial retreat.

In contrast, there are relatively weak enrichments of Mo, V and U in the organic-rich black shales of the Cryogenian Datangpo Formation. The Mo/Al and V/Al ratios vary between 0.25–4.4 and 7.7–25 respectively, with averages of 2.2 and 14.3 (Figure 1c, g), which are similar to the PAAS shale standard, but much lower than the modern Black Sea. The lesser enrichments of trace metals in the Cryogenian Datangpo black shales may record a local environment with less reducing conditions that was not conducive to redox-sensitive metal sequestration. This situation is also supported by V/Cr, V/(V+Ni) and a relatively good metal-TOC correlation. The suboxic-anoxic conditions recorded by the black shales suggest that the Datangpo Formation was deposited near the chemocline with occasionally ventilation of oxygen. This may indicate a temporary ocean oxygenation in the aftermath of the Sturtian Snowball Earth (Lau et al., 2017). This explanation for the lower concentration of trace metal elements preserved in Cryogenian black shales than in the Ediacaran black shales requires further comprehensive testing with other data such as sulphur isotopes (δ^{34} Spyrite) and the possibility of preserved biomarkers, which is currently being tested.

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