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Trace metals and nitrogen in Mo-S-C phases (Cambrian black shales, Southern China)

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Mixed layered Mo-S-C phases, pyrite (py) and Ni-Fe sulfides were analysed for trace metals, N and C, in order to understand its formational environment and the trace element scavanging mechanism. The sulfides occur in a few cm thick polymetallic layer in black shales above phosphorites, cherts, dolomites and baryte. These shales represent the biological explosion at the Precambrian/Cambrian boundary. The bulk sample contains 7 wt.% Mo, 2 wt. % Ni, 19 wt.% S and 13 wt.% C_{org} and C_{tot} (CO_2 : 58 wt.%), 14 wt. % CaO, 1.2 wt.% As, 2000 ppm Se, 5400 ppm Zn and, 450 ppm U and V, respectively. The ore horizon contains up to 1 ppm platinum group elements. Mo-S-C occur as a few hundred micron large rounded 'pebbles' including framboidal pyrite, as relict inclusions in diagenetic pyrite agglomerates and as sub- to euhedral grains around framboidal pyrite. They have an idealized formula of (Mo, Fe, Ni, Cu, Co, Zn, Sb)$_1$ (S, Se, As)$_2$ $C_7N_1O_{0.5}$ composed of $\sim$ 6 at.% Mo, 3.4 at.% Fe, 0.7 at.% Ni, 0.06 at. % Cu, 0.24 at. % As, 0.11 at.% Se, 19 at. % S, 60 at.% C, 1 at.% N, and 0.3-0.8 at.% O. Raman-spectroscopy reveals that C occurs in form of desordered graphite. The average C/N ratio (at.%) is 67. Pd (400-1000 ppm) is homogeneously distributed in Mo-S-C and is positively correlated with C, Se and Mo, and negatively correlated with N and Sb. Platinum is below the detection limit (50 ppm) in Mo-S-C, but reaches up to 80 ppm in py and Ni-Fe-sulfides. The C/N ratio of Mo-S-C is similar to that observed in marine organic matter and clay rich solution-fault breccias related to hy-

drothermal fluids in paleozoic carbonates with similar metal associations in S-China and to that from zooplankton at hydrothermal vents. Mo-enrichments are observed at modern chimney walls (TAG hydrothermal field). Shallow marine sediments infiltrated by hydrothermal fluids ($\sim$35mg/kg Mo) are inhabited by a dense community of hyperthermophilic, sulfur dependent heterotrophs (Japanese islands). Thus the extreme enrichment of Mo and the formation of Mo-S-C phases in the Chinese black shales might be related to a diffuse hydrothermal system favored the growth of N fixing and Mo depending bacteria (hyperthermo- or mesophilic). This is also supported by the incorporation of the biophiles (Pd, Se, As, Sb) in Mo-S-C whereas less biophile (Pt, Ni) are concentrated in later diagenetic py and Ni-Fe-sulfides.