

Copper, zinc, chromium and osmium isotopic compositions of the Teplá-Barrandian unit black shales

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Black shales represent unique sedimentary archives providing important clues into the marine conditions throughout the Earth's history. Transition metals like Cu, Zn and Cr commonly highly enriched in black shales serve as important micronutrients and therefore, inputs and outputs of these elements in the Earth's history is very important for ocean biology [1]. In addition, isotopic composition of Cu and Cr is redox sensitive providing crucial information about the extent of oxygenation if possible post-depositional events are inspected by Re–Os systematics. Here, we present combined isotopic data for Cu, Zn, Cr and Os for two black shale profiles (Hromnice and Kamencec) from the Teplá-Barrandian Unit (Bohemian Massif, Czech Republic) deposited in a semi-isolated basin with restricted seawater circulation and a large influence of hydrothermal activity at Neoproterozoic–Cambrian transition [2,3].

Normal black shales (NBS) and highly metalliferous black shales (HMBS) from both localities display distinctly different elemental and isotopic composition. HMBS have much higher metal concentrations (Mo+Ni+Zn+V > 1500 ppm and locally up to 7600 ppm), compared to NBS but there is no resolvable difference in their $\delta^{66}\text{Zn}$ and $\delta^{53}\text{Cr}$, showing overlapping large variations from -0.19 to $+0.55$ ‰ and -0.24 to $+2.24$ ‰, respectively. In contrast, HMBS show resolvable higher $\delta^{65}\text{Cu}$ values (up to $+1.13$ ‰) than NBS (< 0.77 ‰), combined with an absence of positive correlation between Cu, Zn and Os contents with their $\delta^{65}\text{Cu}$, $\delta^{66}\text{Zn}$ and γOs values. There is also no significant relationship between total organic carbon and isotopic composition. Variable geochemical discrimination plots along with our isotope data suggest mixed Cu, Zn, Cr and Os sources involving mafic, intermediate and felsic igneous rocks, coupled with local hydrothermal venting and dominant sources of dissolved Cu, Zn, Cr and Os in global ocean reservoirs.

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[1] Vance et al. (2016) *Phil Trans R Soc A* 374, 20150294

[2] Pašava et al. (1996) *Econ Geol* 91, 63-79. [3] Kurzweil et al. (2015) *GCA* 171, 121-142.