Speciation of molybdenum and tungsten in euxinic sediment using wavelength dispersive XAFS

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Molybdenum (Mo) is known as a redox sensitive element that indicates global redox change in palaeo environment. Although tungsten (W) belongs to the same group with Mo in the periodic table and has similar chemical properties, their solid-water distribution behaviors are defferent in modern oxic sea water [1]. However, the factors controlling their behaviors in palaeocean are not well known, because few studies have been conducted about speciation of them in anoxic and euxinic sediments. In this study, we determined chemical species of Mo and W in black shale in early Cambrian black shale where oceanic anoxic event was occured. Early Cambrian black shale widely exposed on the Yangtze Platform of South China was studied here [2]. Mineralogical information was examined by observation with optical microscope. Chemical species of Mo and W were determined by X-ray absorption fine structure (XAFS). For high sensitive measurement of W, Bent Crystal Laue Analyzer (BCLA) were introduced in front of the detector.

Concentration of Mo in the black shale was high (>5000 ppm), and its main chemical species was mainly Mo(IV)S_2. Linear combination fitting of obtained spectra indicated the presence of Mo adsorbed on pyrite suggesting that Mo was adsorbed on sulfide minerals such as pyrite and subsequently transformed to molybdenite. On the other hand, concentration of W in the black shale was much lower (30 ppm). Here introduction of BCLA successfully reduced interference X-rays of abundant scattering X-rays, and Ni Kβ and Zn Kα lines which allow us to measure W L_3-edge XAFS spectra. The spectra showed that W formed both sulfur-coodinated and oxigen-coordinated species in euxinic sediment. These species were derived from different distribution mechanisms such as (i) adsorption to sulfide minerals as sulfur-coordinated, and (ii) coprecipitation with carbonates as oxygen-coordinated species.

[1] Kashiwabara et al. (2013) *Geochim. Cosmochim. Acta* **75**, 5762–5784. [2] Xu et al. (2013) *Ore Geol. Rev.* **52**, 66-84.