

Cu and Zn isotope fractionation during weathering of highly metalliferous black shales

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The Cu and Zn isotopic compositions of black shales, which are related to the geochemical cycling of heavy metal elements within oceans, are not well constrained. The concentrations and isotopic compositions of Cu and Zn in the fresh and weathered metalliferous shale and siliceous interbeds of the Maokou Formation in central China are reported to investigate the likely controlling factors of metal mobility and redistribution during continental weathering. For the fresh metalliferous shales and cherts from drill cores, the moderate enrichment of Cu and homogeneous Cu isotopic composition are rationalized in term of quantitative scavenging under anoxic conditions [1]. The high concentrations of Zn and the slightly positive Zn isotopic shift relative to the classic clastic sediments and igneous rocks can be explained by biological uptake of metals during deposition [2].

The weathered shales and cherts have an extremely large range (25.82‰) of Cu isotopic compositions and a small variation (0.53‰) of Zn isotopic ratios. The redox cycling is the primary mechanism for the large range of Cu isotopic variation, in contrast to the small isotopic variation of Zn. The vertical strata and faults could provide pathways for migration of fluids to enhance leaching activities during weathering. The preferential release of heavy Zn and Cu isotopes from the sulfides in shales into leaching fluids during oxidative weathering, may be responsible for the negative isotopic shift in strongly weathered shales and the positive isotopic shift during the re-mineralization of Cu and Zn from the leachate [3]. According to our results, the variations of Cu and Zn isotopes during continental weathering need to be considered when comes to the calculation of flux into oceans. In particular, Zn isotopic composition of riverine flux from shale weathering into oceans may be variable and not be equal to the composition of igneous rocks (0.3‰).

- [1] Lehmann *et al.* (2007) *Geology*, **35**(5), 403-406.
[2] Andersen *et al.* (2011), *EPSL* **301**(1-2), 137-145. [3] Mathur *et al.* (2012), *CG*, **304**,175-184.