



Copper and zinc isotope fractionation during deposition and weathering of highly metalliferous black shales in central China



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ABSTRACT

Black shales represent one of the main reservoirs of metals released to hydrosphere via chemical weathering and play an important role in geochemical cycling of metals in the ocean. The stable isotope systematics of transitional metals (e.g., Cu and Zn) may be used as a proxy for evaluating their geochemical cycling. To investigate the behaviors of Cu and Zn isotopes during metal enrichment of black shales and the migration during weathering, in this study we reported Cu and Zn concentration and isotope data for unweathered and weathered metalliferous shales and siliceous interbeds from the Maokou Formation in central China. The unweathered shales and cherts have moderately enriched Cu and Zn concentrations with silicate-like $\delta^{65}\text{Cu}$ ($+0.14 \pm 0.09\%$, 1σ) but heavy $\delta^{66}\text{Zn}$ ($0.51 \pm 0.11\%$, 1σ). The elevated $\delta^{66}\text{Zn}$ values reflect an important contribution from seawater via sulfide precipitation and/or organic matter (OM) adsorption. The Zn isotopic compositions of these metalliferous shales are different from those of the 'normal' shales, highlighting the potential of Zn isotopes as a tracer for metal enrichment in natural systems.

The weathered shales and cherts have an extreme $\delta^{65}\text{Cu}$ range from -6.42% to $+19.73\%$ and a modest $\delta^{66}\text{Zn}$ range of $+0.25\%$ to $+0.78\%$. The strongly weathered samples have lower Cu and Zn concentrations and lighter isotopic compositions compared to the weakly weathered samples. The leaching of Cu- and Zn-rich sulfides in shallow depths and their downward transport and re-fixation by Fe-sulfide account for the Cu and Zn isotope fractionation, with the huge Cu isotope variation generated by multistage redox leaching. In general, $\delta^{66}\text{Zn}$ values of the weathered shales shift towards light values compared to the unweathered protoliths, suggesting that shale weathering releases Zn which is isotopically heavier than igneous rocks and the global riverine average ($+0.33\%$). Our results therefore indicate that Cu isotopes can be extremely fractionated during weathering of Cu-rich shales and both heavy Cu and Zn isotopes are preferentially released into fluids during shale weathering. These results should be considered when evaluating geochemical cycling of Cu and Zn in the modern or past oceans.

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1. Introduction

Shales account to about 25.4% proportion of exposed continents, linked to the cycling of carbon, nitrogen, phosphorous, sulfur, oxygen and heavy metals such as copper, zinc, iron, molybdenum, vanadium, and uranium (Huyck, 1990; Amiotte Suchet et al., 2003). Trace metals can be enriched in black shales, which become metalliferous so that they are often associated with economically important ore deposits. On the other hand, metalliferous black shales are sometimes the threat to natural environment (Woo et al., 2002). The metals in black shales are mainly in the forms of sulfide and complex incorporated with organic matter (OM) (Nijenhuis et al., 1999; Brumsack, 2006). The sulfide minerals and OM in metalliferous shales tend to decompose under

oxidizing conditions and break down at low pH due to the leaching of sulfide without the buffering material. Subsequently, the release of heavy metals from these shales via weathering is often linked to water pollution, land contamination, instability of ecosystem and potential threat to human health (Woo et al., 2002).

Copper (Cu) and zinc (Zn) are two of the most important transitional metals and micronutrient elements. It has been well known that biological process significantly fractionates Cu and Zn isotopes (Maréchal et al., 2000). For example, Andersen et al. (2011) reported that the biogenic opal extracted from bulk marine sediment samples has heavy Zn isotopic composition ($+0.7\%$ to $+1.5\%$) relative to clastic sediments ($\sim +0.25\%$) in ocean (Maréchal et al., 2000). These findings make Cu and Zn isotopes a new tool for investigating the biological cycling of metals on the modern and ancient Earth (Maréchal et al., 2000; Little et al., 2014). A recent investigation sheds light on the global oceanic budget and modern oceanic mass balance of Cu and Zn using their isotopes (Little et al., 2014). The inputs from rivers and dust have light

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Cu isotope compositions ($\delta^{65}\text{Cu}$ relative to NIST 976; +0.63‰) compared to seawater (+0.9‰), and the oxic sediments are a complement reservoir with light Cu isotope composition (+0.31‰). For Zn, the riverine inputs have the same Zn isotopic composition (+0.33‰) as the lithogenic Zn. However, the Zn isotopic compositions of seawater and the outputs (Fe–Mn crusts and carbonates) are all heavier than that of the inputs. The present model of oceanic mass balance of Zn thus has problems with the missing of an isotopically light sink or an isotopically heavy input. Especially, Zn isotopic signatures of the sink in the euxinic sediments (e.g., shales) are still unclear but may be very important for understanding mass balance of Zn in the ocean.

Because of the biological toxicity with excess concentration (Påhlsson, 1989), the mobility and environmental behavior of Cu and Zn in the critical zone (soils and weathering horizons) have been recognized and the isotope fractionation mechanism has already drawn attention (Fernandez and Borrok, 2009; Liu et al., 2014a; Li et al., 2015). However, the Cu and Zn isotopic compositions of shales and the fractionation during weathering are not well studied or debated. Several experimental and field studies have investigated the isotopic behaviors of Cu and Zn during chemical weathering. For example, the leaching experiments of Cu and Zn sulfide-rich rocks show that the heavy Cu and Zn isotopes are preferentially enriched in fluids (Fernandez and Borrok, 2009; Wall et al., 2011). Experimental studies show that the dissolved Zn fractions are isotopically light during the early stage of biotite granite dissolution (Weiss et al., 2014). For Cu, Mathur et al. (2012) observed that Cu isotope fractionation during weathering of pyrite-bearing soils developed on shales obeys the Rayleigh fractionation model. Liu et al. (2014a) reported that organic matters can play a key role in Cu isotope fractionation with organically-bound Cu enriched in light isotopes. Compared with Cu isotopes, the behavior of Zn isotopes during continental weathering is less constrained. Thus, the study on Cu and Zn isotopic compositions of fresh and weathering shales may hold new constraints on the inputs and outputs of oceanic Cu–Zn budget.

This present study aims to study Cu and Zn isotopic signatures of fresh shales and to investigate the behaviors of Cu and Zn isotopes during shale weathering. The fresh and weathered metal-rich shales and cherts in horizontal and vertical strata from Maokou Formation in central China are chosen for this study. The results shed lights on (1) oceanic mass balance of Cu and Zn and (2) the application of Cu and Zn isotopes as tracers of geochemical cycling and metal mobilization during continental weathering.

2. Samples

The regional geological setting for samples studied in this study was previously described in detail by Zhu et al. (2014) and is briefly summarized below. The fresh and weathered shales and cherts of the Lower Permian Maokou Formation (P_1m^3) were collected from the Yutangba ($30^\circ10'810''\text{N}$, $109^\circ46'728''\text{E}$) and Shadi ($30^\circ20'304''\text{N}$, $109^\circ45'124''\text{E}$) in the Enshi area, central China. Yutangba is located in the northwestern limb of the Shuanghe syncline in the northeastern part of the upper Yangtze Platform fold belt, sited about 81 km southwestern of the Enshi Prefecture in the Hubei Province (Fig. 1). The strata are horizontal at the Shadi and mainly consist of carbonaceous shales and cherts, whereas the strata at Yutangba strike ENE and dip $40\text{--}70^\circ$ SSE. The strata at Yutangba develop SSE-dipping normal faults. The target strata, carbonaceous shales of Maokou Formation (P_1m^3), are extremely polymetallic-enriched and several Se ore deposits occur in the studied area. At the same time, the incidence of Se poisoning is arising since 1960s in this area, leading to the displacement of population (Yang et al., 1983).

Both the unaltered and weathered rocks from Yutangba and Shadi were selected and unaltered samples obtained from drill cores at Yutangba. Samples at Shadi are gathered vertically across the horizontal strata from a newly cut profile, sorted into the strongly weathered, the

weakly weathered and the unweathered samples identified by observations of hand specimens, the distance from the top and the concentrations of total sulfur (TS), total organic carbon (TOC) and total iron (TFe). The weakly weathered and unweathered samples have high TOC, TFe and TS contents and significantly positive correlation between TFe and TS ($R^2 = 0.85$). For strongly weathered samples, TOC is heavily depleted; TS contents are variable due to some efflorescent salts; TFe is enriched and has negative correlation with TS ($R^2 = 0.98$) (Zhu et al., 2014).

At Yutangba, two series of weathered samples were sampled horizontally across the vertical strata. Transect 1 (T1; cp0 prefix) was sampled at 2 m height above the floor at an interval of ca. 0.1 m. Roughly 7 m height above the floor, transect 2 (T2; YTB prefix) was sampled and samples from this transect are weathered more strongly than samples from transect 1 (Zhu et al., 2014). Samples from T2 have much lower TOC, TS and TFe contents than rocks from Shadi and T1. Fault crossed transects and weakened the strength of rocks, tending to accelerate the chemical weathering rate of rocks. Fault developed nearly around the samples YTB 25 and cp015. Totally, five unaltered samples and fifty-six weathered samples from Yutangba and Shadi were selected here for trace elements and Cu and Zn isotope analyses. These samples are well-characterized and have been studied for Se isotopes (Zhu et al., 2014).

3. Methods

3.1. Trace elements analysis

The concentrations of trace elements are analyzed on ELAN DRC-e inductively coupled plasma-mass spectrometry (ICP-MS) at the Institute of Geochemistry, Chinese Academy of Sciences (CAS). The method is outlined in Liang et al. (2000) and described briefly below in summary. Rock powders were completely dissolved in HF (38%) and HNO_3 (68%) at 200°C using high-pressure PTFE bomb. The samples are re-dissolved in 1% HNO_3 for trace element analysis after evaporation to dryness. The measured trace elemental concentrations are corrected with the addition of Rh as an internal standard. The relative standard deviation (RSD) is less than $\pm 10\%$.

3.2. Cu and Zn isotope analysis

All chemical procedures were performed in laminar flow hoods (Class 100) in the clean room (Class 1000) with filtered air. All beakers were PTFE (Savillex®). Double distilled reagents and $\geq 18.2\text{ M}\Omega$ water were used for sample dissolution and all other processes. Approximately 20 mg of powder was digested in Teflon vessels using high pressure Parr reactor bombs with a mixture of HF, HNO_3 and HCl at 190°C . Each portion, added with 2 to 3 ml of HNO_3 , was then heated in oven over 36 h at 160°C after decomposing carbonate minerals in concentrated HF (38 vol.%) and HNO_3 . H_2O_2 was added to decompose the organic matter. If the samples were not dissolved completely, the residues were re-dissolved in 50% HNO_3 . After complete digestion, 1 ml of 8 N HCl was added and the sample was heated to dryness. Dissolved samples were finally prepared in 1 ml of 8 N HCl + 0.001% H_2O_2 for chemical ion-exchange separation.

Copper and zinc were separated with a single-column procedure modified from Maréchal et al. (1999). The procedure for chemical purification and Cu isotopic analysis was reported in previous studies from our group (Liu et al., 2014a, 2014b, 2015; Li et al., 2015). The procedure for Zn isotope analysis is outlined in this study.

The samples were loaded on pre-cleaned column stuffed with 2 ml Bio-Rad strong anion resin AG-MP-1M. Copper was collected in the 24 ml of 8 N HCl after 10 ml of 8 N HCl is applied to elute the matrix. 18 ml of 2 N HCl + 0.001% H_2O_2 was then added to elute the Fe fraction. Zinc was collected in the following 10 ml of 0.5 N HNO_3 after 2 ml of 0.5 N HNO_3 was discarded. After evaporating to dryness at 80°C and

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