The geochemical behavior of Cu and its isotopes in the Yangtze River

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Abstract:

Copper (Cu) isotopes can be a useful tool to constrain the interaction of water and the environment, but they have not been widely applied to riverine research in the preceding decades. Isotopically heavy Cu in rivers (global average: about +0.7‰) compared to rocks (at about 0‰) has been attributed to: a) the mobilization of heavy Cu during oxidative weathering, and b) partitioning between an isotopically heavy, organically complexed dissolved pool, and an isotopically light pool adsorbed to particulates. Here, we report Cu concentrations and isotope ratios of the main stream of the Yangtze River and its several tributaries. We find that the Yangtze River exhibits anomalously heavy Cu isotope compositions compared to other rivers: $\delta^{65}\text{Cu}_{\text{NIST 976}}$ of dissolved Cu for the main stream, from Chongqing to Nanjing, ranges from +0.59 to +1.65‰, while the tributaries vary from +0.48 to +1.20‰. A negative correlation is observed between Cu concentrations and Cu isotope compositions.

We attribute the anomalous Cu isotope geochemistry of the Yangtze River to two key features of the basin: first, the influence of the Three Gorges Dam (TGD), and second, the presence of extensive Cu sulphide deposits close to the lower reaches of
the river. In the upper reaches, downstream towards the TGD, $\delta^{65}$Cu values increase as Cu concentrations decrease, reflecting the preferential adsorption of light Cu by sedimenting particulate phases. $\delta^{65}$Cu values continue to increase to a maximum of +1.65‰ in the middle reaches, at Guangxingzhou. The lower reaches, from Jiujiang to Tongling, are characterized by less positive values of $\delta^{65}$Cu (at about +0.60‰), due to the oxidative weathering of Cu sulphide deposits. The overall Cu-$\delta^{65}$Cu trend in the river reflects mixing of these waters from the lower reaches, influenced by Cu sulphides, with waters from upstream, which have lower Cu concentrations and elevated $\delta^{65}$Cu values.

**Keywords:** Yangtze River; Cu isotopes; Three Gorges Dam; Cu sulphide deposits

1. Introduction

Copper has two stable isotopes, $^{63}$Cu and $^{65}$Cu, and is a principal metal in ore-forming processes. Copper isotopes may be a useful tool to trace the fate of Cu during long-term geological processing, and to shed light on its biogeochemical cycling in the natural environment (Zhu et al., 2000; Larson et al., 2003; Weinstein et al., 2011). In recent years, the application of multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has brought a great improvement in the determination of Cu isotope ratios (Maréchal et al., 1999; Bermin et al., 2006), and Cu isotopes are increasingly being applied in the fields of geology, biology and environmental sciences (Moynier et al., 2017).

Recent work on Cu isotopes in rivers and the oceans has demonstrated that
dissolved Cu (+0.02 to +1.45‰) is isotopically heavy compared to the solid Earth (about 0‰) (Vance et al., 2008; Takano et al., 2014; Little et al., 2018). Several possible mechanisms to explain this phenomenon have been suggested. First, isotopically light Cu may be preferentially adsorbed by clay and oxy(hydr)oxide minerals, either during weathering (Vance et al., 2016; Guinoiseau et al., 2017; Kusonwiriyawong et al., 2017; Little et al., 2019) or via scavenging of Cu from the aqueous phase (Takano et al., 2014). Laboratory sorption experiments indicate that light Cu isotopes are preferentially adsorbed onto kaolinite (Li et al., 2015) and Mn oxides (Ijichi et al., 2018), though heavy isotopes tend to be adsorbed onto iron oxy(hydr)oxide surfaces (Balistrieri et al., 2008; Pokrovsky et al., 2008). In addition, bacteria-metal interaction experiments indicate that live bacteria cells preferentially take up the lighter Cu isotope regardless of the experimental conditions (Navarrete et al., 2011).

Second, organic complexation dominates the speciation of Cu in rivers and oceans (Vance et al., 2008; Takano et al., 2014; Thompson et al., 2014; Thompson and Ellwood, 2014; Little et al., 2018; Baconnais et al., 2019) and organic ligands preferentially complex isotopically heavy Cu in the dissolved phase (Ryan et al., 2014). Dead bacterial surfaces preferentially adsorb the heavier Cu isotope, which likely reflects fractionation due to complexation with organic acid surface functional group sites (Navarrete et al., 2011). During weathering, organic complexation of the heavier Cu isotope has been proposed as one mobilization mechanism for Cu (Bigalke et al., 2011; Vance et al., 2016; Little et al., 2019).
Third, the oxidation (or reduction) of Cu can also lead to isotope fractionation. Oxidised Cu$^{2+}$ species will tend to accumulate heavy Cu isotopes, while reduced Cu$^{+}$ species will be isotopically light (Ehrlich et al., 2004; Asael et al., 2007; Fujii et al., 2013, 2014; Sherman, 2013). The abiotic fractionation of Cu in Cu sulphide-rich ore deposits is associated with the preferential oxidation of $^{65}$Cu$^+$ at the mineral surface and the formation of an isotopically heavy oxidized layer (Kimball et al., 2009). This layer is then leached during further weathering, releasing heavy Cu to the dissolved phase. It has been documented that leachate Cu solutions derived from sulphides such as chalcopyrite (Mathur et al., 2005; Fernandez and Borrok, 2009; Kimball et al., 2009), chalcocite (Mathur et al., 2005), bornite (Wall et al., 2011), and enargite (Kimball et al. 2009) have $\delta^{65}$Cu values that range from +1.0 to +3.5‰ relative to the initial sulphide (Mathur et al., 2014; Song et al., 2016).

Extensive studies on the geochemistry, hydrology and environment of the Yangtze River have been carried out for more than 140 years (Zhang et al., 1998; Chen et al., 2001; Du et al., 2001; Chen et al., 2002; Ding et al., 2004, 2014; Chetelat et al., 2008, 2009, 2013; Wu et al., 2013; Zhang et al., 2014; Wang et al., 2015). Several studies have demonstrated that the Three Gorges Dam (TGD) has led to many changes to the environment of the Yangtze River and surroundings (Xu and Milliman, 2009; Li et al., 2011; Guo et al., 2012; Luo et al., 2012). To date, some Cu isotope data have been presented for the Yangtze River at Wuhan (Vance et al., 2008), showing that the $\delta^{65}$Cu of the Yangtze River is anomalously positive compared to other global rivers, which have a general tendency towards lower dissolved Cu.
concentrations for heavier dissolved Cu isotope compositions. Here, we present a more comprehensive Cu isotope dataset for the Yangtze River and its tributaries, which provides useful information to help understand the geochemical behavior of Cu and its isotopic fractionation during weathering and in the aqueous environment.

2. Methodology

2.1. Geological setting

The Yangtze River is the third-largest river in the world and plays an important role in human society, such as freshwater supply, transportation, flood prevention, and electricity. The Yangtze River, with a length of about 6300 km, lies between $90^\circ33′-122^\circ25′$ E and $24^\circ30′-35^\circ45′$ N and covers a total area of $1.81\times10^6$ km$^2$ (Chen X. et al., 2001; Chen et al., 2002). According to hydrologic and geographic conditions, the Yangtze River can be divided into three sections (Fig. 1): the upper reaches, from river source to Yichang (CJ-30); the middle reaches, from Yichang (CJ-30) to Hukou (near JJ-1); and the lower reaches, from Hukou (near JJ-1) to the East China Sea (Chen Z. et al., 2001).

The Yangtze River is situated in a subtropical monsoon climate region and the annual precipitation of most areas through which it flows ranges from 800 to 1600 mm (Ding et al., 2013). The drainage basin encompasses a very diverse range of rock types, which is mainly overlain by sedimentary rocks composed of marine carbonates, evaporites and alluvium from Precambrian to Quaternary age (Chetelat et al., 2008; Ding et al., 2014). Carbonate rocks are widely spread throughout the basin and are
particularly abundant in the southern part (Yunnan, Guizhou and western Hunan Provinces) and the sub-basin of the Hanjiang (Chen et al., 2002; Chetelat et al., 2009). Clastic rocks are mainly found in the upper reaches (Fig. 1).

The Yangtze River flows from the Qinghai-Tibet Plateau to the East China Sea and passes through the Three Gorges Dam (TGD) at Yichang city, Hubei province (Chen et al., 2002). The intercept of the TGD has affected the Yangtze River discharge, which caused a decrease in sediment supply to the East China Sea (Chen et al., 2008; Li et al., 2011; Guo et al., 2012; Luo et al., 2012).

**2.2. Sampling and analytical methods**

Samples from Wuhan to Nanjing (the main channel and associated tributaries) were collected during September 2013, and samples from Chongqing to Chibi (the main channel and associated tributaries) were collected at the end of July 2014 (Fig. 1). The average annual precipitation and discharge of the Yangtze River basin in 2013 were 1029.6 mm and 27506.7 m³/s. In 2014, the average annual precipitation was 1100.6 mm and the average discharge was 31774.2 m³/s (data from the Changjiang & Southwest Rivers Water Resources Bulletin), with no significant differences of the precipitation and discharge from 2013 (7% and 15%, respectively). The climate of the Yangtze River basin is rainy and hot in both July and September (Changjiang & Southwest Rivers Water Resources Bulletin). Therefore, the two datasets we collected are comparable and can be discussed together. The vertical heterogeneities are present in the river sections (Bouchez et al., 2010; Guinoiseau et al. 2016), and we only collected surface water samples in this study. Samples were collected by boat, distally
from the riverbank. A long (approx. 15 m) rope was attached to the sampling bottle to collect samples (2-4 L) as great a distance from the bow of the boat as possible. The water samples were collected in pre-cleaned plastic bottles (PP) that were leached with ultra-pure HCl (1 M) for 48 h, and then rinsed four times with Milli-Q water. Clean bottles were rinsed twice with ambient river water before final collection of water samples. The pH, electrical conductivity (EC) and dissolved oxygen (D.O.) were measured using a Multi-3410 portable multiparameter digital dual input analyzer (Table 1).

All indoor work was carried out under “class 100” laboratory conditions and all reagents were purified in-house prior to use. Within 5 days of collection, samples were filtered through 0.22 μm cellulose acetate filter membranes by SHZ-D (Ⅲ) SHB-3 Water Circulating Vacuum Pump. These <0.22μm filtered water samples are referred to as “dissolved” (they may contain some colloidal material). Filtered samples were then acidified to pH < 2.5 using double sub-boiling distillation concentrated HNO₃. About 250 mL of each was evaporated to dryness on a hot plate at 100°C. After that, 2-3 mL 8.5 M HCl + 0.03% H₂O₂ was added and samples evaporated to dryness once more, to convert all cations to chloride species. The final dry residues were redissolved in 1 mL 8.5 M HCl + 0.03% H₂O₂ for the purification of Cu using the AG MP-1M anion exchange resin (Bio-Rad, 100-200 mesh) (Hou et al., 2016), which followed a modified protocol from Maréchal et al. (1999). The total procedural blank of the process was <1.0 ng, accounting for less than 1.0% of the Cu concentration of our measured solution samples. A further 50 mL of each filtered
water sample was dried down to analyze Sr isotope ratios. The Sr separation from major elements for isotopic analysis was carried out using an AG50W-X8 cation exchange resin (Bio-Rad, 200-400 mesh) and 2.5 M HCl (1 mL for load, 18.6 mL for rinse, 12 mL for elute) (Hans et al., 2013). The pure Sr solutions were then evaporated to dryness to be measured.

All samples were analyzed for major element (Na, Mg, Ca) and trace element concentrations by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Agilent Technologies 7700 series) in the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), Wuhan, China. Indium was used as an internal standard to correct for instrumental drift and eventual matrix effects. The ICP-MS internal precision was generally lower than 2% for most of the elements, the Cu detection limit was 1 nmol/L and the relative standard deviation (RSD) was lower than 5%.

Copper isotope compositions were measured at GPMR using a Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) (Neptune Plus, Thermo Finnigan Scientific, Bremen, Germany). The samples were introduced using a conventional system that consists of a tandem quartz spray chamber (cyclone + standard Scott double pass) coupled with a low flow PFA nebulizer (50 μL/min). We measured Cu isotope ratios in low-resolution mode and used a combined standard sample bracketing and internal normalization method (C-SSBIN) with Ga addition to correct mass bias. More details are given in Hou et al. (2016).

Copper isotope compositions are reported relative to the NIST SRM 976 standard. Delta per mil (‰) notation for the Cu isotope ratio is employed as follows:
\[
\delta^{65}\text{Cu} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000
\]

(1)

In this equation, \(R_{\text{sample}}\) and \(R_{\text{standard}}\) represent the measured \(^{65}\text{Cu}/^{63}\text{Cu}\) ratios of sample and NIST SRM 976 standard, respectively. As we were not able to duplicate all the samples, the error of 0.06‰ given is an external reproducibility obtained on the repeated analysis of several USGS reference materials from the GPMR MC-ICP-MS.

The \(\delta^{65}\text{Cu}\) for three USGS reference materials are reported in Table 2. Values for BHVO-2, BCR-2 and GSP-2 fall within the ranges recommended in Moynier et al., (2017) and Liu S. et al., (2014).

Strontium isotopes were measured at GPMR using a Thermal Ionisation Mass Spectrometer (TIMS) (Triton, Thermo Finnigan Scientific, Bremen, Germany). The long-term measured value of NIST 987 standard was \(^{87}\text{Sr}/^{86}\text{Sr} = 0.71024 \pm 0.00001\) (2σ, \(n \geq 50\)), which was in good agreement with the given value of 0.71023 ± 0.00001 (Wang et al., 2007). The value of procedural standard “BCR-2” was \(^{87}\text{Sr}/^{86}\text{Sr} = 0.705019 \pm 0.000009\) (2σ), which corresponds with the reference value of 0.705015 ± 0.000013 (Balcaen et al., 2005).

3. Results

The pH of the water samples ranges from 7.37 to 8.36 and dissolved oxygen (D.O.) from 5.06 to 8.64 mg/L. The electrical conductivity (EC) of the main stream ranges from 274 to 404 μS·cm\(^{-1}\), while the tributaries have a wider range of 148 to 709 μS·cm\(^{-1}\). The concentrations of Ca and Mg in the Yangtze River main stream water range from 833 to 1225 μmol/L and 304 to 490 μmol/L, respectively, with decreasing trends from the upper to lower reaches (Fig. 2). The main stream water of
the Yangtze River has considerably higher Sr concentrations (1924 to 4865 nmol/L) and slightly lower $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios (0.709923 to 0.711139) (Table 1) than the global average river values of dissolved Sr (890 nmol/L) and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio (0.7119) (Palmer and Edmond, 1989), consistent with the data of Wang et al. (2007).

The Cu concentration of the main stream and tributaries ranges from 16.0 to 97.4 nmol/L and 17.2 to 72.4 nmol/L, respectively, while the isotopic composition of dissolved Cu ranges from +0.59 to +1.65‰ and +0.48 to +1.20‰, respectively (Table 1). As shown in Figure 3, most of the $\delta^{65}\text{Cu}$ values are consistent with previously published data for global rivers (+0.02 to +1.45‰), but are relatively more positive than that of the global discharge-weighted average (+0.68‰) (Vance et al., 2008). The upper reaches (upstream of the TGD), which show increasing $\delta^{65}\text{Cu}$ values downstream (Fig. 3), have more positive values of $\delta^{65}\text{Cu}$ (+1.01 to +1.45‰) and lower concentrations (16.0-38.9 nmol/L) than the lower reaches (Jiujiang to Nanjing, +0.59 to +1.16‰, 25.3-97.4 nmol/L). The most positive $\delta^{65}\text{Cu}$ values are observed in the middle reaches, downstream of the TGD at Guangxingzhou (+1.65‰) and Leigutai (+1.50‰).

Furthermore, a robust correlation ($r = -0.88$, $p < 0.01$, N = 20) between Cu concentrations and the $\delta^{65}\text{Cu}$ of dissolved Cu in the Yangtze River main channel shows a tendency towards heavier dissolved Cu isotope compositions for lower dissolved Cu concentrations, and the $\delta^{65}\text{Cu}$ values of the Yangtze River are always more positive than other rivers with similar Cu concentrations (Fig. 4). In the
following discussion, we review the possible processes that control this Cu-δ^{65}Cu trend.

4. Discussion

4.1. Atmospheric and anthropogenic sources of Cu

Chetelat et al. (2008) estimated that the proportion of cations supplied by atmospheric input to the Yangtze River ranges from 2 to 10%. The maximum measured Cu concentration of atmospheric precipitation from Chongqing to Shanghai is about 315 nmol/L (Ai, 2011; Hu et al., 2012; Liu G. et al., 2014; Peng, 2014). The average annual precipitation of the Yangtze River basin was 1029.6 mm in 2013 and 1100.6 mm in 2014 (data from the Changjiang & Southwest Rivers Water Resources Bulletin). Therefore, the product of average annual precipitation (i.e. 1029.6 mm, 1100.6 mm) and Cu concentration (i.e. 315 nmol/L) can be used to estimate an atmospheric Cu flux over the Yangtze River basin of up to about 21,000 g/km^2/yr.

Takano et al. (2014) determined δ^{65}Cu values in rainwater of Japan, finding a range of -0.12 to +0.03‰, and thus presumed the δ^{65}Cu value for atmospheric input to be ~0‰, close to that of the bulk silicate Earth (+0.07 ± 0.10‰ (2SD), Liu et al., 2015; Savage et al., 2015; Moynier et al., 2017). Rain is thus one important pathway delivering Cu (both directly in runoff, and in indirectly via the washing in of solid particles) to the Yangtze River. However, assuming a lithogenic Cu isotope composition, rainwater cannot explain the heavy isotopic compositions observed in the river.

Potential anthropogenic Cu inputs to the river include agriculture (fertilizers, soil
amendments), industrial activities (mining and refinery, fossil fuel combustion, chemical industries) and urban activities (waste incineration, traffic), which are spatially and quantitatively variable (Fekiacova et al., 2015).

Copper is an essential micronutrient required for the growth of animals and plants and is usually added into fertilizer. Long-term application of fertilizer leads to the accumulation of Cu in surface soil (Wei et al., 2007). The leaching of fertilized soils (croplands or farmlands) can transfer fertilizer-derived Cu to rivers (Bengtsson et al., 2006). Phosphorus is the main nutrient element that is widely added to the arable land areas in China. About $8.5 \times 10^6$ t P fertilizers were used in 2014, accounting for 14.1% of the total fertilizer ($\sim 6.0 \times 10^7$ t) used in 2014 (data come from National Bureau of Statistics of China). The draft standard for approval of Cu in the fertilizer is less than 0.0050%, and the measured percent content of Cu in fertilizer ranges from 0.00014 to 0.00022% (Yan et al., 2014). Hence, the Cu/P ratio in the fertilizer ranges from 0.000010 to 0.000016. If we assume that all the dissolved P in the Yangtze River water comes from fertilizer, the dissolved Cu concentration derived from fertilizers can be estimated by using the Cu/P ratio. In so doing, we find that Cu from P fertilizers accounts for less than 0.3% of the Cu concentration in the Yangtze River (see the supplement for details). If we assume a similar Cu content in all (i.e. P and non-P fertilizers), this increases the fertilizer-derived Cu in the river to $\sim 2.1\%$. Hence, the input of Cu derived from fertilizer is likely small and can be neglected in the analysis of Cu isotopes.

The second possible anthropogenic source of Cu to the Yangtze River is the
industrial processing of ore minerals. There is no significant Cu isotope fractionation during smelting because Cu has a higher boiling point than most smelting temperatures (Gale et al., 1999; Mattielli et al., 2006). Therefore, the $\delta^{65}$Cu of emissions from Cu smelting are likely to reflect the Cu isotope composition of the feedstock (Thapalia et al., 2010). Feedstock deposits are predominantly sulphide minerals (Borrok et al., 2008; Kimball et al., 2009; Mathur et al., 2009), which typically have light Cu isotope compositions and high Cu concentrations (see section 4.3). The Cu concentration of industrial wastewater in China is relatively high, up to $6.4 \times 10^3$ nmol/L (Cheng, 2003), while the Cu concentration of mining wastewater in Central South China (located in the Yangtze River basin) is up to $4.6 \times 10^3$ nmol/L (Hu et al., 2014), suggesting that mining may have a significant influence on riverine Cu. Evidence for a local industrial source of Cu to the Yangtze River can be seen at Tongling, a famous Cu industrial city located in the lower reaches, where the river has an elevated Cu concentration (97.4 nmol/L) and a less positive $\delta^{65}$Cu value, of $+0.61\%o$ (Table 1).

Urban activities are a third possible anthropogenic source of Cu. Copper is the most abundant trace element measured in brake pads (~6.6%) (McKenzie et al., 2009). Brake pad waste in China contains high Cu concentrations of 10.6% by weight (Zhang et al., 2019). Brake wear from road traffic vehicles is an important source of atmospheric (particulate) Cu concentrations, and can contribute significantly to deposition fluxes of Cu to surface waters (Hulskotte et al., 2007). Dong et al. (2017) found that the Cu concentrations of PM$_{10}$ (particulate matter, diameter $\leq 10$ μm)
collected at a heavily traveled street (Marylebone) were much higher than those from a lightly traveled open urban site (North Kensington) in London, UK (Table 3). About 40% of the total Cu present in the brake wear debris can be leached into solutions by synthetic rainwater after 18 h in batch reactors (Hur et al., 2004). Similarly, about half of the Cu present in PM$_{10}$ can be leached in acetate buffer solution at pH 4.5 (Canepari et al., 2008). To our knowledge, no Cu isotope compositions for Chinese traffic emissions have yet been reported. However, $\delta^{65}$Cu values for European tyres and breaks range from +0.17 to +0.63‰ (Table 3, Dong et al., 2017). By comparison, dissolved Cu isotope compositions close to the huge cities along the Yangtze River, e.g. Chongqing and Wuhan, are characterized by distinctly positive values (+1.04‰, +1.37‰, Table 1), and do not exhibit significantly elevated Cu concentrations (27.3 nmol/L, 25.9 nmol/L, Table 1). Therefore, despite the relatively high Cu concentrations of brake pads, we suggest that urban activities are likely a minor contributor to the distribution of Cu and Cu isotopes in the Yangtze River.

4.2. Lithological control on the enrichment of isotopically heavy dissolved Cu

Bulk silicate Earth has an average $\delta^{65}$Cu of $+0.07 \pm 0.10$‰ (2SD) while different rocks have some measurable differences in $\delta^{65}$Cu (cratonic peridotites: -0.64 to +0.68‰; orogenic peridotites: -0.34 to +1.82‰; basalts: -0.19 to +0.47‰; andesites/dacites: +0.04 to +0.38‰) (Liu et al., 2015; Savage et al., 2015; Moynier et al., 2017). Weathering can also drive isotopic fractionation (e.g. Mathur et al., 2012; Vance et al., 2016). The lithological distribution and the weathering of rocks in the drainage basin may therefore influence riverine dissolved Cu isotope compositions.
Carbonates are characterized by relatively high Ca/Na and Mg/Na ratios, while silicates and evaporites have lower ratios (Gaillardet et al., 1999; Dessert et al., 2003). The Na-normalized ratios (Mg/Na vs. Ca/Na, Fig. S1 in supplement) for the Yangtze River water samples indicate that carbonates and silicates control the dissolved concentrations of major cations. Typically, carbonates and/or evaporites have high concentrations of Sr and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, while silicates have low concentrations and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Palmer and Edmond, 1989; Palmer and Edmond, 1992). A plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus 1/Sr (Fig. S2 in supplement) shows that the Yangtze River mainstream water chemistry is mainly dominated by the contribution of carbonate weathering. Decreasing concentrations of Ca and Mg from the upper to lower reaches (Fig. 2) suggest a gradually increasing contribution of silicate rocks in the middle-lower reaches.

Dissolved Cu/Ca ratios (µmol/mol) decline from ~30 to ~15 in the upper reaches, then increase markedly in the middle-lower reaches to a maximum of ~100 (Fig. 5). These changes are consistent with changing Cu/Ca ratios of the major source rocks. Silicate rocks have an average Cu concentration of 28 µg/g and CaO percentage of 3.59% (Rudnick and Gao, 2003), leading to a high Cu/Ca ratio of ~690 µmol/mol. The extensive Cu sulphide deposits present close to the lower reaches of the Yangtze River (see section 4.3) will also exhibit very elevated Cu/Ca ratios. By contrast, carbonate rocks have an average Cu concentration of 14 ± 9 µg/g (Graf, 1960). For limestone, with 95-100% CaCO$_3$, carbonate Cu/Ca will range from ~8 to ~40 µmol/mol, while for pure dolomite (CaMg(CO$_3$)$_2$) it will range from ~15 to ~70 µmol/mol.
Thus, the increasing Cu/Ca ratios in the lower reaches are consistent with an increasing contribution of solutes from the weathering of silicates or Cu sulphide deposits with high Cu/Ca ratios.

Dissolved Cu isotope compositions exhibit the reverse trend to Cu/Ca, becoming isotopically heavier downstream in the upper and middle reaches, and then isotopically lighter in and lower reaches (Fig. 3). In fact, most data from the main stream of the Yangtze fall close to a mixing line in 1/Cu vs. $\delta^{65}$Cu space (Fig. 6), suggesting that dissolved Cu and Cu isotope compositions could reflect mixing of two sources: (1) a low Cu concentration, high $\delta^{65}$Cu end-member (at about +1.6‰) from the upper reaches and (2) a higher Cu concentration, lower $\delta^{65}$Cu end-member (at about +0.6‰) in the lower reaches (Fig. 6).

Clastic silicate rocks exhibit Cu isotope compositions of +0.08 ± 0.20‰ (2SD, Moynier et al., 2017). However, a range of soils developed on silicate (granitoid and basaltic) rock substrates exhibit the preferential loss of isotopically heavy Cu during oxic weathering, suggested to reflect partitioning between aqueous organic complexes and/or incorporation in Fe (hydr)-oxides retained in the soil (Vance et al., 2016; Little et al., 2019). Oxidative weathering of sulphides is also expected to mobilise isotopically heavy Cu (e.g., Kimball et al., 2009; Mathur et al., 2005, 2012), discussed in detail in section 4.3. Therefore, weathering of silicates and/or sulphides is a plausible driver of heavy Cu isotope compositions (compared to the solid Earth, at about ~0‰) in the dissolved pool of the Yangtze River.

The upper reaches of the Yangtze are primarily under the influence of carbonate
weathering, providing one possible origin of the high $\delta^{65}\text{Cu}$ end-member. At present, little is known about the Cu isotope composition of carbonate rocks, or any potential isotopic fractionation during carbonate weathering. In ore bodies, Cu carbonate minerals are isotopically heavy compared to coexisting Cu sulphides (e.g. Asael et al., 2007), consistent with predictions from ab initio calculations (e.g., Fujii et al., 2013). However, we consider it unlikely that the unusually heavy Cu isotope compositions observed in the upper-middle reaches of the Yangtze (up to $+1.65\permil$) reflect a carbonate Cu source. We return to discuss the origin of these high $\delta^{65}\text{Cu}$ values in section 4.4.

Rather than mixing between two end-members with different Cu-$\delta^{65}\text{Cu}$ characteristics, the evolution of dissolved $\delta^{65}\text{Cu}$ values in the Yangtze River could instead result from variability in the trapping efficiency of isotopically light Cu in soils across the basin. The greater the trapping efficiency, the lower the riverine dissolved Cu concentration and heavier its isotopic composition, which would lead to a negative correlation between Cu concentrations and $\delta^{65}\text{Cu}$ values (Fig. 4). For example, from Chongqing to Yichang, the Cu concentration decreases (Fig. S3 in supplement) (as the water discharge increases by $\sim30\%$); this decrease is associated with an accumulation of isotopically heavy Cu in the middle reaches (Fig. 3). However, this hypothesis is speculative; testing it would require a means to estimate the trapping efficiency of Cu in soils across the basin.

4.3. Copper isotope fractionation during weathering of ore deposits
Markedly elevated dissolved Cu concentrations (69 to 97 nmol/L) and less positive δ\textsuperscript{65}Cu values (+0.59 to +0.63‰) are observed in the lower reaches of the Yangtze River, from Jiujiang to Tongling (Figs. 3, S3). We suggest that these values reflect leaching of the extensive Cu sulphide-rich deposits located near the mainstream of Yangtze River in this region (Fig. 7). These deposits have variably light Cu isotope compositions (-2.10 to +0.17‰, Ouyang et al., 2017; -0.54 to +0.95‰, Wang et al., 2014) (Fig. 3), but the oxidative weathering of sulphide-rich rocks is thought to lead to the mobilization of isotopically heavy Cu (Kimball et al., 2009; Mathur et al., 2005, 2012; Mathur and Fantle, 2015; Lv et al., 2016). Surface water and groundwater samples in the Tongling area have wide-ranging δ\textsuperscript{65}Cu values (-0.13 to +6.90‰), generally heavier than the primary ore materials (chalcopyrite: -0.04 ± 0.26‰ (n = 9); pyrite: +0.61 ± 0.94‰ (n = 4), Su et al., 2018). Dissolved Cu isotope compositions of +0.59‰ to +0.63‰ from Jiujiang to Tongling in the Yangtze main stream, and of +0.48‰ for the Hongxing River tributary (TLHX-1), are close to those of mine leachates from the Tongling ore fields (+0.30‰, Su et al., 2018), suggesting that this section of the Yangtze is significantly influenced by Cu that originated from mining.

4.4. Fractionation of Cu isotopes in the river channel

The construction of the TGD led to sedimentation of particulate material and an increase in the transparency and dissolved oxygen content of the water column in the TGR (Huang, 2008). As a result, phytoplankton, consisting of Cyanophyta, Bacillariophyta and Chiorophyta, increase in abundance from Chongqing to Yichang.
Total biomass increases from 0.0019 mg/L to 0.0040 mg/L (Huang, 2008). Cellular Cu uptake by phytoplankton favours incorporation of light Cu isotopes (e.g. Navarette et al., 2011), and could thus lead to the enrichment of isotopically heavy Cu in the dissolved phase. However, assuming a mean cellular Cu:C ratio of 4.1 μmol/mol for phytoplankton (Sunda and Huntsman, 1995), we estimate that less than 0.01% dissolved Cu is incorporated into phytoplankton cells in the TGR, with a resultant negligible influence of biological uptake on the fractionation of Cu isotopes.

The free Cu$^{2+}$ ion occurs primarily as an aquacomplex in inorganic freshwater solutions, as Cu(H$_2$O)$_5^{2+}$ (Sherman, 2001). However, many previous studies have concluded that dissolved Cu in rivers and oceans is very strongly bound to organic ligands (e.g., Skrabal et al., 1997; Wells et al., 1998; Shank et al., 2004; Moffett and Dupont, 2007), with less than 1% of the total dissolved fraction present as free Cu$^{2+}$ (Moffett and Dupont, 2007; Thompson et al., 2014). This organic complexation may lead to isotopically heavy Cu in the dissolved phase because of the preferential complexation of heavy Cu isotopes by organic ligands (Schauble, 2004; Vance et al., 2008; Bigalke et al., 2011; Ryan et al., 2014). Experimental estimates of $\Delta^{65}$Cu$_{\text{complex-free}}$ vary with ligand-binding strength, from +0.14 to +0.84‰ (Ryan et al., 2014).

While organic complexation retains isotopically heavy Cu in the dissolved phase, scavenging may remove isotopically light Cu to the particulate phase (e.g., Takano et al., 2014). For example, sorption of Cu to kaolinite favours light Cu isotopes, with experimental estimates of $\Delta^{65}$Cu$_{\text{sorbed-free}}$ = -0.2 to -0.8‰ at low ionic strength (Li et
As discussed, the construction of the TGD caused a significant amount of sediment deposition in the Three Gorges Reservoir (TGR, from Chongqing to Yichang), as well as a decrease in the concentration of suspended particulate material in the river from ~1000 mg/L to ~100 mg/L in July 2003, 2005 and 2007 (Huang, 2008; Ding et al., 2013). Copper concentrations in sediments of the TGR range from 36.5 to 93.9 μg/g (Bing et al., 2016), almost all of which are enriched compared to the detrital background Cu concentration of 35 μg/g (Zhao et al., 2017). The sediments, which consist of numerous clay minerals and organic/inorganic colloids, are likely to be enriched in Cu by adsorption.

Consistent with the hypothesised scavenging removal of isotopically light Cu on particles, dissolved δ⁶⁵Cu values increase and Cu concentrations decrease downstream towards the TGD (Fig. 3, Fig. S3). Furthermore, sorption of cations on negatively charged mineral surfaces is more energetically favourable at higher pH; we observe a positive correlation (r = 0.78, p < 0.01, N = 10) between dissolved Cu isotope compositions and pH in the upper reaches (Fig. 8), consistent with increased adsorption of light Cu onto clay particles.

The most positive δ⁶⁵Cu values (up to +1.65‰) are observed in the middle reaches downstream of the TGD, from Yichang to Chibi (Fig. 3). To our knowledge, Cu isotope compositions in this section of the Yangtze are the heaviest yet reported in any river system worldwide. We suggest that these values reflect the continued impact of the TGD downstream. Notably, δ⁶⁵Cu values increase in concert with dissolved oxygen, both upstream and downstream of the TGD (Fig. S4). This relationship
suggests an impact on Cu isotope geochemistry of enhanced productivity, via the enhanced production of strong organic ligands, and/or the presence of particulate phases (e.g., Fe-Mn oxides, clays), which continue to scavenge isotopically light Cu (e.g., Little et al., 2014; Li et al., 2015; Ijichi et al., 2018). More detailed evaluation of these possibilities requires an analysis of particulate phase Cu isotope compositions.

Though we cannot isolate the individual roles of organic complexation and scavenging, their combined impact on aqueous Cu isotope compositions can be modelled following Vance et al. (2008), by assuming equilibrium partitioning between the dissolved and particulate phase, illustrated in Figure 9. For a starting Cu pool with the maximum measured Cu concentration (~100 nmol/L) and minimum dissolved $\delta^{65}$Cu value (at +0.6‰), the best fit $\Delta^{65}$Cu_{diss-part} is about +1‰. However, this model (dashed curve, Fig. 9) does not provide a good fit to the dataset, particularly at intermediate Cu concentrations. If we assume that the samples from the lower reaches (with high Cu concentrations and less positive $\delta^{65}$Cu values) record the impact of Cu supply from the weathering of Cu sulphide deposits (section 4.3), and instead set the initial Cu concentration and $\delta^{65}$Cu at 40 nmol/L and +1‰, the best fit $\Delta^{65}$Cu_{diss-part} is about +0.8‰. This alternative model (solid line, Fig. 9) provides a significantly improved fit to the data from the upper and middle reaches of the Yangtze mainstream. A fractionation factor of +0.8‰ is also broadly consistent with experimental constraints on organic complexation and sorption to particulates, and with the observed offset between the two phases in a small natural river system (the Itchen, UK; Vance et al., 2008).
To conclude, we suggest that sedimentation and scavenging of Cu driven by the intercept of the TGD has a significant impact on the Cu isotope geochemistry of the Yangtze River, and is likely responsible for the globally anomalous heavy Cu isotope compositions observed in its upper and middle reaches. Future work should test this hypothesis by coupling particulate and dissolved phase Cu isotope ratio analysis.

Finally, we note that the most downstream site (NJ-1, Nanjing) also has more positive $\delta^{65}\text{Cu}$ than the three upstream sites influenced by Cu sulphide-rich ore deposits. About 75% of Cu is lost between these upstream sites and NJ-1, suggesting that strong adsorption of Cu onto particles occurs at this location due to the tidal influence that enhances the concentration of suspended particulate matter.

5. Conclusions

This study presents dissolved Cu isotope compositions and Cu concentrations for the main channel of the Yangtze River and its several tributaries. The Yangtze River exhibits more positive $\delta^{65}\text{Cu}$ values (range: +0.59 to +1.65‰) than other rivers at similar Cu concentrations, and there is a tendency towards heavier dissolved Cu isotope compositions at lower Cu concentrations.

Isotopically heavy Cu in global rivers (compared to lithogenic Cu, at about 0‰) is believed to reflect a) oxidative weathering, which mobilises isotopically heavy Cu, and b) partitioning in the river between an isotopically heavy, organically complexed dissolved pool, and an isotopically light pool, sorbed to particulates. While these processes are undoubtedly important in the Yangtze River, they do not explain its apparently anomalous Cu isotope geochemistry compared to other rivers.
We find two key features of the Yangtze River basin that contribute to the unique Cu isotope geochemistry of the river. First, we suggest that the Three Gorges Dam (TGD) has had a major impact on the Cu isotope geochemistry of the upper and middle reaches. Second, we suggest that weathering of extensive Cu sulphide deposits between Jiujiang and Tongling dominates the geochemistry of the lower reaches.

In the upper reaches, upstream of the TGD, we observe increasing $\delta^{65}$Cu values and decreasing Cu concentrations associated with increasing pH. The construction of TGD has led to extensive sedimentation, and we suggest that the sorptive removal of isotopically light Cu onto particles explains the observed trend towards isotopically heavy Cu in the dissolved phase. Downstream of the TGD, in the middle reaches, $\delta^{65}$Cu values increase to a maximum of $+1.65\%$. We suggest that this trend reflects the downstream influence of the TGD, which is associated with increasing dissolved oxygen levels that may drive elevated primary productivity.

In the lower reaches, oxidative weathering of isotopically light Cu sulphide-rich deposits leads to elevated Cu concentrations and lighter Cu isotope compositions in the river. The overall relationship between dissolved Cu and $\delta^{65}$Cu in the Yangtze mainstream thus reflects mixing between these high concentration, low $\delta^{65}$Cu, Cu sulphide-influenced waters, and the lower concentration, higher $\delta^{65}$Cu waters from upstream.

Acknowledgments

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**Figure captions**

Fig. 1. The lithologic map and sampling sites of the Yangtze River drainage area. Modified from Ding et al. (2014). The green sites (Wuhan to Nanjing) and associated tributaries (white sites) were collected in September 2013; the red sites (Chongqing to Chibi) and associated tributaries (white sites) were collected at the end of July 2014. The abbreviations (blue for main channel, green for tributaries) in this figure correspond to the locations listed in Table 1. TGD means the Three Gorges Dam, with a sample site CJSX-01. GXZ-1 and LGT-1 represent Guangxingzhou and Leigutai, respectively. WHHJ-1 and CJHJ-1 overlapped in the figure represent the tributaries “Hanjiang” in Wuhan. JJ-1 and TL-1 represent Jiujiang and Tongling, respectively. Evaporitic rocks which are not marked in the figure can also be found in the Yangtze River basin (Chetelat et al., 2008).

Fig. 2. The concentrations of Ca and Mg in the Yangtze River mainstream water.

Fig. 3. $\delta^{65}$Cu of the Yangtze River. The average mean and range of $\delta^{65}$Cu in global rivers is referred from Vance et al. (2008); the data for Dongxiang and Dongguashan ore deposits are referred from Ouyang et al. (2017) and Wang et al. (2014), respectively.

Fig. 4. Riverine Cu isotope compositions plotted against Cu concentrations. The data of other world rivers are referred from Vance et al. (2008) and Guinoiseau et al.
New data for the main stream of the Yangtze River are shown in blue circles. The dashed line shows the Cu-$^{65}$Cu trend in the main stream of the Yangtze River.

Fig. 5. Molar Cu/Ca ratios for the dissolved load in the Yangtze River mainstream water.

Fig. 6. Plot of $\delta^{65}$Cu vs. 1/Cu in the Yangtze River. An illustrative linear mixing line is shown between two hypothetical end-members (black diamonds); see text for details. Correlations (blue text) are calculated for the data of main channel only.

Fig. 7. The distribution of Cu deposits in the Yangtze River basin. The map of deposits is modified from information in: http://www.mining120.com/

Fig. 8. (a) The changes in pH (green circles) and Cu concentrations (orange diamonds) in the upper reaches of the Yangtze River. Inset (b) Correlation of pH and $\delta^{65}$Cu for the upper reaches of the Yangtze River. Open symbols represent an outlier that is considered to be inaccurate.

Fig. 9. Cu isotope compositions plotted versus 1/Cu concentration. Model curves represent equilibrium partitioning of Cu between the dissolved and particulate phases in the main channel. The dashed curve represents the modeled evolution from a starting composition of the maximum measured Cu concentration (~100 nmol/L) and
The lightest Cu isotope composition (+0.6‰). The solid curve represents the evolution from a starting pool of 40 nmol/L and +1‰, assuming that the three circled points are influenced by Cu supply from the weathering of Cu sulphide deposits. $\Delta_{\text{diss-part}}$ values give the modelled Cu isotopic fractionation between dissolved and particulate phases ($\delta^{65}\text{Cu}_{\text{diss}} - \delta^{65}\text{Cu}_{\text{part}}$) in each scenario. See text for full details.
Figure 5

Figure 6
Figure 7

Figure 8
Figure 9

Influence of sulphide on the isotope fractionation of copper in the Yangtze River.
1  
2  
3  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Latitude (N)</th>
<th>Longitude (E)</th>
<th>Water discharge* (m³/s)</th>
<th>Distance (km)</th>
<th>pH</th>
<th>EC (µS cm⁻¹)</th>
<th>D.O. (mg/L)</th>
<th>δ⁶⁵Cu (‰)</th>
<th>2 SD (‰)</th>
<th>δ⁸⁷Sr</th>
<th>2σ (Mg)</th>
<th>Ca (µmol/L)</th>
<th>Na (µmol/L)</th>
<th>Cu (µmol/L)</th>
<th>Sr (µmol/L)</th>
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<td>421</td>
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<td>109.885</td>
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<td>8.36</td>
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<td>465</td>
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<td>11 CJXK-01</td>
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<td>30.825</td>
<td>111.006</td>
<td></td>
<td>615</td>
<td>-</td>
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<td>-</td>
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*The discharge was recorded from the web of the hydrological information for the main rivers in China (http://xxzx.mwr.gov.cn/).

**Table 2**
δ⁶⁵Cu (%) and 2SD for three USGS reference materials compared to recommended values

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<tr>
<th>Reference</th>
<th>δ⁶⁵Cu (‰)</th>
<th>2SD</th>
<th>n</th>
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<td>0.17</td>
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<td></td>
<td>0.30</td>
<td>0.04</td>
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<td>Liu S. et al., 2014</td>
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**Table 3**
Cu concentrations and δ⁶⁵Cu in different sources

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<tr>
<th>Site</th>
<th>Sample type</th>
<th>Cu concentration (µg/g)</th>
<th>Cu concentration (ng/m³)</th>
<th>δ⁶⁵Cu (%) ± 2SD</th>
<th>Reference</th>
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<td>close to Marylebone and North Kensington</td>
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<td>6.1</td>
<td>0.62</td>
<td>0.13</td>
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<td></td>
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<td>0.63</td>
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<td>25</td>
<td>0.28</td>
<td>0.1</td>
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<td></td>
<td>Tire</td>
<td>43</td>
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<td>0.09</td>
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<td>0.17</td>
<td>0.1</td>
<td></td>
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<td></td>
<td>26</td>
<td>0.33</td>
<td>0.12</td>
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</tr>
<tr>
<td>North Kensington PM₁₀</td>
<td>1.9 ~ 3.6</td>
<td>-0.01 ~ +0.46</td>
<td></td>
<td>Dong et al., 2017</td>
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<tr>
<td>Marylebone Road PM₁₀</td>
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<td>+0.01 ~ +0.51</td>
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<td>Dong et al., 2017</td>
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Supplementary material for on-line publication only
Click here to download Supplementary material for on-line publication only: Supplement_data-R3.xlsx
**Declaration of interests**

☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

No