Are Cu isotopes a useful tool to trace metal sources and processes in acid mine drainage (AMD) context?

Jérôme Viers a, *, Jose Antonio Grande b, Cyril Zouiten a, Rémi Freydier c, Jérémy Masbou a, Teresa Valente d, Maria-Luisa de la Torre b, Christine Destrigneville a, Oleg S. Pokrovsky a

a Geosciences Environnement Toulouse (GET), Université de Toulouse, CNRS, IRD, 14 avenue Edouard Belin, 31400 Toulouse, France
b Centro de Investigación para la Ingeniería en Minería Sostenible, Escuela Técnica Superior de Ingeniería, Universidad de Huelva, Ctra. Palos de la Frontera, s/n, 21819 Palos de la Frontera, Huelva, Spain
c HydroSciences UMR 5569, CNRS, Universités Montpellier 1 & II, IRD, Place Eugène Bataillon, CC MSE, 34095 Montpellier Cedex 5, France
d Instituto de Ciências da Terra (ICT), DCT (ECUM) Polo da Universidade do Minho, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

HIGHLIGHTS

- Oxidative dissolution of sulfides releases preferentially heavy isotope in solution.
- Preferential uptake of light isotope with the precipitation of secondary minerals.
- The sampling location determines the isotope signature of a river impacted by mines.
- Potential bias of the Cu isotopic composition of the world riverine flux.

ABSTRACT

In the South-West Europe (Iberian Pyrite Belt), acid mine drainage (AMD) processes are especially problematic because they affect the environmental quality of watersheds, restricting the use of surface water. Recent studies have shown that Cu isotopes are fractionated during the oxidative dissolution of primary sulfide minerals and could be used to trace metal cycling. However, the chemistry of Cu in such environment is complex because Cu is redistributed within numerous secondary minerals and strongly dependent on the hydroclimatic conditions that control key parameters (pH, redox conditions). Finally, it remains difficult to compare the various field studies and deliver some strong general tendencies because of these changing conditions. For these reasons, concerted studies on Cu isotopes fractionation in waters impacted by AMD may help to reveal the sources and transport pathways of this important pollutant. To address this issue, we used a representative scenario of strong contamination by AMD in the Iberian Pyrite Belt (SW Spain), the Cobica River. The aim of our study is to measure the Cu isotopes signature in the waters (river, mine lake, water draining waste) of the small Cobica River system (Huelva, Spain), sampled during a short period (8 h) to avoid any change in the hydro-climatic conditions. This provided an instantaneous image of the isotopic Cu signature in a small mining systems and helped us to constrain both the processes affecting Cu isotopes and their use a potential tracer of metals in contaminated environments.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Acid mine drainage (AMD) that emerges from sulfide and coal mines attracts significant attention of the environmental scientists. The AMD phenomena lead to surficial waters with low pH, and a high metal and sulfate load (e.g., Amils (2006), Andújar et al. (2006), Aroba et al. (2007), Azcue (1999), Borrego (1992), Borrego et al. (2002), Braungardt et al. (1998), Cabrera et al. (1992), Cruzado et al. (1998), Davis et al. (2000), de la Torre et al. (2009), Elbaz-Poulachet et al. (2000, 2001), Fernández-Rubio and Lorca
The aim of our study is to measure the Cu isotopes signature in the Andevalo dam, which delivers its waters to the Andevalo dam. The Andevalo dam supplies water for irrigation and human consumption to an area of ~20,000 km². The main contributor of the Andévalo dam is the Malagon River, of high hydrological relevance, with a watershed of 405 km². The hydrological conditions of the area, mainly made up of impermeable materials, cause practically all the rainfall received by these watersheds to flow as runoff into the channels and, therefore, into the dam. This results in hydric regimes with torrential characteristics, with large floods in winter and almost empty channels in summer (Grande et al., 2005a).

The study area, in the Huelva province, has a Mediterranean climate, which can be classified as semi-arid. Annual precipitation is about 630 mm/year, being mostly concentrated in the wet season from October to May. Monthly precipitation ranges from 3 to 121 mm, corresponding to June and December, respectively. The average annual temperature is 17.1 °C, with January being the coldest month (mean 9.8 °C), and July and August being the hottest (mean 25.7 °C) (Instituto Nacional de Meteorología; unpublished data). July also has much higher evapotranspiration (162 mm) than January (19 mm).

3. Materials and methods

3.1. The sampling location

We have collected three types of samples: river water, open mine lakes water and shallow subsurface water percolating through wastes of the Herreries and Lagunazo mines. The location of samples is shown in Fig. 1 and their main environmental parameters are listed in Table 1. The Cobica River is firstly fed at the East of the studied zone by the clean dam (LZ4) also called Embalse del Lagunazo. Then the Cobica River has been sampled just after the Lagunazo mine (LZ6) and at the Puente (CO1), at mid distance between the mine and the dam. The Chorrillo River has been sampled after the Herreries mine (CO5) and before the Andevalo dam (CO6). In the Lagunazo mining area we collected the open lake (LZ1), the black water lake (LZ5), and two surficial waters flowing through waste dump (LZ3) and pyrite-rich waste (LZ2). In the Herreries mine, we sampled two open mine lakes (Santa Barbara open lake...
(CO3) and Guadiana open lake (CO2), and the waters at the outlet of the Santa Barbara waste (CO4) and Guadiana waste (CO7). Finally, the tap water originated from the Andevalo dam was collected at the city of El Portil.

### 3.2. Sampling protocol

All the samples were collected the 14 of October 2015, between 10 a.m. and 6 p.m. The temperature, pH, Eh and conductivity were measured in the field. pH was measured on unfiltered solution after a calibration of the pH meter with two buffer solutions (pH 4.00 and pH 7.00). A conductimeter was calibrated with a $10^{-2}$ M KCl solution (1413 μS/cm at 25 °C) and all conductivities were given at the temperature of 25 °C. The Eh electrode was calibrate using a standard Zobell solution (250 mV).

Water samples were filtered in the field immediately after sampling using Nalgene®Rapid-Flow™ filtration unit, that had a cellulose nitrate membrane with a pore size of 0.22 μm. About 80 mL of water were successively filtered three times to rinse the membrane and the final 250 mL of the filtrate were stored in three 60 mL HDPE bottles: one for cations and trace elements analyses, one for anions analyses, and one for copper isotopes analysis. The HDPE bottles used for solution storage were cleaned at the laboratory with HCl 1 N and MilliQ® deionised water. Solution for major cations and trace elements analyses were acidified to – pH 2 with double distilled HNO3. In the field, a blank filtration was performed to check the level of contamination induced by both our materials and the field protocol. All values (see Table 1) show that the level of contamination is negligible with respect to metal concentrations of these waters.

### 3.3. Analysis

Major and trace cations concentrations were measured using ICP-MS (iCAP Q, Thermo Scientific—Kinetic Energy Discrimination mode using He) at the AETE-ISO platform (OSU OREME/Université de Montpellier). Concentrations were determined with external calibration using (Be, Sc, Ge, In, Rh) as internal standards to correct potential sensitivity drifts. The quality of the analysis was checked by analyzing international certified reference waters (CNRC SLRS-5, NIST SRM 1643e). The accuracy was better than 5% relative to the certified values and the analytical error (relative standard deviation) was better than 5% for concentrations ten times higher than the detection limits. Anions concentrations were determined by ionic chromatography (ICS, 2000 Dionex) at the Géosciences Environnement Toulouse (GET) laboratory. The Certified Reference Materials ION 015 was analyzed to check both the accuracy and the reproducibility of the analyses. The concentrations we determined are in agreement with the certified concentrations taken into account the associated uncertainties. Cu isotopic analyses were performed on water samples from rivers and lakes. Water sample aliquots containing approximately 1000 ng of Cu were purified using anion exchange chromatography on AG-MP1 resin (BIORAD) following an adapted protocol from Borrok et al., 2007. The protocol was repeated twice in order to ensure a complete separation of Cu from the matrix. The total procedure blank was negligible in comparison with the amount of Cu in the samples (<1%). Column yields and remaining elements such as (Na, Mg, Ca, Ti, Cr) that can interfere with Cu and Zn isotopes (Petit et al., 2008) were checked for each samples using Q-ICP-MS iCAP Q (Thermo Scientific). The yield was 100 ± 5% and no interfering elements were found in the solutions.
Cu isotopic analyses were performed on a multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) Neptune (Thermo Scientific®) at GET (Toulouse, France). Each sample was analyzed three times and was bracketed with the SRM NIST 976 copper solution. Cu isotopes (\(^{63}\text{Cu},\ 65\text{Cu})\), Zn isotopes (\(^{64}\text{Zn},\ 66\text{Zn},\ 67\text{Zn},\ 68\text{Zn})\), and Ni isotope (\(^{62}\text{Ni})\) were monitored simultaneously. Measurements of \(^{62}\text{Ni})\) signal allowed correcting the possible isobaric interference of \(^{64}\text{Ni}\) on \(^{64}\text{Zn}\). A Zn solution JMC standards, the SRM NIST 976: (64Zn, 66Zn, 67Zn, 68Zn), and Ni isotope (62Ni) were monitored and the method of sample-standard bracketing was used to correct instrumental mass bias using the \(^{66}\text{Zn}/^{64}\text{Zn}\) ratio (exponential law).

Cu isotopic deviation relative to NIST 976; TDS indicates Total Dissolved Solid.

\[
\delta^{65}\text{Cu} = \left( \frac{\left( \frac{\text{Cu}}{\text{Cu}} \right)_{\text{sample}}}{\left( \frac{\text{Cu}}{\text{Cu}} \right)_{\text{NIST 976}}} - 1 \right) \times 1000
\]

### Table 1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample type</th>
<th>Sampling date (and hour)</th>
<th>Position</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Conductivity ms/cm</th>
<th>TDS mg/L</th>
<th>Eh mV</th>
<th>d65Cu ‰</th>
<th>Cl mg/L</th>
<th>SO4²⁻ mg/L</th>
<th>NO3⁻ mg/L</th>
<th>Na mg/L</th>
<th>Mg mg/L</th>
<th>K mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-1</td>
<td>Field blank</td>
<td>Cobica River (Puente)</td>
<td>14/10/2015 (2:51 PM)</td>
<td>N 37°38’33” W 7°15’57”</td>
<td>24.9</td>
<td>3.17</td>
<td>2.34</td>
<td>1355</td>
<td>488</td>
<td>0.36</td>
<td>(-0.01)</td>
<td>&lt;1LD</td>
<td>&lt;1LD</td>
<td>&lt;1LD</td>
<td>&lt;1LD</td>
</tr>
<tr>
<td>CO-5</td>
<td>Chorrito River</td>
<td>14/10/2015 (4:55 PM)</td>
<td>N 37°37’37” W 7°18’16”</td>
<td>27.1</td>
<td>3.20</td>
<td>2.64</td>
<td>1909</td>
<td>429</td>
<td>0.67</td>
<td>(-0.004)</td>
<td>72.41</td>
<td>1378</td>
<td>0.42</td>
<td>65293</td>
<td>120555</td>
</tr>
<tr>
<td>CO-6</td>
<td>Chorrito River (before Andevalo dam)</td>
<td>14/10/2015 (5:10 PM)</td>
<td>N 37°37’37” W 7°18’30”</td>
<td>26.1</td>
<td>5.07</td>
<td>0.32</td>
<td>179</td>
<td>287</td>
<td>1.75</td>
<td>(-0.01)</td>
<td>29.70</td>
<td>90</td>
<td>0.12</td>
<td>22641</td>
<td>13448</td>
</tr>
<tr>
<td>CO-2</td>
<td>Guadiana open mine lake</td>
<td>14/10/2015 (3:21 PM)</td>
<td>N 37°36’55” W 7°17’31”</td>
<td>26.9</td>
<td>3.22</td>
<td>5.76</td>
<td>6059</td>
<td>510</td>
<td>0.66</td>
<td>(-0.02)</td>
<td>50.04</td>
<td>4408</td>
<td>0.10</td>
<td>50795</td>
<td>472306</td>
</tr>
<tr>
<td>CO-3</td>
<td>Santa Barbara open mine lake</td>
<td>14/10/2015 (3:53 PM)</td>
<td>N 37°37’03” W 7°17’57”</td>
<td>24.4</td>
<td>5.50</td>
<td>5.64</td>
<td>5665</td>
<td>n.m.</td>
<td>0.77</td>
<td>(+0.01)</td>
<td>101.18</td>
<td>4031</td>
<td>0.04</td>
<td>140730</td>
<td>662715</td>
</tr>
<tr>
<td>CO-4</td>
<td>Santa Barbara waste colector</td>
<td>14/10/2015 (4:23 PM)</td>
<td>N 37°37’07” W 7°18’09”</td>
<td>27.2</td>
<td>3.07</td>
<td>6.53</td>
<td>8583</td>
<td>558</td>
<td>-1.52</td>
<td>(+0.04)</td>
<td>9.25</td>
<td>6693</td>
<td>1.62</td>
<td>4607</td>
<td>460814</td>
</tr>
<tr>
<td>CO-7</td>
<td>Guadiana waste colector</td>
<td>14/10/2015 (6:00 PM)</td>
<td>N 37°37’02” W 7°17’37”</td>
<td>25.2</td>
<td>3.18</td>
<td>2.71</td>
<td>2114</td>
<td>511</td>
<td>0.27</td>
<td>(+0.04)</td>
<td>62.71</td>
<td>1539</td>
<td>4.49</td>
<td>56818</td>
<td>73187</td>
</tr>
<tr>
<td>LZ-4</td>
<td>Clean dam (11:57 AM)</td>
<td>14/10/2015</td>
<td>N 37°37’17” W 7°09’44”</td>
<td>21.1</td>
<td>6.86</td>
<td>0.60</td>
<td>275</td>
<td>230</td>
<td>n.m.</td>
<td>62.73</td>
<td>100</td>
<td>0.31</td>
<td>50554</td>
<td>22869</td>
<td>3976</td>
</tr>
<tr>
<td>LZ-6</td>
<td>Cobica River (after Lagunazo mine) (12:35 PM)</td>
<td>14/10/2015</td>
<td>N 37°37’16” W 7°10’19”</td>
<td>25</td>
<td>2.32</td>
<td>13.1</td>
<td>17743</td>
<td>496</td>
<td>0.15</td>
<td>(+0.07)</td>
<td>43.68</td>
<td>12221</td>
<td>0.23</td>
<td>73090</td>
<td>210706</td>
</tr>
<tr>
<td>LZ-1</td>
<td>Lagunazo open mine lake (10:18 AM)</td>
<td>14/10/2015</td>
<td>N 37°37’42” W 7°10’02”</td>
<td>21.1</td>
<td>3.21</td>
<td>1.10</td>
<td>638</td>
<td>311</td>
<td>0.05</td>
<td>(+0.12)</td>
<td>31.11</td>
<td>410</td>
<td>1.68</td>
<td>37390</td>
<td>27969</td>
</tr>
<tr>
<td>LZ-2</td>
<td>Pyrite rich waste (11:00 AM)</td>
<td>14/10/2015</td>
<td>N 37°37’39” W 7°10’05”</td>
<td>19.2</td>
<td>2.15</td>
<td>28.3</td>
<td>81369</td>
<td>503</td>
<td>-0.70</td>
<td>(+0.03)</td>
<td>31.78</td>
<td>61472</td>
<td>3.19</td>
<td>6241</td>
<td>285352</td>
</tr>
<tr>
<td>LZ-3</td>
<td>Ash waste colector (11:45 AM)</td>
<td>14/10/2015</td>
<td>N 37°37’17” W 7°09’55”</td>
<td>18.5</td>
<td>2.38</td>
<td>13.61</td>
<td>38725</td>
<td>530</td>
<td>-0.08</td>
<td>(+0.12)</td>
<td>17.26</td>
<td>26238</td>
<td>0.87</td>
<td>2923</td>
<td>177631</td>
</tr>
<tr>
<td>LZ-5</td>
<td>Black water lake (12:24 PM)</td>
<td>14/10/2015</td>
<td>N 37°37’16” W 7°10’15”</td>
<td>24.8</td>
<td>1.50</td>
<td>75.0</td>
<td>108920</td>
<td>445</td>
<td>0.19</td>
<td>(+0.05)</td>
<td>27.55</td>
<td>76133</td>
<td>0.66</td>
<td>111989</td>
<td>485943</td>
</tr>
<tr>
<td>PO-1</td>
<td>tap water (El portil, Huelva)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 4. Results

#### 4.1. Physico-chemical parameters and major elements

All the hydro chemical and isotopic data are reported in Table 1. The specific conductivity ranged from 0.32 ms/cm (CO6, Chorrito River before Andevalo dam) to 75 ms/cm (LZ5, black water lake from Lagunazo mining area) and pH between 1.5 (LZ5) and 6.86 (LZ4). The Cobica River has a neutral pH (6.86) and a low conductivity (0.59 ms/cm). After the Lagunazo mine the Cobica River presents a neutral pH (6.86) and a low conductivity (0.59 ms/cm). The waters draining the wastes stored in the mining zone of Lagunazo have very high conductivities with values ranging from 13.6 to 75 ms/cm and low pH (between 1.50 and 2.38). The Lagunazo open mine lake presents a pH of 3.21 and a conductivity of 1.10 ms/cm. After the Lagunazo mine towards the Andevalo dam, the conductivity presents a pH of 3.2 and a conductivity of 13.1 ms/cm. Therefore, from the Lagunazo mine towards the Andevalo dam, the conductivity decreases and the pH increases. These values are similar to those of the
the Chorrito River draining the Herrerias mine (pH of 3.2 and conductivity of 2.6 mS/cm). In the Herrerias mine the open lakes and the water from the waste collectors present a conductivity between 2.7 and 5.8 mS/cm and a pH between 3.07 and 5.5. The pH of the Santa Barbara open lake is relatively high (5.5) compared to the Guadiana open lake (pH ~3.2), which is another open lake of the Herrerias mine. Just before the Andevalo dam the Chorrito River presents a pH of 5.05 and a conductivity of 0.32 mS/cm.

The concentrations of both major and trace elements are reported in Table 1. Table 2 presents the relative distribution (with respect to the Total Dissolved Solid, TDS) of the major elements in the different samples. The sulfates account for 64–78% of the TDS. In some samples chloride represents a significant fraction of the TDS; this is particularly true in the case of the clean dam (up to 23% of the TDS) and for the Cobica River (up to 17% of the TDS) before the Andevalo dam. The major cations (Na, K, Ca, Mg, and Fe) account for the remaining fraction and compensate the negative charges. Note that Fe accounts for 14–26% in the waste samples (LZ2, LZ3, LZ5) and in the Cobica River sampled just after the Lagunazo area. The concentrations and the relative distributions of major dissolved components and pH obtained in this study are in agreement with previous works and in particular, that of Grande et al. (2010), who collected more than 230 samples during one hydrological year (October 2003–May 2004).

### 4.2. Copper concentrations and isotopic composition

The three mine lakes present Cu concentrations varying by a factor of 50. In the case of the Herrerias mine, we observe a large difference of Cu concentrations between the Santa Barbara open mine lake (~0.9 mg/L) and the Guadiana open mine lake (23 mg/L). These values are in good agreement with the study of Sanchez-Espana et al. (2008) that reported a Cu concentration of 0.5 mg/L, 8 mg/L and 25 mg/L for Lagunazo, Santa Barbara and Guadiana mine lakes, respectively. By contrast, the level of Cu concentration is much lower in the Guadiana waste collector (5.5 mg/L) compared to the Santa Barbara waste collector (170 mg/L). Cu concentrations in the waste samples collected in the Lagunazo area are between 189 and 403 mg/L. Cu concentration in the Cobica River strongly decreases from the Lagunazo area (LZ6, ~33 mg/L) to the Cobica.
River Puente (CO-1, 1.5 mg/L). The Chorrito River draining the Herrerias mine zone contains 4.4 mg/L of Cu after the mining area. Before the Andevalo Dam, Cu concentration in this river strongly decreases (CO-6, 26 μg/L). Cu concentrations measured in the Chorrito and Cobica Rivers are in good agreement with those published by Jiménez (2009) and Grande et al. (2005b). The clean dam (close to the Lagunazo mine) and the tap water from EL Portil exhibit a low concentration (close to 5 μg/L).

The $\delta^{65}$Cu value measured in the waters draining the various deposits in the Lagunazo mine ranges between $-0.70$ and $+0.19\%$. The isotopic composition measured in the lake of the Lagunazo mine is close to zero ($0.05 \pm 0.12\%$). The Cobica River sampled just after the Lagunazo mining area has $\delta^{65}$Cu = 0.15%. The isotopic composition increases along the river since the value obtained for the Cobica River Puente sample is 0.36%. In the Herrerias mining zone the waters percolating through the waste present an isotopic composition between $-1.52$ and $+0.27\%$. The two open lakes present similar isotopic composition, 0.66 and 0.77% in the Guadiana and Santa Barbara open mine lakes, respectively. The isotopic composition of the open mine lake of Herrerias is much higher than the value of the Lagunazo mine lake. Again, as in the case of the Cobica River, the isotopic composition measured in the Chorrito River increases downstream from the mine to the lake. Indeed, the $\delta^{65}$Cu is 0.67% just after the mine and reaches 1.75% just after the Andevalo Dam, 2 km after. Considering all samples together, there was no any statistically significant between the water chemistry parameters (pH, E.C. Cu and SO$_4^{2-}$ concentrations) and $\delta^{65}$Cu.

5. Discussion

Before discussing our results, we have to report the main general trends revealed by previous studies on Cu isotopes in the mining areas. The Cu isotopic composition of solids present a large variability both for primary sulfides and secondary minerals; for illustration Mathur et al. (2014) obtained a range of $-9.2$ to $+1.7\%$ ($\delta^{65}$Cu) for 15 massive sulfide deposits in South West Spain. In a study of 9 porphyry copper deposits from USA, Chile and Turkey Mathur et al., 2009 reported a range of $-16.5$ to $+3.6\%$ ($\delta^{65}$Cu) for secondary products derived from these deposits. Despite this variability for primary and secondary materials, several clear general tendencies could be reported. From both field sampling and laboratory experiments, it appears that aqueous Cu resulting from the oxidative dissolution of sulfate minerals (e.g., chalcocite CuFeS$_2$) is isotopically heavier than the remaining solid phase (Mathur et al., 2005, 2014; Fernandez and Borrok, 2009; Kimball et al., 2009; Pekala et al., 2011). The $\Delta^{65}$Cu$_{\text{solution-solid}}$ (=$\delta^{65}$Cu$_{\text{solution}}$-$\delta^{65}$Cu$_{\text{solid}}$) ranges between 0 and 3% depending on the identity of solid phases and the experimental conditions (Mathur et al., 2005, 2014; Fernandez and Borrok, 2009). The preferential oxidation of $^{65}$Cu$^+$ at the surface of sulfide produces a surface layer that is enriched in $^{65}$Cu$^{2+}$. Thus heavy Cu($II$) isotope is preferentially transferred to the solution. Leaching experiments also reveal that the fractionation between the solid and the solution is smaller in the presence of bacteria (e.g. Thiobacillus ferrooxidans) (Mathur et al., 2005; Kimball et al., 2009) that may sequester heavy isotopes fraction when the cells are closely associated with secondary precipitates. In some cases, the $\delta^{65}$Cu$_{\text{solution-solid}}$ becomes negative in the presence of bacteria since they may reduce Cu$^{2+}$ to Cu$^0$ before incorporation within the cell (Navarrete et al., 2011). Overall, there are 3 main processes that may fractionate Cu isotopes in Earth-surface environment: the release of Cu from primary sulfide minerals, the adsorption or incorporation of Cu onto secondary minerals, and the adsorption + intracellular assimilation by live microbial cells (Mathur et al., 2005; Pokrovsky et al., 2008; Moynie et al., 2017).

In this study, Lagunazo and Herrerias mine waters percolating through the waste deposits present either negative or lowest values measured in sampled waters ($\delta^{65}$Cu $=-1.52$ to $0.27\%$) (see Table 1, Fig. 2). These waters drain complex heterogeneous wastes inherited from more than one century of mining activity. Taking into account the variability of isotopic composition for both primary and secondary minerals, a straightforward interpretation of Cu isotopic data in these waters is not possible. The open mine lakes of these two mines present positive values ($\delta^{65}$Cu $= +0.05$–$0.77\%$) which are higher than the values measured for percolating waters through the waste deposits ($\delta^{65}$Cu $= -0.70$ to $+0.19\%$). Waters of the lakes contain a fraction of rainwater falling directly on the area of the open mine and a fraction (the most important in terms of Cu concentration) of groundwater percolating from the bottom of the lake and from old lateral mine galleries. Within this region, the average annual evapotranspiration (~850 mm) exceeds the annual average precipitation (~650 mm) (Santisteban Fernandez Maria, 2015).

We observed a clear difference in the isotopic composition of the rivers draining these two mines. The Cobica River presents a value of 0.15% ($\delta^{65}$Cu) just after the mine of Lagunazo while the Chorrrio River presents a value of 0.67 ($\delta^{65}$Cu) just after the mine of Herrerias. Both rivers present an isotopic composition similar to those of the open mine lakes. We observe a similar evolution of the river water hydrochemistry and Cu isotopic composition when progressing downstream for both rivers; together with a drastic loss of Cu, Fe, Al and many other elements (see Fig. 3), there is an increase in the pH. The Cu isotopic composition becomes progressively heavier, and the $\delta^{65}$Cu value increases from $+0.15$ to $+0.36\%$ and from $+0.67$ to $+1.75\%$ in the Cobica River and Chorrrio River, respectively.

Table 2

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample type</th>
<th>Cl</th>
<th>SO$_4$</th>
<th>NO$_3$</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-1</td>
<td>Cobica River</td>
<td>6</td>
<td>68</td>
<td>0</td>
<td>6</td>
<td>5</td>
<td>0</td>
<td>7</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO-5</td>
<td>Chorrrio River</td>
<td>4</td>
<td>72</td>
<td>0</td>
<td>3</td>
<td>6</td>
<td>1</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>CO-6</td>
<td>Chorrrio River (before Andevalo dam)</td>
<td>17</td>
<td>50</td>
<td>13</td>
<td>8</td>
<td>2</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO-2</td>
<td>Guadiana open mine lake</td>
<td>1</td>
<td>73</td>
<td>0</td>
<td>1</td>
<td>8</td>
<td>0</td>
<td>9</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>CO-3</td>
<td>Santa Barbara open mine lake</td>
<td>2</td>
<td>71</td>
<td>0</td>
<td>2</td>
<td>12</td>
<td>0</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO-4</td>
<td>Santa Barbara waste collector</td>
<td>0</td>
<td>78</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>1</td>
<td>7</td>
<td>0</td>
<td>1</td>
<td>5</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>CO-7</td>
<td>Guadiana waste collector</td>
<td>3</td>
<td>73</td>
<td>0</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LZ-4</td>
<td>Clean dam</td>
<td>23</td>
<td>36</td>
<td>0</td>
<td>18</td>
<td>8</td>
<td>1</td>
<td>11</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LZ-6</td>
<td>Cobica River after Lagunazo mine</td>
<td>0</td>
<td>69</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>24</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LZ-1</td>
<td>Lagunazo open mine lake</td>
<td>5</td>
<td>64</td>
<td>0</td>
<td>6</td>
<td>4</td>
<td>1</td>
<td>14</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>LZ-2</td>
<td>Pyrite rich waste</td>
<td>0</td>
<td>75</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LZ-3</td>
<td>Ash waste collector</td>
<td>0</td>
<td>68</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>26</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>LZ-5</td>
<td>Black water lake</td>
<td>0</td>
<td>70</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>26</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PO-1</td>
<td>tap water (El portil, Huelva)</td>
<td>31</td>
<td>23</td>
<td>1</td>
<td>20</td>
<td>7</td>
<td>2</td>
<td>14</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Along the Cobica River is stronger than that along the Chorrito concentration at the more distal point. The decrease of Cu concentration Valente et al., 2013), contributing to the decrease of Cu concentration, goethite could also precipitate (Sanchez-Espana et al., 2005; capacity for metals retention, such as jarosite and low crystallinity sul(Valente et al., 2013). Moreover, minerals well-known for their organic complexes become significant (~18%) despite that the dissolved organic carbon concentration was only 1.5 mg/L. Concerning the saturation index it appears that the upstream waters of the Cobica River are over saturated with respect to ferrihydrite, goethite, K- and Na-jarosite (mainly K-jarosite) and schwertmannite and under saturated with respect to aluminous minerals (gibbsite and hydrobasaluminite). In the downstream point of the Chorrito River, the solution is under saturated with respect to ferrihydrite, goethite and schwertmannite but undersaturated with respect to K- and Na-jarosite. In the Cobica River the speciation of the dissolved Cu is dominated by Cu2+ (~67%) and CuSO4 (~32%). Downstream the percentage of the Cu2+ increases up to 75% and organic complexes become significant (~18%) in the downstream point of the Cobica River channel. It is unlikely that the sorption of Cu onto solid or biological (cell) phases induces a such high fractionation since Balistrieri et al. (2008) and Pokrovsky et al. (2008) revealed that Cu sorption on common mineral and organic surfaces favors the heavy isotope. The removal of light Cu isotope from the river water can be also explained by a preferential incorporation of light isotopes into bacteria, peryphytic biofilm or algae via intracellular assimilation (Navarrete et al., 2011; Coutaud et al., 2017) that could reduce Cu (Cu2+ → Cu+) before incorporation. Unfortunately, the degree of later processes impact could not be quantified. Note that the Cu sulfide precipitation which retains light isotope in the solid phase would also explain the enrichment of remaining solution in heavy isotope. However, this process is not evidenced in bed sediments of rivers from this region even if it could happen in the anoxic zone of sediments in lakes affected by acid mine drainage (Torres et al., 2013).

The Cu isotope data for World Rivers and the oceans show that the dissolved riverine Cu is enriched in heavy isotopes (~1.45‰) relative to the solid Earth (0–0.2‰) (Vance et al., 2008). The proposed mechanism of this fractionation is the redistribution between the dissolved and particle phases and the complexation by aqueous organic ligands that favors heavy isotopes in the complexed forms (Ryan et al., 2014). Vance et al. (2008) estimated a discharge-weighted average δ13Cu of ~0.69‰ (n = 29) for the dissolved riverine flux to the ocean. Our study shows that Cu removal due to the precipitation of secondary materials in mining areas could also produce heavy isotope enrichment of the dissolved fraction in river (up to 1.7‰). We also suggest that the distance between the sulfide source and the sampling point constrain the isotopic signature, that is, Cu isotopes are not conservative in the river water of mining areas. An environmental significance of these observations is that the proximity of Cu mine water source to the respectively.

Thermodynamic analysis included calculation of the speciation and the saturation indexes of aqueous solutions (Cobica and Chorrito Rivers) with respect to the common minerals of mining environments. These calculations were done using Visual MINTEQ ver. 3.0. The saturation index for two other minerals (Schwertmannite: Fe8O8(SO4)y(OH)x and hydrobasaluminite: Al4(SO4)3(OH)12–36H2O) were calculated using the apparent solubilities products of Bigham et al. (1996) and Bigham and Nordstrom (2000). In the upstream Chorrito River the speciation of the dissolved Cu is dominated by Cu2+ (~67%) and CuSO4 (~32%). Downstream the percentage of the Cu2+ increases up to 75% and organic complexes become significant (~18%) despite that the dissolved organic carbon concentration was only 1.5 mg/L. Concerning the saturation index it appears that the upstream waters of the Cobica River are over saturated with respect to ferrihydrite, goethite, K- and Na-jarosite (mainly K-jarosite) and schwertmannite and under saturated with respect to aluminous minerals (gibbsite and hydrobasaluminite). In the downstream point of the Chorrito River, the solution is under saturated with respect to ferrihydrite, goethite and schwertmannite but undersaturated with respect to K- and Na-jarosite. In the Cobica River the speciation of the dissolved Cu is dominated by Cu2+ (~65–75%) and CuSO4 (34–25%) with no strong differences between the upstream and downstream points. The upstream point of the Cobica River presents an over saturation with respect to ferrihydrite, goethite, K- and Na-jarosite (mainly K-jarosite) and schwertmannite but much less (not far from equilibrium) than in the Chorrito River. The solutions are under saturated with respect to gibbsite and hydrobasaluminite. In the downstream point, the solution appears to be undersaturated with respect of all the minerals considered above.

The decrease of Cu concentrations between the sulfide sources and the sampling point could result from precipitation of sulfate efflorescences. Former studies on mining areas of this region of Huelva have described the precipitation of Cu sulfate phases such as chalcantite (CuSO4·7H2O) and alpersite ((Mg,Cu)SO4·7H2O) near the sulfides source, contributing to the immobilization of Cu (Valente et al., 2013). Moreover, minerals well-known for their capacity for metals retention, such as jarosite and low crystallinity goethite could also precipitate (Sanchez-Espana et al., 2005; Valente et al., 2013), contributing to the decrease of Cu concentration at the more distal point. The decrease of Cu concentration along the Cobica River is stronger than that along the Chorrito River. This is coherent with Cu removal via precipitation along the stream since the last Cobica sampling point is much far from the sulfide source compared to the last Chorrito sampling point (10 and 2 km, respectively). Additionally, an increase in underground water input when progressing downstream may lead to dilution as another attenuation factor of Cu concentration in the river. However, it remains difficult to quantify these freshwater inputs reaching the surface through the fractured rock zone.

This increase of δ65Cu along the river main course implies that the fraction of Cu which is progressively removed from the dissolved phase is enriched in light isotope. We therefore hypothesize that the most likely process responsible for removal of light Cu isotope is Cu coprecipitation with jarosite and goethite along the river channel. It is unlikely that the sorption of Cu onto solid or biological (cell) phases induces a such high fractionation since Balistrieri et al. (2008) and Pokrovsky et al. (2008) revealed that Cu sorption on common mineral and organic surfaces favors the heavy isotope. The removal of light Cu isotope from the river water can be also explained by a preferential incorporation of light isotopes into bacteria, peryphytic biofilm or algae via intracellular assimilation (Navarrete et al., 2011; Coutaud et al., 2017) that could reduce Cu (Cu2+ → Cu+) before incorporation. Unfortunately, the degree of later processes impact could not be quantified.

Note that the Cu sulfide precipitation which retains light isotope in the solid phase would also explain the enrichment of remaining solution in heavy isotope. However, this process is not evidenced in bed sediments of rivers from this region even if it could happen in the anoxic zone of sediments in lakes affected by acid mine drainage (Torres et al., 2013).
river can be traced via positive isotopic signature of the river water. In this regard, the value proposed by Vance et al. (2008) has probably to be reconsidered because the contribution of Cu sulfide mines - located on coastal regions all around the world — to the riverine Cu dissolved flux is underestimated. For illustration, Olias et al. (2006) estimated that the Tinto and Odiel Rivers could account for 20% of the global gross flux of dissolved Cu. Thus, Cu isotope mapping of large rivers draining the mine regions is necessary to constrain the isotope signature of riverine flux to the Ocean.

6. Conclusion

This study established new features of Cu isotope fractionation in rivers draining the mining area:

- The Cu isotopic composition of AMD-affected Cu is heavier than the background mining waters, percolating shallow groundwater and the lake water. This confirms that the oxy-
  dative dissolution of sulfides preferentially releases heavy isotope in solution.
- Downstream the river, the removal of total dissolved Cu is accompanied by an increase in the $\delta^{65}$Cu value. We interpret this increase as a precipitation of Cu-bearing secondary minerals which preferentially incorporate light isotope. The non-
  conservative behavior of both Cu concentration and isotope composition downstream the same river highlights the importance of the sampling point location for characterizing the isotope composition of a river.
- Rivers draining Cu mining areas are enriched in $^{65}$Cu compared to the global average value (Vance et al., 2008). Considering that the riverine flux of Cu delivered to the world ocean from mining areas located on coastal regions is probably largely under-
  estimated, the global Cu isotopic composition of riverine flux to the ocean may be 0.2–0.3% higher than currently thought.
- Finally, our study shows that Cu isotopes may help us to understand the processes controlling Cu behavior within a mining area such as prefential uptake of the light isotope secondary Cu-
  bearing minerals which should be, however, confirmed by laboratory experiments. At the same time, the change in Cu isotopic composition along the river reveals that Cu isotopes do not allow straightforward tracing of metal sources in mining areas since the isotopic composition of the river is highly sensitive to the sampling location.

Acknowledgements

This work was supported by the french national programme EC2CO Bioheffect/Ecodyn/Dril/MicrobiEen (INSU/CNRS, France), the Paul Sabatier University (France) and the Department of Mining, Mechanical, Energetic and Construction Engineering of the University of Huelva (Spain).

References

  mica Acta 72, 311–328.
  mannette and the chemical modeling of iron in acid sulfate waters. Geochimica Cosmo-
  mica Acta 12, 2111–2121.
  teristics of heavy metal pollution in surface sediments of the Tinto and Odiel rivers estuaries (SW Spain). Environ. Geol. 41 (7), 785–796.
  mica Acta 72, 329–344.
  ference. Abstract 51.
Coutaud, A., Meheut, M., Viets, J., Rols, J.-L., Pokrovsky, O.S., 2017. Cu Isootope Frac-
  tionation During Cu Efflux from Phototrophic Biofilm: Possible Role of Cu Reduction and Comparison with Zn (Chemical Geology, submitted).
  ron. Geol. 39 (10), 1095–1101.


Santisteban Fernandez Maria, 2015. Incidencia de procesos AMD en la hidroquimica del río Cobica. Tesis Doctoral. Universidad de Huelva (Ined.).


