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# Dissolved versus colloidal U and Th under acid mine drainage conditions in Río Tinto area (Spain)

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## Abstract

Results of ultrafiltration experiments performed in acid waters from the Río Tinto acid mine drainage system in order to evaluate the role of colloids under acid mine drainage conditions indicate that for U and Th, a constant permeation model is applicable and does produce results that are compatible with the predicted behavior of these elements under acidic conditions. Results show that around 8,7% of total U is in the colloidal fraction. Results considering the 234, 235 and 238 U isotopes show similar percentages of retention in the colloidal fraction. Th is dissolved in the acid waters of Río Tinto, which agrees with the predicted dissolved character of Th under acid and high sulfate concentration conditions

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## 1. Introduction

U and Th series constitutes excellent tools for estimating rates in a wide variety of surficial scenarios including weathering rates, scavenging of different elements, comminution ages (timescale associated with the origin of sediments from bedrock transformation by physical weathering). Under neutral pH and oxidizing conditions, U is highly mobile in the hexavalent form, forming uranyl ion $UO_2^{2+}$ or soluble complexes mainly with carbonate and phosphate. This is not the case of the acidic conditions prevailing in Río Tinto where pH values are generally low (<

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2.5), redox conditions are oxidant (Eh values form 400 to 800 mV) and carbonate and phosphate ligands are almost absent. Instead, sulfate concentrations are very high (up to 10000 mg/l), the dominant U(VI) species having two coordinated sulfates, the concentration of uranyl ion $UO_2^{2+}$ being negligible. On the other hand, Th is considered to be a inmobile under neutral and oxidizing conditions. This is not the case of the acid mine drainage conditions in which, due to the low pH and high sulfate concentrations Th species are dominated by soluble sulfate complexes such as $Th(SO_4)^{2+}$ and $Th(SO_4)_{2(aq)}$ (Kim & Osseo-Asare, 2012). Depending on the sulfate concentration, at pH values higher than 2.8 to 3.8 Th precipitates as solid $ThO_2$ (Kim & Osseo-Asare, 2012).

Normal practice in surface- or groundwater sampling includes procedures such as acidification and filtering of samples and transport to the laboratory under refrigerating conditions. Filtering is normally performed by the use of 0.22 or 0.45 μm membrane filters and analysis on acid mine drainage waters, despite the high abundance of suspended matter, are usually performed with no further filtering. This is the case of the composition reported for the acid mine drainage system in the Río Tinto and Río Odiel basin in the Iberian Pyrite Belt (Spain) (see for example Olías et al., 2004; Sánchez-España et al., 2005; Villa et al., 2011; among others).

### *1.1. U and Th in Río Tinto waters*

Figure 1 shows the variation of the U and Th concentration with pH after 0.45 μm filtering. As expected from the theoretical behavior of these elements under low pH and oxidizing conditions, both exhibits high concentrations at pH below 2.5 and values below detection limit at higher pH values. U in Río Tinto water is likely derived from the rhyolite rocks in the headwaters but also from certain sulfides such as sphalerite. This is evidenced by the high correlation coefficients between dissolved U and Zn, Cd, Cu, and K in agreement with the previous data of Sánchez-España et al. (2005). For Th, high correlation coefficients are obtained for Al and K, which point also the rhyolites as the main source for this element. High correlation coefficients for light rare earth elements such as La, Nd and Sm are also obtained, which is typical of adsorption of these elements onto particles or colloids.

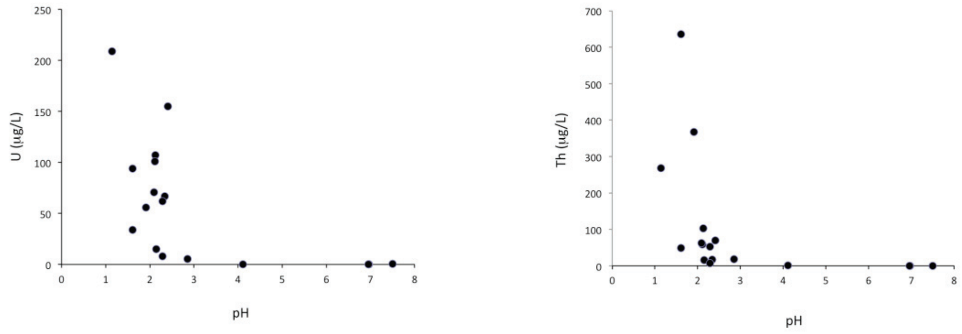

Fig. 1. (a) U concentration against pH at Río Tinto waters; (b) Th concentration against pH in the same samples.

$^{234}U/^{238}U$ activity ratios are in the range of 1.5 to 3 (Ketterer et al., 2011), which is the consequence of several processes occurring during weathering of the outcrops at the headwaters but also due to processes related to acid mine drainage (Barbero et al. submitted). $^{230}Th/^{234}U$ ratios vary in a very wide range from 0.0046 to 170,352 in analysis performed in 0.22 μm filtered samples, indicating a very different behavior of Th in between different samples.

The main objective of this preliminary study is to estimate the role of colloids when considering Th and U concentrations and isotopes under conditions prevailing in acid mine drainage, as colloids are very abundant in these scenarios when iron oxi-hydroxides and secondary sulfates precipitates as pH is raised.