

Study of the origin, migration and precipitation of Th-U in acid rock drainage (León, Spain)

E. SANTOFIMIA^{1*}, F.J. GONZÁLEZ¹, E. LÓPEZ-PAMO¹

¹¹Geological Survey of Spain (IGME), Madrid, Spain

(* correspondence: e.santofimia@igme.es)

Since the construction of a highway, the La Silva Stream is affected by acid rock drainages (ARDs), which were generated after the oxidative dissolution of pyrite in organic-rich shales excavated. ARDs in La Silva are acid water (pH 3-4), with high concentrations of SO_4^{2-} and heavy metals [1].

An anomaly was detected as respect to dissolved Th-U values (up to 300 and 150 $\mu\text{g/L}$ respectively), observing an enrichment of several orders of magnitude if these values are compared with natural waters. This enrichment was also observed in stream-sediments and precipitates studied.

The study of the lithology includes petrographic, mineralogical and geochemical methods (XRD, EPMA, SEM XRF and ICP-AES and ICP-MS). Organic-rich Ordovician shales (TOC 1.16%) show abundant pyrite crystals ($<100 \mu\text{m}$), dispersal in the matrix and forming veins. These shales, with average contents of Th and U of 18 and 2 $\mu\text{g/g}$ respectively, contain disseminated detrital micro-grains of highly resistant to weathering minerals, bearing Th-U, like monazite and xenotime. Th-U is probably also sorbed onto clay minerals in the organic-rich shales.

Th is considered to be immobile under neutral and oxidizing conditions, but a low pH, Th-U in sulphated waters can be dissolved as a sulphated ionic complex [2]. After running the calculations with Phreeqc [3] on the chemical speciation of Th-U, we know that Th is present in solution as $\text{Th}(\text{SO}_4)_2$ at 65% and $\text{Th}(\text{SO}_4)_3^-$ at 27% and U as UO_2SO_4 at 71%, UO_2^{+2} at 20% and $\text{UO}_2(\text{SO}_4)_2^{-2}$ at 9%.

The study of precipitates was carried on using a set of analytical techniques (XRD, XRF and SEM), which revealed that these mineral phases were mainly schwertmannite and goethite. A typical characteristic of schwertmannite is its high specific surface, whereby it is capable of removing dissolved metals through adsorption. The sampled iron precipitate has shown an enrichment of the following trace elements: $\text{Th} > \text{Cr} > \text{As} > \text{Cu} > \text{Zn} > \text{Ni} > \text{V} > \text{U}$, Th being the most abundant trace element, with contents up to 798 $\mu\text{g/g}$, showing a strong affinity for iron precipitation.

[1] Santofimia & López-Pamo (2017) Environ Sci Pollut Res 23:14502-14517. [2] Langmuir & Herman (1980). Geochim Cosmoch Ac 44:1753-1766. [3] Parkhurst & Appelo (1999) U.S. Geological Survey 99-4259.