Solid speciation of As, Pb and Sb-rich anthropogenic residues

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We studied As, Pb and Sb solid speciation to better understand the geochemical pathways and mobility of these potentially toxic elements, which are released upon weathering of mining and industrial waste products. Such studies are indispensible to understand soil and water contaminations and to propose remediation solutions. Studied samples are mining residues (mill tailings and slags) from the French Massif Central, generated by former activities over a century (1830 to 1970). They were collected at two different mining districts: Pontgibaud, which was one of the largest production site for Ag and Pb (c.a. 50’000 t Pb) and Brioude-Massiac, which produced around 40’000 t of Sb (second largest nationwide production). Samples were also studied to compare the evolution of industrial processes and to test the variations in Pb or Sb retention.

Mining residues from the two locations show elevated concentrations in As, Pb and Sb, up to 0.16%, 6.6% and 1.1% respectively. However spatially concentrated accumulations of As (up to 11 wt.%), Pb (up to 70 wt%) and Sb (up to 28 wt.%) are also observed. The mineralogical characterization of the products with such contents is essential for the modeling of the geochemical processes controlling the toxicity of these elements. Arsenic, Pb and Sb have only been detected in secondary products resulting from oxidation of Pb or Sb-rich sulfides (galena, stibnite and berthierite) but only few relics of primary sulfides have been observed. Synchrotron X-ray microdiffraction (beamline 12.3.2, Advanced Light Source, USA) and micro-Raman investigations indicate that Sb forms complex mixing phases with goethite and/or lepidocrocite. Antimony is also trapped by jarosite suggesting a substitution of $Fe^{3+}$by Sb^{5+} (up to 3% Sb). Antimony is present as oxides, stibiconite $SbSb_2O_6(OH)$ and associated with Fe, and possibly Mn (oxy-)hydroxides within solid phases of highly heterogenous compositions. Arsenic is also typically associated to iron (oxy-)hydroxides presenting various cristallinity. Main Pb host phases are sulfates (e.g., anglesite $Pb(SO_4)$, beudantite $Pb(Fe_{2.54}A_{1.46})(As_{1.07}O_4)(S_{0.93}O_4)(OH)_6$) but Pb is also associated to complex mixing of silicates and Fe oxides.

S isotopes distinguish two S pulses at terrestrial Cretaceous-Paleogene boundary sections

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The Cretaceous-Palaeogene (K-Pg) boundary marks a major biotic turnover in Earth’s history that may have resulted, at least in part, from a massive bolide impact.

Two of the northernmost occurrences of the K-Pg boundary in terrestrial sediments have been positively identified on the Knudsen’s *T. rex* Ranch in the Scollard Formation of south-central Alberta, Canada. We conducted a high-resolution (2-cm intervals) study of bulk sulfur isotopes and sulfur content across a ~50-cm stratigraphic interval spanning the K-Pg boundary, representing a time interval of ~500 Ka.

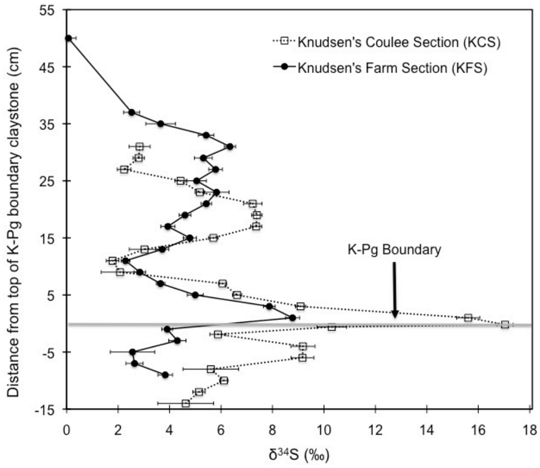

Figure 1: $\delta^{34}S$ profiles at the Knudsen’s *T. rex* Ranch

Positive $\delta^{34}S$ excursions at both sites reveal a pulse of ^{34}S-enriched sulfur at the boundary, likely originating as oceanic sulfate and evaporite target rocks. Post-boundary $\delta^{34}S$ excursions may reflect injection of volcanically-derived sulfate aerosols; at least one peak (KFS) is contemporaneous with a major phase of Deccan trap volcanism. Analyses of minor S isotopes (^{33}S, ^{36}S) offer the possibility to validate our interpretation of the origins of the boundary and post-boundary S injections into the freshwater environment.