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TEM study on the localisation of Th in an Al-ore industrial residue

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Thorium is a significantly radioactive element that occurs in most rocks and soils, with relatively high concentrations of ~10 ppmw on the Earth's crust. Thorium is also present in Al-ores (bauxites) and is concentrated into their metallurgical residues produced through the industrial Al production process [1]. However, the nature of Th in the metallurgical residues is not fully understood. Here, we use advanced electron microscopy to identify the location of Th and its carrier minerals in a metallurgical residue. The sample was provided from the Aluminium of Greece S.A. company and contains a significant amount of Th, ~110 ppmw [2].

The sample is composed of gibbsite ($\text{Al}(\text{OH})_3$), diaspore (AlOOH), hematite (Fe_2O_3), calcite (CaCO_3), cancrinite- and hydrogarnet-like phases as major minerals along with fine-grain aggregates with the "Na, Al, Si, Ca, Ti, Cr, Fe" composition, which was examined by XRD and SEM [2]. There is no sign of Th in the SEM observations, implying either the very low concentration over the sample or the local accumulation with below submicron size (in minerals or as precipitate). Several major mineral phases are identified by TEM; diaspore, hematite, anatase (TiO_2) and clay-like minerals but none of them contains detectable Th. However, long dwell time and high count rate TEM-EDS measurements allowed Th in a perovskite-type (CaTiO_3) mineral to be detected with sufficient signal levels, ~700 ppmw Th. The identified perovskite-type mineral has typically ~200 nm in size and contains a significant amount of Na ($\text{Na}/\text{Ca}=0.25$). Electron diffraction patterns from this phase show diffraction spots additional to those from perovskite, which might be caused from the presence of Na and/or O vacancies. The incorporation of Th into perovskite also has been supported by EXAFS study [2]. Our measurements suggest the perovskite-type mineral can be one of the major Th carriers but from the small volume fraction of the perovskite ($\ll 1\%$) in this sample, Th should also exist in other forms, in which the concentrations of Th are below the detection limit of the used instrument (<100 ppmw).

[1] Adams & Richardson (1960) *Econ. Geol.* 55, 1653.

[2] Gamaletos et al. (2016) *Sci. Rep.* 6, 21737 (in press)