Geophysical Research Abstracts
Vol. 20, EGU2018-16696-1, 2018
EGU General Assembly 2018

Synchrotron X-ray cryomicrospectroscopy on radiation sensitive samples: Thallium speciation in contaminated soils

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Thallium, a highly toxic trace metal, occurs in the environment mostly as Tl(I) and Tl(III). Relatively soluble monovalent Tl(I) can sorb onto clay minerals and mineral oxides.....[1], whereas less soluble trivalent Tl(III) precipitates as Tl_2O_3or sorbs onto Mn-oxides.....[2]. Given these differences, speciation information is of primary importance to evaluate the mobility and potential toxicity of Tl in the environment.

Synchrotron-based X-ray absorption spectroscopy (XAS) allows to gain information on the redox state and speciation of trace elements, with down to micrometric spatial resolution when using a micro-focused X-ray beam. However, third-generation synchrotrons are characterized by increasingly higher photon flux density, which raises concerns about beam-induced chemical changes due to the breaking of chemical bonds and/or the promotion of the formation of radical species...[3]. A number of studies have shown that the rate of radiation-induced damage can be slowed down at low (cryogenic) temperatures. Additionally, sample exposure to the beam can be reduced by collecting energy maps at discrete energies across X-ray absorption edges that allow discriminating relevant chemical species. With the combination of low sample exposure and temperature, we can obtain spatially-resolved speciation information on dilute samples with minimal instrumental artifacts.

Thallium is a radiation sensitive element, therefore speciation information as obtained by X-ray techniques available in third generation synchrotrons may be affected by measurment artifacts. In this study, we show that beam-induced artifacts (speciation change) can be reduced by lowering sample temperature and X-ray exposure. By carrying out chemical redox mapping at discrete energies on thin-sections, we monitored variations in the oxidation state of Tl associated with Mn-concretions in geogenically Tl-rich soils from the Swiss Jura mountains. The observed heterogeneity in the redox-state of Tl associated with Mn-concretions points to complex redox dynamics in association with the biogeochemical cycle of Mn in these soils, which will be further explored in ongoing cryo-microspectroscopy work.

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