

International Master 2 Atmospheric Sciences: Research Training 2022-2023

Laboratory: LPCA - Laboratoire de Physico-Chimie de l'Atmosphère (ULCO)

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Eventually CaPPA Work Package: WP2. Aerosol microphysical, chemical and optical properties from fundamental heterogeneous processes to remote sensing

A computational insight of the isotopic composition during hematite dissolution in acidic oxalate solutions

Isotopic compositions have been employed to address the transport and transformation processes that various light elements undergo in nature. Fortunately, advances in analytical techniques such as *Multiple-Collector Inductively Coupled Plasma Mass Spectroscopy* (MC-ICP-MS) have made possible the extension of this quantity to the study of transition metal isotopes. For instance, isotopic composition can potentially be used to trace the natural and anthropogenic atmospheric sources of iron to the oceans, where this element is an essential micronutrient for marine phytoplankton, i.e. for the sequestration of CO₂ by the oceans.

However, a previous study has shown that the isotopic composition of Fe-bearing aerosols may change during their atmospheric transport [1]. In fact, the formation of complexes on the particles surface seems to constrain the release of soluble heavier Fe isotopes [2]. Therefore, a computational study turns out to be useful in order to shed light onto this process at a molecular scale.

The internship aims at complementing the experiments realized within our group mimicking the dissolution of hematite particles (a proxy for Fe-bearing aerosols) in cloud water, this latter simulated by an acidic oxalate solution. Specifically, the structure, energy and vibrational frequencies of oxalate-hematite model clusters, representing the possible oxalate complexes adsorbed on the hematite surface, will be computed by means of density functional theory (DFT) calculations. Fractionation factors between dissolved and surface Fe-oxalate complexes will be theoretically estimated from their respective vibrational frequencies following the approach described in reference [3] and compared to available experimental data.

[1] Mulholland *et al.*, *Atmospheric Environment* **2021**, 259, 118505.

[2] Maters *et al.*, *Chemosphere* **2022**, 299, 134472.

[3] Urey, *J. Chem. Soc.* **1947**, 562.

Key words: atmospheric chemistry, iron oxides, aerosols, isotope fractionation