

Structural incorporation of Mo⁶⁺ into iron oxides

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Molybdenum is a significant prerequisite for the biosynthesis of several metalloenzymes and essential for all known life forms on earth. Especially in recent years, the mobility and bioavailability of Mo in soil attracted large interest with particular focus on the most abundant molybdenum specie in environmental systems, Mo⁶⁺. In soils, molybdenum belongs to the trace elements and occurs in a range of 0.2 – 6 mg/kg (He et al., 2005) from which a major fraction is considered to be not bioavailable. Interactions of Mo with the mineral fraction of the soil, which strongly binds Mo by surface adsorption or structural incorporation, are the most likely the cause for this low bioavailability. Various studies emphasized the adsorption mechanisms of Mo to many different soil constituents, whereas information about the structural incorporation of Mo in soil minerals remains scarce. Studies by Lang (2000) and Lang & Kaupenjohann (1999) show that the major fraction of Mo in forest soils is associated with the crystalline Fe phases in these soils. Therefore, we investigated some of the most common iron oxides in soils as possible scavengers for Mo⁶⁺, including goethite (α -FeOOH), hematite (α -Fe₂O₃), magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃) and ferrihydrite (Fe₂O₃·nH₂O).

Mo-bearing iron oxides were synthesized after modified procedures described in Schwertmann & Cornell (1991). During the formation of the iron oxides, Na₂MoO₄·2H₂O was added in various concentrations, ranging from molar Mo:Fe ratios in the starting solution from 0.01 to 1. After synthesis, surface-bound Mo⁶⁺ was removed by treating all iron oxides with a 0.2 M K₂HPO₄/KH₂PO₄ solution (Liang & Zhu, 2016). Phase purity was checked by powder X-ray diffraction. Elemental composition of all samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). X-ray absorption near edge structure (XANES) spectra of the Mo L_{2,3}-edge were obtained at the SUL-X beamline, Angströmquelle Karlsruhe (ANKA), Germany, and extended X-ray absorption fine-structure (EXAFS) spectra of the Mo K-edge at the Diamond Light Source, UK. All obtained spectra were processed and fit with the IFEFFIT software package (Ravel & Newville, 2005).

The loss of Fe, indicated by ICP-OES suggests that all investigated iron oxides structures, except goethite, incorporate Mo⁶⁺, while the highest Mo concentrations can be found in ferrihydrite (6-line) with 7.4 wt% Mo. Magnetite and maghemite, in comparison, incorporate a maximum of about 0.4 wt%. The XANES spectra of all our samples, except magnetite, displayed significant peak splitting of the white line, ranging from 2.59-3.27 eV, indicating Mo in octahedral coordination with oxygen (Bare, 1993, Aritani, 1996). Magnetite is the only exception in our samples as there is no peak splitting at the Mo L₃-edge visible which indicates the tetrahedral incorporation of Mo in its structure. The ongoing analysis of the EXAFS regions supports the structural incorporation of Mo into the iron oxides.

These results indicate that iron oxides might belong to the major sinks of molybdenum in soils and reduce the bioavailability of this vital trace metal for plants and microorganisms alike.

References

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