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Adsorption of mono- and poly-molybdate (MoO_4^{2-}) onto Fe-oxides: A multi-technique approach

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Molybdenum (Mo) is a key trace element and exists as molybdate [Mo(VI)O_4^{2-}] in oxic soil environments associated with mining, and other extractive industries. At high concentrations molybdate in soils can be toxic to plants/animals. Iron oxide minerals, uiquitous in the environment, such as hematite ($Fe^{3+}_2O_3$) and magnetite ($Fe^{2+}Fe^{3+}_2O_4$) can control the mobility of Mo; in particular through absorption due to high surface area and redox processes.

We characterised molybdate adsorption processes to hematite and magnetite under key environmental conditions including pH (3-13) and Mo concentration (1-200 ppm) using a multi-technique approach. Wet chemistry, geochemical modelling (PHREEQC), Infrared Spectroscopy (ATR-FTIR) and X-ray Absorption Spectroscopy (XAS) were used holistically to identify adsorption mechanisms and changes in chemical state.

ATR-FTIR indicates that for hematite both pH and Mo concentration are key variables in the formation of poly- vs. mono-molybdate (Figure 1), which has also been verified by PHREEQC. XAS indicates the formation of a inner-sphere bidentate monomolybdate adsorption complex above pH 5, and a polymolybdate complex below pH 5, at the hematite surface. XAS also indicates Mo(VI) is reduced to Mo(IV) when adsorbed to magnetite.

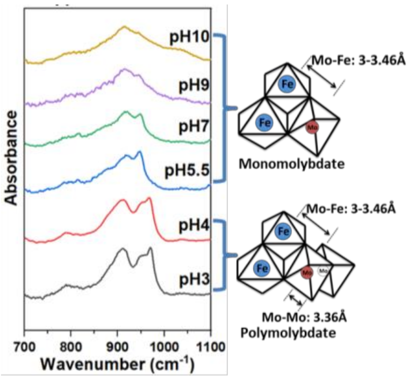

Figure 1. ATR-FTIR analysis for 50 ppm Mo adsorption to hematite.

This provides a detailed understanding of Mo adsorption at the molecular scale providing a comprehensive dataset for determining the environmental speciation and mobility of Mo in varying geochemical scenarios.