Stability and Transformation of Amorphous Fe-oxyhydroxides in the Presence of Environmenatlly Relevant Ligands

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Fe-oxyhydroxides play a vital role in Fe bioavailability and heavy metal adsorption in the environment. Amorphous phases are more bioavailabile and have a higher sorption capacity than crystalline phases, but the residence time of amorphous phases in the environment is not known. Natural ligands can influence the longevity of the amorphous phase by coordinating to evolving Fe-oxyhydroxide polymners. If ligands bind strongly to the amorphous Fe-oxyhydroxide phase, they can block polymerization reactions and slow the transformation to crystalline Fe-oxyhydroxide phases. This is expected for strongly complexing ligands, such as SO_4^{2-}, SiO_4^{4-} and HCO_3^-. Ligands such as NO_3^- and Cl^- are not expected to complex strongly with amorphous Fe-oxyhydroxide phases. The growth and transformation of amorphous Fe-oxyhydroxide precipitates were monitored by IR and x-ray absorption spectroscopy at pH 5.5 and 8.0 in the presence of the aforementioned ligands.

The stability of amorphous Fe-oxyhydroxides formed in the presence of Cl^-, NO_3^-, SO_4^{2-} varied significantly. Chloride had the strongest effect on the longevity of the amorphous phase, delaying goethite formation 2.2x longer than NO_3^- and 3x longer than SO_4^{2-} at pH 5.5. At pH 8, SO_4^{2-} had the strongest effect, delaying goethite formation 4.9x longer than NO_3^- or Cl^-. The rate of goethite formation at both pH 5.5 and pH 8.0 also varied with ligand. The addition of dissolved SiO_4^{4-} did not influence the stability of the amorphous phases significantly unless it was added after the precipitates had formed. The use of HCO_3^- as the base (instead of OH^-) caused changes to the bulk structure of the Fe-oxyhydroxide precipitates at both pH 5.5 and pH 8.0. Over time, ligand concentrations in amorphous Fe-oxyhydroxides decreased, indicating that ligand expulsion is closely tied to the structural reorganization of the amorphous phase.

These results indicate that the associated ligands play a significant role in the stability of amorphous precipitates, and their transformation to crystalline phases. This must be taken into account if the role of Fe-oxyhydroxide phases in biological metal acquisition and heavy metal storage in the environment is to be fully understood.