Effect of metal cations on Fe(II)-induced phase transformation of ferrihydrite

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Iron minerals are one of the most active constituents of soils and play important roles in the biogeochemical cycles of soil elements. Besides the dissimilatory iron reduction and ferrous oxidation, the direct interplay between aqueous Fe(II) species and the structural Fe(III) in soil iron-bearing minerals is one of the most important reactions of the iron cycle. Fe(II)-induced phase transformation of iron (hydr)oxides during the interplay has been reported and the coexisting metal pollutants have been found to inhibit the phase transformation rates. However, the underlying mechanisms of the metal cation effect and the most critical property of metal cations responsible for the inhibition remain unclear. The present study focused on the cation effect of seven divalent cations (indicated as Me(II), including Mg(II), Ca(II), Ba(II), Mn(II), Co(II), Ni(II), and Zn(II)) and herein the influencing mechanisms on Fe(II)-induced transformation processes of ferrihydrite. The stability constant (logK) of Me(II) was explored to be critical in affecting the ferrihydrite transformation. The Me(II) with higher binding stabilities (higher logK values) decreased the bound-Fe(II) intensity on ferrihydrite and reduced the redox activity of the Fe(II)-catalyzed system, so as to more inhibit the transformation rates of ferrihydrite. The phase transformation rates were negatively correlated with the logK values of Me(II). Besides the inhibition effect, Me(II) were partly stabilized in the formed secondary iron minerals. The binding stabilities of Me(II) also affected the ferrihydrite transformation pathways of ferrihydrite through affecting the intensity of bound-Fe(II) on ferrihydrite. Ferrihydrite was first transformed to lepidocrocite and then to goethite and magnetite when with Me(II) that had lower logK values than Fe(II), whereas directly transformed to goethite and magnetite when with Me(II) that had higher logK values than Fe(II).