Spectroscopic evidence reveal the contribution of aqueous Fe(II) to the recrystallization of lepidocrocite

MANJIA CHEN[1], YUHUI LIU[2], CHENGSHUAI LIU[2*], JIAN HUA[1], FANGBAI LI[1]

[1] Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management, Guangdong Institute of Eco-environmental Science & Technology, Guangzhou 510650, P. R. China

[2] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550009, P. R. China

*correspondence: liuchengshuai@vip.gyig.ac.cn

The aqueous Fe(II) ($Fe(II)_{aq}$)-induced phase transformation of iron mineral is an important part of soil iron cycling, which plays a critical role in the behavior of pollutants. The Fe atom exchange and electron transfer between $Fe(II)_{aq}$ and structural Fe(III), and thus induced phase transformation are well-known. However, the reletive contribation of initial $Fe(II)_{aq}$ and iron mineral to the phase transformation is unclear. In this study, we focus on and the relative contributions of initial $Fe(II)_{aq}$ and lepidocrocite during the phase transformation of lepidocrocite induced by $Fe(II)_{aq}$. Enriched ^{57}Fe isotope tracer and Mössbauer spectroscopy (MS) studies demonstrated that $^{57}Fe(II)_{aq}$ undergoes electron transfer and atom exchange with lepidocrocite, and lepidocrocite was transformed into new lepidocrocite and goethite. When compared the abundance of goethite detected by MS analysis with that detected by X-ray diffraction (XRD) analysis, the higher abundance of goethite in the XRD results confirmed the initial $Fe(II)_{aq}$ and lepidocrocite both involved the phase transformation of lepidocrocite during the process. A brief model was established by the reaction of ^{57}Fe(II) + ^{56}lepidocrocite, with ^{56}lepidocrocite, ^{57}lepidocrocite, ^{56}goethite, and ^{57}goethite as products. Based on the model, the relative contributions of initial $Fe(II)_{aq}$ and lepidocrocite on the phase transformation were derived. The relative contribution of initial $Fe(II)_{aq}$ to the phase transformation decreased during the reation, whereas the contribution of relative contribution of lepidocrocite increased. The relative contribution of initial lepidocrocite to the phase transformation was higher than that of initial $Fe(II)_{aq}$, and about 60% of phase transformation depended on the initial lepidocrocite after reaction 14 days. These findings provide a quantitative interpretation of the contribution of initial $Fe(II)_{aq}$ and iron mineral to the phase transformation, which could assist the mechanistic understanding of the iron cycling in soil environment.