## Oxidation mechanism of Fe( $\Pi$ )<sub>aq</sub>-induced crystalline phase reconstruction of goethite coupling with As( $\Pi$ )

LIU Ya-nan<sup>1,2,3#</sup>, CHEN Man-jia<sup>2#</sup>, TONG Hui<sup>1,2</sup>, LI Fang-bai<sup>2</sup>, LIU Cheng-shuai<sup>1,2\*</sup>, HUA Jian<sup>2</sup>, LONG Sheng-qiao<sup>1,3</sup>, GAO Ting<sup>1,3</sup>, LIU Yu-hui<sup>1,3</sup>, XIA Ya-fei<sup>1,3</sup>

(1. State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences,
Guiyang 550081, China; 2. Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management,
Guangdong Institute of Eco-Environmental Science & Technology, Guangzhou 510650, China; 3. The University of
Chinese Academy of Sciences, Beijing, 100049, China)

Abstract: Arsenic is an important heavy metal pollutant in the soil. Its toxicity is mainly controlled by its morphology and redox state in the environment. Aqueous Fe( $\mathbb{II}$ )<sub>aq</sub>-induced crystalline phase reconstruction of iron (hydroxides) oxides is an important part of the iron cycling in the soil. This significantly affected environmental behaviors, such as the adsorption, stabilization, and passivation, of heavy metals in the soil. In this study, the redox and morphology variation of arsenic in the process of Fe( $\mathbb{II}$ )<sub>aq</sub>-induced crystalline phase reconstruction of goethite, which was coupled with As( $\mathbb{III}$ ), under the anaerobic condition has been investigated by using <sup>57</sup>Fe iron stable isotope tracing method. Results show that As ( $\mathbb{III}$ ) was not oxidized by the goethite though more than 83% of As( $\mathbb{III}$ ) was adsorbed on the surface of goethite which was only existed for the comparison treatment of the system. In the Fe( $\mathbb{II}$ )<sub>aq</sub> and goethite coexisted system, the Fe( $\mathbb{II}$ )<sub>aq</sub> could exchange atoms of the Fe( $\mathbb{II}$ ) which is the structural state of goethite. The existence of As( $\mathbb{II}$ ) in the system reduced the iron atom exchanging velocity. Meanwhile, in the process of Fe( $\mathbb{II}$ )<sub>aq</sub>-induced crystalline phase reconstruction of goethite, 77% As( $\mathbb{III}$ ) was oxidized to As( $\mathbb{V}$ ) and the As activity was decreased. Furthermore, small part of As( $\mathbb{II}$ ), which was adsorbed on the surface of goethite, and the As( $\mathbb{V}$ ) transformed from the oxidation of As( $\mathbb{III}$ ) were fixed into the structure of goethite in forms of inclusions in lattice unit or substituting the structural position of Fe. This will further reduce the activity of As.

**Keywords:** iron (hydroxide) oxide; heavy metal; iron atom exchange; stable isotope tracing method; crystalline phase reconstruction