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Ferric vs. ferrous arsenate amorphous precursors: Properties and controls on scorodite mineralization

PEI CHANG[1], XIANGYU ZHU[1,*], HONGMING CAI[1], JIANCHAO ZHANG[1], SILIANG LI[1], XIANCAI LU[2], RUCHENG WANG[3], AND HUI HENRY TENG[1,*]

[1]Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China
[2]Key Laboratory of Surficial Geochemistry, Ministry of Education, School of Earth Sciences and Engineering, Nanjing University, Nanjing, Jiangsu 210023, China
[3]State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing, China

ABSTRACT

Amorphous iron-arsenate precipitates are significant As sinks in natural and industrial settings and often serve as precursors to the crystallization of ferric arsenate minerals such as scorodite ($FeAsO_4 \cdot 2H_2O$) and kankite ($FeAsO_4 \cdot 3.5H_2O$). These amorphous phases have varied structures and compositions depending on the geochemical conditions under which they form but have not been well characterized except for the frequently encountered amorphous ferric arsenate (represented as AFe^{III} in the present study). Here, we intend to characterize another phase, amorphous ferrous arsenate (AFe^{II}), which is formed in partially oxidized Fe(II)-As(V) systems, and carry out a comparative study on the properties and related scorodite mineralization processes relative to those of AFe^{III}. We synthesized both AFe^{II} and AFe^{III}, determined their compositions and structures, and finally examined the amorphous-crystalline phase transition processes leading to scorodite mineralization. Computed chemical formulas showed AFe^{III} and AFe^{II} can be represented by $Fe(III)_{0.99}AsO_4 \cdot 4.1H_2O$ and $Fe(III)_{0.48}Fe(II)_{0.43}(HAsO_4)_{0.7}(AsO_4)_{0.3} \cdot 4.0H_2O$, respectively, with AFe^{II} containing 47.3% Fe(II), as deduced from the pre-edge data of Fe *K*-edge X-ray absorption spectroscopy. Structurally, the Fe-O bond at 2.02 ± 0.01 Å in AFe^{II} was significantly longer than that of 1.99 ± 0.01 Å in AFe^{III} and scorodite. In addition, AFe^{II} appeared to have a higher stability (slower kinetics of scorodite crystallization) under either atmospheric or aqueous conditions. Together with solution chemistry measurements, these findings suggest AFe^{II} controls scorodite formation by limiting the occurrence of aqueous Fe^{3+} and retards the amorphous-scorodite phase transition compared to the case of AFe^{III}. These findings improve our understanding of iron arsenate system and may find industrial applications to arsenic sequestration via scorodite mineralization.

Keywords: Iron arsenate crystallization, non-classical nucleation, Fe^{2+}- vs. Fe^{3+}-amorphous phases, XAFS structural analyses