

## **Synthesis, characterization, and thermodynamics of arsenates forming in the Ca-Fe(III)-As(V)-NO<sub>3</sub> system: Implications for the stability of Ca-Fe arsenates**

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### **ABSTRACT**

Arseniosiderite and yukonite are among the important arsenate minerals occurring as secondary alteration products in relation to the oxidation of arsenopyrite and arsenian pyrite and as discrete grains in some gold ores, mine tailings, and contaminated soils. Characteristics of these Ca-Fe arsenate species are not well known and our understanding of the conditions promoting their formation and dissolution is limited. Long- and short-range structural characteristics and thermodynamic properties of the Ca-Fe arsenates forming in the Ca-Fe(III)-As(V)-NO<sub>3</sub> system were determined to better predict the mineralogical transformations taking place in neutralized sludge and tailings environments, and their influence on arsenic mobilization. Yukonite and arseniosiderite readily form from solutions with highly variable compositions at a wide pH range from slightly acidic to alkaline conditions. Calcium concentrations corresponding to molar Ca/(Ca+Fe+As) ratios as low as 0.1 appear to be adequate for their formation. Our experimental results confirm observations in natural settings and mine tailings where scorodite is progressively replaced by yukonite and arseniosiderite. The initial amorphous precipitates made of small oligomeric units of edge-sharing FeO<sub>6</sub> octahedra with bridging arsenate evolve to yukonite through the establishment of corner linkages between the FeO<sub>6</sub> chains. Yukonite represents a nanocrystalline precursor and Ca-deficient variety of arseniosiderite. Formation of arseniosiderite is kinetically controlled with faster development of crystallinity at neutral to slightly acidic pH and slower kinetics under alkaline conditions. Calorimetric measurements provided an enthalpy of formation value of  $-1950.3 \pm 3.1$  kJ/mol and standard entropy of  $237.4 \pm 4.4$  J/(mol·K) for arseniosiderite [with composition Ca<sub>0.663</sub>Fe<sub>1.093</sub>(AsO<sub>4</sub>)(OH)<sub>1.605</sub>·0.827H<sub>2</sub>O], the corresponding Gibbs free energy of formation is  $-1733 \pm 3.4$  kJ/mol. A rough estimate of the thermodynamic properties of yukonite is also provided. Arseniosiderite is a stable arsenate between pH 3.5 and 7.5 in solutions saturated with respect to soluble Ca minerals such as calcite, gypsum, anorthite, or Ca-montmorillonite. Arsenic release from mine wastes and contaminated soils can be effectively controlled by arseniosiderite and the conditions promoting its formation such as lime-treatment leading to gypsum saturation in ferric arsenate solutions would prove to be desirable for stabilizing arsenic in the form of arseniosiderite in mine wastes.

**Keywords:** Arsenic, arsenate, arseniosiderite, yukonite, arsenic control, mine wastes