Reaction pathways of iron-sulfide mineral formation: an in situ X-ray diffraction study

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Abstract: Iron sulfides were synthesized via a co-precipitation method. In addition, synchrotron-radiation experiments were performed under a range of pH and temperature conditions (up to 100 °C) to compare the results of in situ and ex situ crystal growth investigation of iron sulfides. In acidic environments, H2S acts as an oxidant, oxidizing Fe2+ to Fe3+ and allowing formation of greigite from mackinawite. However, under neutral conditions, due to very low H2S concentrations, the oxidant may be S (instead of H2S), allowing mackinawite to transform into greigite. Both mackinawite and magnetite were present under alkaline conditions, with possible transitions of Fe(OH)2, followed by 3Fe(OH)2 → Fe3O4 + 2H2O + H2. In situ X-ray diffraction results indicate that the mineral transformation rate under acidic conditions is faster than under neutral and alkaline conditions. This means that acid environments can enhance rapid phase transformation of iron sulfides. The results under different experimental conditions suggest that there is a variety of formation pathways for iron-sulfide minerals owing to the presence of different oxidants in different geochemical environments.

Key-words: iron sulfide; crystal growth; co-precipitation method; ex situ and in situ; reaction pathway; pyrite; greigite; mackinawite; X-ray diffraction; synchrotron.

1. Introduction

Iron sulfides constitute one of the most common mineral groups on Earth; variations in their chemical composition and structure result in different minerals, e.g. mackinawite (tetragonal FeS), greigite (Fe3S4), pyrite (FeS2), troilite (hexagonal FeS), and pyrrhotite (Fe1−xS). Among them, mackinawite is metastable with a layered structure. Greigite is also a metastable phase, with an inverse spinel structure in which all Fe(II) atoms occupy octahedral sites and Fe(III) atoms occupy both tetrahedral and octahedral sites. Pyrite is the most stable iron sulfide, and has a cubic structure. Crystal structures of mackinawite, greigite, and pyrite (Skinner et al., 1964; Lee, 2004; Oertzen et al., 2005; Devey et al., 2009; Brocho & Miller, 2012; Bai et al., 2014; Birkholz, 2014; Kwon et al., 2015; Mehlape et al., 2015) are shown in Fig. S1, freely available as Supplementary Material linked to this article on the GSW website of the journal, http://eurjmin.geoscienceworld.org/.

The abovementioned minerals are of special geological significance. For example, greigite is used as an indicator for the presence of methane in natural gas hydrate (Horng & Chen, 2006; Larrasoána et al., 2007); it is also the best recorder of geomagnetic fields in sedimentary rocks (Horng et al., 1998; Jiang et al., 2001; Horng & Roberts, 2006). The growth process and phase transformation of iron sulfides also play an important role in the global sulfur cycle and in the origin of life (Berner, 1983; Schoonen et al., 1999; White et al., 2015). Moreover, the transformation of iron sulfides can influence trace-metal concentrations in groundwater (Jeong & Hayes, 2007; Hayes et al., 2009), and shallow (less than 450 m deep) storage of nuclear waste (Bourdouiseau et al., 2010; Sergeev et al., 2015). Particle size, morphology, and degree of pyrittisation of these minerals are indicative for their formation environments, and thus can provide insights into paleoenvironmental conditions (Bolshakov & Dolotov, 2012; Chang et al., 2014; Fu et al., 2015). Furthermore, these minerals have many applications for batteries and medical sciences (Li et al., 2014; Liu et al., 2014). However, the formation mechanisms of different types of iron sulfides in sediments and the chemical conditions required for their stable existence remain partly unclear.

There are three common iron sulfide formation pathways in sediments identified from previous studies (Benning et al., 2000; Hunger & Benning, 2007; Lan & Butler, 2014):

\[ 3 \text{FeS} + S = \text{Fe}_3\text{S}_4, \quad \text{Fe}_3\text{S}_4 + 2S = 3\text{FeS}_2, \quad (1) \]
\[ \text{FeS} + \text{H}_2\text{S} = \text{FeS}_2 + \text{H}_2, \quad (2) \]
\[ \text{FeS} + S_n^2- = \text{Fe}_3\text{S}_4, \quad \text{Fe}_3\text{S}_4 + S_n^2- = \text{FeS}_2. \quad (3) \]