



Metastability, nanocrystallinity and pseudo-solid solution effects on the understanding of schwertmannite solubility



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ABSTRACT

The role of metastable nanocrystalline precursors, like schwertmannite, in iron and sulfate rich acidic waters is commonly underestimated or even neglected. In addition to schwertmannite metastability, its heterogeneous chemical composition and the current use of disparate solubility products result in an incongruous understanding of this mineral. In order to characterize schwertmannite stability in acid mine drainage settings, we used coincident schwertmannite and solution samples to determine how its solubility product is related to its composition. The solubility products (as $\log K_{sp}$) for 30 natural samples of this study span a range of $\log K_{sp}$ values from 5.8 to 39.5. These values show a gradual distribution on the pH–pe space from pH 1.93 to 4.71 and pe values from 8.5 to 13.7. A set of three predictive equations to select the best schwertmannite solubility product for each new specific case study was obtained. This approximation allows generating an appropriate solubility product for schwertmannite despite the lack of information in certain environments (e.g., absence of former water chemistries on Mars). The trend observed for Fe and S contents in schwertmannite can be interpreted as a pseudo-solid solution ranging from high to low S and Fe concentrations. The polyphasic nature of schwertmannite was studied by means of a thermodynamic model assuming equilibrium between a hydrous ferric oxide (HFO), schwertmannite, and solution. All the results obtained in this study support the understanding of schwertmannite as a polyphasic nanomineral and encourage using a broad $\log K_{sp}$ range to model the solubility of schwertmannite in nature.

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1. Introduction

Surficial iron rich waters often precipitate the Fe-bearing nanominerals ferrihydrite and schwertmannite (Banfield and Zhang, 2001). The study of Fe-bearing nanominerals and mineral nanoparticles is being considered from many different angles, including: crystal growth by oriented attachment (Li et al., 2012), size-driven thermodynamic complexity (Navrotsky et al., 2008), catalytic and sorption processes (Madden and Hochella, 2005) and environmental pollutant transport (Hasselov and von der Kammer, 2008; Plathe et al., 2013). However, an understanding of the connection between water chemistry and nanomineral solubility and bulk composition can help to tie together these approaches.

Acidic waters rich in sulfate and iron control an important part of the iron cycle under Earth-surface conditions. Acid mine drainage (AMD) is the primary example of these types of waters. This pollution is the result of the interaction between sulfides (mainly pyrite), water and air. Acid

mine drainage water chemistry is greatly influenced by jarosite, schwertmannite and ferrihydrite solubilities at very low (1.5–2.5), low (2.5–5.5) and intermediate (>5.5) pHs (Bigham et al. 1996), respectively; however there is not a consensus about the extent of the solubility field for each of these three mineral phases and quite disparate pH ranges and solubility products have been proposed (Cornell and Schwertmann, 2003; Majzlan et al., 2004). Notwithstanding, schwertmannite has been proposed as a metastable iron mineral controlling iron precipitation, and concomitantly water chemistry, over a wide range of pH (Bigham et al., 1996; Bigham and Nordstrom, 2000; Majzlan et al., 2004). Three quite different $\log K_{sp}$ values for schwertmannite are commonly accepted and used indiscriminately to model schwertmannite solubility, namely: 7.06 ± 0.09 (Kawano and Tomita, 2001), 10.05 ± 2.5 (Yu et al., 1999) and 18.0 ± 2.5 (Bigham et al., 1996).

Schwertmannite is widely present in acidic sulfate and iron rich waters (Bigham and Nordstrom, 2000) and is a metastable precursor leading to jarosite or goethite formation (Acero et al., 2006). Apart from the well-known locations in mine districts in association with AMD (pit lakes, underground galleries, spoil heaps, tailings and rivers),

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schwertmannite has been reported in a broad variety of other environments such as acidic soils (Burton et al., 2008), gossan deposits in arctic environments (West et al., 2009), intertidal marshes (Johnston et al., 2011) and oxic microenvironments beneath polar glaciers (Raiswell et al., 2009). Schwertmannite has also been reported to play an essential role in toxic metal removal (mainly arsenic), in AMD passive remediation systems (Caraballo et al., 2011; Macías et al., 2012).

Recent studies suggest the presence of schwertmannite on Mars and as a precursor to the Banded Iron Formations (BIF) generated during Precambrian times. After the presence of schwertmannite was suggested as a component in Meridiani outcrop materials (Farrand et al., 2009) and the Meridiani Planum region (Bibring et al., 2007), it has become a keystone mineral phase in several recent studies that model the current mineral composition of the Martian surface. These models incorporate schwertmannite as a metastable precursor to other mineral phases like jarosite or goethite (Marion et al., 2008; Tosca et al., 2008; Hurowitz et al., 2010). In the case of the BIFs, ferrihydrite is unanimously accepted as a precursor of goethite (and finally hematite) in the seawaters generating these sediments (Hoashi et al., 2009). Based on Mo–Rh (Anbar et al., 2007), Ni (Konhauser et al., 2009) and Cr (Konhauser et al., 2011) concentrations in the rocks forming BIFs today, some studies have proposed the oxidative weathering of crustal sulfide minerals (and the concomitant generation of acidic iron and sulfate rich waters) as a mechanism increasing the concentration of sulfate in Precambrian seawaters. This new theory opens an exciting research area where a better understanding of schwertmannite solubility is essential to understand the control that this “paleo-AMD” could have in the generation of some very specific formations corresponding to shallow-water deposits like the Granular Iron Formations (Konhauser et al., 2011).

The growing awareness of the influence of Fe-bearing nanominerals, particularly schwertmannite, in the hydrochemistry of present and past Earth and Mars environments, calls for a better understanding of how their solubility is controlled by water chemistry, mineral crystallinity, and aggregation state. The goal of this study is to unify our knowledge of schwertmannite solubility and composition using a new approach.

2. Methods

Compositional data for coexisting schwertmannite and natural waters were obtained from hydrochemical and mineral field samples. These data were supplemented with data from the literature. It is important to emphasize that the current study is focused on schwertmannite samples formed under natural conditions. Therefore, the use of any bibliographic information involving synthetic schwertmannite samples, produced by titration (or by any other method) of synthetic or natural AMD waters, has been purposely and necessarily excluded from our analyses, calculations, and conclusions despite its great value in the general understanding of this material.

The current research follows the path opened by pioneering studies in this subject (Bigham et al., 1996; Yu et al., 1999) which require: 1) schwertmannite precipitation in a system close to equilibrium, and 2) working with schwertmannite samples that have no other Fe minerals present. As shown in the following sections, many strict limitations have been imposed on the sampling methods used in this particular study in order to comply with these two fundamental requirements. Unfortunately, some inherent limitations of this approach cannot be completely ruled out, among them: 1) natural solutions in contact with schwertmannite may be slightly different from the solutions present during the growth of the original schwertmannite due to hydrochemistry evolution, 2) the existence of a possible kinetic barrier for schwertmannite precipitation may require some degree of oversaturation before precipitation, and 3) compositional factors inhibiting or enhancing mineral precipitation (e.g.,

organic matter). Nevertheless, the restrictive methodology employed in the present study offers a reliable and robust foundation to address the study of natural schwertmannite solubility.

2.1. Field sampling

Field sampling was carried out within the Iberian Pyrite Belt (IPB), SW Spain. This region suffers ubiquitous and severe AMD pollution due to more than a remarkable five millennia of mining activity (Nocete et al., 2005). The iron- and sulfate-rich acidic waters show wide variations in physicochemical parameters and water compositions making our field dataset representative of a wide range of conditions where schwertmannite forms in AMD (Sarmiento et al., 2009).

Two extensive field campaigns in 2010 and 2011 yielded 20 samples. At each site, solutions were sampled in the vicinity of the schwertmannite precipitates or directly from the waters containing colloidal schwertmannite samples. The solutions were filtered immediately after collection through 0.1 µm Millipore filters, acidified in the field to pH < 1 with Suprapur® HNO₃, and stored at 4 °C in 60 mL sterile polypropylene containers until analysis. The unequivocal presence of schwertmannite as the only mineral phase in the precipitates in contact with the AMD was imposed to (1) ensure that the waters were close to equilibrium with schwertmannite and rule out the possibility that the presence of jarosite or goethite might influence the calculated solubility products, and (2) to guarantee that the chemical composition of the solid corresponds exclusively to schwertmannite. Only nine of the 20 initial samples satisfied these restrictions (Fig. 1 and Table 1).

2.2. Bibliographic sampling

A total of 20 publications with more than 60 potential “bibliographic” sampling points were selected from the extensive peer-reviewed literature available. However, this information was refined by requiring that the solution and solid be sampled at the same time and place, specification of the field pe values or Fe speciation (Fe⁺³–Fe⁺²) was required, the solution charge balance error was limited to less than ±15%, and schwertmannite had to be the only Fe-bearing mineral phase comprising the solid sample.

The complete final dataset containing nine field-derived data from the IPB plus 21 “bibliographic” sampling data from around the world is offered in the supplementary information (Table S1, n = 30), whereas a summary of the most relevant parameters on this study is shown in Table 1. An additional dataset (Electronic Appendix A, Table A2, n = 46) was specifically generated to study the Fe and S contents in schwertmannite. Due to the very specific purpose of this complementary dataset it was not necessary to apply any restriction to the collection of these data beyond the existence of S and Fe concentrations for each pure, natural schwertmannite sample.

2.3. Analytical methods

Water pH and redox potential were measured in the field using a PH25 meter (Crison®). Redox potential was checked using 240 and 468 mV Crison® standard solutions whereas pH was calibrated using a 3 point curve (pH 4.01–7.00–9.21, Crison® standard solutions). Redox potential measurements were corrected to the Standard Hydrogen Electrode (SHE) and finally converted to pe (Nordstrom and Wilde, 1998). To this end, the temperature dependence of the reference cell electrode (platinum electrode and Ag/AgCl reference electrode with 3 M KCl electrolyte) was corrected using the conversion table provided by Crison® and according to the following equation:

$$Eh_{\text{corr.}} = Eh_{\text{field}} + 22.4 - 0.7 T \quad (1)$$

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