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A revised analysis of ferrihydrite at liquid helium temperature using Mössbauer spectroscopy

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Abstract

Short-range-ordered Fe(III) minerals such as ferrihydrite (Fh) are ubiquitous in the environment, are key players in biogeochemical cycling, and sorb trace elements and nutrients. As such, it is important to be able to identify the presence of such minerals in natural samples. Fh is commonly observed to be X-ray amorphous and cannot be easily analyzed using X-ray diffraction, meaning that spectroscopic methods such as X-ray absorption or ^{57}Fe Mössbauer spectroscopy (MBS) are necessary for accurate identification and quantification. Despite decades of research into Fh using MBS, there is a discrepancy in the literature about the exact parameters applicable to the mineral when measured at liquid helium temperature. Fh is frequently fitted with either one, two, or three hyperfine sextets with little interpretation applied to the meaning of each, which is problematic as a one sextet model does not account for the asymmetric lineshape frequently observed for Fh. Here, we address inconsistencies in the fitting of Fh and provide a more standardized approach to its identification by MBS. We present a systematic comparison of different fitting methods, notably based on Lorentzian and Voigt functions. We suggest that the most suitable approach to fitting pure Fh at liquid helium temperature is with two sextets (A and B) fitted using an extended Voigt-based function with the ability to apply probability distributions to each hyperfine parameter. 2-line Fh: A (δ = 0.49 mm/s; ε = 0.00 mm/s; B_{hf} = 50.1 T) and B (δ = 0.42 mm/s; ε = –0.01 mm/s; B_{hf} = 46.8 T) 6-line Fh: A (δ = 0.50 mm/s; ε = –0.03 mm/s; B_{hf} = 50.2 T) and B (δ = 0.40 mm/s; ε = –0.05 mm/s; B_{hf} = 47.1 T). We interpret the two sextets to be due to either differences in the coordination environment of iron, i.e., in tetrahedral or octahedral sites, the presence of a disordered surface phase, or a combination of both. We hope that provoking a discussion on the use of MBS for Fh will help develop a greater understanding of this mineral, and other short-range ordered iron minerals, which are so important in environmental processes.

Keywords: 2-line ferrihydrite, 6-line ferrihydrite, iron oxide, Mössbauer, fitting, parameters, hyperfine field