Revisiting the nontronite Mössbauer spectra

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ABSTRACT

The distribution of ferric iron (Fe3+) between the octahedral and tetrahedral sheets of smectites is still an active problem due to the difficulty of identifying and quantifying the tetrahedral ferric iron ([4]Fe3+). Mössbauer spectroscopy has often been used to address this problem, with the spectra being fitted by a sum of doublets, but the empirical attribution of each doublet has failed to yield a uniform interpretation of the spectra of natural reference Fe3+-rich smectites, especially with regard to [4]Fe3+, because little consensus exists as to the [4]Fe3+ content of natural samples. In an effort to resolve this problem, the current study was undertaken using a series of synthetic nontronites [Si4-x[4]FexO10(OH)2Nax with x ranging from 0.51 to 1.3. Mössbauer spectra were obtained at 298, 77, and 4 K. Statistically acceptable deconvolutions of the Mössbauer spectra at 298 and 77 K were used to develop a model of the distribution of tetrahedral substitutions, taking into account: (1) the [4]Fe3+ content; (2) the three possible tetrahedral cationic environments around [0]Fe3+, i.e., [4Si]-(3[6]Fe3+), [3Si]-(4[6]Fe3+)-(3[6]Fe3+), and [2Si 2[4]Fe3+)-(3[6]Fe3+); and (3) the local environment around a [4]Fe3+, i.e., [3Si]-[2(6)Fe3+] respecting Lowenstein’s Rule. This approach allowed the range of Mössbauer parameters for [6]Fe3+ and [4]Fe3+ to be determined and then applied to spectra of natural Fe3+-rich smectites. Results revealed the necessity of taking into account the distribution of tetrahedral cations ([6]Fe3+) around [0]Fe3+ cations to deconvolute the Mössbauer spectra, and also highlighted the influence of sample crystallinity on Mössbauer parameters.

Keywords: Clay minerals, iron, Mössbauer spectroscopy, nontronite, smectites, tetrahedral iron

INTRODUCTION

Iron (Fe) is a major element in terms of abundance in the Earth’s crust. Many minerals contain Fe and some of them, such as Fe (oxyhydr)oxides and Fe-bearing swelling clay minerals, play a significant role in many natural processes occurring at the Earth’s surface and in its subsurface (Murad 2013; Stucki 2013). Virtually all swelling clay minerals, known as smectites, contain Fe and are ubiquitous in the Earth’s surface. Fe can exist in the structure of the smectites in either the ferrous (Fe2+) or the ferric (Fe3+) state. The structure of the smectite layers consists of one central octahedral sheet that shares O atoms (O) with two tetrahedral sheets, one on each side. The cations in the octahedral sheet are coordinated by four O atoms and two hydroxyl groups, while the cations in the tetrahedral sheet are coordinated by four O atoms. The octahedral sheet consists of three different crystallographic sites, two cis sites and one trans site relative to the hydroxyl group positions. In the case of dioctahedral smectites, the octahedral sites are mainly occupied by trivalent cations (R3+) [R = aluminum (Al) or Fe3+] and only two-thirds of these sites are filled, whereas the tetrahedral sites are mainly occupied by silicon (Si) cations. Heterovalent substitutions can occur in both the tetrahedral (where Al or Fe3+ can substitute for Si) and the octahedral (where magnesium (Mg), nickel (Ni2+), or Fe3+ can substitute for Al or Fe3+) sheets, which creates a net negative charge on the smectite layer. The charge imbalance is generally compensated by the incorporation of alkaline cations in the interlayer space. Nontronite is the general name for the dioctahedral Fe3+-rich end-member of the smectite clay minerals group.

The negative charge induced by heterovalent substitutions partially controls the physical-chemical properties of Fe3+-rich smectites. Fe3+ has been observed in both tetrahedral and octahedral sites in the nontronite structure. The [6]Fe3+ content is relatively easy to quantify, whereas quantifying the [4]Fe3+ content has proven to be a challenge (Gates et al. 2002). Petit et al. (2015) and Baron et al. (2016) recently proposed several formulas to estimate the [4]Fe3+ and [6]Fe3+ contents, based on infrared spectroscopy from a series of synthetic smectites.

Mössbauer spectroscopy is used in clay science mainly for mineralogical identification of various Fe-containing phases (oxides, sulfides, sulfates, carbonates, and phosphates) and to study magnetic impurities [in particular Fe (oxyhydr)oxides], the oxidation state of Fe, and the location of Fe atoms in clay mineral samples (Murad 2013; Stucki 2013). It was used also for mineralogical identification of Fe (oxyhydr)oxides on Mars (Klingelhöfer et al. 2004, 2006; Morris et al. 2004; Schröder et al. 2011). The capability of this type of spectroscopy to identify silicate minerals remains a matter of debate due to the lack of specific features uniquely attributable to specific silicate minerals (Dyar and Schaefer 2008; Murad 2008).

OCTAHEDRAL Fe3+

The capability of Mössbauer spectroscopy to study the distribution of Fe3+ cations between both the octahedral and the