Controls on tetrahedral Fe(III) abundance in 2:1 phyllosilicates—Discussion

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ABSTRACT

Cuadros et al. (2019) used a wide range of data from dioctahedral and trioctahedral Fe3+-bearing, 2:1 phyllosilicates to propose a model describing how tetrahedral occupancy by Fe3+ takes place in both dioctahedral and trioctahedral 2:1 phyllosilicates. The partition coefficient approach (Decarreau and Petit 2014) focusing on the distribution of Al3+ and Fe3+ between octahedral and tetrahedral sites of dioctahedral smectites has been disregarded in the study of Cuadros et al. (2019). This approach was applied here on the set of data from Cuadros et al. (2019). The partition coefficient value linked to the distribution of Al3+ and Fe3+ between octahedral and tetrahedral sites determined from natural and synthetic dioctahedral smectites applies well to trioctahedral phyllosilicates too. Data from synthetic iron-rich 2:1 smectites also fit well with both Cuadros et al. (2019) and Decarreau and Petit (2014) models.

Keywords: 2:1 phyllosilicates, tetrahedral Fe, partition coefficient, smectite, nontronite

Cuadros et al. (2019) used a wide range of data (70 samples) concerning dioctahedral and trioctahedral Fe3+-bearing 2:1 phyllosilicates to propose a model describing how tetrahedral occupancy by Fe3+ takes place in both dioctahedral and trioctahedral 2:1 phyllosilicates. The data came from the investigation of 2:1 phyllosilicates of submarine hydrothermal origin (29) and from literature (41).

Cuadros et al. (2019) wrote: “With respect to cation competition for specific sites in phyllosilicates, it appears that the radius and charge of Si4+, Al3+, Fe3+, Fe2+, and Mg2+ only allow Al3+ and Fe3+ to occupy both tetrahedral and octahedral sites. The relative stability of these two cations in the two sites should be a control for Fe(III) distribution between both sites”. On the basis of this largely accepted assumption, and using the formalism for intra-crystalline, homovalent ion exchange between two nonequivalent sites, Decarreau and Petit (2014) previously proposed a model based on a partition coefficient approach, contradicting the claim of Cuadros et al. (2019) to report for the first time a model of Fe3+ distribution in 2:1 phyllosilicates. Decarreau and Petit (2014) showed that the distribution of Al3+ and Fe3+ between octahedral and tetrahedral sites of dioctahedral smectites was controlled by a partition coefficient \( K_{d(4/6)} = [Fe^{3+}_{tetrahedra}/Al^{3+}_{octahedra}] / [Fe^{3+}_{octahedra}/Al^{3+}_{tetrahedra}] \), \( (Fe^{3+} = Fe^{3+}/(Fe^{3+}+Al^{3+})) \) molar ratio in tetrahedra, 4 and 6 referring to tetrahedral and octahedral sites (similar relations for Al3+), and a \( K_{d(4/6)} \) value of 0.006 was obtained from the fit of data from natural smectites formed at low temperature. This very low \( K_{d(4/6)} \) value was consistent with the physical model of Brice (1975), widely used for the partitioning of elements in geochemistry. The model of Brice (1975) also predicts an increase in \( K_{d(4/6)} \) with the increase of temperature of mineral formation. Accordingly, a \( K_{d(4/6)} \) value of 0.02 was measured from synthesis experiments of dioctahedral smectites at 200 °C (Decarreau and Petit 2014). All data from Cuadros et al. (2019) were plotted on a classical geochemical diagram (\( Fe^{3+}_{tetrahedra} vs. Fe^{3+}_{octahedra} \)) to evaluate a Kd value (Fig. 1). Most of the data are consistent with \( K_{d(4/6)} \) values ranging from 0.006 to 0.02 except two trioctahedral samples (ferrriphlogopite with no Al3+ and talc/smectite with almost no Fe3+ and Al3+) and three nontronites (HQ and two NG1 with different structural formulas). The partition coefficient approach of Decarreau and Petit (2014), established for dioctahedral smectites, appears efficient for a large variety of both di- and tri-octahedral 2:1 phyllosilicates. A single \( K_{d(4/6)} \) value suits to most samples irrespective of their di- or tri-octahedral character and of their amount of M2+ (Fig. 1).

It is possible to evaluate the amount of tetrahedral Fe3+ from the total amount of Fe3+ and the \( K_{d(4/6)} \) value determined by Decarreau and Petit (2014) by fixing the amount of octahedral M2+ cations and the layer charge. The data of Cuadros et al. (2019) of Figure 1 were reported on Figure 2. Most of the di- and trioctahedral samples are fit well using a \( K_{d(4/6)} \) value of 0.006, a tetrahedral charge of 1, and an amount of M2+ cations from 0.2 to 0.8 [for \( O_{20}(OH)_{4} \)] (Fig. 2). The trioctahedral samples that are

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Figure 1. Plot of \( Fe^{3+}_{tetrahedra} vs. Fe^{3+}_{octahedra} \) molar ratio (see text). Squares = dioctahedral phyllosilicates; triangles = trioctahedral phyllosilicates. Open symbols = outlying data (see text). Red curve: \( Fe^{3+}_{tetrahedra} vs. Fe^{3+}_{octahedra} \) in the case of a partition coefficient \( K_{d(4/6)} = 0.006 \). Green curve: \( Fe^{3+}_{tetrahedra} vs. Fe^{3+}_{octahedra} \) in the case of a partition coefficient \( K_{d(4/6)} = 0.02 \). (Color online.)