1 **Revision 1**

2 # 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 Fe^{3+}-bearing 2:1 phyllosilicates, to propose a model describing how tetrahedral occupancy by Fe^{3+} takes place in both dioctahedral and trioctahedral 2:1 phyllosilicates. The partition coefficient approach (Decarreau and Petit, 2014) while focusing on distribution of Al^{3+} and Fe^{3+} between octahedral and tetrahedral sites of dioctahedral smectites has been disregarded in the Cuadros et al. (2019)'s study. This approach was applied here on the Cuadros et al. (2019)'s set of data. The partition coefficient value linked to the distribution of Al^{3+} and Fe^{3+} 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 fit also well with both Cuadros et al. (2019) and Decarreau and Petit (2014) models.

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

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Cuadros et al. (2019) used a wide range of data (70 samples) concerning dioctahedral and trioctahedral Fe^{3+}-bearing 2:1 phyllosilicates, to propose a model describing how tetrahedral occupancy by Fe^{3+} 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 Si^{4+}, Al^{3+}, Fe^{3+}, Fe^{2+}, and Mg^{2+} only allow Al^{3+} and Fe^{3+} 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 ions exchange between two nonequivalent sites, Decarreau and Petit (2014) proposed a preexisting model based on a partition coefficient approach contradicting Cuadros et al. (2019)'s claim to report for the first time a model of Fe^{3+} distribution in 2:1 phyllosilicates. Decarreau and Petit (2014) showed that the distribution of Al^{3+} and Fe^{3+} between octahedral and tetrahedral sites of dioctahedral smectites was controlled by a partition coefficient $Kd_{(4/6)} = [Fe^{3+}{}_4 * Al^{3+}{}_6]/ [Fe^{3+}{}_6 * Al^{3+}{}_4]$, ($Fe^{3+}{}_4 = Fe^{3+}{}_/ (Fe^{3+} + Al^{3+})$ molar ratio in tetrahedra, 4 and 6 referring to tetrahedral and octahedral sites; similar relations for Al^{3+}), and a $Kd_{(4/6)}$ value of 0.006 was obtained from the fit of data from natural smectites formed at low temperature. This very low $Kd_{(4/6)}$ 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 $Kd_{(4/6)}$ with the increase of temperature of mineral formation. Accordingly, a $Kd_{(4/6)}$ value of 0.02 was measured from synthesis experiments of dioctahedral smectites at 200°C (Decarreau

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and Petit, 2014). All data of Cuadros et al. (2019) (supplementary file S1) were plotted on a classical geochemical diagram (Fe^{3+}_4 *vs* Fe^{3+}_6) to evaluate a Kd value (Fig. 1). Most of the data are consistent with $Kd_{(4/6)}$ values ranging from 0.006 to 0.02 except two trioctahedral samples (ferriphlogopite with no Al^{3+}_6 and talc/smectite with almost no Fe^{3+}_6 and Al^{3+}_6) and three nontronites (HQ and two NG1 with different structural formulae). 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 $Kd_{(4/6)}$ value suits to most samples irrespective of their di- or tri-octahedral character and of their amount of M^{2+} (Fig.1).

It is possible to evaluate the amount of tetrahedral Fe^{3+} from the total amount of Fe^{3+} and the $Kd_{(4/6)}$ value determined by Decarreau and Petit (2014), fixing the amount of octahedral M^{2+} cations and the layer charge. The Cuadros et al (2019)'s data of figure 1 were reported on figure 2. Most of di- and tri-octahedral samples fit well using a $Kd_{(4/6)}$ value of 0.006, a tetrahedral charge of 1, and an amount of M^{2+} cations from 0.2 to 0.8 (for O_{20} $(OH)_4$) (Fig.2). The trioctahedral samples that are out of the range are micas and Fe-rich saponites with none or very-low total amount of Al. Nevertheless, the data are consistent with a low $Kd_{(4/6)}$ value (Fig.2).

For the selection of literature data, Cuadros et al. (2019) disregarded some relevant data concerning micas (Semenova et al., 1984) and excluded some data from synthetic nontronites (Petit et al., 2015; Baron et al., 2016) because tetrahedral Fe^{3+} was mainly obtained using IR spectroscopy. Due to their high total Fe^{3+} and high Fe^{3+}_4 amounts compared to natural samples, the series of well characterized synthetic nontronites are interesting samples to study iron status in clay minerals (Petit et al., 2017). Several studies gave strong evidence that the wavenumber of several IR bands, and notably the main Si-O band at about 1000 cm^{-1} can be used efficiently to quantify the octahedral and tetrahedral Fe^{3+} amounts (Petit et al., 2015; Baron et al., 2016). These

78 samples of Baron et al. (2016) were also studied by chemical analysis using scanning electron
79 microscope equipped with an energy dispersive spectrometer, Mössbauer spectroscopy (Baron et
80 al., 2017), and by X-ray diffraction that supported well the IR results. Cuadros et al. (2019)
81 alleged that these data from synthetic nontronites fit their regression. Why thus exclude these data
82 for their study?

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112 **Figure captions**

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Figure 1: Plot of Fe^{3+}_4 *vs* Fe^{3+}_6 molar ratio (see text). Squares: dioctahedral phyllosilicates; triangles: trioctahedral phyllosilicates. Open symbols: outlying data (see text). Red curve: Fe^{3+}_4 *vs* Fe^{3+}_6 values in the case of a partition coefficient $Kd_{(4/6)} = 0.006$; green curve: Fe^{3+}_4 *vs* Fe^{3+}_6 values in the case of a partition coefficient $Kd_{(4/6)} = 0.02$.

Figure 2: Plot of Fe^{3+}_4 *vs* total Fe^{3+} (for O_{20} $(OH)_4$). Squares: dioctahedral phyllosilicates; triangles: trioctahedral phyllosilicates. Open symbols: outlying data (dioctahedral data in Fig. 1); Curves were calculated with $Kd_{(4/6)} = 0.006$. Blue curve: $M^{2+} = 0.2$ and tetrahedral charge = 1; green curve: $M^{2+} = 0.8$ and tetrahedral charge = 1; violet curve: $M^{2+} = 3$ and tetrahedral charge = 1; red curve: $M^{2+} = 3.85$ and tetrahedral charg e= 2.

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Figure 1

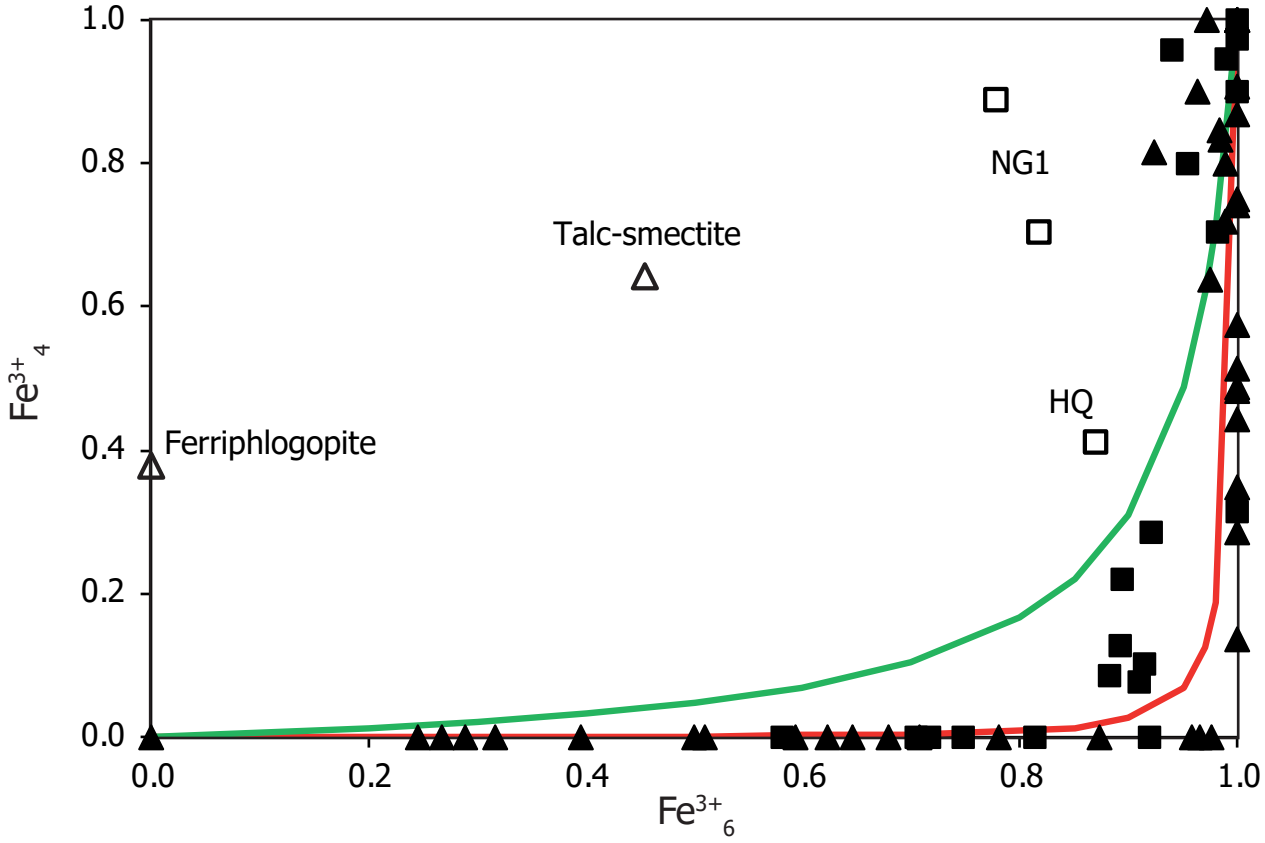

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Figure 2