Controls on tetrahedral Fe(III) abundance in 2:1 phyllosilicates - Reply

Javier Cuadros[1], Joseph R. Michalski[1,2], and M. Darby Dyar[3]

[1]Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

[2]Department of Earth Sciences and Laboratory for Space Research, University of Hong Kong, Hong Kong, China

[3]Department of Astronomy, Mount Holyoke College, South Hadley, Massachusetts 01075, U.S.A.

Corresponding author: Javier Cuadros, j.cuadros@nhm.ac.uk

Abstract

The model of Fe^{3+} distribution between octahedra and tetrahedra in dioctahedral smectites by Decarreau and Petit (2014) used data from infrared analysis. From their own and other general evidence, resulting data are likely to be affected by significant uncertainty. This aside, their model has limited application because it is based on synthetic smectites containing only Si, Al, and Fe^{3+}.

Keywords: Dioctahedral 2:1 phyllosilicates, Fe, tetrahedral Fe

In their discussion of our article (Cuadros et al., 2019), Petit et al. (this discussion) ask why their model of Fe^{3+} distribution between octahedral and tetrahedral sites in smectites (Decarreau and Petit, 2014) was not mentioned. It was essential in our investigation to obtain the most reliable data of Fe octahedral and tetrahedral occupancy found in the literature to establish or disprove the universal validity of the correlations that we had found in our collection of submarine hydrothermal samples (Cuadros et al., 2019). The criteria for the selection of studies providing Fe distribution between tetrahedral and octahedral sites were stated in Cuadros et al. (2019). Our experience suggests that infrared data alone are not sufficient to obtain the reliable distributions that we were looking for. This can be illustrated from studies directly relevant to this discussion. In Petit et al. (2015), a method of distributing Fe^{3+} between tetrahedral and octahedral sites using near-infrared data (based on curve-fitting and quantification of individual bands) was described and applied. Their assignment of the infrared bands is not straightforward, requiring a good deal of interpretation. Band overlap, unexplained differences in band position, band width and band multiplicity, and one band of unknown origin with as much as 10% of the intensity of the largest band of interest all contribute to their uncertainties (Petit et al, 2015). These problems are common in infrared investigations. Further, Decarreau and Petit (2014) provided tetrahedral Fe^{3+} occupancy based on the above method and obtained some negative values ranging -0.03 to -0.14 per 8 tetrahedral sites, which also reflects uncertainty in the interpretation and quantification of infrared data. Given that the amount of tetrahedral Fe^{3+} is frequently small, infrared data alone are likely to generate results with uncertainties equal to or above the investigated values. Similar reasons apply to quantification of tetrahedral Fe^{3+} content based on the position of the large infrared band at ~1000 cm^{-1} (Petit et al., 2015; Petit et al., this discussion). This is a wide, complex band (with obvious overlapping components) modified by multiple variables that is likely to produce tetrahedral Fe^{3+} contents of significant uncertainty. In summary, while we consider the above methods valid and with a wide range of applications, their level of accuracy was considered insufficient for our particular study.

Setting aside the accuracy of the Fe^{3+} distributions between tetrahedral and octahedra used by Decarreau and Petit (2014), their model for such distribution is based on synthetic smectite samples containing only Si, Al and Fe^{3+}. Application of their model is thus limited by the almost universal presence of significant amounts of Mg and frequent presence of Fe^{2+} in dioctahedral phyllosilicates. Their results represent a specific case of the general phenomenon. Decarreau and Petit (2014) stated that Mg does not seem to modify the distribution of Fe^{3+} between tetrahedra and octahedra, whereas our model shows the central role played by Mg in this distribution, increasing the average dimensions of the octahedral and tetrahedral sites. Where tetrahedral sites have a minimum threshold size, Fe^{3+} is accommodated. We suggest that the fit of the model of Decarreau and Petit (2014) for many non-synthetic samples containing Al, Mg, Fe^{3+} and Fe^{2+} (Petit et al., this discussion) is partly due to the use of cation ratios in which major divalent octahedral cations are not included. Where divalent cations are in low abundance, the model of Decarreau and Petit (2014) is a good approximation. Where divalent cations are abundant, ratios of (Fe^{3+}/Al+Fe^{3+}) may still fit the model but it is not reasonable to assume that these two cations are the only control of the crystal-chemical characteristics of the corresponding samples. The misfits in Fig. 1 of Petit et al. (this discussion) are an indication that the model is incomplete. In our opinion, such misfits include not only the samples highlighted as such by them, but also those samples that do not follow the bending part of their curves (bottom, right of their Fig. 1) and those away from the merging of their two curves at the top, right (their Fig. 1). Inclusion of divalent cation contents in the model of Decarreau and Petit (2014) requires ad hoc fixing of divalent cation content and layer charge values to allow the calculation of distribution curves that can then be tested against experimental data. The result of this test shown in Petit et al. (this discussion) (their Fig. 2) is ambiguous, with a broad distribution of data points within the limits of some of the curves. It would be necessary to check the charge and divalent cation content of each sample to test whether the data points plot on their corresponding curve or away from it.

References

Cuadros, J., Michalski, J. R., Darby Dyar, M., and Dekov, V. (2019) Controls on tetrahedral Fe(III) abundance in 2:1phyllosilicates. American Mineralogist, 104, 1608–1619. DOI: https://doi.org/10.2138/am-2019-7036

Decarreau, A., and Petit, S. (2014) Fe^{3+}/Al^{3+} partitioning between tetrahedral and octahedral sites in dioctahedral smectites. Clay Minerals, 49, 657-665. DOI: 10.1180/claymin.2014.049.5.03

Petit, S., Baron, F., and Decarreau, A. (this discussion) Controls on tetrahedral Fe(III) abundance in 2:1 phyllosilicates - - Discussion. American Mineralogist

Petit, S., Decarreau, A., Gates, W., Andrieux, P., and Grauby, O. (2015) Hydrothermal synthesis of dioctahedral smectites: The Al-Fe^{3+} chemical series. Part II: Crystal-chemistry. Applied Clay Science, 104, 96–105. DOI: http://dx.doi.org/10.1016/j.clay.2014.11.014.