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

JAVIER CUADROS[1,*], JOSEPH R. MICHALSKI[1,2], M. DARBY DYAR[3], AND VESSELIN DEKOV[4]

[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.
[4]Department of Ocean Sciences, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan

ABSTRACT

Fe(II) only occupies octahedral sites in phyllosilicates, whereas Fe(III) can occupy both octa-hedral and tetrahedral sites. The controls on Fe(III) distribution between tetrahedral and octahedral sites have been a matter of great interest to understand the interplay between formation environment (Fe abundance, redox conditions) and crystal-chemical factors (stability of the crystal lattice) during crystallization of Fe-phyllosilicates. Here, for the first time, we present a model of Fe(III) distribution in 2:1 phyllosilicates. We investigated 21 samples of 2:1 phyllosilicates of submarine hydrothermal origin using XRD, chemical analysis, and Mössbauer spectroscopy (and other supporting techniques not presented here). An additional data set of 49 analyses of 2:1 phyllosilicates from the literature was also used. Overall, the data cover a wide range of dioctahedral and trioctahedral phyllosilicates, including end-member minerals and interstratified phases. Dioctahedral phyllosilicates have a steric control whereby tetrahedral Fe(III) is only allowed if at least five out of six octahedral atoms are larger than Al (typically Fe[III], Fe[II], Mg) that produces an expanded structure where tetrahedral sites can accommodate Fe(III). After this threshold, further Fe(III) atoms occupy tetrahedral sites preferentially (~73% of further Fe[III] atoms) over octahedral sites. In trioctahedral 2:1 phyllosilicates there is no steric hindrance to tetrahedral Fe(III) because the crystal dimensions are such that tetrahedral sites can accommodate Fe(III). On average, Fe(III) enters tetrahedral and octahedral sites in similar pro-portion, and the only apparent control on tetrahedral Fe(III) abundance is Fe(III) availability during crystallization. This model allows to predict Fe(III) distribution between structural sites, provides an avenue for further exploration of the thermodynamic stability of phyllosilicates using cationic size, and provides a tool to better describe stability/reactivity of Fe-rich phyllosilicates, the most reactive of phyllosilicates and very relevant in geochemical and biological processes.

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