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

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ABSTRACT

Fe(II) only occupies octahedral sites in phyllosilicates, whereas Fe(III) can occupy both octahedral 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 proportion, 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

INTRODUCTION

Iron-rich phyllosilicates are important because they are more reactive than their Al- and Mg-rich counterparts. Phyllosilicates with significant Fe(II) content, typically trioctahedral, are weathered more rapidly than Al- and Mg-rich ones (Wilson 2004). Iron in phyllosilicates may undergo oxidation and reduction, which has an immediate effect on mineral stability, due to modifications to the layer charge. Typically, Fe oxidation state in non-expanding phyllosilicates is not affected by inorganic agents, unless they are extreme (e.g., hydrothermal fluids, strong acid attack). However, microorganisms can modify Fe oxidation state to a certain extent in non-expandable phyllosilicates (e.g., illite, chlorite; Dong et al. 2009). In expandable phyllosilicates (smectite, vermiculite), Fe oxidation state is influenced by both external redox conditions (Fialips et al. 2002) and the direct action of microorganisms (Jaisi et al. 2005). The above reactions are important for microorganism respiration and, more generally, in soils, where water saturation conditions, microbial activity, and organic matter concentration change Fe oxidation state in phyllosilicates. As a consequence, these minerals may experience changes of particle size, particle aggregation state, cation exchange capacity, and even their mineralogy (Stucki et al. 2002; Cuadros 2017). Such changes influence further bio-geochemical processes. Recent articles have demonstrated that Fe in environments with redox fluctuations causes rapid formation of Fe-illite or glauconite from kaolinite or smectite, in reactions of geochemical significance at a global scale (Baldermann et al. 2015; Cuadros et al. 2017). As a consequence of all the above, Fe in phyllosilicates promotes faster mineralogical and chemical changes and a greater, more intense interaction of these minerals with their biological and inorganic environment. Improved understanding of the crystal-chemistry of Fe-phyllosilicates will help to better establish their reactivity.

Iron most frequently occupies octahedral sites in phyllosilicates. In a first evaluation, it appears that both Fe(II) and Fe(III) fit better within the larger octahedral site than in the smaller tetrahedral site. Iron (III) occupies tetrahedral sites, but no Fe(II) has been found so far occupying tetrahedral sites in phyllosilicates or, more generally, in silicates. In phyllosilicates, Fe(II) does not enter tetrahedral sites probably due to the combination of large ionic radius (0.71 Å in a tetrahedral environment according to Whittaker and Muntus 1970; compare

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