

Iron speciation in smectites of different charge and charge location

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Smectites are essential minerals in soils and sediments, in which they control the availability of cationic nutrients and molecules. They are extensively used as constituents of engineered barriers for the isolation of pollutants because of their good hydraulic and chemical properties. This reactivity is related to their layered structure made by one octahedral sheet sandwiched between two silicate tetrahedral sheets, and to the presence of layer charges. It is thus important to understand the crystallochemical properties which control their reactivity. For example, the chemical form of structural Fe in these minerals can influence their reactivity. Under the reducing conditions expected to develop in the near-field of a deep geological waste repository, octahedral Fe(III) can be reduced and provide electrons able to reductively immobilize pollutants. In contrast, tetrahedral Fe(III) reduction is less likely. For the safety assessment of deep repositories, it is thus important to know the distribution of Fe(III) between possible structural sites.

To explore the variety of Fe crystallochemistry, a set of ten smectites with different chemical composition and charge locations was selected. Eight natural smectites were purified and fractionated; two synthetic saponites where $^{44}\text{Fe}^{3+}$ substitutes for $^{44}\text{Si}^{4+}$ were used without fractionation. The extent of Al for Si substitution in tetrahedral sites was determined by ^{27}Al MAS NMR, and information on Fe speciation was obtained by Fe K-edge polarized XAS on textured samples at the INE beamline at KARA and at BM30B at ESRF.

All samples were identified as smectites by XRD and FTIR spectroscopy, and further distinguished as dioctahedral (2/3 of octahedral sites filled by trivalent cations) or trioctahedral (all octahedral sites filled by divalent cations) frameworks. NMR data showed that all or most of Al is located in the tetrahedral sheet of saponites and hectorite, in contrast to montmorillonites. The Fe content in nontronites was too high for NMR measurements. All samples contain only ferric iron, with no evidence of cluster formation. In the synthetic saponites, the presence of 3-4 O atoms at 1.86 Å indicates a tetrahedral environment, which is confirmed by the detection of in-plane Si at ~3.19 Å and out-of-plane Mg at ~3.33 Å. No octahedral Fe could be evidenced, meaning that substitution of ^{44}Fe for ^{44}Si operates and that these samples can be used as model compounds for natural smectites. Dioctahedral smectites have a Fe content ranging from low/moderate in montmorillonites to high in nontronites. In all these samples, Fe is bound to 6 O oriented in-plane and located at ~2.00 Å, suggesting insertion in the octahedral sheet. This is confirmed by the detection of in-plane Al/Fe at ~3.06 Å and out-of-plane Si at ~3.26 Å. In one nontronite particularly rich in Fe, the detection of ~0.5 O at 1.88 Å suggests a concomitant Fe insertion in the tetrahedral sheet. The investigated trioctahedral saponite and hectorite have a low Fe content. In both samples, Fe is bound to 6 O oriented in-plane, and low numbers of octahedral cations were detected. The presence in adjacent octahedral sites of vacancies in saponite and Li in hectorite for charge balance can best explain these findings.

All natural smectites contain octahedral Fe(III), and one nontronite particularly rich in Fe contains additional low amounts of tetrahedral Fe(III). Results show that smectites containing ^{54}Fe can be successfully obtained in the laboratory, but is rare in nature or present in amounts below the detection limit of EXAFS.