Cation Migration in Smectite Minerals: Electron Spin Resonance of Exchanged Fe^{3+} Probes

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Abstract: The migration of interlayer Fe^{3+} cations into the structure of heated montmorillonite and Laponite has been studied by electron spin resonance (ESR), Mössbauer spectroscopy, and magnetic susceptibility measurements. The intensity of the ESR signal corresponding to interlayer Fe^{3+} in air-dried montmorillonite and Laponite increased linearly as the amount of interlayer Fe^{3+} increased. Changes in the spectra after thermal treatment indicate that Fe^{3+} cations migrated into the pseudohexagonal cavities of dehydrated montmorillonite and Laponite. The electrostatic interaction between the Fe^{3+} and the oxygen atoms defining the entrance to these cavities and the proton of the structural OH groups at the bottom of the cavities differ for the two smectites. Ferric cations were apparently bound more strongly within the pseudohexagonal cavities of the dehydrated montmorillonite than within the cavities of Laponite, because the montmorillonite did not rehydrate after heating. The differences in the binding of Fe^{3+} cations within the pseudohexagonal cavities of montmorillonite and Laponite were probably due to variations in the ability of the protons of the structural OH groups to reorient. An additional electronic interaction occurred in the heated Laponite, in which small cations were able to promote the formation of structural defects, which gave rise to a sharp ESR signal at g = 2.00. No evidence for the penetration of Fe^{3+} cations into the vacant octahedral sites of montmorillonite was found.

Key Words: Electron spin resonance • Hofmann-Klemen effect • Ion migration • Iron • Laponite • Montmorillonite • Mössbauer spectroscopy

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