Nuclear Magnetic Resonance and X-ray Photoelectron Spectroscopic Investigation of Lithium Migration in Montmorillonite

B. K. G. Theng[1], S. Hayashi[2], M. Soma[3,†] and H. Seyama[3]

[1] Manaaki Whenua-Landcare Research, Private Bag 11 052, Palmerston North, New Zealand
[2] National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan
[3] National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305, Japan

[†] Present address: Graduate School of Nutritional and Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422, Japan.

Abstract: When Li-saturated montmorillonite is heated to 200 – 300 ° C, the Li ions migrate from interlayer positions to sites in the layer structure. However, the identity of these sites has not been clearly established. Here we have investigated the migration of Li ions in montmorillonite, after heat treatment at 250 ° C, using chemical and instrumental analyses. The latter include X-ray diffractometry (XRD), ^{7}Li-nuclear magnetic resonance (NMR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Heating causes a large reduction in cation exchange capacity (CEC) and an almost complete loss of interlayer expansion with glycerol as shown by XRD. Static and magic angle spinning (MAS) ^{7}Li-NMR spectroscopy shows that the quadrupole coupling constant of Li increases markedly over the corresponding value for unheated Li-montmorillonite (where Li occupies exchange sites in the interlayer space) and for hectorite (where Li is located in the octahedral sheet). This would indicate that, in heated montmorillonite, Li occupies structural sites of low symmetry which, however, cannot be identified with octahedral vacancies in the layer structure as is commonly assumed. XPS shows that the binding energy (BE) for Li in unheated montmorillonite is comparable to that for other exchangeable cations. Heating broadens the Li 1*s* band and decreases the BE. The BE for Li in heated montmorillonite is significantly higher than that in either spodumene or lepidolite, where Li is known to occupy octabedral sites. The combined data suggest that heating induces Li to migrate from interlayer sites to ditrigonal cavities in the tetrahedral sheet, rather than into vacancies in the octahedral sheet, of montmorillonite.

Key Words: Lithium • Migration • Montmorillonite • NMR Spectroscopy • X-ray Photoelectron Spectroscopy

Clays and Clay Minerals; October 1997 v. 45; no. 5; p. 718-723; DOI: 10.1346/CCMN.1997.0450510

Clay Minerals Society (www.clays.org)