Charge Reduction, Octahedral Charge, and Lithium Retention in Heated, Li-Saturated Smectites[1]

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Abstract: Reference smectites were examined to determine relationships between Li uptake, cation-exchange capacity (CEC), and octahedral layer charge after Li saturation and heating at 250 ° C (Hofmann-Klemen effect). Direct measurements of exchangeable Li after heating led to overestimates of charge reduction due to entrapment of Li in collapsed interlayers. Expansion of interlayers by sequential washings with 1 N $MgCl_2$, 0.01 N $MgCl_2$, and ethanol and subsequent determinations of exchangeable Mg provided accurate measurements of reduced charge. The CEC reductions observed in dioctahedral samples as a result of Li saturation and heating equaled octahedral charge values derived from published mineral formulae, and interlayer charge estimates obtained by alkylammonium exchange confirmed that measured CEC reductions were a consequence of uniform decreases in octahedral layer charge.

Dioctahedral specimens retained 1 to 10 meq/100 g of non-exchangeable Li in excess of CEC reduction and were acidified in direct proportion to their total Fe contents, apparently as a result of the deprotonation of structural hydroxyl groups. Mild acid treatment reprotonated these hydroxyl groups, released excess Li, and resulted in total Li contents comparable to measured CEC reductions. Heating (250 ° C Mg-saturated hectorite induced a loss of octahedral Li, acidification, and a reduction of CEC, indicating that Mg had partially replaced octahedral Li. These results suggest that octahedral Li is mobile at low temperatures and that cation movement into or out of the octahedral sheet is favored if the layer charge is reduced.

Key Words: Alkylammonium exchange • Cation-exchange capacity • Hofmann-Klemen effect • Layer-charge reduction • Lithium • Octahedral charge

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