

## Structural Properties of Reduced Upton Montmorillonite

W. P. Gates<sup>1,2</sup>, J.W. Stucki<sup>2</sup>, R.J. Kirkpatrick<sup>3</sup>

<sup>1</sup> Savannah River Ecology Laboratory, University of Georgia, Drawer E, SC 29802,

<sup>2</sup> Dept Natural Resources and Environmental Sciences, University of Illinois, 1102 South

Goodwin, Urbana, IL 61801

<sup>3</sup> Dept Geology, University of Illinois, 1301 West Green, Urbana, IL 61801

**Abstract** – Reduction of octahedral Fe in the crystalline structure of smectites influences, possibly controls, surface-sensitive physical and chemical properties. The purpose of this study was to investigate if reduction of structural Fe by Na-dithionite or bacteria affects the chemical environment of constituent cations in montmorillonite, employing solid state multinuclear ( $^{29}\text{Si}$  and  $^{27}\text{Al}$ ) magic angle sample spinning nuclear magnetic resonance (MAS NMR) spectroscopy. Reduction of structural Fe resulted in a positive (downfield) chemical shift of the main Si Q<sup>3</sup> (Q<sup>3</sup>(0Al)) site which was strongly correlated with Fe(II) content and inferred that distortions in Si–O–T (T=Si, Al) bond angles and Si–O bond lengths occur with increasing layer charge. The line width ( $W$ ) of the  $^{29}\text{Si}$  Q<sup>3</sup> signal also increased with increasing levels of reduction. No change occurred in the position of the peak maximum for the octahedral Al ( $^{27}\text{Al}$ ) signal; however, an increased  $W$  was observed for this peak with increasing Fe(II) content. These results are attributed to decreases in Si–O–T bond angles and Si–O bond distances, corresponding to a better fit between the tetrahedral and octahedral sheets brought about by the presence of Fe(II) in the clay structure. The increased  $^{27}\text{Al}_{\text{VI}}$  signal width ( $W$ ) may also be due to a lessening of the paramagnetic influence of Fe(III) nuclei and enhancement of  $^{27}\text{Al}_{\text{VI}}$

signals with different quadrupole coupling constants (QCC). Multinuclear MAS NMR analysis of dithionite- and microbial-reduced montmorillonite indicate that reduction of structural Fe caused reversible changes in the smectite structure as far as this method could discern.