

CHEMISTRY AND MINERALOGY OF EARTH'S MANTLE

**Influence of hydration on  $^{23}\text{Na}$ ,  $^{27}\text{Al}$ , and  $^{29}\text{Si}$  MAS-NMR spectra of sodium saponites and sodium micas†**

**JESUS SANZ<sup>1,\*</sup>, ISABEL SOBRADOS<sup>1</sup> AND JEAN-LOUIS ROBERT<sup>2</sup>**

<sup>1</sup>Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain

<sup>2</sup>IMPMC, UMR 7590, CNRS-Université Pierre et Marie Curie, Case courrier 115, 4 place Jussieu, 75252 Paris Cedex 05, France

**ABSTRACT**

Synthetic sodium saponites,  $\text{Na}_x\text{Mg}_3(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , with  $0.33 \leq x \leq 1$ , and trioctahedral sodium micas series,  $\text{Na}(\text{Mg}_{3-y}\text{Al}_y)(\text{Si}_{3-y}\text{Al}_{1+y})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , with  $0 \leq y \leq 1$ , have been investigated by MAS-NMR spectroscopy. The presence of anhydrous, one-layer and two-layer hydrates, deduced by X-ray diffraction, has been associated with specific lines detected in  $^{23}\text{Na}$  MAS-NMR spectra. In these phyllosilicates, the location of tetra- and octahedral charge has been analyzed by  $^{27}\text{Al}$  MAS-NMR spectroscopy. The salient result is the major effect of the interlayer charge on  $^{29}\text{Si}$  chemical shift of the four NMR components ascribed to  $\text{Si}_1$ ,  $\text{Si}_2\text{Al}$ ,  $\text{SiAl}_2$ , and  $\text{Al}_3$  environments. This effect is much more important than the most commonly accepted contribution of the ditrigonal distortion of tetrahedral sheets. In saponites,  $^{29}\text{Si}$  MAS-NMR spectra change considerably with the sodium hydration. In dehydrated samples, where Na cations are engaged in two pseudo-hexagonal cavities,  $^{29}\text{Si}$  MAS-NMR components split as a consequence of the partial sodium occupancy of three neighboring hexagonal rings that surrounds a particular tetrahedron. In hydrated samples, where  $\text{Na}^+$  cations interact with water, chemical shifts of resolved components are averaged as a consequence of interlayer water and cation mobilities.

**Keywords:** 2:1 phyllosilicates;  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ , and  $^{23}\text{Na}$  MAS-NMR spectroscopy; Si-Al distribution; charge location; hydration state