CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE

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

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ABSTRACT

Synthetic sodium saponites, Na$_x$Mg$_{1-x}$Si$_6$O$_{18}$OH$_2$·nH$_2$O, with 0.33 ≤ x ≤ 1, and trioctahedral sodium micas series, Na(Mg$_{1-y}$Al$_y$)$_3$Si$_3$O$_{10}$(OH)$_2$·nH$_2$O, with 0 ≤ y ≤ 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 $^{23}$Na MAS-NMR spectra. In these phyllosilicates, the location of tetra- and octahedral charge has been analyzed by $^{27}$Al MAS-NMR spectroscopy. The salient result is the major effect of the interlayer charge on $^{29}$Si chemical shift of the four NMR components ascribed to Si$_x$, SiAl, SiAl$_2$, and Al$_3$ environments. This effect is much more important than the most commonly accepted contribution of the ditrigonal distortion of tetrahedral sheets. In saponites, $^{29}$Si MAS-NMR spectra change considerably with the sodium hydration. In dehydrated samples, where Na cations are engaged in two pseudo-hexagonal cavities, $^{29}$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 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; $^{29}$Si, $^{27}$Al, and $^{23}$Na MAS-NMR spectroscopy; Si-Al distribution; charge location; hydration state

INTRODUCTION

In trioctahedral 2:1 Na-phyllosilicates Na$_{x_1}$Mg$_{x_2}$T$_{1}$O$_{12}$(OH)$_2$, where M stands for Mg, Al and T for Si, Al; tetrahedra T share three O atoms with neighboring tetrahedra to form hexagonal rings (Fig. 1). In these silicates, charge deficits introduced by the substitution of Si$^{4+}$ by Al$^{3+}$ are compensated by the incorporation of interlamellar Na$^+$ cations in saponites Na$_{x_1}$Mg$_{x_2}$T$_{1}$O$_{12}$(OH)$_2$·nH$_2$O or by the substitution of Mg$^{2+}$ by Al$^{3+}$ in the octahedral sheet of micas Na(Mg$_{1-y}$Al$_y$)$_3$Si$_3$O$_{10}$(OH)$_2$·nH$_2$O.

In phyllosilicates 2:1, Al for Si substitution increases the tetrahedral layer dimensions making difficult the matching of the octahedral with two tetrahedral layers. This dimensional misfit is compensated by the opposite rotation of adjacent tetrahedra by an angle α around the c* direction (Fig. 1), and by the flattening of octahedra into trigonal antiprisms (Bailey 1984; Sanz and Robert 1992). From this fact, the size of the interlamellar cations can limit the tetrahedral distortion in anhydrous phases (Bailey 1984; for a compilation). In hydrated samples, single and double-layer phases, with basal spacings near 12 and 15 Å, are the most frequent hydration states of Na-phyllosilicates (Carman 1974; de la Calle and Suquet 1988; Güven 1988). In these phases, the arrangement of water and sodium cations changes appreciably with the hydration state.

NMR spectroscopy has been extensively used to study the tetrahedral framework of phyllosilicates 2:1 (Sanz and Serratosa 1984; Sanz and Robert 1992). The detection of tetra- and octahedral Al components in $^{27}$Al MAS-NMR spectra make possible the analysis of substitutional schemes in phyllosilicates. On the other hand, it was shown that $^{29}$Si MAS-NMR chemical shifts associated with Si in Si$_x$-Al$_{(1-x)}$ environments (n = 0, 1, 2, and 3) depend on the interlayer charge, playing a secondary role the octahedral one (Sanz et al. 2006a). Some characteristics of the Si-Al distribution have been previously deduced from the analysis of the relative intensities of Si$_x$-Al$_{(1-x)}$ components. In particular, it was shown that the distribution of Si and Al complies besides the Loewenstein’s rule (Al-O-Al, avoidance), with the homogeneous dispersion of charges (HDC) model, proposed by Herrera et al. (1985) and Cirone et al. (1991). In this model, the number of Al per hexagonal ring was assumed to be as close as possible to the mean value deduced from structural formulas.

Finally, hydration states deduced by X-ray diffraction (Fig. 2) can be correlated with information obtained by $^{23}$Na NMR spectroscopy, as anhydrous, one-layer and two-layer hydrates give specific lines at different chemical shift values (Laperche et al. 1990). In two-layer hydrates, the analysis of $^1$H NMR spectra afforded information about interactions of water with compensating cations and tetrahedral layers (Hougaard et al. 1970 and 1976). In one-layer hydrated Na-micas, contiguous layers are shifted relative to each other, favoring a stronger interaction of hydrated sodium cations, Na$^{2+}$H$_2$O, with four tetrahedra of two contiguous layers (de la Calle and Suquet 1988;