Multiple oxygen sites in synthetic phyllosilicates with expandable layers: \(^{17}\)O solid-state NMR study

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**ABSTRACT**

Recent advances in high-resolution solid-state NMR enabled us to resolve the previously unknown details of atomic configurations around quadrupolar nuclides such as O \(^{17}\)O (spin 5/2) and aluminum \(^{27}\)Al (spin 5/2) in phyllosilicates. Here, we report the \(^{17}\)O 1D and 2D NMR (MAS and MQMAS) spectra of synthetic kaolinite-montmorillonite mixtures. Various O sites in the mixtures revealed from O-17 NMR include apical O \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Al}\), multiple basal O atoms \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{V}}\text{Al}\) and two \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Al}\) sites in tetrahedral layers, and hydroxyl group with distinct ranges for NMR parameters (quadrupolar coupling constant, \(C_q\) and isotropic chemical shift, \(\delta_{\text{iso}}\)). In particular, the structurally relevant NMR parameters \(\text{\textsuperscript{17}}\text{O} \delta_{\text{iso}}, C_q\), and asymmetry parameter, \(\eta\) for two resolved \(\text{\textsuperscript{17}}\text{O-\textsuperscript{IV}}\text{Al}\) sites are about 52 ± 2 ppm, 2.6 ± 0.2 MHz, and 0.5 for \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Al}\) (I) and about 44.5 ± 2 ppm, and 3.1 ± 0.2 MHz, and 0.5 for \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Al}\) (II), respectively. These sites may stem from crystallographically distinct \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Al}\) sites of varying bond length and \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Al}\) bond angle or \(\text{\textsuperscript{IV}}\text{Al-O-\textsuperscript{IV}}\text{Al}\) site in the montmorillonite.

**Keywords:** High-resolution solid-state NMR, phyllosilicates, oxygen sites, 3QMAS NMR, montmorillonite

**INTRODUCTION**

Phyllosilicates are among the major components in terrestrial surface environments and have important implications for diverse geological processes, such as weathering, diagenesis in sedimentary basins, and dehydration and serpentization processes at tectonic plate margins (Altaner et al. 1987; Brindley and Brown 1980). They also have technological applications in advanced materials including clay-polymer nano-composites and for the oil and pharmaceutical industries.

Whereas the long-range structures of phyllosilicates are well known (Brindley and Brown 1980), important questions about their short-range structure (e.g., Si/Al disorder and bond angle and lengths) and their effects on the macroscopic properties (crystallographic sites dependent reactivity in contact with fluids) remain to be solved. For instance, the distribution of Si and Al in the tetrahedral layer determines the types of corner-sharing configurations (e.g., \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Si}\), \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Al}\), as well as \(\text{\textsuperscript{IV}}\text{Al-O-\textsuperscript{IV}}\text{Al}\) and these distinct basal-O sites can exhibit varying reactivity in contact with fluids and thus play an important role in macroscopic reactivity (Cheng et al. 2000; Lasaga 1995; Lee and Stebbins 2003; Stebbins et al. 1999; Xu and Stebbins 1998). The Si-Al disorder in the phyllosilicates predicted from solid-state NMR and theoretical calculations suggests that the short-range structure seems to satisfy “the Al avoidance rule” in the tetrahedral layers, but the longer range constraints on the distribution of Si/Al seems to depend on composition (e.g., Si/Al ratio) (e.g., Circone et al. 1991; Herrearo et al. 1987; Palin et al. 2001). While Si/Al distribution in the layer silicates with high crystallinity (e.g., muscovite) appears to obey the Al-avoidance rule, the extent of Si/Al disorder in metastable low-temperature phyllosilicates, such as montmorillonites (clay minerals with expandable layers due to negative surface charge) with low crystallinity have not been fully understood.

Whereas it is difficult to directly quantify the degree of Al/ Si disorder by investigating cation environments in the phyllosilicates, similar information can be effectively obtained by exploring the connectivity among coordination polyhedra (e.g., \(\text{\textsuperscript{IV}}\text{Si-O-\textsuperscript{IV}}\text{Al}\) and \(\text{\textsuperscript{IV}}\text{Al-O-\textsuperscript{IV}}\text{Al}\) using \(\text{\textsuperscript{17}}\text{O}\) NMR (e.g., Walter et al. 1988; Lee and Stebbins 1999). Particularly, we have shown that high-resolution \(\text{\textsuperscript{17}}\text{O}\) 2D MQMAS NMR (triple quantum magic angle spinning; Frydman and Harwood 1995) at relatively high magnetic field (e.g., 14.1 Tesla) can provide resolution among chemically distinct O environments in model phyllosilicates (Lee and Stebbins 2003; Lee et al. 2003). These results revealed previously unknown details of atomic configurations around O \(\text{\textsuperscript{17}}\text{O}\) (spin 5/2) as were also demonstrated for aluminosilicate glasses (e.g., Dirken et al. 1997; Stebbins and Xu 1997). \(\text{\textsuperscript{27}}\text{Al}\) MAS NMR at high magnetic field has been useful in exploring the Al environment in Al hydroxides, layer silicates, and aluminosilicate glasses (e.g., Allwardt et al. 2005; Lee et al. 2003; Neuville et al. 2006; Stebbins et al. 2000). While paramagnetic impurities (e.g., Fe) in the natural dioctahedral layer silicates lead to a broadening of the NMR spectrum due to strong interaction between unpaired electrons and nuclear spins (e.g., natural muscovite, Lee and Stebbins 2003), synthetic samples free from...