O atom sites in natural kaolinite and muscovite: $^{17}$O MAS and 3QMAS NMR study

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ABSTRACT

The layer silicates are among the most common minerals in the Earth’s surface environment, play important roles in many geological processes, and have diverse technological applications. While it has been suggested that O isotope exchange and dissolution kinetics in aqueous solutions are controlled by chemical bonding and local atomic structures, the effect of atomic environment around O atom sites in clay minerals on their site-specific reactivities with H$_2$O are not well known, mainly because direct experimental evidence is lacking.

Here, we present for the first time detailed high-resolution $^{17}$O NMR data for $^{17}$O-exchanged natural kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$] and muscovite [KAl$_4$(AlSi$_3$)O$_10$(OH)$_2$] using $^{17}$O triple quantum magic angle spinning (3QMAS) and MAS NMR at high fields. At least two basal O atom sites in kaolinite are resolved: O$_4$, and (O$_3$ + O$_5$). Apical O atoms ([Si-O-2[Al$_6$]Al] and hydroxyl groups are also shown in these spectra. The $^{17}$O 3QMAS spectrum for muscovite shows improved resolution over the $^{17}$O MAS NMR spectrum, allowing us to resolve several basal O atoms, including ([Si-O-][Al]), as well as hydroxyl groups. The fraction of each O atom appears to deviate somewhat from the stoichiometric value, suggesting that each crystallographically distinct site may have a different rate of exchange with the O atom in H$_2$O.

INTRODUCTION

The interaction between layer silicates and water has long been studied theoretically and experimentally because of its importance in O atom isotope exchange fractionation and geologic processes such as weathering and diagenesis (Savin and Lee 1988). Layer silicates have large surface areas and thus also have important applications to nuclear waste storage and industrial catalysis (Sposito et al. 1999).

Extensive macroscopic isotope exchange measurements and statistical thermodynamic analyses have suggested that the kinetics of isotope exchange and of dissolution may be strongly affected by average chemical bonding in specific silicate and oxide minerals (Cole and Ohmoto 1986; Savin and Lee 1988; Sverjensky 1992; Cole 2000). Some examples include faster O atom isotope exchange for minerals with more non-bridging O atoms (for example, chain silicates vs. tectosilicates) (Cole 2000). The rate-determining step of mineral dissolution is usually metal-O atom bond dissociation. Thus, dissolution behavior of specific minerals has been semi-quantitatively modeled using their relative average bond strengths (Sverjensky 1992; Lasaga 1995). Several theoretical approaches, including quantum chemical calculations, have revealed the importance of bonding environment and topology in the kinetics of mineral-fluid interactions, including kaolinite dissolution (Xiao and Lasaga 1994; Lee et al. 2001). Recent experimental studies including liquid-state $^{17}$O NMR on a simple aqueous aluminum complex (Al$_{13}$) (Phillips et al. 2000), and solid state $^{17}$O NMR on zeolites (Xu and Stebbins 1998; Stebbins et al. 1999; Cheng et al. 2000), have buttressed the theoretical results, revealing that each O atom site in these systems has a distinct reactivity (rate of exchange of O atoms) with H$_2$O.

Testing these results on more complex but more common minerals at the Earth’s surface, such as clay minerals, is particularly important, because clays are among the most important indicators of geologic processes in the environment. This testing, however, is experimentally challenging and can be limited by the resolutions of spectroscopic and diffraction methods.

As has been previously demonstrated, element-specific solid-state $^{17}$O NMR is one of the most effective and promising probes of O atom sites and their specific reactivities (Walter et al. 1988; Xu and Stebbins 1998; Lee et al. 2001), $^{17}$O is, however, a quadrupolar nuclide. Interactions between the electric field gradient and the quadrupolar moments of the nuclei, combined with overlap in chemical shifts, often yield heavily broadened NMR spectra for O atom sites with similar environments in complex materials. As a result, there have been few $^{17}$O NMR studies of clay minerals. Previous $^{17}$O static NMR studies of t alc [Mg$_6$Si$_4$O$_{10}$(OH)$_2$] combined with cross-polarization from protons revealed three O atom sites, including Si-O-Mg, Si-O-Si and Mg-OH, that have distinct ranges of structurally relevant NMR parameters, coupling constants (C$_h$), asymmetry parameter (τ), and isotropic chemical shift (δ$_{iso}$), but $^{17}$O static NMR has not allowed further resolution among O atom sites (Walter et al. 1988). A possible solution for achieving high resolution in solid-state NMR is magic-angle spinning (MAS) NMR at higher magnetic fields, which reduces the quadrupolar broaden ing (Stebbins et al. 2000). Further advances, such as triple-quantum magic-angle spinning (3QMAS) NMR at high fields, can provide much improved resolution, free from quadrupolar