

LETTER

Reactive Al-O-Al sites in a natural zeolite: Triple-quantum oxygen-17 nuclear magnetic resonance

JONATHAN F. STEBBINS,* PEIDONG ZHAO, SUNG KEUN LEE, AND XING CHENG

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

ABSTRACT

In framework aluminosilicate materials (e.g., feldspars, zeolites and many others), it is generally assumed that AlO_4 tetrahedra do not share corners, i.e., that Al-O-Al oxygen sites are avoided when stoichiometry permits. This assumption plays a key role in models of thermodynamic properties and of reaction kinetics. We present a new approach to directly test this assumption, based on ^{17}O triple-quantum magic-angle spinning nuclear magnetic resonance (3QMAS NMR). We show that thermodynamically significant concentrations of Al-O-Al sites can be observed in a naturally occurring zeolite (stilbite), and that these sites react faster with H_2O vapor than do Si-O-Si and Si-O-Al sites.

INTRODUCTION

Framework aluminosilicates, which are based on three-dimensional networks of corner-shared AlO_4 and SiO_4 tetrahedra, comprise the most common minerals of the Earth's crust (feldspars), are the predominant components of many natural magmas and glasses, and are important constituents of many glasses and ceramics used in technology. Zeolites are a group of aluminosilicate minerals that are common in natural low-temperature hydrothermal systems and are of widespread utility as catalysts in petroleum refinement and in industrial chemical synthesis. One of the most important aspects of the structure of such materials is the arrangement of AlO_4 and SiO_4 groups in the tetrahedral network. The extent of ordering among these groups has a major influence on the configurational entropy of the material and hence on temperature and compositional conditions of formation, in either nature or the laboratory. Al-Si order-disorder affects reaction kinetics as well, for example in the distribution and number of acid sites in catalysts, and in the rate at which different sites react with water (Xu and Stebbins 1998a, 1998b).

Direct determination of the extent of Al-Si ordering in aluminosilicates is often difficult because of the similarity of X-ray scattering by the Al^{3+} and Si^{4+} (T) cations. Long range average Al-Si site occupancies must therefore often be estimated from average T-O bond lengths. Data on short range order, which is generally of greater energetic significance, have recently been greatly extended by high-resolution ^{29}Si magic-angle spinning (MAS) NMR (Engelhardt and Michel 1987). This technique, when applied to relatively simple structures, can quantify the concentrations of Si sites with varying numbers of Al first neighbors and hence elucidate the framework

ordering state. However, it is less useful in complex structures that have multiple, overlapping ^{29}Si peaks. The most general conclusion from many diffraction and NMR studies (Engelhardt and Michel 1987) is that in systems where the molar ratio $R = \text{Si}/\text{Al}$ is greater than or equal to 1 (by far the most common situation), Al-O-Al oxygen sites are absent or are at least minimized with respect to mixtures of Si-O-Al and Si-O-Si sites. This conclusion is supported by theoretical and experimental estimates of relative energetic stability (Navrotsky et al. 1982; Tossell 1993). Although this "aluminum avoidance principle" (Goldsmith and Laves 1955) or "Loewenstein's rule" (Loewenstein 1954) is acknowledged by many crystallographers to be only a first approximation (Smith 1988), it is almost always assumed in models of order-disorder in framework silicates. Experimental observation of variations from ideal "aluminum avoidance" have been limited, primarily occurring in alkaline-earth containing aluminosilicates with $\text{Si}/\text{Al} \leq 1$ (Phillips et al. 1992; Putnis 1992; Benna et al. 1999).

The utility of high-resolution ^{17}O nuclear magnetic resonance (NMR) spectroscopy in measuring structural disorder in solid silicates has advanced significantly with the introduction of techniques that average out second-order quadrupolar effects, which can severely broaden conventional magic-angle spinning (MAS) spectra (Chmelka et al. 1989; Fernandez and Amoureux 1995; Frydman and Harwood 1995; Baltisberger et al. 1996; Florian et al. 1996). In particular, the triple quantum MAS technique (3QMAS) is relatively easy to implement, and although not strictly quantitative, has been shown to clearly resolve Si-O-Si, Si-O-Al, and other oxygen sites in aluminosilicates (Dirken et al. 1997; Stebbins and Xu 1997; Xu et al. 1998; Xu and Stebbins 1998b). Recently, Al-O-Al sites were observed by ^{17}O 3QMAS NMR in model compounds and in Al-rich aluminosilicate glasses and shown to be clearly distinguishable from Si-O-Si and Si-O-Al sites (Stebbins et al. 1999). This report uses ^{17}O 3QMAS NMR to show that in many cases

*E-mail: stebbins@pangea.stanford.edu

the direct detection and, potentially, the quantitation of Al-O-Al sites in aluminosilicate crystals and glasses is possible, and hence, the extent of aluminum avoidance can be directly evaluated. We also present evidence for the existence of a significant concentration of Al-O-Al sites in an aluminosilicate zeolite with $R \gg 1$, and show that such sites have a relatively high reactivity toward oxygen exchange with H_2O .

EXPERIMENTAL METHODS

Using a naturally occurring zeolite starting material (stilbite) ^{17}O -enriched samples were prepared by hydrothermal exchange with isotopically enriched H_2O . Stilbite samples from Nasik, India, approximately $Na_{0.46}Ca_{2.0}Al_{4.5}Si_{13.5}O_{36} \cdot 10.8H_2O$ (Xu and Stebbins 1998a) were crushed and reacted with a roughly equal weights of 45% ^{17}O H_2O in sealed gold tubes at 200 °C for several weeks in cold-seal reaction vessels. Subsequent "back reaction" with isotopically normal water vapor at about 21 torr pressure was done on dehydrated samples at elevated temperature, followed by re-hydration at 25 °C (Xu and Stebbins 1998a). All NMR spectra were collected with a Varian Inova 600 spectrometer, at 119.1 MHz for ^{29}Si and 81.3 MHz for ^{17}O . A 3.2 mm Varian/Chemagnetics MAS probe, with sample spinning rates of about 16 kHz, was used. Spectra are referenced to external tetramethyl silane for ^{29}Si and water for ^{17}O , and were collected with delay times that were tested to ensure against differential relaxation among sites. Single-pulse acquisition with delay times of 30 s were used for the ^{29}Si spectra. A three-pulse 3QMAS sequence with a 180° selective echo, followed by shear transformation, was used for ^{17}O spectra as described previously (Xu and Stebbins 1998b). An rf (radiofrequency pulse) power of about 80 kHz was used for excitation and reconversion pulses, which were 5 and 1.6 μs long.

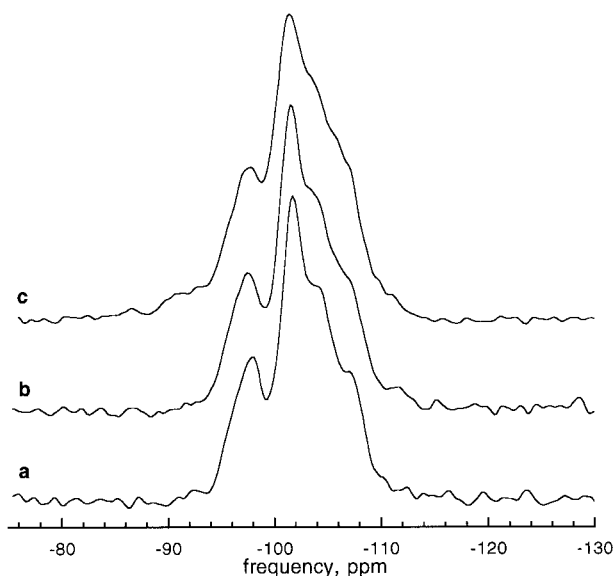


FIGURE 1. ^{29}Si MAS spectra of (a) unmodified stilbite; (b) stilbite after initial hydrothermal enrichment in ^{17}O ; (c) stilbite after "back reaction" at 200 °C for 40 h. The slight broadening in the latter case is probably caused by a slight variation in the hydration state.

RESULTS AND DISCUSSION

^{29}Si MAS NMR spectra (Fig. 1) as well as previous NMR and X-ray diffraction studies (Xu and Stebbins 1998b; Xu and Stebbins 1998a) showed no changes in the aluminosilicate framework connectivity either during initial exchange or in subsequent "back reaction" with isotopically normal water vapor at low pressure. The two-dimensional ^{17}O 3QMAS spectrum of the enriched stilbite (Fig. 2), has three clearly identifiable peaks. The largest two peaks are unambiguously attributable to Si-O-Si and Si-O-Al sites (Timken et al. 1986; Engelhardt and Michel 1987; Stebbins 1995; Dirken et al. 1997; Xu et al. 1998; Xu and Stebbins 1998b). The third, smaller, peak is similar in position to Al-O-Al sites connecting pairs of AlO_4 groups in crystalline $NaAlO_2$ and in a Al-rich Na-aluminosilicate glass (Stebbins et al. 1999). Previous ^{17}O 3QMAS studies of stilbite (Xu and Stebbins 1998b; Xu and Stebbins 1998a) did not report this third peak, because its intensity was not much above noise in spectra collected with a lower-field spectrometer, and its position had not yet been predicted from studies of model compounds.

The observation of Al-O-Al sites in a zeolite is unexpected in view of conventional models of Si/Al ordering in aluminosilicates. It is thus important to ensure that the observed third ^{17}O NMR peak cannot be explained otherwise. Powder X-ray diffraction showed no impurities with a detection limit of a few percent. ^{27}Al MAS NMR showed only AlO_4 groups, ruling out contamination by clays, micas, prehnite and aluminum oxides, or hydroxides at a detection limit of a fraction of 1%. Oxides and hydroxides, as well as non-bridging oxygen sites, are also ruled out by known ^{17}O NMR parameters for these phases (Stebbins 1995). Among other contaminants that might be expected from mineralogical studies of Deccan Traps zeolites (Sukheswala et al. 1974), apophyllite, gyrolite, and okenite have expected ^{29}Si peaks that were not observed in our samples (Stebbins 1995). Chlorite and related minerals are Fe-rich and would not produce detectable spectra. Small amounts of other zeolites or other framework aluminosilicates could be present, but would contribute primarily to the Si-O-Si and Si-O-Al peaks in the ^{17}O spectra.

From the positions of the new peak in the two dimensions, its mean isotropic chemical shift ($\delta_{iso} = 21 \pm 3$ ppm) and quadrupolar coupling product ($P_Q = 3.8 \pm 0.3$ MHz) can be estimated as discussed previously (Baltisberger et al. 1996; Schaller and Stebbins 1998), and are consistent with the observed quadrupolar line shape if the quadrupolar asymmetry parameter η is between about 0 and 0.2. [With C_Q as the quadrupolar coupling constant, $P_Q = C_Q [1 + (\eta^2)/3]^{1/2}$. For ^{17}O in silicates, P_Q typically exceeds C_Q by only 0 to 4% (Baltisberger et al. 1996).] The shift δ_{iso} resembles values for Al-O-Al sites previously determined in $NaAlO_2$ and a sodium aluminosilicate glass [19–31 ppm (Stebbins et al. 1999)], but P_Q is significantly greater (1.8–1.9 MHz). The latter difference is probably caused by the association of H_2O molecules with the highly charged Al-O-Al sites, as is known to occur for Si-O-Al sites in zeolites. The exact effect of this association is not predictable, but it is well known that OH groups in hydrated oxides tend to have large P_Q values (Xu et al. 1998).

The average (X-ray diffraction) structure of stilbite is disordered, with equal and random distributions of Al on all tetra-

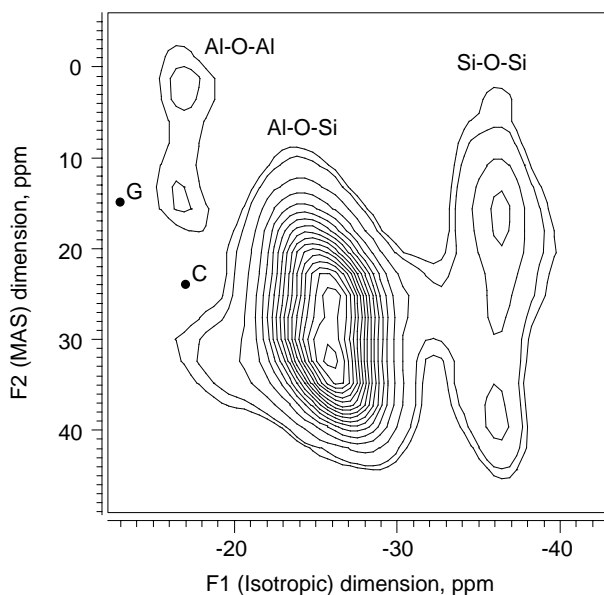


FIGURE 2. ^{17}O 3QMAS spectra of ^{17}O -enriched stilbite. In these 2-dimensional spectra, isotropic spectra appear in the F1 dimension and are free of second-order quadrupolar broadening. In the F2 dimension, spectra that are somewhat distorted versions of standard MAS spectra appear. Plotting conventions are as described previously (Baltisberger et al. 1996; Schaller and Stebbins 1998); contour lines mark intensities at equal intervals from 3 to 100% of the maximum with an extra contour at 4.2% inserted to show the shapes of the low-intensity features. "C" marks the Al-O-Al peak center predicted from recent data on crystalline NaAlO_2 ; "G" marks that for an aluminous sodium aluminosilicate glass (Stebbins 1999).

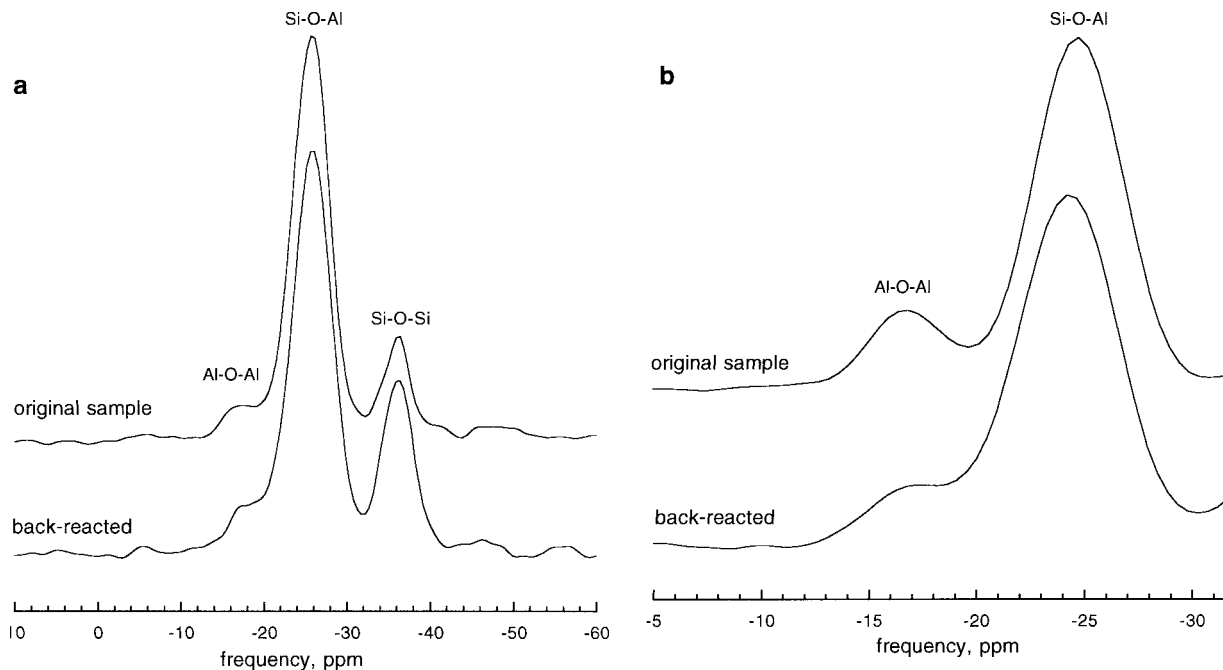


FIGURE 3. Isotropic dimension projections of ^{17}O 3QMAS spectra of stilbite. In each part, the two spectra are normalized to the same maximum peak height. (a) Projections of total spectra. (b) Projections of spectra in region of Al-O-Al peak.

hedral sites (Slaughter 1970), although optical properties have suggested some Si-Al ordering (Akizuki and Konno 1985). Long-range disorder does not, however, constrain short-range aluminum avoidance or the lack thereof. Isotropic projections of the ^{17}O 3QMAS spectra can, on the other hand be used to estimate the relative abundance of Al-O-Al sites. In general, 3QMAS peak intensities depend on C_Q , with excitation and reconversion efficiencies both decreased for sites with higher C_Q . However, the P_Q and hence C_Q of the Al-O-Al and Si-O-Al sites [3.5 MHz (Xu and Stebbins 1998b)] are quite similar, suggesting that their relative intensities should also be comparable. Relative site occupancies were derived from the isotropic dimension projections. The area of the projection of the total spectrum of the Si-O-Al site was compared with that of a partial projection in the region of the Al-O-Al peak to avoid the contribution from the overlapping high frequency shoulder of the Si-O-Al peak. We estimate that the ratio of Al-O-Al to Si-O-Al sites is about $6 \pm 0.5\%$. Given the bulk Si/Al ratio of the stilbite of about three (Xu and Stebbins 1998a), this is equivalent to $3 \pm 0.5\%$ of the total O atoms in the structure as Al-O-Al.

A simple model of the configurational entropy (S_c) of framework aluminosilicates, which assumes ideal mixing of the three oxygen species (Lee and Stebbins 1999), indicates that for an otherwise fully disordered structure, the difference between complete aluminum avoidance (0% Al-O-Al, $S_c = 5.76$ J/K per mole of O) and the observed deviation from aluminum avoidance [3% Al-O-Al, $S_c = 6.60$ J/(K·mol)] is about 15% of the total. This variation could be important in models of free energy and phase equilibria, which almost invariably assume complete aluminum avoidance, particularly for reactions with small overall entropy changes.

The observed extent of violation of aluminum avoidance can be analyzed in terms of an order parameter Q , which varies from 1 for complete Al-avoidance to 0 for a fully random arrangement of Al and Si tetrahedra (Lee and Stebbins 1999). A recent ^{29}Si NMR study of Ca-aluminosilicate glasses, equilibrated with liquids at roughly 1000 K, estimated Q values as low as 0.8 (Lee and Stebbins 1999). The Q value derived from the Al-O-Al content of stilbite is 0.72, which is surprisingly low, especially given that the temperature of formation is likely to be less than about 420 K (Kristmannsdóttir and Tomansson 1978). This disorder thus strongly implies thermodynamic disequilibrium, or, perhaps, unexpected stabilization of Al-O-Al sites by H_2O . Disequilibrium ordering states are not uncommon in aluminosilicates that form at low temperature (Flehmig 1977), but such a violation of Al-avoidance has not previously been reported.

One form of disequilibrium framework disorder can be the structural mismatches that can occur at domain boundaries during crystal growth under conditions of high nucleation density. If we assume repetitive planar stacking faults, approximately 1 fault per eight oxygen layers, or on average roughly one per unit cell, would be required to explain the observed Al-O-Al concentration if Al-avoidance is maintained within each domain. Such an enormous density of defects would, of course, blur the distinction between “defect” and “structure,” and seems unlikely.

Structural sites that have relatively low energetic stability, such as Al-O-Al, are expected to be relatively reactive. In addition, the unusually high concentration of negative charge on such a framework oxygen (formally -0.5 , vs. -0.25 for Si-O-Al and 0 for Si-O-Si), suggests that it is a likely locus of interaction with H_2O molecules and other polar or charged species during reaction with fluids or in catalyst systems. We recently reported that Si-O-Al sites in stilbite exchange more rapidly with O in H_2O vapor than do Si-O-Si sites (Xu and Stebbins 1998a), as predicted from energetic considerations based on ab initio calculations (Xiao and Lasaga 1994). Figure 3 shows the ^{17}O spectra for a stilbite sample after “back-reaction” at 197°C for 40 h, during which more than half of the ^{17}O was exchanged with ^{16}O from water vapor. In the projections of the full spectra, the relative ratio of Al-O-Si to Si-O-Si sites clearly decreases as the former is replaced more rapidly by isotopically normal oxygen. In the projections of the partial spectra, an overlapping shoulder from the Si-O-Al peak is reduced and the intensity of the Al-O-Al peak relative to that of the Si-O-Al peak is more accurately portrayed. Here, it can be seen that the ratio of Al-O-Al to Si-O-Al also appears to decrease with back reaction, indicating that the former is even more reactive to H_2O exchange.

Other variations from perfect aluminum avoidance have been found, but these are generally restricted to metastable disordered phases in systems with $\text{Si}/\text{Al} \leq 1$, and with divalent charge balancing cations, such as cordierite [$\text{Mg}_2\text{Si}_4\text{Al}_2\text{O}_{18}$ (Putnis 1992)], anorthite [$\text{CaAl}_2\text{Si}_2\text{O}_8$ (Phillips et al. 1992)] and the corresponding Pb- and Sr-feldspars (Benna et al. 1999). Another reported exception, based on analysis of a highly overlapped ^{29}Si spectrum, was reported for a synthetic zeolite-like material (Klinowski et al. 1987), and at least trace amounts of

hole centers associated with Al-O-Al sites have been detected by electron paramagnetic resonance (EPR) in radiation-damaged potassium feldspars ($\text{Si}/\text{Al} \gg 1$) and even in quartz (Speit and Lehmann 1982; Weil 1984; Hofmeister and Rossman 1985). Evaluation of the broader implications of our finding of reactive Al-O-Al sites in a zeolite will require the study of many more materials, but certainly suggests that conventional structural models should be re-examined.

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