

## Disordering during melting: An $^{17}\text{O}$ NMR Study of crystalline and glassy $\text{CaTiSiO}_5$ (titanite)

SCOTT KROEKER,<sup>1</sup> DAVID RICE,<sup>2</sup> AND JONATHAN F. STEBBINS<sup>3,\*</sup>

<sup>1</sup>Department of Chemistry, University of Manitoba, 350 Parker Building, Winnipeg, Manitoba, R3T 2N2, Canada

<sup>2</sup>Varian Inc., 3120 Hansen Way, Palo Alto, California 94304, U.S.A.

<sup>3</sup>Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

### ABSTRACT

Although titanite ( $\text{CaTiSiO}_5$ ) has one of the highest known entropies of fusion among silicates, the corresponding melt is a relatively good glass-former, which provides an opportunity to investigate the structural origin of disorder in the liquid. Here we present an  $^{17}\text{O}$  NMR study of  $\text{CaTiSiO}_5$  glass, using detailed new results on the crystalline phase, collected at magnetic fields of 9.4, 14.1, 18.8, and 21.1 Tesla, to interpret the spectra. We find that the glass contains significant concentrations of Si-O-Si and Si-O-Ca sites in addition to the Ti-O-Ti and Ti-O-Si sites of the crystal, suggesting considerable network disorder. Simulations of the spectra for the crystal allow the derivation of isotropic chemical shifts and quadrupolar coupling constants ( $C_Q$ ) for each of the five O atom sites. In addition the Ti-O-Ti site has an unusually large chemical shift anisotropy and an unusually small  $C_Q$  value.

### INTRODUCTION

The structural role of tetravalent titanium ( $\text{Ti}^{4+}$ ) in silicate glasses and melts has recently received widespread attention. Titanium-containing minerals are important accessory phases in igneous rocks and hence in their geochemical differentiation, Ti has important effects on technologically interesting properties such as density, refractive index, and crystal nucleation rates, and  $\text{Ti}^{4+}$  shows intriguing behavior as an “intermediate” between more well-defined network-forming and network-modifying cations (Varshneya 1994). Some titanosilicate melts show anomalously large heat capacities just above the glass transition that decrease with increasing temperature (Tangeman and Lange 1998; Bouhifd et al. 1999); density data for melts have suggested important effects of composition on the coordination of Ti (Liu and Lange 2001); and addition of  $\text{TiO}_2$  to silicate melts has major effects on phase equilibria, markedly increasing the activity coefficient for  $\text{SiO}_2$  (Ryerson 1985). Extensive studies of titanosilicate glass and melt structure by Raman (Mysen et al. 1980) and X-ray absorption spectroscopy (Farges et al. 1996) have been reviewed and linked to thermodynamic and transport properties (Ryerson 1985; Mysen 1988; Brown et al. 1995; Gan et al. 1996; Bouhifd et al. 1999; Liu and Lange 2001).

Most previous structural studies of titanosilicate glasses and melts have focused on cation coordination and bonding environments. For a variety of silicate, aluminosilicate, and boro-

silicate glasses, we have recently emphasized the importance of the complementary view provided by  $^{17}\text{O}$  NMR, which can give a direct, and in many cases, quantitative view of anion coordination, the linkages among network-forming cations, and the extent of disorder among both network-forming and network-modifying cations (Farnan et al. 1992; Florian et al. 1996; Stebbins et al. 1997; Wang and Stebbins 1999; Lee and Stebbins 2000; Zhao et al. 2000; Lee and Stebbins 2002). Here we apply that approach to a glass of  $\text{CaTiSiO}_5$  composition, which represents the structure of the melt at the glass transition temperature of about 740 °C (Villegas et al. 1994). This material is unusual; although crystalline titanite is an “orthosilicate” ( $\text{SiO}_4$  tetrahedra linked to no other tetrahedral groups), the melt is a relatively good glass former, at least in small samples that cool rapidly. At the same time, however, titanite has one of the largest entropies of fusion of any silicate, suggesting a great degree of structural disorder in the melt (Stebbins et al. 1984). Oxygen-17 NMR has also recently been applied to the structure of alkali titanosilicate glasses (Larsen et al. 2001), to titanosilicate gels and titanosiloxanes (Dirken et al. 1995; Gervais et al. 2000; Gervais et al. 2001), and to titania-based xerogels and nanoparticles (Blanchard et al. 1998; Scolas et al. 1999). This growing body of data is particularly useful in interpreting new  $^{17}\text{O}$  NMR results for a glass of  $\text{CaTiSiO}_5$  composition.

In order to better interpret results on the glass, we have also made a detailed  $^{17}\text{O}$  NMR study of crystalline titanite. We report data that provide new information on the relationship of local structure to NMR observables, and show the real utility of spectra collected at very high magnetic fields, including 14.1,

\* E-mail: [stebbins@pangea.stanford.edu](mailto:stebbins@pangea.stanford.edu)

18.8, and 21.1 Tesla. For a quadrupolar nuclide such as  $^{17}\text{O}$  (nuclear spin quantum number  $I = 5/2$ ) with a relatively low resonant frequency, such high fields are particularly useful in decreasing the effects of second-order quadrupolar broadening and enhancing spectral resolution and the structural information that can be obtained.

## EXPERIMENTAL METHODS

### Sample synthesis

$\text{CaSiO}_3$  glass was initially synthesized from isotopically normal  $\text{CaCO}_3$  and  $\text{SiO}_2$  by melting at 1550 °C (Fiske 1993). Approximately 48%  $^{17}\text{O}$ -enriched  $\text{TiO}_2$  was prepared by the hydrolysis of  $\text{TiCl}_4$  by isotopically enriched  $\text{H}_2\text{O}$ , followed by neutralization with  $\text{NH}_3$  and calcination in dry  $\text{N}_2$ . The stoichiometric ratio of this material was mixed with the  $\text{CaSiO}_3$  glass and 0.2 wt% cobalt oxide was added to speed spin-lattice relaxation; the mixture was then melted at 1450 °C in  $\text{N}_2$  for 30 minutes, yielding a bubble-free dark blue glass on air quenching of the small sample (<0.5 g). Neither powder XRD nor optical microscopy revealed any crystallinity. A portion of the glass was crystallized by heating for 12 h at 1200 °C in a welded Pt tube.

### NMR spectroscopy

Oxygen-17 magic-angle spinning (MAS) spectra (referenced to  $\text{H}_2\text{O}$ ) were collected with four Varian spectrometers to allow detailed comparisons of the effects of external magnetic field on spectral resolution and peak shapes. The 21.1 T spectra (122.0 MHz for  $^{17}\text{O}$ ) data were collected with the UnityINOVA 900 spectrometer and Oxford Instruments 900/54 magnet at Oxford Instruments in Eynsham, U.K., with a prototype probe of *Chemagnetics* T3 'H-X design (Varian Inc.) with 3.2 mm  $\text{ZrO}_2$  rotors and a maximum spinning rate of 25 kHz. For the data shown here, thin-walled rotors (about 25  $\mu\text{L}$  sample volume) with a maximum spinning rate of 15 kHz were used. The 18.8 and 14.1 T data (108.4 and 81.3 MHz for  $^{17}\text{O}$ , respectively) were collected with similar spectrometers and probes, with thicker-walled rotors and spinning rates of about 20 kHz. At 9.4 T, a VXR/Unity spectrometer was used with a probe from Doty Scientific, Inc., with 5 mm rotors and sample spinning rate of about 10 kHz (Fiske 1993).

All spectra shown for crystalline titanite were collected with single-pulse acquisition, using small (about 30°) radiofrequency (rf) tip angles to ensure that sites with varying quadrupolar coupling constants ( $C_Q$ ) were quantitatively observed. A spline fitted baseline correction was applied to the spectra. Spectra for the glass were more difficult to collect because of the breadth of the higher frequency Ti-O-Ti peak (see below). Even with a relatively short instrumental "dead time" of about 12  $\mu\text{s}$  (necessitated by probe "ringing"), some of this signal was lost at the beginning of the time-domain raw data set and could only be partially reconstructed by linear back prediction during data processing. Spectra were therefore also collected using a spin-echo pulse sequence (Kunwar et al. 1986) with whole echo data processing to enhance signal-to-noise ratio and eliminate phase corrections (Smith 2000). However, the wide range in  $C_Q$  values for the differing sites in the glass resulted in less

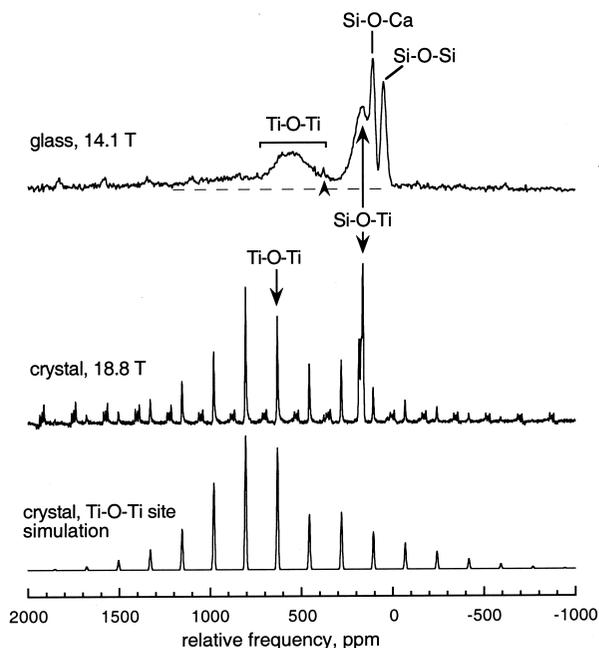
than ideal quantitation for this approach as well, as the rf tip angle varied significantly from site to site regardless of pulse parameters selected. Nonetheless, analysis of the combined data sets allowed at least semi-quantitative measurements of site concentrations in the glass.

NMR parameters for the five distinct O atom sites in the polycrystalline titanite sample were derived by analyzing the positions and intensities of the spinning sidebands (involving a full simulation of all transitions) and the central peaks in the 18.8 T and 14.1 T data collected after careful optimization of the MAS angle, using the STARS software package (Varian, Inc.).

## RESULTS

### Crystalline titanite: the Ti-O-Ti site

The  $^{17}\text{O}$  MAS spectrum of polycrystalline titanite is made up of many narrow peaks (Fig. 1). Most of these can be identified as spinning sidebands by their shifts in position with changes in the sample spinning rate. The sharp (full width at half maximum, FWHM = 6 ppm), featureless peak at 632 ppm can be unambiguously assigned to the Ti-O-Ti O atom, based on previous studies of  $\text{TiO}_2$  polymorphs, Ti-rich gels, and organometallic compounds (Bastow and Stuart 1990; Dirken et al. 1995; Gervais et al. 2000; Gervais et al. 2001), and other



**FIGURE 1.** Oxygen-17 MAS NMR spectra for polycrystalline and glassy  $\text{CaTiSiO}_5$ . (**Top**) Spin-echo spectrum for glass at 14.1 T; dashed baseline is to highlight the poorly resolved broad component associated with the Ti-O-Ti peak. (**Middle**) Data for polycrystalline sample at 18.8 T. (**Bottom**) Simulation of spectrum for the Ti-O-Ti site only. Central peaks are marked; all unlabeled peaks in the experimental spectra are spinning sidebands. The unlabeled arrow in the upper spectrum marks a background signal from the  $\text{ZrO}_2$  sample rotor (natural isotopic abundance).

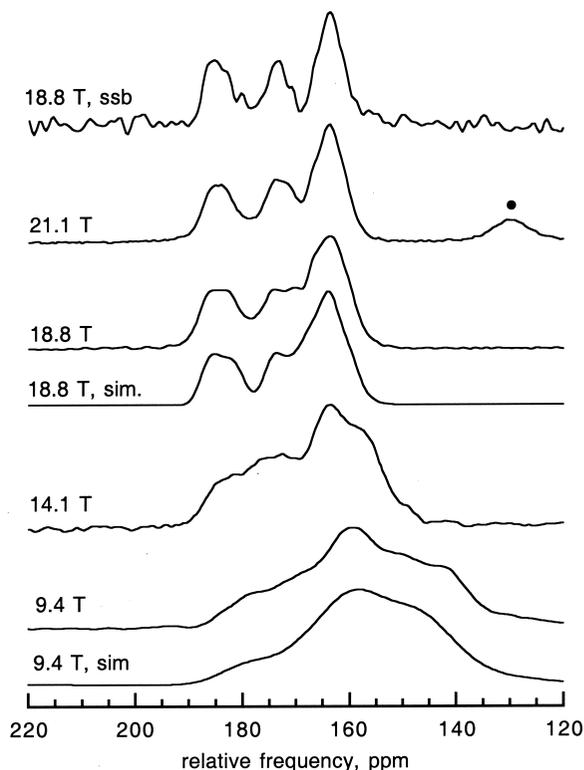
titanite-based materials (Blanchard et al. 1998; Scolan et al. 1999). Associated with this peak is a well-defined manifold of narrow spinning sidebands, the overall shape of which implies an unusually small  $C_Q$  value and significant chemical shift anisotropy. This component of the spectrum can be simulated with the assumption of coincident quadrupolar and chemical shift tensors and all transitions, to yield a  $C_Q$  value of 200 kHz and a chemical shift anisotropy spanning more than 1400 ppm (Table 1, Fig. 1).

### Si-O-Ti sites in titanite

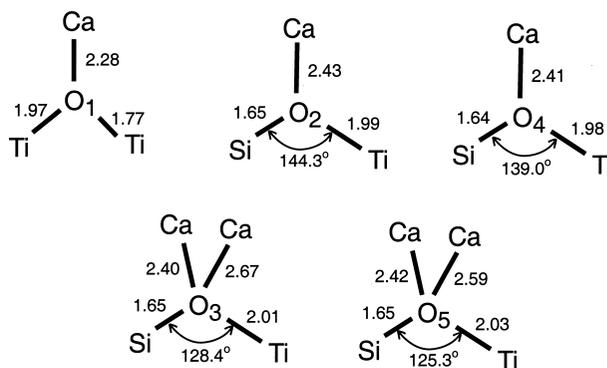
Central peaks for the four Si-O-Ti sites in titanite are found between 160 and 190 ppm at 18.8 and 21.1 T (Fig. 2). At the highest field available (21.1 T), these appear as a group of three roughly Gaussian peaks, one with an area twice that of each of the others. These clearly result from four equal-area contributions from the four crystallographically distinct Si-O-Ti sites, each of which has the same multiplicity. The doubled peak at lowest frequency probably represents the sum of signals either from sites  $O_4$  and  $O_2$ , or  $O_3$  plus  $O_5$ , as each pair has nearly identical local geometry (Speer and Gibbs 1976) (Fig. 3) and thus would be expected to have similar  $\delta_{iso}$  and  $C_Q$  values. In spite of the peak overlap, good estimates of  $\delta_{iso}$ ,  $C_Q$ , and  $\eta$  (the quadrupolar asymmetry parameter) can be generated using the 18.8 T data (Table 1), especially with consideration of the well-resolved satellite transition spinning sidebands (Fig. 1) as has been demonstrated in many studies of nuclides such as  $^{17}O$ ,  $^{23}Na$ , and  $^{27}Al$  (Skibsted et al. 1991; Jäger 1994). These parameters are consistent with experimental data collected at 14.1 and 9.4 T (Fiske 1993; Fiske and Stebbins 1994). At the highest two fields investigated, the peaks do not show obvious quadrupolar features, although second-order quadrupolar broadening still affects their width, and peak maxima are offset from the isotropic chemical shift values by about 3 to 5 ppm. Separation of the peaks is, however, largely controlled by chemical shift differences at these fields. In contrast, at 9.4 T, peak shapes are much more strongly affected by the quadrupolar coupling, which dominates the chemical shift differences, shifts the peaks to lower frequency, and makes resolution among the peaks poor. At 18.8 T, the spinning sidebands for the “inner satellite” ( $\pm 1/2$  to  $\pm 3/2$ ) transitions are somewhat better resolved (Fig. 2) than the spectrum for the central ( $1/2$  to  $-1/2$ ) transitions, because for a spin  $5/2$  nuclide the former are subject to less second-order quadrupolar broadening.

At approximately 3 MHz, the quadrupolar coupling constants are intermediate between typical values for Si-O-Si (4–5 MHz, Stebbins 1995b) and Ti-O-Ti (<1.5 MHz, Bastow and Stuart 1990; Bastow et al. 1996). Isotropic chemical shifts of

166 to 189 ppm are also between typical ranges for Si-O-Si (70–80 ppm) and Ti-O-Ti (500–600 ppm). These are at the low end of the range previously reported for binary titanite gels and titanite siloxanes (Gervais et al. 2000; Gervais et al. 2001), but similar in position to the Si-O-Ti peak in fresnoite ( $Ba_2TiSi_2O_8$ , 190 ppm) and to  $\delta_{iso}$  for this site type in  $Li_2TiOSiO_4$  (157 ppm) (Bastow et al. 1999).



**FIGURE 2.** Central transition ( $1/2$  to  $-1/2$ ) peaks in the  $^{17}O$  MAS spectra for the Si-O-Ti sites in crystalline titanite collected at the fields shown. Simulations at 18.8 and 9.4 T are shown, calculated using the parameters in Table 1. Dot marks a spinning sideband. The topmost spectrum shows the inner satellite transition ( $\pm 1/2$  to  $\pm 3/2$ ), sixth-order spinning sidebands for the Si-O-Ti peaks, shifted down in frequency by about six times the MAS rotor frequency.



**FIGURE 3.** Local bonding environments of O atom sites in titanite, with bond distances in angstroms (Speer and Gibbs 1976).

**TABLE 1.** NMR parameters for O atom sites in crystalline titanite

Site type	$\delta_{iso}$ , ppm $\pm 0.5$	$C_Q$ , MHz, $\pm 0.1$	$\eta$ , $\pm 0.1$
Ti-O-Ti*	$632 \pm 0.2$	0.2	$\approx 1.0$
Si-O-Ti	189	3.2	0.2
	177	3.2	0.1
	169	2.7	0.1
	166	2.9	0.2

\* The chemical shift tensor is described by  $\delta_{11} = 1200 \pm 50$  ppm,  $\delta_{22} = 940 \pm 50$  ppm,  $\delta_{33} = -240 \pm 50$  ppm.

### CaTiSiO<sub>5</sub> glass

Oxygen-17 MAS spectra of silicate glasses usually show at most two well-resolved peaks, generally representing bridging O atoms (BO) and non-bridging O atoms (NBO), although triple quantum MAS spectra are often much better resolved and reveal a much wider range of structural detail (Wang and Stebbins 1999; Lee and Stebbins 2000; Zhao et al. 2000). The spectra for CaTiSiO<sub>5</sub> glass shown in Figures 1 and 4 are thus unusual in displaying four well-defined features. This resolution originates from bonding to the titanium atom (Ti-O-Ti and Ti-O-Si), which shifts the O atom peaks to much higher frequency with respect to Si-O-Si and Si-O-Ca.

The lowest frequency peak, centered around 50 ppm, has a position and width typical of Si-O-Si (BO) O atoms in highly disordered glasses such as Ba- and Ca-silicates (Stebbins et al. 1997). Here, relatively wide ranges of NMR parameters apparently give rise to the roughly Gaussian peak shape, obscuring features from the more typical quadrupolar “doublet” pattern seen for Si-O-Si in materials such as silica gel and alkali silicates (Xue et al. 1994). However, the overall width of this peak is probably still dominated by the second-order quadrupolar broadening caused by the expected large values of  $C_Q$  for such sites, which are typically about 4 to 5 MHz (Stebbins 1995b). The peak centered at about 106 ppm is in exactly the position expected for NBO atoms bonded exclusively to Si and Ca (Stebbins et al. 1997); its narrow width corresponds to the smaller  $C_Q$  values typical of such sites (generally 2 to 3 MHz, Stebbins 1995b). The position of the broader peak centered at 165 ppm corresponds to the chemical shift range for the Si-O-Ti sites in crystalline titanite. The small  $C_Q$  values observed for the latter (about 3 MHz) suggest that the width of the Si-O-Ti peak in the glass is dominated not by quadrupolar broadening but by a range of chemical shifts corresponding to a range of bonding environments, such as number of Ca neighbors, Si-O-Ti angle, and even Ti coordination number (see Discussion).

Centered at 550 ppm is a broad signal ranging from 400 to 700 ppm (emphasized in Fig. 1 by the dashed baseline) and encompassing the chemical shift range for O atoms with two or more Ti neighbors as known from crystalline titanite, TiO<sub>2</sub> polymorphs and xerogels (Bastow and Stuart 1990; Scolan et al. 1999; Bastow et al. 2000), and titanosilicate gels (Dirken et al. 1995; Gervais et al. 2000). The relative intensities of this component and of the three described above are difficult to quantify due to the difference in peak width (see experimental section), but our estimates of the relative areas are ( $\pm 5\%$  absolute): Ti-O-Ti, 24%, Si-O-Ti, 40%, Si-O-Ca, 18%; Si-O-Si, 18%.

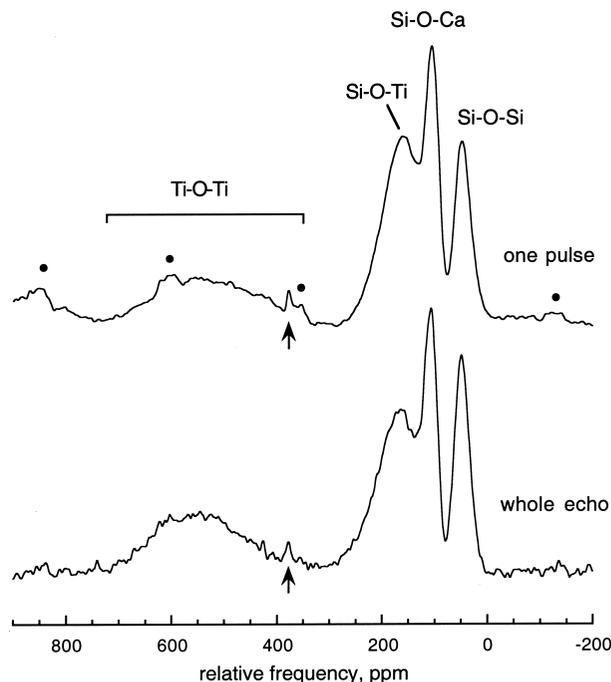
The width of this Ti-O-Ti component is comparable to the magic angle spinning rate, as can be seen in Figure 4 by the spacing of the spinning sidebands for the Si-O-Ca peak. As a result, sidebands for the Ti-O-Ti peak that may be generated by the sample spinning, if they are present, will overlap with the central peak. Disorder in the glass will compound the effects of shielding anisotropy, by analogy with Ti-O-Ti in the crystalline phase, to produce a distribution of resonances that may be much broader than attainable spinning speeds. The net effect may be a broader, unresolved feature that manifests in the spin-echo spectra as a raised baseline (Fig. 1). While its extent is difficult to assess, it appears to be similar to that of

spinning sidebands that map out the chemical shift anisotropy pattern for the Ti-O-Ti site in titanite. However, NMR parameters and their distributions for this site are not well characterized, and very broad “baseline” components are difficult to accurately observe and could have contributions from several sources. In particular, the Ti-O-Ti fraction estimated from the peak at 550 ppm may be underestimated.

## DISCUSSION

### Spectral resolution and NMR parameters

The improvements in NMR resolution provided by increasingly high magnetic fields are well known. The reduction in second-order quadrupolar broadening is especially useful in MAS spectra of non-integer spin nuclides ( $I > 1/2$ ). Here, the extent of the broadening relative to the chemical shift (in ppm) scales as the inverse square of the field. The 21.1 T data shown in Figure 2 are among the first solid state NMR results collected at this extremely high field (900 MHz <sup>1</sup>H frequency). At least for <sup>17</sup>O in crystalline titanite, the improvement in resolution at 21.1 and 18.8 T over that obtainable at lower fields is dramatic, with peak separation dominated by the chemical shift instead of being obscured by second-order quadrupolar broadening. Related enhancements have recently been reported for <sup>17</sup>O in several silicates, <sup>27</sup>Al in zeolites, and <sup>11</sup>B in glasses (Stebbins et



**FIGURE 4.** Central regions of the <sup>17</sup>O MAS spectra for the CaTiSiO<sub>5</sub> glass at 14.1 T. (Top) One-pulse acquisition. (Bottom) Spin-echo spectrum, corrected with a linear baseline to remove the very broad component beneath the Ti-O-Ti peak and allow more direct comparison with the one-pulse data. Dots mark obvious spinning sidebands from the Si-O-Ca peak; others may be present but not visible above noise; arrow marks background signal from ZrO<sub>2</sub> rotor (natural isotopic abundance).

al. 2002; Kroeker et al. 2001; Kroeker and Stebbins 2001).

The utility of detailed chemical shift data now becoming available for  $^{17}\text{O}$  is, however, somewhat limited by incompletely understood relationships between this parameter and local structure. While improvements in *ab initio* calculations of  $^{17}\text{O}$  chemical shifts and electric field gradients are providing new insights (Xue and Kanzaki 2000; Clark et al. 2001; Kubicki and Toplis 2002; Tossell and Cohen 2001), many fundamental questions remain. For example, titanite possesses two types of Si-O-Ti sites: one with a single coordinating Ca cation and hence relatively wide Si-O-Ti angle, and another with two Ca neighbors and a narrower angle (Fig. 3). Although it is likely that one of these pairs gives rise to the nearly coincident  $\delta_{\text{iso}}$  values of 166 and 169 ppm, we cannot yet be sure which pair to assign to these peaks.

The quadrupolar coupling constant,  $C_Q$ , is proportional to the largest principal component of the tensor that describes the electric field gradient at the nucleus of interest. In some simple systems  $C_Q$  for  $^{17}\text{O}$  correlates directly with the local structure. For example,  $C_Q$  is zero for sites with cubic point symmetry, as in MgO (Fiske et al. 1994); in silicates,  $C_Q$  varies systematically with Si-O-Si bond angle (Farnan et al. 1992; Xue et al. 1994; Clark et al. 2001). However, such relationships may not be obvious when O atom coordination numbers are higher and more types of cations are involved. For example, the O3 and O5 O atoms in titanite have distorted tetrahedral coordination while O2 and O4 are in flat pyramidal three coordination; all four sites have  $C_Q$  in the narrow range of 2.7 to 3.3 MHz. The Ti-O-Ti site in titanite has a nearly planar threefold coordinate structure, but a very small  $C_Q$  value, implying a surprisingly symmetrical local electric field gradient. In these cases, it is likely that the effects of ions beyond the first shell contribute significantly to these properties.

The anisotropy in the chemical shift reflects the dependence of nuclear shielding on the orientation of local bonding geometry relative to the external magnetic field. It is characterized by a second-rank tensor with principal components  $\delta_{11}$ ,  $\delta_{22}$ , and  $\delta_{33}$  ( $\delta_{\text{iso}}$  is the mean of these three values) (Duncan 1990). Although quantitative determinations of shift anisotropy for spin 1/2 nuclides such as  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$  are relatively common (Smith et al. 1983; Turner et al. 1986; Duncan 1990; Stebbins 1995b), such results can be difficult to obtain reliably for quadrupolar nuclides (Kroeker and Stebbins 2002). In many materials at typical NMR fields, quadrupolar interactions dominate the spectral appearance and simulations of stationary powder patterns or spinning sideband manifolds are insensitive to chemical shift anisotropy. However, for  $^{17}\text{O}$ , the large known range of  $\delta_{\text{iso}}$  in silicates and oxides suggests that anisotropic shielding (i.e., the range of chemical shifts spanned by  $\delta_{11}$ ,  $\delta_{22}$ , and  $\delta_{33}$ ) could be large as well. The Ti-O-Ti site in titanite is unusual for a non-cubic material in having a small  $C_Q$  value. As a result, the total intensity of the sidebands for all transitions is concentrated into a relatively narrow frequency range (about 200 kHz instead of the more typical several MHz), each sideband is relatively narrow (making each even more intense), and chemical shift anisotropy governs their relative intensities. Hence, the principal components of the shielding tensor can be readily determined by simulation of the sideband mani-

fold. The relative magnitudes of the  $^{17}\text{O}$  quadrupolar and chemical shift interactions for the Ti-O-Ti site in titanite are reminiscent of some metal carbonyl compounds (Oldfield et al. 1985) and vanadyl O atoms in  $\text{V}_2\text{O}_5$  and  $\text{KVO}_3$  (Klug et al., in preparation), where the anisotropic chemical shift also dominates the appearance of the spinning sideband pattern.

For the glass, the relatively good resolution at 14.1 T among signals from various O atom sites is caused by the large range of chemical shifts for O bonded to one or more Ti atoms. This, combined with the relatively large individual peak widths and relatively small  $C_Q$  values that are expected by comparison to the crystal, indicate that two-dimensional, triple-quantum MAS (3QMAS) spectra are unlikely to provide much additional resolution or structural information. Indeed,  $^{17}\text{O}$  MAS spectra at 14.1 T and 9.4 T (Fiske 1993; Fiske and Stebbins 1994) had comparable peak resolution, thus confirming that the peak widths arise from chemical shift effects, and not primarily from second-order quadrupolar broadening. A similar situation was encountered for yttrium and lanthanum aluminosilicate glasses (Schaller and Stebbins 1998). Both contrast with typical aluminosilicates and borosilicates, where relatively small  $^{17}\text{O}$  chemical shift ranges and large  $C_Q$  values generally result in unresolved MAS spectra but highly informative 3QMAS data (Wang and Stebbins 1999; Lee and Stebbins 2000; Zhao et al. 2000; Lee and Stebbins 2002).

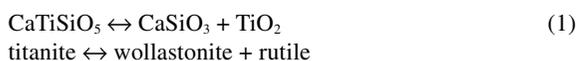
### Glass structure

Despite our limited understanding of structural effects on  $^{17}\text{O}$  chemical shifts, broad ranges of  $\delta_{\text{iso}}$  can be defined that are useful in interpreting NMR spectra of glasses. The O atoms in  $\text{CaTiSiO}_5$  glass occur in bonding environments of the types Si-O-Si, Si-O-Ca (probably with two or three Ca neighbors), Si-O-Ti (probably with one or more Ca neighbors), or Ti-O-Ti (several possible O and Ti coordinations as well as Ca neighbors). Our  $^{17}\text{O}$  NMR results do not provide direct information on Ti coordination number, but if we assume that most Ti atoms have five or six O atom neighbors, the Ti-O-Ti peak is an unusually clear example of O atom sites in a glass that are bonded to no tetrahedral network-forming cations, which have often been described as "oxide" or "O<sup>2-</sup>" ions but have rarely been directly observed. The lack of a well-defined peak between the known value of  $\delta_{\text{iso}}$  for CaO (294 ppm) (Turner et al. 1985) and the known range for Ti-O-Ti sites suggests that O atoms bonded to a single Ti and multiple Ca atoms are not abundant, but does not rule out the presence of a relatively minor concentration of such species, particularly if their environment is highly disordered. Similarly, "apical" O atoms with very short Ti-O bonds in  $\text{TiO}_5$  groups, as suggested by extensive X-ray spectroscopic studies, give narrow  $^{17}\text{O}$  NMR peaks for crystalline  $\text{Li}_2\text{TiOSiO}_4$  and  $\text{Li}_2\text{TiOGeO}_4$  (Bastow et al. 1999) at 740 to 750 ppm. The intensity in this region of the  $\text{CaTiSiO}_5$  glass is quite low (Fig. 4), but it is possible that some broad intensity could be hidden in the baseline noise.

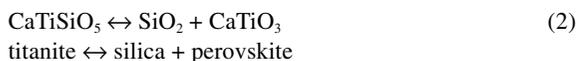
The large widths of the Si-O-Ti and especially the Ti-O-Ti peaks indicate considerable disorder around such sites. For the latter, data on binary titanosilicate gels and titanosiloxanes have indicated that O atoms with two Ti neighbors have  $\delta_{\text{iso}}$  near 730 ppm, with three Ti neighbors near 540 ppm, and with four

Ti neighbors near 370 ppm (Gervais et al. 2000; Gervais et al. 2001). Thus, a range in coordination of O atoms by Ti may be the predominant effect on the width of the Ti-O-Ti peak in CaTiSiO<sub>5</sub> glass. A range in the coordination number of the Ti by O may have a significant but secondary influence, lowering  $\delta_{\text{iso}}$  for Si-O-Ti sites by 30 to 70 ppm as Ti changes from six to four coordination (Gervais et al. 2001). Raman spectroscopy has indicated, however, that sixfold-coordinated Ti is not common in Ca silicate glasses with added TiO<sub>2</sub> (Mysen et al. 1980); X-ray absorption spectroscopy has suggested that most Ti is fivefold-coordinated in this system (Brown et al. 1995; Farges et al. 1996).

The most striking feature of the glass spectrum is the high concentration of O atom sites not found in the crystalline analog, with roughly 15 to 20% each of Si-O-Ca (NBO) and Si-O-Si (BO). To transform the structure of the crystal to that of the glass, some Si-O-Ti linkages may be replaced by a mixture of these new sites types, forming additional Ti-O-Ti groups in the process. Using hypothetical reactions among crystalline phases as a guide, several ways of writing such “reactions” can be imagined. For example, the “reaction”



would produce a mixture with two Si-O-Ca and one Si-O-Si (i.e., NBO/BO greater than that observed), and two O atoms coordinated by three Ti atoms each. Or, the “reaction”



could produce all Si-O-Si (i.e., NBO/BO less than that observed), in addition to O atoms with two Ti plus several Ca neighbors. Such reasoning does not account for changes in Ti coordination, but does suggest the range of processes that can occur. The “Ti-O-Ti” sites in the corresponding crystals have  $\delta_{\text{iso}}$  values that span much of the range observed in the glass, with rutile at 590 ppm, anatase at 558 ppm (Bastow and Stuart 1990), and perovskite at about 445 ppm (Bastow et al. 1996).

For the relatively well-defined Ti-O-Ti NMR peak (700 to 400 ppm), the area estimated above was about 24%. Given the associated uncertainty, this is not significantly greater than the fraction of Ti-O-Ti sites in crystalline titanite and is seemingly inconsistent with the above scenario. As discussed above, however, some additional peak area for such sites may be “hidden” in the poorly resolved, very broad baseline component.

A different initial approach to the glass structure is to imagine an interconnected network of SiTiO<sub>4</sub> stoichiometry made up exclusively of SiO<sub>4</sub> and TiO<sub>4</sub> tetrahedra. Initially, all O atoms in such a system would be two coordinate, with a mixture of Si-O-Si, Si-O-Ti, and Ti-O-Ti depending on the energetics of the following reaction, as in analogous aluminosilicate and borosilicate systems (Lee and Stebbins 2000; Lee and Stebbins 2002):



Addition of CaO could proceed as in simple silicates, forming two moles of NBO for each mole of oxide, which could be distributed over both Ti and Si cations depending on the relative stability of Ti-O-Ca and Si-O-Ca (always assuming that multiple Ca<sup>2+</sup> cations will coordinate NBO values). At the CaTiSiO<sub>5</sub> composition, an average of one NBO per tetrahedron would be formed, with 2/5 of the total oxygen as NBO, and 3/5 in the form of BO as in the analogous sheet silicate phases Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> or a hypothetical tetrahedral CaSi<sub>2</sub>O<sub>5</sub> phase. Alternatively, CaO addition to a Si/Ti tetrahedral network could be envisioned as occurring simply by the addition of one extra O atom to each TiO<sub>4</sub> tetrahedron, creating TiO<sub>5</sub> units with one NBO or tightly bonded “apical” O atom (“Ti = O”), as hypothesized from X-ray spectroscopic studies (Brown et al. 1995; Farges et al. 1996). The observation of a high concentration of NBO on Si in the <sup>17</sup>O NMR spectrum of CaTiSiO<sub>5</sub> glass suggests a combination of these sorts of processes. Again, although no discrete Ti-O-Ca or “Ti = O” peaks are observed, we cannot rule out the presence of some such species unresolved from the broad Ti-O-Ti peak. In these scenarios, a fully Si/Ti ordered glass of CaTiSiO<sub>5</sub> stoichiometry would have no Si-O-Si or Ti-O-Ti; such sites would be generated by randomization of the hypothetical initial ordered network.

The formation of an assortment of structural units in a glass or melt that is more diverse than that present in the corresponding crystal can be viewed as a consequence of (and a contribution to) the increase in disorder that takes place on melting, some of which remains when the melt is quenched into the glass at the glass transition temperature  $T_g$ . Other well-studied examples include the distribution of “Q<sup>n</sup>” species (SiO<sub>4</sub> groups with *n* BO and 4 - *n* NBO) in alkali silicate glasses (Stebbins 1987; Stebbins 1995a) and disorder among BO species in aluminosilicates (Lee and Stebbins 2000; Lee and Stebbins 2002). Reactions such as the following can be considered as “disproportionation” reactions analogous to those above for CaTiSiO<sub>5</sub>:



In all three cases, the mixing of the species produced increases the configurational entropy up to the point where the reaction products predominate, with further reaction potentially leading to “anti-ordering” or even to phase separation. For the Q<sup>n</sup> and BO species, quantitative speciation data show clearly that the former situation prevails in all systems studied, that is, that the products of the reactions as written remain in relatively low concentration, so that their increase at higher temperature contributes to the increase in configurational entropy. For CaTiSiO<sub>5</sub> glass, the remaining high concentration of Si-O-Ti sites suggests that this is also the case, but accurate quantitation is more difficult. The roughly equal concentrations of Si-O-Ca and Si-O-Si sites indicate however, that the spectra are not simply recording the onset of thermodynamically driven phase separation. Although addition of TiO<sub>2</sub> to Ca silicate melts does widen the already large miscibility gap, the CaTiSiO<sub>5</sub> composition remains well outside the stable two-liquid field and the two-liquid compositional tielines are nearly parallel to the

CaTiSiO<sub>5</sub>-SiO<sub>2</sub> join (Levin et al. 1964). Thus, if sub-microscopic, metastable phase separation were significant in CaTiSiO<sub>5</sub> glasses, the high-silica phase would be expected to contain mostly BO, not a mixture of BO and NBO. On the other hand, formation of a separate, low viscosity TiO<sub>2</sub>-rich liquid phase during cooling should promote crystallization. In CaTiSiO<sub>5</sub> glass, <sup>17</sup>O NMR is extremely sensitive to the presence of any of the likely Ti-rich crystalline phases (rutile, perovskite, titanite), as these fortuitously have unusually small C<sub>Q</sub> values and thus very narrow and intense NMR peaks (Bastow and Stuart 1990; Bastow et al. 1996); no evidence for any crystallinity was observed. Such sensitivity is indicated by the observation of a small peak for the ZrO<sub>2</sub> sample-containing rotor (Fig. 4), which, although having a mass about 15 times than that of the glass sample, has a natural <sup>17</sup>O concentration roughly 600 times smaller. Despite such reasoning, which suggests that liquid-liquid phase separation is unlikely, it remains possible that "nano-scale" compositional heterogeneity is present in the glass (Farges et al. 1996). The type of NMR data presented here cannot determine the scale of such heterogeneity, but small angle X-ray scattering of CaMgSi<sub>2</sub>O<sub>6</sub> glasses did show increases in the number and size of "subcritical nuclei" formed on cooling below the liquidus when up to 1 mol% TiO<sub>2</sub> was added (Kuo and Kirkpatrick 1982). Some sort of clustering may also be implied by the utility of TiO<sub>2</sub> as a nucleating agent in aluminosilicate glass ceramics (Beall 1994). The randomization with increasing temperature of modifier-rich domains (associated with fivefold-coordinate titanyl groups) has been used to explain heat capacity anomalies in titanosilicate melts (Farges et al. 1996; Gan et al. 1996), as has the energetically more significant mixing of Si and Ti in the network (Bouhifd et al. 1999). Future NMR studies of samples prepared with differing quench rates may help to resolve this question (Stebbins 1995a).

Another consequence of "reactions" such as reactions 1 and 2, which should also occur in melts with lower TiO<sub>2</sub> concentrations, may be the formation of greater concentrations of Si-O-Si linkages than expected from random mixing of the oxide components. If such groups reflect the presence of silica-like local structural units, an unexpectedly high thermodynamic activity of silica might be expected. Analysis of phase diagrams has shown that addition of TiO<sub>2</sub> to alkaline earth silicate melts does indeed increase the activity coefficient of silica (Ryerson 1985), and similar structural consequences have been suggested in interpretations of Raman spectra (Mysen et al. 1980).

Among silicates, titanite has one of the highest known entropies of fusion, whether considered on a formula unit basis [74.1 J/(mol·K)] or per mole of atoms (9.3 J/g·atom/K) (Stebbins et al. 1984). This is higher than values measured for other orthosilicates such as fayalite (Fe<sub>2</sub>SiO<sub>4</sub>, 8.6 J/g·atom/K), tephroite (Mn<sub>2</sub>SiO<sub>4</sub>, 7.9 J/g·atom/K), and forsterite (Mg<sub>2</sub>SiO<sub>4</sub>, 7.6 ± 1.3 J/g·atom/K) (Stebbins et al. 1984; Navrotsky et al. 1989), although relative values change somewhat when compared at a constant temperature instead of the respective melting points. Although titanosilicates are more "fragile" liquids than corresponding Ti-free melts (viscosity decreases relatively rapidly above T<sub>g</sub>) (Bouhifd et al. 1999), CaTiSiO<sub>5</sub> liquid is a much better glass former than other Al-free orthosilicate melts. Ti<sup>4+</sup> probably plays a structural role intermediate between those

of obvious network forming cations such as Si<sup>4+</sup> and Al<sup>3+</sup>, and those of relatively large, low charge network modifiers such as Na<sup>+</sup> and Ca<sup>2+</sup> (Varshneya 1994). Even if most Ti<sup>4+</sup> is in fivefold-coordinate instead of typically fourfold-coordinate "network-forming" sites, its small size and high charge are still likely to create relatively strong Ti-O bonds that form links to other network cations (Farges et al. 1996). Mixing of Si and Ti cations in the network, or, in a complementary view, mixing of Ti-O-Ti, Si-O-Ti, and Si-O-Si O atoms, may thus make an important contribution to the configurational entropy and to its increase with temperature. Although the extent of disorder that is quenched into the glass at T<sub>g</sub> must be considerably less than that which is present at the melting point, the <sup>17</sup>O NMR data shown here for CaTiSiO<sub>5</sub> glass are consistent with this type of disordering mechanism. Finally, we note that titanite is not the only multicomponent silicate that has an apparently anomalous entropy of fusion: the sheet silicate fluorophlogopite (KMg<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>F<sub>2</sub>) has an entropy of fusion of 9.3 J/g·atom/K (Stebbins et al. 1984), 200 to 300% greater than those for the alkali disilicates (M<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) of the same basic sheet silicate geometry. In fluorophlogopite as for CaTiSiO<sub>5</sub> liquid, considerable mixing of tetrahedral cations is suggested, in this case probably tetrahedral Mg<sup>2+</sup>, Al<sup>3+</sup>, and Si<sup>4+</sup>, possibly with an added contribution from the mixing of fluoride and oxide anions.

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