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High-temperature ^{23}Na MAS NMR data for albite: Comparison to chemical-shift models

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ABSTRACT

Recently, correlations of ^{23}Na chemical shifts with structural parameters such as bond length, coordination number, and bond strength in inorganic compounds have been proposed. When considering only silicate materials we have found that some of these models lead to conflicting predictions.

To test the applicability of these correlations to silicates, we collected ^{23}Na MAS NMR spectra of a pure, ordered albite ($NaAlSi_3O_8$) from 25 to 352 °C. Over this temperature range, the Na-O bond lengths increase, and the measured isotropic shifts relative to 1 *M* NaCl decrease linearly from −7.1 ppm at room temperature to −7.8 ppm at 352 °C. This agrees with the observed trend in silicates of increasing bond length leading to more negative values of δ but is not consistent with the bond-valence model, which predicts a change of several parts per million in the opposite direction over this temperature range.

Quadrupolar coupling constants were also seen to change, decreasing linearly with temperature from 2.69 MHz at 20 °C to 2.30 MHz at 352 °C. Static spectra measured from 22 to 1020 °C yielded values consistent with this in the low-temperature range and continued to decrease linearly to 1.50 MHz at the highest temperature. The ^{23}Na spin-lattice relaxation times (T_1) were collected between 25 and 1140 °C as well. T_1 decreases gradually up to about 500 °C and then drops rapidly, indicating that there is a change in the relaxation mechanism at this temperature.

INTRODUCTION

Chemical shift is an NMR parameter sensitive to the local environment of the atom of interest. For some nuclei in inorganic solids (e.g., ^{27}Al, ^{29}Si, and ^{25}Mg), there exist correlations between chemical shifts and structural properties such as bond lengths and angles, type of neighboring atoms, and bond strengths. These structural variables are often highly correlated with each other. The observed ^{23}Na chemical-shift δ range for silicates is about 50 ppm (Koller et al., 1994; Xue and Stebbins, 1993). To date, several authors have noted possible trends for Na chemical shifts. Koller et al. (1994) correlated ^{23}Na chemical shifts with a function of bond-strength sum and interatomic distances. Xue and Stebbins (1993) observed a relationship between ^{23}Na chemical shifts and coordination number, Na-O distance, and number of nonbridging O atoms per tetrahedral cation (NBO/T). Other studies have also noted a possible correlation between ^{23}Na δ and coordination number (Dec et al., 1990; Dirken et al., 1992). However, these trends are not all consistent. In particular, the predictions of the model of Koller et al. (1994) appear to have the opposite Na-O bond-length dependence for silicate materials as that observed by Xue and Stebbins (1993), leading to a need to test the models further.

The ^{23}Na nucleus is relatively easy to study by NMR. It is 100% abundant and has a high magnetogyric ratio. Determination of isotropic chemical shift in solid materials, however, is more difficult because of the fact that ^{23}Na has a spin-quantum number of $\frac{3}{2}$, causing quadrupolar interactions, broadening of the spectra, and more complicated lineshapes than the single peaks seen for spin $\frac{1}{2}$ nuclei.

There have been few studies of NMR chemical shifts in inorganic materials at high temperature (Fiske et al., 1994; Hafner and Nachtrieb, 1964; Hayashi and Hayamizu, 1992). Knowledge of how thermal expansion affects chemical shift is important for the interpretation of high-temperature spectra of silicate glasses and melts, and, in theory, chemical shift can be an indicator of changes in bonding as temperature increases.

We present new ^{23}Na chemical shift data for albite from room temperature to 352 °C and discuss it in the light of previous models. We also include quadrupolar coupling constants and relaxation times for temperatures up to 1020 °C and discuss their significance.

BACKGROUND

For ^{23}Na chemical shifts in inorganic materials in which Na is coordinated by O, Koller et al. (1994) developed an empirical chemical-shift parameter that depends on bond valences and distances. Bond valence is defined following Brown and Altermatt (1985) as

$$s_{ij} = \exp\left[\frac{r_0 - r_{ij}}{B}\right] \tag{1}$$

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TABLE 1. Predicted and measured ^{23}Na chemical shifts for albite as a function of temperature

T (°C)	Av. $r_{\mathrm{Na\text{-}O}}$ (nm)	A	δ, predicted by model of Koller et al. (1994) (Eq. 4)	δ, predicted by model of Xue and Stebbins (1993)*	Experimental δ, corrected for drift
25	0.2812	0.930	−9.35	−7.1	−7.1
352			−4.38**	−8.69**	−8.8†
500	0.2847	0.876	−2.13	−9.41	

Note: assuming Na coordinated by nine O atoms within 3.5 Å; δ in parts per million relative to 1 *M* NaCl.

* The room temperature value is fixed at the measured value; high-temperature values were predicted using the slope of the δ–bond-length relation in Xue and Stebbins (1993).

** Interpolated.

† The value without correction for probe heating effects is −7.8.

where s_{ij} is the bond valence between atoms i and j, r_{ij} is the bond length between O atom i and cation j, r_0 is the length of a bond with unit valence as given by Brown and Altermatt (1985) and Brese and O'Keeffe (1991), and B is a constant, 0.37. The bond valences around an O atom are summed to get its atomic valence W_i:

$$W_i = \sum_j s_{ij}. \tag{2}$$

This value was close to 2 for all the compounds investigated. The contribution of an O atom to the chemical shift of a neighboring Na atom was assumed to be a function of its atomic valence, W_i, and the Na-O bond distance, and a shift parameter, A, was defined as the sum of all the contributions of O atoms within 3.4 Å of the Na cation:

$$A = \sum_i \left(\frac{W_i}{r_i^n}\right). \tag{3}$$

A $1/r^3$ dependence was assumed because this gave the best correlation between the shift parameter, A, and chemical shift, δ. Linear regression gave

$$\delta = -133.6A + 107.6 \tag{4}$$

(with a correlation coefficient of 0.91) for δ in parts per million relative to solid NaCl. This equation can be used to predict ^{23}Na chemical shifts in a wide variety of inorganic Na-containing compounds.

Other correlations for Na chemical shifts were published by Xue and Stebbins (1993), although no explicit fit equations were derived. From data for crystalline, anhydrous, Na-bearing silicates and aluminosilicates, they found that the ^{23}Na chemical shift correlates with several factors: Na coordination (within a 3.4 Å radius), mean Na-O bond distance, and the number of nonbridging O atoms per tetrahedral cation (NBO/T). The ^{23}Na chemical shifts decrease with increasing Na coordination, reflecting increased ionicity of the cation with increasing coordination and distance, and increase with increasing NBO/T. The relationship with NBO/T may be a function of the number of first-neighbor network modifiers, which increases with higher NBO/T values. The correlation between decreasing ^{23}Na δ and increasing average bond length is especially good, possibly because bond length is related to both coordination and NBO/T.

Comparison of the published correlations is not straightforward because the shift parameter A has a rather complicated dependence on the Na-O bond distance. Not only is there a $1/r^3$ dependence (Eq. 3), but all the individual bond valences around the O atoms have a negative exponential dependence on r (Eq. 1). However, if one assumes that the main contribution is from the Na-O bonds, it appears that the model of Koller et al. (1994) predicts a trend in chemical shift opposite that observed by Xue and Stebbins (1993); if r increases, both $1/r^3$ and $\exp[(r_0 - r_{ij})/0.37]$ decrease, causing A to decrease and δ to increase. If the bond strengths of the other O bonds vary, this r dependence is not so clear.

One way to limit the number of variables in the system and test the applicability of this model to silicate minerals containing Na is to measure chemical shifts as a function of temperature and to compare them with predicted values from A.

Low albite has a single, large, asymmetrical Na site. The nine nearest O atoms include five O atoms within 2.7 Å and four more beyond 3.0 Å (Winter et al., 1977; Smith et al., 1986; Harlow and Brown, 1980). With increasing temperature, the spread between the five closest Na-O distances and those farther out is reduced, and the site becomes less irregular (Winter et al., 1977). The strongly anisotropic thermal ellipsoid observed for the Na atom has led to some controversy about whether Na occupies a single site or is statically disordered in subsites. However, measurements of the isotropic displacement factor over a range of temperatures show that it extrapolates to zero at 0 K except for a small contribution attributed to zero-point motion (Smith et al., 1986). This indicates that the Na anisotropy is due to anisotropic thermal vibrations of Na in a single site and not to averaging between multiple sites (Smith et al., 1986; Winter et al., 1977). Also, neutron diffraction data of low albite are more consistent with a model with a single Na site than with a split-atom model (Harlow and Brown, 1980).

O atoms as far as 3.5 Å from the central Na atom were included in calculations of predicted values of albite chemical shifts from the bond-strength model of Koller et al. (1994). More distant atoms made negligible contributions. The prediction of Equation 4, using structural data from Winter et al. (1977), is that the chemical shift should become more deshielded by 7.1 ppm between 22 and 500 °C (Table 1).

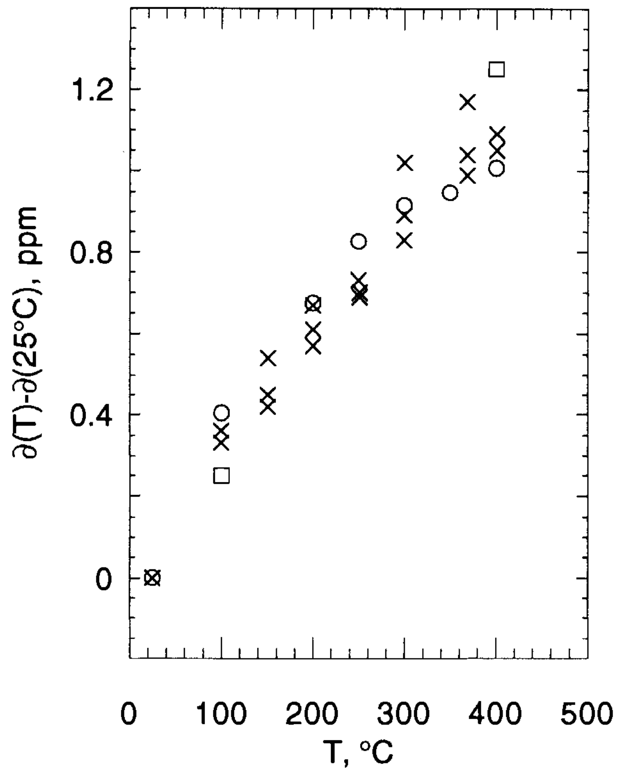

Fig. 1. The effect of heating the high-temperature MAS probe on chemical shift as a function of temperature. Circles indicate the difference between the ^{23}Na peak position for NaCl as measured on the high-temperature static and MAS probes, squares are measurements for ^{29}Si in sillimanite, and Xs are for ^{29}Si in Li_4SiO_4.

EXPERIMENTAL METHODS

The ^{23}Na measurements were made on a pure, ordered albite from Cazadero, California. Electron microprobe data indicate <0.3 mol% An and <0.2 mol% Or component (Neil and Apps, 1979), and ^{29}Si MAS NMR shows that the sample has essentially complete Al-Si ordering. The albite was crushed to 0.5 mm grains. Spectra were collected using a modified Varian VXR-400S spectrometer operating at 105.8 MHz and a high-*T* MAS probe from Doty Scientific. Additional relaxation time measurements and spectra were collected with a home-built high-*T* static probe (Stebbins, 1991). Chemical shifts were referenced to an external 1 *M* NaCl solution at room temperature. A short 1 μs rf pulse length was used to excite the central transition on the Na site. Delay times ranged from 2 s at room temperature to 0.5 s at 358 °C, and relaxation times were checked to pick appropriate delay times for each temperature. Samples were contained in a boron nitride–lined zirconia rotor for the MAS measurements and a boron nitride capsule for the static measurements. MAS sample spinning rates were about 4 kHz, which was fast enough to give a narrowed spectrum and place the spinning sidebands away from the central peak. Between 200 and 2000 free-induction decays were collected and added together for the spectra.

Temperatures inside the MAS probe and static probe were calibrated in separate experiments by comparing temperatures from a thermocouple mounted in the sample container (spinning, in the case of the MAS probe) with those from the control thermocouple. Uncertainty in these calibrations is ±10 °C.

Isotropic chemical shifts, quadrupolar coupling constants, and η values were obtained from the quadrupolar lineshapes for albite using software developed by D. Massiot. The fits were hand adjusted to maximize the fit of the peak maxima and shoulders. The uncertainty in isotropic chemical shift from the fitting program for the MAS spectra is less than ±0.1 ppm; that for the static albite spectra is ±1 ppm. The uncertainty in the obtained quadrupolar coupling constants is ±0.03 MHz in both cases. Chemical-shift anisotropy was not included in the static lineshape fits but probably has only a minor effect. Chemical shifts for NaCl obtained from the experiments using the static probe were corrected for shifts owing to the furnace current polarity, as in Fiske et al. (1994). Uncertainty in the peak position in this probe, after correction, was <0.2 ppm.

To assess the amount of change in the local magnetic field caused by MAS probe heating, chemical shifts for NaCl were obtained using both probes and compared. The difference between the two was taken to be the "drift" in chemical shift caused by changes in the MAS probe as the temperature changed. This drift, as measured for NaCl, is comparable to that seen for earlier measurements for ^{29}Si in sillimanite and Li_4SiO_4 (Fig. 1), suggesting that the change is indeed due to the probe and not the samples. The change in the bond lengths and angles in sillimanite over the temperature range 25–400 °C (Winter and Ghose, 1979) is not enough to cause the observed shift of about 1 ppm, further suggesting that it is indeed a probe effect.

Relaxation time (T_1) measurements were made with the static probe using a saturation-recovery sequence at temperatures <600 °C and both saturation-recovery and inversion-recovery sequences from 600 to 1020 °C with good agreement. Saturation-recovery T_1 measurements made at lower temperatures with the MAS probe agreed well with the static measurements.

RESULTS

Chemical shifts

The MAS albite spectra yielded quadrupolar lineshapes indicating a single site and show marked changes over the temperature range studied (Fig. 2). The spectra narrow with increasing temperature, possibly because of quadrupolar interactions averaging as temperature increases. Simulations of the spectra show that the isotropic chemical shift changes slightly as a function of temperature, decreasing from −7.1 ppm at room temperature to −7.8 ppm at 352 °C before correction for probe effects or −8.8 ppm after correction for probe heating (Fig. 3).

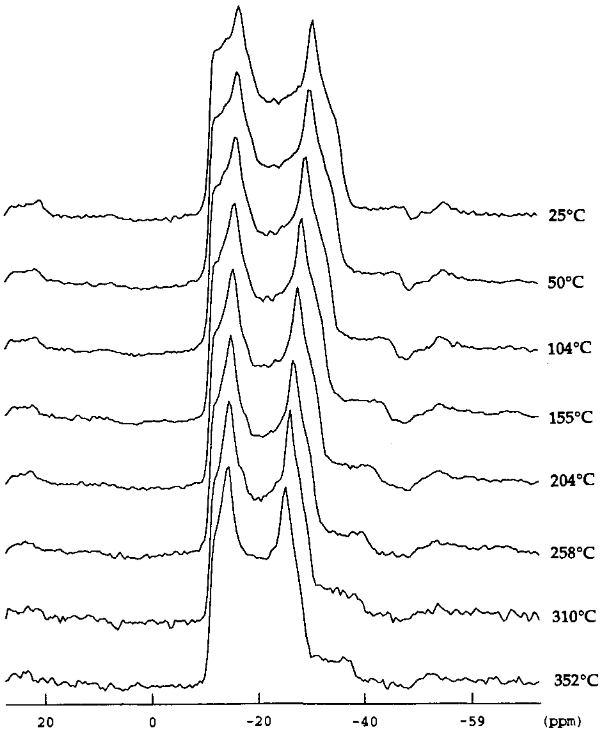

Fig. 2. The ^{23}Na MAS NMR spectra for albite, showing typical quadrupolar lineshapes and the changes with increasing temperature.

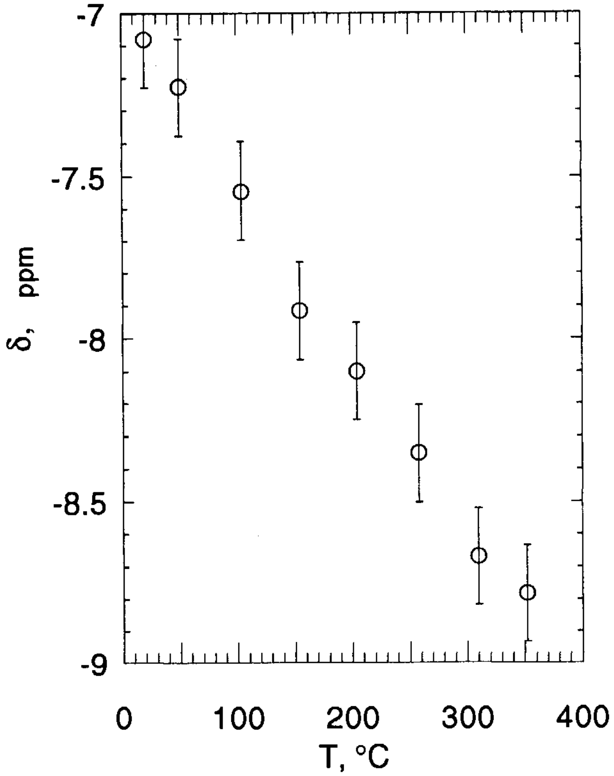

Fig. 3. Albite isotropic chemical shifts as a function of temperature, referenced to 1 *M* NaCl. Data are corrected for probe effects by subtracting the amount of drift for Na shown in Fig. 1.

This change is in the opposite direction of the probe drift of 1 ppm observed for NaCl over this temperature range and thus is probably a real effect caused by thermal expansion. Other published δ values for albite relative to 1 *M* NaCl at room temperature are −6.8 ppm (Kirkpatrick et al., 1985) and −7.3 ppm (Kundla et al., 1981), which agree well with our room temperature value.

This observed trend of δ with temperature has a slope of −0.52 ppm/100 °C and is consistent with that predicted by the Na-O bond-length correlation of Xue and Stebbins (1993). However, it conflicts with the prediction using the Koller et al. (1994) bond-strength formalism (Eq. 4), which yields a change of about 7 ppm in the opposite direction between room temperature and 500 °C (Table 1).

Quadrupolar parameters

The quadrupolar coupling constant (QCC) was also obtained from the simulations. QCCs obtained from both static and MAS spectra were consistent over the overlapping temperature range and decreased linearly as a function of temperature (Fig. 4). The slight systematic offset between the two could be caused by neglect of chemical-shift anisotropy or dipole-dipole coupling in the fitting of the static spectrum, both of which could lead to subtle changes in the lineshape and affect the QCC obtained from the fit. Room temperature measurements of QCC = 2.69 ± 0.03 MHz and η = 0.25 agree well with values of QCC = 2.60 MHz and η = 0.25 obtained by Phillips et al. (1988). Point-charge calculations using the program ptchg (Spearing, 1994), quadrupolar moment of 0.1×10^{28} m^2, ^{23}Na Sternheimer antishielding factor of −4.1 (Mason, 1987), and the high-temperature structural information contained in Winter et al. (1977) predict that the quadrupolar coupling constant should have a value of 2.53 MHz at room temperature, decrease to 2.28 MHz by 500 °C, and further decrease to 2.1 MHz by 970 °C. These results compare with measured values of 2.67 MHz at room temperature, 2.02 MHz at 507 °C, and 1.56 MHz at 905 °C. The calculated change in QCC is consistent in direction with the measured values, although the calculations predict a smaller amount of change than was observed. This is possibly because of uncertainties in the Sternheimer antishielding factor or atomic positions. The QCC is a function of the geometry and charge distribution around the site, and the decrease in measured QCC values is a reflection of the site becoming more symmetric with increasing temperature.

Relaxation times

NMR relaxation occurs by means of fluctuations in the electric-field gradient at the nucleus caused by motion of

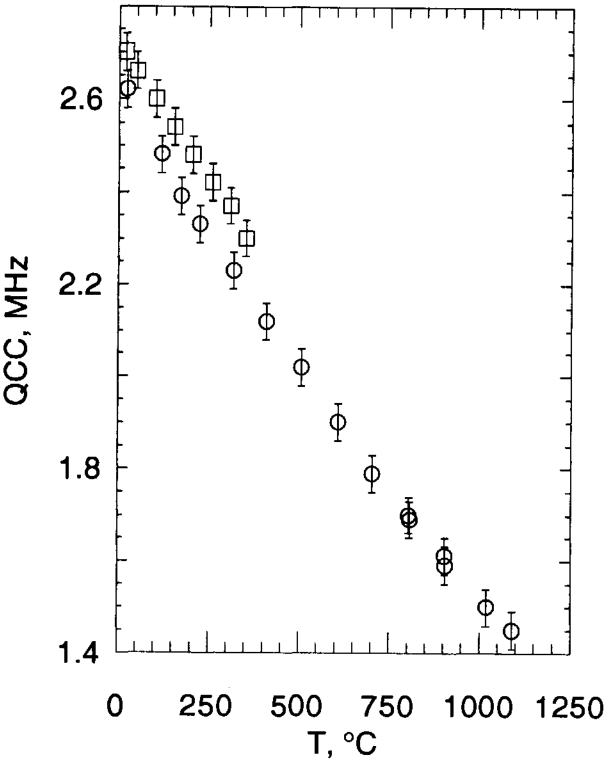

Fig. 4. Quadrupolar coupling constants in albite as a function of temperature. Circles indicate measurements from the static probe; squares, from the MAS probe.

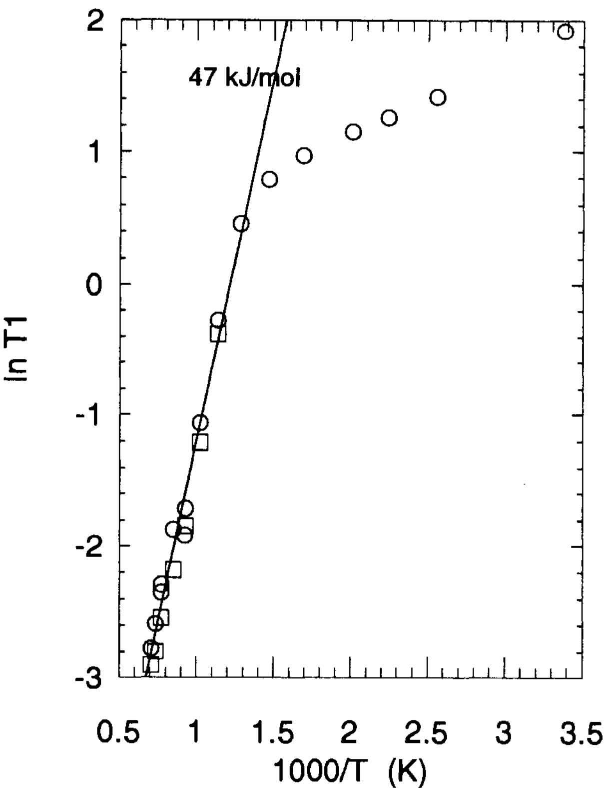

Fig. 5. Na relaxation times in albite. Circles show data obtained using a saturation-recovery pulse sequence, and squares show data obtained from an inversion-recovery pulse sequence.

the atom and nearby defects or by oscillations in the shape of its site. Relaxation-time measurements can thus give information on the dynamics of motion. Relaxation times obtained from both static and MAS measurements are in reasonable agreement. At lower temperatures, T_1 decreases fairly slowly, whereas above 500 °C, the slope increases abruptly and indicates an activation energy of 45.8 ± 2 kJ/mol for the motion responsible for the relaxation (Fig. 5). This abrupt change in slope indicates a change in the dominant relaxation mechanism around 500 °C. The activation energy for Na diffusion in albite has been measured as 176 ± 8 kJ/mol (Kasper, 1975). However, it is difficult to compare directly activation energies measured by NMR with those obtained using other methods because NMR relaxation is affected by Na atoms hopping back and forth locally between sites, by throughgoing motion, and by motion of nearby defects, leading to lower activation energies than those needed for throughgoing ionic diffusion alone.

DISCUSSION

Apparent conflicting trends in chemical shifts have been seen for other elements. An example is ^{29}Si chemical shifts. Empirical relations show both a decrease with increasing coordination number (Engelhardt and Michel, 1987) and an increase with increasing bond length within $^{[4]}$Si sites with four bridging O atoms (Q^4 sites) in silicates (Grimmer, 1985; Grimmer and Radeglia, 1984; Smith et al., 1983). Trends of δ have also been observed with Si-O-T angles in zeolites and SiO$_2$ polymorphs (Engelhardt and Radeglia, 1984; Newsam, 1987; Radeglia and Engelhardt, 1985; Ramdas and Klinowski, 1984; Smith et al., 1983; Thomas et al., 1983) and with the electronegativities of O-metal groups attached to the central atom (Janes and Oldfield, 1985). A bond-strength model similar to that of Koller et al. (1994) also holds for $^{[4]}$Si (Smith and Blackwell, 1983). It is possible to see conflicting trends depending on what particular parameters and set of data are investigated because the many structural parameters used in these correlations are interrelated, and there is often more than one factor affecting the chemical shift. For ^{29}Si, the trend seen for coordination indicates that δ moves to lower frequency as coordination increases, and because cation-O distance increases with coordination, δ would be seen to decrease with increasing bond distance. However, for Q^4 sites, δ increases with increasing $d_{\text{Si-O}}$. This apparent discrepancy stems from the fact that there is more than one factor determining chemical shift, and some of the variables, particularly bond length and angle, are highly correlated. Both trends are valid for the data sets to which they are applied. This seems to be true for Na chemical shifts as well.

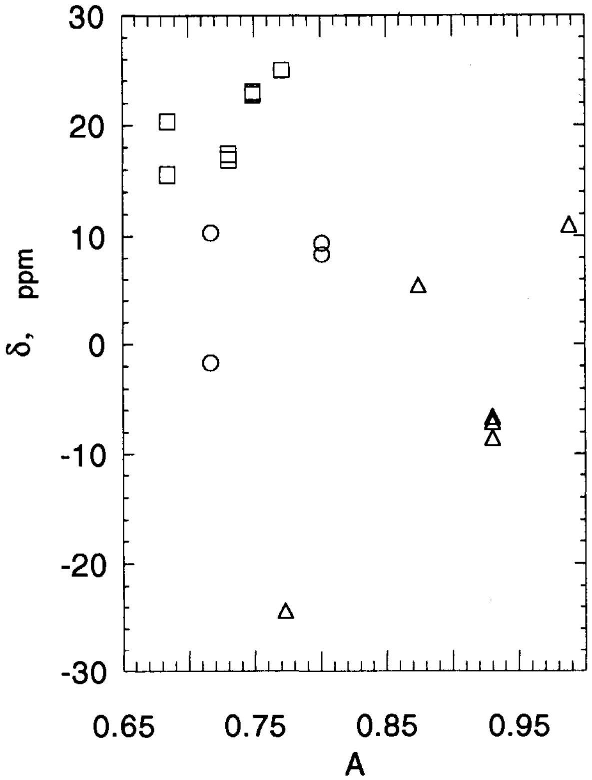

Fig. 6. The ^{23}Na isotropic chemical shift vs. A [the Koller et al. (1994) chemical-shift parameter] for anhydrous silicates only. Squares indicate materials with $^{[5]}$Na, circles show materials with $^{[6]}$Na, and triangles show materials with larger Na sites (eightfold–tenfold coordinated). Chemical-shift data from Xue and Stebbins (1993).

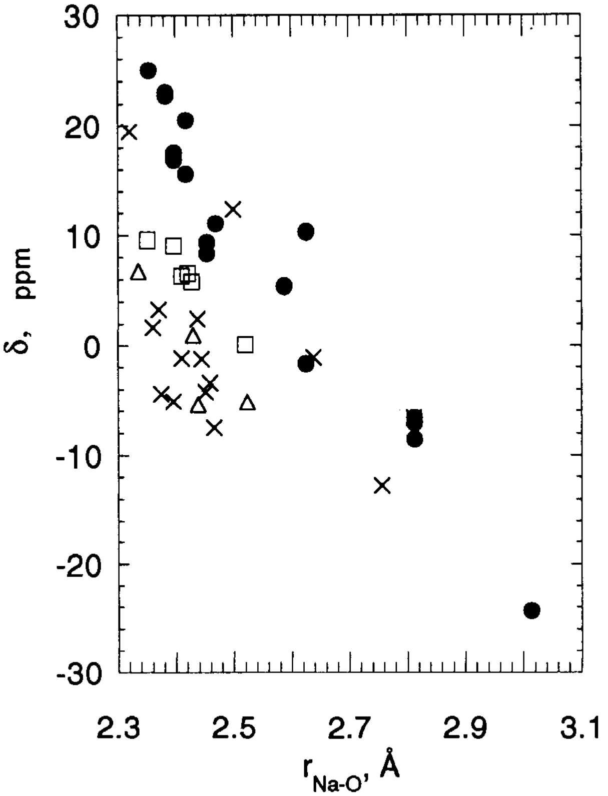

Fig. 7. The ^{23}Na isotropic chemical shift vs. average Na-O bond distance, using data from Koller et al. (1994) and Xue and Stebbins (1993), and newly acquired data for carbonates (George and Stebbins, in preparation). Circles show a linear trend for anhydrous sodium silicates, squares for hydrous sodium silicates, and triangles for sodium carbonates. Data for other materials are shown with Xs. Chemical shifts are referenced to 1 M NaCl.

The difference given by the models of Koller et al. (1994) and Xue and Stebbins (1993) is due to the different Na compounds studied. The bond-strength model is controlled mostly by the many different kinds of compositions included (sodium silicates, sodium silicate hydrates, sodalites, phosphates, sulfates, and other inorganic compounds) and depends on coordination and bond lengths. If silicates alone are considered, the relation between A and δ is not as evident (Fig. 6). If all compositions from both studies are included, the correlation between chemical shift and bond distance is more scattered overall but remains fairly unscattered within compositional subsets of Na compounds (Fig. 7), and it is consistent with the high-T albite data. It appears that the trend of Xue and Stebbins (1993) is more applicable to ^{23}Na chemical shifts in silicates than that of Koller et al. (1994) and should be taken into account when interpreting chemical-shift data for these materials.

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