A theoretical study of the molecular basis of the Al avoidance rule and of the spectral characteristics of Al-O-Al linkages

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Abstract

The molecular basis of the Al avoidance rule has been investigated by performing ab initio self-consistent field molecular orbital calculations on two different isomers of the molecular anion $Si_2Al_2O_4H_8^{2-}$, in which the Si and Al atoms are either alternating, i.e., ...Si-O-Al-O-Si-O-Al..., or paired, i.e., ...Si-O-Si-O-Al-O-Al..., around the four-membered ring. When all geometric parameters are optimized at the polarized split valence SCF level and both a many-body perturbation theory correction to the SCF energy and the zero-point vibrational energy are added, the alternating isomer is found to be more stable than the paired isomer by 63.0 kJ/mol of $Si_2Al_2O_4H_8^{2-}$, as expected from Loewenstein's Rule. Addition of singly coordinated Na^+ ions to the bridging O atoms reduces the energy difference of the isomers by about 22 kJ/mol. This isomeric energy difference is equivalent to an energy decrease of about 10 kJ for the transformation of ¼ mole of Al-O-Al and ¼ mole of Si-O-Si linkages to ½ mole of Si-O-Al linkages. This calculated value compares reasonably well with experimental values of between 9 and 25 kJ found in sodium- and calcium aluminosilicate minerals and glasses. Previous theoretical studies obtained erroneously high values for the instability of the Al-O-Al linkage because the molecular clusters considered were too small and were not properly charge balanced. Similar calculations on a number of $T_2T_2'O_4H_8$ four-membered rings show that the magnitude of instability of the paired geometry isomer depends on both the difference of T and T' valences and the difference of T-O and T'-O bond distances. Nuclear quadrupole coupling constants (NQCC) at O have been calculated for all the species studied and show good agreement with available experimental data. O atoms that bridge two Al atoms are predicted to have a NQCC only about half as large as those in Si-O-Si bonds. Calculations of NMR shieldings indicate that O is deshielded by about 10 ppm in $P_2Al_2O_4H_8$ compared with $Si_4O_4H_8$, whereas it is shielded by about 5 ppm in $Si_2Al_2O_4H_8Na_2^{2+}$, both trends consistent with experiment. The calculated frequencies of the symmetric O breathing vibrational modes decrease from $Si_3O_3H_6$ to $Si_4O_4H_8$, consistent with experiment, and from $Si_4O_4H_8$ to $Si_2Al_2O_4H_8^{2-}$. The best hope for direct spectroscopic identification of Al-O-Al linkages seems to be through their uniquely small ^{17}O NQCC values, but identification based upon O NMR shieldings or upon vibrational spectra is a possibility.

Introduction

The principle of Al avoidance or Loewenstein's Rule (Loewenstein, 1954) is central to the structural chemistry of aluminosilicate crystals and glasses and seems to apply also to aluminosilicate anions in solution (Kinrade and Swaddle, 1989). Numerous quantum chemical studies (Hass et al., 1981; Sauer and Engelhardt, 1982; Navrotsky et al., 1985; Derouane et al., 1990; Pelmenschikov et al., 1992) have found the combination of an Al-O-Al corner-sharing tetrahedral linkage and a Si-O-Si linkage to be higher in energy than two Si-O-Al linkages by >400 kJ/mol of Al-O-Al linkages. As noted by Navrotsky et al. (1985), although these computational results certainly indicate an instability for Al-O-Al linkages, they are not really in good agreement with observations, since many crystalline framework silicates show considerable Al,Si

disorder at high T and must thus contain appreciable numbers of Al-O-Al linkages. The fractions of such linkages in several minerals have recently been determined more quantitatively by solid-state NMR spectroscopy (Putnis and Angel, 1985; Phillips et al., 1992). Recently a lattice energy minimization study of zeolite A based on empirical two- and three-body potentials (Bell et al., 1992) found an energy penalty of only about 40 kJ/mol of Al-O-Al linkages, a result more consistent with the calorimetric data described in Navrotsky et al. (1982, 1985). An inspection of the previous quantum chemical studies show that they all calculated energies for reactions of the type

$$...Si-O-Si + (...Al-O-Al...)^{2-} = 2(...Si-O-Al)^{1-} \quad (1)$$
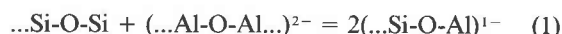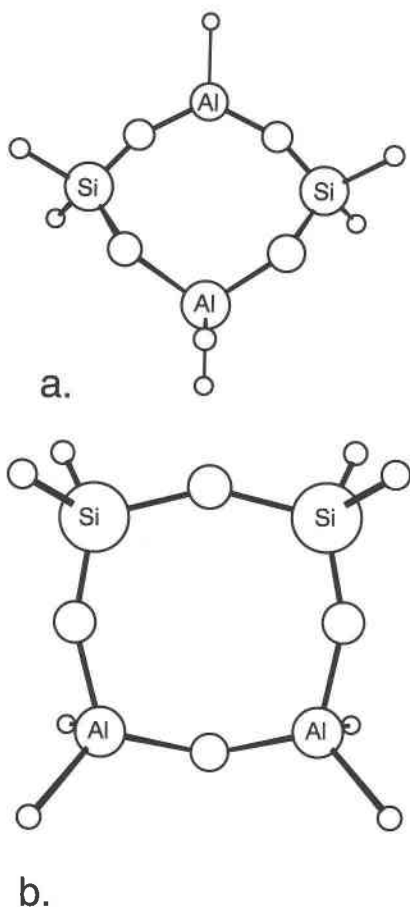
where the coordination of the Si and Al was completed

a.

b.

Fig. 1. Minimum energy geometries of the two isomers of $Si_2Al_2O_4H_8^{2-}$, calculated at the 3-21G* SCF level: (a) alternating ...Si-O-Al-O-Si-O-Al... isomer, (b) paired ...Si-O-Si-O-Al-O-Al... isomer. Circles identify atoms in size order Si > Al > O > H. Si and Al atoms are marked for clarity.

and defensible procedure for choosing the point charge locations so as to overcome this ambiguity in the calculated energy.

One obvious solution to this problem is to carry out the quantum chemical calculations on a molecular cluster large enough so that the different orderings of Al and Si atoms correspond simply to different geometric isomers of the same molecule. A ring structure containing two Si and two Al atoms satisfies these requirements, i.e., one isomer would be of what we will call the alternating form (...Si-O-Al-O-Si-O-Al...) expected from Loewenstein's Rule, and the other of what we will call the paired form (...Si-O-Si-O-Al-O-Al...), as we proceed around the ring of the four tetrahedrally coordinated atoms. Ab initio quantum chemical calculations at reasonably high levels, with full geometry optimization, reasonably large basis sets, and some incorporation of electron correlation and zero-point vibrational effects, can be performed for such species, particularly if the terminating OH groups are replaced by H. We are thus led to explore the energetics of the isomerization reaction for the molecule $Si_2Al_2O_4H_8^{2-}$, the two isomers of which are shown in Figure 1 at their optimized geometries.

Certainly it would be desirable eventually to replace the terminating H atoms in this model by OH groups. However, our calculated energy for Equation 1 when the tetrahedral atoms are terminated by H rather than OH is very similar to that found in previous studies that used OH terminating groups. Previous quantum chemical studies on $TH_3OT'H_3$ and on $(SiH_2O)_n$ ring molecules have shown that many of their properties, such as their structures and vibrational frequencies (O'Keeffe and Gibbs, 1984), electric field gradients at O, and NMR shieldings of O and Si (Tossell and Lazzeretti, 1988; Tossell, 1990b; Lindsay and Tossell, 1991) show magnitudes and trends very similar to those observed in silicates. Thus, at least for these properties, the use of H terminating groups does not preclude agreement with experiment. Calculations on a larger six-membered ring system, i.e., $Si_4Al_2O_6H_{12}^{2-}$, would also be valuable to determine the differences in stability, as the Al atoms are placed in different positions around the ring, i.e., paired, separated by one Si, and separated by two Si atoms. Unfortunately, the difficulty of an ab initio calculation increases by about the fourth power of the number of expansion functions in the basis set (see the discussion in Simons, 1991), so that replacing H by OH or increasing the number of tetrahedrally coordinated atoms in the ring from four to six causes a very significant increase in the computer space and time required for the calculation. We are thus led to study $Si_2Al_2O_4H_8^{2-}$, since it is the smallest model molecule that can reliably address the question at hand.

Besides our studies on Si,Al ordering, we consider it valuable to study the ordering energetics of other pairs of tetrahedrally coordinated atoms, e.g., Si,P and Si,B. One purpose of such comparative studies is to determine just how generally applicable ordering principles like Loewenstein's Rule are and what implications they have for

by −OH groups. Each of the calculations referenced suffers from the defects still endemic to quantum chemical calculations on large molecules, e.g., neglect of electron correlation, use of limited expansion basis sets, and the use of assumed or incompletely optimized geometries, and their discrepancies with experiment (when noted) have generally been ascribed to such effects. We believe, however, that the most serious failing of these studies is in their use of species that are not properly charge balanced. Although calculated geometries of such species are usually accurate if the charge magnitude is no greater than two (Tossell, 1981), the energies may be in error by a large enough amount to make comparisons of species like those in Equation 1 unreliable. This destabilizing effect is much larger for the $(Al-O-Al...)^{2-}$ species than for the $(...Si-O-Al...)^{1-}$ and leads to a totally erroneous instability for the Al-O-Al linkage. This problem was noted by Sauer and Engelhardt (1982), who found that the addition of point charges at various locations could even change the sign of the energy difference they calculated for Equation 1. However, they were unable to devise any systematic

the structures of other minerals and glasses. A second purpose is to gain insight into the electronic mechanism of such ordering principles. Should such principles be interpreted as consequences of underutilization of the bonding capacity of the bridging O in Al-O-Al linkages (as suggested by Pauling, 1929), or are they rather a result of mismatches of distances and angles within the four-membered rings or of local electrostatic effects (as suggested by Cohen and Burnham, 1985)?

Since observations from experiments and our results indicate that Al-O-Al linkages are not so unfavorable as to be completely precluded at high but geologically possible temperatures, we also consider it worthwhile to try to identify spectral signatures for such linkages. Recently considerable progress has been made in measuring O NMR shieldings and nuclear quadrupole coupling constants in solids using multiple-angle rotation methods (Farnan et al., 1992). We have thus calculated electric field gradients at O, which, when multiplied by the quadrupole moment of the O nucleus and divided by Planck's constant, give values for the NQCC. NMR shielding constants at O and at Si have also been calculated with the Hartree-Fock perturbation theory (Tossell and Lazzeretti, 1988). Vibrational spectral energies and IR intensities have also been calculated for $Si_3O_3H_6$, $Si_4O_4H_8$, and the two isomers of $Si_2Al_2O_4H_8^{2-}$ to establish whether changes in ring size, composition, and ordering have observable effects upon the vibrational spectrum.

It is worth noting that theoretical studies on zeolite and aluminosilicate minerals even more computer intensive than those in this work have recently appeared (Ahlrichs et al., 1989; Kramer et al., 1991). These studies focused upon even larger aluminosilicate clusters, typically at a slightly lower level of quantum mechanical rigor, but did not explore the question of Al,Si ordering in the clusters investigated.

COMPUTATIONAL DETAILS

We employ the conventional methods of ab initio self-consistent-field molecular orbital theory as described in quantum chemistry texts (Levine, 1991) and monographs (Hehre et al., 1986), and as implemented in the programs Gamess (Schmidt et al., 1990) and Sysmo (Lazzeretti and Zanasi, 1980). Gibbs (1982) and Tossell and Vaughan (1992) have reviewed the applications of quantum mechanical calculations to a number of mineralogical problems, and Simons (1991) has written a brief experimentalist's guide to the use of ab initio quantum chemical techniques and the interpretation of the results. The basis sets used to expand the molecular orbitals in our studies are of the type generally described as polarized split valence and are specifically described by the symbol 3-21G* (Hehre et al., 1986). All geometrical parameters of the molecules studied have been optimized, within certain symmetry constraints, e.g., assuming C_{2v} symmetry for both isomers of $Si_2Al_2O_4H_8^{2-}$. At the 3-21G* SCF-optimized geometries obtained for the two isomers of $Si_2Al_2O_4H_8^{2-}$, we have calculated (using the same 3-21G*

basis set) a part of the valence correlation energy using Moller-Plesset many-body perturbation theory to the second order (designated MP2) and have also calculated the vibrational spectrum and evaluated the corresponding zero-point vibrational energies. For the isomers of the other T,T′ pairs we have calculated the 3-21G* optimized SCF energies only. The 3-21G* basis set has also been used to calculate the EFG at O and the NMR shielding at Si and O. For the EFG and the NMR shielding, the present basis is too small to give highly accurate results (and is smaller than that used in previous studies of TH_3OTH_3 systems; Tossell and Lazzeretti, 1988), but we expect that trends from one molecule to the next will be accurately described. The present MP2 calculations using a 3-21G* basis at the 3-21G* SCF-optimized geometry are probably about the best presently feasible for such molecules. For $H_3SiOSiH_3$ it is now possible to use larger basis sets and to account more completely for correlation (Nicholas et al., 1992), but that does not seem to be necessary to address the problem of Si,Al ordering accurately. In the NMR calculations, which we consider somewhat preliminary since they utilize basis sets smaller than in our previous studies (e.g., Tossell and Lazzeretti, 1988), we have calculated shieldings for both O and Si with the molecular center of mass (CM) as the gauge origin. We report the diamagnetic and paramagnetic components of the shielding, σ^d and σ^p, with reference to that gauge origin, transforming σ^d from its value with origin on the magnetic nucleus to its value for a CM origin, using the electronic contribution to the electric field at the nucleus, as described by Arrighini et al. (1970). In comparing shieldings for species with and without a set of four Na^+ counterions, we have corrected the diamagnetic shielding for the presence of the Na core electrons, which are not well described within our common origin scheme, as explained by Tossell (1990a).

It is worth noting that for $Si_2Al_2O_4H_8^-$ and all the other clusters with charge magnitudes of 2 or less, all occupied molecular orbitals have negative eigenvalues. As noted by Ahlrichs (1975), an SCF result for an anion in which some of the occupied orbitals have positive eigenvalues is unstable when continuum functions are added to the basis set, and so, at least formally, the properties of the anion are not well defined. Hass et al. (1981) stated that $[(OH)_3Al-O-Al(OH)_3]^{2-}$ had positive eigenvalues for 15 occupied orbitals, indicating a physical instability for such a cluster, which confirmed the Al avoidance rule. In contradiction to this argument, they also noted that such linkages do in fact occur in crystalline potassium aluminate. We think this argument is unsound. The formal instability of the SCF wavefunction for a dinegative ion does not imply that an analogue species may not occur when charge compensated in a crystalline solid. The O^{2-} anion itself is unstable in a vacuum but appears to exist (slightly perturbed) in many crystalline environments. Such instability simply means that the gas phase model chosen to represent this species in a solid is a poor one. Even the caveats of Ahlrichs with respect to the accuracy

TABLE 1. Calculated total energies for Si-O-Al-O-Si-Al and Si-O-Si-O-Al-O-Al isomers of $Si_2Al_2O_4H_8^{2-}$ and energy difference of isomers, obtained at different quantum mechanical levels

| Method | $Si_2Al_2O_4H_8^{2-}$ [E(h)] | | ΔE (kJ/mol) |
	Si-Al-Si-Al isomer	Si-Si-Al-Al isomer	
3-21G SCF	−1358.8412	−1358.8121	76.4
3-21G* SCF	−1359.2783	−1359.2497	75.1
MP2/3-21G*	−1359.4237	−1359.3996	63.3
+ Zero-point	−1359.3369	−1359.3129	63.0

of calculated properties of anions have to be assessed in the light of computational results. As Hotokka and Pyykko (1989) have shown, distances and vibrational frequencies calculated for anions using conventional basis sets (without diffuse functions and certainly without continuum functions) are in quite good agreement with experiment, even if the anion has positive eigenvalues for many occupied orbitals. Thus, the problem of positive eigenvalues may be more formal than real for many properties of interest. We emphasize, however, that in this case the increased number of atoms in the dianions spreads out the negative charge and thus stabilizes all the orbitals so that we have no occupied orbitals with positive eigenvalues for any of the dianions considered. For $Al_4O_4H_8^{4-}$, on the other hand, we do find positive eigenvalues for many occupied orbitals, and so for this species we focus on the optimized geometry and the EFG at O, since the relative energetics of this anion are probably unreliable.

RESULTS

Geometries and energetics

In Table 1 we present the total energies (in hartree atomic units, one hartree per molecule equals 2625.5 kJ/mol) for the two isomers of $Si_2Al_2O_4H_8^{2-}$ and the energy difference between the isomers (in kilojoules per mole) obtained at different computational levels. The first point to notice is that the 3-21G results (no polarization functions) and the 3-21G* results (*d* polarization functions on Si, Al, and O) are very similar. The effect of the valence-shell electron correlation evaluated at the MP2 level on the energy difference is fairly modest (about 12 kJ/mol), and the zero-point vibrational contributions are identical to within a few tenths of a kilojoule per mole for the two isomers. Even the energy difference of 86 kJ/mol evaluated at the minimum basis level STO-3G is in reasonable agreement with the more accurate split valence calculations.

By contrast, the 3-21G* SCF energies of Si_2OH_6, $Al_2OH_6^{2-}$, and $SiAlOH_6^{1-}$ give a ΔE value of −421.8 kJ for Equation 1; corresponding to that magnitude of destabilization for every mole of Al-O-Al linkages. Thus, as we suspected, the problem with previous studies of the energetics of Al-O-Al linkages did not lie in basis set limitations nor neglect of correlation, and probably not with

inadequate geometry optimization. Rather, the main problem was simply in the use of too small a cluster model, forcing the comparison of the energies of clusters with unbalanced charges. For properly defined clusters, even minimum basis sets give a reasonable energy difference, although we do not expect them to accurately reproduce other spectral and charge distribution properties and so would not generally recommend their use.

Navrotsky et al. (1985) have determined the enthalpy of the reaction

$$\tfrac{1}{2}M^{n+}_{1/n}AlO_2 + \tfrac{1}{2}SiO_2 = M^{n+}_{1/2n}Al_{0.5}Si_{0.5}O_2 \qquad (2)$$
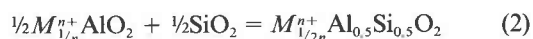
to be −22.6 kJ/mol for M = Na and −9.2 kJ/mol for M = Ca in the glassy state and −25.1 and −18.9 kJ/mol, for Na and Ca, respectively, in the crystalline state, based on the calorimetric data of Navrotsky et al. (1982). This reaction corresponds to ¼ times Equation 1, i.e., it corresponds to the formation of ½ mole of Si-O-Al linkages from ¼ mole of Si-O-Si and ¼ mole of Al-O-Al linkages. For the molecule $Si_2Al_2O_4H_8^{2-}$, transformation of the Si-O-Si-O-Al-O-Al isomer to the Si-O-Al-O-Si-O-Al isomer changes 4 mol of Si-O-Al linkages to 2 mol of Si-O-Al linkages, 1 mol of Si-O-Si linkages, and 1 mol of Al-O-Al linkages, for a net 2 mol of Si-O-Al linkages changing to 1 mol of Si-O-Si and 1 mol of Al-O-Al linkages. Thus, the energy difference of the $Si_2Al_2O_4H_8^{2-}$ isomers should be divided by 4 to correspond to the experimental values for Equation 2 quoted in Navrotsky et al. (1985). Thus, the internal energy change calculated for Equation 2 based on our $Si_2Al_2O_4H_8^{2-}$ model at the MP2/3-21G* computational level is about −16 kJ/mol. Other estimates of the experimental enthalpy change for Equation 1 are −39 ± 12 kJ/mol for anorthite from Phillips et al. (1992) and −34 and −25 kJ/mol in corderite and albite, respectively, from Putnis and Angel (1985). The enthalpy values quoted by Phillips et al. (1992) and Putnis and Angel (1985) correspond to that for a mole of Si,Al exchanges and thus should be equivalent to our calculated energy difference of isomers of $Si_2Al_2O_4H_8^{2-}$, since these two isomers also differ by a single Si,Al exchange. Our calculated value is somewhat larger than that from Phillips and co-workers or Putnis and Angel, but, as we will see below, addition of Na+ counterions to the bridging O atoms somewhat reduces the isomerization energy. We have engaged in this rather labored and detailed discussion of the comparison of experiment and theory because some studies do not give sufficient detail to determine how many moles of what are actually being referred to in phrases such as "x kJ/mol."

In previous studies, such as Sauer and Engelhardt (1982), a strong dependence of reaction energy on the nature of the point-charge stabilization was found. We have explored this point for our $Si_2Al_2O_4H_8^{2-}$ model by allowing H+ or Na+ to bond to each of the bridging O atoms of the four-membered ring, resulting in the species $Si_2Al_2O_4H_{12}^{2+}$ or $Si_2Al_2O_4H_8Na_4^{2+}$. The 3-21G* SCF-optimized geometries for the alternating isomers of these cations show R(Si-O) = 1.707 and 1.630, R(Al-O) = 1.956

and 1.720 Å, and $\angle$Si-O-Al = 159.0 and 150.0° for the H$^+$ and Na$^+$ modified species, respectively, with R(O-H) = 0.982 and R(O-Na) = 2.297 Å. The calculated energy differences of alternating and paired Si,Al isomers in these compounds at the 3-21G* SCF level (3-21G on Na and H) were 84 and 53 kJ/mol, respectively, fairly similar to the 75 kJ/mol value for the Si$_2$Al$_2$O$_4$H$_8^{2-}$ case. The result for Si$_2$Al$_2$O$_4$H$_8$Na$_4^{2+}$ was not optimized to quite so high a precision as that for the dianion species, and the singly coordinated Na$^+$ ions in Si$_2$Al$_2$O$_4$H$_8$Na$_4^{2+}$ are only a simple approximation to the actual cations with large coordination numbers present in a real aluminosilicate. However, using our four-membered-ring model cluster even the strong perturbation of H$^+$ or (singly coordinated) Na$^+$ added to all the bridging O atoms does not dramatically alter the energetics of Si,Al ordering, although the effects of the two cations do seem to be somewhat different.

How then can one explain the existence of Al-O-Al linkages at geological temperatures? If we assume that ΔG for Equation 2 has the same magnitude as the ΔE we have calculated using the Si$_2$Al$_2$O$_4$H$_8^{2-}$ model (i.e., its value is about -16 kJ), the equilibrium constant at 1250 °C would be only about 3.6, and so at equilibrium a significant fraction of Al-O-Al linkages would remain. Taking into account configurational entropy effects that favor disordered paired geometries over the more ordered alternating geometries would further increase the fraction of Al-O-Al linkages. It is also possible that specific local environments could stabilize the Al-O-Al linkage. For example, we expect that cations in general will coordinate more strongly to Al-O-Al linkages than to Si-O-Si linkages. A single cation coordinated to the Al-O-Al linkage of the paired isomer of Si$_2$Al$_2$O$_4$H$_8^{2-}$ might stabilize the paired isomer, compared with the alternating isomer with a single cation coordinated to one of the Si-O-Al linkages.

To understand better the source of the Si,Al ordering energetics we have calculated energy differences at the 3-21G* SCF level for a number of T,T′ pairs. Our results are shown in Table 2. We see that for Si,B and P,Si pairs the energy difference of alternating and paired isomers is very similar to that for Si,Al. For the P,Al pair the energy is about four times larger, whereas for Si,C (with no difference in valence but a considerable one in atomic radius) the ordering energy is comparable to that for Si,Al. This suggests that avoidance rules of the Loewenstein type are a general feature of the energetics of such four-membered-ring systems. Previous studies based on dimers with uncompensated charges [e.g., (...P-O-P...)$^{2+}$, (...Al-O-Al...)$^{2-}$, (...P-O-Al...)], also obtained large destabilizations for P-O-P and Al-O-Al interactions, but these were exaggerated by the charge inbalance. Our results, however, certainly support the idea that P and Al cations should be much more highly ordered into alternating pairs than should Si and Al. The fairly large ordering energy for the Si,C case makes clear that a difference of T and T′ valence (or equivalent over- and underbonding of the bridging O atom) is not the sole source of the ordering energy.

TABLE 2. Calculated energy differences between alternating and paired isomers of T$_2$T′$_2$O$_4$H$_8^q$ obtained at the 3-21G* SCF level

T	T′	q	ΔE (kJ/mol)	$|\Delta v|$	$|\Delta r|$
Si	Al	2−	75	1	0.13
Si	B	2−	80	1	0.14
P	Si	2+	76	1	0.09
Al	P	0	315	2	0.22
Si	C	0	83	0	0.24

Note: differences of crystal radii from Shannon and Prewitt (1969). Symbols are defined as follows: q = charge; $|\Delta v|$ = difference in the number of valence electrons between T and T′; $|\Delta r|$ = difference in the atomic radii between T and T′ in ångströms.

It is worthwhile to note that although the isomerization energy for a Si,B pair is actually calculated to be slightly larger than that for a Si,Al pair, the mineral danburite, CaB$_2$Si$_2$O$_8$, the B analogue of anorthite, has both B-O-B and Si-O-Si bonds in its T$_2$,T′$_2$ four-membered rings, i.e., it is a paired structure. Clearly, bonding effects outside the T,T′ containing ring must modify the relative energies of the paired and alternating isomers in this mineral. In the crystal structure of danburite (Phillips et al., 1974) the O atom bridging between the two Si atoms (O4) is the only O atom not also coordinated to Ca. Thus, the danburite structure is stabilized by selective coordination of Ca ions to only the underbonded O atoms in the structure. It is not immediately clear why such selective coordination of underbonded O atoms could not stabilize a paired structure in CaAl$_2$Si$_2$O$_8$.

To give an idea of the effect of the different orderings and compositions on the bond distances and angles, we present in Table 3 the geometric results for Si$_4$O$_4$H$_8$, Al$_4$O$_4$H$_8^{2-}$, and the two isomers of Si$_2$Al$_2$O$_4$H$_8^{2-}$, with the results for the more stable alternating isomer being given first in this and subsequent tables. For the Si$_4$... and Al$_4$... cases the calculated bond distances are a few hundredths of an ångström too short compared with experiment, and the $\angle$T-O-T are about 5–10° too large, as observed in other studies using this basis set (Tossell, 1991). For example, the electron diffraction geometry of gas-phase Si$_4$O$_4$H$_8$ (Glidewell et al., 1970) shows R(Si-O) = 1.634 Å and $\angle$Si-O-Si = 144.1°. A more important consideration is the change in geometric parameters in going from the end-member four-membered rings to the two isomers of the Si$_2$Al$_2$... species. For the alternating isomer, the Si-O distance is slightly smaller than in the Si$_4$..., case and the Al-O bond is slightly longer than in Al$_4$. The $\angle$Si-O-Al is also slightly larger than either $\angle$Si-O-Si or $\angle$Al-O-Al in the end-members, and the order of $\angle$O-Si-O and $\angle$O-Al-O are reversed compared with the end-members. In the paired isomer there are nonequivalent R(Si-O) of 1.631 (in the Si-O-Si linkage) and 1.565 Å (in the Si-O-Al linkages) and nonequivalent R(Al-O) of 1.700 (in the Al-O-Al linkage) and 1.792 Å (in Al-O-Si linkages). There are also three nonequivalent $\angle$T-O-T′, which average to 155.3°. The paired isomer of course shows more chemically inequivalent bond distances and angles than does

TABLE 3. Equilibrium bond distances (Å) and angles (°) calculated at the 3-21G* SCF level

Molecule	R(Si-O)	R(Al-O)	∠Si-O-Si	∠Si-O-Al	∠Al-O-Al	∠O-Si-O	∠O-Al-O
$Si_4O_4H_8$	1.619		150.0			109.8	
$Al_4O_4H_8^{4-}$		1.718			151.0		118.6
$Si_2Al_2O_4H_8^{2-}$	1.592	1.744		155.9		116.9	111.0
$Si_2Al_2O_4H_8^{2-}$	1.631	1.700	152.0	158.6	155.3	116.8	111.0
	(SiOSi)	(AlOAl)					
Si...Si...Al...Al...	1.565	1.792					
	(SiOAl)	(AlOSi)					

the alternating one, but it also shows slightly longer average Si-O and Al-O distances of 1.598 and 1.746 Å, respectively, compared with 1.592 and 1.744 in the alternating isomer. Although such differences seem small, inserting them into the semiempirical expressions for Si-O and Al-O bond energies given by Bell et al. (1992), V(T-O) $= A \exp[-R(\text{T-O})/\rho]$ where V(T-O) is the bond energy in electron volts, $A = 1283.9$ eV for Si and 1460.3 eV for Al, and $\rho = 0.3296$ Å for Si and 0.2991 Å for Al, gives an energy difference of about 80 kJ/mol between the two isomers, quite close to the 3-21G* SCF energy difference. Thus we can interpret the difference in energy of the isomers as arising from longer average bond distances in the paired case. In the same way, the average P-O and Al-O distances increase by 0.0249 and 0.0338 Å, respectively, in going from the alternating to the paired isomer of $P_2Al_2O_4H_8$.

Explaining the calculated differences in energies and bond distances at a more fundamental level is difficult. Perhaps the increased π bonding capacity of the tetrahedral atoms of higher valence cannot be completely utilized when they are connected to formally overbonded O atoms. Local electrostatic effects may also be important. As discussed by Cohen and Burnham (1985), the difference in next nearest neighbor electrostatic energies for the alternating and paired isomers of a T,T′ structure with T and T′ differing in charge by one unit of electronic charge, e, is just $e/(\epsilon_{eff}R_{T-T'})$, where ϵ_{eff} is the effective dielectric constant and $R_{T-T'}$ is the T-T′ distance. One can readily show that the difference of electrostatic energies between the alternating and paired isomers scales as the square of the charge difference. If that were the dominant effect, we would expect to see the isomerization energy scale approximately with the square of the charge difference. Although there is no unique way to define the charge on an atom within a molecule, we would expect calculated Mulliken charges to give roughly correct values for relative charges. For the Si,Al; Si,B; and Si,P pairs the differences of calculated Mulliken charges are 0.43, 0.64, and 0.08 electrons, respectively, whereas the calculated isomerization energies are all within 75–80 kJ/mol at the 3-21G* SCF level. This indicates that the degree of charge separation is probably not a significant determinant of the isomerization energy.

NMR AND VIBRATIONAL SPECTRA OF FOUR-MEMBERED RING MOLECULES

The possible presence of Al-O-Al linkages in aluminosilicates has been previously evaluated, mainly by study of their ^{29}Si NMR and their vibrational spectra. Determination of Al-O-Al abundances from ^{29}Si NMR is necessarily indirect, focusing upon the effect of such linkages upon the number of distinct Si(OT)$_4$ groupings, where T = Si,Al, and the corresponding number and intensity of peaks in the Si NMR spectrum. Analysis of the assignment of Raman or IR peaks to specific local units or specific modes of motion within a solid is also difficult, relying mainly upon fingerprinting comparisons to well-characterized crystalline materials and general trends related to the effects of varying bond strengths and angles upon the vibrational frequencies.

To help in the characterization of Al-O-Al linkages we have calculated a number of their spectral properties. In Table 4 we compile calculated values for the electric field gradient at O and the nuclear quadrupole coupling constant, NQCC. To determine the quadrupole coupling constant, we first calculate the gradient of the electric field, eq, at each O nucleus, diagonalize the EFG tensor to obtain the principal components (in atomic units), and convert to the nuclear quadrupole coupling constant, e^2qQ/h, by multiplying the magnitude of the largest principal component by the ^{17}O nuclear quadrupole moment, assumed to have the value of 0.02233 barns, which is appropriate to the use of Hartree-Fock level wave functions (Schaefer et al., 1968). The results for the Si-O-Si linkage are certainly in reasonable agreement with the average experimental value given by Timken et al. (1986). Exact agreement should not be expected, since the experimental values are somewhat uncertain (to within a few tenths of a megahertz), the exact value is a function of the T-O-T′ angle, the basis set used is fairly modest (actually less flexible than that used in Lindsay and Tossell, 1991), and electron correlation has been neglected. More important are the relative values for the different linkages. The ranking of NQCC values for the bridging O linkages studied is for the T-O-T case: P-O-P > B-O-B > Si-O-Si > Al-O-Al. This is the trend expected from our general understanding of the degree of covalency of the different bonds and is consistent with the experimental data (Timken et al., 1986). For the cases of T-O-T′, T ≠ T′, the NQCC values are almost always intermediate between the values for T-O-T and T′-O-T′. For example, Si-O-Al values are always intermediate between Si-O-Si and Al-O-Al. An Al-O-Al bridge is always characterized by an NQCC value slightly larger than half that of Si-O-Si. The various linkages show quadrupole couplings that depend only slightly on the particular four-membered ring considered, but there does seem to be a general tendency for the NQCC

TABLE 4. Calculated values of the magnitude of $|\mathbf{q}|$ and NQCC at the O nucleus in a series of four-membered-ring molecules

Molecule	Bridging bond	$\|q\|$ (au)	NQCC (MHz)
$Si_4O_4H_8$	Si-O-Si	0.945	4.96 (5.02)
$Al_4O_4H_8^{4-}$	Al-O-Al	0.516	2.71
$Si_2Al_2O_4H_8^{2-}$	Si-O-Al	0.746	3.91 (3.18)
$Si_2Al_2O_4H_8^{2-}$	Si-O-Si	0.935	4.91
...Si...Si...Al...Al...	Si-O-Al	0.727	3.82
	Al-O-Al	0.512	2.68
$Si_2B_2O_4H_8^{2-}$	Si-O-B	1.025	5.38 (est. 6.40)
$Si_2B_2O_4H_8^{2-}$	Si-O-Si	0.980	5.14
...Si...Si...B...B...	Si-O-B	0.903	4.74
	B-O-B	1.192	6.26
$Si_2P_2O_4H_8^{2+}$	Si-O-P	1.318	6.92
$Si_2P_2O_4H_8^{2+}$	Si-O-Si	1.032	5.42
...Si...Si...P...P...	Si-O-P	1.278	6.71
	P-O-P	1.535	8.06
$P_2Al_2O_4H_8$	P-O-Al	1.088	5.71 (5.67)
$P_2Al_2O_4H_8$	P-O-P	1.396	7.33
...P...P...Al...Al	P-O-Al	0.955	5.01
	Al-O-Al	0.540	2.83
$Si_2Al_2O_4H_{12}^{2+}$	Si-(OH)-Al	1.476	7.75
$Si_2Al_2O_4H_{12}^{2+}$	Si-(OH)-Si	1.616	8.48
...Si...Si...Al...Al...	Si-(OH)-Al	1.435	7.53
	Al-(OH)-Al	1.367	7.17
$Si_2Al_2O_4H_8Na_4^{2+}$	Si-(ONa)-Al	0.699	3.67 (3.18)
$Si_2Al_2O_4H_8Na_4^{2+}$	Si-(ONa)-Si	0.882	4.63
...Si...Si...Al...Al...	Si-(ONa)-Al	0.726	3.81
	Al-(ONa)-Al	0.447	2.34

Note: average experimental values are from Timken et al., 1986, in parentheses.

TABLE 5. Calculated values of the ^{17}O NMR shielding

| Molecule	σ^d (O)	σ^p (CM)	σ^d (CM)	σ (CM)
$Si_4O_4H_8$	725.4	−221.3	623.2	401.9
$P_2Al_2O_4H_8$	721.7	−235.5	621.4	385.9
$Si_2Al_2O_4H_8^{2-}$	711.5	−236.3	608.0	371.7
$Si_2Al_2O_4H_8^{2-}$				
...Si...Si...Al...Al				
Si-O-Si	716.8	−236.4	604.7	368.3
Si-O-Al	712.1	−242.1	615.0	372.9
Al-O-Al	702.8	−231.6	596.1	364.5
Av.	710.9	−238.0	607.7	369.7
$Si_2Al_2O_4H_8PC_4^{2+}$	707.8	−270.6	598.0	327.4
$Si_2Al_2O_4H_8Na_4^{2+}$	707.9*	−216.3	616.0	399.7

Note: all contributions to the shielding are given in parts per million, and the gauge origin used for evaluation of the shielding contribution is given in parentheses.
* For the Na_4 containing molecules the value of σ^d (O) has been corrected for the presence of the core electrons on Na, as described in Tossell (1990a).

in T-O-T' linkages to be somewhat smaller in the paired isomers than in the alternating isomers. The effect of Na^+ complexation is to slightly reduce the EFG, bringing the results for Si-O-Al linkages into somewhat better agreement with experiment, as suggested by Tossell and Lazzeretti (1988). Overall, the most dramatic signature of the Al-O-Al linkage is probably the small value of the O NQCC. Note that bonding a Na^+ to the O bridging two Al atoms in $Si_2Al_2O_4H_8Na_4^{2+}$ gives a slight reduction in the value of the O EFG. Thus, this feature of the Al-O-Al bond does not seem too sensitive to the next shell of atoms.

The calculation of the NMR shieldings of the four-membered-ring systems considered here is even more demanding than the calculation of their geometries and vibrational spectra. Accordingly, we here present NMR shieldings for only some of the species. In Table 5 we present the ^{17}O NMR shieldings calculated for $Si_4O_4H_8$, $P_2Al_2O_4H_8$, $Si_2Al_2O_4H_8^{2-}$ (both isomers), and $Si_2Al_2O_4H_8Na_4^{2+}$ (the ...Si...Al...Si...Al... isomer only). Experimentally, the O NMR shielding is found to decrease (i.e., the shift, δ, becomes more positive compared with liquid H_2O) by around 10 ppm in going from Si-O-Si to P-O-Al linkages. On the other hand, Si-O-Al linkages are found to show O shieldings larger by about 10 ppm than those in Si-O-Si linkages (Timken et al., 1986). As described in Tossell and Lazzeretti (1988) accurate calculation of even the relative NMR shielding (i.e., the chemical shift) is quite difficult, requiring large basis sets, some study of the effect of the choice of gauge, and careful correction for the effects of core electrons on distant centers, which

are not well described by the common gauge origin calculations implemented in the Sysmo program. It may well be that slightly different computational schemes will be needed to accurately model shieldings in some of the larger systems, i.e., the modern formulation of the gauge-including AO method (Wolinski et al., 1990) may be more efficient and accurate than the common origin approach.

Nonetheless, we find that O in a P-O-Al linkage is indeed calculated to be deshielded by about 16 ppm with respect to that in a Si-O-Si linkage, almost identical to the difference previously calculated between H_3POAlH_3 and $H_3SiOSiH_3$ (Tossell and Lazzeretti, 1988). It thus seems that the calculation of relative shieldings for Si-O-Si vs. P-O-Al linkages, with both O atoms in charge-balanced environments that can be modeled by neutral molecules, is fairly easy. By contrast, calculating accurate relative shieldings for Si-O-Si vs. Si-O-Al linkages has proved to be difficult for both ^{17}O and ^{29}Si. The main difficulty is implicit in the qualitative MO analysis of Tossell (1984), which attributed the deshielding of ^{29}Si in the Si-O-Al linkage (compared with that in Si-O-Si) to the reduction in excitation energies arising from close interaction with the charge-balancing univalent cations. As seen in Table 5, we find for both isomers of the $Si_2Al_2O_4H_8^{2-}$ anion a deshielding of the O, compared with $Si_4O_4H_8$. To improve our modeling of the environment of the O we have also calculated the shielding for the 3-21G* SCF optimized geometry of the molecule $Si_2Al_2O_4H_8Na_4^{2+}$, but so far only for the isomer with alternating Si,Al. The O shielding for this molecule with four Na^+ added is substantially higher than for $Si_2Al_2O_4H_8^{2-}$, but it is still slightly lower than that calculated for the $Si_4O_4H_8$ molecule. This suggests that an even better description of the environment of O, with the proper number of properly coordinated counterions, will be needed to accurately reproduce the Si-O-Al vs. Si-O-Si shielding trend. Previous studies have shown that replacing H^+ or other cations in the second coordination sphere by point charges, PC, gives results in good agreement with those for the original system (Tossell, 1991). For the O shielding, however, a $Si_2Al_2O_4H_8PC_4^{2+}$ model, with

TABLE 6. Calculated values of the ^{29}Si NMR shielding

Molecule	σ^d (T)	σ^p (CM)	σ^d (CM)	σ (CM)
$Si_4O_4H_8$	1135.7	−542.6	994.1	451.5
$Si_2Al_2O_4H_8^{2-}$	1132.9	−497.4	1000.0	502.6
$Si_2Al_2O_4H_8^{2-}$				
...Si...Si...Al...Al	1133.9	−499.7	1001.2	501.5
$Si_2Al_2O_4H_8PC_4^{2+}$	1126.4	−550.1	981.5	431.4
$Si_2Al_2O_4H_8Na_4^{2+}$	1126.4	−544.6	967.3	422.7

Note: all contributions to the shielding are given in parts per million, and the gauge origin used for evaluation of the shielding contribution is given in parentheses. For the Na_4 containing molecules, the value of σ^d (T) has been core corrected, as described in Tossell (1990a).

charges of $+1$ replacing Na^+ ions at their equilibrium positions, gives a very poor result. The O is even more highly deshielded than in the original dianion. Note, of course, that in this case the replacement of a real atom by a point charge occurs in the first coordination sphere about the magnetic nucleus. It thus appears that at this point we do not yet have a model and a method with sufficient accuracy to determine the effects of network-modifying cations on the shielding of O in T-O-T' linkages. Our studies do suggest, however, that the effects of the counterions on the ^{17}O NMR shielding will be substantial and may thus provide a means for monitoring this aspect of the local geometry of aluminosilicate glasses.

In Table 6 we present ^{29}Si NMR shieldings calculated for $Si_4O_4H_8$, $Si_2Al_2O_4H_8^{2-}$, $Si_2Al_2O_4H_8PC_4^{2+}$, and $Si_2Al_2O_4H_8Na_4^{2+}$. Experimentally, Si is observed to be deshielded by about 5 ppm when one Si-O-Si linkage is replaced by a Si-O-Al linkage (Kinsey et al., 1985). For the four-membered-ring anions $Si_2Al_2O_4H_8^{2-}$, our calculated Si shieldings are actually larger than that for $Si_4O_4H_8$, in the wrong direction compared with experiment, just as in our previous study using $H_3SiOAlH_3^{1-}$ compared with $H_3SiOSiH_3$ (Tossell and Lazzeretti, 1988). However, when we include a representation of the second coordination sphere about the Si, using either Na^+ ions or point charges, we get the correct deshielding of the Si. Thus, the PC for cation replacement works reasonably well for the second coordination shell about the Si. Given the substantial change in Si NMR shielding introduced by the second coordination sphere, we cannot at present establish with certainty the nature of the difference in ^{29}Si NMR shieldings between the alternating and paired $Si_2Al_2...$ four-membered rings.

**Vibrational spectra**

Certain defect features in the vibrational spectra of amorphous SiO_2, labeled D1 and D2, were attributed by Galeener (1982) to the existence of symmetric O-breathing modes in three-membered and four-membered rings that were decoupled from the rest of the lattice vibrations. Experimental evidence from polarized and ^{18}O isotopically labeled Raman spectra and ^{29}Si NMR spectra (Brinker et al., 1990) has supported these assignments, as have quantum mechanical calculations of the energies and normal modes of such ring systems (O'Keeffe and Gibbs,
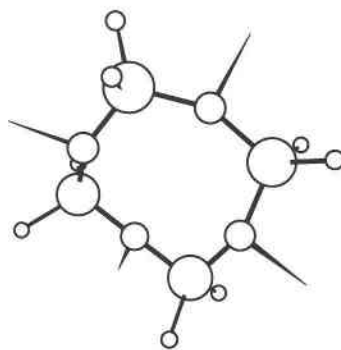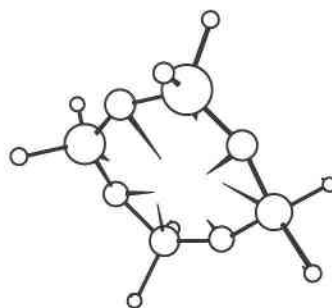

$Si_4O_4H_8$ S_4 3-21G* SCF ν=504.5 cm^{-1}

a.
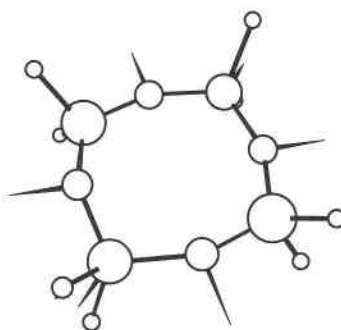
$Si_2Al_2O_4H_8^{-2}$ ..Si-O-Al-O-Si-O-Al.. C_{2v}
3-21G* SCF ν=454.7 cm^{-1}

b.

$Si_2Al_2O_4H_8^{-2}$ ..Si-O-Si-O-Al-O-Al.. C_{2v}
3-21G* SCF ν=446.5 cm^{-1}

c.

Fig. 2. Calculated O breathing normal modes of vibration for **(a)** $Si_4O_4H_8$, **(b)** the alternating isomer of $Si_2Al_2O_4H_8^{2-}$, and **(c)** the paired isomer of $Si_2Al_2O_4H_8^{2-}$, all calculated at the 3-21G* SCF level. Calculated vibrational frequencies are given in the figure. Circles identify atoms as in Figure 1, with the order of size Si > Al > O > H. The atomic motions within the normal modes are shown by the arrows projecting from the atoms.

1984; Tossell, 1990b). Using the same 3-21G* bases as in our calculations on the four-membered-ring systems, we have calculated the vibrational spectrum of $Si_3O_3H_6$ in D_{3h} symmetry and have confirmed the existence of a symmetric O-breathing mode with no IR intensity (Raman active only) and with a frequency of 696 cm^{-1}. Since calculations at the 3-21G* SCF level typically overestimate vibrational frequencies by about 10% (Hehre et al., 1986; p. 226–261), this suggests an experimental stretching frequency of about 626 cm^{-1}, only slightly larger than the 606 cm^{-1} value observed in amorphous SiO_2. This result is in reasonable agreement with that estimated for an O symmetric breathing mode in $Si_3O_3H_6$ from a series of single point energy calculations by Tossell (1990b) and O'Keeffe and Gibbs (1984). For $Si_4O_4H_8$ in S_4 symmetry, the vibrational spectrum calculated at the 3-21G* SCF level has a mode at 504.5 cm^{-1}, which is predominantly a symmetric O breathing mode, although there is also a small Si and H contribution. Scaling down this calculated vibrational energy by 10% gives 454 cm^{-1}, about 50 wavenumbers smaller than that observed for the D1 band of amorphous SiO_2. This result provides further support for the assignment of the D1 band to symmetric O stretching vibrations in rings like $Si_4O_4H_8$. This normal mode is shown in Figure 2a.

For the alternating isomer of $Si_2Al_2O_4H_8^{2-}$, we calculate what is predominantly a symmetric O breathing mode at 454.7 cm^{-1}, substantially lowered from that for the $Si_4O_4H_8$ molecule. This normal mode is shown in Figure 2b. We believe that this lowering in energy of the symmetric breathing mode is a real effect, associated with the smaller T-O force constants in the Si_2Al_2... ring, but we cannot exclude the possibility that it is exaggerated by the double negative charge, which we expect to weaken all the bonds somewhat. For the paired isomer of $Si_2Al_2O_4H_8^{2-}$, we find the normal modes to be less symmetric, as expected from the presence of three different T-O-T' linkages. There are no completely symmetric O breathing modes. The normal mode with a calculated frequency of 446.5 cm^{-1} is shown in Figure 2c. Although the two isomers of $Si_2Al_2O_4H_8^{2-}$ do show some differences in their calculated vibrational spectra, these differences are subtle and could well be masked by features from other more delocalized normal modes within the spectrum of the solid. The presence of Si and Al motions within the normal modes, particularly for the paired isomer, may also prevent the uncoupling from the lattice vibrations that is characteristic of the defect bands of amorphous SiO_2 (Galeener, 1982).

CONCLUSIONS

The energetics of Si,Al ordering can be accurately calculated by quantum mechanics using molecular cluster models for aluminosilicate rings, so long as the clusters chosen are large enough. The calculations confirm that alternating Si,Al structures are favored over paired structures, but by only a modest amount of energy, so that paired structures, e.g., Al-O-Al linkages, are indeed pos-

sible in high-temperature disordered materials. The energy difference of the isomers can be related to their calculated differences in average Si-O and Al-O distances, although this may not be the most fundamental explanation for their energy difference. For all the T_2, T'_2 four-membered rings studied the alternating isomer is favored, with the magnitude of the difference depending upon both the valence difference and the radius differences of T and T'. The existence of O in Al-O-Al linkages can be most easily determined from the value of the ^{17}O NQCC, which is calculated to have only about half as large a value as that in Si-O-Si linkages. The effects of alternating vs. paired Si,Al on the ^{17}O and ^{29}Si NMR shielding have been investigated, but no definite conclusions can yet be drawn. The O shielding depends substantially upon the details of its coordination to univalent cations, and the Si shielding is also somewhat affected by the presence of counterions in the second coordination sphere. The calculated value of the symmetric O breathing frequency in $Si_4O_4H_8$ is consistent with its attribution to the D1 defect band in amorphous SiO_2, and the $Si_2Al_2O_4H_8^{2-}$ anion is calculated to have a symmetric O breathing frequency that is about 50 cm^{-1} smaller and involves substantial T atom motion.

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