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Molecular orbital modeling of aqueous organosilicon complexes: Implications for silica biomineralization

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Abstract—Researchers recently have proposed that hypercoordinate Si-organic complexes can form in biologically relevant fluids, and they have reported the first evidence for a transient organosilicon complex generated within the life cycle of an organism (Kinrade et al., 2001b, 2002). These interpretations are based upon peak assignments of ^{29}Si NMR spectra that invoke Si-polyol (e.g., Si-sorbitol) complexes with Si in five- and six-fold coordination states. However, ab initio analyses of the proposed organosilicon structures do not reproduce the experimentally observed ^{29}Si NMR chemical shifts (Sahai and Tossell 2001, 2002 and this work). In place of the originally proposed structures, we have modeled one of the observed $\delta^{29}\text{Si}$ values with a 5-fold Si-disorbitol complex involving 5-membered ring configurations (i.e., Si–O–C–C–O). The calculated $\delta^{29}\text{Si}$ value of this new structure closely matches the observed $\delta^{29}\text{Si}$ peaks in the -100 to -102 ppm range. Likewise, ^{29}Si NMR peaks near -144 ppm were well fit by a model complex in which a 6-fold Si was complexed to three sorbitol molecules in 5-membered ring configurations. The ability to reproduce the observed NMR peaks using molecular orbital calculations provides support for the controversial role of hypercoordinate organosilicon species in the uptake and transport of silica by biological systems. The existence of such complexes in turn may explain other puzzles in Si biogeochemistry, such as the persistence of dissolved silica in concentrated biological fluids, the biofractionation of Si isotopes, and fractionation of Ge from Si. Copyright © 2003 Elsevier Ltd

1. INTRODUCTION

Silica (SiO_2) is essential to the growth and development of a host of organisms, but the mechanism by which biologic systems transport this compound is incompletely understood. The functionalities of biogenic silica are diverse. In marine organisms such as diatoms, radiolaria, and sponges, siliceous tests and skeletons provide protection against predation. Analogously, siliceous bodies called phytoliths enhance the structural stability, photosynthetic capacity, and defensive strength in higher plants (reviewed in Simpson and Volcani, 1981; Simkiss and Wilbur, 1989; Birchall 1995; Perry and Keeling-Tucker, 2000). Some scientists have postulated that bacterially-mediated precipitation of Fe-rich siliceous coats enabled Archean life forms to survive the intense ultraviolet radiation that bathed the surface of the early Earth (Pierson et al., 1993; Phoenix et al. 2001). Higher order organisms (including humans) require silica for the formation of bone and connective tissue, and a growing body of evidence indicates that silica serves as a detoxification agent against dissolved Al (Carlisle 1981; Birchall et al., 1989; Edwardson et al., 1993; Hodson and Sangster 1999; Desouky et al., 2002).

Just as our appreciation for the manifold biologic roles of silica is increasing, scientists also have made significant strides in unraveling some of the processes that govern the deposition of silica within organisms. Certain polyamines and silaffins found in the cell walls of diatoms and sponge spicules have been shown to control the condensation of polymeric silica from orthosilicic acid (H_4SiO_4) (Iler 1979; Mizutani et al., 1998; Kröger et al., 1999, 2000, 2001; Coradin and Livage

2001). These catalysts of silica biomineralization suggest self-assembly routes for mimetic materials with complex nanoscale patterning (Morse 1999; Cha et al., 1999, 2000; Brott et al., 2001; Sumper 2002).

Despite advances in our understanding of biogenic silica precipitation, surprisingly little is known of the way in which organisms extract silica from inorganic sources and endogenously transport it. Plants, for example, must remove silica from groundwater solutions in which silica concentrations typically fall below the solubility of quartz ($6\text{--}12$ ppm SiO_2), and they then must concentrate it beyond the solubility of amorphous silica (~ 120 ppm SiO_2) to precipitate siliceous phytoliths. Takahashi and Okuda (1962) report that when rice plants are grown in solutions with 10 to 100 ppm SiO_2 , the xylem saps contain silica concentrations of 120 to 650 ppm after 37 h. Likewise, Kaufman et al. (1981) measured silica concentrations of 250 ± 25 ppm in natural xylem saps of the horsetail *Equisetum hyemale*. The ability of such organisms to concentrate silica while maintaining silicic acid in monomeric, dimeric, or trimeric forms during transport has suggested to many authors that inorganic silica is extracted and conveyed as a complex with an organic compound (Lewin and Reimann, 1969; Iler 1979; Simkiss and Wilbur 1989).

Evidence for the existence of an organosilicon complex, or even a Si–O–C bond sequence, in biologic systems had not been forthcoming despite a long and intensive search; and several scientists had expressed doubt that any such species occurs (Birchall 1995; Exley 1998). Moreover, Pokrovski and coworkers (Pokrovski and Schott, 1998; Pokrovski et al., 2000) have demonstrated that octahedral Ge-organic complexes readily form in aqueous solutions, but Si-organic complexation is significantly weaker if it occurs at all. Recently, however, Kinrade et al. (2002) have observed evidence for a transient

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organosilicon complex in the fresh water diatom *Navicula pelliculosa* using in vivo ^{29}Si nuclear magnetic resonance (NMR) spectroscopy. A peak observed near -131.5 ppm was assigned to a hexacoordinate Si-organic complex of unknown origin. This coordination state is surprising because the vast majority of silicate minerals that form under crustal pressures contain Si in four coordination with oxygen. Hypercoordinate states are extremely rare, though exceptions, such as thaumassite, do occur. Similarly, Si in biogenic amorphous varieties of silica has consistently been shown to exist in the usual tetrahedral coordination with O (De Jong et al., 1987; Bertermann and Tacke 2000). Nevertheless, Kinrade and colleagues (Kinrade et al., 2001b) have suggested that aliphatic carbohydrate molecules may complex with dissolved orthosilicic acid, even in relatively dilute neutral solutions, and these organosilicon complexes favor Si in fivefold coordination.

Understanding the detailed structures of Si-organic complexes is critical to predict whether a given organic compound is favored to complex with Si and to determine what kind of complex forms. Whereas Pokrovski and Schott (1998) observed negligible Si complexation with carboxylic acids (e.g., citric acid), Kinrade et al. (1999) observed peaks they assigned to 4-, 5- and sixfold Si species in alkaline solutions with polyols (e.g., sorbitol). They concluded that "complexes only form in significant quantities when the aliphatic polyol additive has four or more adjacent hydroxy groups, with two being in *threo* configuration." In dilute, neutral aqueous silicate solutions, these same authors observed Si monomers, dimers and penta-coordinate species in solution with sodium D-gluconate as the ligand, but the hexacoordinate species was not detected (Kinrade et al., 2001b). When polyol ligands with terminal carboxylic acid groups (e.g., monopotassium D-saccharic acid) were used, they exhibited a significantly stronger affinity for silica, and the hexacoordinate species appeared to be dominant (Kinrade et al., 2001a).

In light of the role that hypercoordinate organosilicon complexes may play in the transport of dissolved silica in biologic systems, and in their possible applications in novel materials synthesis preparations (Laine et al., 1991), it is important to determine the local structure of these complexes. The configurations proposed in the work of Kinrade and colleagues were not generated using extensive structure data; and, as is detailed below, their specific conformations are probably inaccurate. Empirical models for organosilicon configurations can be tested by comparison of experimental ^{29}Si -NMR analyses with theoretically derived spectra. As shown by Sahai and Tossell (2001, 2002), molecular orbital (MO) simulations offer a promising means of determining the true state of Si when complexed to organic moieties. These evaluations of peak assignments are critically important for a number of reasons: 1) the existence of hypercoordinate Si species in natural systems remains controversial; 2) assignments of ^{29}Si bands that are routinely reported in the literature are based on analogies with reference compounds rather than on determinations by first principles; and 3) one-dimensional NMR experiments do not give detailed structural information with respect to the complexes, whereas MO calculations provide three-dimensional configurations of organosilicon species.

In this paper, we report the results of MO analyses of the complexation between silica species with sorbitol, which was

one of the ligands examined by Kinrade et al. (1999). Previous efforts have challenged the interpretations of Kinrade and co-workers (Sahai and Tossell 2001, 2002). We successfully modeled the ^{29}Si spectral peaks observed by Kinrade and colleagues when 5-membered ring configurations were formed between the Si and sorbitol. Our MO analyses support the existence of hypercoordinate organosilicon complexes in the silica-polyol aqueous systems studied by Kinrade and coworkers.

2. COMPUTATIONAL METHODS

Model clusters were generated with Cerius² (Accelrys, Inc., San Diego, CA). MO calculations on molecular clusters were carried out using Gaussian 98 (Frisch et al., 1998). Structures were energy minimized with HF/3-21G(d,p) (Binkley et al., 1980) and B3LYP/6-31G(d) (Gordon et al., 1982, Becke 1988; Lee et al., 1988) basis sets. NMR chemical shieldings (σ) were calculated based on these structures. ^{29}Si chemical shieldings were computed with the HF/6-311+G(d,p) basis set (McLean and Chandler 1980; Krishnan et al., 1980). This basis set has been shown to reproduce experimental ^{29}Si chemical shifts (Casanovas et al., 1999). Calculated chemical shifts ($\delta^{29}\text{Si}$) were based on the difference in theoretical chemical shielding of the model molecules and the NMR standard, tetramethylsilane, $(\text{CH}_3)_4\text{Si} = \text{TMS}$. (The chemical shielding for TMS calculated using the HF/6-311+G(d,p)//HF/3-21G(d,p) method is 397 ppm and with HF/6-311+G(d,p)//B3LYP/6-31G(d) σ is 396 ppm.). This methodology has been shown to generate accurate $\delta^{29}\text{Si}$ values compared to experiment (Sykes et al., 1997; Kubicki and Toplis M. J. (2002)). The accuracy of computed NMR parameters were tested on models representing commonly accepted Si species in aqueous solution. NMR chemical shifts were calculated on isolated molecules and with explicit hydration of the cluster (i.e., addition of H_2O molecules) to test for solvation effects on structure and NMR chemical shifts.

3. RESULTS

3.1. MO Calculations: Comparison with Reference Compounds

To verify the accuracy of our calculated $\delta^{29}\text{Si}$ values, we compared model ^{29}Si shifts with those observed for a series of Si compounds whose peak assignments are well established (Table 1). In aqueous solutions, observed NMR peaks at -71.0 and -80.2 ppm have been assigned to orthosilicic acid (H_4SiO_4) and the dimer ($\text{H}_6\text{Si}_2\text{O}_7$), respectively (Mann and Chmelka 2000; Kinrade et al., 2001b). Our models of these two aqueous species resulted in calculated $\delta^{29}\text{Si}$ values of -74 and -82 ppm, respectively. Negative charges on these species did not adversely affect our ability to model the ^{29}Si -NMR chemical shifts. As evidence, we calculated $\delta^{29}\text{Si}$ for $\text{H}_3\text{SiO}_4^- \cdot 9(\text{H}_2\text{O})$ and obtained a value of -69 ppm, as compared to ~ -71 ppm from experiment (Kinrade and Swaddle 1988). Polymerization and coordination state changes did not significantly affect the model accuracy. Si bonded to 4 bridging O atoms (designated as Q^4Si), Si bonded to 3 bridging O atoms (designated as Q^3SiOH), and hexacoordinate ^{16}Si model species were all found to agree closely with observed $\delta^{29}\text{Si}$ values

Table 1. Comparison of calculated and experimental $\delta^{29}\text{Si}$ values for known compounds.

Compound	Experiment	Model	Calculated
<i>Hydrated monomeric and dimeric silicic acids</i>			
$\text{H}_4\text{SiO}_4(\text{aq})$	-71 ^a	$\text{H}_4\text{SiO}_4 \cdot 9(\text{H}_2\text{O})$	-74
$\text{H}_3\text{SiO}_4^-(\text{aq})$	-71 ^b	$\text{H}_3\text{SiO}_4^- \cdot 9(\text{H}_2\text{O})$	-69
$\text{H}_6\text{Si}_2\text{O}_7(\text{aq})$	-80 ^a	$\text{H}_6\text{Si}_2\text{O}_7 \cdot 19(\text{H}_2\text{O})$	-82
<i>Variations in Si-O polymerization and coordination</i>			
$\text{Q}^3 \text{SiOH}$	-100 ^c	$((\text{OH})_3\text{SiO})_3\text{SiOH}$	-98
$\text{Q}^4 \text{Si}$	-112 ^d	$((\text{OH})_3\text{SiO})_4\text{Si}$	-112
$^{16}\text{SiO}_6$	-170 to -220 ^e	$\text{H}_6\text{SiO}_6^{2-} \cdot 12(\text{H}_2\text{O})$	-182
$\text{SiH}_4(\text{g})$	-92 ^f	SiH_4	-89
<i>Organosilicon compounds</i>			
$^{14}\text{Si}-(\text{O}_2\text{C}_6\text{H}_{12})_2$	-81 ^g	$\text{Si}-(\text{O}_2\text{C}_6\text{H}_{12})_2$	-81
$^{14}\text{Si}-(\text{O}_2\text{C}_6\text{H}_{12})_2^\ddagger$	-44 ^g	$\text{Si}-(\text{O}_2\text{C}_6\text{H}_{12})_2^\ddagger$	-45
$^{15}\text{Si}-(\text{O}_2\text{C}_6\text{H}_{12})_2(\text{OC}_6\text{H}_{12}\text{OH})$	-135 ^g	$(\text{OH})\text{Si}-(\text{O}_2\text{C}_6\text{H}_{12})_2$	-136
$^{15}\text{Si}-(\text{O}_2\text{C}_2\text{H}_4)_2(\text{OC}_2\text{H}_4\text{OH})^\ddagger$	-103 ^g	$(\text{OH})\text{Si}-(\text{O}_2\text{C}_2\text{H}_4)_2^\ddagger$	-106
$^{15}\text{Si}-(\text{O}_2\text{C}_6\text{H}_{12})_2(\text{OC}_6\text{H}_{12}\text{OH})^\ddagger$	-111 ^g	$(\text{OH})\text{Si}-(\text{O}_2\text{C}_6\text{H}_{12})_2^\ddagger$	-112
$^{15}\text{Si}-(\text{OCH}_2\text{CH}_2\text{O})_3^\ddagger$	-105 ^h	$\text{Si}-(\text{OCH}_2\text{CH}_2\text{O})_3^\ddagger$	-110
$^{16}\text{Si}-(\text{O}_2\text{CH}_2\text{CH}_2)_3^\ddagger$	-143.3 & -145.5 ⁱ	$\text{Si}-(\text{O}_2\text{CH}_2\text{CH}_2)_3^\ddagger$	-153
$^{16}\text{Si}-(\text{O}_2\text{C}_6\text{H}_4)_3^{2-}$	-139 ^j	$\text{Si}-(\text{O}_2\text{C}_6\text{H}_4)_3^{2-}$	-151
$^{16}\text{Si}-(\text{O}_2\text{C}_6\text{H}_4)_3^{2-}$	-139 ^j	$\text{Si}-(\text{O}_2\text{C}_6\text{H}_4)_3^{2-*}$	-145
$^{16}\text{Si}-(\text{O}_2\text{C}_6\text{H}_4)_3^{2-}$	-139 ^j	$\text{Si}-(\text{O}_2\text{C}_6\text{H}_4)_3^{2-\ddagger}$	-153

[†] - 5-membered ring structure.

* - Structure optimized with B3LYP/6-311+G(d,p).

[‡] - Structure optimized with HF/3-21G(d,p) and PCM.

^a - Kinrade et al. (2001) and Mann and Chmelka (2000); ^b - Kinrade and Swaddle (1988); ^c - Farnan et al. (1987); ^d - Murdoch et al., (1985);

^e - Grimmer et al. (1986); ^f - Niemann and Marsmann (1975); ^g - Kemmitt and Milestone (1995); ^h - Cheng et al. (2000); ⁱ - Hoppe et al. (1993);

^j - Cella et al. (1980).

(Table 1). Calculated peak assignments for these test cases all fell within ± 3 ppm of the accepted experimental values.

To test our methodology for calculating ^{29}Si chemical shifts in Si species with bonds other than Si(OH) and Si-O-Si, comparisons between modeled and experimental ^{29}Si shifts for other bonding environments were made. In general, these models also agreed well with experiment (Table 1). For example, modeled SiH_4 yielded -89 ppm (Table 1) compared to -92 ppm from experiment (Niemann and Marsmann 1975). Similar accuracy was also found for the Si-organic complexes tested (e.g., $^{15}\text{Si}-(\text{O}_2\text{C}_2\text{H}_4)_2$). The seven Si-organic model complexes with aliphatic ligands in Table 1 were selected to represent the range of variation observed in ^{29}Si chemical shifts within the tetrahedral and pentacoordinate states (i.e., $^{14}\text{Si} = -44$ to -82 ppm; $^{15}\text{Si} = -103$ to -137 ppm (Kemmitt and Milestone 1995)). Agreement of the model calculations with the previous assignments for Si-organic complexes (Cella et al., 1980; Murdoch et al., 1985; Grimmer et al., 1986; Farnan et al., 1987; Hoppe et al., 1993; Kemmitt and Milestone 1995; Cheng et al., 2000) consistently fell within 10 ppm (Table 1). Thus, we consider a 10 ppm difference between experimentally derived values and our model calculations to be an estimate of the possible uncertainty. Most importantly, the MO results reproduce the experimental observation of Kemmitt and Milestone (1995) that pentacoordinate Si with 6-membered rings (Si-O-C-C-C-O) have $\delta^{29}\text{Si}$ values near -135 ppm whereas those with 5-membered rings are between -102 and -112 ppm (Table 1).

However, not all models agreed so closely with observed values. In silica/catechol aqueous solutions, a $\text{Si}(\text{O}_2\text{C}_6\text{H}_4)_3^{2-}$ complex is believed to form that gives rise to a ^{29}Si -NMR peak near -139 ppm (Kinrade and Swaddle 1988). The HF/3-21G(d,p) optimized model of this complex yielded a calculated

$\delta^{29}\text{Si}$ value of -151 ppm. Thus, this simulation was marked by a 12 ppm discrepancy between experiment and theory, possibly because solvation was neglected and/or the catechol aromatic rings were modeled within the Hartree-Fock approximation. Re-optimization of the $\text{Si}(\text{O}_2\text{C}_6\text{H}_4)_3^{2-}$ complex with the B3LYP/6-311+G(d,p) basis set generated a structure with a $\delta^{29}\text{Si}$ value of -145 ppm, which is closer to the experimental observation. However, solvation did not help reduce the discrepancy. Re-optimization of the structure with the polarized continuum model (PCM) (Miertus et al., 1981) and the HF/3-21G(d,p) basis set resulted in a calculated $\delta^{29}\text{Si}$ of -153 ppm, farther from the observed value. Hence, the error most likely was caused by inadequate representation of the aromatic catecholate with the HF/3-21G(d,p) basis set. Because the complexes considered in this paper do not contain aromatic groups, this limitation should not have affected the $\delta^{29}\text{Si}$ values calculated in this paper. If this error nevertheless appeared in our analyses, then the estimated errors in our calculated values of $\delta^{29}\text{Si}$ would be on the order of 12 ppm.

3.2. MO Analysis of Published Silica-Sorbitol ^{29}Si NMR Peak Assignments

Kinrade et al. (1999, 2001a, 2001b) examined Si-organic aqueous solutions by ^{29}Si -NMR and observed peaks near -102 ppm and -144 ppm. By comparison with $\delta^{29}\text{Si}$ peak assignments for organosilicon complexes in the solid state and as dissolved species in non-aqueous solutions, they interpreted those NMR bands as evidence for hypercoordinate ^{15}Si and ^{16}Si complexes, respectively, with aliphatic polyols. Hence, we modeled penta- and hexacoordinate organosilicon structures similar to those posited by Kinrade et al. (1999, 2001a) using ab initio energy minimizations (Fig. 1) and NMR calculations

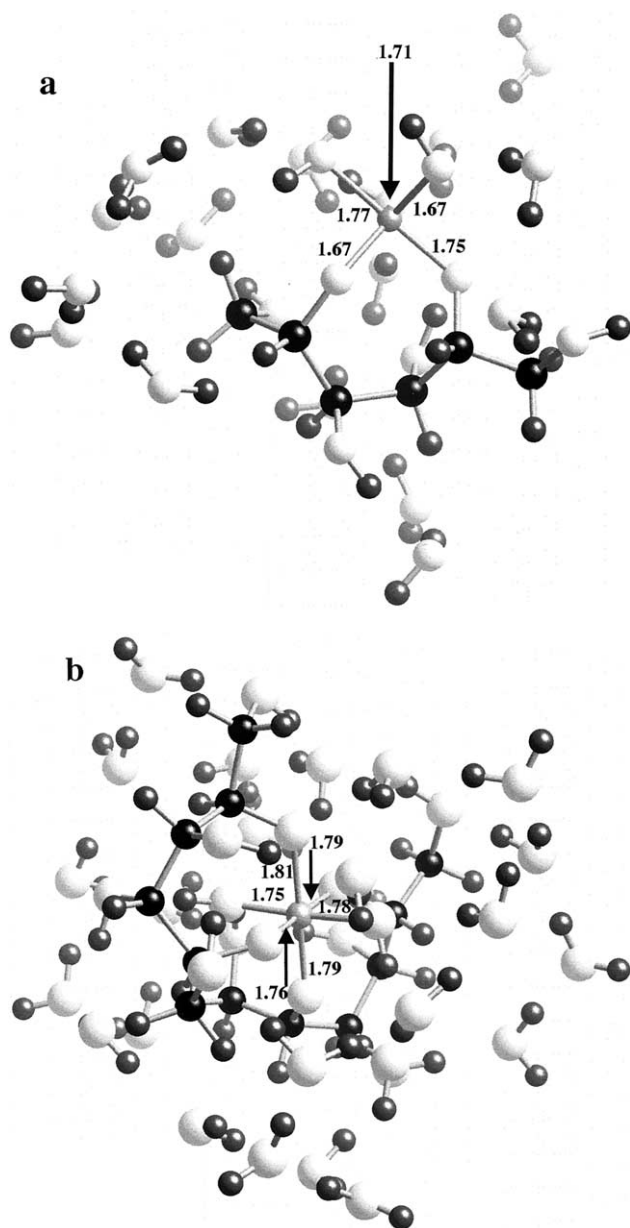


Fig. 1. HF/3-21G(d,p) optimized models of two configurations proposed in Kinrade et al., 1999. (a) ^{15}Si -sorbitol and (b) ^{16}Si -disorbitol complexes with explicit solvation.

(Table 2). In contrast to the good agreement obtained between observed and calculated NMR peak assignments for a series of reference compounds (Table 1), we were unable to reproduce the $\delta^{29}\text{Si}$ values reported by Kinrade et al. when we used the organosilicon configurations that they proposed. The isolated ^{15}Si -sorbitol and solvated ^{15}Si -sorbitol_(aq) clusters resulted in modeled $\delta^{29}\text{Si}$ values of -123 and -129 ppm, respectively, compared to observed values that range between -100 and -102 ppm (Table 2). An NMR calculation using a larger basis set (i.e., HF/6-311+G(3df,2p)) on the ^{15}Si -sorbitol complex resulted in a predicted value for $\delta^{29}\text{Si}$ of -135 ppm (Table 2), farther from the experimentally observed peak position. Re-optimization of the ^{15}Si -sorbitol complex with the B3LYP/6-

31G(d) basis set resulted in a calculated $\delta^{29}\text{Si}$ of -118 ppm (Table 2). Thus, neither solvation nor basis set effects brought the theoretical value for this complex within error of the observed peak.

Similar disagreement between observed and calculated model values were found for the highly charged species, $\text{SiO}_3^{4-}(\text{O}_2\text{C}_6\text{H}_7(\text{OH})_2\text{COO}^-)$, proposed in Kinrade et al. (2001a). Our calculated ^{29}Si -NMR shift for this compound was -123 ppm, whereas Kinrade et al. reported an observed value of -102 ppm (Table 2). (Note: A gluconic acid- $^{15}\text{SiO}_3 \cdot 10(\text{H}_2\text{O})$ structure was generated by default values in Cerius² (Accelrys, Inc.) because the structure was not stable during energy minimizations with Gaussian 98. This instability arose because the SiO^- bonds were basic and attracted H^+ from surrounding H_2O molecules. The Cerius² "CLEAN" algorithm that generated the model structure we used here does not allow this hydrolysis reaction to occur.)

We experienced similar inconsistencies in our efforts to model the hexacoordinate complexes suggested by Kinrade et al. (1999), who assigned resonances observed near -144 ppm to ^{16}Si complexes in aqueous solutions. We calculated a $\delta^{29}\text{Si}$ value for the aqueous ^{16}Si -disorbitol configuration suggested by these authors and obtained a value of -181 ppm (Table 2). Kinrade et al. assigned the observed $\delta^{29}\text{Si}$ peak at -144 ppm to a hexacoordinate Si center because Cella et al. (1980) demonstrated that Si-triscatecholate forms an aqueous octahedral complex with a peak shift of this magnitude (-139 ppm). However, significant differences exist between the Si-triscatecholate complex and the complexes proposed by Kinrade et al. (1999), such as the number of atoms in the Si-O-C rings and the aromaticity of the ligands. We also note that the calculated $\delta^{29}\text{Si}$ values presented here are consistent with values calculated previously by Sahai and Tossell (2001, 2002).

3.3. MO Analysis of Inorganic Si Species

Because previously proposed structures failed to reproduce the ^{29}Si peak shifts observed by Kinrade et al. (1999, 2001), we searched for alternative configurations that could give rise to the observed peaks. Previous work has shown that silica monomers, dimers, and higher-order oligomers are likely to co-exist when silica concentrations are sufficiently high (Iler 1979). Consequently, we modeled the monomeric and oligomeric silica species listed in Table 3 to determine whether any polynuclear structures might give rise to NMR peaks near -102 and -144 ppm. Only $((\text{OH})_3\text{SiO})_3\text{SiOH} \cdot 9(\text{H}_2\text{O})$ yielded a calculated value for $\delta^{29}\text{Si}$ that fell within the computational error of the observed values (-98 ppm). This value is closer to the observed value than the calculated ^{15}Si -sorbitol complexes in Table 2 and might be a reasonable assignment for the -102 ppm peak. However, the peaks observed under circumneutral and alkaline conditions have close to the same $\delta^{29}\text{Si}$ values (Kinrade et al., 1999, 2001). Under the highly alkaline conditions employed in the experiments of Kinrade et al. (1999), polymerized silica species should be partially de-protonated (Iler 1979). When $((\text{OH})_3\text{SiO})_3\text{SiOH} \cdot 9(\text{H}_2\text{O})$ was modeled as a singly charged de-protonated species, $((\text{OH})_3\text{SiO})_3\text{SiO}^- \cdot 9(\text{H}_2\text{O})$, the calculated value for $\delta^{29}\text{Si}$ moved to a less negative value (-93 ppm), away from the observed peak near -102 ppm. Thus, a more realistic representation of the Q^3 Si species does not result in good agreement with observation.

Table 2. Comparison of experimental $\delta^{29}\text{Si}$ values (ppm) previously assigned to complexes and calculated values (HF/6-311 + G(d,p)//HF/3-21G(d,p) for models of the experimental assignments.

Compound	Experiment	Model	Calculated
^{14}Si -sorbitol(aq)	—	$(\text{OH})_2\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8) \cdot 15(\text{H}_2\text{O})$	-73
^{15}Si -sorbitol(aq)	-100 to -102 ^a	$(\text{OH})_3\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)$	-123
^{15}Si -sorbitol(aq)	-100 to -102 ^a	$(\text{OH})_3\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)^\S$	-135
^{15}Si -sorbitol(aq)	-100 to -102 ^a	$(\text{OH})_3\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)^\forall$	-118
^{15}Si -sorbitol(aq)	-100 to -102 ^a	$(\text{OH})_2\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8) \cdot 18(\text{H}_2\text{O})$	-129
$^{15}\text{SiO}_3$ -gluconate ⁴⁻ (aq)	-102 ^b	$\text{O}_3\text{Si}^{4-}(\text{O}_2\text{C}_6\text{H}_7(\text{OH})_2\text{COO}^-) \cdot 10(\text{H}_2\text{O})^\ddagger$	-123
^{16}Si -disorbitol(aq)	-143.3 & -145.5 ^a	$(\text{OH})_2\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)^\forall$	-177
^{16}Si -disorbitol(aq)	-143.3 & -145.5 ^a	$(\text{OH})_2\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_2 \cdot 18(\text{H}_2\text{O})$	-181
^{16}Si -trisorbitol(aq)	-143.3 & -145.5 ^a	$(\text{OH})_2\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_2^\forall$	-180

[§] = HF/6-311 + G(3df,2p)//HF/3-21G(d,p) value.

[¶] = B3LYP/6-31G* structure.

* = "CLEAN" structure from Cerius².

‡ = Structure not stable within HF/3-21G(d,p) energy minimization.

^a - Kinrade et al. (1999); ^b - Kinrade et al. (2001a).

The pentacoordinate monomeric species listed in Table 3 yielded $\delta^{29}\text{Si}$ shifts that are 10 to 27 ppm more negative than the observed peak near -102 ppm. The complex that most closely matched the observed value was $\text{Na}_2\text{H}_4\text{SiO}_5 \cdot 14(\text{H}_2\text{O})$, which presumably could be a stable species at high pH. However, Kinrade et al. (2001b) observed the ^{29}Si -NMR peak near -102 ppm at near-neutral pH conditions where $\text{Na}_2\text{H}_4\text{SiO}_5 \cdot 14(\text{H}_2\text{O})$ is unlikely to exist. Of the pentacoordinate inorganic species tested, the cluster $\text{H}_5\text{SiO}_5^- \cdot 9(\text{H}_2\text{O})$ predicted a value for $\delta^{29}\text{Si}$ that was closest to the observed peak near -144 ppm. This complex yielded a $\delta^{29}\text{Si}$ shift of -129 ppm (Table 3), but this value falls outside the estimated model error of the observed peak. Sahai and Tossell (2001) also noted discrepancies between inorganic models with ^{15}Si centers and experimental measurements. Hence, we conclude that inorganic ^{15}Si species do not give rise to the ^{29}Si -NMR intensity observed near -102 ppm.

We also tested a hexacoordinate inorganic ^{16}Si model, $\text{H}_6\text{SiO}_6^{2-} \cdot 12(\text{H}_2\text{O})$, which resulted in a $\delta^{29}\text{Si}$ value of -182 ppm (Table 3). This and other calculated $\delta^{29}\text{Si}$ values for octahedral Si (Table 3) are consistent with NMR spectra of crystalline phases that contain ^{16}Si , with $\delta^{29}\text{Si}$ shifts that range between -180 and -221 ppm (Grimmer et al., 1986). None of these values are close to the peak observed near -144 ppm.

Table 3. Calculated $\delta^{29}\text{Si}$ values in ppm for inorganic models hypothesized in this study.

Model	Calculated
$((\text{OH})_3\text{SiO})_3\text{SiOH} \cdot 9(\text{H}_2\text{O})$	-98
$((\text{OH})_3\text{SiO})_3\text{SiO}^- \cdot 9(\text{H}_2\text{O})$	-93
$((\text{OH})_3\text{SiO})_3\text{SiSiO}(\text{OH})_2^-$	-95
$\text{H}_5\text{SiO}_5^- \cdot 9(\text{H}_2\text{O})$	-129
$\text{H}_4\text{SiO}_5^{2-} \cdot 9(\text{H}_2\text{O})$	-123
$\text{NaH}_5\text{SiO}_5 \cdot 9(\text{H}_2\text{O})$	-127
$\text{NaH}_4\text{SiO}_5 \cdot 14(\text{H}_2\text{O})$	-121
$\text{Na}_2\text{H}_4\text{SiO}_5 \cdot 14(\text{H}_2\text{O})$	-112
$((\text{OH})_3\text{SiO})_4\text{Si}(\text{OH})$	-120
$\text{H}_6\text{SiO}_6^{2-} \cdot 12(\text{H}_2\text{O})$	-182
$\text{H}_4\text{SiO}_6^{4-} \cdot 12(\text{H}_2\text{O})$	-171
$\text{Na}_2\text{H}_6\text{SiO}_6 \cdot 12(\text{H}_2\text{O})$	-179
$((\text{OH})_3\text{SiO})_4\text{Si}(\text{OH})_2$	-182

Again in agreement with Sahai and Tossell (2001), we conclude that inorganic ^{16}Si species are not associated with the NMR intensity in this region.

3.4. Matching MO Calculations with Hypercoordinate Silica-Sorbitol Complexes

The model Si-sorbitol $\delta^{29}\text{Si}$ values based on the complexes proposed by Kinrade et al. (1999) consistently were 20 to 40 ppm more negative than the observed values, so we explored Si-sorbitol configurations that might match the experimentally derived NMR spectra more closely. As mentioned above, Kemmitt and Milestone (1995) have shown that the formation of 5-membered (Si-O-C-C-O) rings decreases the absolute value of ^{29}Si chemical shifts by 20 to 40 ppm. Hence, ^{15}Si and ^{16}Si complexes with sorbitol could be responsible for the peaks near -102 and -144 ppm, respectively, if 5-membered rings are present. The results of our calculations for Si-sorbitol complexes with 5-membered ring structures are presented in Table 4. The ^{15}Si -disorbitol complex optimized with the HF/3-21G(d,p) method was associated with a calculated chemical

Table 4. Calculated values for model 5-membered ring Si-organic complexes hypothesized in this study.

Model	Calculated
$(\text{OH})_3\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)$	-114
$(\text{OH})_3\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)^\ast$	-117
$(\text{OH})_3\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)^\ast\ast$	-100
$(\text{OH})_3\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)^\ast$	-108 [¶]
$(\text{OH})\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_2$	-109
$(\text{OH})\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_2^\forall$	-101 [¶]
$(\text{OH})_2\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_2$	-159
$(\text{OH})_2\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_2^\ast\ast$	-161
$(\text{OH})_2\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_2^\forall$	-157
$\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_3$	-154
$\text{Si}(\text{O}_2\text{C}_6(\text{OH})_4\text{H}_8)_3^\forall$	-147 [¶]

[∗] = PCM optimized structure.

^{∗∗} = "CLEAN" structure from Cerius².

[¶] = B3LYP/6-31G(d) optimized structure compared to B3LYP/6-31G(d) optimized TMS HF/6-311 + G(d,p) chemical shielding (396 ppm).

shift of -108 ppm, which deviates from the observed peaks by only 6 ppm. Re-optimization with the more accurate B3LYP/6-31G(d) basis set (Fig. 2a) resulted in a closer fit to experiment (-101 ppm). The closest fit to the peaks near -144 ppm was obtained for the Si-trisorbitol model complex with 5-membered rings optimized with B3LYP/6-31G(d) (Fig. 2b); this calculation yielded a shift of -147 ppm. As discussed above, Kinrade et al. (2001a) proposed 7- rather than 5-membered ring complexes, and re-optimization of these 7-membered ring ^{15}Si -sorbitol and ^{16}Si -disorbitol species with the B3LYP/6-31G(d) basis set resulted in modeled $\delta^{29}\text{Si}$ values of -118 and -180 ppm (Table 2). These values fall outside our model error, so basis set effects in the energy minimization do not explain these results. Thus, if Si-sorbitol complexes form, the 5-membered ring chelation mechanism with two and three sorbitol ligands, respectively, appear to give the best fit to experiment for both the observed NMR peaks.

4. DISCUSSION

Two questions arise from the assignment of the observed NMR peaks to Si-organic complexes with 5-membered rings. First, why do the complexes tend to form with 5-membered rings? One might hypothesize that the strain energy (Kemmitt and Milestone, 1995) required to change the structure of the ligand into a 5-membered ring would be so significant as to inhibit the reaction. However, the HF/6-311+G(d,p)//B3LYP/6-31G(d) energies calculated for the complexes presented here predict that the 5-membered ring configuration is actually -25 kJ/mol more stable than the 7-membered ring configuration for the 5-coordinate Si-disorbitol complex whether as an isolated cluster or within the aqueous phase (as represented by the IEFPCM). Preferred stability of the 5-membered ring complexes has been predicted previously by Bennett and Casey (1994). We were unable to complete an IEFPCM calculation for the 6-coordinate Si-trisorbitol complex, but HF/6-311+G(d,p)//B3LYP/6-31G(d) calculations predict that the 5-membered ring structure is -150 kJ/mol more stable. This value probably overestimates the energy difference, but it strongly suggests energetic favorability of the 5-membered ring configuration. Consequently, we conclude that any strain energy generated within the sorbitol itself is more than offset by the gain in energy provided by maximizing the Si-sorbitol bonding interaction.

The second question is why the formation of a 5-membered Si-O-C-C-O ring should change the $\delta^{29}\text{Si}$ value by 20 to 40 ppm. Both experimental (Kemmitt and Milestone, 1995) and the model results presented here indicate that switching from a configuration with 6- or 7-membered rings to one with 5-membered rings significantly affects $\delta^{29}\text{Si}$. Indeed, this shift is the key factor in identifying the proposed Si-organic complexes. Kemmitt and Milestone (1995) attributed the large shift to strain energy in the complex. However, as Sahai and Tossell (2002) pointed out, there is no a priori reason why strain in the ligand should translate into a change in $\delta^{29}\text{Si}$. For example, in the disorbitol- ^{16}Si complex, the Si-O bond lengths to sorbitol average 1.81 Å and the Si-(OH) bonds are 1.82 Å. In the 7-membered ring complex, the bonds are 1.81 and 1.83 Å, respectively. The O-Si-O angles formed with the O atoms of sorbitol are 87° and 92° in the 5- and 7-membered ring com-

plexes, respectively. Thus, there does not appear to be a large difference between these two configurations in terms of bond strains within the Si-O-C-C-O rings. However, a significant difference between the two configurations is calculated for the Si-O-C angles. These values are 113° and 128° , respectively, for the 5- and 7-membered ring complexes of disorbitol- ^{16}Si . The fact that $\delta^{29}\text{Si}$ values are a function of the Si-O-Si angle in phases with 4-coordinate Si has been known for some time (Oestrike et al., 1987 and references therein), and this trend has been explained theoretically (Wolff et al., 1989; Moravetski et al., 1996). Hence, it is logical to explain the observed and calculated changes in $\delta^{29}\text{Si}$ values for Si-organic complexes in terms of the Si-O-C angle.

Finally, it is interesting to note that the calculated $\delta^{29}\text{Si}$ shift for a tetrahedrally coordinated ^{14}Si center in complexation with a sorbitol 6-ring configuration was -73 ppm (Table 2; Sahai and Tossell, 2001, 2002), which is close to the experimentally observed value of -71 ppm for orthosilicic acid (Table 1). Although the experiments of Kinrade et al. (1999, 2001a, 2001b, 2002) have yielded surprising evidence for the existence of hypercoordinate silicon species in aqueous solutions, it is important to remember that generally the most intense peaks occur around -71 ppm. Thus, orthosilicic acid is interpreted to be the predominant species in these solutions. Nevertheless, our calculations demonstrate that complexation of sorbitol to tetrahedral Si does not necessarily lead to a dramatic chemical shift in the NMR signal. While it seems unlikely that at neutral pH an organic ligand to tetrahedral Si would be thermodynamically favored over a hydroxyl group (Kubicki et al., 1996; Sahai and Tossell, 2001, 2002), it also is clear that some organisms are capable of maintaining dissolved silica in monomeric (or dimeric and trimeric) form at silica concentrations in excess of the solubility of opal (Kaufman et al., 1981). Our calculations suggest that if biogenic silica is maintained as monomeric ^{14}Si through the complexation of organic moieties, the ^{29}Si -NMR signal associated with the complex might not differ significantly from that associated with pure orthosilicic acid.

5. CONCLUSIONS

If Si-organic complexes form in nature via a mechanism similar to that suggested here, then there are several implications for biologic and materials research. First, Si may not necessarily be transported as $\text{Si}(\text{OH})_4$ through plants or diatoms, thereby allowing the solubility of monomeric silica in solution to be increased. If silica is transported as hypercoordinate ^{15}Si or ^{16}Si centers in organic complexes, then those species ultimately must engage in a back reaction to ^{14}Si , as is found in amorphous silica phytoliths (Bertermann and Tacke 2000). The mechanism underlying this condensation reaction merits further investigation, but both the initial complexation and the ultimate precipitation reactions might serve to fractionate Si isotopes in plants and diatoms (Shahack et al., 1996; Kelly et al., 1998; Jähren et al., 1998; Webb and Longstaffe 2000). De La Rocha et al. (1997) have demonstrated that diatoms discriminate against ^{30}Si , and recently these authors have documented that the Si isotopic composition of groundwaters are shifted away from igneous values of Si. They infer that land plants also might select against ^{30}Si , but at this point

the style and degree of Si fractionation in plants remains unknown.

Second, the specific conformation into 5-membered rings required to reproduce the observed $\delta^{29}\text{Si}$ values suggests that compounds with the ability to achieve this configuration with minimal distortion will be the most favored carriers of Si. Specific Si complexing agents, similar to siderophore compounds, may be produced that can efficiently increase the solubility of Si, move Si through the organism, and deposit Si at specific sites where it will be utilized (Perry et al., 1991; Larcher et al., 1991; Cowan et al., 1997; Hodson and Sangster 1999).

Third, several groups (Mortlock and Froelich 1987; Murnane and Stallard 1990; Kurtz et al., 2002) have demonstrated that Ge is enriched in soil solutions and stream waters relative to bedrock, with Ge/Si ratios up to 10 times greater than that of the source material. Pokrovski and colleagues (Pokrovski and Schott 1998, Pokrovski et al. 2000) argue convincingly that Ge enrichment is at least partly attributable to the ease of formation of Ge-carboxylic acid complexes. The investigations of Pokrovski et al. and other groups (e.g., Poulson et al., 1997) have revealed little evidence for Si chelation with carboxylic acids (e.g., citric, oxalic, acetic, tartaric, and salicylic acids). The preferred complexation of Ge over Si with carboxylic acid functional groups is one likely mechanism of fractionating the two elements because humic and fulvic acids contain high percentages of carboxylic acid functional groups.

Pokrovski and Schott (1998) did observe an increase in amorphous silica solubility in the presence of catechol, which has two hydroxyl groups and no carboxylic acid groups. These authors propose the formation of a hexacoordinated Si-catechol complex based on work by Iler (1979) and Öhman et al. (1991), but they point out that the high catechol concentrations required to make silica-catechol complexes in significant numbers are not typical of natural aqueous systems.

Nevertheless, the present study in tandem with the work of Kinrade et al. (1999, 2000) implies that aliphatic polyols may be more effective than catechols in forming complexes with aqueous silica. Moreover, Kinrade et al. (2001) observed that polyol chains with terminal carboxylic acid groups exhibit a much stronger tendency to complex with silica than their counterparts that contain only polyols. Direct bonding to the carboxylate group is not hypothesized for these compounds. Thus, the affinity of silica centers for organic ligands is sensitive to the functional groups that do not participate directly in the bonding process. Because most of the organic acids examined by Pokrovski et al. would require complexation with carboxylate groups, the absence of silica-organic ligands in their experiments may not rule out the existence of these species in natural systems. In any event, it is clear that a complete understanding of the organic complexation behaviors for both Ge and Si must be achieved before Ge/Si ratios can be reliably applied to paleoenvironmental analysis.

Lastly, investigations into hypercoordinate silica have intensified over the last decade since these species are simply and cheaply produced in both aqueous and non-aqueous solutions, and the structures are sufficiently simple that they can serve as the feedstock for the synthesis of a variety of inorganic and organometallic silicon compounds (Laine et al., 1991; Herreros et al., 1994; Blohowiak et al., 1994). Our results suggest that

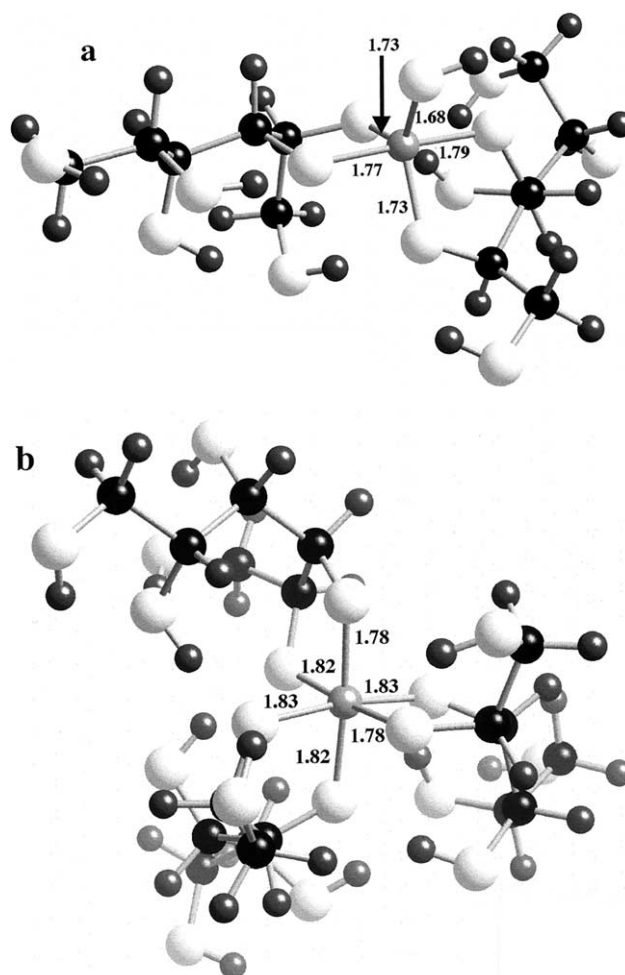


Fig. 2. B3LYP/6-31G(d) energy minimized models of the structures that best match the observed $\delta^{29}\text{Si}$ -NMR shifts reported by Kinrade et al. (1999) (a) 5-membered ring ^{51}Si -disorbitol complex and (b) 5-membered ring ^{61}Si -trisorbitol complex.

materials processing may be optimized by examining organic ligands with the ability to form 5-membered rings. In addition, it may be possible to discriminate among compounds that favor ^{51}Si versus ^{61}Si where one or the other is needed for specific applications (Holmes 1990).

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