Deep-sea biogenic silica: new structural and analytical data from infrared analysis – geological implications

François Fröhlich
Laboratoire de Géologie du Museum, 43 rue Buffon, 75005 Paris. France

ABSTRACT

The main parameters of infrared spectra have been investigated for marine siliceous skeletons and for silica polymorphs. From infrared (IR) data, the mean values for the Si–O bond length (1.62 Å) and for the Si–O–Si angle (about 142°) are inferred for biogenic silica. A model is proposed for the molecular structure of biogenic, amorphous silica, which consists of a discontinuous, three-dimensional framework of short chains of [SiO₄] tetrahedra, bounded with apical hydroxyls. According to the relationship between the structure of the silica polymorphs and their infrared spectra, it is shown that a quantitative analysis of biogenic silica seems to be possible in quartz-rich sediments. Some geological implications of these data are emphasized, including the processes of siliceous skeleton sedimentation and diagenetic evolution.

Terra Nova, 1, 267–273

INTRODUCTION

Biogenic silica is an important constituent of deep-sea sediments from the high primary production areas (e.g. equatorial and polar divergences areas), particularly since the Miocene period. Although the molecular structure of high-temperature silica glasses has been well documented (Bell and Dean, 1966; Mozzi and Warren, 1969; Taylor, 1972; Moenke, 1974; Da Silva et al., 1975; Wong and Angell, 1976; Calas and Petiau, 1983; Navrotsky et al., 1985), the molecular constitution of biogenic silica has been poorly investigated. In general, silica particles of biological origin have a very fine size and are mixed with other minerals, (mainly carbonates and silicates). Due to its amorphous nature, mineralogical studies of biogenic silica are quite difficult, and qualitative and quantitative determination in marine sediments are inaccurate when using X-ray diffraction or chemical analysis.

Nevertheless, the quantitative infrared method proposed by Chester and Elderfield (1968) provides a determination of biogenic silica content, without any chemical treatment. Previous IR analysis of sediments proved to be successful, giving a satisfactory estimate of the main components of deep-sea sediments (van der Marel, 1966; Flechig and Kutze, 1973; Fröhlich, 1981, 1982; Pichard and Fröhlich, 1986).

Very few IR spectra of biogenic silica, or even of inorganic glasses, have been yet published (Bolduirev, 1976; van der Marel and Beutelspacher, 1976), probably because the absorption bands are broadened when the particle size of the powdered samples is too large (Farmer and Russell, 1966). However, according to Pichard and Fröhlich (1986), a strict control of the particle size allows the performance of an accurate quantitative analysis. Thus, IR quantitative analysis appears to provide a promising method for the study of the amorphous structure of biogenic silica and for a routine determination in sediments.

MATERIALS

Infrared analyses were performed on the most common biogenic siliceous remains deposited in deep-sea sediments: radiolarian skeletons, diatom frustules and sponge spicules. Sedimentary crystalized silica phases and high-temperature amorphous silica were also analysed for comparison studies on the molecular pattern of biogenic silica. A good definition of this molecular structure is a prerequisite for a quantitative analysis of biogenic silica in deep-sea sediments.

Biogenic silica (opal-A, after Jones and Segnit, 1971)

Radiolarian skeletons were picked out of Quaternary deep-sea surface sediments cored in the Equatorial Indian Ocean. Hexactinellid sponge spicules, up to 300 mm long, of Holocene age, were collected in the Central Indian Basin. Quaternary diatoms were sampled in equatorial and antarctic diatom oozes from the Indian Ocean.

Inorganic amorphous silica

Samples of geyserite, an hydrated amorphous silica phase, of hydrothermal origin (Yellow Stone, USA), and Libyan glass (anhydrous silica glass, likely to be an impactite in origin, from the Libyan Desert) were also analysed.

Crystalline silica

Different hexagonal crystalline phases which are the most common silica minerals in deep-sea sediments, were analysed: a bipyramidal crystal of quartz from Oisans Range (French Alps), chalcedony samples from Oregon (USA) and from Kerguelen Islands (Southern Indian Ocean). Non-hexagonal silica minerals were also studied: opal-CT (using the nomenclature of Jones and Segnit, 1971, 1972) samples (pure opal-CT sand, composed of isolated lepi- spheres, from the upper Cretaceous deposits of the Indre area, France), and a precious opal sample given by the Gallery of Mineralogy, Museum, Paris. All these silica minerals were analysed using X-ray diffraction (XRD) in order to ascertain their crystallinity. Quartz and chalcedony have an identical XRD pattern. The opal-CT XRD pattern ex-
METHOD

Preparation of samples

Samples are mechanically ground with small agate balls in an agate vial under acetone and in a refrigerated area (4°C) in order to prevent heating and structural changes of particles. A particle size of less than 2 μm is required because excessive scattering of IR radiation is observed for larger particles. The size of the particles is constantly controlled on smear slides and under a microscope till the particle size is less than 2 μm. Then the powder is mixed by hand with KBr in an agate mortar for about 7 min. A dilution of 0.2%, or 0.25%, is suitable for common minerals and for sediments. Weighing is performed within a dry atmosphere. A 10⁻² g accuracy is required. After drying the mixture at 110°C over one night, a 300-mg pellet, 13 mm in diameter, is made by pressing the mixture in a vacuum die, with up to 10³ kg cm⁻² of compression.

Spectral parameters (Fig. 1)

Four main absorption parameters are taken into account from the IR spectra:
(1) The wavenumber \( N \) (i.e., the frequency, in cm⁻¹) of the maximum of absorption for the elemental bands of the [SiO₄] tetrahedra. This frequency is related to one, or several, vibration modes of the molecule. (2) The absorbance \( A \) at the frequency \( N \) (i.e., the absorption intensity, a parameter specific to each band). (3) The half-width \( \Delta N \) (i.e., width in cm⁻¹ of an absorption band at half-absorbance). This parameter provides indications concerning the scattering of frequencies near \( N \), at the maximum of absorption. (4) The integrated intensity \( I \) (sum of absorbances) which takes account of the scattering in frequency of the absorbed energy. Assuming a Gaussian distribution of the absorbed energy, symmetrical on both sides of the maximum of absorption, \( I \) is approximately computed from: \( I = \Delta N \cdot A \). When an absorption band is overlapped, as it is for quartz near 800 cm⁻¹ (see further), \( I \) is computed from the half-band that is not overlapped (left or right from \( N \)), and then extrapolated for the whole band.

Quantitative analysis

The absorbance \( A \) is measured for the spectrum in using the empirical method of the baseline (Chester and Elderfield, 1968; Flehmig and Kurtze, 1973). This technique provides a quick graphical method for correcting errors. The baseline is obtained by constructing a virtual spectrum after bypassing the absorption band (Frohlich, 1981; Pichard and Frohlich, 1986). Drawing a tangent to the minima of absorption on both sides of the absorption band can provide a good approximation of the baseline (Fig. 1). The absorbance \( A \) is computed as shown in Fig. 1. The content \( C \) (i.e., mg of a silica phase per mg of total samples analysed) is directly computed from the absorbance \( A \) (see Pichard and Frohlich, 1986). When the particle size is smaller than 2 μm, the absolute error \( \Delta A \) which is a constant for different values of \( C \), depends on the accuracy of the baseline plotting. Thus, the relative error \( \Delta A/A \) increases when the content \( C \) decreases. For instance, the accuracy for the quartz content computed with this method is about 1% for \( C > 0.37 \), and 8% for \( C < 0.06 \) (Pichard and Frohlich, 1986).

Calibration curves of weight (mg) versus absorbance for particular absorption bands are prepared, using pure reference minerals (Fig. 2). Correction of errors due to overlapping bands will be discussed further. For absorption with a low molar extinction coefficient (ε) and/or substantial dilutions, the calibration curve is a straight line which projects to the origin of the coordinate axes (Fig. 2). For \( A > 0.5 \), \( T > 80\% \) or \( T < 20\% \), \( \Delta A/A \) increases quickly. With double-beam spectrophotometers, a simultaneous analysis of two pellets also provides accurate calibration curves (Pichard and Frohlich, 1986).
RESULTS

Within the silicate vibration range (1200–200 cm⁻¹), radiolarian skeletons, diatom frustules, and sponge spicules exhibit infrared spectra, with strictly identical parameters. Thus, the structure of the biogenic silica does not appear to be a characteristic of the nature of the secreting organisms. The IR data can be considered representative of sponge, radiolarian and diatom silica, only when dealing with recent to subrecent material. Further examination of older material shows that slight differences can be observed on the spectra of these different biogenic silica components (Frohlich, work in progress). Hurd and Theyer (1977) have observed substantial changes with age in the physical and chemical properties of biogenic silica from Pacific sediments: this evolution is an indication of structural changes with depth.

Infrared spectra of amorphous silica, either biogenic in origin or chemically precipitated, exhibit only the three IR-active absorption bands of condensed tetrahedra (four-fold coordination of silicon) predicted by the theory (Lecomte, 1949). The weak subsidiary band that is seen at 950 cm⁻¹ (Fig. 3a,b), is assigned to a Si-OH vibration mode (Moenke, 1974). The Si (O–H) stretching mode is seen near 3600 cm⁻¹ (Lecomte, 1949). This very low number of vibration modes is related to the high symmetry (cubic) of the unit-tetrahedron. The regular, three-dimensional reticular setting of [SiO₄] tetrahedra lowers the symmetry and gives rise to translation modes of the lattice. As a consequence, the number of absorption bands increases for quartz and chalcedony (hexagonal silica minerals). The lack of additional bands on the spectra of tetragonal and orthorhombic phases (opal-CT) provides evidence of a bi-dimensional periodicity of the lattices of α-cristobalite and α-tridymite (Frohlich, 1981).

The three elemental bands of the tetrahedral pattern are common to all the silica minerals studied. Changes in the symmetry and in the bridging angle (Si–O–Si) between adjacent tetrahedra, affect the IR parameters: shifting of the frequencies (Table 1), shifting of the half-width, and of the absorbances for the three elemental absorption bands (Table 2).

(1) The 1100-cm⁻¹ band is assigned to a Si–O stretching, triply degenerated vibration mode. The frequency of this band is strongly affected by the surroundings of the unit-tetrahedron (Lecomte, 1949), and then by the structure. Relatively small differences are seen in absorbance (Table 2). Usually, the higher the absorbance, the higher is the crystallinity (i.e., three-dimensional continuity of the lattices). But for crystallized silica, this broad absorption band is regarded as the envelope of several, poorly resolved bands. As a result, ΔN and I (Table 2) are not significant.

(2) The 470-cm⁻¹ band is assigned to a Si–O bending vibration mode. Shifts in frequency (Table 1) are roughly related to the frequency shifts observed for the 1100-cm⁻¹ band. The relatively small

Table 1. Frequencies, in cm⁻¹, of the absorption bands assigned to the three elemental vibration modes of the tetrahedra [SiO₄], and to the Si–OH bonds for various silica polymorphs. (1) Si–O (stretching mode); (2) Si–O (bending mode); (3) Si–O–Si (intertetrahedral bridging bonds); (4) Si–OH (stretching mode); (5) Si–OH (bending mode).

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<td>3640</td>
<td>950</td>
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<td>801</td>
<td>3650</td>
<td>950</td>
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<td>Libyan glass</td>
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<td>473</td>
<td>801</td>
<td></td>
<td></td>
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<tr>
<td>Precious opal</td>
<td>1103</td>
<td>475</td>
<td>793</td>
<td>3640</td>
<td>951</td>
</tr>
<tr>
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<td>477</td>
<td>793</td>
<td></td>
<td></td>
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<tr>
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<td>Quartz</td>
<td>1084</td>
<td>462</td>
<td>798</td>
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Table 2. Spectral parameters for the three elemental bands of their [SiO₄] tetrahedra. \(A_s\) = specific absorbance computed for 1 mg; \(I_s\) = specific integrated intensity computed for 1 mg; \(\Delta N = \) half-width computed for 0.3 mg.

|                  | \(N(\text{cm}^{-1})\) | \(A_s\) | \(I_s\) | \(
\) \(\Delta N(\text{cm}^{-1})\) |
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<tr>
<td></td>
<td>1100</td>
<td>470</td>
<td>800</td>
<td>1100</td>
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<tr>
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<td>520</td>
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<tr>
<td>Precious opal</td>
<td>4.58</td>
<td>2.07</td>
<td>0.359</td>
<td>492</td>
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<tr>
<td>Opal-CT</td>
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<td>2.07</td>
<td>0.515</td>
<td>491</td>
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<tr>
<td>Chalcedony</td>
<td>5.10</td>
<td>1.82</td>
<td>1.140</td>
<td>545</td>
</tr>
<tr>
<td>Quartz</td>
<td>5.14</td>
<td>2.10</td>
<td>1.350</td>
<td>595</td>
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Differences in absorbance (Table 2) are distinctive for amorphous silica (low values) and for crystalline silica (high values). Hexagonal phases exhibit a 470-cm\(^{-1}\) band, sharper (\(\Delta N \approx 31\) cm\(^{-1}\)) than for the other phases (about 50 cm\(^{-1}\)). These particular details are clearly not unique to the molecular pattern.

(3) The 800-cm\(^{-1}\) band is assigned to the pulsation of the bridging oxygen atom in the plane of the Si-O-Si bonds between two adjacent tetrahedra (Lecomte, 1949). The relative motion results in a distortion of the Si-O-Si angle (angle \(\alpha\)) in the direction of its bissectrix (Parke, 1974). The spectra of the hexagonal phases exhibit a doublet at 780 and 798 cm\(^{-1}\). According to theoretical considerations and to infrared reflection data (Lecomte, 1949), the 798-cm\(^{-1}\) band is assigned to the intertetrahedral vibration mode. The 780-cm\(^{-1}\) overlapping band which is absent on the spectra of the other silica polymorphs, is not taken into account for the calculation of the spectral parameters for this vibration mode.

The frequency of this band is distinctive for the amorphous phases (about 800 cm\(^{-1}\)), the hexagonal phases (798 cm\(^{-1}\)), and for the cristobalitic opals (793 cm\(^{-1}\)). The absorbance gradually increases from biogenic silica to quartz: the values observed for quartz are five times higher than for biogenic silica (Figs 2 and 3, Table 2). As seen for the 1100-cm\(^{-1}\) band, this increase is clearly linked to the degree of crystallinity. The substantial changes found for \(\Delta N\) between these two phases (up to 3.5 times: Table 2) are also related to the crystallinity. Thus, only small differences in the integrated intensity \(I\) are seen between the different silica phases: i.e., the total energy involved in the intertetrahedral vibration is nearly the same for all of the tetrahedrally coordinated species. Then, the variations of the angle \(\alpha\) affect the frequencies of the 800-cm\(^{-1}\) band: the variability of the angle \(\alpha\) would produce a frequency scattering of the vibration energy, and therefore, account for the broadening of the 800-cm\(^{-1}\) band for poorly crystallized or amorphous silica minerals.

**Quantitative analysis of biogenic silica**

The amorphous, hydrated silica is easily identified from its IR spectrum. Moreover, owing to the constant molecular structure of the recent siliceous skeletons, quantitative analyses are also available. For older sediments, distinct calibration curves should be established. Chester and Elderfield (1968) and Fröhlich (1981) have experimented with such analysis for deep-sea sediments.

The amount of biogenic silica is accurately computed from the 800-cm\(^{-1}\) band when the rate of quartz is < 5% (Chester and Elderfield, 1968). Overlapping of the 800-cm\(^{-1}\) band by the doublet of quartz at 798 and 780 cm\(^{-1}\) inhibits a direct computation. However, an indirect determination of the biogenic silica content is possible whatever value the quartz ratio is. The quartz percentage may always be computed from its specific band at 693 cm\(^{-1}\) or from the band at 370 cm\(^{-1}\) (see Fig. 3): these bands are rarely overlapping on the spectra related to deep-sea sediments. The contribution of the quartz to the absorbance of the 800-cm\(^{-1}\) band is then easily computed. If we consider that the absorbances at 798 cm\(^{-1}\), and at 800 cm\(^{-1}\), are nearly identical for the biogenic silica, then the biogenic silica content is directly deduced from the residual absorbance obtained in subtracting the quartz contribution.

Some results obtained by the proposed determination of biogenic silica content from artificial quartz-biogenic silica mixtures are displayed in Table 3. The accuracy is lower than for direct measurements, but would be better for deep-sea sediments where the quartz content is commonly lower than 10%.

The IR determination of biogenic silica content becomes more difficult, even occasionally impossible, in the presence of minerals whose spectra include rather strong bands near 800 cm\(^{-1}\); mainly goethite and Fe\(^{3+}\) · Mg\(^{2+}\) or Fe\(^{3+}\) · Fe\(^{2+}\) diotahedral clay minerals (e.g. celadonite, glauconite, nontronite).

**DISCUSSION**

High-temperature vitreous silica, such as Libyan glass, is known to be composed of a [SiO₄] tetrahedra framework. According to Lecomte (1949), and Wong and Angell (1976), this framework consists of discontinuous chains of tetrahedra. The angular value of \(\alpha\) may then fluctuate within the 120°–160° range (Bell and Dean, 1966), even 120°–180° (Taylor, 1972). In contrast, the angle \(\alpha\) is unvarying for crystallized silica phases. From statistical studies of random network models for vitreous silica, it appears that the most common value of \(\alpha\) lies between 140° and 150° (Bell and Dean, 1966). This range includes the angle of highest stability for Si-O-Si bonds (Pauling, 1980), i.e., the quartz angle: 143.6° (L. P. Page and Donnay, 1976), 144° for Li and Ching (1985). According to Mozzin and Warren (1969), the most probable mean angle \(\alpha\) for amorphous silica is 144°. This value is quite close to that of quartz. Hydroxyl ions easily removed on heating, are condensed at the external surfaces of the glasses (Parke, 1974).

Hydrated amorphous silica (here, biogenic silica and geyserite) exhibits a slightly different structure, owing to
the content of OH ions, as shown by the 950-cm\(^{-1}\) band (Fig. 3). The integrated intensity I of the 800-cm\(^{-1}\) band is the lowest value calculated for both biogenic silica and geyserite (Table 2). This lowering of the total energy (roughly 25%) of the intertetrahedral Si-O-Si vibration, and the presence of a rather intense band at 950 cm\(^{-1}\) (Si-OH bond), are the result of a high level of OH for O substituents at the apex of tetrahedra, possibly one in four. In the case of the discontinuous chain network of biogenic silica, these substitutions imply the formation of short chains of tetrahedra, consisting of only a few tetrahedra: less than 10 according to Wong and Angelı́ (1976), three or six according to Lecomte (1949). Thus, hydroxyl ions do not occur mainly on the surface of the particles, as previously assumed (Juillet, 1980).

The total potential energy slowly varies with the angle \(\alpha\) (Gibbs, 1982), and it has been demonstrated that the frequency of the Si-O-Si vibration mode increases when the angle \(\alpha\) decreases (Brawer, 1975). Hence, the frequency variation observed between \(\alpha\)-tridymite and amorphous silica (Table 1) most probably depends on the variation of the angle \(\alpha\). A linear relationship is actually observed for \(\alpha\)-tridymite, \(\alpha\)-cristobalite and quartz, between the frequency of the Si-O-Si band and sin \(\alpha\) (Fig. 4). Then \(\alpha\) is empirically assessed from Fig. 4 for other silica phases: the angle \(\alpha\) for the amorphous, biogenic silica is 146°6 with a 800-cm\(^{-1}\) frequency, and 146°5 for opal-CT with a 793-cm\(^{-1}\) frequency. Thus, according to infrared data, the most frequent angle \(\alpha\) for biogenic silica, and generally speaking for silica glass, is lower than previously assumed (153°—Bell and Dean 1972; 152°—Da Silva et al., 1975; 144°—Moizzi and Warren, 1969), even slightly lower than for quartz. According to the relationship established by Louis-nathan and Gibbs (1972), the Si-O bond length computed for biogenic silica in this study is 1.62 Å, when \(\alpha = 142°6\). This value is in better agreement with the theoretical values expected for this bond length, than those computed from larger angles (Vieillard, 1986). The density and the refractive index are related to the value of the angle \(\alpha\) for crystallized silica. But for biogenic silica, in spite of a rather small angle \(\alpha\), the discontinuous, inhomogenous molecular structure is consistent with a low density and a low refractive index (Table 4).

**CONCLUDING REMARKS: GEOLOGICAL IMPLICATIONS**

Owing to the unvarying molecular structure of biogenic silica, IR spectra are not distinctive for the various organisms collected from recent deep-sea sediments. This structure consists of short chains including only a few tetrahedra (probably less than 10) and bounded with OH ions, each tetrahedron probably having one hydroxyl. In the model proposed, the mean values for the Si-O bond lengths and for the bridging Si-O-Si angle, both quite close to those of quartz, are the highest and lowest of the four-fold coordinated silica polymorphs respectively. The hydration of the biogenic silica and the low value of the mean angle \(\alpha\) probably affect its physical and chemical properties and would play a decisive role in the sedimentary and diagenetic processes.

<table>
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<tr>
<th>(n)</th>
<th>(d\ A)</th>
<th>(\alpha)</th>
<th>(N\ \text{cm}^{-1})</th>
<th>(D\ \text{(g cm}^{-3})</th>
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<td>1.62(^{(1)})</td>
<td>142°6(^{(4)})</td>
<td>800(^{(4)})</td>
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<tr>
<td>Quartz</td>
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<td>1.609(^{(1)})</td>
<td>143°7(^{(1)})</td>
<td>798(^{(4)})</td>
</tr>
<tr>
<td>Opal-CT</td>
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<td>1.607(^{(2)})</td>
<td>147°9(^{(2)})</td>
<td>793(^{(3)})</td>
</tr>
</tbody>
</table>

\(^{(1)}\)Vieillard (1986); \(^{(2)}\)average value computed from \(\alpha\)-cristobalite and \(\alpha\)-tridymite data quoted by Vieillard (1986); \(^{(3)}\)Le Page and Donnay (1976); \(^{(4)}\)this work.

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**Table 3. Quantitative analysis of quartz/biogenic silica mixtures.** (1) % of biogenic silica weighed in the mixture; (2) % of biogenic silica computed on the IR spectra by subtracting the quartz contribution to the 800-cm\(^{-1}\) band; (3) % of quartz weighed in the mixture; (4) % of quartz computed from the 693-cm\(^{-1}\) band; (5) % of quartz computed from the 370-cm\(^{-1}\) band.

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<tr>
<td>95</td>
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<td>100</td>
<td>100.0±2.0</td>
<td>100.10±1.0</td>
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**Fig. 4. Frequency of the intertetrahedral vibration as a function of the angle \(\alpha\) (Si-O-Si).** \(T = \alpha\)-tridymite (data from van der Marel and Beutelspacher, 1976; and from Vieillard, 1986); \(C = \alpha\)-cristobalite (data from van der Marel and Beutelspacher, 1976; and from Etchepare et al., 1978); \(Q = \) quartz (data from this work; and from Le Page and Donnay, 1976).

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**Table 4. Parameters related to the Si-O-Si bond.** \(n = \) refractive index\(^{(1)}\); \(d\ A = \) length of the Si-O bond\(^{(2)}\); \(\alpha = \) mean Si-O-Si angle; \(N\ \text{cm}^{-1} = \) maximum of absorption for the Si-O-Si vibration mode; \(D = \) density.

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<th>(n)</th>
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**TELL RESEARCH**
Sedimentary processes

The rather high solubility of the frustules just after the diatom depth, and their dissolution at the sediment/water interface probably arises from their molecular structure. Releasing bonds, and then starting a depolymerization of tetrahedra, the decay of the silica-bound proteins is most likely responsible for this increase in solubility. This process must become partly inhibited when siliceous skeletons accumulate, probably by interaction of hydroxyl ions with the free apex of the [SiO₄] tetrahedra.

Diagenesis

As the values of angle $\alpha$ are quite close for both quartz and biogenic silica, the energy required for converting the biogenic amorphous frame into a quartz network, would be low. This mineralogical conversion must be greatly facilitated if we consider that the elemental chains of the biogenic silica framework include a low number of tetrahedra. Such a solid–solid conversion would account for the chaledony-replaced radiolarian skeletons and sponge spicules which usually occur in cherts and flints. On the other hand, a solid–solid transformation from amorphous silica to opal-CT is inconsistent with their structural parameters: this hypothetical transformation would occur at the values of quartz, for the Si–O–Si angle and Si–O bond length, which are the most stable values (Pauling, 1980).

These inferences lead to further possibilities in the study of the formation of cherts. As for biogenic silica, the IR determination of opal-CT and chaledony content in cherts should result in a discrimination between distinct diagenetic processes.

ACKNOWLEDGEMENTS

The author is grateful to P. Clement for providing silica samples, and to Professor T. Monod, Membre de l'Institut, for valuable discussions and for providing many specimens of various silica phases. Dr J.P. Cautel has gathered a great amount of radiolarian skeletons and has cooperated during the sampling in the field and experimentation in the laboratory. I am especially grateful to him for his assistance and for discussions and improvements to the manuscript. I thank Professors H. Chamley and J. Decourt, and Drs M. Recq and B.C. Schreiber for their critical reviews and valuable suggestions for improvements to this paper.

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Received 5th February 1989,
Accepted 4th June 1989