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A solid state ^{29}Si nuclear magnetic resonance study of opal and other hydrous silicas

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Abstract

A range of opal and natural silica samples, as well as calcined flint and fused silica, were examined by solid state ^{29}Si nuclear magnetic resonance (NMR). The chemical shifts from 1-pulse magic angle spinning (MAS-NMR) spectra do not distinguish among opal-AG, opal-C, or opal-CT. However, the ^{29}Si line widths decrease with increasing structural order—opal-AG 9.8–9.9 ppm (two examples), opal-CT 6.0–7.5 ppm (12 examples), and opal-C $<$ 5 ppm (one example)—and may be used to discriminate among these three phases. Most samples show silanol (Q^3) ^{29}Si resonances in the ^{29}Si-{^{1}H} cross-polarization (CP) MAS-NMR spectra, but there is no evidence of resonances due to $Si(OH)_2$ (Q^2) units. For eight chalcedony and flint samples, in which the silanol groups are believed to be on the silica surface, the Q^3 resonances are in the range $\delta = -98.5$ to -99.5 ppm, and the difference in chemical shift between the Q^3 and Q^4 resonances is in the narrow range of 7.8–8.1 ppm. The chemical shift range for Q^3 resonances in the less well resolved spectra of the 15 opal samples is $\delta = -101.0$ to -103.7 ppm, and the corresponding $Q^3 - Q^4$ difference is in the range 9.0–12.5 ppm. These opal samples may contain both internal and surface Q^3 units, but in view of the increased structural disorder for the opal samples, the difference in their chemical shift parameters compared with the chalcedony and flint samples cannot be used as a basis for establishing the presence or absence of internal silanol groups in opal.

Introduction

Opal is a compact form of natural hydrous silica that occurs in many sedimentary and diagenetic environments. This study seeks to use ^{29}Si MAS-NMR to probe the physical and chemical binding of H_2O or OH in the silica structure. Opal has been classified by Jones and Segnit (1971) according to the nature of its X-ray diffraction pattern. Opal-C yields a sharp X-ray diffraction pattern for α-cristobalite and minor evidence of tridymite; opal-CT yields a pattern of broadened but well-defined peaks for α-cristobalite with varying degrees of stacking disorder leading to maxima attributable to tridymite; and opal-A is amorphous and yields a diffuse band. Jones and Segnit (1971) also considered an H_2O content greater than 1 wt% to be essential for opal.

In a combined X-ray, chemical, thermoanalytic, and quantitative infrared (IR) spectroscopic study, Langer and Flörke (1974) further classified amorphous opal as opal-AN with a glasslike network structure (including hyalite) and opal-AG with a gel-like structure (including many precious and potch opal samples). In that study, they proposed a model for H_2O and OH incorporated into opal-AG that is based upon a particulate structure for the opal of primary and secondary spheres (Jones et al., 1964; Darragh et al., 1966). The model proposes that molecular H_2O occurs in two distinct environments, and silanol (SiOH) groups also occur in two environments but not as $Si(OH)_2$ groups as proposed earlier by Hockey and Pethica (1961). On the basis of ^{1}H/^{2}H isotope exchange experiments on Monterey diatomite (opal-A), Knauth and Epstein (1982) identified five forms of H_2O or OH based on hydration state and isotope exchange properties; however, a detailed physico-chemical model for H_2O or OH incorporation was not proposed. In related studies employing IR spectroscopy, both structural SiOH and molecular H_2O were identified in chalcedony (Frondel, 1982) and in chalcedony and opal-C from Brazilian agate geodes (Graetsch et al., 1985). In a subsequent investigation

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TABLE 1. Location and description of opal and silica samples

	Specimen	Location	Color
S1	opal	Australia, location unknown	yellow-brown, black
S2	wood opal	U.S.A., location unknown	brown
S3	"Beltane" opal	Napa Valley, Sonoma, California, U.S.A.	white
S4	wood opal	Location unknown	brown
S5	quartz/opal	Cyprus	white
S6	Fire opal	Mexico, location unknown	orange, clear
S7	flint	Hornchurch, Essex, England	gray-brown
S8	opal	St. Austell, Cornwall, England	white, translucent
S9	chalcedony	Dubai, location unknown	white opaque
S10	"semi" opal	Nevada, U.S.A.	green, translucent
S11	wood opal	U.S.A., location unknown	white
S12	wood opal	U.S.A., location unknown	light brown
S13	wood opal	U.S.A., location unknown	white
S14	flint	Guildford, Surrey, England	light gray
S15	opal	Turin, Italy	translucent yellow/light brown
S16	opal	Le Puy, France	lustrous, resinous brown
S17	opal	Location unknown	pinky/red and cream
S18	polyhedroid quartz	Paraiba State, Brazil	milky white
S19	calcined flint	Blue Circle Cement Co., England	white opaque
S20	chalcedony	Huel Gout, France	white opaque
S21	quartz/opal	Sedgewick Holstein	gray
S22	opal	Australia, location unknown	pale pink chips, some milky
S23	fused silica (FSR)	Tilcon Industrial Minerals, Staffs., England	colorless
S24	opal/chalcedony	Unknown	pale cream/white
S25	opal	St. Austell, Cornwall, England	off white, lustrous, slight iridescence
S26	potch opal	Williamstown, Australia	honey colored, vitreous luster
S27	opal	Idaho, U.S.A.	white, some Fe oxide
S28	opal	Nebraska, U.S.A.	white, pale blue areas, some white spots
S29	rock crystal	Brazil	clear, colorless

of structural defects in microcrystalline silica, Graetsch et al. (1987) summarized the above results and related studies of the role of H_2O and OH in opal, chalcedony, flint, moganite, and quartz. It is clear that knowledge of the precise nature of H_2O and OH in natural hydrous silicas is essential to an understanding of their genesis and their physical and chemical properties.

Solid state NMR is now established as an important technique for the study of bonding in minerals that exhibit a wide range of structural ordering from amorphous to highly crystalline. In particular, recent advances in the methodology of ^{1}H NMR allow the identification of OH groups in mineral samples (Eckert et al., 1988; Yesinowski et al., 1988; Bronnimann et al., 1988), and high resolution ^{29}Si NMR provides information about the substitution at Si in polymeric silicate structures (Engelhardt and Michel, 1987; Kirkpatrick, 1988). Additionally NMR experiments using ^{29}Si-{^{1}H} cross polarization (CP), which result in enhanced ^{29}Si resonances from Si close to a proton in the silicate structure, have attempted to quantify the surface OH contents of silica gels (e.g., Sindorf and Maciel, 1983). In view of the above NMR results, it is surprising that de Jong et al. (1987) did not obtain any evidence for the existence of silanol groups in their ^{1}H and ^{29}Si NMR study on a range of opal-A and opal-CT samples that contained up to ca. 8 wt% H_2O. Graetsch et al. (1990) reported a ^{29}Si MAS-NMR study of short range order in two amorphous opal samples and one opal-CT sample. These studies prompt our report of a ^{29}Si NMR study of opal and other naturally occurring hydrous silicas.

EXPERIMENTAL

Chemical analysis

Major elements. The samples were prepared for solution by initial crushing in a Sturtevant jaw crusher and subsequent grinding in a Fritsch Pulverisette (with agate mortar and pestle) until the powder passed a 63-μm sieve. Dissolution of the samples closely followed the method of Walsh and Howie (1980), which is based on an HF/$HClO_4$ acid attack. All sample solutions were analyzed for major elements (except silica) using a Philips PV 8060 simultaneous inductively coupled plasma emission spectrometer (ICPS).

H_2O. Total H_2O content of the samples was determined gravimetrically by the method of Shapiro and Brannock (1955), whereby the sample is fused with anhydrous sodium tungstate and the expelled H_2O is absorbed on a filter paper that is then weighed.

Silica. The silica content was calculated as the difference between 100% and the sum of the percentages of the remaining major elements including H_2O.

Mineralogical analysis

All samples were examined as powders using X-ray diffraction (XRD) (Philips PW 1743 generator using PW 1390 channel control, Cu*Kα* radiation, graphite monochromator) and a 1°/min scan rate.

NMR spectroscopy

Spectra of ^{29}Si MAS-NMR were recorded at 79.5 MHz with a Bruker WH-400 spectrometer and at 59.6 MHz

TABLE 2. Minerals* of opal and silica samples from X-ray powder patterns

Sample	Quartz ($\Delta 2\theta$)**	Cristobalite	CT	Kaolinite	Calcite	Amorphous	Class†
S1		X					opal-CT
S2	X (0.25)	trace					Ch
S3	X	X		X			opal-C
S4			X			X	opal-CT
S5	X (0.30)	trace			X		Ch
S6	trace		X				opal-CT
S7	X (0.35)	trace					Fl
S8			X				opal-CT
S9	X (0.28)	trace					Ch
S10			X				opal-CT
S11	X (0.50)	X (ca. 30%)					Ch-opal-CT
S12	X (0.45)	X (ca. 30%)					Ch-opal-CT
S13	trace		X				opal-CT
S14	X (0.33)						Fl
S15			X				opal-CT
S16	trace		X				opal-CT
S17	trace	trace	X				opal-CT
S18	X (0.17)						Q
S19	trace	X					Cr
S20	X (0.17)		trace				Q
S21	X (0.20)	X (ca. 10%)			trace		Ch-opal-CT
S22						X	opal-AG
S23						X	
S24	trace		X				opal-CT
S25			X				opal-CT
S26	trace		X				opal-CT
S27						X	opal-AG
S28	X (0.45)	X (ca. 30%)					Ch-opal-CT
S29	X (0.17)						Q

* The symbol X indicates the detection of a significant amount of the mineral phase indicated.
** Full width at half maximum of the $11\bar{2}0$ reflection.
† Our classification of the minerals: Ch = chalcedony, Q = quartz, Fl = flint, Cr = cristobalite.

using Bruker MLS-300 spectrometers. Rotational frequencies were in the range 3–4 kHz, and the 1-pulse data acquisition sequence, using 90° (4 μs) flip angle pulses, was repeated typically every 25 s to accumulate ca. 300 scans. For ^{29}Si spectra measured with the ^{29}Si-{^{1}H} CP technique (Pines et al., 1972a, 1972b, 1973; Fyfe, 1983), the ^{29}Si-{^{1}H} contact time was typically 10 ms. All ^{29}Si NMR chemical shifts are referenced to external liquid tetramethylsilane (TMS). We have not attempted to interpret the 1-pulse MAS ^{29}Si spectra in a quantitative manner because this would require the use of repetition times much longer than the ^{29}Si spin-lattice relaxation times (T_1). These relaxation times may vary in the range 10^{-3} to 10^3 s (Engelhardt and Michel, 1987), and measurements of T_1 are beyond the scope of this study.

RESULTS

Samples, X-ray diffraction, and chemical analysis

The samples used in this study and their origins are described in Table 1. The descriptions, e.g., wood opal, are not rigorous classifications but are the descriptive names under which the samples were obtained; indeed, Scurfield and Segnit (1984) have shown that wood opal may variously be composed of opal-A, opal-CT, chalcedony, quartz, quartz + chalcedony, or opal + chalcedony. The calcined flint sample (S19) is predominantly α-cristobalite (Frondel, 1962). Polyhedroid quartz, an unusual form, has been described by England (1976), Gunther (1982), and Cassedanne (1983).

The results of the analysis of the XRD patterns for the powdered samples are summarized in Table 2 (see also Fig. 1); assignments for peaks caused by quartz, cristobalite, kaolinite, and calcite are made by comparison with standard patterns (ASTM Standard Data Cards). None of the samples gives a well-defined tridymite pattern, but many samples do display the somewhat broadened pattern shown by Jones and Segnit (1971) to be characteristic of opal-CT. The main features of the opal-CT pattern are three peaks with d values near 2.5, 4.1 (major peak), and 4.3 Å; the opal-CT samples studied in this work give peak maxima for the major peak at 4.08 (S1), 4.09 (S6, S8, S13, S24, and S26), 4.10 (S4, S15, and S25), and 4.13 Å (S10 and S16). Sample S3 (Fig. 1), in addition to kaolinite (not shown in Fig. 1) and quartz-like impurities, has a relatively sharp major peak at 4.06 Å with minor peaks at 2.85 and 3.15 (cristobalite) and 2.98 and 3.25 Å (tridymite). The tridymite peak at 4.3 Å is relatively more intense than in the opal-C example given by Jones and Segnit (1971), but it is much less intense than in the other opal-CT samples. We therefore classify S3 as opal-C. Graetsch et al. (1985) summarized evidence that chalcedony is a fibrous quartz containing 1–2 wt% H_2O and subsequently Graetsch et al. (1987) showed that the full width at half maximum ($\Delta 2\theta$) of certain XRD reflections is greater for chalcedony than for quartz. We have mea-

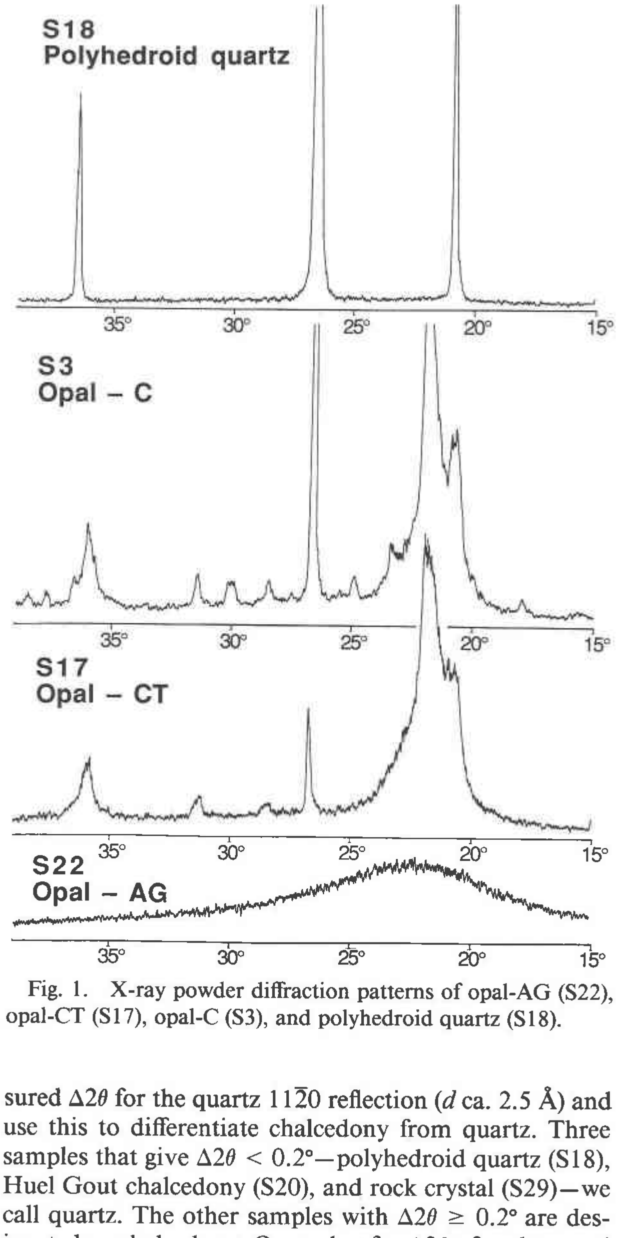

Fig. 1. X-ray powder diffraction patterns of opal-AG (S22), opal-CT (S17), opal-C (S3), and polyhedroid quartz (S18).

sured Δ2θ for the quartz $11\bar{2}0$ reflection (d ca. 2.5 Å) and use this to differentiate chalcedony from quartz. Three samples that give Δ2θ < 0.2°—polyhedroid quartz (S18), Huel Gout chalcedony (S20), and rock crystal (S29)—we call quartz. The other samples with Δ2$\theta \geq$ 0.2° are designated as chalcedony. Our value for Δ2θ of rock crystal is greater than the 0.07° of Graetsch et al. (1987), and we attribute this to the coarser particle size of our samples.

The classification of the mineral phases in Table 2 falls broadly into three groups—the quartz-like materials (including chalcedony and flint), cristobalite, and opal—and we use these classifications as a basis for the discussion of the ^{29}Si NMR spectra.

Samples that are not composed of more than one mineral (i.e., all except S3, S5, S20, and S21) show clear trends with regard to total H_2O content (Table 3). The opal-CT samples (S1, S4, S6, S8, S10, S13, S15, S16, S17, S24, S25, and S26) all have H_2O contents in the range 5.0–9.3 wt%, and the two opal-AG samples, S22 and S27, have 15.31 and 6.38% H_2O, respectively. There is no distinction between opal-CT and opal-AG on the basis of total H_2O content alone, in accord with the findings of Langer and Flörke (1974). Our classification of S3 as opal-C is substantiated by the H_2O content (4.66%) and the findings of Graetsch et al. (1987) that opal-C contains from 1 to 4 wt% H_2O, whereas opal-CT has from 5 to 10 wt%. The flint and chalcedony samples (S2, S7, S9, and S14) contain 1.3–1.8% H_2O, in agreement with Graetsch et al. (1987). Polyhedroid quartz (S18), calcined flint (S19), and fused silica (S23) all contain <0.4 wt% H_2O. As expected, there was no detectable H_2O in the rock crystal sample (S29).

Concentrations of the major and trace element analyses are available in Table 4.[1]

NMR spectroscopy and peak assignments

The ^{29}Si NMR spectra were obtained using three different spectrometers, and the reproducibility of the chemical shifts (δ, referenced to the external TMS standard) is ca. ±0.2 ppm on the different spectrometers using the sharp resonances of polyhedroid quartz (S18), calcined flint (S19, α-cristobalite), and kaolinite in the beltane opal sample (S3). These ^{29}Si chemical shifts (Table 3) are in excellent agreement with published data on quartz and cristobalite (Lipmaa et al., 1980; Smith and Blackwell, 1983) and kaolinite (Barron et al., 1983). For two of the samples, ^{1}H decoupling improves the resolution in the 1-pulse ^{29}Si spectrum (Fig. 2), and this is discussed below.

The ^{29}Si NMR data from the experiments without cross polarization are summarized in Table 3. In addition, there are both new and enhanced resonances in the ^{29}Si-{^{1}H} cross-polarization spectra (Table 5). With the exception of the kaolinite resonances (δ = ca. −91 to −92 ppm) from samples S3 and S20, the ^{29}Si chemical shifts in Tables 3 and 5 may be grouped into three regions: $\delta = -98.5$ to -104.2 ppm, $\delta = -107.1$ to -108.6 ppm, and $\delta = -109.0$ to -114.3 ppm. Those resonances in the highest frequency (less negative) region generally appear as shoulders on the main lower frequency resonances. Assignment of resonances in the three regions is made by comparison with published data (see, e.g., Engelhardt and Michel, 1987; Kirkpatrick, 1988). The highest frequency region includes silanol (Q^3) units. This assignment is consistent with the strong enhancement of these resonances in the CP-MAS ^{29}Si spectra. In addition, the spectrum of one opal sample, S27, measured with different contact times shows the expected relative enhancement of the Q^3 resonance at shorter contact time (Fig. 3). (See, e.g., Maciel and Sindorf, 1980; Farnan et al., 1987; Dessau et al., 1987.) These results reinforce the argument, presented by Maciel and Sindorf (1980), that the higher frequency resonances are caused by Si in a Q^3 unit that has proton two bonds removed, in contrast to the Q^4 units from which the protons are more remote and hence have a reduced rate of cross polarization.

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[1] To receive a copy of Table 4, order Document AM-91-478 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036. Please remit $5.00 in advance for the microfiche.

TABLE 3. ^{29}Si MAS-NMR data* (without cross polarization) for opal and silica samples

Sample	Total H_2O (wt%)	Chemical shift (ppm)			$\Delta\nu_{1/2}$ (ppm)‖
S1**	5.02	−107.3‡	−111.6		6.0
S2**	1.53	−107.2			1.6
S3** †	4.66	−91.8§	−107.9‡	−112.2	5.0
S4**	7.01	−102.6‡	−112.7		7.8
S5**	2.26	−107.3			2.0
S6**	9.16	−104.2‡	−112.4		6.9
S7**	1.46	−107.3			2.3
S8**	7.43	−111.5	−112.6		6.6
S9**	1.77	−107.2			1.8
S10**	8.47	−112.6	−114.0		6.7
S11**	4.13	−107.3	−111.6		8.1
S12**	4.12	−107.2	−110.6		7.4
S13**	6.17	−112.8			7.0
S14**	1.32	−107.2			2.3
S15†	7.00	−112.8			6.1
S16** †	6.77	−104.1‡	−108.1‡	−113.0	6.3
S17** †	8.22	−101.2‡	−114.3		7.5
S18** †	0.22	−107.2			2.0
S19**	0.26	−109.0			1.1
S20†	3.54	(−91.5, −90.9)§		−107.7	1.0
S21**	4.13	−107.3	−112.5		12.1
S22†	15.31	−101.7	−111.5		9.8
S23†	0.40	−110.6			12.4
S24†	8.32	−112.7			6.0
S25†	9.28	−112.6			6.0
S26**	8.35	−112.4			6.8
S27**	6.38	−101.6	−111.7		9.9
S28**	6.82	−107.4	−112.6‡		1.7
S29†	0.00	−107.2			0.9

* Chemical shifts are in ppm to low frequency of external liquid tetramethylsilane reference.
** Spectra recorded with high power ^{1}H decoupling.
† Spectra recorded without high power ^{1}H decoupling.
‡ This indicates minor resonances which usually appear as a partially resolved shoulder on the main peak.
§ This resonance is due to clay.
‖ Full width of main resonance at half height.

The signals in the region −107.1 to −108.6 ppm are relatively sharp and are readily assigned to Q^4 units in quartz or the quartz-like structures of chalcedony or flint. Samples S19 (calcined flint, α-cristobalite, 0.26% H_2O), S23 (fused silica, 0.4% H_2O), and S29 (rock crystal, quartz, 0.0% H_2O) yield no detectable ^{29}Si-{^{1}H} CP-MAS-NMR signal under the same conditions as employed for the other samples. Polyhedroid quartz (S18, 0.22% H_2O) did yield very weak CP-MAS signals at $\delta = -98.5$ and −107.3 ppm because of Q^3 and Q^4 units. The extremely weak Q^4 signal for S20 and the absence of a Q^3 signal reinforces our earlier conclusion that this "chalcedony" sample is a mixture of quartz and kaolinite and that the H_2O present is associated with the clay. All other samples that are classified as chalcedony yield much stronger signals in the −107 to −108 ppm region of the CP-MAS spectra.

Those signals in the region −109.0 to −114.3 ppm (except α-cristobalite, S19) are quite broad with $\Delta\nu_{1/2}$ = 5.0 to 12.4 ppm. The fused silica (S23) spectrum with $\delta = -110.6$ ppm and $\Delta\nu_{1/2} = 12.4$ ppm agrees closely with that found by Murdoch et al. (1985) for silica glass ($\delta = -110.9$ ppm, $\Delta\nu_{1/2} = 13.2$ ppm). The remaining samples with resonances in this low frequency region are those that were shown by XRD analysis to contain more than a trace of opal-AG, opal-C, or opal-CT (Table 2). The ^{29}Si spectrum of tridymite comprises overlapping resonances (Smith and Blackwell, 1983) with the most intense having chemical shifts $\delta = -109.3$, −110.7, and −114.0 ppm. The ^{29}Si spectra from samples classified mainly as opal-CT (S1, S4, S6, S8, S10, S13, S15, S16, S17, S24, S25, and S26) have quite broad ($\Delta\nu_{1/2}$ = 6.0 to 7.5 ppm) featureless resonances with maxima in the region δ = −111.6 to −114.3 ppm, and they do not appear to be composed of superimposed well-defined cristobalite and tridymite resonances. The full range of ^{29}Si peak maxima that we find (−110.6 to −114.3 ppm) for opal-CT considerably extends the range (−111.9 to −112.4 ppm) reported by de Jong et al. (1987) and Graetsch et al. (1990).

Samples S3 and S20 contain significant Al (5.32 and 9.84 wt% Al_2O_3, respectively), and because these samples show strong kaolinite ^{29}Si resonances, the bulk of this Al is surely associated with the kaolinite. All other samples contain much less Al, and this probably occurs as impurities rather than as structural Al within the bulk silicate structure. If the Al did occur as next-nearest neighbors to Si, e.g., forming Q^4 (1Al) units, the ^{29}Si resonance would be expected to have a chemical shift similar to that from Q^3 units (Engelhardt and Michel, 1987), but the Q^4 (1Al) would not be enhanced in the ^{29}Si{^{1}H} CP-MAS spectra.

Spectra of 1-pulse MAS and CP-MAS ^{29}Si of S11 (a wood opal sample) were measured after heating the sam-

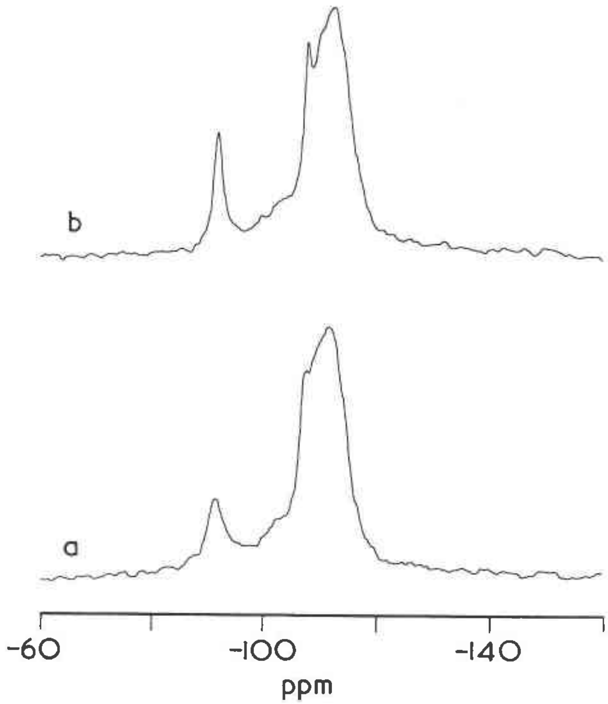

Fig. 2. Spectra of ^{29}Si MAS-NMR (MSL-300) of Beltane opal (S3); a = with MAS only and b = with both MAS and high power ^{1}H decoupling.

Table 5. Additional and enhanced high frequency ^{29}Si resonances in CP-MAS spectra

Sample	Chemical shift (ppm)*	Calculated Q^3 chemical shift
S1	−101.1, −108.6, −111.8	−98.0 to −106.8
S2	−99.2, −107.1	
S3**	−91.4†, −102.3	−99.1 to −106.9
S4	−101.0, −103.7, −111.3, −113.0	−98.2 to −108.8
S5	−99.5, −107.3	
S6	−102.9, −111.7	−98.4 to −108.1
S7	−99.2, −107.3	
S8	−102.0, −112.6	−98.7 to −108.1
S9	−99.1, −107.3	
S10	−101.8, −110.1, −112.6	−100.1 to −109.6
S11	−99.3, −107.7	
S12	−99.5, −107.6	
S13**	−101.6, −103.5, −107.8 to −113.6	−98.7 to −108.5
S14	−99.4, −107.5	
S15**	−102.6, −108.9 to −116.1	−99.2 to −108.1
S16**	−102.0, −107.2 to −112.7	−99.3 to −108.4
S17	−101.8, −103.5, −108.9, −111.6	−100.0 to −110.3
S18	−98.5‡, −107.3‡	
S20	(−91.5, −90.9)†, −107.2‡	
S21	−101.3, −107.5 to −114.5	
S22	−100.2, −101.8, −111.3	−96.0 to −108.6
S24**	−102.9	−99.1 to −107.9
S25	−102.9, −112.9	−99.0 to −107.8
S26	−101.9, −109.9	−98.4 to −108.0
S27	−99.5, −111.7	−96.2 to −108.9
S28	−99.5, −107.5	

* Chemical shifts are in ppm to low frequency of external liquid tetramethylsilane reference.

** Very broad spectrum covering the region ca. −9610–116 ppm.

† This resonance is due to clay.

‡ This resonance is very weak.

ple at 160, 360, and 1150 °C for 8 h. The 1-pulse spectra (Fig. 4, sections a–c) are essentially the same, showing a resonance at $\delta = -107.3$ because of a quartz-like Si environment (probably chalcedony) and a broader resonance at $\delta = -111.6$ ppm owing to opal-CT. After heating at 1150 °C, however, the spectrum (Fig. 4, section d) is a single resonance ($\Delta\nu_{1/2}$ 4.5 ppm) at $\delta = -110.5$ ppm, consistent with a significant degree of recrystallization of the sample to cristobalite (Wahl et al., 1961). The CP-MAS ^{29}Si spectra of these samples show minor changes on heating at 360 °C (Fig. 4, sections e–g), but no CP-MAS ^{29}Si spectrum was obtained for the sample heated to 1150 °C. The spectrum before heating (Fig. 4, section e) shows ^{29}Si resonances at −99.3 (silanol Q^3) and −107.7 ppm (Q^4). After heating at 160 °C to remove most surface molecular H_2O (Graetsch et al., 1985; Iler, 1979), the spectrum is largely unchanged (Fig. 4, section f). The sample heated at 360 °C (Fig. 4, section g) yields a slightly reduced Q^3 resonance at −99.3 ppm and also a weaker signal at −102.5 ppm.

Discussion

Si structural environments

The bulk Q^4 ^{29}Si resonances (Table 3) from the opal samples reflect short range structural order (de Jong et al., 1987), and the line widths are best considered as arising from Si environments with a range of Si-O-Si angles. Various studies that relate bond angles and distances with ^{29}Si chemical shifts have been summarized by Oestrike et al. (1987), Oestrike and Kirkpatrick (1988), and Sherriff and Grundy (1988). Using the corrleation assembled by Oestrike et al. (1987) between ⟨Si-O-Si⟩ bond angle for Q^4 (0Al) sites and ^{29}Si chemical shift, the opal ^{29}Si shifts (−110.6 to −114.3 ppm) indicate mean ⟨Si-O-Si⟩ angles in the range 148–153°. The ^{29}Si chemical shifts of the opal-C and opal-AG samples are in the same range as the opal-CT samples and, thus, there is no differentiation among the opal classes based on chemical shift alone. However, increasing line widths ($\Delta\nu_{1/2}$) for the Q^4 resonances indicate a greater distribution of ⟨Si-O-Si⟩ angles for the less ordered samples, and our data show that we can group the opal samples in this way, i.e., opal-C $\Delta\nu_{1/2}$ = 5.0 ppm, opal-CT 6.0 to 7.5 ppm, opal-AG 9.8 to 9.9 ppm.

H_2O and OH environments in opal

The model proposed by Langer and Flörke (1974) for water incorporation in opal-AG is a useful reference for discussion of our ^{29}Si{^{1}H} CP-MAS results. In that model, molecular H_2O can occur as isolated molecules trapped within the silicate matrix (e.g., 2.0 wt%) or as H-bonded liquidlike H_2O (e.g., 3.1 wt%) on the surfaces of silicate spherulites. Chemically bound H is present as silanol (Q^3) groups. These silanol groups may be on the surfaces of the spherulites (e.g., 0.5 wt%) and therefore extensively H bonded, or they may be internal, i.e., within the silica matrix (e.g., 0.4 wt%) and more weakly H bonded. It is likely that the enhanced ^{29}Si Q^3 and Q^4 resonances in the

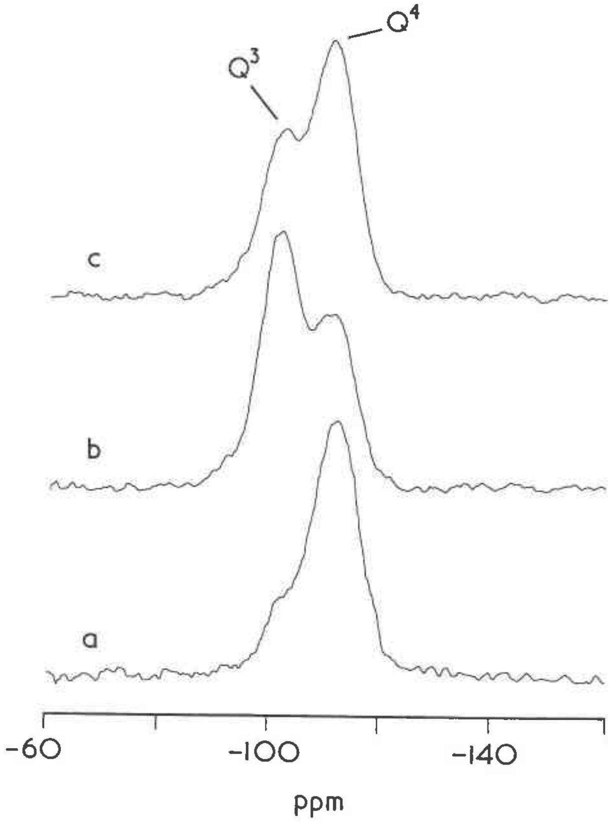

Fig. 3. Spectra of ^{29}Si NMR (MSL-300) of opal sample S27; a = with MAS and high power ^{1}H decoupling, b = with MAS + decoupling + CP with 1-ms contact time, and c = with MAS + decoupling + CP with 4-ms contact time.

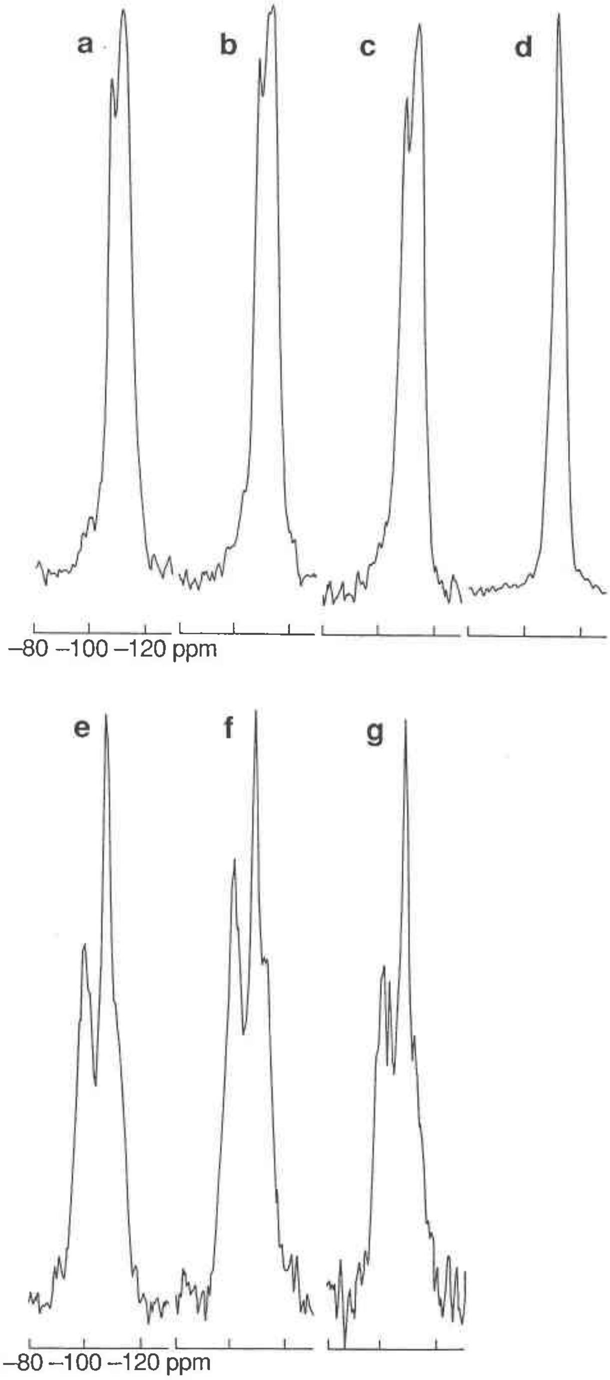

Fig. 4. Spectra of ^{29}Si MAS-NMR of wood opal (S11); a–d = with MAS only and e–g = with CP-MAS and 10-ms contact time. a and e before heat treatment, b and f after heating at 160 °C for 8 h, c and g after heating at 360 °C for 8 h, and d after heating at 1150 °C for 8 h.

CP-MAS spectra result from the proximity of the silanol protons rather than the molecular H_2O (see for example Farnan et al., 1987). This conclusion is reinforced by the retention of the Q^3 and Q^4 resonances in the CP-MAS spectrum of wood opal S11 after prolonged heating at 360 °C (Fig. 4, section g). At this temperature, most molecular H_2O will have been removed (Langer and Flörke, 1974). The remaining question concerns the possibility of distinguishing between surface and internal silanol groups from our ^{29}Si NMR data. Typical ^{29}Si Q^3 chemical shifts have been reported in the range -91 to -98 ppm (Magi et al., 1984), and there are a few reports of lower frequency Q^3 resonances: -99.8 ppm (Maciel and Sindorf, 1980) and -101.6 ppm (Fyfe et al., 1985) from silica gel and -100.5 ppm (Farnan et al., 1987) from a silica glass. Nagy et al. (1982) reported a Q^3 resonance from a highly dealuminated ZSM-5 zeolite ($<0.5\%$ Al) at a significantly lower frequency (-103 ppm), and this was subsequently assigned to internal silanol groups (Woolery et al., 1986; Dessau et al., 1987). On this basis, it is tempting to assign our lower frequency ^{29}Si Q^3 resonances at <-103 ppm from the opal-CT samples S4, S13, and S17 (Table 5) to such internal groups. However, we discount this for the following reasons. In chalcedony and flint a high proportion of the total H occurs as surface silanol groups located at structural defects (Graetsch et al., 1985, 1987). The sharp Q^3 resonances from such samples in this study (S2, S5, S7, S9, S11, S12, S14, and S28) are in the narrow range −98.5 to −99.5 ppm (Table 5) and have a very consistent difference in chemical shift to the Q^4 resonances, $\Delta\delta(Q^3 - Q^4)$ = 7.8–8.1 ppm. Corresponding $\Delta\delta$ values for surface silanol $-Q^4$ shift differences in silica gels have been reported to be 9.5 ppm (Maciel and Sindorf, 1980), 8.4 ppm (Fyfe et al., 1985), and 10.0 ppm (Bayer et al., 1983). All our opal samples exhibit Q^3 resonances in the range −101.0 to −103.7 ppm (Table 5) with corresponding $\Delta\delta(Q^3 - Q^4)$ values between 9.0 and 12.5 ppm. The higher frequency Q^3 resonances from S4, S13, and S17 referred to above are at 9.0 ± 3.9, 9.3 ± 3.5, and 10.8 ± 3.8 ppm, respectively, from the bulk Q^4 resonances (Table 3, errors are half the $\Delta\nu_{1/2}$ values) and are therefore consistent with the surface $\Delta\delta(Q^3 - Q^4)$ values obtained above.

In order to decide if it is reasonable to expect a characteristic Q^3 chemical shift or $\Delta\delta$ value for an internal silanol, we propose that the principal factor providing a surface-internal ^{29}Si shift difference would be the decreased H bonding at the internal group. Barron and Frost (1985) found that the removal of H bonding at the innermost Q^3 group of sepiolite, by driving off the zeolitic H_2O, imparted a low frequency shift ca. 2 ppm in the ^{29}Si resonance. Such a small change is within the error limits given above for $\Delta\delta(Q^3 - Q^4)$ in the opal-CT samples, and we conclude that our ^{29}Si NMR data do not provide evidence for or against the occurrence of internal silanols.

Effect of decoupling

Few solid state ^{29}Si NMR studies of polymeric silicate and aluminosilicate structures employ ^{1}H decoupling because MAS in the range 3–4 kHz is usually sufficient to eliminate broadening effects in the ^{29}Si spectra resulting from ^{29}Si-^{1}H dipole-dipole interactions. This is presumably the reason why de Jong et al. (1987) found no improvement in ^{29}Si line width with ^{1}H decoupling—an observation that led them to conclude the absence of silanol groups in opal. However, we have observed experimentally that in two cases (S3, see Fig. 2, and S20) ^{1}H decoupling improves the resolution of the ^{29}Si spectrum beyond that achieved using MAS alone. Fyfe et al. (1985) suggested that ^{1}H decoupling may improve ^{29}Si MAS-NMR spectral line widths if the samples have very high proton concentrations. Engelhardt and Michel (1987) noted that high-power ^{1}H decoupling is sometimes helpful in removing residual ^{29}Si-^{1}H dipolar interactions, and Woessner (1989) routinely used ^{1}H decoupling to improve the resolution of ^{27}Al spectra of clay minerals. If the proton resonance experiences ^{1}H-^{1}H homogeneous broadening that is much greater than the heteronuclear broadening (e.g., Yesinowski et al. 1988), MAS may no longer be sufficient for optimum ^{29}Si resolution. We suggest that this is the situation for samples S3 and S20, and the effect is the subject of continuing investigations.

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