

Fig. 3 Comparison of rain noise spectral samples due to Franz (—), Bom (— —), Nystuen (---) and Scrimger (wind $< 1.5 \text{ m s}^{-1}$ (+—+), wind $> 1.5 \text{ m s}^{-1}$ (— —)). Spectrum level is expressed in dB relative to $1 \mu\text{Pa}^2 \text{ Hz}^{-1}$. Numbers adjacent to curves are rain rate in mm h^{-1} .

with increasing frequency. Figure 3 compares our results with those reported by other workers.

The use of a distrometer permitted the determination of the drop size distributions in the rain producing the acoustic noise samples. These are given in Table 1, which shows the number of drops in a given drop-size interval, expressed in terms of the drop diameter, falling on 1 m^2 of the surface per s. Also given is the rain rate derived from the drop counts and the power input per m^2 at the surface due to the kinetic energy of the drops, expressed in dB, referred to the power associated with the rain noise of spectrum f . The latter was chosen as it was obtained from the lightest rainfall of the samples considered. The distrometer samples were 30 s long, so that three contiguous samples were added to correspond to a single 90-s sample obtained in near coincidence with the 100 s needed to produce the acoustic spectrum.

These data are remarkable for the abrupt fall-off in level of the rain noise spectra below 13 kHz and particularly for the sharp contrast in form between the spectra of the rain noise taken in winds of speeds $< 1.5 \text{ m s}^{-1}$ compared with those taken in winds of greater speed. In the 17 spectra obtained in winds of speeds below 1.5 m s^{-1} , which might well be considered 'pure' rain noise spectra, the peak occurs at 13.5 kHz within a few hundred hertz and the cutoff on the low-frequency side of the peak is extremely sharp, dropping the spectrum level over 15 dB in a 2-kHz frequency interval. Evidently, the wind, as it increases in speed above 1.5 m s^{-1} , affects the noise generation mechanism in such a way that the 13.5-kHz peak is rounded off and extended over several kHz and the slope on the low-frequency side of the cutoff is diminished. The hail spectrum above 15 kHz is essentially the same as the rain spectra but it does not exhibit the cutoff near 13.5 kHz, and peaks at 3.0 kHz. Considering the different properties of hail and rain—the rigidity of the hail and the fluidity and surface tension of the rain—the simplicity of the hail spectrum compared with that of the rain is not surprising. Also, *a priori*, the negative slopes of the respective spectra towards high frequencies are consistent with the concept that the higher-frequency energy in the noise is generated by the smaller drops (or stones) and that these input less energy (both kinetic and, in the case of rain, potential) at the water surface.

The noise spectrum of falling snow is unique in that it increases uniformly at 3 dB per octave as frequency increases over its entire range. As the kinetic energy of the falling snow is negligible compared with hail or rain, the noise must arise from a process associated with the melting of the snow.

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Polymerization of silicate anions in solutions at low concentrations

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Adsorption of tetrahedral-forming ions, such as silicates and phosphates, is considered to be the main cause of retention of these anions on the surfaces of hydrated Al- and Fe-oxides. The importance of this retention in natural and man-caused phenomena has been the subject of many investigations. When adsorption studies are conducted, the role of the surface and the charges developed on it by the potentially determining ions tend to be emphasized, while the nature of the sorbate is rarely considered or investigated. Nevertheless, the excluded or equilibrium solution is the seminal source of information in the formulation of adsorption mechanisms or models. The ionic species present in the equilibrium solution are practically always taken for granted, that is, from data previously published. They are thought to be a simple function of solution pH, without further analysis of ionic speciation changes that occur during the sorption process. Here, we provide direct experimental evidence, using an advanced and sensitive spectroscopic technique, laser Raman spectroscopy (LRS), that aqueous equilibrium silicate solutions at low concentrations contain polymeric and/or other anionic complexes and not just monomeric species. These low concentrations are similar to those used in most previous sorption experiments on Fe- and Al-sesquioxides and on tropical acidic soils. Our findings clearly indicate that any mechanisms and models that are proposed to describe anion sorption on sesquioxides should consider that silicates, and probably some other tetrahedral-forming anions, are not present in solution solely as monomeric ionic species as most investigators have assumed^{1–11}. Irregularities in fitting experimental data to models previously reported prompted this research^{2–4,6,12}.

We determined that a spectrum of Na- or Ca-silicate could be obtained at very low Si concentrations and that the 'fingerprint' approach (Fig. 1) is applicable to the spectra obtained because they have lines distinctly placed, well separated, and of adequate intensity to determine the frequencies at which the peaks or bands occur. The published Raman spectra of Na silicates in solution were determined from Si solutions of concentrations 200–1,000 times larger than the solutions used in this study^{13–16}. No laser Raman (LR) spectra of Ca-silicates in solution have been published.

The spectrum of a Na-silicate solution at a Si concentration of $75 \mu\text{g cm}^{-3}$ is presented in Fig. 1. Numerous precautions were taken to exclude CO_2 from the alkaline solutions. Air-tight plastic bottles were used to store the silicate solution and all of the samples were freshly prepared just before the experiments with degassed water. The solution pHs were measured with a combination electrode immersed in a sealed plastic container to restrict any CO_2 contamination. Unless otherwise stated, all the solutions examined were adjusted to pH 10 since this pH is close to the reported pK of monosilicic acid, that is 9.5 (refs

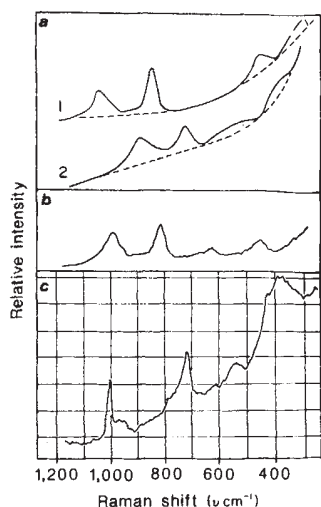


Fig. 1 Comparison of spectra of Na_2SiO_3 solutions reported by different authors. *a*, Raman spectrum as reported by Fortnum and Edwards¹³. 1, NaH_2PO_4 , 4 M solution (used as silicate analogue); 2, Na_2SiO_3 , 2.5 M. *b*, Laser Raman spectrum of Na_2SiO_3 1.5 M as reported by Freund^{14,15}. *c*, Laser Raman spectrum of Na_2SiO_3 (multipass device) ($\text{Si} = 75 \mu\text{g per g} \approx 0.003 \text{ M}$).

7-9). This pK_a is a crucial component of the conclusions of many previous investigations. As a basis for comparison, Raman spectra of 1.5 and 2.5 M silicate solutions previously reported¹³⁻¹⁵ are also shown. The remarkable intensity of the Raman lines for the low Si concentration solution is attributed to the enhancement of the signal due to the multipass device used in the studies. A very satisfactory spectrum may also be obtained with Si concentrations as low as $30 \mu\text{g Si cm}^{-3}$. More details of the methodology and the analogue structures suitable for these analyses will be published elsewhere.

Consideration of the position and number of the Raman shifts in the $400\text{--}500 \text{ cm}^{-1}$, 600 cm^{-1} , 785 cm^{-1} , and at the ≈ 900 and $1,050 \text{ cm}^{-1}$ regions agree fairly well. The slight displacement in the 900 and $1,000 \text{ cm}^{-1}$ regions may be due to pH differences. Solutions that are 1.5 or 2.5 M obviously have much higher pHs (> 12) than the $25\text{--}75 \mu\text{g cm}^{-3}$ working range of our Si solutions.

Calcium as well as Na salts are frequently supporting electrolytes in sorption studies, and soluble silicates occur at low concentrations in the soil solution, and in numerous other aqueous environments. When we examined solutions of low Si concentrations, 'anomalies' led to the suspicion that silicate species other than monomers were present. The indications of silicate polymerization or the formation of complexes other than monomeric silicates or silicic acid are reflected in the following LR spectral characteristics: (1) the band at $1,070\text{--}1,090 \text{ cm}^{-1}$ is considered to indicate the presence of a dimer (Si-O-Si band)^{13-15,17} or Si polymers^{13-16,17-20}; (2) changes in the band features, that is, splitting and/or broadening of peaks, shifts of the band frequencies to higher values, and changes of intensity (band height). The lines at $\approx 780 \text{ cm}^{-1}$ are especially sensitive to these changes^{14,15,17-19,21,22}.

The increase in polymerization of the silicate solution is reflected qualitatively by an increase in the intensity of the Raman lines at 780 and $1,070 \text{ cm}^{-1}$ (Fig. 2) in spectrum *b* compared with spectrum *a*. With increasing Si concentration, polymerization of Si rapidly occurs as shown by the development of the peak at $1,070 \text{ cm}^{-1}$ (refs 15, 16, 19-22).

Using times and ionic environments comparable to most other previous sorption studies^{1-6,12}, we determined that a silicate solution of low concentration is not only in monomeric form. Fresh monosilicic acid solutions ($75 \mu\text{g cm}^{-3}$) were prepared using the H-resin method⁸ and brought to pH 10 with NaOH and examined immediately by LRS (Fig. 3). Spectra were run at 15-min intervals and when the solution 'aged' at 3 h, distinct changes in the spectrum as appears in Fig. 3 inset *b* were clearly noticed.

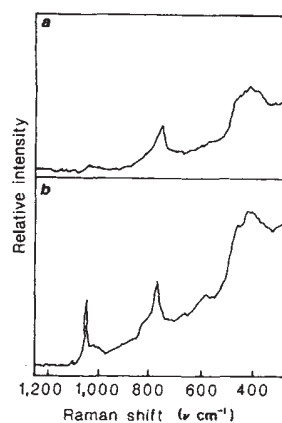


Fig. 2 Laser Raman spectra of aqueous solutions of Na_2SiO_3 with varying concentration. The increase in polymerization in graph *B* is reflected by an increment in the band = $1,070 \text{ cm}^{-1}$, which corresponds to a silicate dimer (Si-O-Si band) or higher polymer. *a*, Na_2SiO_3 solution at $75 \mu\text{g cm}^{-3}$; *b*, Na_2SiO_3 solution at $100 \mu\text{g cm}^{-3}$.

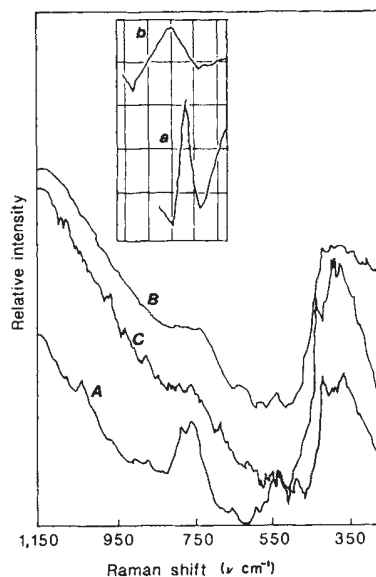


Fig. 3 Laser Raman spectra of Si-solutions at a Si concentration of $75 \mu\text{g per g}$. $\text{Ca}(\text{OH})_2$ or $\text{Na}(\text{OH})$ were added to reach a pH = 10. This pH was selected because between pH 8.5 and 10.5 'maximum adsorption' or 'adsorption envelopes' are reported to occur. *A*, A freshly prepared solution of monosilicic acid and $\text{Ca}(\text{OH})_2$. *B*, Solution *A* examined after 'ageing' for 3 h after exposure to the laser beam. *C*, Solution *A* examined after ageing for 3 h with no previous exposure to the laser beam. No differences between *B* and *C* were detected, therefore the Si-solution was not polymerized by photocatalysis. Inset: *a*, A freshly prepared solution of monosilicic acid and NaOH. *b*, Solution *a* after ageing for 3 h. The $\approx 782 \text{ cm}^{-1}$ peak broadens, splits and shifts frequency as a sign of polymerization. The labelling of the axes are as in *A*.

The 782 cm^{-1} frequency observed (Fig. 3, insets *a* and *b*) was taken as a reference and it was shown from experimental evidence^{17,22} that the ≈ 780 peak is perturbed when Si polymerizes. This is evident because inspection of the spectra revealed three very distinct alterations of the aged solution in comparison with that at 'zero-time', (Fig. 3, insets *a* and *b*): (1) the band width broadened to twice the value at 'zero-time'; (2) the intensity (band height) decreased nearly 50%; (3) the frequency was displaced from 782 to 803 cm^{-1} . Effects of photocatalysis, due to the laser beam, on the rate of polymerization were ruled out by additional experiments in which Ca was the complementary cation (Fig. 3, *A*, *B*, *C*). Although not shown, a sample of $30 \mu\text{g cm}^{-3}$ Si was examined in similar conditions and even at

this concentration, variations of the 782 cm^{-1} peak occurred 3 h after sample preparation.

The present results are simply a predictable extension of proven facts which explain polymerization, anion bridging and/or gelation of inorganic polymers from solutions at higher concentration than in our studies^{8,9,21,23-28}. They indicate that it is difficult to define a boundary Si concentration, high or low, where silicate monomers are the sole species, which has been the repeated assumption in many previous investigations. Our results confirm that the formation of at least a silicate dimer, at pH 10, predicted from theoretical and experimental reported data^{23,28} occurs at any silicate concentration (in fact, 35% as silicate-dimer, Iler, unpublished data). Even at low concentra-

tions and after a short period of time, a substantial part of the silicate solution is non-monomeric. Moreover, the widely accepted concept that maximum adsorption of silicate on sesquioxides occurs at the $pK_a = \text{pH}$ of monosilicic acid^{1-6,12} without consideration that polymeric species exist has led to incorrect explanations and non-fitted models for those 'adsorption' systems. At $\text{pH} = pK_a$ the conditions are optimal for polymerization to occur^{25,26}. Indeed, our statements do not proscribe sorption of silicates on various sesquioxides in nature and in the laboratory^{1-6,12,22}. Work is in preparation which explains polymerization mechanisms at low concentration, and the possible configurations of dimers and polymeric species, based on evidence from spectroscopy and complementary techniques.

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Laboratory models for aromatization and isomerization of hydrocarbons in sedimentary basins

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With increasing depth in the Earth's crust, changes take place in the sedimentary distributions of aromatic steroid hydrocarbons and of stereoisomers of certain types of alkanes^{1,2}. The changes occur before and during the early stages of hydrocarbon generation and have been interpreted as resulting from aromatization and configurational isomerization reactions respectively³. We have now brought about an aromatization reaction and an isomerization reaction in the laboratory under free radical conditions, sulphur being chosen as a convenient source of radicals, and have extracted rate constants from the absolute concentration-time functions of the organic substrates. The activation energies and pre-exponential factors were then deduced from the temperature dependence of the rate coefficients. The values of these activation parameters show that, in the laboratory, the aromatization is more temperature dependent than the isomerization reaction, as suggested previously from the distributions of steroidal compounds in sedimentary basins³⁻⁵.

The relative extents to which the proposed reactions occur for steroid hydrocarbons in the sedimentary column have been suggested as being indicative of the thermal history of sediments³. These data, in conjunction with a geophysical model describing sedimentary basin formation, have been used to derive both activation energies and pre-exponential factors governing the rates of the reactions⁴⁻⁶. However, such studies have used kinetic schemes based on the following assumptions: (1) the reactions obey unimolecular first-order rate laws, and (2) the total concentration of reactant plus product remains constant throughout each reaction. In addition, rate coefficients have been derived from the relative abundances of presumed products to reactants, as measured from peak areas in mass chromatograms, rather than from absolute concentrations. The activation energy of a reaction is dependent upon its mechanism⁷; hence, if laboratory-derived values are ever to be extrapo-

lated to the sedimentary column, the same mechanism must be followed in both cases. Previous authors⁸⁻¹² have proposed the importance of free radical mechanisms in petroleum generation and associated processes. Significant concentrations of free radicals have also been measured, even at room temperature, in many kerogens¹³.

In the present study, intimate mixtures of the organic substrate, powdered sediment and elemental sulphur were heated at temperatures where high concentrations of sulphenyl and polysulphenyl radicals are observed¹⁴. Typically, the mixture in Pyrex glass tubes sealed *in vacuo* (after three N₂ purges) was heated in an oven and the temperature monitored using a chromel-alumel thermocouple. The substrate for aromatization was an isomeric mixture of ring-C monoaromatic hydrocarbons (compounds I, Fig. 1)¹⁵ and the matrix was a solvent-extracted carbonate sediment (Cretaceous, Abu Dhabi), with 0.08% w/w of elemental sulphur added. For the isomerization, one stereoisomer [(6*R*, 10*S*) = *meso*-pristane] of 2,6,10,14-tetramethyl pentadecane (IIIa, Fig. 1) was used, with a solvent-extracted shale as matrix (Semécourt shale, Lower Toarcian,

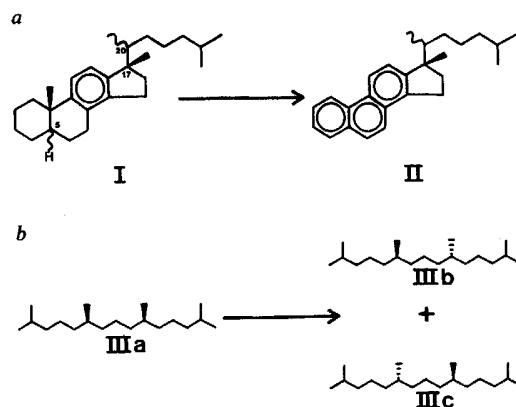


Fig. 1 a, Aromatization of the 5 α (H) and 5 β (H) isomers of (20*R*)- and (20*S*)-17 β -methyl-18-norcholesta-8,11,13-triene (I) to (20*R*)- and (20*S*)-17 β -methyl-18,19-dinorcholesta-1,3,5(10), 6,8,11,13-heptaene (II) (numbering based on steroid skeleton). b, Isomerization of (6*R*,10*S*)-pristane (IIIa) to (6*R*,10*R*)- plus (6*S*,10*S*)-pristane (IIIb and IIIc respectively).