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Chemical heterogeneity in phosphosilicate gels by NMR magnetisation exchange

Nigel J. Clayden,[*a] **Serena Esposito**[b] **and Antonio Aronne**[b]

[a] *School of Chemical Science, University of East Anglia, Norwich, UK NR4 7TJ.*
E-mail: n.clayden@uea.ac.uk
[b] *Department of Materials and Production Engineering, University of Naples, Federico II Piazzale Tecchio, 80125 Napoli, Italy*

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Nanometre scale chemical heterogeneity has been revealed in a phosphosilicate gel by ^{31}P spin exchange. Monomeric phosphorus was found near to phosphorus singly cross-linked with phosphorus. Phosphorus doubly cross-linked with phosphorus was found to be remote from both other types of phosphorus species. Radiofrequency driven magnetisation exchange through ^{31}P–^{31}P dipolar coupling was rather ineffective, even with recoupling times of up to 30 ms, demonstrating the weak ^{31}P–^{31}P dipolar coupling and the effect of residual ^{1}H–^{31}P dipolar coupling. Effective ^{31}P spin exchange was possible in the laboratory frame through the ^{1}H spin interactions, when mixing times from 100 ms to 2 s were used.

1 Introduction

Conventional humidity sensors are mainly based on porous sintered oxide ceramics.[1] Recently, however, humidity sensitive amorphous phosphosilicate films have been prepared by sol–gel methods.[2] A clear understanding of the chemical structure of these films is required in order to design a sensitive and stable sensor. This is particularly true given that the sensitivity of the phosphosilicate films to the relative humidity is strongly dependent on their phosphorus content and the temperatures used in processing the film. Extensive study of the chemistry of phosphosilicate sol–gels has allowed the broad outline of the reactions involved to be discerned.[3–8] In the initial gelation step monomeric phosphorus species can be considered as being trapped within a silica gel matrix, there being no evidence for the formation of P–O–Si or P–O–P bonds at this stage. NMR studies have also shown that, upon heating the gel, the phosphorus monomer reacts with either other phosphorus monomers or the silicate matrix with the type and degree of cross-linking dependent on the phosphorus content, the temperature used in the heat treatment and the duration of the heating. For example, at low temperature, 300 °C, with 10 mole% P_2O_5 Q_0, Q_1 and Q_2 are found with Q_1 predominating where Q_N denotes the number of cross-links, N, made by the phosphorus.[7,8] Although clearly demonstrating the nature of the short range order there is no indication of the proximity of the various Q_N units, and thus the chemical heterogeneity on the nanometre scale. The aim of the current work is to determine the connectivity of the Q_N resonances in a phosphosilicate gel.

One approach to the question of spatial connectivities is the use of two-dimensional (2-D) NMR techniques[9] where the proximity of the structural units giving rise to resonances with unique chemical shifts is determined by magnetisation exchange arising through their dipole–dipole coupling.[10–16] Magnetisation exchange experiments in the solid state can be carried out using either the standard solution three pulse sequence,[9] in which case the exchange is referred to as being in the laboratory frame, or by using dipolar recoupling. One method of dipolar recoupling, involving a series of π pulses during the mixing time, is known as radiofrequency (rf) driven.[10] The essential difference between these two experiments lies in their response to chemical shift terms. In laboratory frame magnetisation exchange, because the exchange must be energy conserving, the rate of exchange depends on the spectral overlap between the nuclei involved. The maximum rate will be observed when the resonances have the same chemical shift and can be represented as delta functions. Any difference in chemical shifts between the resonances will reduce the overlap and thus decrease the rate of exchange. In the limit of the resonances not overlapping the rate of exchange will be zero. On the other hand radiofrequency driven dipolar recoupling is not dependent on spectral overlap, with the effective dipolar coupling constant and hence rate of exchange being dependent on the ratio of the chemical shift difference to the spinning speed. Radiofrequency driven dipolar recoupling is therefore possible between non-overlapping resonances. Dipolar recoupling variants of the magnetisation exchange experiment are usually necessary in the solid state because the magic angle spinning which is used to give high resolution NMR spectra not only averages the dipolar interaction to zero, it also minimises spectral overlap, making laboratory frame magnetisation exchange exceedingly slow.[10,13,14] Heteronuclear ^{1}H–^{31}P dipolar coupling is a hindrance to rf driven magnetisation exchange because it interferes with the reintroduction of the homonuclear ^{31}P–^{31}P dipolar coupling and must be removed during the dipolar recoupling by high power decoupling. However, in the laboratory frame magnetisation exchange ^{1}H–^{31}P heteronuclear dipolar coupling can be beneficial as it provides a mechanism whereby resonances with different chemical shifts can have overlapping bandshapes. To fulfil this role properly the ^{1}H–^{31}P dipolar coupling must be of the appropriate strength to maximise the spectral overlap of the phosphorus resonances[11] whilst minimising the overall spread of the resonances. Usually rf driven dipolar recoupling is more efficient than laboratory frame magnetisation exchange, however in the case of weak ^{31}P–^{31}P dipolar coupling the latter may be more effective because of the long recoupling times. During these long recoupling times cumulative errors in the radiofrequency pulse can destroy the magnetisation of the rf driven experiments, preventing the observation of spin exchange. Small dipolar couplings may arise from either the ^{31}P nuclei being remote or

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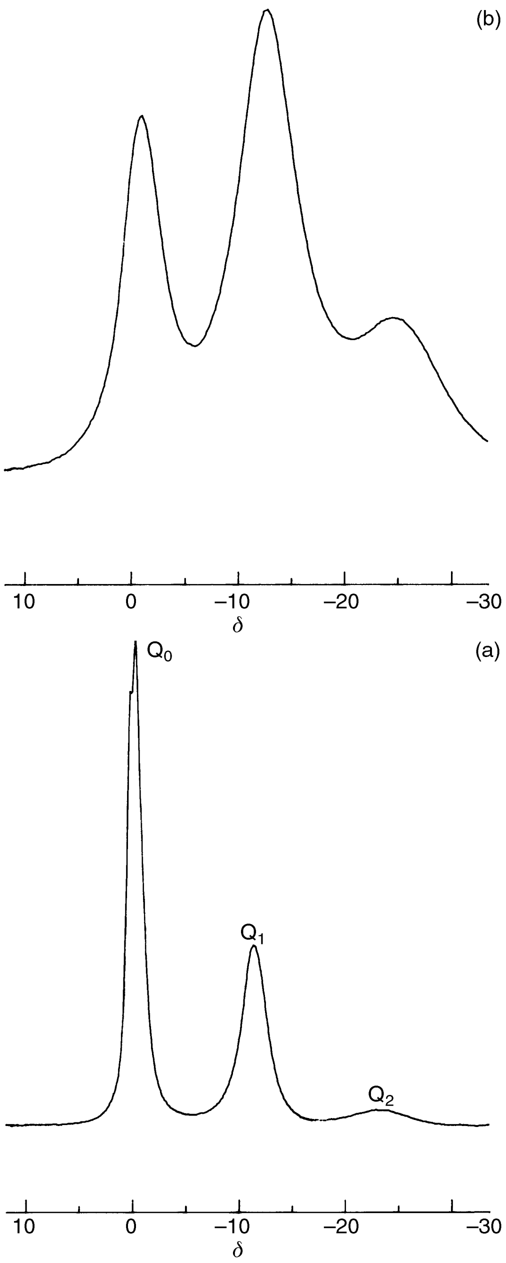

Fig. 1 81 MHz ^{31}P MAS NMR spectrum of a phosphosilicate gel with a composition 10% P_2O_5–90% SiO_2. Spinning speed 5 kHz (a) with and (b) without high power ^1H decoupling. The types of phosphorus (Q_N) and their chemical shift assignments are shown.

the presence of molecular dynamics. Dynamic processes by decreasing the homonuclear ^{31}P–^{31}P dipolar coupling will tend to reduce the maximum rate of magnetisation exchange for both the rf driven and laboratory frame mechanisms. However, in the case of the laboratory frame magnetisation exchange, the simultaneous reduction in the heteronuclear ^{31}P–^1H dipolar coupling will tend to increase the actual rate of exchange towards this lowered maximum value, by reducing the resonance linewidths. The theoretical maximum is only observed when the resonances have the same chemical shift and delta function lineshapes.

2 Results and discussion

A one-dimensional ^{31}P NMR spectrum of the phosphosilicate gel is shown in Fig. 1(a). Three resonances can be seen; one at δ *ca.* 0 corresponds to the monomeric phosphorus, Q_0, one at δ *ca.* −10 is phosphorus singly cross-linked with phosphorus, Q_1 and the one at δ *ca.* −20 is phosphorus doubly cross-linked with phosphorus, Q_2. Structure is seen to the resonance at δ 0 because the monomeric phosphorus is present as a mixture of ethyl esters $OP(OEt)_{3-x}(OH)_x$ where $x = 0$–3. However, the poor resolution in the spectrum prevents the clear observation of the resonances corresponding to the individual ester forms. No evidence for cross-linking with the silicate matrix was found by ^{29}Si NMR, where a resonance around δ −115 would be expected.[4,5] Two-dimensional spectra showing rf driven ^{31}P–^{31}P magnetisation exchange are in Fig. 2. Two features are important in these spectra, resonances along the diagonal and off-diagonal or cross peaks. Resonances lying along the diagonal usually indicate no exchange though they can occur through the exchange of magnetisation between like Q_N units. Cross peaks show the exchange of magnetisation and hence proximity of unlike Q_N units. Cross peak intensities in the ^{31}P–^{31}P dipolar recoupled magnetisation exchange spectra and hence distances can, in principle, be calculated from a number of parameters including the magnitude of the dipolar coupling, the chemical shift anisotropy and the mixing time used in the 2-D experiment.[16] In the present case precise calculations are unimportant; only an approximate idea of the limiting distance for the observation of the magnetisation exchange is required. This can be estimated readily by assuming that the magnetisation exchange is a pure dipolar process, in which case the initial cross peak intensity is expected to be proportional to $D^2\tau_m$ where D is the dipolar coupling and τ_m the mixing time.[17] Empirically, for a mixing time of *ca.* 2.5 ms the magnetisation exchange is dominated by the ^{31}P–^{31}P interaction of neighbouring PO_4 tetrahedra, corresponding to a distance of 0.2 nm and a dipolar coupling of 1 kHz.[13] Since D is proportional to r^{-3} where r is the internuclear distance, the limiting distances obtained in a magnetisation exchange can therefore be estimated. On this basis a 30 ms mixing time would only be sensitive to distances of up to 0.4 nm. Indeed, such is the strong dependence of the dipolar coupling on the internuclear separation that even using a mixing time two orders of magnitude larger will only increase the range to 0.6 nm or so. Thus, the magnetisation exchange experiment is sensitive to very short range ordering within a lattice.

In the case of the phosphosilicate gel, Fig. 2, cross peaks are seen between the Q_0 and Q_1 phosphorus even when the dipolar recoupling mixing time is zero. Furthermore, only a small increase is seen in the Q_0/Q_1 cross peak intensity when the recoupling time is increased to 30 ms. No cross peaks were seen between Q_0 and Q_2 or Q_1 and Q_2. The behaviour of the cross peak intensity demonstrates not only that magnetisation exchange can occur between the Q_0 and Q_1 resonances in the absence of dipolar recoupling but also that ^{31}P–^{31}P dipolar recoupling is rather ineffective. The explanation for the cross peaks in the absence of the rf pulse recoupling time is that magnetisation exchange must take place in the laboratory frame by a three spin mechanism. Thus, in the absence of the dipolar recoupling mixing time the pulse sequence used is equivalent to a standard 2-D exchange NMR experiment with the dephasing time of $2t_d = 100$ ms equal to the mixing time. Note that the interactions between the third spin and the two ^{31}P spins only act to ensure the spin exchange is energy conserving: magnetisation still passes directly between the two ^{31}P spins and not through the third spin. This raises the question of why the direct ^{31}P–^{31}P mechanism is inefficient, since with proper recoupling the rate of magnetisation transfer should exceed that by the three spin mechanism. Gross instrumental errors can be ruled out since in control experiments on $LiSn_2(PO_4)_3$ cross peaks were seen after a mixing time of 10 ms. Even so, this result in itself does suggest poor recoupling for instrumental reasons since 10 ms is a rather long dipolar recoupling time for nuclei known to be ≈0.3 nm apart, values closer to 5 ms would be more appropriate. Thus a combination of residual heteronuclear-^1H dipolar coupling which is known to interfere with the rf driven recoupling and pulse imperfections may account for the poor recoupling. The presence of residual ^1H

dipolar coupling is clearly demonstrated by the line broadening seen in the ^{1}H coupled ^{31}P MAS NMR spectrum. Despite these possible reasons for the recoupling being less than maximally efficient, the observed weak cross peaks do imply that the dipolar coupling is small, either because the ^{31}P nuclei are remote or because some dynamic process is averaging the dipolar coupling. Dynamic averaging of the dipolar coupling between the Q_1 and Q_2 resonances is unlikely and therefore the absence of a cross peak indicates that these are on average further apart than the limiting distance of 0.6 nm. On the other hand the Q_0 and Q_1 resonances must lie within this 0.6 nm radius. Since the limiting intensities in the magnetisation exchange cannot be determined it is not possible to say from the rf driven experiments what fraction of the Q_0 and Q_1 is proximate. In view of the ambiguity in the mechanism giving rise to the cross peaks, attempts were made to demonstrate unambiguously that rf driven recoupling can be achieved by using a shorter dephasing period.[16] However, these proved to be unsuccessful because of strong artifacts arising from the residual transverse magnetisation from the Q_0 resonance. Despite this remaining uncertainty it is clear that rf driven recoupling is weak because very little change took place in the cross-peak intensity as the recoupling period was increased from zero to 30 ms.

Laboratory frame magnetisation exchange between chemically inequivalent nuclei requires the presence of a third spin to provide a mechanism for energy conservation. The only possible candidate spins in the phosphosilicate gels to act in this role are ^{1}H and ^{29}Si. ^{29}Si is unlikely to play a part because of its low natural abundance (4.7%) and the weak dipolar coupling to the ^{31}P spins caused by its moderate magnetogyric ratio and its distance from the ^{31}P spins. On the other hand previous experiments have shown that magnetisation exchange can indeed occur between inequivalent ^{31}P nuclei by a three spin mechanism involving ^{1}H–^{31}P interactions[12] in similar circumstances. The role of the ^{1}H–^{31}P interactions is to broaden the ^{31}P resonances sufficiently to give a finite zero quantum transition rate. A similar role has been seen for lithium (^{6,7}Li 100% abundant) in lithium phosphate glasses[16] as well as $LiSn_2(PO_4)_3$.[18] Evidence for these residual ^{1}H–^{31}P interactions can be seen by comparing the ^{31}P MAS NMR spectra with and without high power ^{1}H decoupling during acquisition, Fig. 1(b). In the absence of decoupling the resonances at δ 0 and −11 are substantially broadened, whereas changes in the resonance at δ −22 are unclear. Upon decoupling the resonances narrow so that the peak heights increase, however the integrated intensities of the Q_N resonances stay the same. This effect is most marked for the Q_0 resonance. Owing to the broad nature of the Q_2 resonance its change in linewidth on decoupling does not unambiguously demonstrate protons are close by. However, the fact all three resonances cross-polarise together with the variation in intensity in the variable contact time cross polarisation spectra,

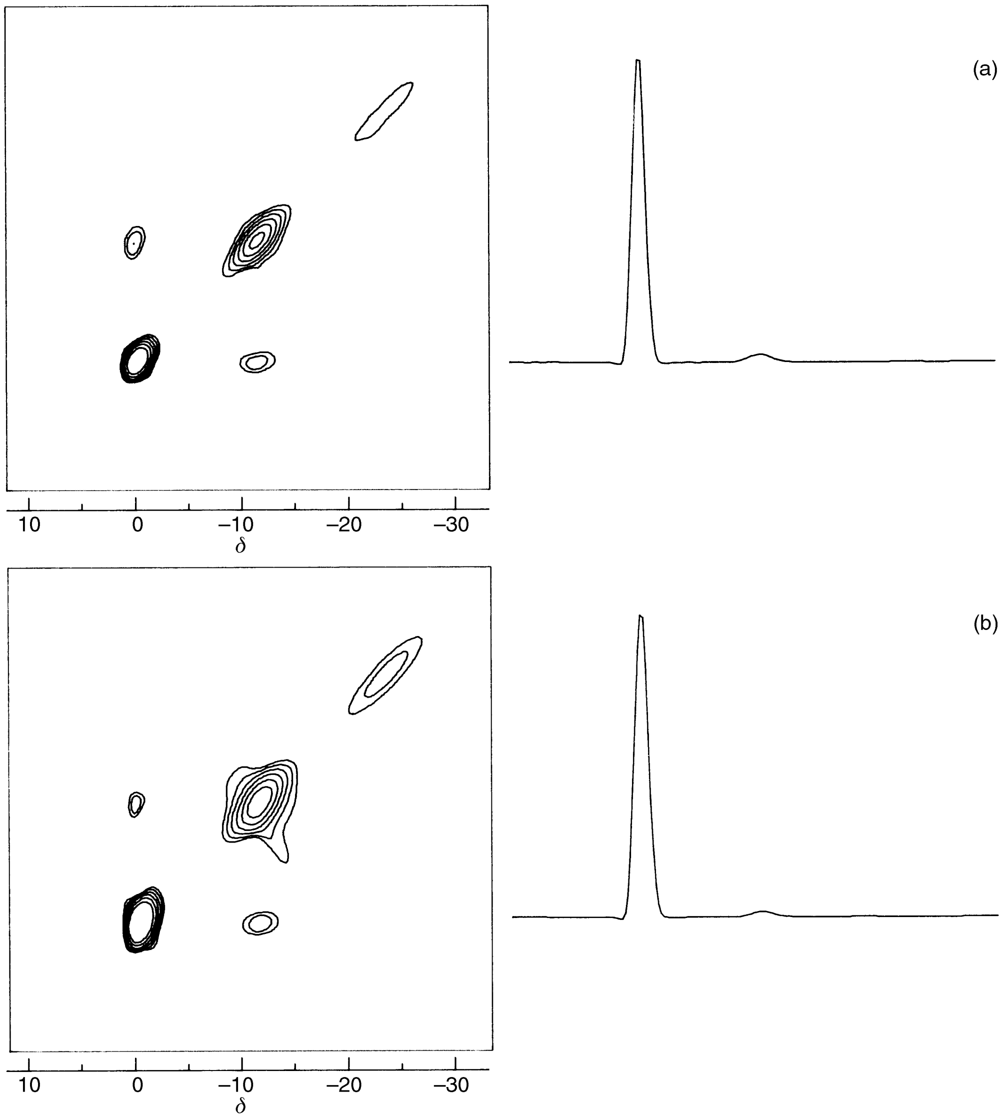

Fig. 2 Contour plots of the two-dimensional ^{31}P MAS NMR exchange spectra with rf driven dipolar recoupling based on the XY-8 cycle for different mixing times $\tau_m = 0$ (a) and 30 ms (b). A cross section at the position of the Q_0 resonance is shown to the right.

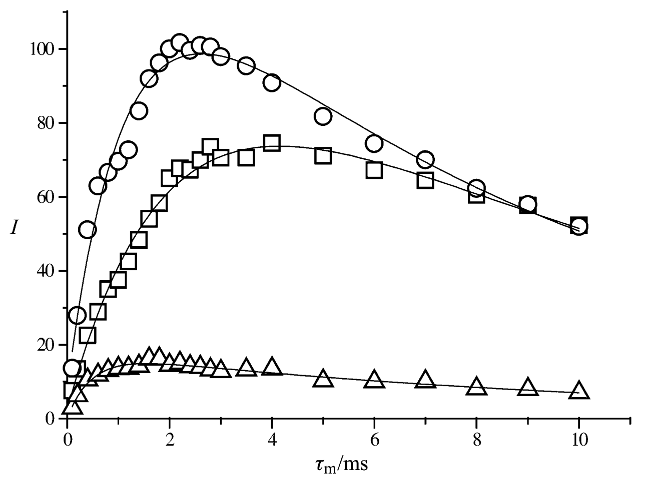

Fig. 3 Variation of the intensity of the resonances in the ^{31}P CPMAS NMR spectrum as a function of the contact time. The solid lines represent a fit to the function[20] $I = I_0 \exp(-\tau_m/T_{PH}^{eff})[1 - \exp(-\tau_m/T_{1\rho}^{eff})]$ where I is the intensity of the resonance, I_0 the fitted maximum intensity, τ_m the contact time in the cross-polarisation pulse sequence, T_{PH}^{eff} the effective rise time constant and $T_{1\rho}^{eff}$ the effective ^1H spin–lattice relaxation time in the rotating frame. (○) Q_0, (□) Q_1 and (△) Q_2.

Fig. 3, clearly shows that all the phosphorus sites are close to protons. Good fits were obtained to the cross polarisation data using a simplified model for the cross polarisation dynamics where the rise time constant T_{PH}^{eff} depends not only on the true T_{PH} but also $T_{1\rho}^{H}$ and $T_{1\rho}^{P}$. T_{PH} is a function of the PH dipolar coupling and a spectral density representing processes modulating the dipolar coupling. The similarity in T_{PH}^{eff} for the three phosphorus sites (Q_0, 2.65: Q_1, 1.3: and Q_2, 0.5 ms), therefore demonstrates that each is, to a first approximation, equally coupled to nearby protons. If anything the cross polarisation dynamics demonstrates a stronger coupling and hence closer proximity between the phosphorus and protons in the Q_2 case than in the Q_0 one. In all likelihood though this is simply a reflection of the greater dynamics of the Q_0 rather than any difference in the distances.

To investigate the possibility of ^1H mediated magnetisation exchange further, the standard 2-D exchange MAS NMR experiment was used with mixing times of 1 and 2 s; the spectra are shown in Fig. 4. Cross sections of the contour plots at a mixing time of 2 s at the isotropic chemical shifts of the Q_N units are shown in Fig. 5. Increasing the mixing time led to an increase in the intensity of the Q_0 to Q_1 cross peak but again no cross peaks were seen between the Q_2 resonance and the Q_0 or Q_1 resonances. Based on the intense cross peaks seen between the Q_0 and Q_1 resonances when longer mixing times are used, the majority of the nuclei giving rise to these two resonances must be close together in the structure of the gel. Although precise distances cannot readily be obtained, the limiting distances will not be significantly different from those seen in dipolar recoupling since the driving force for the magnetisation exchange is still the ^{31}P–^{31}P dipolar coupling. One possible model for the interaction involves a hydrogen bonded pair as shown in Fig. 6. In this model the hydrogen bonding must be weak to ensure the average distance between the two phosphorus atoms is of the order of 0.4–0.5 nm. Independent evidence for a weak hydrogen bonded P–OH is provided by the ^1H chemical shift of δ 9.45 seen for the P–OH group.[17]

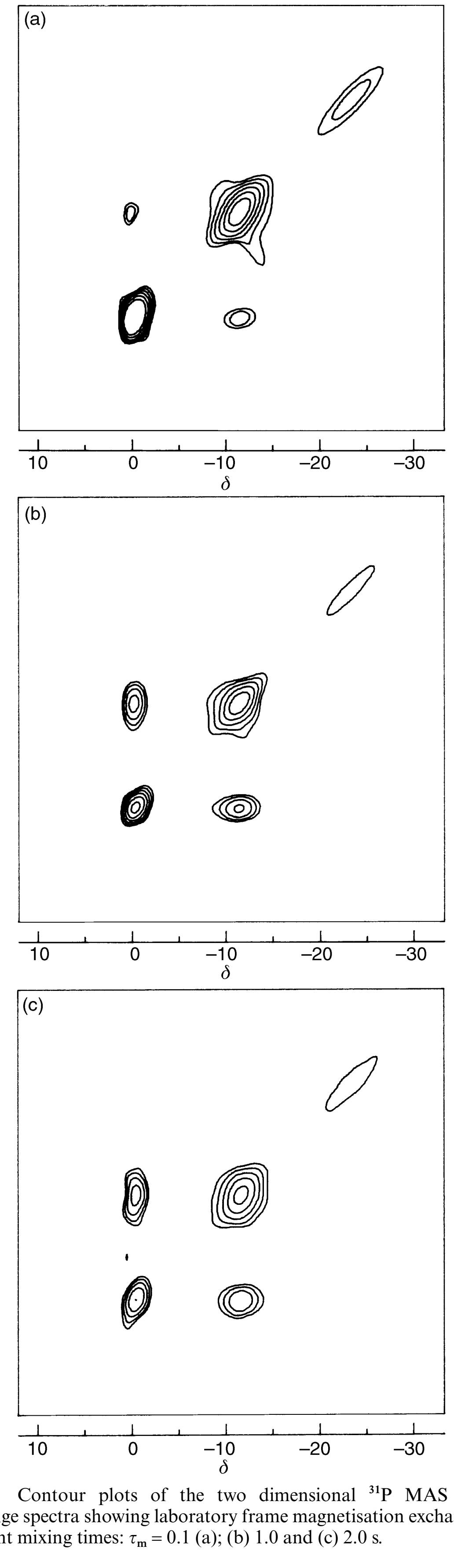

Fig. 4 Contour plots of the two dimensional ^{31}P MAS NMR exchange spectra showing laboratory frame magnetisation exchange for different mixing times: τ_m = 0.1 (a); (b) 1.0 and (c) 2.0 s.

Interpretation of the ^1H mediated magnetisation exchange is in fact less clear cut than the direct exchange. Despite the presence of cross peaks, conclusively proving the proximity of the resonances involved, the absence of a cross peak does not necessarily prove they are distant. This is so because the magnetisation exchange mechanism relies not just on the strength of the dipolar coupling but also on the ^1H interactions providing spectral overlap between the resonances with different isotropic chemical shifts. Thus the greater chemical shift difference between the resonances the poorer the spectral overlap and the smaller the zero quantum transition rate will be, leading in turn to a reduced cross peak intensity. Although this is a possible explanation for the absence of a cross peak between the Q_0 and Q_2 resonances it is unlikely to be the case

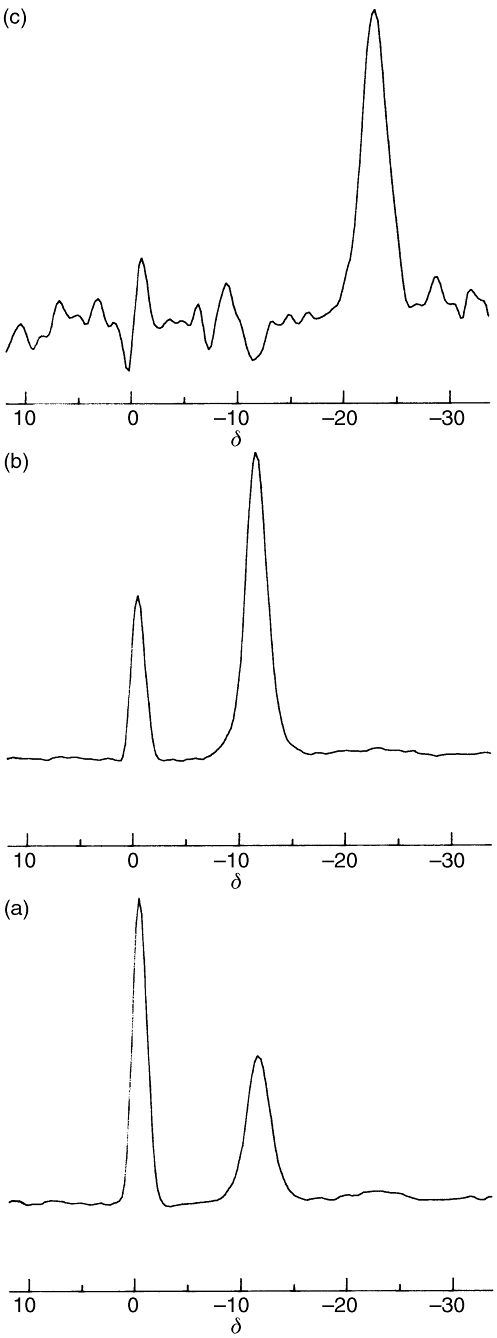

Fig. 5 Cross sections of the two dimensional ^{31}P MAS NMR exchange spectra contour plots at a mixing time of 2s at the position of the isotropic Q_N resonances. (a) δ 0; (b) −10 and (c) −20.

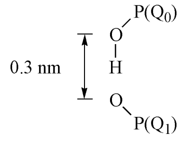

Fig. 6 Schematic structure of the Q_0 and Q_1 phosphorus interaction.

for the Q_1/Q_2 cross peak given that these resonances strongly overlap. Hence the absence of the Q_1/Q_2 cross peak shows that these structural types are further apart than about 0.6 nm. Both direct and ^1H–^{31}P mediated magnetisation exchange are clearly inefficient, requiring long mixing times. The relative inefficiency of the rf driven recoupling is of uncertain origin. Instrumental factors play some part as well as residual ^1H dipolar coupling. Significant chemical shift anisotropy of the ^{31}P spins involved in the magnetisation exchange is known to reduce the efficiency of rf driven dipolar recoupling.[15] Yet this will also adversely affect the laboratory frame magnetisation exchange. Another possibility is interference in the coherent transfer of rf driven recoupled magnetisation brought by a dynamic process or indeed the laboratory frame mechanism.

Relating the observed magnetisation exchange to the reactions taking place within the phosphosilicate gel is complicated by the cut-off distance seen in the ^{31}P–^{31}P dipolar coupling mediated exchange process, where the absence of a cross peak is consistent with any distance above the limiting distance of about 0.6 nm. Despite this limitation of the distance scaling the data reported are consistent with a picture of the phosphosilicate gel with distinct domains of different phosphorus connectivity. Three models are consistent with the presence of only Q_2 in a part of the silicate matrix. One, cyclic phosphates are formed so no Q_1 would be attached to Q_2. Two, very long chain polyphosphate is formed making the $Q_2 : Q_1$ ratio large with the consequence that the cross peak has negligible intensity. Three, Q_2 is cross-linked with the silicate matrix. In this case no Si–O–P linkages are seen in the ^{29}Si NMR, however, this does not rule out the third model because only a small fraction of the total ^{29}Si would be involved. On the basis of the current results it is not possible to distinguish between these models. A better technique for determining the separation of the Q_N sites would be an experiment based on ^1H spin diffusion experiments,[19] however these were not possible in this case because of the low signal-to-noise ratio after the ^{31}P to ^1H cross polarisation step.

3 Conclusion

Chemical heterogeneity has been demonstrated in a phosphosilicate gel by use of two dimensional NMR magnetisation exchange spectroscopy. Magnetisation exchange was observed in the laboratory frame as well as in rf driven ^{31}P–^{31}P dipolar recoupling. Rf driven exchange was inefficient indicating weak dipolar coupling between Q_0 and Q_1 phosphorus; no exchange peaks to Q_2 were observed. Laboratory frame magnetisation exchange was only observed between Q_0 and Q_1 and was attributed to three spin interactions involving ^1H spins. Based on the intense cross peaks seen, the majority of the Q_0 and Q_1 phosphorus must participate in the exchange process suggesting a close association of these two structural types. A model for this association has been proposed involving a hydrogen bonded interaction between the Q_0 and Q_1 units. The pattern of the magnetisation exchange is consistent with a variable degree of reaction of the phosphorus monomer in the silicate matrix.

4 Experimental

The phosphosilicate gel was prepared by the controlled hydrolysis of phosphoryl chloride $POCl_3$ and tetraethoxysilane $Si(OC_2H_5)_4$ to give a gel of molar composition 10% P_2O_5–90% SiO_2.[2] Gelation took place in ten days at room temperature. After drying at 100 °C for one day the gel was heated to 300 °C and allowed to cool.

^{31}P magic angle spinning NMR spectra were obtained on a Bruker MSL200 NMR spectrometer operating at 81.0 MHz for ^{31}P and 200.13 MHz for ^1H. Neighbouring phosphorus spins were identified by spin exchange occurring through the dipole–dipole interaction. Two related pulse sequences were used. First, a standard 2-D exchange NMR sequence with TPPI (Time Proportional Phase Increment) adapted for high power ^1H decoupling during both t_1 and t_2 periods.[9] Second, a modified 2-D exchange NMR sequence with TPPI incorporating rotor synchronised π pulses (XY-8 cycle) during the mixing period for ^{31}P–^{31}P dipolar recoupling.[10] Magic angle spinning (MAS) at 5 kHz was employed throughout the experiment to give high resolution ^{31}P NMR spectra thereby allowing the observation of the Q_N resonances. Typical $\pi/2$ pulses of 3.2 µs and π pulses of 6.4 µs were used together with recycle times of 10 s; 16 or 32 transients per t_1 increment were acquired. A time domain data size of 512 points in both dimensions was used over a spectral width of 5 kHz giving a time increment of 100 µs. Transverse magnetisation was allowed to decay during two 50 ms dephasing periods one before and one after the mixing time. Variable contact time ^1H–^{31}P cross polarisation were carried out with the contact time ranging from 0.2 to 10 ms. ^{31}P chemical shifts are referenced to 85% phosphoric acid as δ 0.0.

Acknowledgements

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