

## Application of the MAS-J-HMQC experiment to a new pair of nuclei $\{^{29}\text{Si}, ^{31}\text{P}\}$ : $\text{Si}_5\text{O}(\text{PO}_4)_6$ and $\text{SiP}_2\text{O}_7$ polymorphs

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### Abstract

We report the results of the two-dimensional MAS-J-HMQC experiment providing scalar correlations between  $^{29}\text{Si}$  and  $^{31}\text{P}$  nuclei in solid state NMR, and we give the first evaluation of the  $^2J_{\text{Si-O-P}}$  coupling constants ( $\sim 15$  Hz) for a crystalline silicophosphate phase  $\text{Si}_5\text{O}(\text{PO}_4)_6$ . The experiment is applied to the characterization of complex mixtures of  $\text{SiP}_2\text{O}_7$  phases, through editing of  $^{31}\text{P}$  spin pairs by the heteronuclear  $^2J_{\text{P-O-Si}}$  interaction.

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### 1. Introduction

In the field of materials chemistry, the local structure of compounds can be probed efficiently by NMR spectroscopy. The scalar interaction is characteristic of the existence of chemical bonds and the measurement of the corresponding  $J$  coupling constants is known to provide detailed insights in the structure of crystalline phases or amorphous materials [1]. The heteronuclear correlation experiment MAS-J-HMQC [2,3] shows in particular, that the transfer through scalar  $J$  coupling has one major advantage over dipolar transfer by selecting the chemical bond correlations. We should note that other schemes based on  $J$  interaction, such as INEPT [4], have been proposed in the frame of solid state NMR.

In the last few years, silicophosphate gels and materials have attracted much attention. Indeed, these materials present very interesting technological and structural properties suitable for fast proton conductor [5–7] and for applications as biomaterials and catalysts [8]. Very few  $^{31}\text{P}/^{29}\text{Si}$

correlation experiments were published in the literature [9], based on dipolar CP transfer ( $^{31}\text{P} \rightarrow ^{29}\text{Si}$ ). The use of  $J$ -mediated correlation experiments appears as very promising for the fine structural characterization of such materials.

The results published so far in the literature and dealing with the MAS-J-HMQC experiment concern the following spin pairs: ( $^1\text{H}$ ,  $^{13}\text{C}$ ), ( $^1\text{H}$ ,  $^{15}\text{N}$ ) [2,10] (spin  $\frac{1}{2}$ , spin  $\frac{1}{2}$ ); ( $^{31}\text{P}$ ,  $^{27}\text{Al}$ ) [3] (spin  $\frac{1}{2}$ , spin  $\frac{5}{2}$ ); ( $^{27}\text{Al}$ ,  $^{17}\text{O}$ ) [11] (spin  $\frac{5}{2}$ , spin  $\frac{5}{2}$ ). No example of such an experiment involving  $^{31}\text{P}$  and  $^{29}\text{Si}$  nuclei in Si-O-P bonds has been reported. We show that this experiment efficiently applies to the  $^{31}\text{P}/^{29}\text{Si}$  pair of nuclei.

The experiment was set up by using various crystalline silicophosphate phases. We shall first consider the simple case of the  $\text{Si}_5\text{O}(\text{PO}_4)_6$  phase, which has been used very recently for the implementation of  $^{31}\text{P} \rightarrow ^{29}\text{Si}$  CP MAS experiments [9]. This particular phase is obtained with amorphous silica  $\text{SiO}_2$  as secondary product. It will be demonstrated that the MAS-J-HMQC sequence acts as an editing sequence. Then, we will show that the MAS-J-HMQC approach can be extended to more complex systems, such as mixtures of silicophosphate ( $\text{SiP}_2\text{O}_7$ ) polymorphs and of  $\text{Si}_5\text{O}(\text{PO}_4)_6$ . In this case, the spectroscopic

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goal is to extract, via  $J$  coupling, pairs of  $^{31}\text{P}$  nuclei (belonging to various pyrophosphate units) bonded to the  $^{29}\text{Si}$  nuclei.

## 2. Experimental details

Solid state NMR experiments were performed on a Bruker AVANCE 300 spectrometer at  $B_0 = 7\text{ T}$  with  $\nu_0(^{31}\text{P}) = 121.49\text{ MHz}$  and  $\nu_0(^{29}\text{Si}) = 59.63\text{ MHz}$ , using a 4 mm triple resonance Bruker MAS probe. The spinning rate was 14 kHz and samples were spun at the magic angle using  $\text{ZrO}_2$  rotors.  $^{31}\text{P}$  NMR chemical shift was referenced to 85% aqueous  $\text{H}_3\text{PO}_4$  and to TMS for  $^{29}\text{Si}$ . Full experimental details are given in the Figure captions.  $^{31}\text{P}$ - $^{29}\text{Si}$  MAS-J-HMQC experiment was detected on the  $^{31}\text{P}$  channel to enhance sensitivity.

The synthesis protocol of the  $\text{Si}_5\text{O}(\text{PO}_4)_6$  phase has been recently reported [9]. Amorphous silica is a side product involved in the synthesis. The  $T_1(^{31}\text{P})$  of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  was estimated to  $\sim 450\text{ s}$ . To obtain 2D MAS-J-HMQC spectra with a good signal to noise ratio in a reasonable time, it has been necessary to decrease the  $T_1$  relaxation time. For that purpose, the doping of the  $\text{Si}_5\text{O}(\text{PO}_4)_6$  phase by a paramagnetic complex (namely,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) has been performed (1%). The % molar ratio was adjusted to obtain shortened  $T_1(^{31}\text{P})$  ( $\sim 1\text{ s}$ ), without drastic modification of the characteristic  $T_2$  of the sample (the definition of  $T_2$  is given below). XRD powder patterns of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  with, and without  $\text{Ni}^{2+}$ , were similar.

Following the same purpose,  $\text{Ni}^{2+}$  was added during the synthesis of the mixture of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  and the polymorphic forms of  $\text{SiP}_2\text{O}_7$ : after the dissolution of 0.05 g (0.22 mmol) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in ethanol, 5.16 g (44.8 mmol) of phosphoric acid ( $\text{H}_3\text{PO}_4$  85%) were added, followed by 4.67 g (22.4 mmol) of tetraethoxysilane  $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ . A gel was obtained after 2 h at room temperature and then heated at 100 °C for 48 h, before a final heat treatment at 1000 °C for 2 h. It should be noted that  $T_1(^{29}\text{Si})$  are also drastically decreased.

## 3. Results and discussion

The structure of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  described by Mayer [12] (trigonal, R-3,  $a = 7.869\text{ \AA}$ ,  $c = 24.138\text{ \AA}$ ) involves one unique P site and three inequivalent Si sites (two 6-fold coordinated  $\text{Si}_{\text{VI}}$  atoms,  $\text{Si}_1$  and  $\text{Si}_2$ , and one 4-fold coordinated  $\text{Si}_{\text{IV}}$  atom,  $\text{Si}_3$ ). The  $\text{Si}_1/\text{Si}_2/\text{Si}_3$  ratio is 1:2:2. The structure consists of  $[\text{SiO}_6]$  and  $[\text{Si}_2\text{O}_7]$  groups linked by  $[\text{PO}_4]$  groups. Each  $[\text{PO}_4]$  tetrahedron is surrounded by three  $\text{Si}_{\text{VI}}$  atoms ( $\text{Si}_2 \times 2$ ) and  $\text{Si}_1$  and one  $\text{Si}_{\text{IV}}$  atom ( $\text{Si}_3$ ) (Fig. 1A). The four involved P-O-Si bonds are inequivalent. The  $^{31}\text{P}$  MAS spectrum reveals a unique resonance located at  $\delta(^{31}\text{P}) = -44.1\text{ ppm}$ , while the  $^{29}\text{Si}$  MAS spectrum exhibits three resonances located at  $\delta = -119.8$ ,  $-214.0$ , and  $-217.7\text{ ppm}$ . A broad resonance centered at  $\delta(^{29}\text{Si}) \approx -110\text{ ppm}$  associated to amorphous silica  $\text{SiO}_2$  is also evidenced (Fig. 1B).

The first experiment presented in this paper is the measurement of the  $T_2'$  time constant, by a spin-echo experiment under MAS for the unique  $^{31}\text{P}$  signal, corresponding to the *non refocusable line width* (namely,  $\Delta' = 1/\pi T_2'$ ) which is usually significantly less than the “apparent line” width. Following the discussion of Emsley and coworkers [13–16], we use the notation  $T_2'$  which clearly states the experimental nature of this relaxation time, and makes no hypothesis on its underlying mechanism [3]. The echo sequence that measures the  $T_2'$  relaxation time is one of the most useful building block used in NMR: at the end of the  $2\tau$  delay, the chemical shift and field inhomogeneity are refocused. It thus provides a measurement of the coherence life time under the actual MAS and rf conditions. Long  $T_2'$  are key points for all  $J$ -mediated solid state NMR experiments [3,11,14–16].

Fig. 1C shows the spin-echo sequence and the corresponding decay curve. The curve was fitted by a single exponential decay in time domain according to:

$$I = \exp(-2\tau/T_2') \quad (1)$$

leading to  $T_2' = 65 \pm 3\text{ ms}$ . This rather long  $T_2'$  value is favourable for the creation and evolution of coherences during the HMQC pulse scheme (Fig. 1D). As the optimum  $\tau$  value for a given compound depends strongly on the  $^2J_{\text{P-O-Si}}$  value and  $T_2'$ , various 1D  $^{31}\text{P}$ - $^{29}\text{Si}$  MAS-J-HMQC experiments at variable  $\tau$  were performed. Fig. 1D shows the intensity curve of the HMQC signal. We consider the case of spin pairs because, due to the low abundance of  $^{29}\text{Si}$  (4.7%), the probability to encounter one  $^{31}\text{P}$  spin coupled to two (or more)  $^{29}\text{Si}$  spins is very weak ( $< 1.2\%$ ). For one given spin pair, the evolution of the HMQC signal as a function of  $\tau$  can be modelled by [2,17]:

$$I_{\text{HMQC}} = I_0 \sin^2(\pi J_{\text{P-O-Si}} \tau) \exp(-2\tau/T_2'), \quad (2)$$

where  $T_2'$  is given by the MAS spin-echo experiment. By using Eq. (2) and taking into account a unique  $^{31}\text{P}$ - $^{29}\text{Si}$  coupling constant, an averaged  $^2J_{\text{P-O-Si}}$  value can be extracted from the data shown in Fig. 1D (for the fit of the build-up curve,  $T_2'$  was fixed at 65 ms). This crude approach leads to  $^2J_{\text{P-O-Si}} \sim 15\text{ Hz}$ . To the best of our knowledge, such constants have not been reported so far in the literature, neither in the frame of solid state NMR nor in high resolution NMR. More accurate values should be obtained by implementing frequency selective pulse sequences, such as those proposed recently by Amoureux et al. [18] or by using  $^{31}\text{P}/^{29}\text{Si}$  INEPT sequences. Moreover, experimental data such as those presented in Fig. 1D allow the determination of reasonable  $\tau$  values for the study of silicophosphate derivatives by HMQC-like experiments (namely,  $\tau \approx 20\text{--}35\text{ ms}$ ).

The  $^{29}\text{Si}$ - $^{31}\text{P}$  MAS-J-HMQC sequence is easily extended to 2D, as shown in Fig. 2A. Fig. 2B presents the 2D  $^{29}\text{Si}$ - $^{31}\text{P}$  MAS-J-HMQC spectrum obtained for  $\text{Si}_5\text{O}(\text{PO}_4)_6$ . The three  $^{29}\text{Si}$  resonances are correlated with the unique  $^{31}\text{P}$  resonance located at  $-44.1\text{ ppm}$ . As expect-

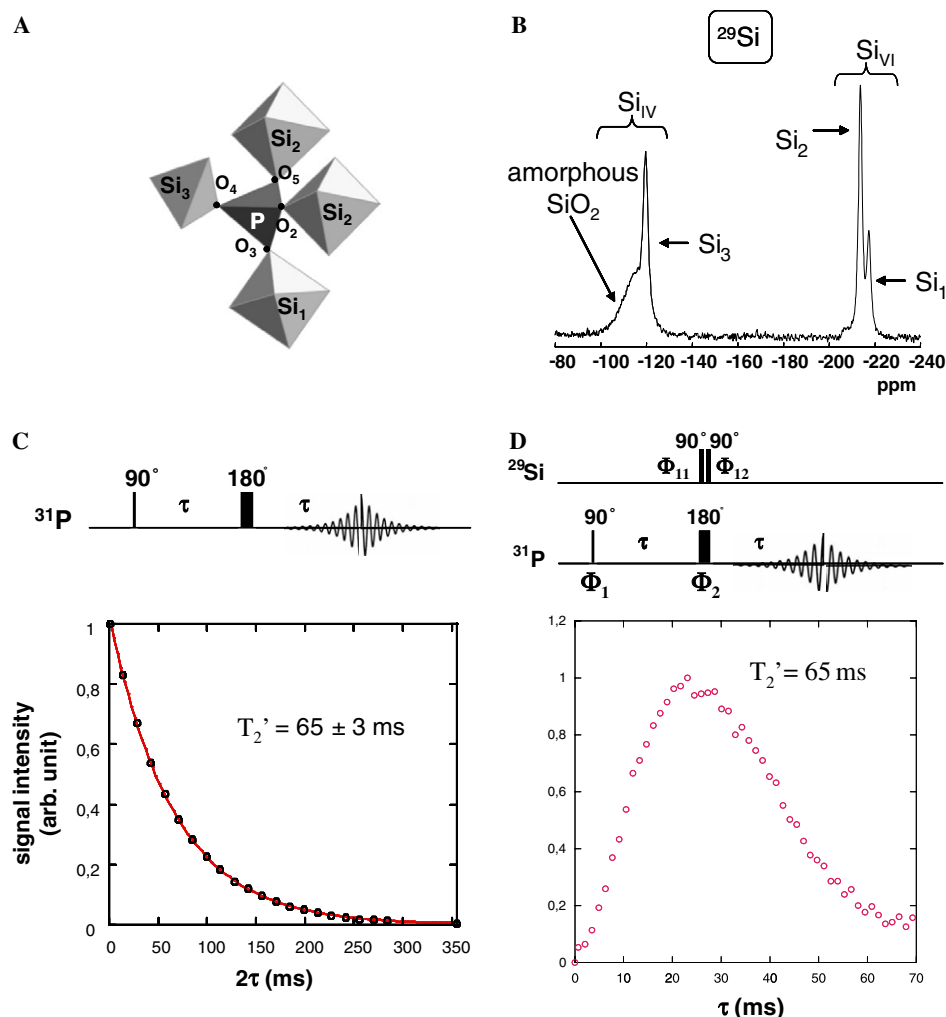


Fig. 1. (A) Part of the structure of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  around P atom. The labelling scheme of atoms are given according to [12]. The four P-O-Si bonds are inequivalent. (B)  $^{29}\text{Si}$  MAS spectrum of  $\text{Si}_5\text{P}_6$  ( $\varnothing$ : 4 mm, rotation frequency (RO): 14 kHz, number of co-added transients (NS): 1760, recycle delay (RD): 10 s,  $90^\circ$  ( $^{29}\text{Si}$ ): 4.5  $\mu\text{s}$ , LB = 10 Hz). (C) Evolution of  $^{31}\text{P}$  intensity for  $\text{Si}_5\text{O}(\text{PO}_4)_6$  in a spin-echo MAS experiment (RO = 14 kHz). (D) Evolution of  $^{31}\text{P}$  intensity for  $\text{Si}_5\text{O}(\text{PO}_4)_6$  in 1D  $^{31}\text{P}/^{29}\text{Si}$  MAS-J-HMQC experiment (RO = 14 kHz). Phase cycling scheme for the MAS-J-HMQC sequence:  $\Phi_1 = +x$ ;  $\Phi_2 = +x, +x, +y, +y, -x, -x, -y, -y$ ;  $\Phi_{11} = +x$ ;  $\Phi_{12} = +x, -x$ ; receiver =  $+x, -x, -x, +x, +x, -x, -x, +x$ .

ed, the experiment edits the chemically bonded  $^{29}\text{Si}$ : no correlation is observed at  $\delta(^{29}\text{Si}) \approx -110$  ppm, as this resonance corresponds to amorphous  $\text{SiO}_2$  (see above).

The synthesis of  $\text{SiP}_2\text{O}_7$  phases (see above) leads generally to mixtures of polymorphs and to complex  $^{31}\text{P}$  MAS NMR spectra [19]. We will then show that the 2D  $^{29}\text{Si}$ - $^{31}\text{P}$  MAS-J-HMQC experiment is helpful for the determination of the various phases involved. The X-ray diffraction (XRD) powder pattern of the sample (not shown here) indicates, that besides the  $\text{Si}_5\text{O}(\text{PO}_4)_6$  crystalline phase presented before, three polymorphs of  $\text{SiP}_2\text{O}_7$  were synthesized as major constituents, namely a tetragonal (JCPDS 22-1320) and two monoclinic forms (39-0189 and 25-0755) [20]. As shown in Fig. 3B, the  $^{31}\text{P}$  MAS spectrum reveals also the presence of the cubic form of  $\text{SiP}_2\text{O}_7$ , but as a very minor component. This particular phase was not clearly evidenced by XRD. The isotropic chemical shifts of the various  $\text{SiP}_2\text{O}_7$  polymorphs are reported in Table 1 [19,21,22]. For the  $\text{SiP}_2\text{O}_7$  polymor-

phs, it is known from XRD data that the pyrophosphate groups (involving generally two non equivalent P sites) are linked exclusively to  $\text{Si}_{\text{VI}}$  atoms (Fig. 3A). Fig. 3C shows the corresponding  $^{29}\text{Si}$  MAS NMR spectrum. Resonances corresponding to 4-fold and 6-fold coordinated Si atoms are observed, with resolved components in the  $-220/-210$  ppm region. Fig. 4 presents the 2D  $^{29}\text{Si}$ - $^{31}\text{P}$  MAS-J-HMQC spectrum of the  $\text{Si}_5\text{O}(\text{PO}_4)_6/\text{SiP}_2\text{O}_7$  mixture. First, we note three cross peaks associated to the  $\text{Si}_5\text{O}(\text{PO}_4)_6$  phase (the  $^{31}\text{P}$  resonance at  $-43.8$  ppm correlates with three  $^{29}\text{Si}$  resonances at  $-217.0$ ,  $-213.3$ , and  $-119.1$  ppm). Moreover, the 2D spectrum reveals the presence of four other cross peaks. The  $^{29}\text{Si}$  resonance at  $\delta(^{29}\text{Si}) = -212.8$  ppm is correlated with two  $^{31}\text{P}$  resonances located at  $-45.5$  and  $-52.9$  ppm and assigned to the  $\text{SiP}_2\text{O}_7$  tetragonal form. The  $^{29}\text{Si}$  resonance at  $\delta(^{29}\text{Si}) = -214.9$  ppm is correlated with two  $^{31}\text{P}$  resonances at  $\delta(^{31}\text{P}) = -47.6$  and  $-55.3$  ppm, which are characteristic for the  $\text{SiP}_2\text{O}_7$  monoclinic 1 form (Table 1). It

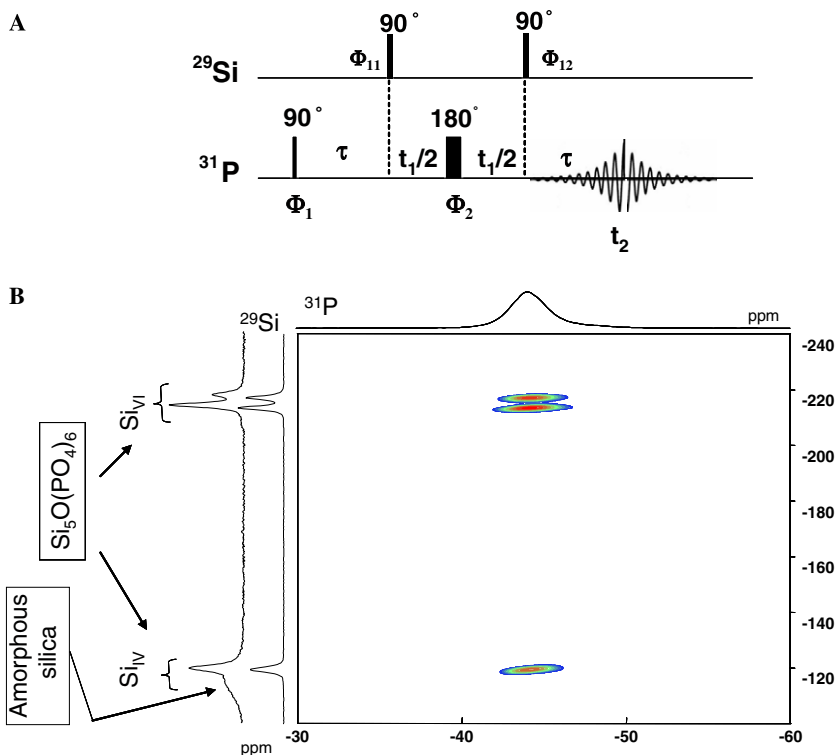


Fig. 2. (A) 2D MAS-J-HMQC  $^{31}\text{P}/^{29}\text{Si}$  pulse sequence. (B) 2D MAS-J-HMQC  $^{31}\text{P}/^{29}\text{Si}$  spectrum of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  ( $\varnothing$ : 4 mm, RO: 14 kHz, NS: 104 for each  $t_1$  increment, RD: 3 s,  $90^\circ$  ( $^{31}\text{P}$ ): 6  $\mu\text{s}$ ,  $90^\circ$  ( $^{29}\text{Si}$ ): 4.9  $\mu\text{s}$ ,  $\tau = 35$  ms, states mode with 512  $t_1$  increments, 44 h, LB = 20 Hz in F2 ( $^{31}\text{P}$ ), LB = 10 Hz in F1 ( $^{29}\text{Si}$ )). 1D  $^{29}\text{Si}$  and  $^{31}\text{P}$  spectra, as well as the projections, are also presented. The bottom contour is at 5% with a multiplicative increment of 1.40.

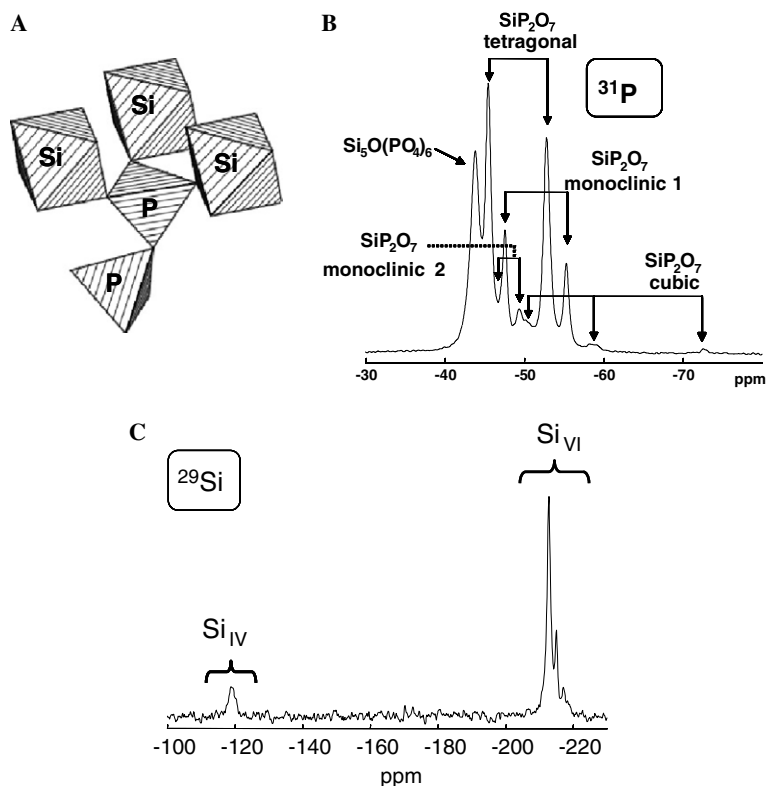


Fig. 3. (A) Structural scheme for  $\text{SiP}_2\text{O}_7$  pyrophosphate phases: one given P atom is bonded to one P atom and three 6-fold coordinated Si atoms. (B)  $^{31}\text{P}$  MAS spectrum of the mixture of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  and several polymorphs of  $\text{SiP}_2\text{O}_7$  (tetragonal, monoclinic 1, monoclinic 2, and cubic) ( $\varnothing$ : 4 mm, RO: 14 kHz, NS: 8, recycle delay: 5 s,  $90^\circ$  ( $^{31}\text{P}$ ): 6  $\mu\text{s}$ , LB = 0 Hz). (C) The corresponding  $^{29}\text{Si}$  MAS spectrum ( $\varnothing$ : 4 mm, RO: 14 kHz, NS: 800, RD: 5 s,  $90^\circ$  ( $^{29}\text{Si}$ ): 5.3  $\mu\text{s}$ , LB = 20 Hz).

Table 1  
 $^{31}\text{P}$  and  $^{29}\text{Si}$  isotropic chemical shifts for the mixture of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  and  $\text{SiP}_2\text{O}_7$  polymorphs

Phase (JCPDS)	$\delta_{\text{iso}}$ (ppm) $^{31}\text{P}$ (Fig. 3B)	$\delta_{\text{iso}}$ (ppm) $^{31}\text{P}$ (Fig. 4)	$\delta_{\text{iso}}$ (ppm) $^{29}\text{Si}$ (Fig. 4)
$\text{Si}_5\text{O}(\text{PO}_4)_6$ (70–2071)	–43.8	–43.8	–119.1 –213.3 –217.0
$\text{SiP}_2\text{O}_7$ tetragonal (22–1320)	–45.5	–45.5	–212.8
$\text{SiP}_2\text{O}_7$ monoclinic 1 (39–0189)	–47.6	–47.6	–214.9
$\text{SiP}_2\text{O}_7$ monoclinic 2 (25–0755)	–46.1	–55.3	
$\text{SiP}_2\text{O}_7$ cubic (22–1321)	~–50 ~–58 ~–70		

follows that the 2D  $^{29}\text{Si}$ – $^{31}\text{P}$  MAS-J-HMQC experiment is clearly able to edit the  $^{31}\text{P}$  MAS spectrum in terms of the  $^{31}\text{P}$  pairs involved in each  $\text{SiP}_2\text{O}_7$  pyrophosphate phase. Moreover, the unique  $^{29}\text{Si}$  isotropic shift corresponding to each  $\text{SiP}_2\text{O}_7$  polymorph is determined with great accuracy. We note that the relative intensities of the cross peaks corresponding to  $\text{Si}_5\text{O}(\text{PO}_4)_6$  are high, when compared to the  $\text{SiP}_2\text{O}_7$  cross peaks. This tends to prove that variations of the  $^2J_{\text{P-O-Si}}$  values may occur from one silicophosphate structure to another. The absence of cross peaks for the monoclinic 2 and the cubic forms is surely related to the low amount of these particular phases and/or to much lower  $^2J_{\text{P-O-Si}}$  coupling constants. We also note that in all cases, the involved  $^2J_{\text{P-O-Si}}$  ( $\sim 15$  Hz) scalar coupling is significantly smaller than the  $^{31}\text{P}$  linewidths

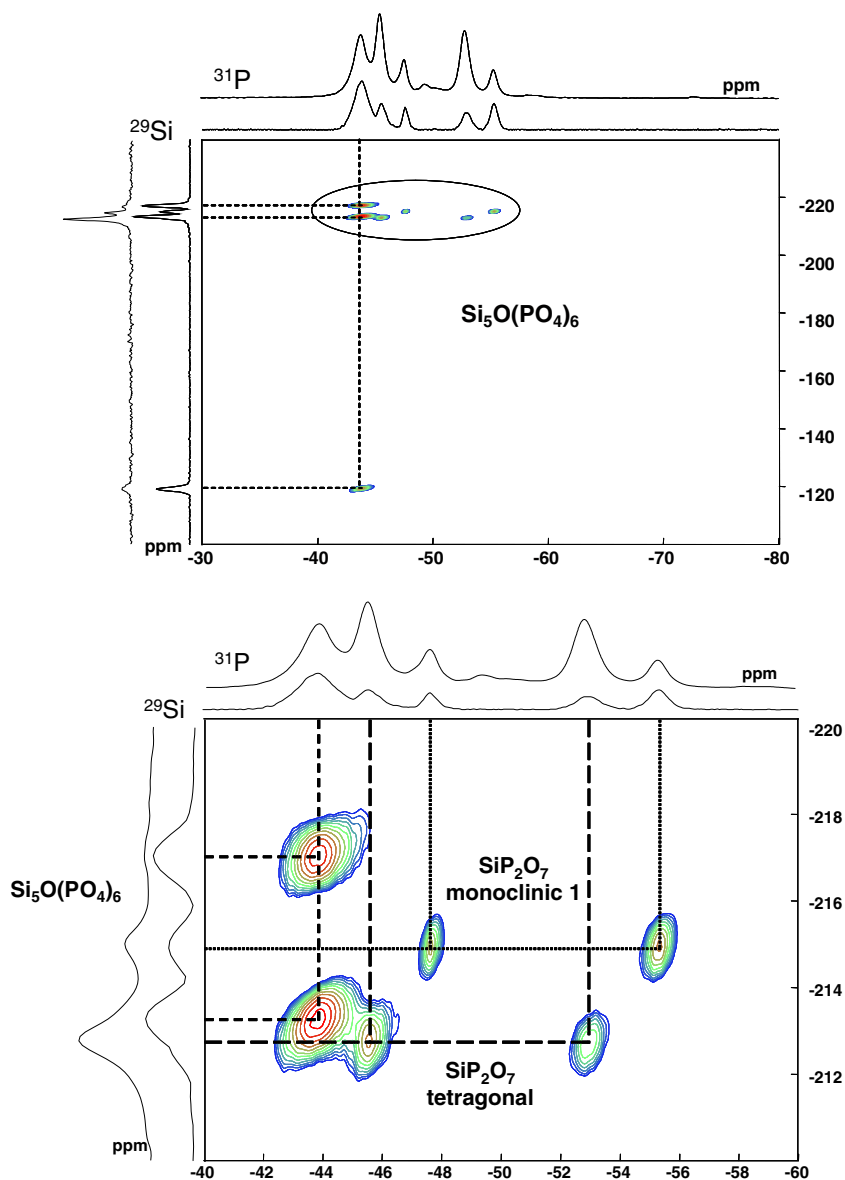


Fig. 4. 2D MAS-J-HMQC  $^{31}\text{P}/^{29}\text{Si}$  spectrum of the mixture of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  and  $\text{SiP}_2\text{O}_7$  polymorphs ( $\varnothing$ : 4 mm, RO: 14 kHz, NS: 136 for each  $t_1$  increment, RD: 5 s,  $90^\circ$  ( $^{31}\text{P}$ ): 6.8  $\mu\text{s}$ ,  $90^\circ$  ( $^{29}\text{Si}$ ): 5.3  $\mu\text{s}$ ,  $\tau$  = 25 ms, States mode with 208  $t_1$  increments, 40 h, LB = 0 Hz in F2 ( $^{31}\text{P}$ ), LB = 0 Hz in F1 ( $^{29}\text{Si}$ ), presaturation on the  $^{31}\text{P}$ ). 1D  $^{29}\text{Si}$  and  $^{31}\text{P}$  spectra, as well as the projections, are also presented. Below: expansion of the oval region. The bottom contour is at 8% with a multiplicative increment of 1.37.

[80–300 Hz], precluding the observation of doublets in the 1D  $^{31}\text{P}$  spectra.

#### 4. Conclusions

In conclusion, we have shown that the MAS-J-HMQC experiment can be extended to the  $\{^{29}\text{Si}, ^{31}\text{P}\}$  spin pair. The potential of this experiment is demonstrated through the study of a model compound ( $\text{Si}_5\text{O}(\text{PO}_4)_6$ ) and a complex mixture of  $\text{SiP}_2\text{O}_7$  polymorphs. The build-up curves of the HMQC experiment allowed the estimation of the  $^2J_{\text{P-O-Si}}$  coupling constants. In the case of mixtures of silicophosphates, the MAS-J-HMQC experiment allowed the editing of the  $^{31}\text{P}$  MAS spectrum, as well as the precise determination of the corresponding  $^{29}\text{Si}$  chemical shifts. This approach seems promising for the characterization of silicophosphates, for which no XRD data are available, and more generally for silicophosphate derived materials.

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