

Supporting Information: **How high concentrations of proteins stabilize the amorphous state of calcium orthophosphate: a solid-state NMR study of the casein case**

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**alpha1 (37.5% total)**

RPKHPIKHQGLPQEVLNENLLRFFVAPFPEVFGKEKVNELSKD**I**GSESTEDQAMEDIKQM  
EAESISSSEEIVPNNSVEQKH**I**QKEDVPSERYLGYLEQLLRLKKYKVPQLEIVPN**S**AEE**R**L  
HSM**K**E**I**HAQQKEPMIGVNQELAYFYPELFRQFYQLDAYPSGAWYYVPLGTQYT**D**APSFS  
DIPNPIGSE**N****E**KTTMPLW

**BETA (37.5% total)**

RELEELNVPG**E**IVES**S**SSSEE**S**ITRINK**K**IEKFQ**S**EEQQQT**E**DELQDK**H**PFAQTQSLVY  
PFPGPIPNSLPQNIPPLTQTPVVPPFLQP**E**VMGVSK**V**KEAMAP**K**H**K**EMPFPK**Y**PV**E**PFT  
ESQSLTLTD**V**ENL**H**LPLPLLQSWM**H**QPH**H**QPLPPTVMFPPQSVLSSQS**K**VLPVPQ**K**AVPY  
PQR**D**MPIQAFLLY**Q**EPVVLGPV**R**GPFP**I**IV

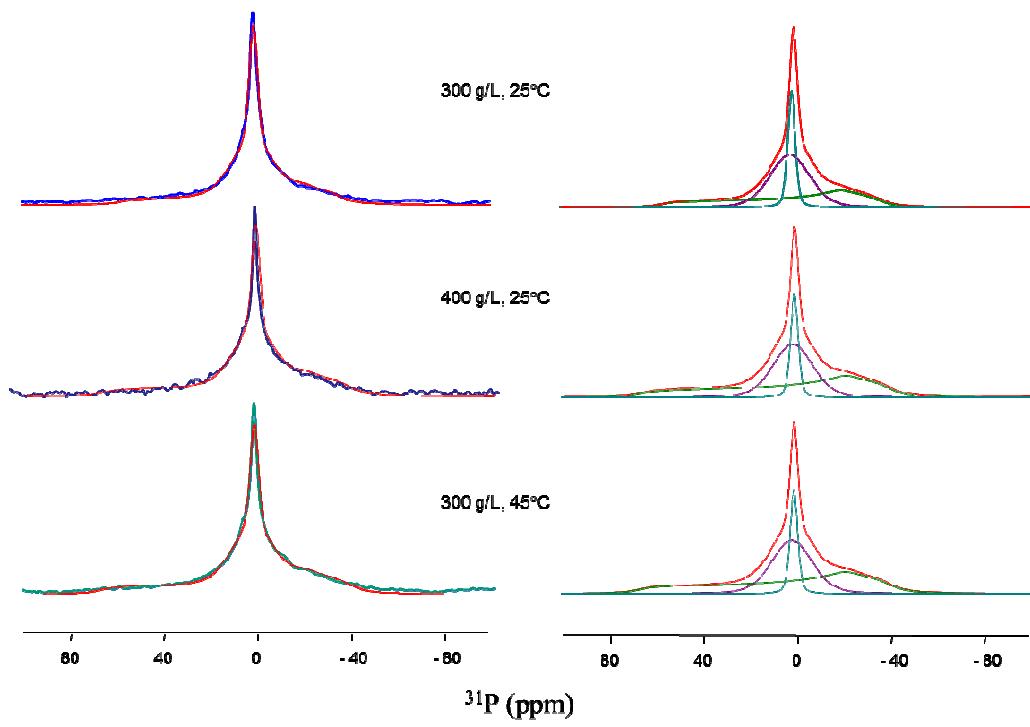
**Alpha2 (12.5% total)**

KNTMEHVSSSEESII**S**QETY**K**QEKNMAINPS**K**ENLCSTFC**K**EVVRNAN**EEE**YSIG**S**SSEE  
SAEVATEEV**K**ITVDD**K**HY**Q**KALNE**I**NQFY**Q**K**F**PQYLQYLY**Q**GPIV**L**NPW**D**QVK**R**NAVPIT  
PTLN**R**EQ**L****S**T**S**E**E****N****S**KKTVDM**E**STE**V**FT**K**K**T****K**L**T****E****E****K**N**R**LNFLKK**I**S**Q****R****Y****Q****K**FALPQYL  
**K**TVY**Q****H****Q****K****A****M****K****P****W****I****Q****P****K****T****K****V****I****P****Y****V****R****Y****L**

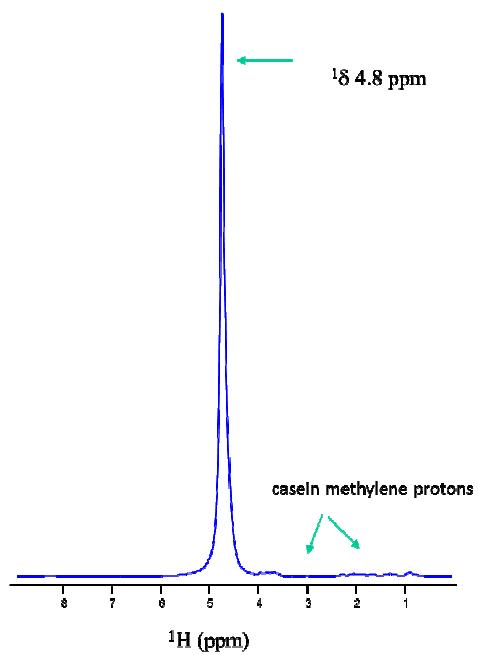
Phosphoserine **S**

**EMBOSS** (<http://emboss.sourceforge.net/>)

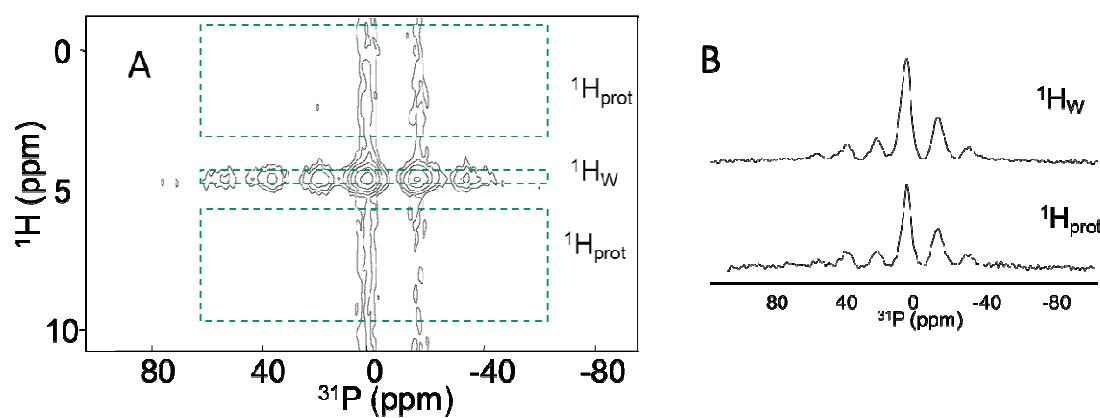
**Figure 1. Casein sequences.** Aminoacid letters are higlighted in green or yellow for positives and negatives charged



**Figure 2. One dimensional  $^{31}\text{P}$  quantitative static spectra of casein gels at different temperatures and concentrations.** The red lines correspond to the simulated spectrum respectively. On the right hand side, the three components of the spectrum are displayed: a narrow Gaussian peak,  $^{31}\text{P}_{\text{free}}$  (blue), a broad Gaussian peak,  $^{31}\text{P}_{\text{ACP}}$  (green) and a chemical shift anisotropy (CSA),  $^{31}\text{P}_{\text{pSer}}$  component (violet). No significant difference is found in the relative intensities of each component in the different conditions.



**Figure 3.** A 1D  $^1\text{H}$  spectrum at MAS 5kHz,  $300 \text{ g.L}^{-1}$ ,  $25^\circ\text{C}$ . The proton chemical shift of the intense water peak is 4.8 ppm.



**Figure 4.** CP 2D  $^1\text{H}$  - $^{31}\text{P}$  HETCOR spectra at 45°C (MAS 3.5 kHz) of casein gel at 400 g.L $^{-1}$ . (A) 2D spectrum; (B) sum of  $^{31}\text{P}$  slices extracted from the proton regions of the  $\text{H}_2\text{O}$  protons  $^1\text{H}_w$  and from the protons region of protein protons