^{1}H and ^{31}P NMR Spectroscopy of Dynamic Structures in Nano- and Mesostructured Hydroxyapatites

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Materials based on **calcium phosphates** have found many applications in

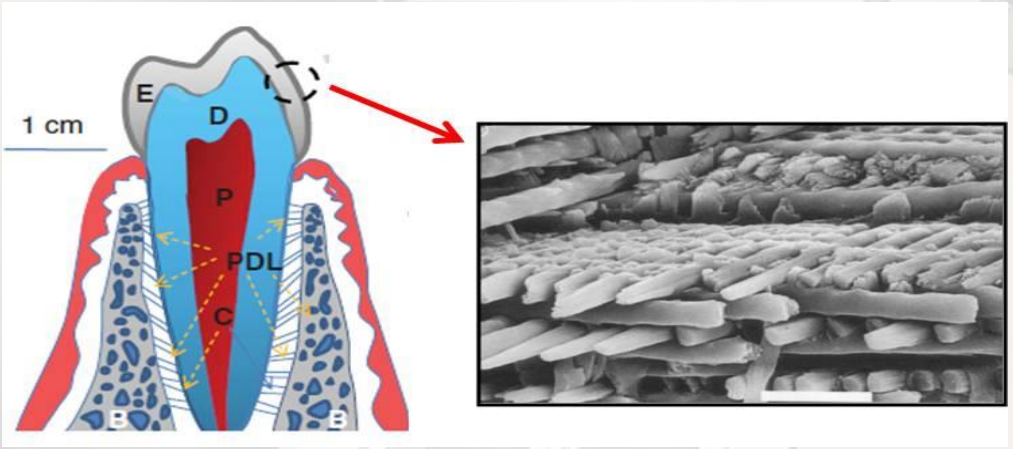
implantology, orthopedic and periodontal surgery.

A special place in these areas is occupied by

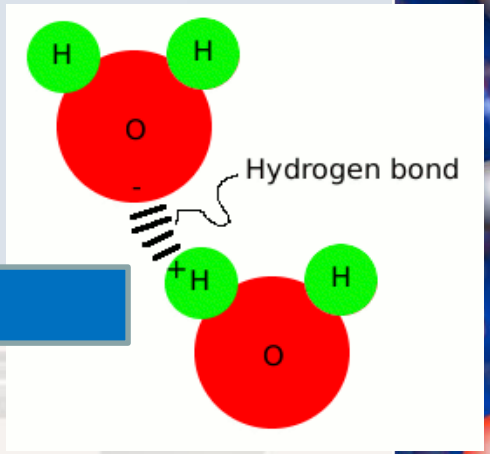
calcium hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2$

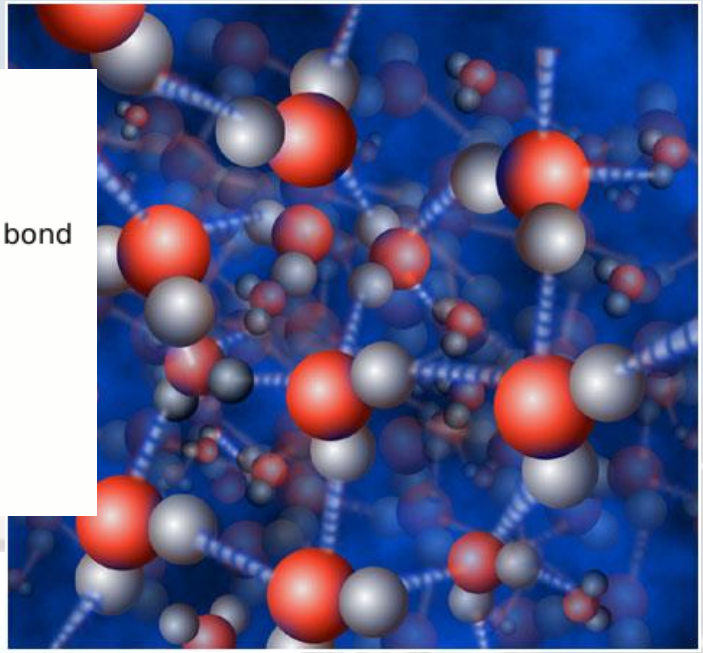
(further **CaHA**),

which shows close similarity to the mineral of hard tissues (bone, enamel, dentin, *etc.*) and therefore has high biocompatibility with them.

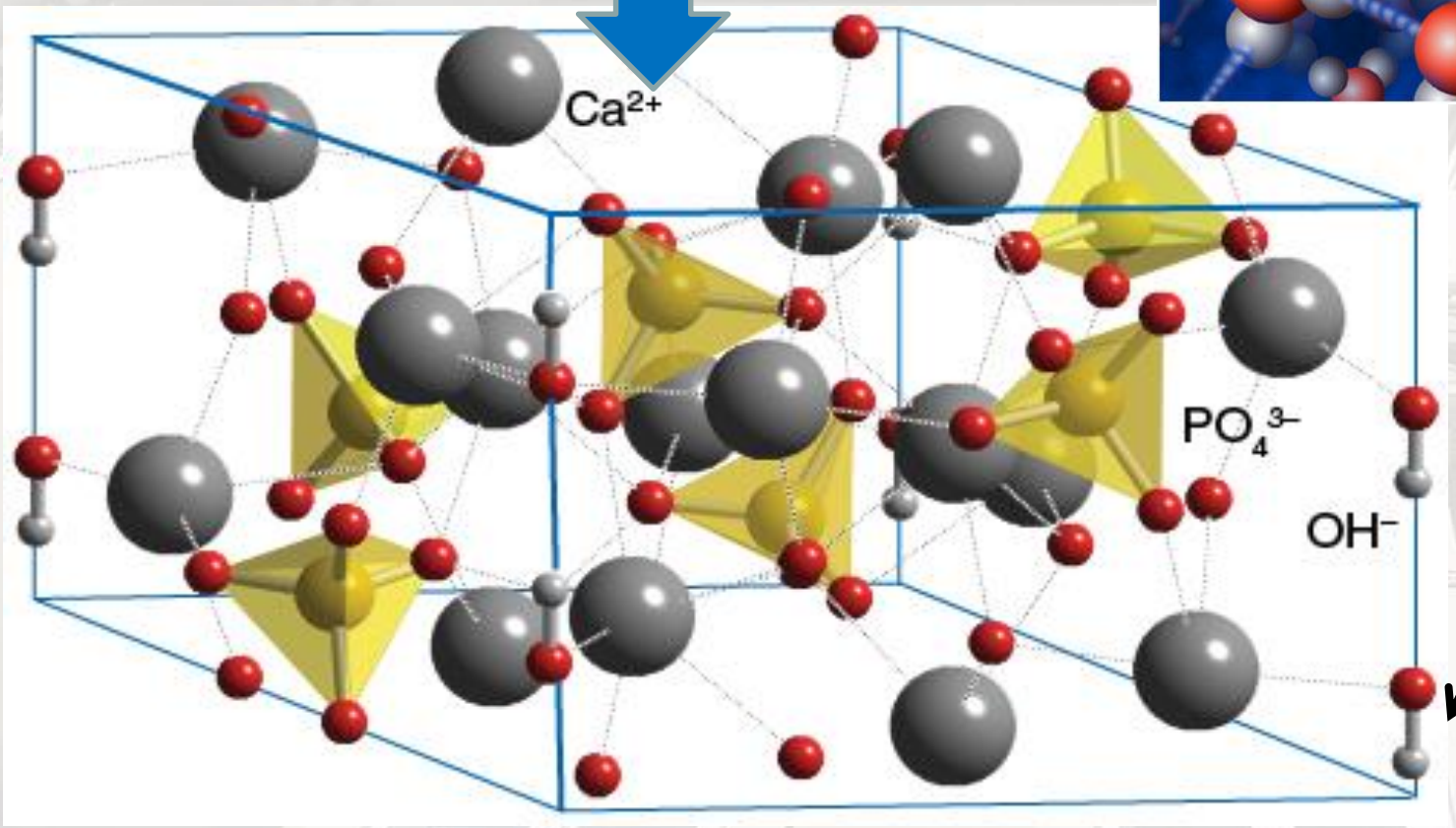


Physics:



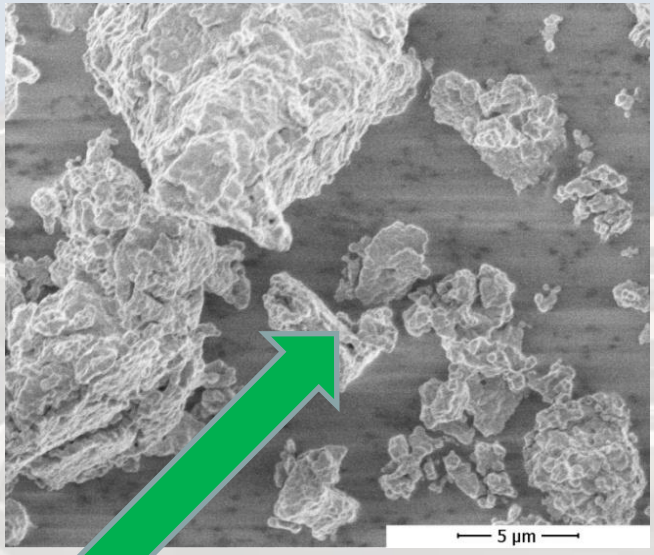


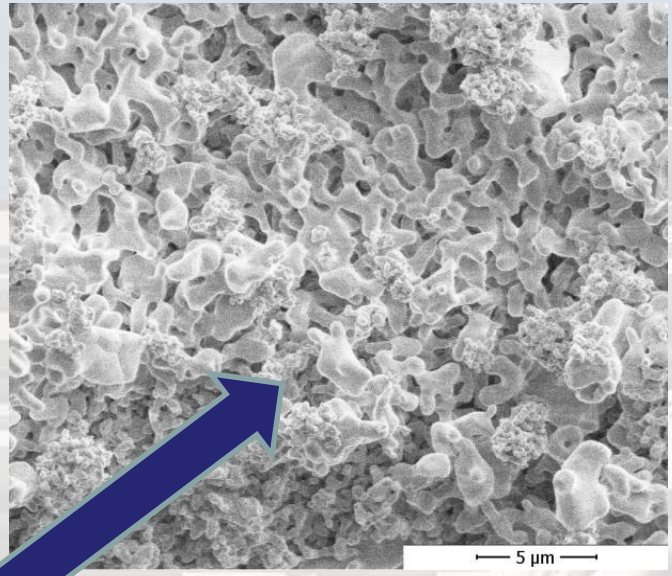
adsorbed water



structural hydroxyls

Materials studied: Sol-gel derived CaHAs

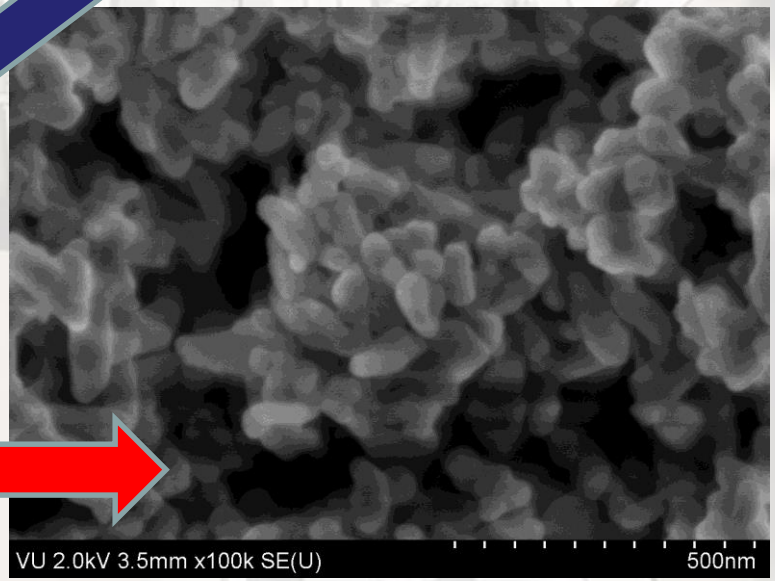




Amorphous phosphate phase (ACP-CaHA)

Nano-structured hydroxyapatite (CaHA)

Commercial nano-structured CaHA



The purposes of present work :

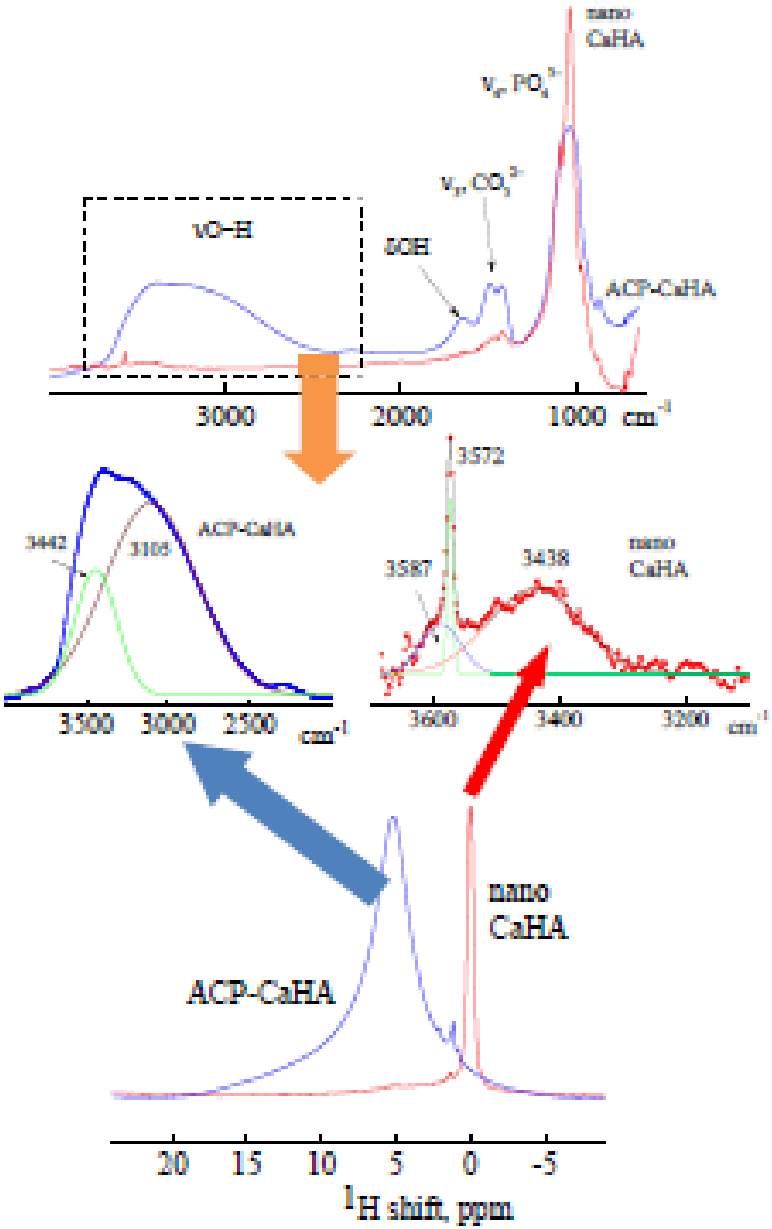
(i) analysis of ^{1}H MAS NMR and FTIR spectra in order to compare synthetic CaHAs respect to **the structural organization of hydroxyl groups** surround ^{31}P nuclei and to evaluate the relative contributions of static and dynamic structures in the samples;

(ii) the **high data point density** measurements of ^{1}H and ^{31}P NMR spectra and ^{1}H–^{31}P cross-polarization kinetics;

(iii) the development of proper methods of processing of CP MAS data that would allow to describe the **oscillatory kinetics and CP curves in nano-structured materials** over the wide range of contact time;

(iv) to determine the **characteristic size profile** and composition and **dynamic features** of the spin clusters in nano-structured materials.

The structural organization respect to the hydroxyl groups: the comparison of FTIR and ^{1}H MAS NMR spectra of calcium hydroxyapatite containing amorphous phosphate phase (ACP-CaHA) and nano-structured CaHA. *NMR spectra are normalized to a maximum intensity*.



Cross-polarization (CP)

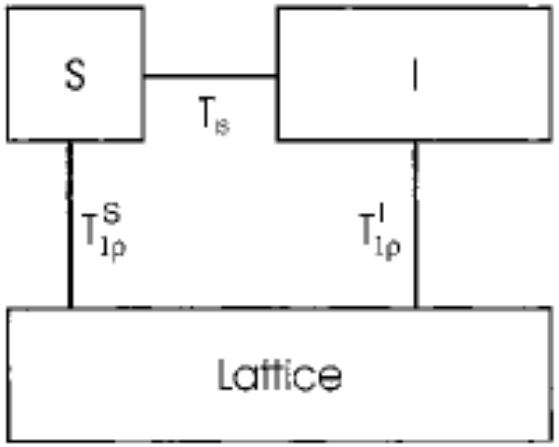
is a solid-state NMR technique originally developed for enhancing the peak intensities of rare nuclei by the polarization transfer from abundant nuclei, typically from protons.

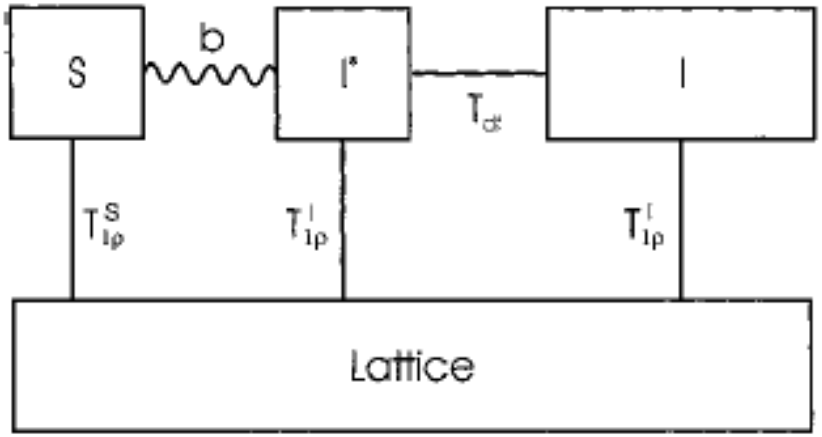
CP is also feasible between abundant nuclei. In such case, the CP enhancement is ineffective and sometimes the signals can be even weaker than those obtained from a conventional single pulse-acquire Bloch-decay (BD) experiments.

However, the CP technique between abundant nuclei is very useful, sometimes even unique in physical characterization of solid materials having complex structures.

Two CP models: ‘non-clasical’

‘clasical’





$$I(t) = I_0 \exp(-t/T_{1\rho}^{I})\left[1 - \frac{1}{2}\exp(-t/T_{df}) - \frac{1}{2}\exp\left(-\frac{3}{2}t/T_{df}\right)\cos(bt/2)\right]$$

$$\lambda = 1/(n+1)$$

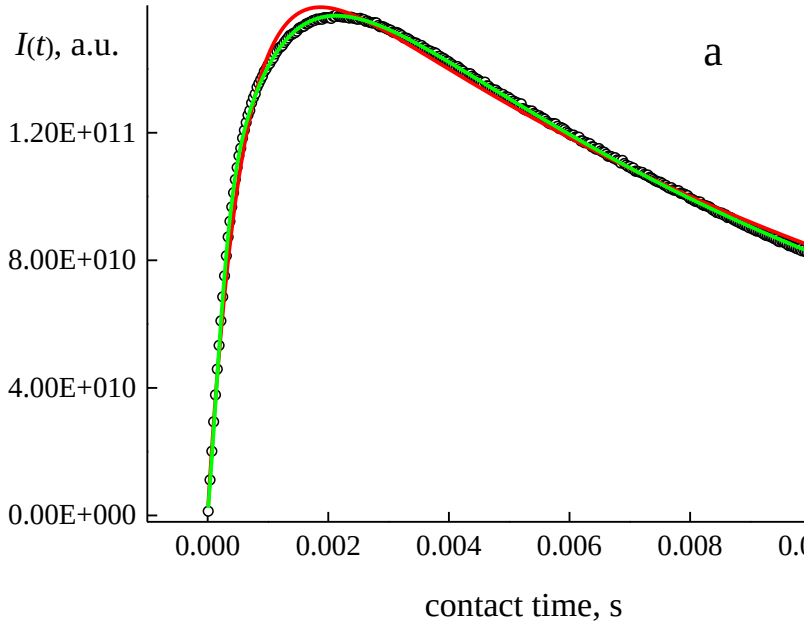
$$\overline{\cos(b_i t/2)} = \frac{\sum_i I_i \cos(b_i t/2)}{\sum_i I_i}$$

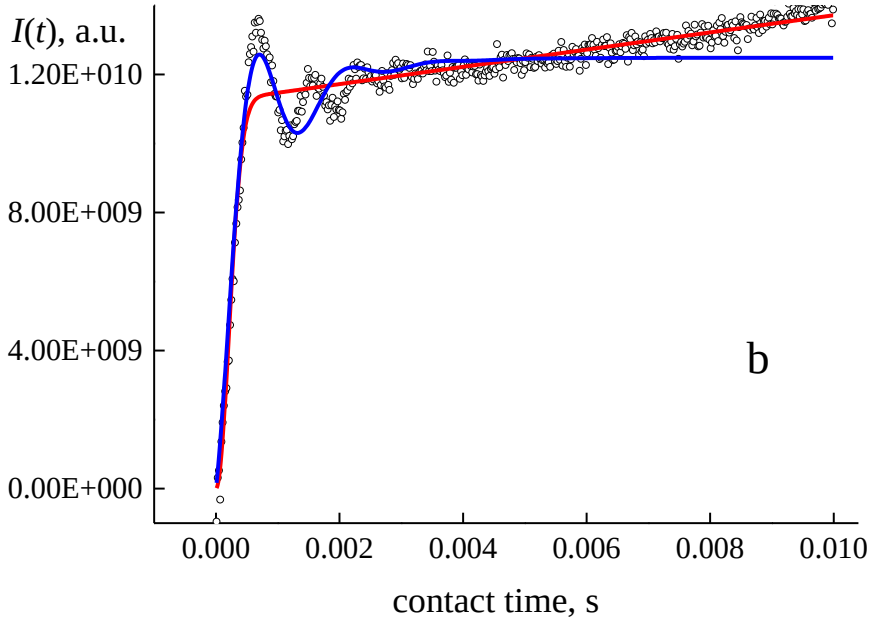
$$I(t) = I_0 \exp(-t/T_{1\rho}^{I})\left[1 - \lambda\exp(-t/T_{df}) - (1-\lambda)\exp\left(-\frac{3}{2}t/T_{df}\right)\exp\left(-\frac{1}{2}t^2/T_2^{\,2}\right)\right]$$

CP MAS kinetics

CaHA containing amorphous phosphate phase (ACP-CaHA)

nano-structured CaHA



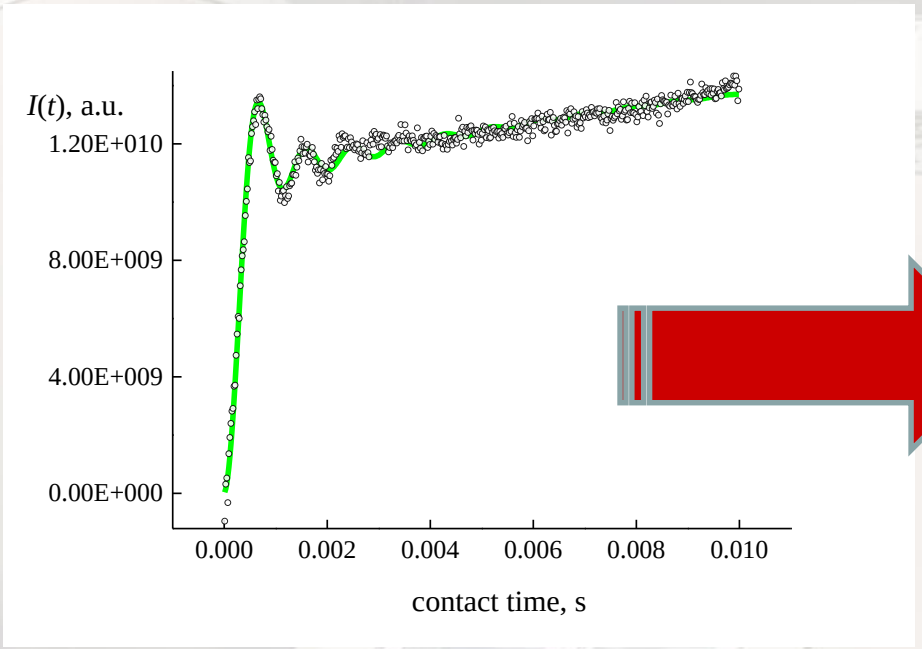


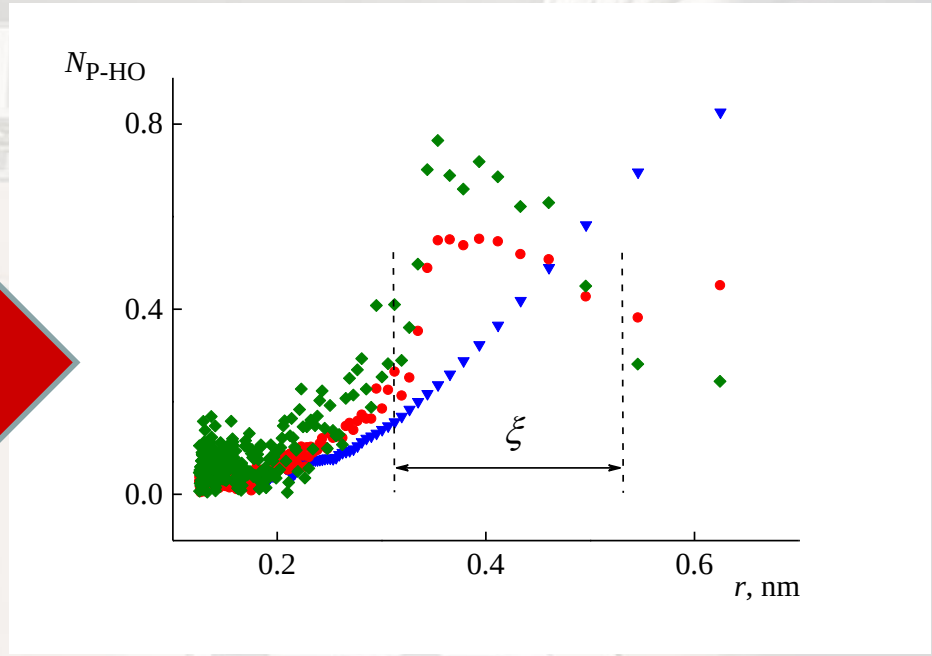
CP MAS kinetics

Method of processing for nano-structured CaHA:

$$\frac{\sum_i I\left(\frac{b_i}{2}\right)\cos\left(\frac{2\pi b_i t}{2}\right)}{\sum_i I\left(\frac{b_i}{2}\right)} \rightarrow \frac{1}{A}\sum_i^{\infty} I\left(\frac{b_i}{2}\right)\cos\left(2\pi\frac{b_i}{2}t\right) = \frac{1}{A}\,\mathrm{Re}\overline{\mathrm{FT}}\left\{I\left(\frac{b}{2}\right)\right\}$$

$$I(b/2) \sim \left|\overline{\mathrm{FT}}^{-1}\frac{1-\lambda f_1 - I(t)/(I_0 f_3)}{(1-\lambda)f_2}\right| \Longleftrightarrow b = \frac{\mu_0}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r^3}\frac{(1-3\cos^2\theta)}{2}$$





CONCLUSIONS

- The structural organization respect to hydroxyl groups has been determined by means of ^{1}H MAS NMR and FTIR spectroscopy. It has been shown that the amount of structural –OH groups in nano-structured CaHA is significantly higher than that from adsorbed water and *vice-verse* in ACP-CaHA.
- High data point density measurements of ^{1}H–^{31}P cross-polarization kinetics have been carried out for calcium hydroxyapatite containing amorphous phosphate phase (ACP-CaHA) and nano-structured calcium hydroxyapatites (CaHA). The chosen setting of the sampling frequency allowed to resolve the ^{1}H–^{31}P cluster structures with the internuclear distances $r \geq 0.125$ nm.

CONCLUSIONS

- The advanced processing of CP MAS data has been developed introducing the variable cut-off distribution of the dipolar coupling. The characteristic size of $^{31}P–(^{1}H)_{n}$ spin cluster being within 0.3÷0.5 nm has been determined for nano-structured CaHA.
- The non-classical spin coupling model is more preferable to describe the CP kinetics in the calcium hydroxyapatites containing amorphous phosphate phase.

Acknowledgments

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Thank you for your attention!