Concentration of hydroxyl groups in dental apatites: a solid-state ^{1}H MAS NMR study using inverse ^{31}P→^{1}H cross-polarization

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Kinetics of direct and reverse cross-polarization

Enamel serves as the intensity standard in our inverse-CP solid-state NMR experiments on dentin and cementum. In order to quantify the amount of structural hydroxyl groups in this way, one has to demonstrate that all three dental tissues exhibit the same ^{31}P → ^{1}H CP kinetics. However, longitudinal relaxation times T_1 for ^{31}P are very long: 190 ± 5, 210 ± 4 and 223 ± 7 s for enamel, dentin and cementum, respectively (a progressive saturation method). It follows that recycle delays of ca. 600 s are required. Furthermore, at least 32 transients for dentin and cementum are needed to acquire reasonable signal and ca. 15 contact times should be applied to properly monitor the inverse CP kinetics. Such variable-contact time experiment for dentin or cementum would last ca. 80 hours, which is time-consuming and inappropriate because of limited long-term stability of the NMR spectrometer.

Instead, we provide indirect evidence that the presented methodology is correct. Our reasoning is based on direct ^{1}H → ^{31}P CP. It was previously found that the ^{1}H → ^{31}P CP kinetics in bone and dental tissues is composed of two components,[1,2] characterised by different $T_{1\rho}$ relaxation times of protons. The fast-relaxing component is from the surface of apatite crystals and the slow-relaxing component comes from the crystal interior. In the former case the polarization transfer is from water protons to surface ^{31}P sites, while in the latter case there is CP from structural OH groups to ^{31}P nuclei located in the crystal lattice. The two mechanisms were nicely visualized by 2D ^{1}H-^{31}P HETCOR experiments.[3] The slow-relaxing component can be easily extracted using an additional ^{1}H spin lock (15 ms) just before the CP contact.[1]

For our purpose, we need to know this slow-relaxing component, because the initial build-up of the ^{1}H → ^{31}P CP signal, that is for short contact times, should match that from the

corresponding $^{31}P \rightarrow {}^{1}H$ CP experiment. Consider that in both cases CP proceeds between the same spin pools, i.e. between protons of structural OH groups and ^{31}P sites inside the apatite crystal lattice, though in the opposite directions. Indeed, we have found for the synthetic apatite HA100 very similar time constants of the $^{1}H \rightarrow {}^{31}P$ and $^{31}P \rightarrow {}^{1}H$ cross-polarization (T_2 in the non-classical kinetic model[4]): 0.20 ± 0.02 and 0.25 ± 0.03, respectively. The measurements were done for MAS at 7 kHz and with the same power levels for the direct and reverse CP experiments. We have also checked that $T_{1\rho}$ for ^{1}H and ^{31}P can be assumed indefinitely long under those experimental conditions. It turns out that similar behaviour of the slow-relaxing components of the $^{1}H \rightarrow {}^{31}P$ CP kinetics in the studied materials can be indicative of their similar $^{31}P \rightarrow {}^{1}H$ CP kinetics.

The adequate experimental results for enamel, dentin and cementum are presented in Figure 1.

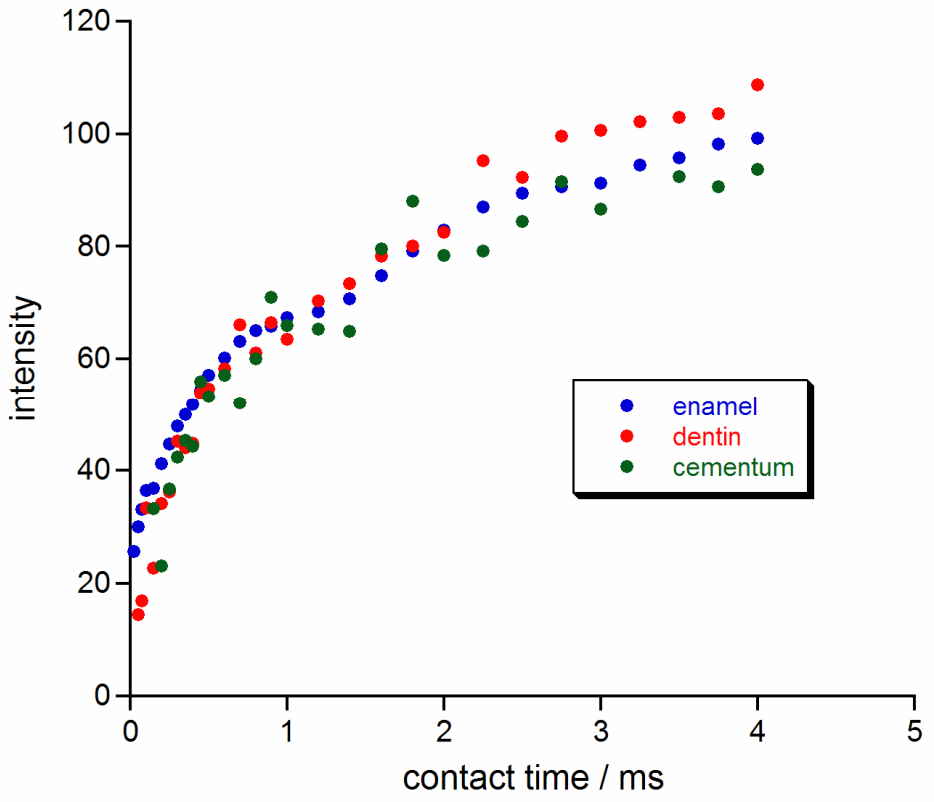

Fig. 1 Kinetics of $^{1}H \rightarrow {}^{31}P$ CP for enamel, dentin and cementum. The solid-state NMR experiments were done under MAS at 7 kHz with the additional ^{1}H spin-lock of 15 ms, applied prior to cross-polarization. Therefore, only polarization transfer from structural OH groups to proximate ^{31}P sites in the apatite crystal lattice has been monitored.[1,2] The optimized recycle delays of 10 s were used, while power levels for the Hartmann-Hahn condition were the same as during the $^{31}P \rightarrow {}^{1}H$ experiments.

It is clear that the direct $^{1}H \rightarrow {}^{31}P$ CP kinetics from protons of the structural OH groups to the ^{31}P sites inside the apatite crystal lattice are similar for all three dental tissues, especially up to the 2 ms contact time. In consequence, one should expect similar inverse $^{31}P \rightarrow {}^{1}H$ CP kinetics in the dental apatites for that contact-time region and the intensities of their inverse-CP proton peaks at 0 ppm from the structural hydroxyl groups can be reliably compared for the applied 2 ms contact time.

References

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