ON THE NATURE OF THE ASSYMETRIC LINE IN THE ESR SPECTRUM OF IRRADIATED BIOAPATITES

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Enamel is a dental tissue constituted of 95% to 98% hydroxyapatites and a few percent organic material. ESR studies of irradiated enamel, started more than 20 years ago, rapidly established that the principal signal in the g=2.00 region of the spectrum was attributable to the mineral phase.

Intensive investigations on irradiated enamel and/or synthetic apatites resulted in contradictory interpretations of the ESR spectra. Thus, while some assume that the assymetric main signal of irradiated bioapatites is due to the superposition of lines of one isotrope species and one species presenting an axial symmetry (Doi et al. 1979), others favor one interpretation into which all lines would have to be attributed to one (Bacquet et al. 1981) or more (Callens et al. 1979) species with an orthorhombic symmetry. From observations led on enamel single fragments, we propose that this assymetric signal be due to the superposition of lines belonging to two species, one with an axial symmetry and the second one with an orthorhombic symmetry.

In enamel, needle-shaped apatite crystals are organized within prisms of diameter < 1μm. Within each prism, the crystallites have their sixfold screw cristallographic axis about parallel to the prism elongation direction. In some regions of teeth, the prims are practically parallel to each other. Thus, careful sampling may allow to obtain single enamel fragments behaving, from an ESR point of view, as partially oriented systems. In this respect, teeth from large mammals, especially herbivores, whose enamel may locally reach a thickness of several millimeters, appear as a particularly interesting material.

We selected for this work enamel from ten fossil mammals and one shark tooth with ages between about 200 ka and 5 Ma. ESR measurements were led on small (± 10 mg) single enamel fragments. Angular variations were taken at 9.5 GHz and 35 GHz in planes containing the sixfold apatite symmetry axis, or perpendicularly to it, either before and after laboratory gamma-irradiation with a Co60 source (delivering 0.17 Gy/min).

The natural ESR spectrum of fossil enamel is composed of several lines in the g=2.00 region : one hyperfine septet M, with g=2.0033 and an hf splitting of 21.6 G, two isotropic species C and D with respectively g=2.0058 and g=2.0008 and one assymmetric line, with g_1=2.0026 and g_2=1.9975. The latter is almost systematically the most intense line of the spectrum. All lines, - except the M septet -, increase in intensity with laboratory gamma-doses, which apparently do not create other stable species.

Several observations : response to klystron power; angular variations of g factors; modification of spectral shape when temperature is lowered from ambiant to 120°K; thermal annealing to temperature up to 620°K, converge to suggest that the assymetric signal is a composite one, made out of at least two components, A and B. It is possible, upon moderate heating (e.g. 350°C for 1 hour), to anneal totally all initially present lines in the spectrum near g=2.00 but line A, which then presents a width of 2.5 G when observed at 9.5 GHz and a symmetric, gausssian shape.

Angular variations of the A line g factors in two perpendicular planes are shown in figure 1 for one enamel single fragment where all other lines had been thermally erased. It shows that this species presents an axial symmetry around the screw symmetry axis of order 6 of hydroxyapatites, with $g_{\perp}$=2.0026 and $g_{//}$=1.9975. Q-band studies confirm this result. Noteworthy, that reorientation is determined by the fast moving site and the exchange process, causing motional narrowing. In order to summarize the effect of slow rotational motion on FIT we plot in Fig.6 FIT(max) (maximum of FIT taken over the range of exchange times in [2]) as a function of κ_S. The figure shows that FIT(max) increases with κ_S and, for κ_S=1, reaches a value of about 0.02 which can be detected experimentally. The slower the rotational motion gets the bound site is approaching rigid limit and FIT(max) reaches asymptotic value which depends on the fraction of the slow moving site.

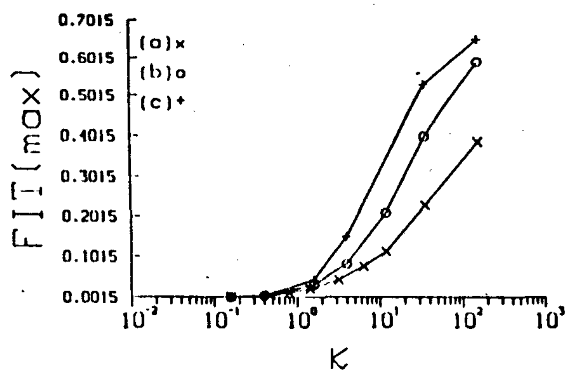

Fig.6 FIT(max) vs. κ_S. (a) χ_S=2MHz, P_S=0.01 (X) ; (b) χ_S=10MHz, P_S=0.01 (O) ; (c) χ_S=10MHz, P_S=0.28 (+)

C. Analytical expression for the longitudinal relaxation with unrestricted amount of spins in the slow motion limit.

Longitudinal relaxation for slow and fast moving spins is calculated by methods similar to the ones described in Ref.1 for the transverse relaxation. We find it to be adequatly described by the limit of SOPT. Since the exchange process is assumed to be independent of spin state it seemed to us that the expressions of ref.7 for the lineshape can be adopted to give the Fourier transform of z-component of the magnetization for exchanging spins. This leads to:

$$M_{Iz}(\omega)= 2M_0 \,\mathrm{Re} \sum_{k=1}^{2} k^2 \frac{P_I(r_{kS}+i\omega+P_S\lambda)}{(r_{kS}+i\omega)(r_{kI}+i\omega)-P_SP_I} \quad [4]$$

with:

$$r_{kS}=0.4\pi^2\chi_S^2 J_k+P_I\lambda$$

$$r_{kI}=0.4\pi^2\chi_I^2 J_k+P_S\lambda$$

$$J_k=\frac{\tau_R}{1+(k\omega_0\tau_R)^2}$$

Similarly one obtains M_{Sz} by interchanging indices I and S. To verify Eq.4 we solved the Liouville equation in Ref.1 for the longitudinal relaxation and compared the results with Eq.4. We got a good fit (FIT<0.006) for any ratio of concentration of the two sites.

Conclusion

For systems containing a site which is in the slow motion limit a good fit to biexponential decay may be obtained, though the widths (decay rates) and second order shifts may differ significantly from their values as predicted by SOPT, and one should analyze the experimental results using a fit to models that are based on numerical solutions of the Liouville Equation.

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