Decomposition of the angular ESR spectra of fossil tooth enamel fragments

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ABSTRACT

The ESR spectra of a fragment of fossil tooth enamel were measured by rotating it in 10° increments over 360° around its three major axes. We used an automated simulated annealing (SA) procedure for the mathematical decomposition of the spectra. The SA approach is particularly robust in finding global solutions rather than getting stuck in local minima. All angular measurements could be fitted with four Gaussian lines, all of which could be attributed to components of CO2 radicals. The results imply that the tooth enamel fragment contains at least two different types of oriented CO2 radicals, plus about 9% of non-oriented CO2 radicals. The oriented components were tentatively attributed to axial and orthorhombic CO2 radicals. Their explicit locations in the crystal domains of the tooth enamel remain unresolved.

1. Introduction

To minimize the impact of the analysis on important archaeological samples, non-destructive ESR analysis has been carried out on tooth enamel fragments rather than powders (Grün, 2006). Nevertheless, the use of fragments for dose reconstruction has strongly complicated the task due to the high anisotropy of tooth enamel crystal. Grün et al. (2008) showed that the angular irradiation response of fragments is different to that of powders due to the presence of at least two different types of CO2 radicals (oriented and non-oriented). The non-oriented CO2 radicals (NOCORs) give rise to a powder spectrum of the same intensity at all angles, while the intensities of the anisotropic CO2 radicals (AICORs) are angular dependent. Because of different relative distributions and thermal stabilities of these two types of CO2 radicals in the natural and irradiated spectrum components, the calculated dose values become angular dependent.

AICORs may occur in two varieties: axial CO2 radicals (with \( g_2 \) around 1.9925 and \( g_1 \) around 1.9974, e.g. Callens et al., 1987; Ishchenko et al., 2002) occur through carbonate substitution of the PO4 tetrahedron (e.g. Vugman et al., 1995). Their axial symmetry is explained by rotation around the O–O axis which is in direction of the mineralogical c-axis of the hydroxyapatite crystals. Orthorhombic CO2 radicals (with \( g_x, g_y \) and \( g_z \) around 2.0030, 2.0015 and 1.9973, respectively, e.g. Callens et al., 1987; Ishchenko et al., 2002; Rudko et al., 2007) are associated with carbonate substitution of (OH)\(^{-}\). Their explicit location is disputed. Some speculated that they are located at the surface of the hydroxyapatite crystals (Callens et al., 1995; Brik et al., 2000, 2005), while others argued them to be in the same position as the axial CO2 radicals (Ishchenko et al., 2002; Vorona et al., 2005).

At specific angles, when the \( g_x, g_y \) or \( g_z \) of the AICORs are largest (T1–B1 dominant, Fig. 1), the \( g_x, g_y \) or \( g_z \) components, which correspond to the B2 dip (Fig. 1C), are mainly composed by NOCORs. Using these specific positions, the fitting of a powder spectrum (obtained by merging all angles of configurations) into the spectra allows the estimation of the amount of NOCORs in the sample. The NOCORs are then subtracted at every angle. Nonetheless, some B2 component of the AICORs may also be removed with the subtraction of the NOCORs. One has to keep in mind that the T1–B1 peak may consist of a range of radicals (methyl, CO3\(^{-}\), CO\(^{-}\), CO\(_2\) etc., for a compilation see Callens et al., 1998; Vanhaelwelyn et al., 2000b). Only CO2 radicals, which may occur as orthorhombic, axial or non-oriented types, have any signal intensity in the B2 region through their \( g_x, g_y \) or \( g_z \) components. Tumbling CO2 radicals give rise of an isotropic line at \( g = 2.0006 \pm 0.0001 \) (Callens et al., 1987; Debuyst et al., 1993; Vanhaelwelyn et al., 2000b; Vorona et al., 2006).

Thus far, all papers dealing with the description and interpretation of the ESR spectra of enamel fragments focused only on specific angles, particularly when the peaks in the T1–B1 and B2 positions were largest or smallest. The spectra recorded for intermediate angles were usually not further discussed. However, these are important for validating proclaimed interpretations. For example, we found that it was not possible to fit intermediate spectra of irradiated fossil tooth enamel with a linear combination of the natural signal and a NOCOR powder spectrum. This means that there are more than just two radicals involved in the natural and/or irradiated spectra of fossil tooth enamel. This was already...
pointed out in the heating experiments by Joannes-Boyau and Grün (2009). In this paper, we present the decomposition of all ESR spectra of a fossil tooth enamel fragment that was rotated around its three major axes in 10° increments.

2. Materials and methods

In this paper X, Y and Z denote configurations, x, y and z the main axes of the measured fragment (Fig. 2). T1, B1 and B2 are positions in the measured or simulated ESR spectra (Fig. 1). R1, R2, R3 and B2 fitted Gaussian components (Fig. 4).

The experiments were carried out on a tooth enamel fragment of a fossil bovid from the archaeological site of Holon (Porat et al., 1999). A long lamella was separated from the tooth using a dentist’s diamond saw and series of consecutive fragments were cut and used for a range of heating and irradiation experiments (e.g. Grün et al., 2008; Joannes-Boyau and Grün, 2009).

The fragment (H5) was successively mounted into three separate Teflon holders containing Parafilm moulds. This allowed for the rotation of the fragment around its three major axes along with the incremental measurements of ESR spectra. We used the following configurations: X: rotation around the axis perpendicular to the dentine—enamel junction, Y: around the axis of tooth growth and Z: perpendicular to X and Y (Fig. 2). The sample holders were inserted in a Bruker ER 218PG1 programmable goniometer and measured with a Bruker Elexys E500 ESR spectrometer in 10° increments over 360° with the following measurement conditions: 2 mW microwave power, 0.1 mT modulation amplitude 12 mT sweep width with a sweep time of 21 s. The spectra were accumulated from 50 consecutive measurements.

All spectrum decompositions and simulations were carried out on the measured derivative spectra. Initially we used the Matlab software with the easyspin add-on (Stoll and Schweiger, 2006, 2007). For simplification, only line shapes defined by the first derivative of the Gaussian function were used, although there were indications that in some cases Lorentzian or Voigtian line shapes were perhaps more appropriate. Some apparent signals in the residual (measured minus simulated) spectra seemed to be due to

![Fig. 1. Stacked ESR spectra of X- and Z-configuration (A,B) and indication of the major spectrum positions (C).](image-url)
the error induced by the Gaussian approximation. After several subjective manual approaches to spectrum analysis, decomposition was optimised and automated using a simulated annealing (SA) procedure. SA is a Monte Carlo method used for combinatorial optimisation problems (for details see Metropolis et al., 1953; Kirkpatrick et al., 1983; Černý, 1985; Mosegaard and Sambridge, 2002). Our SA procedure is able to randomly generate a large number of synthetic spectra defined by a linear combination of four Gaussian lines. Each simulated spectrum is compared to the measured spectra in terms of a least square misfit. The particular advantage of the SA algorithm is the search of the global minimum misfit without getting stuck in local solutions. As we shall see below, SA can resolve completely overlapping signals, which are very difficult to decompose with alternative decomposition approaches.

The Gaussian lines had prescribed limits with respect to the g-value range to avoid unrealistic solutions outside the regions for the CO$_2$ radical in hydroxyapatite (see above). No restrictions were set on the intensity and maximum line width, however, a minimum width (0.10 mT) was defined to avoid aberrations.

3. Results and discussion

ESR spectra of fragments differ from those of powders due to the pronounced anisotropy of the CO$_2$ radical (e.g. Fig. 1). The angular variations of the ESR spectra vary from one configuration to the other. The anisotropy of the measured spectra of the Z-configuration (Fig. 1B, Table 2) is significantly larger than of the other two configurations. The X-configuration shows the smallest anisotropic effects (Fig. 1A), while the Y-configuration appears to show a mixed pattern of the other two.

3.1. Spectrum decomposition

When a single orthorhombic crystal is rotated around the y or z axis, a signal will appear at different g-values, shifting from the parallel ($g_x, g_z$) to the perpendicular position ($g_y$), as shown in Fig. 3. In contrast, enamel fragments are a partially ordered system and mostly only minor g-value shifts have been observed for the T1–B1 and B2 components. This could be the result of a combination of interfering oriented and non-oriented radicals or multiple orientations of the main CO$_2$ radical. Spectrum decomposition should help the understanding of the behaviour of known radicals that are supposedly involved in the spectra.

The ESR spectra of tooth enamel have a range of non-CO$_2$ components, such as dimethyl radicals. To subtract these, a merged spectrum was produced (the average of all measured spectra). In the range used for decomposition, the measured spectra contain a dimethyl triplet and two wide lines (Fig. 4A). W1, around $g = 2.0061$, was also described by Grün (2002) but could not be attributed to a specific radical. W2, around $g = 2.0051$, relates most likely to a combination of SO$_2$ and CO radicals which occur at $g = 2.0056$ and $g = 2.0047$, respectively (Bouchez et al., 1988; Schramm and Rossi, 2000, see also the fitting of Grün, 2002, his Fig. 1G and H). The intensity of the central dimethyl line was derived from the next two outer lines assuming a septet with

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Fig. 2. Direction of axes and configurations used for the measurement of the tooth enamel fragment.
Intensity distribution of a Pascal triangle. None of these components exhibited any quantifiable angular variation, thus they were assumed to be isotropic. The two wide lines were combined with the dimethyl lines into an iso-combined (IC) spectrum (Fig. 4A) which has an intensity of about 25% of the merged spectrum (Fig. 4A). However, most of the IC intensity lies outside the range of CO₂/C₀ radicals and will have little effect on the decomposition results. The IC spectrum was subtracted from all angular measurements.

While the X-configuration can be reasonably fitted with just three components (R₁, R₂, and B₂, see Fig. 4B), the Y- and Z-configurations require an additional component (R₃) to obtain a satisfactory match between experimental spectrum and simulation. The introduction of R₃ resulted in a division of the original B₂ signal that was abnormally wide and intense (compare the fitting results in Fig. 4B and C). In this context we prefer the use of B₂ rather than R₄, since all our previous papers uses B₂ for the dip around g = 1.9976 (see also Fig. 1C).

At this stage, we did not subtract a NOCOR component from the measured spectra, as this does not have an influence on the angular behaviour of the various components (it only causes constant offsets). In the first instance, its maximum intensity can be derived from the minimum B₂ position in X-configuration and cannot exceed 13% of the total radical concentration.

### 3.2. Decomposition of the spectra of the three configurations

The description of the results starts with the Z-configuration, which showed the largest angular changes. The radical concentrations were derived from the double integration of the fitted lines to account for changes in the line width (Table 2 and Figs. 5I, 6I and 7I). The angular variation is expressed in the difference between maximum and minimum concentration divided by the average concentration of the fitted component (C_max − C_min)/C ave. For features in the measured ESR spectra, T₁−B₁ and B₂, it was not possible to carry out double integrations, their angular variations were derived from their intensities (Table 1). The results for the various fitted components are listed in Table 2.

#### 3.2.1. Z-configuration

The Z-configuration shows the largest angular dependency of the measured spectra between the T₁−B₁ maximum and the B₂ maximum 90° later (see Fig. 5A, H and I), with large angular variations in the T₁−B₁ and B₂ intensities of 0.60 and 0.74, respectively. Fig. 5 shows the results of the fitting. Generally, there is a very good match between the measured and fitted spectra (Fig. 5A–C, top row). The intensities in the residual stack (measured minus fitted spectrum, Fig. 5C) are well below 5% of the measured spectra (Fig. 5A). The results on the individual components are shown in the rows below.

As expected from the measured spectra, B₂ shows the largest radical concentrations (0.55) of all configurations and large angular variations (0.54, see Fig. 5H,I). In contrast to the behaviour in the...
other configurations, B2 changes its line width (between 0.33 and 0.42 mT) and g-value (between 1.9981 and 1.9987) considerably (see Fig. 5G and Table 2). This has some influence on the calculation of the B2 concentrations. As a result, the angular variability of the B2 component is somewhat smaller than expected from the intensity changes in the B2 position.

R1 and R2 show very similar angular behaviours, with their maxima and minima offset from B2 by about 90°. The main intensity changes in T1–B1 (0.60) are due to the angular response of R1 (0.56) while R2 shows significantly less angular variation (0.29). Similar to B2, the line width of R1 changes significantly (0.28 to 0.36 mT), but its g-value remains within a narrow range (2.0025–2.0027).

Fig. 5. Decomposition of the spectra in Z-configuration. A: 3D view of measured spectra. The arrows indicate widening of the T1–B2 complex which is due to R3 (see Fig. 5H). B: 3D view of simulated spectra. C: 3D view of residual (measured minus simulated). D–G: Intensity maps of Gaussian components R1, R2, R3 and B2. The scale is the same as in A–C. The lines indicate the position of \( g = 2.0030 \) (solid line) and \( g = 1.9975 \) (dotted). H: decomposition of selected spectra (starting angle where T1–B2 intensity is maximum, over 90° with 30° steps) with lines indicating \( g = 2.0030 \) and \( g = 1.9975 \). I: Summary of all decomposition results. Note that D–I show ESR intensities while H shows radical concentrations (obtained by double integration). These take into account changes in line width. R3 shows a 90° symmetry (arrows).
R1, R2 and B2 show a 180° symmetry, which is expected from an oriented CO2 component. In contrast, R3 shows a pronounced 90° symmetry (Fig. 5I). While this is surprising, the stack of the measured spectra shows a widening of the T1–B1 peak with a 90° symmetry (arrows in Fig. 5A).

The sum of the radical concentrations of the four fitted components (Fig. 5I) shows some angular dependency (0.2). However, any other combination (i.e., excluding one the fitted components) would lead to larger angular variations. We therefore conclude that all fitted components are associated with CO2 radicals.

3.2.2. Y-configuration

The angular responses in the Y-configuration are rather similar to Z (Fig. 6). T1–B1 and B2 vary by 0.62 and 0.53, respectively. The differences between Y and Z for B2 are smaller variations in width and g-value as well as a significantly smaller average intensity. R2 shows a larger angular variation (0.49) and R3 has a somewhat smaller average concentration and converts into a 180° symmetry. R1 and R2 show similar angular behaviours and their maxima and minima are offset by 90° from B2. The angular response of R3 is similar to B2. The intensity variations in T1–B1 are caused in equal measures by the variations in R1 and R2. The

Fig. 6. Decomposition of the spectra in Y-configuration. For the description of the diagrams see Fig. 5.
3.2.3. X-configuration

The X-configuration shows the smallest angular variability in \( T_1 - B_1 \) and \( B_2 \) of 0.31 and 0.40, respectively (Fig. 7). \( R_2 \) and \( R_3 \) show the smallest variations in line widths and angular variations. \( R_3 \) has its largest intensity while \( R_1 \) and \( B_2 \) their smallest. \( R_3 \) has its largest line width. The variations in \( T_1 - B_2 \) are caused in equal measure by \( R_1 \) and \( R_2 \) (the latter has a smaller angular variation, but much higher concentrations). As in the previous configurations, \( R_1 \) and \( R_2 \) show similar angular behaviours and their maxima and minima are offset by 90° from \( B_2 \) and \( R_3 \). The sum of the four fitted components shows a small angular dependency of 0.1.

It is perhaps noteworthy that any peak-to-peak measurements on powders for geochronology purposes or retrospective dosimetry should be carried out on \( T_1 - B_2 \), as their interdependency minimises the angular variability of AICORs (see last column in Table 1). Nevertheless, further studies are required on dose reconstruction to be able to propose a clear statement on peak-to-peak measuring protocols.

Fig. 7. Decomposition of the spectra in X-configuration. For the description of the diagrams see Fig. 5.
components. Based on its and minima from B2, we conclude that R1 and R2 are AICOR remarkable as R1 and R2 completely overlap. Most previous 36:64 and 37:63 for H5 and H4, respectively. This is particularly 3.4. Discussion signals. Altogether, we consider our results as robust.

9%, with an average of 1.3%. The relative contributions of R1:R2 were angular variation of spectral features.

In order to assess the uncertainties of our decomposition approach, we firstly ran our Monte Carlo simulation several times on the same spectra with different values of initial parameters (i.e. initial g and width values, seed of the random number generator). Relatively small differences were observed resulting from the robustness of the fitting strategy. Secondly, a simulation was carried out on a second fragment (H4) immediately adjacent to the fragment discussed in this paper (H5). The results are summarised in Table 3. In spite of using different moulds resulting in somewhat different measurements positions in the cavity, the simulation results on the three configurations are very comparable. The changes in minimum and maximum g-values and widths range between −0.0002 and −0.0001 (average ± 0.00034) and −0.03 and +0.03 mT (average ± 0.01 mT), respectively. The changes in g-values are virtually within measurement error, and the line width changes are well below 5%. Changes in the minimum and maximum radical concentrations as well as changes angular variation are significantly larger, reaching up to 36% (average 9%) and 46% (average 20%), respectively. These large changes in the intensity derived parameters are not entirely surprising, considering discontinuous nature of the radical concentration curves (Figs. 5I, 6I and 7I). More importantly, the average relative radical concentrations of R1, R2, R3, and B2 changed only to a maximum of 9%, with an average of 1.3%. The relative contributions of R1;R2 were 36:64 and 37:63 for H5 and H4, respectively. This is particularly remarkable as R1 and R2 completely overlap. Most previous decomposition approaches on X-band (e.g. Jonas, 1995; Grün, 1998; Vanhaelewyn et al., 2000a) could not resolve closely overlapping signals. Altogether, we consider our results as robust.

Table 2 Results of the decomposition of enamel fragment H5, using the SA protocol with a mix of four Gaussian lines.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Minimum g-value Angle (°)</th>
<th>Maximum g-value Angle (°)</th>
<th>Minimum width (mT)</th>
<th>Maximum width (mT)</th>
<th>Minimum radical conc. Angle (°)</th>
<th>Maximum radical conc. Angle (°)</th>
<th>Angular variation</th>
<th>Average radical conc.</th>
</tr>
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<td>Z-configuration</td>
<td>R1 2.0025 180</td>
<td>2.0027 230</td>
<td>0.28 330</td>
<td>0.36 100</td>
<td>0.31 100</td>
<td>0.54 340</td>
<td>0.05 0.0041</td>
<td>0.40 0.32</td>
</tr>
<tr>
<td>R2 2.0020 290</td>
<td>2.0023 50</td>
<td>0.33 170</td>
<td>0.42 310</td>
<td>0.52 30</td>
<td>0.70 160</td>
<td>0.29 0.61</td>
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<tr>
<td>R3 2.0003 60</td>
<td>2.0006 160</td>
<td>0.38 80</td>
<td>0.44 190</td>
<td>0.59 150</td>
<td>0.86 190</td>
<td>0.39 0.70</td>
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<tr>
<td>B2 1.9981 230</td>
<td>1.9987 0</td>
<td>0.33 240</td>
<td>0.42 10</td>
<td>0.41 350</td>
<td>0.70 80</td>
<td>0.53 0.55</td>
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<tr>
<td>Y-configuration</td>
<td>R1 2.0025 100</td>
<td>2.0028 340</td>
<td>0.28 170</td>
<td>0.35 280</td>
<td>0.30 80</td>
<td>0.54 360</td>
<td>0.57 0.41</td>
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<tr>
<td>R2 2.0020 120</td>
<td>2.0023 340</td>
<td>0.39 110</td>
<td>0.42 320</td>
<td>0.46 60</td>
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<td>R3 2.0005 270</td>
<td>2.0006 120</td>
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<td>0.45 310</td>
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<tr>
<td>B2 1.9985 350</td>
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<td>0.41 300</td>
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<td>X-configuration</td>
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<td>0.27 170</td>
<td>0.30 280</td>
<td>0.24 210</td>
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<td>R2 2.0020 20</td>
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A question remains with respect to the nature of R3. The fact that R3 is needed for minimising the angular dependency of the sum of all fitted components points to anisotropic CO₂ radicals. To recapitulate, enamel fragments are a partially ordered system with some preferential direction of the hydroxyapatite crystals, but there is also a significantly number of crystals in random orientation (Macho et al. 2003). What is seen in the measurements are the extreme values of the preferential directions (gₓ, gᵧ, g₁, and g₂) whilst the other orientations are lumped into R3, see also Liidija (2001). These may arise from the misalignments of the preferential mineralogical axes with the x, y, and z-axes of the fragment, but also from misalignments of certain crystal domains with the preferential mineralogical axes. It is interesting to note that the fitted parameters of R3, apart from its width in X-configuration, hardly change in the three configurations. Its average g-value of 2.0005 ± 0.0001 is indistinguishable from the average value of isotropic CO₂ radicals in hydroxyapatite (see above).

If R3 is the composite of all misalignments, it would consist of a semi-infinite series of Gaussian components between the T1 and B2 positions. If there is no spatial preference, R3 would basically present a Gaussian error function. While such a series is difficult to simulate, it can be approximated by a Gaussian line. However, if the misalignments are not randomly distributed (see Fig. 8B, below), the shape of R3 may change with angle (see e.g. Fig. 9B, below) and its Gaussian approximation may create mathematical artefacts. Our decomposition approach does not allow an accurate assessment of the line shape of R3. As a result, it cannot entirely be excluded that R3 is part of misaligned crystal domains or an artefact of the assumption that R3 has a Gaussian line shape.

Two previous observations on enamel fragments of this tooth support the existence of two oriented CO₂ components. Firstly, heating experiments showed angular shifts of the T1–B1 maximum position by about 30° (Joannes-Boyau and Grün, 2009), which could be most readily explained by a transfer of orthorhombic to axial CO₂ radicals. Secondly, we found that it is not possible to fit the irradiation spectra of fossil tooth enamel fragments with a linear combination of the spectra of the natural sample and isotropic CO₂ radicals. This should be possible if only one oriented and one non-oriented type of CO₂ radicals were

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Table 3
Results of the decomposition of enamel fragment H4, using the SA protocol with a mix of four Gaussian lines.

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</tr>
<tr>
<td>R1</td>
<td>2.0026</td>
<td>2.0028</td>
<td>150</td>
<td>0.27</td>
<td>150</td>
<td>0.31</td>
<td>260</td>
<td>0.22</td>
</tr>
<tr>
<td>R2</td>
<td>2.0020</td>
<td>2.0023</td>
<td>290</td>
<td>0.41</td>
<td>110</td>
<td>0.42</td>
<td>280</td>
<td>0.60</td>
</tr>
<tr>
<td>R3</td>
<td>2.0003</td>
<td>2.0006</td>
<td>200</td>
<td>0.47</td>
<td>130</td>
<td>0.54</td>
<td>300</td>
<td>0.62</td>
</tr>
<tr>
<td>R2</td>
<td>1.9984</td>
<td>1.9987</td>
<td>220</td>
<td>0.39</td>
<td>70</td>
<td>0.42</td>
<td>300</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Fig. 8. A: The orientation of each radical has been estimated using the angular variation response. Each intensity maximum of each configuration corresponds to the strongest projection of the vector (reflecting the radical orientation and intensity) on the opposite plane parallel to the rotation plane. B: Directions of R1, R2, R3 and B2 with respect to the main axes of the fragment and their relative position (B). The grey circle corresponds to the plane perpendicular to the enamel/dentine junction.

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Fig. 9. Rotation of the fragment around an axis perpendicular to $B_2$ and the resultant of $R_1$ and $R_2$. A: Subtraction of the 9% powder spectrum in $B_2$ minimum position. B: Rotation from $T_1$—$B_1$ maximum to the $B_2$ maximum. C: 3D view of stacked spectra. D: map of intensities of stacked spectra.
present with different ratios in natural and irradiated spectra (Grüner et al., 2008). The fits are particularly poor at intermediate angles between the T1–B1 and B2 minima and maxima.

Q-band studies on enamel powders found additional lines in the region of the $g = 2.0007$ (Jonas and Grüner, 1997; Skinner et al., 2001), which can be attributed to tumbling CO$_2$ radicals (see above). In addition, the intensity in the B2 position could not be fitted by a simulation of axial CO$_2$ radicals (Jonas and Grüner, 1997). Q-band studies on fragments of fossil tooth enamel clearly shows the presence of orthorhombic CO$_2$ radicals (Bouchez et al., 1988; Rossi and Poupeau, 1990), which (i) had a somewhat different orientation to the axial CO$_2$ radicals and (ii) were theromally less stable than the axial (and tumbling) CO$_2$ radicals (Rossi and Poupeau, 1990). Taken all lines of evidence into consideration, we are confident that R$_2$ represents a component of orthorhombic CO$_2$ radicals.

For the two fragments analysed, the ratio between R$_1$:R$_2$ is around 36:64. Thus far, we do not have any data for fossil tooth enamel. Vorona et al. (2006) found a relative distribution between axial and orthorhombic CO$_2$ radicals in irradiated modern tooth enamel of approximately 20:75. They showed that orthorhombic CO$_2$ radicals could convert into axial by heating. One would expect that the same happens over geological time scales of hundreds of thousands of years.

We can now use the measurements of the three configurations to calculate the main directions of the fitted components (Fig. 8A). Firstly, there is a clear separation between R$_1$ and R$_2$ of about 23° (Fig. 8B). This is very similar to the angular separation of 30° of CO$_2$ components observed in previous heating experiments (Joannes-Boyau and Grüner, 2009). The angle between R$_1$ and R$_2$ is 76° and between R$_2$ and B$_2$ 98°. The angles are different from 90° because B$_2$ is a composite. The calculated angle between B$_2$ and the resultant vector of R$_1$ and R$_2$ is 86°. The direction of R$_1$ (Fig. 7A) is perhaps less meaningful, but may indicate a general preferential direction of the misaligned crystal domains.

Subsequent to these calculations, we inserted the enamel fragment into the goniometer so that it was rotated around the plane of the B$_2$ vector and the resultant vector of R$_1$ and R$_2$ (Fig. 9). After subtraction of a powder spectrum with 9% of the total radical concentration (Fig. 9A), we can clearly observe a behaviour that is closer to that described for single crystals (compare Figs. 3 and 9B). T1–B1 and B2 intensities can be virtually eliminated at 0° and 90°, respectively. However, in these two positions, the ESR spectrum cannot be fitted with a single Gaussian line, both require at least two components. This clearly indicates a large ‘misalignment’ component, as simulated by Lii.dja (2001), see his Fig. 13. At intermediate angles, a wider line occurs which resembles R$_3$ with a 90° symmetry, peaking between the T1–B1 and B2 maxima (compare to Fig. 5I). From these measurements we can also conclude that the maximum contribution of the NOCORs is 9%. This agrees well with a value of 10% derived from the annealing experiments on another fragment of this tooth (Grüner et al., 2008).

We also tried to decompose this data set. The problem of R$_3$ not being of Gaussian line shape (particularly obvious between 170° and 200° in Fig. 9B) made it impossible to track R$_1$ and R$_2$ when their intensity decreased. Instead, R$_1$ was widening which then had a knock-on effect on the calculation of the line width of B$_2$. We are continuing to work on this problem.

At this stage it is not possible to deduce whether the R$_1$ and R$_2$ components are located in the same or different mineral domains, e.g. inside or on the surface of crystals with different sizes of average crystal sizes etc... If orthorhombic CO$_2$ radicals can be transferred into axial (as observed by Vorona et al., 2006) then these should be located in the same crystal domains.

**4. Conclusions**

We have developed a rapid method for the decomposition of the angular spectra of tooth enamel. The simulated annealing procedure seems particularly well suited to decompose overlapping signals, such as R$_1$ and R$_2$. All spectra can be satisfactorily decomposed using four Gaussian Lines, R$_1$, R$_2$, R$_3$, and B$_2$. All fitted components seem related to anisotropic CO$_2$ radicals. R$_1$ has been tentatively related to the $g_R$ of orthorhombic and R$_2$ to $g_A$ of axial radicals. B$_2$ is a combination of $g_R$ and $g_A$ of the two anisotropic CO$_2$ radicals. R$_3$ presents an envelope for misalignments, resulting from angles between the dominant axial directions and the principal axes of the fragment as well as misalignments of various crystal domains with the dominant axial directions. We found an angle of 23° between the directions of R$_1$ and R$_2$. The occurrence of two different anisotropic CO$_2$ radicals in fossil tooth enamel is supported by Q-band studies on fossil enamel fragments (Bouchez et al., 1988; Rossi and Poupeau, 1990) and our earlier observations on the ESR response to heating (Joannes-Boyau and Grüner, 2009) and that the irradiation spectra of irradiated fossil tooth enamel fragments cannot be fitted by a linear combination of the spectra of the natural sample and isotropic CO$_2$ radicals.

Our decomposition approach will now allow the investigation of the irradiation effects in fossil tooth enamel and assess their relevance for dose response and dating.

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**References**


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