

ESR-Dating of Non-marine Mollusc Shells

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In the present work some results of terrestrial and fresh-water shell investigations are reported. It is shown that the energy parameters of the $g=2.0012$ center in terrestrial shells studied ($E=1.62\pm 0.01$ eV, $s=(2.3\pm 0.4)\times 10^3$ s⁻¹, $\tau=3.2\times 10^8$ y at 5°C) essentially differ from those in marine shells ($E=1.52\pm 0.01$ eV, $s=8\times 10^{13}$ s⁻¹, $\tau=1.14\times 10^6$ y at 5°C). There are some differences in other paleodosimetric properties as well (e.g., sensitivity to irradiation, saturation dose, fading, etc.). The shapes of main spectral peaks of shells and some other carbonates are also compared. Besides, problems connected with the $g=2.0012$ center concentration measurements are discussed.

KEYWORDS: Dating; electron spin resonance (ESR); molluscs; chronostratigraphy; age.

INTRODUCTION

Chronostratigraphical research into continuous sedimentary sequences of shelf seas, continental deposits and deep-sea sediments enables the chain of correlation reconstructions in the natural sea-land system to be closed. An important precondition for successful solving of the problem is the use of material which is genetically uniform and ubiquitous in time and space. Mollusc shells are acknowledged as this kind of material. However, if a great number of works were devoted to investigations of marine malacofauna remains (Ikeya and Ohmura, 1981; Radtke *et al.*, 1985; Katzenberger *et al.*, 1989; Skinner, 1989; Molodkov, 1988; 1989), then the data on palaeodosimetric and radiospectroscopic properties of non-marine mollusc shell substance are rather scanty at present, being mainly represented by the results of earlier studies on fresh-water gastropod *Lymnaea peregra* f. *balthica* (Molodkov *et al.*, 1986; Molodkov, 1988) and by series of land-snails ESR-spectra, reported in the Katzenberger's thesis (1989). The aim of the present work is the continuation of the earlier started non-marine mollusc shell investigations and the estimation of their applicability for solving essential problems of Quaternary stratigraphy.

SPECTRA

The comparative analysis of marine and terrestrial shell ESR-absorption spectra, the comparison of the experimental absorption curves with a calculated Lorentz line of an individual component of ESR spectrum (Fig. 1a) and also a series of other experiments (e.g., Molodkov, 1988; 1989) have shown that in marine, terrestrial and fresh-water mollusc shells among others there is a $g=2.0012$ center (probably CO_3^{2-} , Marshall *et al.*, 1968). Its concentration can be used as a measure of accumulated energy of ionizing radiation. True enough, the corresponding signal is not usually detected in multi-component differential spectra of the shells due to interference from the signals of other centers, including those of non-radiation origin. Nevertheless, it can be separated (Fig.1), and one of its parameters (e.g., height) can be used as an equivalent of the $g=2.0012$ center concentration. This is possible even at conventionally used microwave power (around 2 mW), as the wings of the nearest most intense peaks at $g_3=2.0020$ and $g_5=1.9976$ have practically no effect on the height of the $g=2.0012$ center signal. Otherwise, their contribution to the signal amplitude can be minimized by recording the spectrum at a higher (up to 100 mW) klystron power (Molodkov, 1988).

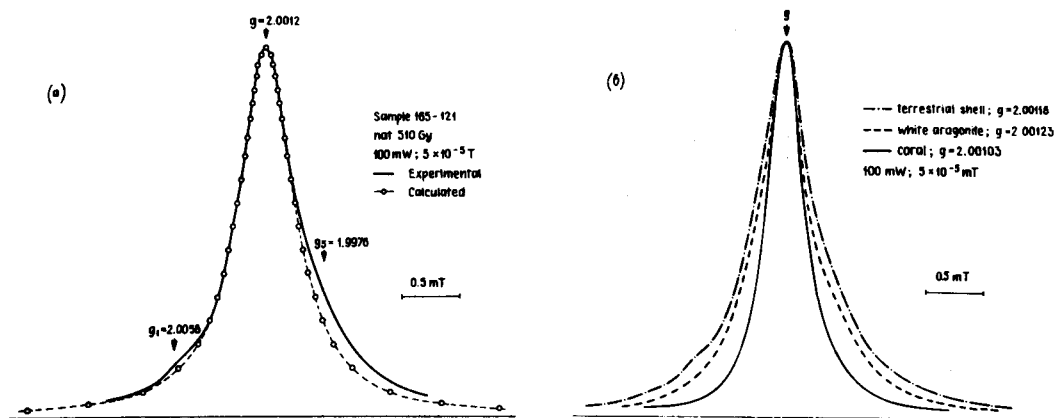


Fig. 1. Calculated Lorentz line (○) and experimental ESR absorption curve at $g=2.00120 \pm 0.00020$ separated in the ESR spectra of terrestrial mollusc shells (a) and some other natural carbonates (b).

The height of the spectral peak at $g=2.0012$ is proposed to be measured using a higher amplitude of magnetic field modulation (method OM, see Molodkov, 1988). Its value is chosen by requiring the least first derivative signal distortion on a spectrometer output by low- and high-field wings of the lines at $g_1=2.0058$ and $g_3=1.9976$, respectively (Fig. 2a). To meet the requirement and keep the proportionality of the analytical parameters, the modulation amplitude, B_1 , was usually chosen five times as much as the width of the $g=2.0012$ signal: $B_1 \approx 5\Delta b_{pp}$ (Molodkov, 1988; 1992). If the amplitude of the absorption signal in the region of one of the adjacent peaks (e.g., g_3) exceeds the amplitude of the 2.0012 peak, a higher microwave power has to be applied to suppress g_3 and enhance the signal at $g=2.0012$.

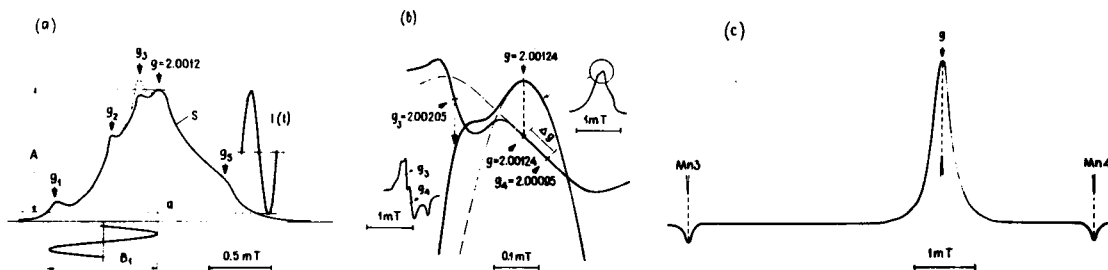


Fig. 2. Determination of some parameters of shell ESR signal. (a) The measurement of the amplitude, A , of the spectral peak at $g=2.0012$ by the overmodulation (OM) method. The read-out level, a , is determined by modulation amplitude, B_1 . (b) Due to the interference of the signals at $g=2.00124$, $g_3=2.0025$, $g_5=1.99760$, the so-called "dating line" at g_4 arises. Its g -factor (2.00095) differs from the real one (2.00124) by the value of ΔG . (c) Precise determination of the g -factor value with the use of electronic integration and low (spikes!) sweep time. Mn3 and Mn4 spikes denote the signals of the Mn marker.

In consequence of interference distortion, false signals can be frequently observed in differential spectra of shells. For instance, consider the signal at $g=2.0009(2.0006)$ that many researchers (e.g., Barabas, 1989; Grün, 1989; Katzenberger *et al.*, 1989) ascribe to one of the paramagnetic centers in the shell substance. As evidence, results of computer simulation of the ESR spectra were adduced (Barabas, 1989; Katzenberger *et al.*, 1989). In fact, as earlier reported (Molodkov, 1988) and as is seen in Fig. 2b, the so-called "dating signal" at $g=2.0009(2.0006)$ is a product of interference of the spectral peak at $g=2.0012$ with at least two adjacent signals: $g_3=2.0020$ and $g_5=1.9976$. It seems the generally used recording of differential spectra should be supplemented with recording the spectra in integrated form. In some cases it will help to avoid misunderstanding in analyzing complicated ESR spectra.

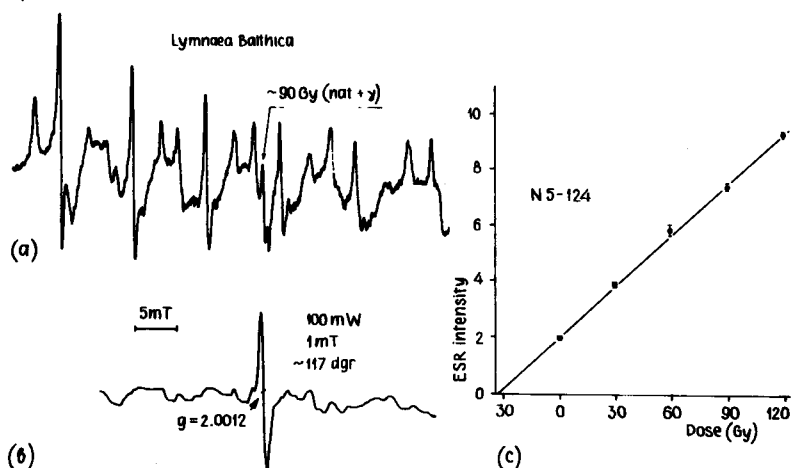


Fig. 3. Analytical line at $g=2.0012$ (b), separated by phase sensitive (PS) technique from the multicomponent spectrum (a) of calcitic fresh-water mollusc shells ~ 10 ky in age. (c) Dose-response for PS technique applied to shell; each point shows the mean of 10 read-out values.

Some of the fresh-water shells studied were composed of calcite. Their ESR spectra are strongly affected by the superposition of a very intense Mn^{2+} signals which mask weak radiation-induced lines. In this case concentration measurements of the 2.0012 centers were performed using the phase sensitive (PS) technique (Fig. 3), which consists of OM, HMP (high-microwave-power) methods and precise (± 0.5 dgr) detector phase shift, providing the greatest suppression of manganese signals and separation of the analytical line at $g=2.0012$ (Molodkov, 1988).

RESULTS AND DISCUSSION

Research into the terrestrial mollusc shells showed that mineralogical composition, even of the oldest shells, is represented by aragonite, i.e., an original structure of the skeletal substance has been preserved. This fact is of great consequence because an inversion of initial crystalline structure and corresponding loss of accumulated palaeodosimetric information in terrestrial mollusc shells was thought to be quite probable.

The results of kinetic studies proved somewhat unexpected; energy parameters of the 2.0012 center in the terrestrial mollusc shell substance ($E=1.62 \pm 0.01$ eV, $s=(2.3 \pm 0.4) \times 10^{13}$ s $^{-1}$, $\tau=3.2 \times 10^8$ y at 5°C) differ significantly from those of marine shells ($E=1.52 \pm 0.01$ eV, $s=8 \times 10^{13}$ s $^{-1}$, $\tau=1.14 \times 10^6$ y at 5°C; Molodkov, 1989). In the former, the annealing of the $g=2.0012$ center down to the level of e^{-1} is ensured on heating at 338°C for a second, in the latter - at 274°C. It is quite probable that the differences observed are due to different impurity ions stabilizing the $g=2.0012$ center in terrestrial and marine shells.

Comparison of the signals of terrestrial shells with the signals of the shells irradiated at a dose of 5×10^3 Gy (Fig. 4a) or heated at 180°C for 12 h (Fig. 4b) has revealed only small differences in their shapes in the region of interest. This is indicative of the similarity between the lifetimes of the signal at $g=2.0012$ and other (with the exception of $g=2.0058$) spectral components, as well as the similarity of dose dependencies of the signals up to the saturation dose, and, probably, energy parameters of corresponding centers.

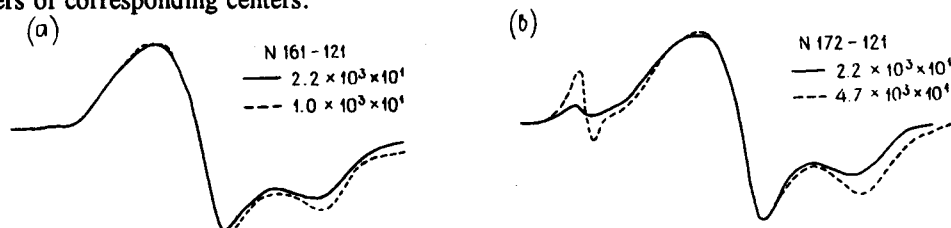


Fig. 4. Comparison of ESR signals of terrestrial mollusc shells (*Monacha caucasicala* (Lindh.)). Solid line: nature samples; dotted line: shells irradiated to a dose of 5 kGy (a) or heated for 12 h at 180°C (b). The spectra were recorded with different amplification factors.

Sensitivity to irradiation, which was determined on 15 aragonitic and calcitic non-marine shell samples, is $(12.1 \pm 3.0) \times 10^{-4} \text{ Gy}^{-1}$, i.e., approximately twice as much as for marine ones $((6.3 \pm 2.1) \times 10^{-4} \text{ Gy}^{-1}$, see Table in Molodkov, 1989). The signal-vs-dose dependence of non-marine shells, at least in the range of doses applied (up to 1 kGy) was well described by exponential function and reached saturation at about 4 kGy. Saturation intensity was determined by an iterative approach.

CONCLUSION

The results obtained by studying non-marine shells may be summarized as follows:

- (1) The signal at $g=2.0012 \pm 0.0001$ (linewidth $(2.65 \pm 0.55) \times 10^{-4} \text{ T}$ at microwave power of 100 mW) seems to be most suitable for concentration analyses and dating. The so-called "dating signal" (2.0006) is its high-field fragment.
- (2) The energetic parameters of the $g=2.0012$ center in terrestrial shells studied are as follows: $E=1.62 \pm 0.01 \text{ eV}$, $s=(2.3 \pm 0.4) \times 10^{13} \text{ s}^{-1}$, $\tau=3.2 \times 10^8 \text{ y}$ at 5°C .
- (3) Lifetimes of other relevant radiation-induced components of the spectrum seem to have the same order of magnitude.
- (4) Concentration measurements of the $g=2.0012$ center in the shell substance can best be made by unconventional techniques: overmodulation (OM), high-microwave-power (HMP), phase sensitive (PS), etc. (see Molodkov, 1988).
- (5) Sensitivity to irradiation is about $12 \times 10^{-4} \text{ Gy}^{-1}$, i.e., about twice as much as for marine shells.
- (6) The dose-response curve is well described by an exponential function and saturates at $\sim 4 \text{ kGy}$.
- (7) The upper limit of the dating at middle and high altitudes is probably $\sim 10^6$ years or even higher.

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