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Paper

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Paramagnetic characterization of fossil mollusc shells at eastern part of the old Konya lake: its importance for EPR dating

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Abstract

Fossil mollusc shells are used for dating geological materials because they are well preserved throughout geological time. In this study, the radicals in the structure of fossil mollusc shells (*Dreissena iconica, Valvata piscinalis, Bithynia tentaculate, Unio pictorum*) collected from the Eastern Part of Old Konya Lake in Türkiye were investigated by EPR technique. For all fossil shells, microwave and temperature dependence of the signals were examined, and the signals suitable for dating are discussed. Characteristic features of intrinsic and impurity-related radicals were identified and the importance of paleontological evaluation of molluscs to get a reliable equivalent dose in EPR dating studies was emphasised.

Introduction

EPR is a unique technique used for the direct detection and characterisation of radicals. With this feature, EPR is widely used in geological studies to determine the naturally existed and/or radiation-induced radicals in the crystal structure of the material. Furthermore, when the radicals are radiation sensitive and thermally stable, EPR can be safely used as a dating method for materials containing them[(1)]. Molluscs have many species that are sensitive to the environmental conditions[(2)]. They can provide information about the changes in the temperature, salinity, water chemistry and depth of the water where they live in. Molodkov stated that fossil mollusc shells are the most promising materials for EPR dating studies and may even provide an overview for paleo-environmental studies. He also reported that mollusc remains could provide Quaternary scientists with important paleo-environmental data on marine, terrestrial and lacustrine sources[(3)].

There are several studies using the mollusc shells as dating materials[(4–6)]; however, the identity and characteristics of radicals in different mollusc species have not been compared and discussed, and there are not enough data on the microwave and temperature dependence of radicals. Since the fossil shells are indices of geological ages and markers of paleo-climatic changes, the purpose of this study is to identify the radicals and to determine their characteristic properties systematically using EPR spectroscopy for the fossil mollusc shells (*Dreissena iconica*, *Valvata piscinalis*, *Bithynia tentaculate*, *Unio pictorum*) collected from the Eastern Part of the Old Konya Lake in Türkiye.

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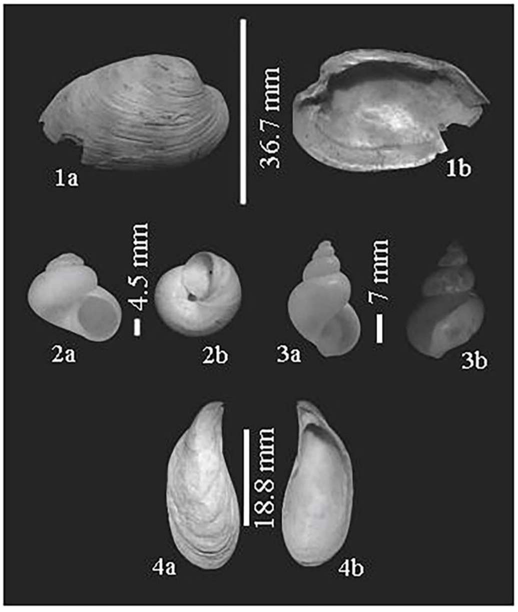

Figure 1. Mollusc species from Eastern Part of the Konya Closed Basin. (1**a**, 1**b**) *Unio pictorum*, (2a, 2b) *Valvata piscinalis*, (3a, 3b) *Bithynia tentaculata*, (4a, 4b) *Dreissena iconica*.

Materials and methods

The fossil mollusc shells were systematically collected from the designated locations (labelled as L4, L7, L8) from Eastern Part of the Konya Closed Basin shown in Figure 1(a) of the study[7]. Paleontological evaluation was performed to define the species of the molluscs, for all the shells taken from the stratigraphic sections of the geological splittings. *Dreissena iconica*[8] is a species in Bivalvia class and defined in the Konya Closed Basin during the Pleistocene and they can live in very low salinity freshwater lakes. *Valvata piscinalis*[9] is small snail found in freshwater streams, rivers and lakes, preferring running water and tolerating water with low calcium levels. *Bithynia tentaculate*,[10] a member of the Gastropoda class, lives in diverse habitats such as low rivers, canals, dikes and fishponds, in spring waters with abundant vegetation and in plant-rich habitats. *Unio pictorum*,[10] belonging to the class Bivalvia, lives in calm streams and fresh and still waters. The mollusc species in Figure 1 abundant in the studied layers were investigated.

The fossil shells were brought to the laboratory with avoiding sunlight and humidity. The samples were washed by distilled water and etched with diluted acetic acid to clean the adherent impurities. Then, they were gently crushed with agate mortar and sieved to 125–250 μm grain sizes. The samples were irradiated by ^{60}Co gamma source located in Turkish Energy, Nuclear and Mineral Research Agency (Istanbul/Türkiye). The gamma source activity was 740 GBq, and at the irradiation point, the dose rate was 269 Gy/hour. EPR experiments of powdered samples were performed at 0.1- and 0.05-mT modulation width between 123 and 298 K and 0.01–200 mW microwave powers with JEOL JES-FA300 X-band EPR spectrometer located in Selçuk University Advanced Technology Research and Application Center (Konya/Türkiye). Low-temperature measurements were performed by JEOL ES-DVT4 variable temperature controller.

Results and discussions

EPR analysis were performed for determination of intrinsic defects induced by radiation, and impurity-related defects due to environmental effects in the structures of mollusc species. As it was observed that there were differences in the EPR spectra of the shells of different species of molluscs, the changes in the EPR signals depending on temperature and microwave power were monitored and *g* values defined as fingerprints were measured.

Mollusc shells of the same species have a similar EPR spectral pattern. As can be seen in Figure 2a displaying the spectra of natural and 500-Gy irradiated fossil shells of *Dreissena iconica* mollusc samples, which is an endemic species of the Old Konya Lake, four distinct signals were observed in the EPR spectra and their intensities increased after irradiation. The *g* values of the signals in the spectral pattern for 500-Gy irradiated *Dreissena iconica* mollusc species (Figure 2a) belong to the g_{iso} values of the freely rotating (SO_2^-), isotropic (SO_3^-), freely rotating (CO_2^-) radicals and the g_{zz} component of the $(CO_2^-)_{orth}$ radical, respectively. The spectrum recorded at 123 K in Figure 2(b) includes the EPR signals that are the signal components of $(CO_3^{3-}Y^+)_{orth}$ and $(CO_3^{3-})_{axial}$ radicals[1].

Further, the $g = 1.9973$ signal of the $(CO_2^-)_{orth}$ radical can be observed at both room temperature and low temperatures, whereas the other signal components of this radical are not visible (because of superimposition with other signals) at room temperature but appear more clearly at 123 K (red *g* values in Figure 2b).

To accurately determine the radicals, the spectrum of Figure 2(a) was recorded at 3 mW microwave power and 0.1 mT modulation amplitude at room temperature, whereas the spectrum of Figure 2(b) was recorded at 0.01 mW microwave power, 0.05-mT modulation amplitude, and 123 K. For the *Dreissena iconica* shells, the graphs of microwave power and temperature dependence of the signals were given in Figure 2(c) and (d), respectively. The *g* values given in these figures belong to the radicals defined in Figure 2(a) and (b). As the optimal spectrometer

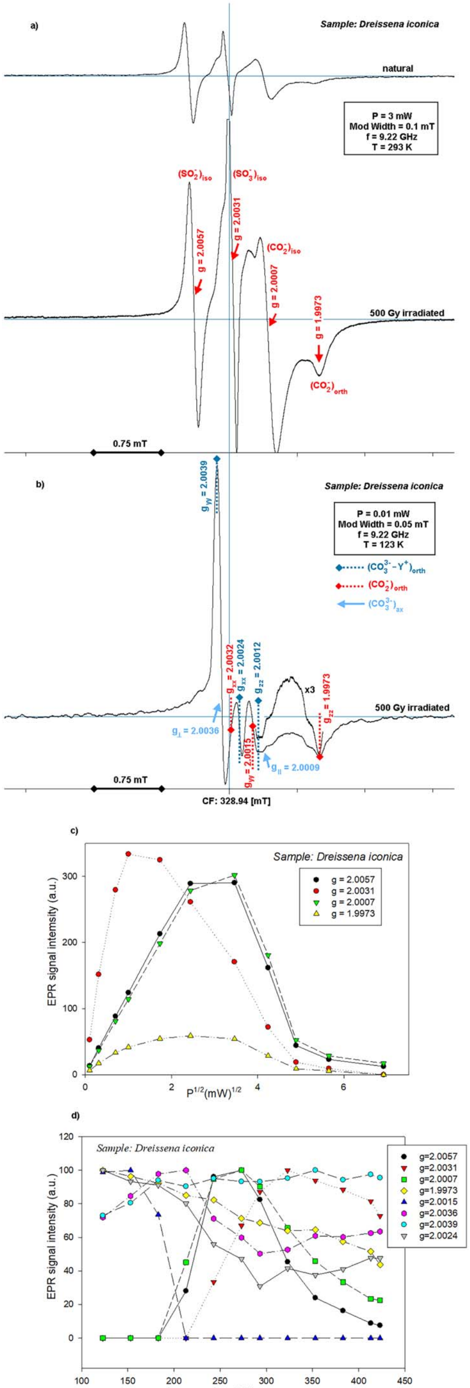

Figure 2. EPR spectra observed in *Dreissena iconia* shells (**a**) at room temperature and (**b**) at 123 K, and (**c**) the microwave power dependence (0.001–48 mW) at room temperature and (**d**) the temperature dependence (123–423 K with a microwave power of 0.1 mW) of the signal intensities observed in the sample.

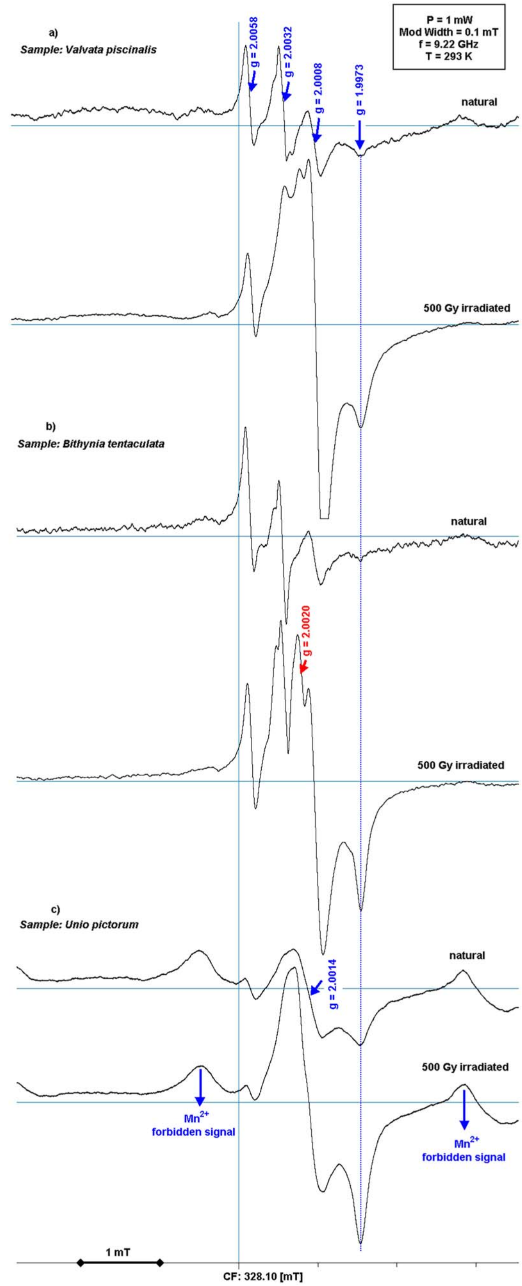

Figure 3. EPR spectra of fossil mollusc shells. (**a**) *Valvata piscinalis*, (**b**) *B. tentaculata*, (**c**) *U. pictorum*.

conditions for each radical are different, the temperature dependence study (Figure 2d) was performed at the power value of 0.1 mW at which all signals appear, and normalised signal intensities versus temperature were provided to observe the temperature dependence for each signal more clearly. Microwave power and temperature dependence should be considered for the radicals to be used in EPR dating. The microwave power where signal intensity is well below saturation and the temperature where spectrum resolution is best should be used for the dating signal.

EPR spectra of natural (non-irradiated) and 500-Gy irradiated samples recorded at room temperature for the mollusc species *V. piscinalis*, *Bithynia tentaculata, U. pictorum* are shown in Figure 3. Temperature dependence of the signals observed in 500-Gy irradiated shells is given in Figure 4, and microwave dependence that the signals observed at 123 K is given in Figure 5. According to the figures, the signal $g = 2.0008$ (*2.0007 in Dreissena iconica*) has the highest intensity at room temperature and it is not observable at 123 K. While the signal $g = 1.9973$ can be measured at 123 K, it has lower intensity and saturates below 1 mW microwave power at this temperature (Figure 5). For this reason, it can be said that in dating studies using $(CO_2^-)_{orth}$ radical it would not be practical to use low temperature.

The fossil shells of *V. piscinalis* and *B. tentaculata* molluscs species have the similar EPR spectral patterns. As for the *Dreissena iconica* shells, it is promising that there are $(CO_2^-)_{iso}$ and $(CO_2^-)_{orth}$ radicals with the *g* values of *2.0008* and *1.9973*, respectively, which are suitable for EPR dating in these mollusc species. Moreover, the resolution of their spectra is also quite good. However, intense Mn^{2+} signals were observed in the EPR spectral pattern (Figure 3c) of the *U. pictorum* mollusc species. A very intense signal with $g = 2.0014$ is observed, and it has been determined from the EPR spectra recorded at 0.1-mW power and 0.05-mT modulation width that this signal is formed by the overlapping of $g = 2.0011$ and *2.0020* signals. There is no precise definition of radical for these signals in the literature. At 123 K, the intensity of the *2.0014* signal increases and the line width decreases (Figure 4c). The $g = 2.0020$ (or *2.0019*) signal observed in *V. piscinalis* and *B. tentaculata* shells (Figure 3a and b), as in *U. pictorum*, is thought to be one of the signal components of the $(CO_2^-)_{ax}$ radical observed in tooth enamel, bone and egg shell samples[11–13]. As allowed and forbidden signals of impurity related Mn^{2+} ions overlap with dating signals, *U. pictorum* mollusc species cannot be used for EPR dating. A shoulder was observed on the left magnetic field region side of the $g = 1.9973$ signal observed at room temperature. This indicates that there is actually more than one radical signal component in the region where the $g = 1.9973$ signal, which is one of the components of the $(CO_2^-)_{orth}$ center. Although the $g = 1.9973$ signal is suitable for dating, as it is right next to the Mn^{2+} forbidden transitions in the spectrum, the signal intensity is not measurable, so it cannot be used for dating.

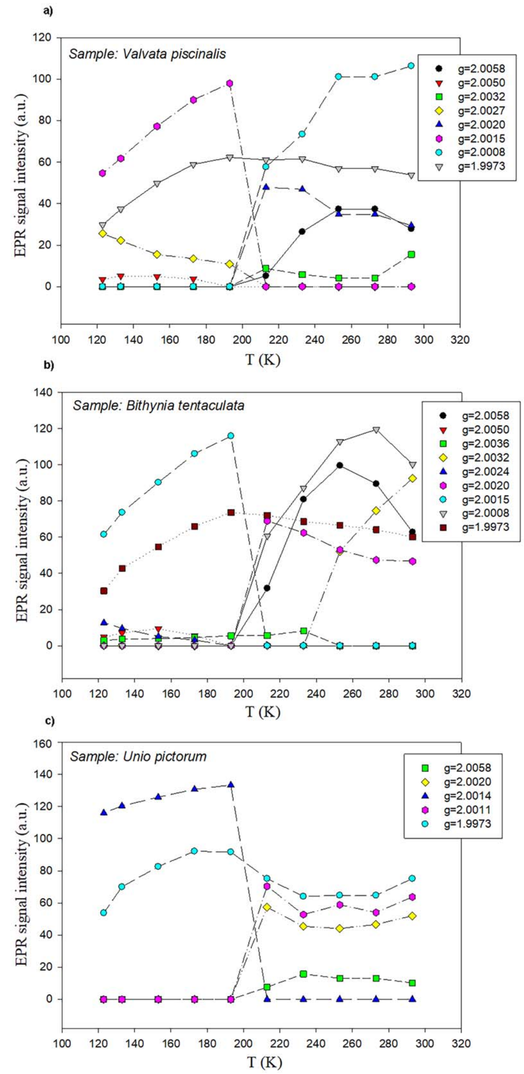

Figure 4. Temperature dependence of the signals for 500-Gy irradiated shells. (**a**) *V. piscinalis* (*P* = 1 mW), (**b**) *B. tentaculata* (*P* = 1 mW), (**c**) *U. pictorum* (*P* = 0.1 mW).

For the mollusc species, the observed EPR signals and the radicals they belong to were given in Table 1. These radicals have been defined in the literature for bio-carbonates with aragonitic crystal structure[1, 14–16]. The observation of $(SO_3^-)_{iso}$ radicals with a value of $g_{iso} = 2.0031$ indicates that the crystal structures of the shells are aragonitic[1, 15], that is, there is no recrystallisation throughout geological time. The signals $g = 2.0007$ and $g = 1.9973$ that are belonging to $(CO_2^-)_{iso}$ and $(CO_2^-)_{orth}$ respectively, are suitable for EPR dating of fossil mollusc shells[1, 4, 5, 17–19]. The signal with $g = 2.0031$ is also suggested to be used for dating of young shells[1].

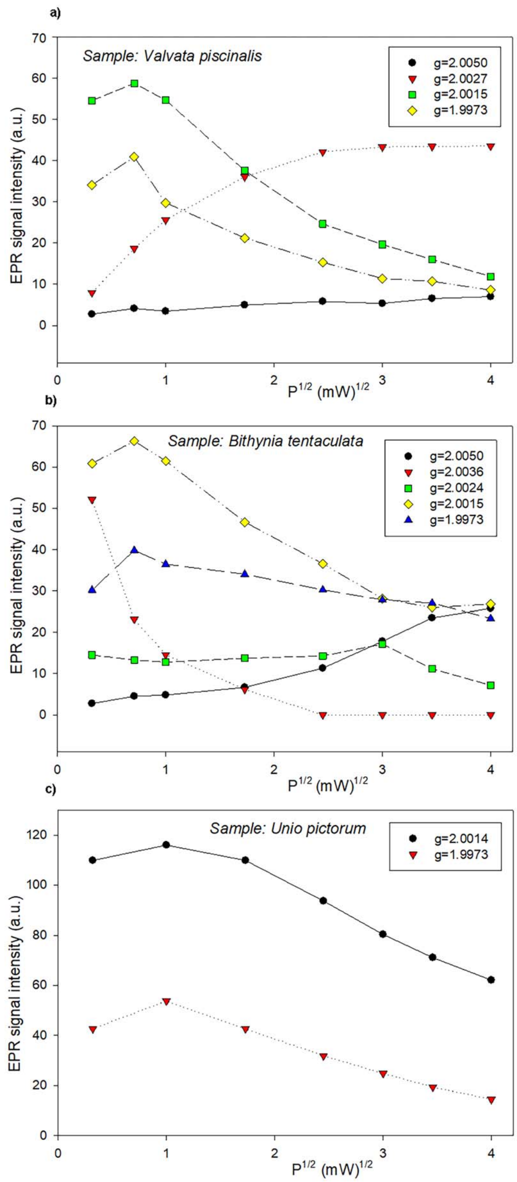

Figure 5. Microwave dependence of the signals observed at 123 K for 500-Gy irradiated samples.

Table 1. EPR signals seen in mollusc species and the radicals to which they belong.

Dreissena iconica	
EPR signals	**Radicals**
$g_{iso}=2.0007$	$(CO_2^-)_{iso}$
$g_1 = 2.0032, g_2 = 2.0015, g_3 = 1.9973$	$(CO_2^-)_{orth}$
$g_{iso} = 2.0057$	$(SO_2^-)_{iso}$
$g_{iso} = 2.0031$	$(SO_3^-)_{iso}$
$g_1 = 2.0039, g_2 = 2.0024, g_3 = 2.0012$	$(CO_3^{3-}\text{-}Y^+)_{orth}$
$g_\perp = 2.0036, g_\parallel = 2.0009$	$(CO_3^{3-})_{ax}$
Valvata piscinalis	
EPR signals	Radicals
$g_{iso} = 2.0008$	$(CO_2^-)_{iso}$
$g_1 = 2.0032, g_2 = 2.0015, g_3 = 1.9973$	$(CO_2^-)_{orth}$
$g_{iso} = 2.0058$	$(SO_2^-)_{iso}$
$g_{iso} = 2.0032$	$(SO_3^-)_{iso}$
$g_1 = 2.0039, g_2 = 2.0024, g_3 = 2.0011$	$(CO_3^{3-}\text{-}Y^+)_{orth}$
$g = 2.0027$	Unknown
$g = 2.0050, g = 2.0020$	Unknown
Mn^{2+} forbidden transition signals (weak)	
Bithynia tentaculata	
EPR signals	Radicals
$g_{iso} = 2.0008$	$(CO_2^-)_{iso}$
$g_1 = 2.0032, g_2 = 2.0015, g_3 = 1.9973$	$(CO_2^-)_{orth}$
$g_{iso} = 2.0058$	$(SO_2^-)_{iso}$
$g_{iso} = 2.0032$	$(SO_3^-)_{iso}$
$g_1 = 2.0039, g_2 = 2.0024, g_3 = 2.0012$	$(CO_3^{3-}\text{-}Y^+)_{orth}$
$g_\perp = 2.0036$	$(CO_3^{3-})_{ax}$
$g = 2.0050, g = 2.0020$	Unknown
Mn^{2+} forbidden transition signals (weak)	
Unio pictorum	
EPR signals	Radicals
$g_3 = 1.9973$	$(CO_2^-)_{orth}$
$g_{iso} = 2.0058$	$(SO_2^-)_{iso}$
$g = 2.0020, g = 2.0014, g = 2.0011$	Unknown
Mn^{2+} forbidden transition signals (intense)	

Some distinctive features, determined in this study, of radicals detected in fossil mollusc shells found in the Eastern Part of the Old Konya Lake can be summarised as follows by also adding the information given in the literature.

Isotropic SO_2^- radical[15, 20, 21]: The signal intensity increases with microwave power and saturation is observed at 10 mW. It was observed that the signal intensity of the $(SO_2^-)_{iso}$ radical decreased from room temperature to about 400 K, whereas the intensity of $(SO_3^-)_{iso}$ increased. During thermal annealing, the signal intensity of $(SO_2^-)_{iso}$ increases with the consumption of $(SO_3^-)_{iso}$ signal. Signal intensity increases at approximately 423 K and goes to zero at 673 K. It is observed most intensely at 273 K, whereas it cannot be seen below 200 K.

Isotropic SO_3^- radical[15, 20, 21]: It is observed better below 0.1 mW microwave powers and it gets saturated at high powers. It is observed most severely at 323 K, while cannot be seen below 230 K. It is still observed at low microwave power values at 423 K but fully annealed at a temperature of about 573 K.

Isotropic $CO_2^{\ -}$ radical[17, 21–23]: It is an electron center. Signal intensity increases with microwave power and saturation is observed at 10 mW. The *g* values of *2.0007* and *2.0008* were measured in different species. It is used as a dating signal since the lifetime given in the literature is $\tau = 1$ Ma (at 288 K) and its signal intensity increases with gamma irradiation. It is observed most intensely at 273 K value, whereas it cannot be observed below 200 K. It is fully annealed at a temperature of about 578 K. The signal width from peak to peak was reported as 0.18 mT (±0.02) at room temperature.

Orthorombic $CO_2^{\ -}$ radical[24, 25]: It is an electron center. The optimum microwave power value at room temperature is between 1 and 3 mW away from saturation. The lifetime is reported as $\tau = 1$ Ma (at 288 K). Signal intensity increases with gamma irradiation. It can be observed between the temperatures of 123 and 423 K and between the microwave powers of 0.1 and 50 mW. It is fully annealed at a temperature of about 573 K.

Axial $CO_3^{\ 3-}$ radical[26, 27]: It is an electron center. It is available between 0.1 and 50 mW but can be more clearly observed at low microwave powers. It can be observable between the spectrometer temperatures of 123–423 K. It is thermally stable at low temperatures.

Orthorhombic $CO_3^{\ 3-}\ Y^{\ +}$ radical[16]: It can be precisely observed at low microwave power (0.1 mW), low modulation amplitude (0.05 mT) and at low temperature (123 K). It goes into saturation at powers greater than 3 mW. At this power value, it is as a hump on the left side of the $g = 2.0031$ peak. Hyperfine splitting was not observed.

Conclusions

For mollusc shells to be used in EPR dating studies, it is necessary to do radical characterisation and determine the optimum spectrometry conditions for a possible dating signal. *Dreissena iconica, V. piscinalis* and *Bithynia tentaculate* species have high resolution spectral pattern including the signals *2.0007* (signal of isotropic CO_2^- radical) and *1.9973* (signal of orthorhombic CO_2^- radical) that are suitable for dating purposes, and the X-band EPR spectra should be recorded at room temperature, in the microwave power range of 1–3 mW away from saturation, and modulation amplitude of 0.1 mT. However, the spectrum of *U. pictorum* species has intense Mn^{2+} signals preventing to use the $g = 1.9973$ signal for dating; thus, the species cannot be an EPR dating material. A notable finding is that the $(CO_2^-)_{orth}$ radical is found in all mollusc species. The only issue that might prevent this radical from being used in dating is the presence of manganese impurity signals in the structure. Although the $(CO_2^-)_{iso}$ radical is usually suggested for dating purposes, the $(CO_2^-)_{orth}$ radical is a suitable alternative when measurement of the isotropic radical is difficult or not observed in the structure. Additionally, it should be noted that there are a few papers that have recommended performing pre-annealing treatment for the signal at $g = 1.997$ before a dose-response study[7, 24]. In our previous study results of EPR dating used by $(CO_2^-)_{iso}$ radical provided beneficial information about Late Quaternary paleoclimatic and paleoenvironmental changes in the Konya Closed Basin[28].

Although shells of different mollusc species contain similar radicals, other signals (i.e., unknown signals and Mn^{2+} forbidden signals) may also be present. It is critical to use the shells of single species mollusc for dating since mixing shells of various mollusc species may inhibit precise detection of the dating signal and result in unreliable ages. EPR analysis support that paleontological assessment is essential before dating experiments. The obtained findings are regarded to be beneficial for EPR dating studies as they reflect the change in the observed signals depending on the species and are a systematic analysis of microwave dependence and temperature dependence of the recorded signals.

Data availability

Data will be provided to the researcher when requested.

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Conflict of interest

There is no conflict of interest in this study.

References

1. Ikeya, M. *New Applications of Electron Spin Resonance: Dating, Dosimetry and Microscopy*. (Singapore: World Scientific Publishing Co. Pte. Ltd.) (1993).
2. Mc Kerrow, W. S. *The Ecology of Fossils*. (London: Duckworth) p. 383 (1978).
3. Molodkov, A. *The late paleoenvironmental evolution in Northern Eurasia through the prism of the mollusc shell-based ESR dating evidence*. Quat. Int. **556**, 180–197 (2020).
4. Engin, B., Kapan-Yeşilyurt, S., Taner, G., Demirtaş, H. and Eken, M. *ESR dating of Soma (Manisa, West Anatolia –*

Turkey) fossil gastropoda shells. Nucl. Instrum. Methods Phys. Res., Sect. B **243**, 397–406 (2006).

5. Schellmann, G., Schielein, P., Burow, C. and Radtke, U. *Accuracy of ESR dating of small gastropods from loess and fluvial deposits in the Bavarian Alpine Foreland*. Quat. Int. **556**, 198–215 (2020).
6. Cano, N. F., Ayala-Arenas, J. S., Javier-Ccallata, H. S. and Watanabe, S. *OSL and EPR dating of shells and sediments from Congonhas II sambaqui, Santa Catarina, Brazil*. Radiat. Phys. Chem. **167**, 108240 (2020).
7. Ekici, G., Sayin, U., Aydin, H., Isik, M., Kapan, S., Demir, A., Engin, B., Delikan, A., Orhan, H., Biyik, R. and Ozmen, A., (2018) *The importance of pre-annealing treatment for ESR dating of mollusc shells: a key study for İsmil in Konya closed Basin/Turkey*, AIP Conference Proceedings **1935**, 140002, https://doi.org/10.1063/1.5026005
8. Schütt, H. *Fossile Mollusken dreier anatolischer Ovas*. Archiv für Molluskenkunde der Senckenbergischen Naturforschenden Gesellschaft **120**(4–6), 131–147 (1991).
9. Myzyk, S. *Life cycle of Valvata cristata O.F. Müller, 1774 (Gastropoda: Heterobranchia) in the laboratory*. Folia Malacol. **10**, 47–75 (2002).
10. Linneaus, C. *Systema naturae, per regna tria naturae: sevundum classes, ordines, genera, species cum characteribus, differentiis, synonymis, locis*. Abbreviated: Syst. Nat. (ed. 13). https://doi.org/10.5962/bhl.title.559. (1707–1778).
11. Ikeya, M. and Miki, T. *Electron spin resonance dating of animal and human bones*. Science **207**(4434), 977–979 (1980).
12. Wieser, A., Haskell, E., Kenner, G. and Bruenger, F. *EPR dosimetry of bone gains accuracy by isolation of calcified tissue*. Appl. Radiat. Isot. **45**(4), 525–526 (1994).
13. Engin, B. and Demirtas, H. *The use of ESR spectroscopy for the investigation of dosimetric properties of eggshells*. Radiat. Phys. Chem. **71**, 1113–1123 (2004).
14. Barabas, M., Bach, A., Mudelsee, M. and Mangini, A. *General properties of the paramagnetic center at g=2.0006 in carbonates*. Quat. Sci. Rev. **11**(1–2), 165–171 (1992).
15. Kai, A. and Miki, T. *Electron spin resonance of sulfite radicals in irradiated calcite and aragonite*. Int. J. Radiat. Appl. Instrum. C. Radiat. Phys. Chem. **40**(6), 469–476 (1992).
16. Marshall, S., McMillan, J. and Serway, R. *Electron spin resonance absorption Spectrum of Y^{3+}-stabilized CO_3^{3-} molecule–ion in single-crystal calcite*. J. Chem. Phys. **48**(11), 5131–5137 (1968).
17. Barabas, M., Mudelsee, M., Walther, R. and Mangini, A. *Dose-response and thermal behaviour of the ESR signal at g=2.0006 in carbonates*. Quat. Sci. Rev. **11**(1–2), 173–179 (1992).
18. Skinner, A. F. and Mirecki, J. E. *ESR dating of molluscs-is it only a "shell game"*. Appl. Radiat. Isot. **44**, 139–143 (1993).
19. Schellmann, G. and Radtke, U. *Problems encountered in the determination of dose and dose rate in ESR dating of mollusc shells*. Quat. Sci. Rev. **18**(13), 1515–1527 (1999).
20. Ikeya, M. and Ohmura, K. *Dating of fossil shells with electron spin resonance*. J. Geol. **89**(2), 247–251 (1981).
21. Katzenberger, O., Debuyst, R., De Canniere, P., Dejehet, F., Aper, D. and Barabas, M. *Temperature experiments on mollusc samples: an approach to ESR signal identification*. Int. J. Radiat. Appl. Instrum. A. Appl. Radiat. Isot. **40**(10–12), 1113–1118 (1989).
22. Hughes, R. C. and Soos, Z. G. *EPR of CO_2^- defects in calcite: motional and nonseclar contributions*. J. Chem. Phys. **52**(12), 6302–6310 (1970).
23. Kai, A., Murata, T. and Miki, T. *Effects of trivalent metal impurities on radiation-induced radicals in calcite*. Appl. Radiat. Isot. **44**(1–2), 311–314 (1993).
24. Takano, M. and Fukao, Y. *ESR dating of Pleistocene fossil shells of the Atsumi group. Central Honshu, Japan: On the discrepancy in TD value among different ESR peaks*. Appl. Radiat. Isot. **45**(1), 49–56 (1994).
25. Walther, R., Barabas, M. and Mangini, A. *Basic ESR studies on recent corals*. Quat. Sci. Rev. **11**(1–2), 191–196 (1992).
26. Serway, R. and Marshall, S. *Electron spin resonance absorption spectra of CO_3^- and CO_3^{3-} molecule-ions in irradiated single-crystal calcite*. J. Chem. Phys. **46**(5), 1949–1952 (1967).
27. Eachus, R. and Symons, M. *Unstable intermediates. Part L. The NO_3^{2-} impurity centre in irradiated calcium carbonate*. J. Chem. Soc. A: Inorg. Phys. Theor. 790–793 (1968).
28. Orhan, H. *et al. Late quaternary paleoclimatic and paleoenvironmental changes in the Konya Closed Basin (Konya, Turkey) recorded by geochemical proxies from lacustrine sediments*. Arab. J. Geosci. **14**, 766 (2021).