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RESEARCH ARTICLE

ELECTRON SPIN RESONANCE DATING AND XRD ANALYSIS OF ANCIENT MARINE SHELL RECENTLY EXCAVATED IN TAMILNADU, INDIA

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ABSTRACT

Electron spin resonance (ESR) dating of ancient marine shell has been made using the paramagnetic defects produced by natural radiation. The total dose of natural radiation of the materials termed as archaeological dose estimated from ESR signals of defects in marine shell recently excavated from the archaeological site Alagankulam, Tamilnadu state, India. The sample was divided into nine sets which were given an artificial dose (AD) by using γ irradiation of 50Gy, 100Gy, 200Gy, 400Gy, 600Gy, 800Gy, 1600Gy, 2400Gy and 3200Gy respectively. From the observed ESR spectra with g factor 2.0036, 2.0007 and 1.9973 have been used to estimate the age by assuming the external dose rate to be 1.12 ± 0.08 mGy/a. The calculated age of the sample is 232 ± 74 ka, which correspond to the middle stage of the Pleistocene epoch. The ESR studies on marine shells have potential in evaluating the relative importance of sea level changes paleoclimate and events shaping coastal zones. The X-ray diffraction (XRD) reveals the preservation condition of the shell sample and evidences the diagenesis in the shell over the burial period.

INTRODUCTION

Fundamental knowledge of the physics of defects has been usefully applied to material science related with technological applications. The damage occurred in the solid materials by radiation forms the basis for electron spin resonance (ESR) dating. The radiation creates paramagnetic centers and free radicals with long lifetimes, whose concentration is proportional to the total radiation dose absorbed by the sample. The first successful experiment to observe ESR was performed by Zavoisky [1]. Since then, ESR technique has found wide variety of applications in Chemistry, Physics, Biology and even in the process control and clinical analysis. Zeller et al. [2], Zeller [3] and Levy [4] suggested that ESR could also be used in geology and archaeology as a new dating technique. ESR dating was introduced to earth sciences when Ikeya [5] dated a speleothem from Akiyoshi Cave, Japan. It permits dates on minerals which are precipitated, such as secondary carbonates (speleothems, mollusk shells, corals) or tooth enamel, as well as materials which were heated in the past such as volcanic minerals [6]. The ESR dating method has been widely used to the geological shells (biocarbonates). Biomineralized calcium carbonate samples arise due to the formation of calcium carbonate by secretion from certain organism. After the death of the organism; these become important components of quaternary age deposits [7]. The shells may be calcite, aragonite, or combination of both. The shells of marine, terrestrial and fresh-water mollusks are often composed of aragonite. The new method of ESR dating will be useful for sediment age determination and for other geological studies.

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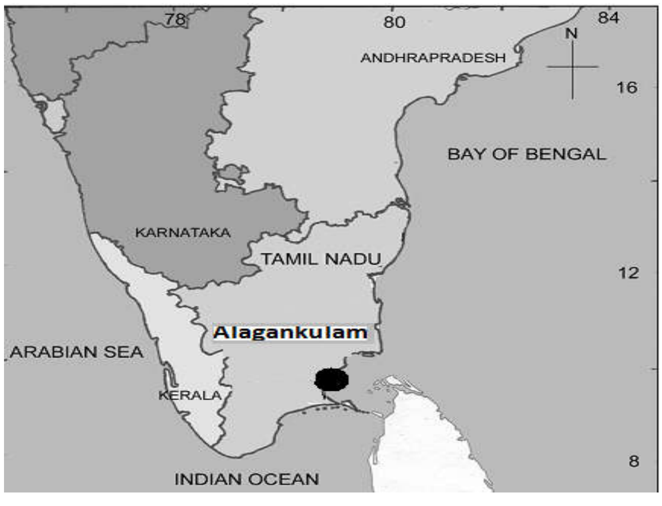
SITE DETAILS

The marine shell was excavated from the archaeological site Alagankulam (lat. 9º31´ N and long. 78º 67´S). It is a village located on the east coast of Ramanathapuram district in the state of Tamilnadu, India. It is sited on the bank of the river Vaigai and is about three kilometers away from the seashore of Bay of Bengal. The excavation in this site was carried out by the State Department of Archaeology, Government of Tamil Nadu, India. The archaeological site studied is shown in site map 1.



Site Map 1. Alagankulam Archaeological site (●) in Tamilnadu (South India).

EXPERIMENTAL DETAILS

The aragonite type of marine sample has been collected from the archaeological site and subjected to the ESR dating method. Aragonite is one of the trimorphous forms of $CaCO_3$, which differs from calcite and vaterite. Aragonite is less common and less stable than calcite. Many organisms (mollusks and corals) build their skeleton of aragonite. The structure of aragonite is orthorhombic, having higher density and hardness than calcite [6]. The photograph of the aragonite marine shell is shown in Fig.1.

Fig. 1. Photograph of the sample AGS

The shell sample was prepared by the following standard procedures and ESR spectra were recorded on a JEOL TES100 ESR spectrometer, having 100 kHz field modulation and phase sensitive detection. DPPH with a g value of 2.0036 was used as an internal standard for g factor calculations. The ESR defects, i.e., unpaired electrons are created in the samples by α-, β- or γ-rays. The concentration of the unpaired electrons can be determined directly by microwave absorption giving the ESR signal intensity. These unpaired electrons are trapped by an impurity or left at a hole, either of which is simply called "defects".

Procedures for ESR Dating (Additive Dose method)

Dose versus magnetic field plots on derivative or absorption spectra yield dose values with similar high precisions. However, this precision can hide complexity of the spectrum (such as from fossils) and independently varying components, so care must be exercised. Also ESR signal intensity doesn't indicate the radiation dose or the age unless the intensity (defect concentration) is calibrated to the dose; if one could know the defect concentration at a certain future time, it would be possible to estimate past passage of time from the present concentration. In conventional TL dating [8] and ordinary ESR dating [9], known additive doses of artificial irradiation are used to produce additional defects which can be used to calibrate the concentration within a sample and to determine the production yield of defects. In other words, artificial irradiation usually by γ- rays from a $_{60}Co$ source is used as a "time machine" to produce the defect concentrations which would be found in future if natural irradiation continued. If the dose rate *D* (usually in mGy/a) is obtained, the age T_{EPR} may be expressed (in ka) using the relation:

$$T_{EPR}\ [\text{ka}] = ED\ [\text{Gy}] / D\ [\text{mGy/a}].$$

The *ED* and *D* estimation for geological and archaeological samples constitutes the main part of ESR dating. In our case, the samples were collected from the field area by digging through the sand to about 2 feet in the absence of sunlight. The sample was washed with dilute acetic acid and powdered by agate mortar and exposed to γ irradiation at a rate of 810 Gy/hr. The resulting artificial doses received were labeled as 50Gy, 100Gy, 200Gy, 400Gy, 600Gy, 800Gy, 1600Gy, 2400Gy and 3200Gy irradiation respectively. All the ESR spectra were recorded at room temperature with an optimum microwave power (1.0 mW), sweep time (2 min) and time constant (0.03 s) to get good resolution. The g factor was determined using the equation

$$g = 71.44836\ (\nu/B)$$

Here υ is the microwave frequency in GHz and *B* is the magnetic field in mT.

Determination of equivalent dose (ED)

The equivalent dose for a particular intensity versus the artificial dose plot is obtained by extrapolating the saturation fit towards the negative direction and allowing it to intersect the negative *x*-axis. The negative value of the dose obtained is the equivalent dose acquired in the past and is related to age of the shell. In the present case, the average ED was determined by taking the mean of closely spaced ED values of different signals derived from similar slope curves. Here, D_{EX} is assumed on the basis of values quoted [6] and considered to have been constant throughout the past. $D_{EX} = 1.12 \pm 0.08$ mGy/a.

XRD analysis

XRD analysis is a major mineralogical tool used extensively in the identification, characterization, and quantification of phases in mineral clusters [10,11,12]. The phase analysis of the chemical structure of the powdered sample was carried with the use of Mini Flex II XRD manufactured by the Rigaku Corporation with the operating voltage 30 KV and the current 15 mA on X-ray tube. The data were compared with the JCPDS (Joint Committee on Powder Diffraction Standards, 2011) database. Alternately, the comparison was done with the Match (Crystal Impact) program.

RESULTS AND DISCUSSION

Single crystals of natural aragonite shells and corals show ESR signals almost identical to those of calcite. The signals at g – 2.0036, 2.0007 and 1.9973 are due to the presence of SO_3- isotropic, freely rotating CO_2- and orthorhombic CO_2- respectively. Carbonate in a shell is not randomly oriented but the crystal directions are oriented to harden the shell. The signal at g - 2.0031 in aragonite is different from similar signals in calcite *g*- 2.0036 due to SO_3^- radical. The former is isotropic SO_3^- and the latter is axial SO_3^- radical [13]. The ESR spectra for the samples were recorded after different doses of gamma irradiation. The intensity of the peaks for all the signals is calculated from the ESR spectra and plotted against Artificial Dose which shown in Fig 3. The Intensity values for corresponding artificial dose and g – factors of the sample AGS was mentioned in Table 1. The equivalent dose rate is determined as 260 ± 67 Gy and the calculated age is 232 ± 74 ka corresponding to middle stage (Ionian) of the Pleistocene epoch respectively which is noted in Table 2. Hence the method introduced here show great promise for solving the problems such as to calculate the age of the archaeological samples and also shows the accuracy in dating. After death and burial of the organism, physical, chemical, and biological factors may cause alteration to the carbonate skeleton. The diagenesis of the carbonate shell skeletons implies replacement of the original crystal structure and carbon exchange with the burial environment [7]. The XRD pattern of the shell sample is shown in Fig 4. In this sample, the occurrence of the characteristic calcite peak at the (104) reflection (~29.4º 2θ) and the aragonite peak at the (012) reflection (~33º 2θ) are clearly indicating that the partial transformation of aragonite into calcite. A chalky appearance is usually associated with aragonite dissolution and precipitation of single crystal calcite, in micro regions where the dissolution rate is higher than that of precipitation [14]. It ought to be noted, however, that aragonite is more soluble than calcite [15, 16] which means that chemical etching could preferentially increase the proportion of diagenetic calcite in the sample

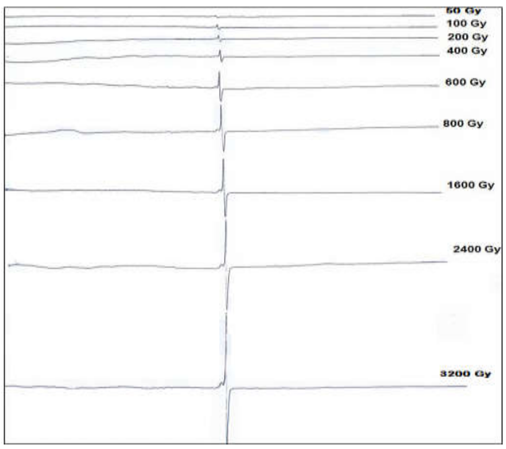


Fig. 2. ESR Spectra of sample AGS

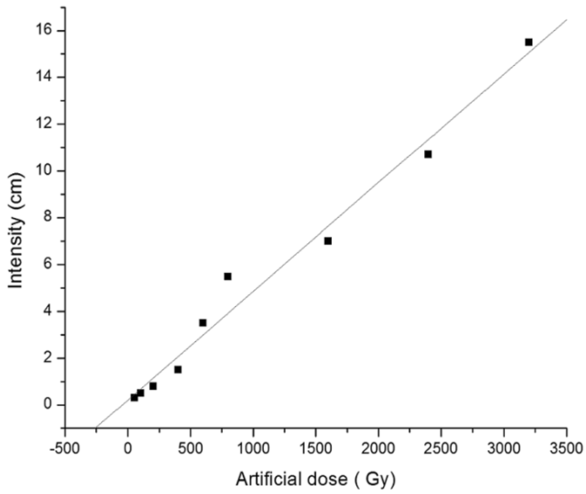


Fig. 3 Artificial dose Vs ESR intensity graph for sample AGS

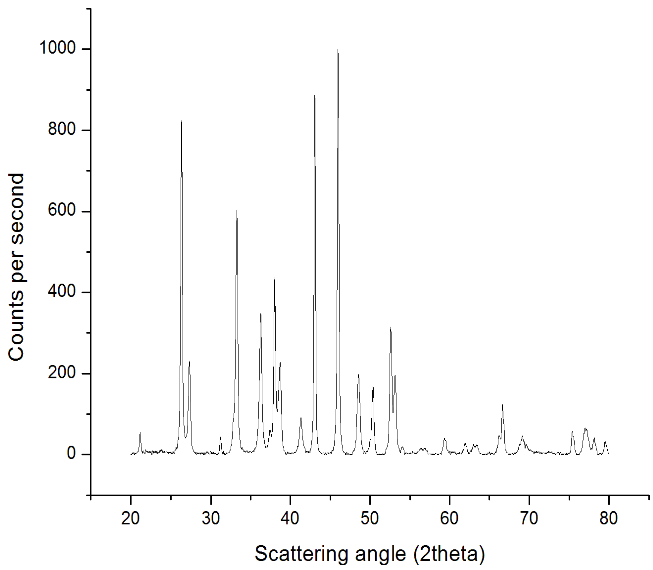


Fig. 4. XRD spectrum of the sample AGS

Table.1 The Intensity values for corresponding artificial dose and g – factor of the sample AGS

Artificial dose (Gy)	g - values	ESR signal Intensity (cm)
50	1.9983	0.3
100	2.0009	0.5
200	2.0036	0.8
400	1.9976	1.5
600	1.9974	3.5
800	2.0008	5.5
1600	1.9976	7.0
2400	2.0007	10.7
3200	2.0007	15.5

Table 2. The estimated ages of the samples

Sample code	External dose (mGy/a)	Equivalent dose (Gy)	Age of the sample T_{ESR} (Ka)	Geological period In Pleistocene epoch
AGS	1.12±0.08	260 ± 67	232 ± 74	Middle stage (Ionian)

CONCLUSION

The ESR dating has been carried out for the ancient marine shell from the coastal zone of the archaeological site Alagankulam in Tamilnadu state, India. Based on knowledge of the physics of stable radiation defects created in mineral part CO_2- present in the shell, it has been possible to determine the accumulated dose by plotting intensity of ESR lines against artificial irradiation and age of the shell calculated as 232 ± 74 ka which correspond to the middle stage of the Pleistocene epoch respectively. These results indicate dates that are coherent with other archaeological and paleontological findings in specified site. Annual variation in the signal SO_3- is useful for assessing the historical environmental change and climate fluctuation. From the XRD studies, the appearance of the aragonite peak confirms the transformation of aragonite into secondary calcite. The identification of secondary calcite in shells that were evidences the diagenesis. Electron spin resonance dating and chemical analysis of marine shells exploits the information about the sea level changes and uplift of the islands due to Quaternary tectonic movements.

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