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**JAPA**

## Investigation of Natural Silica Minerals from the Kizilirmak with EPR Spectroscopy

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### Abstract

A silica mineral contained in gravel taking from the Kizilirmak deposit and bearing organic radicals in its structure was investigated by EPR spectroscopy. The type of radicals in the silica mineral determined under different temperatures and different microwave power were by examining the intensity distributions of the EPR lines. In EPR spectra, the signals with different intensity distributions were detected.  $g$  and  $A$  spin-Hamiltonian parameters for these signals were calculated and given in Table 1. These signals are attributed to the  $\dot{C}H_2$ ,  $\dot{C}H_3$ ,  $\dot{C}H$ ,  $CO_2^-$ ,  $O_3^-$  radicals in the glassy structure by comparing with the literature.

**Key Words:** EPR, Radical, Glassy structure.

## Kızilirmak Yatağından Çıkarılan Doğal Silis Mineralinin EPR Spektroskopisi ile İncelenmesi

### Özet

Kızilirmak yatağından alınan çakıl içinde bulunan ve yapısında organik radikaller bulunduran bir silis minerali EPR spektroskopisi ile incelenmiştir. Farklı sıcaklıklarda ve farklı mikrodalga gücü altında incelenen silis minerali içerisindeki radikallerin türü, EPR çizgilerinin şiddet dağılımlarına bakılarak belirlenmiştir. EPR spektrumlarında şiddet dağılımları birbirinden farklı olan sinyaller tespit edilmiş ve bu sinyallere ait  $g$  ve  $A$  spin-Hamiltonien parametreleri hesaplanmış ve Tablo 1'de verilmiştir. Literatür ile karşılaştırılarak, sinyaller camı yapı içerisindeki  $\dot{C}H_2$ ,  $\dot{C}H_3$ ,  $\dot{C}H$ ,  $CO_2^-$ ,  $O_3^-$  radikallerine atfedilmiştir.

**Anahtar Kelimeler:** EPR, Radikal, Camı yapı.

## **1. Introduction**

The root of natural stones is based on the molten magma of the Earth's core, which constantly moves and always tries to reach the outer surface. Some of this extremely hot mass brings volcanic activity and lava flow. Magma often flows into underground cracks in the lower layer of the planet. Boiling water, steam and gases have also accompanied with the molten rock and minerals. It has been occurring the crystals and precious stones by combining with many minerals that accumulates in the cracks while gasses are become cold.

The surrounding mineral is shaped by pressure, heat and chemically acid or basic media. The small change in environmental conditions can even allow a mineral to grow, stop, change or even form a new one. This may cause to show different properties in the same mineral found in different places [1, 2]. There are many active fault lines in Turkey. There are many different natural phenomena and occurrences around these lines. For example, hot water sources and springs are in these regions. In addition to these, various geological events are also observed in these regions. Granites, syenite, monzonite, quartz diorite, biotite granites are present in the massifs along the Kızılırmak. Marble, fluorite, copper, zinc, chromite and magnesite were also detected in the region. One of these is the  $\text{SiO}_2$  mineral in the glassy or the crystal forms (quartz, etc.), which is very common in nature. This mineral, in general called as silica or siliceous compound, present in pure form and it composes precious and semi-precious stones in different colors by keeping various metals in impurities, such as opal or amethyst.

Besides these well-known forms, well-known organic radicals can also be trapped within various silica composite located near moving fault lines as mentioned. There is no accurate information about the trapping mechanisms of most active organic radicals trapped in the cavities formed in the  $\text{SiO}_2$  matrix. But the most comment one is, the trapped organic compounds which is in silica composite melted within the fossil deposits such as coal, natural gas or oil leaked due to hot magma approaching the surface in faults are fragmented by exposure to high-energy radiation as radiated from radioactive radon (or someone else) leaked from fault fissures. These chemically important and active radicals have continued their existence almost indefinitely since thousands, perhaps millions of years, despite being exposed to various natural conditions [1].

Electron paramagnetic resonance (EPR) spectroscopy is, as well known, a powerful technique for detecting and analyzing trace amounts of paramagnetic impurities at various temperatures. EPR deals only with transitions between spin states. It is not only the external magnetic field that is effective in spin transition. Local magnetic fields produced in the paramagnetic center also affect the spin transitions. The sources making up the local magnetic fields are the nuclei having non-zero spin and other paramagnetic centers located the orbit of the electron and near, which interacts with the paramagnetic ions. In this way, EPR gives detailed information about the orbit of the paramagnetic ion and its interacting nuclei. It can be comments on by taking advantage of the properties of the EPR spectrum such as line intensity, line position, line width and line splitting.

The hyperfine interaction between the magnetic moment of an electron and the magnetic moment of a nucleus can be studied with various experimental techniques [3]. In Electron Paramagnetic Resonance (EPR) spectroscopy, hyperfine interactions manifest as line splittings in the spectrum.

Such splittings, originating from copper nuclei with spin  $I = 3/2$ , have first been observed by R.P. Penrose in 1949 [4] in a single crystal of a copper doped magnesium tutton salt. Since then, measurements of hyperfine interactions with EPR have developed to an indispensable tool for the study of paramagnetic entities in single crystals, in polycrystals, and in frozen and liquid solutions [5-8]. Hyperfine data are particularly helpful in understanding the electronic and geometric structure of paramagnetic species. They enable one to draw up a detailed mapping of the electron spin density distribution, and contain precise information about the spatial arrangement of the nuclei close to the unpaired electron [9, 10].

Electron paramagnetic resonance (EPR) spectroscopy is, as well known, a powerful technique for detecting and analyzing trace amounts of paramagnetic impurities which is assumed to be reflecting the lattice structure of the host at various temperatures. In this study, the types of radicals are determined by examining a silica mineral containing organic radicals and located in pebbles taken from the bed of the Kızılırmak with an EPR spectrometer. This research is particularly interesting for those who work on natural formations, organic radicals, and spectroscopic techniques. It is estimated that the silica mineral was probably formed by the drift of Kızılırmak along the active North Anatolian fault line.

## **2. Materials and Method**

Silica minerals containing organic radicals were extracted from the Kızılırmak deposit. Samples were cleaned to remove any contamination and sized appropriately for EPR measurements. EPR spectra of minerals are recorded in a magnetic field modulation frequency of 100 kHz by using a Varian E-104 X-band EPR spectrometer. The  $g$  values were achieved by comparison with a 2,2-diphenyl-1-picrylhydrazyl (DPPH) sample of  $g = 2.0036$ .

## **3. Results and Discussion**

EPR spectroscopy is the most powerful tool known for examining and determining these important radicals, in trace amounts, in the minerals containing silicon dioxide and in the glassy structure. An X-band EPR spectrometer was used through the experimental work. The EPR spectra taken this glassy structure found in nature at room temperature shown in Fig. 1 and at 433 K in Fig. 2. The line widths of the signals represented by A and B are increased by rising the temperature to 433 K and therefore the line amplitudes are decreasing. By increasing the microwave power applied to the sample at this temperature, the EPR signals lost in the spectra due to the high Signal to Noise ratio have become evident.

When the permitted transitions are considered in the EPR, if an unpaired electron interacts with a nucleus having the spin  $I$ ,  $2I + 1$  lines with the identical EPR intensity distributions are observed. If there are  $n$  identical nuclei interacting with the unpaired electron, the  $2nI + 1$  lines appear, whose intensities are not identical. EPR signal groups with different the intensity distributions were observed in the spectrum given in Fig. 2. Existing more than one radical group with the same intensity

distribution indicate that they are taking place in different chemical environments. The hyperfine spin-Hamiltonian has the form

$$\mathcal{H}_{hfs} = S\bar{A}I$$

In first order, the measured hyperfine angular frequency consists of two contributions, the isotropic Fermi contact term;

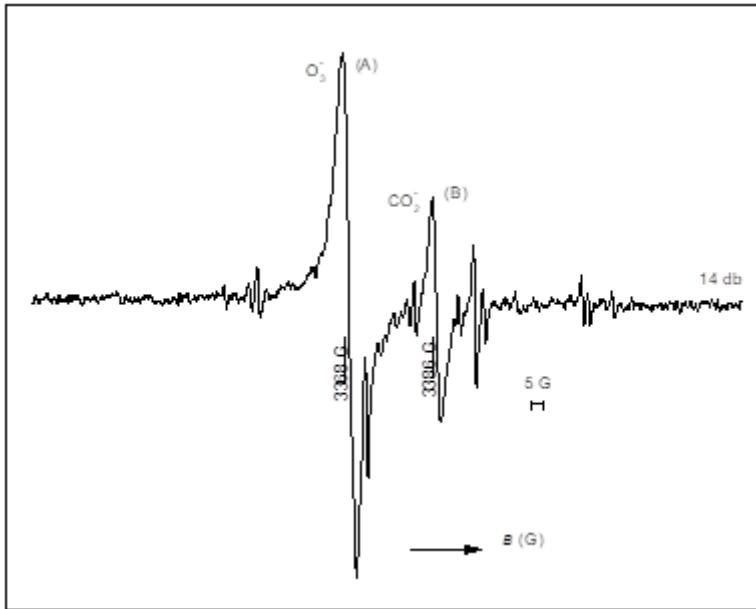
$$a_{iso} = \frac{8\pi}{3\hbar} g_e \beta_e g_n \beta_n \langle \psi_0 | \delta(r) | \psi_0 \rangle$$

and the electron-nuclear dipole-dipole coupling;

$$A_{ij}^{DD} = \frac{g_e \beta_e g_n \beta_n}{\hbar} \left\langle \psi_0 \left| \frac{3r_i r_j - \delta_{ij} r^2}{r^5} \right| \psi_0 \right\rangle$$

where  $\psi_0$  is the orbital of the unpaired electron and  $r_i$  is a component of the radius vector from the electron to the nucleus. The spin-only coupling tensor  $A^{DD}$  is traceless and symmetric [11].

$g$  values and superfine splitting constants ( $A$ ) were found for every radical appears in this glassy. These values indicate which of the signal is belong to which radical. The measured  $g$  and  $A$  parameters are given in Table 1.

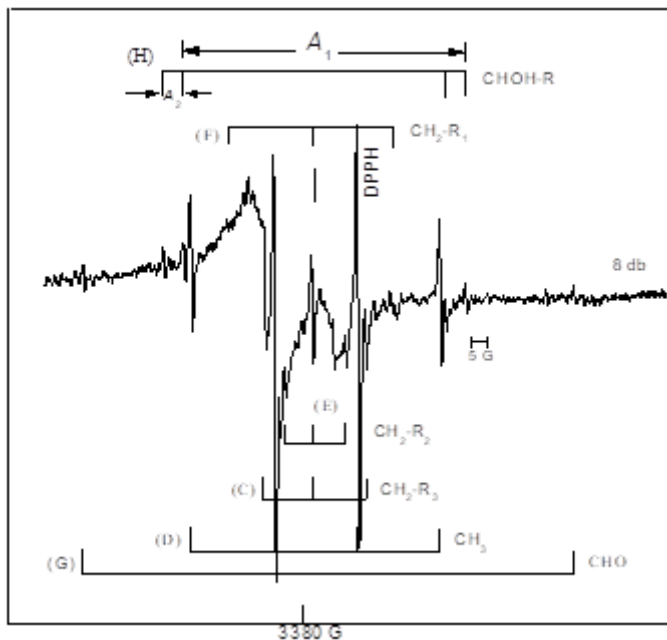


**Figure 1.** EPR spectrum of natural glassy at room temperature (microwave power= 14 dB).

From the calculated  $g$  values of the EPR lines marked as A and B and varied the line widths and intensities as depending on temperature, this EPR signals were determined that belong to  $O_3^-$  and  $CO_2^-$  radicals, respectively. The  $g$  values for these radicals are in agreement with the  $g$  values obtained in previous studies [12-14, 17, 22].

**Table 1.** Spin-Hamiltonien parameters of radicals in natural glassy structure.

Radical	$g \pm 0.0003$	$A_1 \pm 0.5$ (G)	$A_2 \pm 0.5$ (G)	Radical	$g \pm 0.0003$	$A_1 \pm 0.5$ (G)	$A_2 \pm 0.5$ (G)
A	2.0111	-	-	E	2.0024	8.75	-
B	2.0002	-	-	F	2.0026	22	-
C	2.0018	27	-	G	2.0011	123.5	-
D	2.0022	22.5	-	H	2.0033	76	5.5



**Figure 2.** EPR spectrum of natural glassy taken at 433 K (microwave power = 8dB).

The quartet signal (D) shown in Fig. 2 and having a 1: 3: 3: 1 intensity distribution originates from three identical protons of the methyl ( $\bullet \text{CH}_3$ ) group. The  $g$  and  $A$  values found for this signal is compatible with the literature for the  $\bullet \text{CH}_3$  radical [13]. Although the methyl radical is extremely active and mobile, the silica continues its existence in the lattice since thousands of years.

The hyperfine structure splits of the two triplet signals (E and F) in Figure 2 are quite different from each other and the E and F signals have identical shape but belong to two different group in the structure. The  $g$  values calculated for these radicals are equal to each other. The difference of hyperfine structure splits is due to  $\text{CH}_2$  radicals are linked to different inactive groups [15].

The doublet line indicated by "G" in Figure 2 with the hyperfine splitting of 123.5 G and  $g = 2.0011$  belongs to  $\bullet$  HCO radical. The calculated values of  $g$  and  $A$  for this signal are in good agreement with the published data in the literature [16].

Another doublet with 27 G splitting and  $g = 2.0018$  value appears in Fig. 2. This signal previously represented with a "C" belongs to the  $\bullet$  CH<sub>2</sub> radical attached to an inactive group R<sub>3</sub> [18-20]. "H" signal appearing as quadruple signals in the spectrum in Fig. 2 attributed to  $\bullet$  CHOH radical. The unpaired electron interacted with one of the non-identical protons and signaled the doublet. The unpaired electron then interacts with the beta proton to cause a doublet repeat splitting [20, 21].

#### 4. Conclusions

The EPR spectra of the natural glassy structures containing silicon are given in Fig. 1 and Fig. 2. The  $g$  values of signals A and B in Figure 1 were determined as 2.0111 and 2.0002 and attributed to radicals  $O_3^-$  and  $CO_2^-$ , respectively. It was observed that the line widths and intensities of the EPR signals of these radicals changed with temperature. According to the  $g$  values of the EPR signals represented by C, D, E, F, G and H in Fig. 2, they can be assigned to the organic radicals  $\bullet$  CH<sub>2</sub>,  $\bullet$  CH<sub>3</sub>, CH<sub>2</sub>-R<sub>1</sub>, CH<sub>2</sub>-R<sub>2</sub>,  $\bullet$  HCO and  $\bullet$  CHOH respectively. The spin Hamiltonian parameters of each signal were found and are given in Table 1. The results show that this mineral was probably deposited by the Kızılırmak drifting along the active North Anatolian fault line.

#### Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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