

Electron Paramagnetic Resonance of Organic and Inorganic Centers in γ -Irradiated Natural Sepiolite Minerals

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Natural sepiolite minerals and their γ -irradiated forms were investigated by electron paramagnetic resonance (EPR) at room temperature and at 113 K. The EPR signals in powders of natural sepiolite were observed due to clusters of Fe^{3+} ions. The paramagnetic centers produced by γ -irradiation of natural sepiolite minerals were attributed to the CH_3 at room temperature and SO_2^- and SO_3^- radicals at 113 K. These centers were found to be perfectly observable above 20 mW microwave power. The g values of all paramagnetic centers have been measured and the A values of some of them have been reported. The results were consistent with the literature data for similar paramagnetic centers.

Key words: EPR; Paramagnetic Centers; γ -Irradiation; Sepiolite Minerals.

1. Introduction

Sepiolite is a hydrated magnesium silicate. It is non-metallic, porous with a large specific surface, and has a low chemical activity belonging to the polygorskite mineral family. Its chemical formula is $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot n\text{H}_2\text{O}$, where $n = 6–8$.

Sepiolite is applied in cosmetics, paints, industrial waste, friction control, catalysis, fertilizers, asphalt, drilling mud, acoustics, insulation, absorption, filtering, moisture control, supports, bleaching, animal feed, plastics, rubber, paper and construction. It is also used in the removal of microbial contaminants, such as viruses, bacteria and protozoa, in public water systems,

and in the filtration of human blood plasma. Therefore, this and similar minerals are important for health services and industrial production in developed countries.

Natural and synthetic clay minerals are known to contain stable paramagnetic centers observable by electron paramagnetic resonance (EPR), arising from impurity ions in the lattice, trapped radicals, electron holes or vacancies [1].

EPR is a nondestructive standard method which enables a quick and very sensitive measurement of paramagnetic radicals in solids. This method has been successfully applied to identify paramagnetic defects in miscellaneous natural minerals in their γ -irradiated [2–12] and unirradiated [13,4] forms as well as volcanic tuffs [4]. In these studies, performed on different minerals, CO_2^- , CO_3^- , CO_3^{3-} , CH_2OH , CH_3 , SO_2^- , SO_3^- , PO_4^{2-} , E' and peroxy paramagnetic centers were found. These centers are found either in the natural states of the minerals as impurities or as a result of γ -irradiation. On the other hand, some minerals exhibited the existence of Mn^{2+} , Al^{2+} and especially Fe^{3+} paramagnetic ion species [4,14–16], but studies in this field with EPR are still limited by the complexity of the broad signal due to magnetic impurities producing ferromagnetic resonance [17].

Most of the natural minerals contain traces of iron ions in sufficient quantity to generate an intense EPR spectrum. The observed paramagnetism is due to Fe^{3+} , which has an electronic spin $S = 5/2$ [13]. Thus, the EPR spectrum of a mineral reveals two broad signals at $g = 4.3$ and near $g = 3$ [18] and a much thinner signal near $g = 2$. The first two signals are due to Fe(III) in different environments. The EPR signal at $g = 4.3$ arises from Fe^{3+} localized in orthorhombic sites [19]. The third signal, located near $g = 2$, is attributed to hydrated Fe^{3+} giving rise to oxides such as Fe_2O_3 or FeOOH [20]. In the same field of the spectrum at around $g = 2$, another narrow signal can be observed. This signal arises from effects of natural irradiation, which induces the formation of radicals or trapped electrons and holes [8].

In the present study we have investigated by EPR the paramagnetic centers in natural sepiolite minerals and their γ -irradiated forms at room temperature and at 113 K. The spin Hamiltonian parameters of the paramagnetic centers and also their local symmetries are explained.

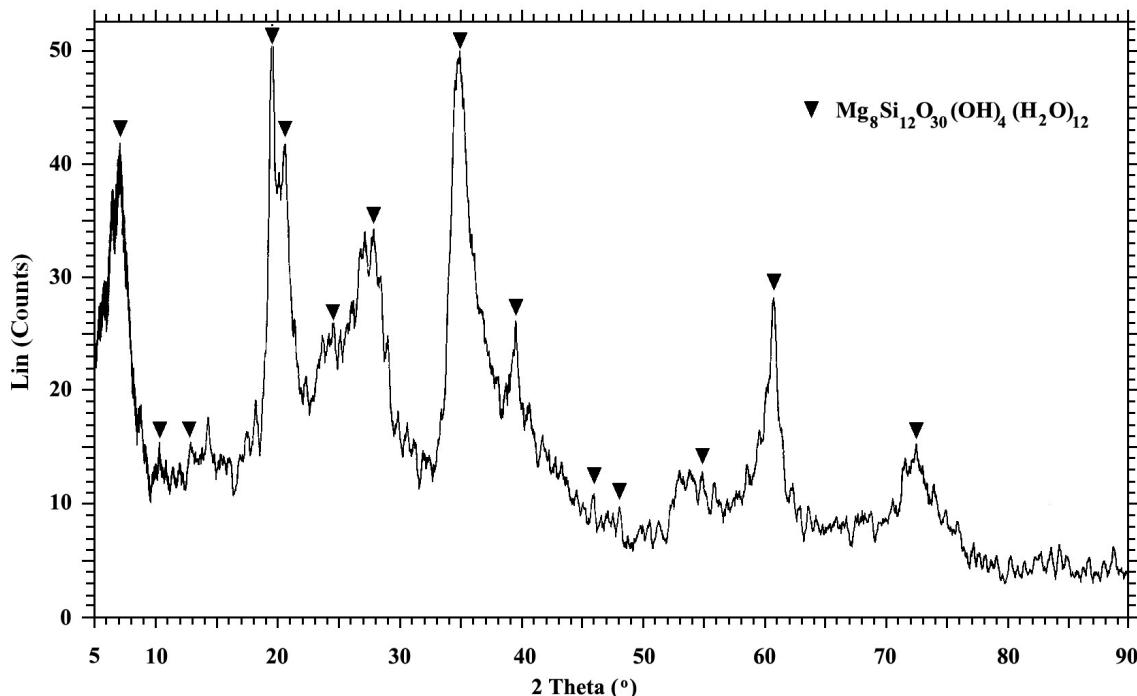


Fig. 1. The X-ray powder diffraction pattern of sepiolite mineral.

2. Experimental

Natural sepiolite mineral samples were obtained from the Mihalıççık-Eskişehir region of Anatolia (Turkey). The samples were washed, dried and finely powdered, using an agate mortar. The samples were first investigated by X-ray powder diffraction (XRD). These measurements were carried out at the Erciyes University, Kayseri, Turkey, with a Bruker AXS D8 Advance model instrument with a Cu^{2+} X-ray tube operating at $\lambda = 1.5405 \text{ \AA}$. Then, the powdered samples were irradiated with a ^{60}Co γ -ray source at room temperature to a dosage around 25 kGy. The EPR measurements on the samples were carried out with a Varian E-line 109C model X-band EPR spectrometer using a microwave power within the range of 0.1–150 mW and a 100 kHz field modulation frequency with an amplitude of 0.1 mT. The low temperature studies were carried out using a Varian variable temperature control unit. The *g*-factors were found by comparison with the position of the line of a diphenylpicrylhydrazyl sample of $g = 2.0036$. The EPR measurements were carried out at room temperature and at 113 K. Some of the EPR spectra were simulated using the Bruker Win EPR simulation programme.

3. Results and Discussion

The X-ray powder diffraction pattern of sepiolite mineral is shown in Figure 1. The signals marked with “▼” in Fig. 1 show the presence of $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot n\text{H}_2\text{O}$. On the other hand, in the literature the chemical composition (in %wt) of the sepiolite mineral is reported to be 60.0% SiO_2 , 25.4% MgO , 0.3% Al_2O_3 , 0.5% K_2O , 0.6% CaO , 0.05% TiO_2 , 0.05% Na_2O , 0.01% P_2O_5 , 0.01% MnO , 0.04% $\Sigma(\text{Fe}_2\text{O}_3 + \text{FeO})$ and 13.4% loss on ignition [21].

On the low field side of the EPR spectrum of natural sepiolite mineral before γ -irradiation at room temperature only two EPR signals are observed, the first one near $g_{\text{eff}} = 3.2$ and the other near $g_{\text{eff}} = 4.3$. These signals are due to the $\text{Fe}(\text{III})$ species located in different environments. We attributed the first single signal to paramagnetic Fe^{3+} ions ($m_s = 1/2 \rightarrow -1/2$ transition), localized in tetrahedral coordination with rhombic distortion. The other signal, near $g_{\text{eff}} = 4.3$, is attributed to high spin Fe^{3+} ions localized in the orthorhombic crystal field. Additionally, on the high field side of the EPR spectrum at 113 K, a single signal around $g = 2$, whose intensity increases with the tem-

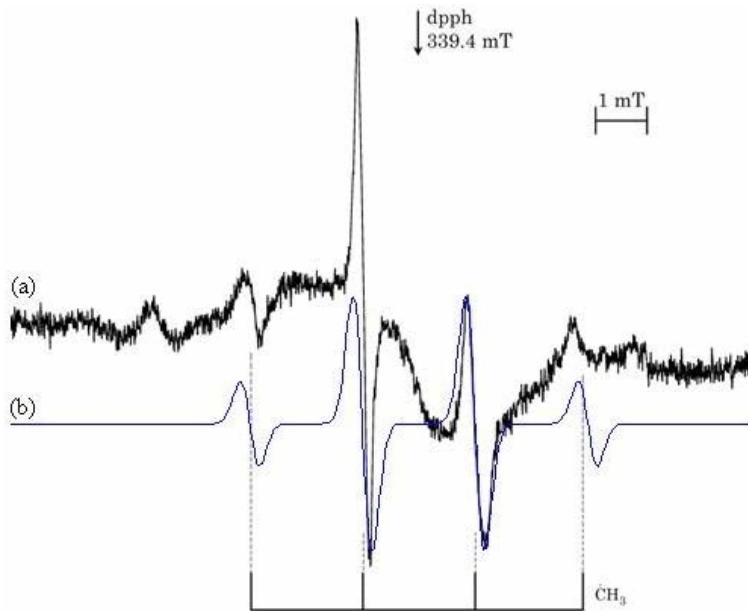


Fig. 2. a) EPR spectrum of γ -irradiated sepiolite mineral powders at room temperature. b) Simulation of the CH_3 radical; simulation parameters: $a_{\alpha}^{(1,2,3)} = 2.33$ mT, $\Delta H = 0.15$ mT.

perature, is also observed. We attributed this single signal with the linewidth $\Delta H = 0.7$ mT at $g_{\text{eff}} = 2.04$ to the hydrated Fe^{3+} , giving rise to oxides such as Fe_2O_3 or FeOOH [20]. Also, the EPR spectrum of paramagnetic Fe^{3+} ions can be adequately described by the spin Hamiltonian [16]

$$H = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2), \quad (1)$$

where β is the Bohr magneton, \mathbf{H} is the magnetic field, $D(3B_2^0)$ and $E(B_2^2)$ are the axial and orthorhombic structure parameters, respectively, which describe the splitting of the Fe^{3+} Kramers doublets in the crystal field, \mathbf{g} is a second rank tensor with the eigenvalues g_x, g_y, g_z , \mathbf{S} is the total spin operator, and S_x, S_y, S_z are the spin matrices. The orthorhombic character of the field is expressed by the ratio $E/D = \lambda$, where a completely rombic field is achieved if $\lambda = 1/3$. If $\lambda = 0$, this means that the iron ion is located in axial symmetry of the crystal field. A single EPR signal with $g_x = g_y = g_z = g_{\text{eff}} = 4.3$ will be observed when $\lambda = 0.333$ and $h\nu/D < 1$, where $h\nu$ is the microwave energy. It should be noted that λ lies in the range $0 \leq \lambda \leq 1/3$.

After γ -irradiation, the EPR spectrum of sepiolite mineral at room temperature was observed as in Figure 2a. The quartet signals observed as in Fig. 2a are probably due to the CH_3 free radical, and its average

Table 1. The EPR parameters of paramagnetic ions and γ -irradiation-induced paramagnetic centers in sepiolite mineral in this study.

Center	Local symmetry	g	$a_{\alpha}^{(1,2,3)}$ (mT)	Linewidth (mT)
Fe^{3+}	orthorhombic	$g_{\text{eff}} = 4.3$		
Fe^{3+}		$g_{\text{eff}} = 3.2$		
Fe_2O_3 or FeOOH at 113 K	orthorhombic	$g_{\text{eff}} = 2.04$		0.7
CH_3		$g_{\text{av}} = 2.0038$	2.33	0.15
SO_2^-	freely rotating	$g = 2.0057$		0.07
SO_3^-	freely rotating	$g = 2.0033$		

g value is calculated to be $g_{\text{av}} = 2.0038$, and the hyperfine coupling constants of free electron with the three equivalent α protons in the methyl radical are measured as $a_{\alpha}^{(1,2,3)} = 2.33$ mT, the linewidth is $\Delta H = 0.15$ mT. These signals appear clearly when the microwave power is around 20 mW. The simulated spectrum, presented in Fig. 2b, is made using the Bruker Win EPR programme. The agreement between the experimental and simulated EPR spectrum is very good. Their spin Hamiltonian parameters are given in Table 1. The reported values are found to be consistent with the literature values [6, 10, 17, 22–24]. The inhomogeneous broadening of the observed lines arises probably from the slow motion of the radicals over the clay surfaces, which is expected if we consider that the methyl radicals are trapped in a rigid matrix. Methyl

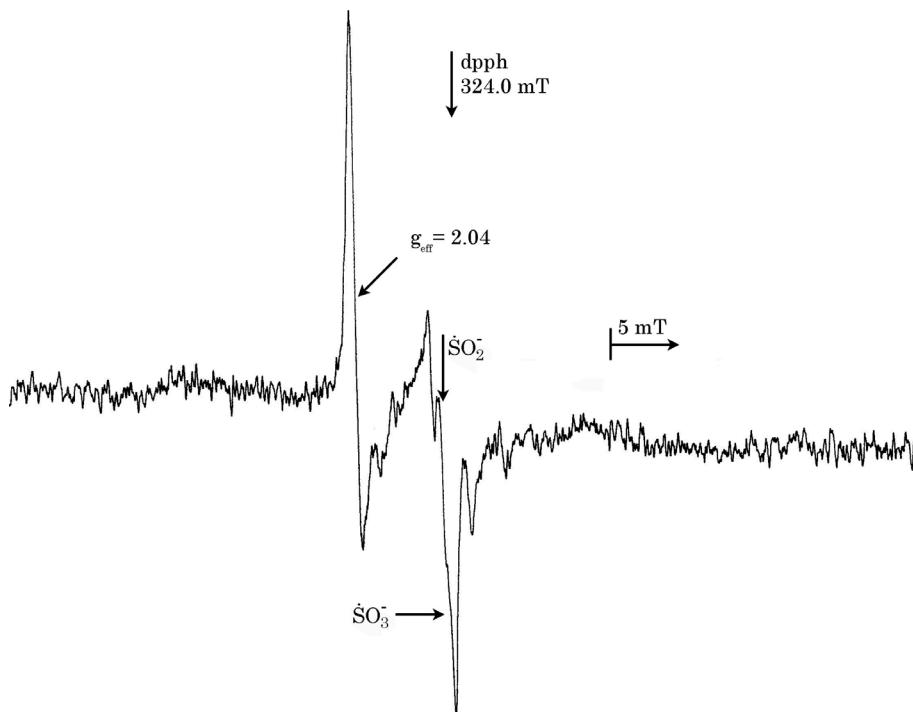


Fig. 3. EPR spectrum of γ -irradiated sepiolite mineral powders at 113 K.

radicals can be generated from the radiolysis of organic molecules existing as impurities in the crystal structure of the clay minerals. These traces of organic matter are found in most clay deposits and are presumably acquired from the minerals by percolation of water-carrying organic matter from surrounding areas [25]. The organic impurities are associated either with external surfaces or with the interlayer sorption sites or the broken edge sites of the clay minerals [3]. At 113 K, in addition to the quartet signals of the methyl radical, some signals between the second and third lines of the methyl radical, arising from two different centers, are also observed, as shown in Figure 3. We attributed these signals to the $\dot{\text{SO}}_2^-$ and $\dot{\text{SO}}_3^-$ free radicals. The EPR signals at $g = 2.0057$ ($\Delta H = 0.07$ mT) and 2.0033 may be due to freely rotating $\dot{\text{SO}}_2^-$ and $\dot{\text{SO}}_3^-$ radicals [6, 26], respectively. It seems that the observed lines belonging to the $\dot{\text{SO}}_2^-$ and $\dot{\text{SO}}_3^-$ free radicals may probably appear due to the anisotropic behaviour of the hyperfine interaction of the $\dot{\text{CH}}_3$ protons, at 113 K. This shows that in the $g = 2.0036$ region, the spectra are composed by superposition of three different paramagnetic species. Furthermore, at 113 K we have observed that, while the intensities of signals be-

longing to clusters of Fe^{3+} ions increase, the intensities of the other observed paramagnetic center signals decrease.

4. Conclusions

As a result, in this study of organic and inorganic free radicals the paramagnetic ions were identified in inorganic sepiolite mineral, and their spin Hamiltonian parameters were determined by the EPR method. These centers, mentioned above, were observed either in the natural states of the minerals as impurities, or as a result of γ -irradiation. The EPR signals belonging to clusters of Fe^{3+} transition metal ions on the low field side and hydrated Fe^{3+} species giving rise to oxides such as Fe_2O_3 or FeOOH on the high field side were only observed before γ -irradiation. After γ -irradiation, in addition to them, signals due to the $\dot{\text{CH}}_3$ radical at room temperature and $\dot{\text{SO}}_2^-$, $\dot{\text{SO}}_3^-$ radicals at 113 K were also observed.

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- [1] J. M. Gaite, F. Muller, and S. Jemai, *Phys. Chem. Minerals* **30**, 366 (2003).
- [2] R. W. A. Franco, F. Pelegrini, and A. M. Rossi, *Phys. Chem. Minerals* **30**, 39 (2003).
- [3] D. Gournis, A. E. Mantaka-Marketou, M. A. Karakasides, and D. Petridis, *Phys. Chem. Minerals* **28**, 285 (2001).
- [4] F. Köksal, R. Köseoğlu, and E. Başaran, *Z. Naturforsch.* **58a**, 293 (2003).
- [5] F. Köksal, R. Köseoğlu, İ. Şaka, E. Başaran, and F. Şener, *Radiat. Eff. Def. Solids* **159**, 393 (2004).
- [6] R. Köseoğlu, F. Köksal, E. Çiftçi, and M. Akkurt, *J. Mol. Struct.* **733**, 151 (2005).
- [7] R. Köseoğlu, E. Köseoğlu, F. Köksal, E. Başaran, and D. Demirci, *Radiat. Meas.* **40**, 65 (2005).
- [8] M. Plötze, G. Kahr, and R. Hermanns Stengele, *Appl. Clay Sci.* **23**, 195 (2003).
- [9] R. Pushkareva, E. Kalinichenko, A. Lytovchenko, A. Pushkarev, V. Kadoczhnikov, and M. Plastynina, *Appl. Clay Sci.* **21**, 117 (2002).
- [10] H. Sasaoka, C. Yamanaka, and M. Ikeya, *Appl. Radiat. Isot.* **47**, 1415 (1996).
- [11] S. Sorieul, T. Allard, G. Morin, B. Boizot, and G. Calas, *Phys. Chem. Minerals* **78**, 1 (2005).
- [12] E. G. Yukihara, E. M. Yoshimura, and E. Okuno, *Nucl. Inst. Meth. Phys. Res. B* **191**, 266 (2002).
- [13] Y. Bensimon, B. Deroid, F. Dijoux, and M. Martineau, *J. Phys. Chem. Solids* **61**, 1623 (2000).
- [14] A. V. Chandrasekhar, M. Venkata Ramanaiah, B. J. Reddy, Y. P. Reddy, P. S. Rao, and R. V. S. S. N. Ravikumar, *Spectrochim. Acta A* **59**, 2115 (2003).
- [15] N. O. Gopal, K. V. Narasimhulu, and J. Lakshmana Rao, *J. Phys. Chem. Solids* **65**, 1887 (2004).
- [16] H. Rager and H. Schneider, *Am. Mineral.* **71**, 105 (1986) and references therein.
- [17] M. Ikeya, *New Applications of Electron Spin Resonance: Dating, Dosimetry and Microscopy*, World Scientific, Singapore 1993.
- [18] B. R. Angel and W. E. J. Vincent, *Clays Clay Miner.* **26**, 263 (1978).
- [19] J. Bartoll, A. Tani, M. Ikeya, and T. Inada, *Appl. Magn. Reson.* **11**, 577 (1996).
- [20] D. Bonnin, S. Muller, and G. Calas, *Bull. Miner.* **105**, 467 (1982).
- [21] S. Akyüz and T. Akyüz, *J. Mol. Struc.* **651 – 653**, 205 (2003).
- [22] D. R. Griffiths, G. V. Robines, N. J. Seeley, H. Chandra, A. C. McNeil, and M. C. R. Symons, *Nature* **300**, 435 (1982).
- [23] A. S. Marfunin, *Spectroscopy, Luminescence and Radiation Centers in Minerals*, Springer, Berlin 1979.
- [24] K. Takeya, A. Tani, T. Yada, M. Ikeya, and K. Ohgaki, *Jpn. J. Appl. Phys.* **43**, 353 (2004).
- [25] H. Z. Friedlander, C. R. Frink, and J. Saldick, *Nature* **199**, 61 (1963).
- [26] R. Köseoğlu, F. Köksal, and E. Çiftçi, *Radiat. Eff. Def. Solids* **159**, 497 (2004).