Electron Paramagnetic Resonance of Rhyolite and γ-Irradiated Trona Minerals

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Rhyolite from the "Yellow Stone of Nevşehir" and γ-irradiated trona from the Ankara Mine have been investigated by electron paramagnetic resonance at ambient temperature and at 113 K. Rhyolite was examined by X-ray powder diffraction and found to consist mainly of SiO_2. Before γ-irradiation, the existing paramagnetic species in rhyolite were identified as $\dot{P}O_4^{2-}$, $\dot{C}H_2OH$, $\dot{C}O_3^-$, $\dot{S}O_2^-$, $\dot{C}O_3^{3-}$, and $\dot{C}O_2^-$ free radicals and Fe^{3+} at ambient temperature. At 113 K $\dot{S}O_2^-$, $\dot{C}O_3^{3-}$, and $\dot{C}O_2^-$ radicals and Fe^{3+} were observed. The γ-irradiation produced neither new species nor detectable effects on these free radicals. The disappearance of some of the radicals at 113 K is attributed to the freezing of their motions. Before γ-irradiation, the trona mineral shows only Mn^{2+} lines, but after γ-irradiation it indicated the inducement of $\dot{C}O_3^{3-}$ and $\dot{C}O_2^-$ radicals at ambient temperature, 113 K, in addition to the Mn^{2+} lines. The *g* and *a* values of the species were determined.

Key words: Electron Paramagnetic Resonance; Free Radicals; Silicate; Rhyolite; Trona; γ-Irradiation.

1. Introduction

Various kinds of stones, geothermal samples and lava systems have been investigated by electron paramagnetic resonance (EPR) [1, 2]. The samples studied were either natural state or in their γ-irradiated [3 – 14]. These studies revealed the presence of various kinds of sulphur oxy and carboxy radicals in these substances. Around the Erciyes mountain in inner Anatolia, and its neighbouring province Nevşehir, the mostly encountered remnants are various kinds of stones or tuffs. One of these stones is rhyolite, locally named Yellow Stone of Nevşehir. It was investigated in this study. We expected to detect paramagnetic centers in rhyolite due to the thermal effects of the close mountain Erciyes, which was active earlier. Due to it is use in house constraction, this stone is important in that region. To our knowledge there exists no investigation of this mineral with EPR. Also trona, which is widely used in soda and glass production, seemed interesting to study with EPR. Rhyolite and trona were first studied in their natural states, and then their γ-irradiated states were considered. Before γ-irradiation the results indicated the existence of Fe^{3+} ions and $\dot{P}O_4^{2-}$, $\dot{C}H_2OH$, $\dot{C}O_3^-$, $\dot{S}O_2^-$, $\dot{C}O_3^{3-}$, and $\dot{C}O_2^-$ radicals in rhyolite and Mn^{2+} ions in trona. After γ-irradiation $\dot{C}O_3^{3-}$ and $\dot{C}O_2^-$ free radicals were detected in trona and no detectable effects in rhyolite.

2. Experimental

Rhyolite was obtained in Nevşehir (Karadağ) from the bulk of the region, and trona in bulk form from the Mine Investigating and Searching Department of Turkey in Ankara. Trona is a natural source and obtained in Ankara (Beypazarı). Pure $Na_3H(CO_3)_2$ samples were obtained from the grey parts of the bulk trona substance. The γ-irradiation was performed at the Ankara Nuclear Training and Research Centre at ambient temperature to a dose of around 20 kGy.

The spectra were recorded with a Varian E-109 C model X-band EPR spectrometer at ambient temperature and at 113 K. The microwave power was around 2 mW, and the modulation frequency was 100 kHz with an amplitude of 0.1 mT. The low temperatures were attained by a Varian temperature controller.

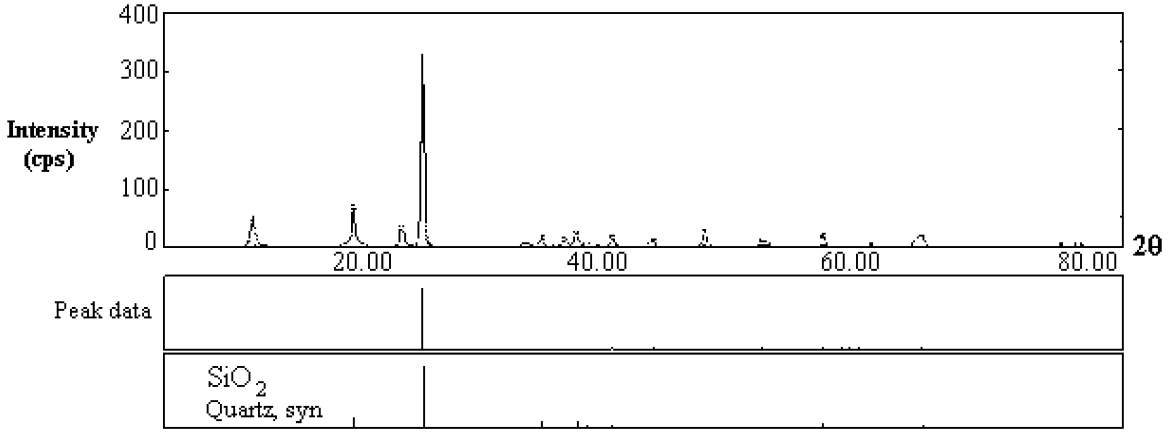

Fig. 1. X-ray powder diffraction pattern of rhyolite.

The g values were determined in comparison with a diphenylpicrylhydrazyl sample of $g = 2.0036$.

The X-ray powder diffraction was made in the High Technology Institute at Gebze with a Rigaku dmask 2200 powder X-ray diffractometer. The results in this paper are completely reproducible, and the samples were obtained from colossal bulks of the minerals.

3. Results and Discussion

The X-ray powder diffraction results of rhyolite are shown in Figure 1. This figure indicates that the so called Yellow Stone of Nevşehir consists mainly of SiO_2, which is normal for a rhyolite. The EPR spectrum at ambient temperature of this mineral is shown in Fig. 2(a), and that at 113 K in Fig. 2(b). The spectrum of the γ-irradiated sample is not displayed because there was no appreciable difference between the irradiated and unirradiated one. The spectrum in Fig. 2(a) can be explained by the existence of the radicals $\dot{P}O_4^{2}-$, $\dot{C}H_2OH$, $\dot{C}O_3^-$, $\dot{S}O_2^-$, $\dot{C}O_3^{3-}$, and $\dot{C}O_2^-$. The $\dot{P}O_4^{2-}$ and $\dot{C}H_2OH$ radicals can not be observed above 20 mW microwave power. The g values of all of the observed radicals and the hyperfine coupling constants of ^{31}P and H nuclei with the free electron in $\dot{P}O_4^{2-}$ and $\dot{C}H_2OH$ are given in Table 1. The reported values were found to be consistent with the literature data [1 – 14]. For the $\dot{P}O_4^{2-}$ radical the g value was reported as 2.0079, and for the hyperfine interaction of the ^{31}P nucleus with the free electron it was given as 3.44 mT [13 – 15]. In the $\dot{C}H_2OH$ radical the hyperfine interaction of α protons with the free electron is 1.738 mT and for β protons is 0.115 mT, and the g value is 2.0030 [16 – 17].

Table 1. The EPR parameters of the $\dot{P}O_4^{2-}$, $\dot{C}H_2OH$, $\dot{C}O_3^-$, $\dot{S}O_2^-$, $\dot{C}O_3^{3-}$, and $\dot{C}O_2^-$ radicals in rhyolite.

Radical	g	a (in mT)
$\dot{P}O_4^{2-}$	2.0057	$a_P = 3.42$
$\dot{C}H_2OH$	2.0031	$a_H = 1.75$
		$a_{OH} = 0.115$
$\dot{C}O_3^-$	2.0112	
$\dot{S}O_2^-$	2.0071	
$\dot{C}O_3^{3-}$	2.0026	
$\dot{C}O_2^-$ (free rotating)	2.0007	
$\dot{C}O_2^-$ (axial) at ambient temperature	$g_\perp = 2.0028$	
	$g_\parallel = 1.9975$	
$\dot{C}O_2^-$ (orthorhombic) at 113 K	$g_{xx} = 2.0026$	
	$g_{yy} = 2.0019$	
	$g_{zz} = 1.9875$	

These values agree with the results of this paper. The g value for $\dot{C}O_3^-$ is reported as 2.015 [5, 18] and is very close to the present value of 2.012. The g values of free rotating $\dot{S}O_2^-$ and $\dot{C}O_3^{3-}$ radicals are 2.0059 [19 – 20] and 2.0025 [21], respectively. The g value for the free rotating $\dot{C}O_2^-$ is reported to be 2.0007 [22], which is equal to the g value obtained in this work. The components of g for the axial $\dot{C}O_2^-$ are $g_\parallel = 1.9975$ and $g_\perp = 2.0025$, and in the orthorhombic $\dot{C}O_2^-$ are: $g_{xx} = 2.0032$, $g_{yy} = 2.0018$, $g_{zz} = 1.9973$ [1, and the references therein].

It seems that the signals belonging to the $\dot{P}O_4^{2-}$, $\dot{C}H_2OH$ and $\dot{C}O_3^-$ radicals disappear due to the freezing of their motions at 113 K, as their EPR parameters become anisotropic and the signal broadens at these temperatures. The signals for the $\dot{S}O_2^-$ and $\dot{C}O_3^{3-}$ radicals stay as they are at room temperature. The signals of $\dot{C}O_2^-$ change their places, see the principal values of g given in Table 1.

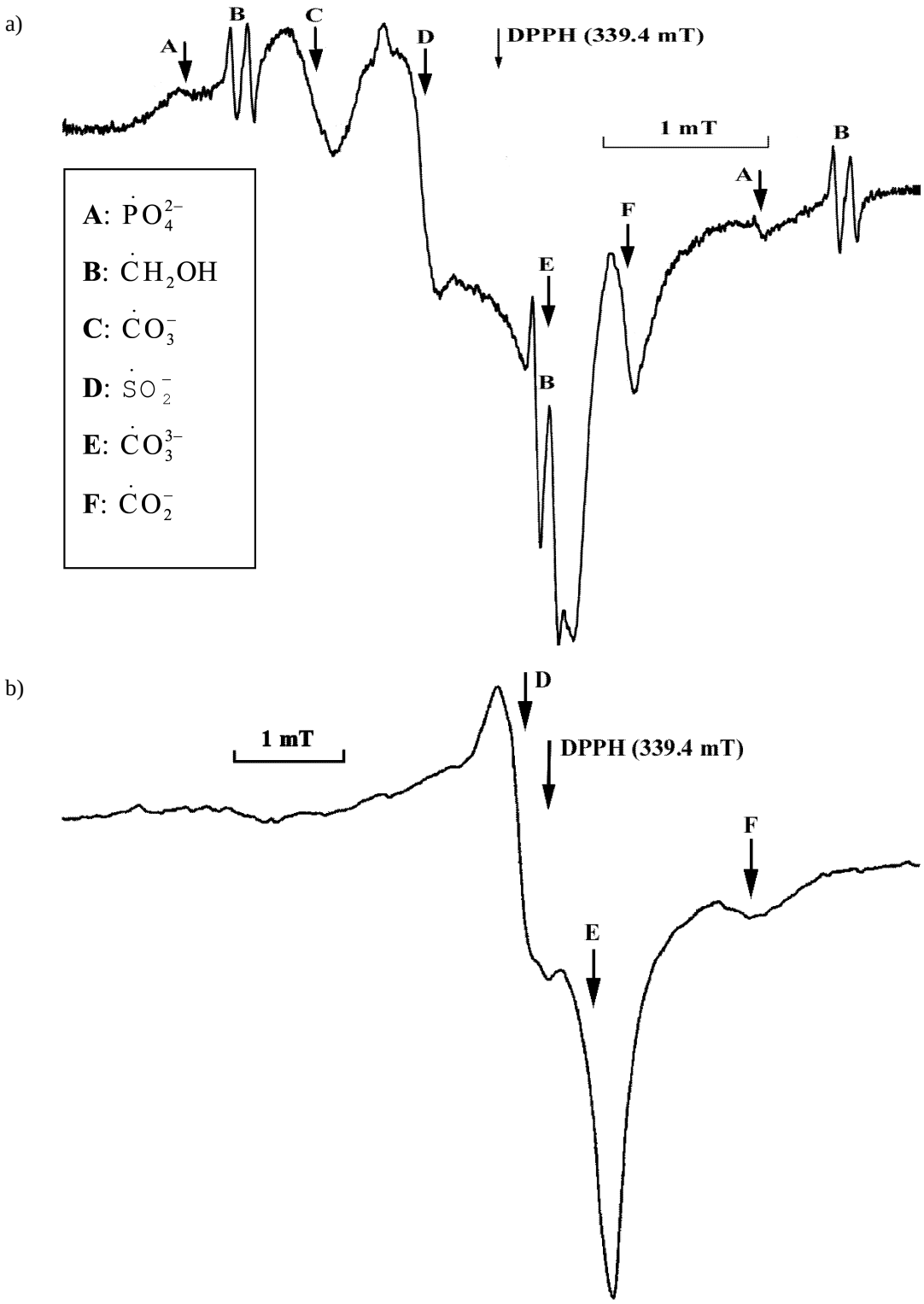

Fig. 2. a) EPR spectrum of rhyolite from the Yellow Stone of Nevşehir at ambient temperature, and b) at 113 K.

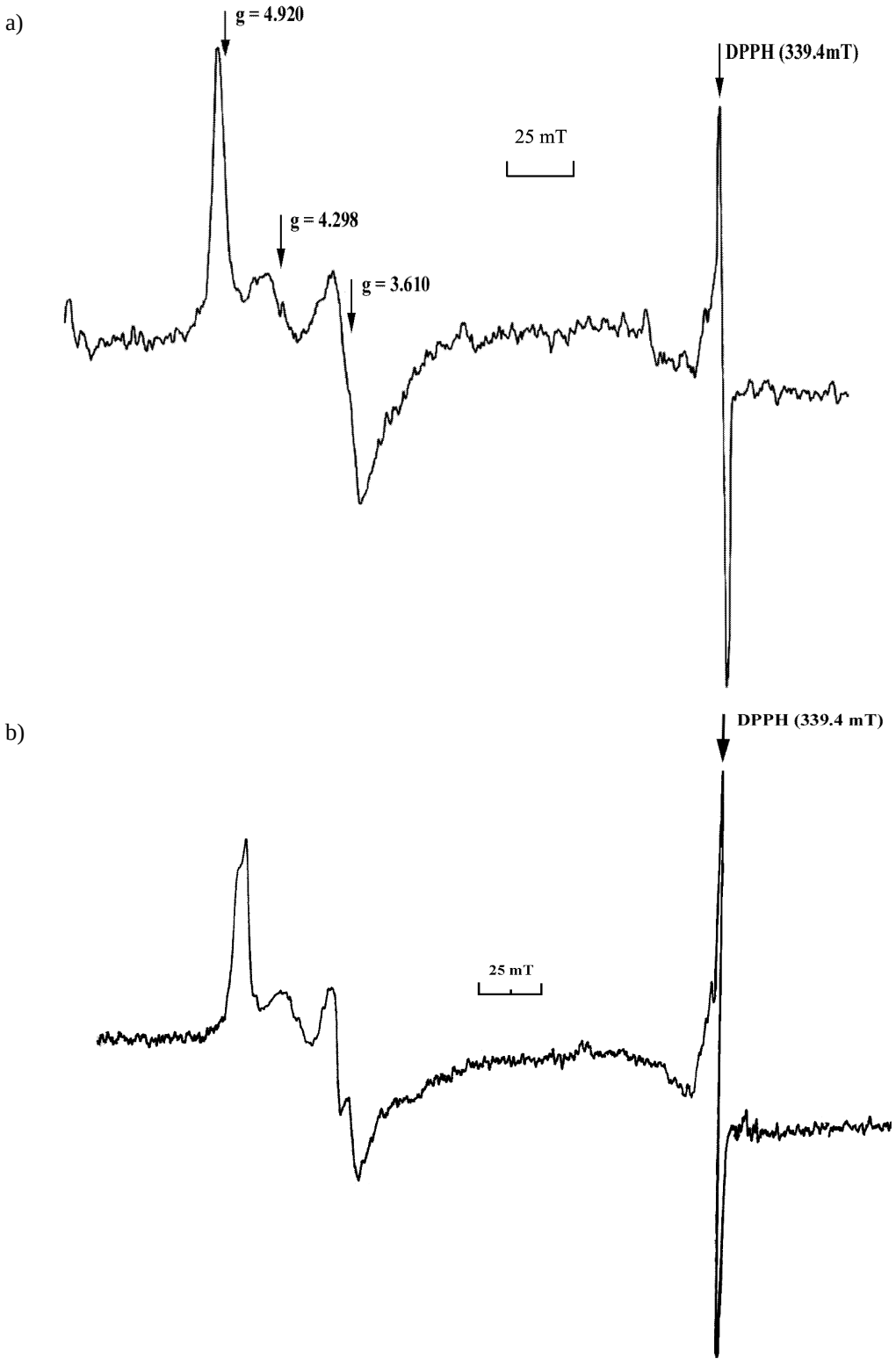

Fig. 3. a) Low field part of the EPR spectrum of rhyolite from the “Yellow Stone” at ambient temperature, and b) at 113 K.

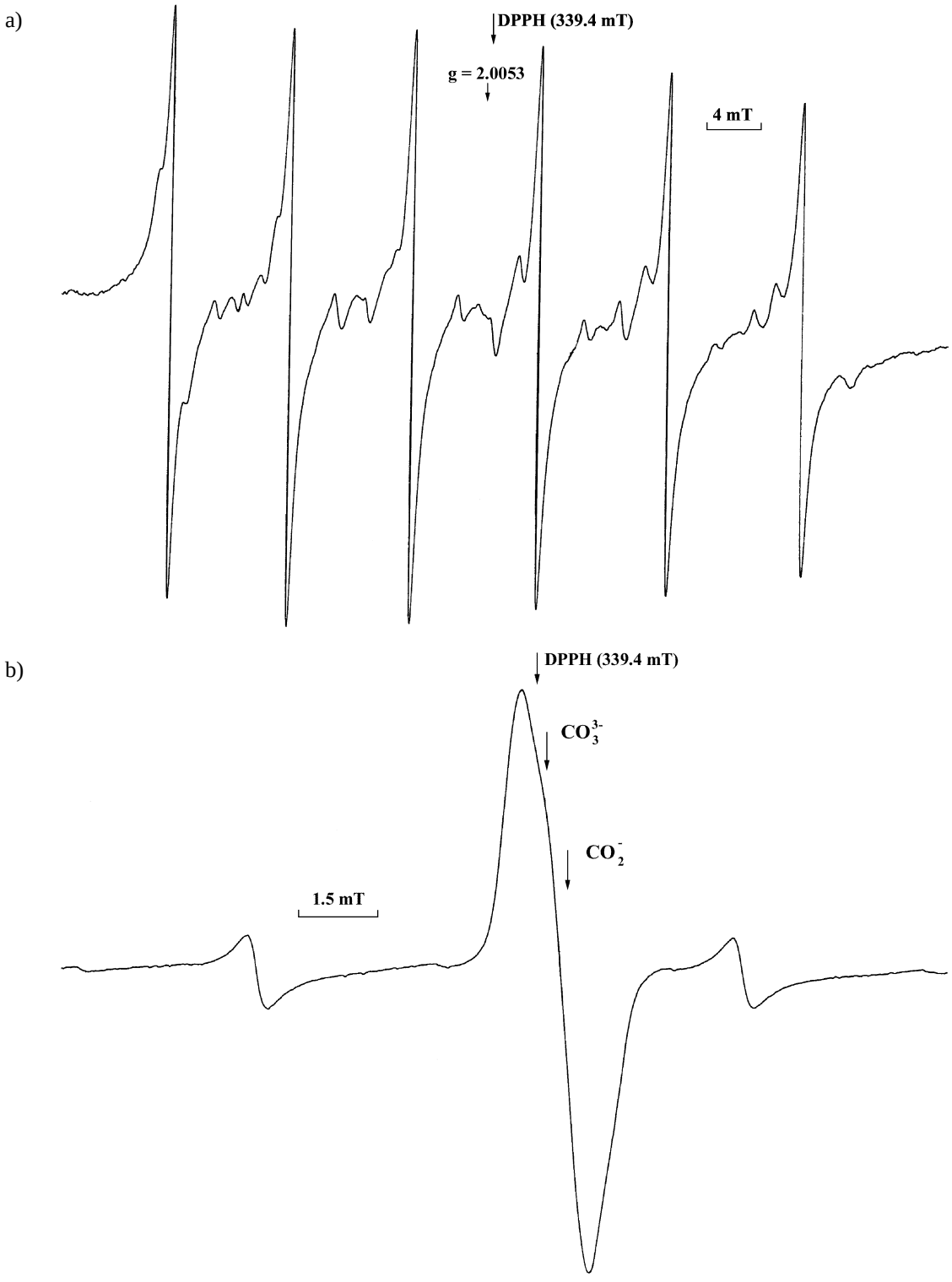

Fig. 4. a) EPR spectrum of trona from the “Ankara Trona Mine” at ambient temperature before the γ-irradiation, and b) after the γ-irradiation.

The low field part of the spectrum at ambient temperature is shown in Fig. 3(a) and can be explained with the existence of Fe^{3+}. For the central line $g = 4.298$ the signals on both sides correspond to $g = 4.29 \mp \frac{E}{D}$ lines with $g = 4.92$ and $g = 3.61$, where E and D are the usual zero field splitting parameters [1]. The low field part of the spectrum seems to be splitted into two at 113 K as in Fig. 3(b). This splitting is presumably due to the different environments of Fe^{3+} in the rhyolite, and is better observed at 113 K where some of the motions cease.

The ambient temperature EPR spectrum of trona, before γ-irradiation, is shown in Fig. 4(a). The spectrum consists of six EPR lines of Mn^{2+} with the g value 2.0053 and the hyperfine constant $a \cong 9.2$ mT. After γ-irradiation, the spectrum turns out to be as in Fig. 4(b). Between the third and the fourth lines of the Mn^{2+} spectrum there appears a signal as a consequence of γ-irradiation. When this signal is observed in appropriate field scanning range, it seems that it consists of two lines which we interpreted as the EPR lines of $\dot{C}O_3^{3-}$ and $\dot{C}O_2^-$ radicals. The g values of the radicals are 2.0024 and 2.0007, respectively. These are due to the free rotating $\dot{C}O_3^{3-}$ and $\dot{C}O_2^-$. Pure trona, $Na_3H(CO_3)_2$, could be obtained from the grey parts of its bulk matter. In this case, the EPR lines of Mn^{2+} do not appear, leaving only the spectrum that corresponds to the radicals stated above. The EPR spectrum of γ-irradiated trona at 113 K exhibits somewhat line broadening, but it is not that much appreciable to add the spectral features at the ambient temperature. That means that the free rotations of the $\dot{C}O_3^{3-}$ and $\dot{C}O_2^-$ radicals are still effective at 113 K.

4. Conclusions

The EPR results presented in this study indicate the existence of the radicals $\dot{P}O_4^{2-}$, $\dot{C}H_2OH$, $\dot{C}O_3^-$, $\dot{S}O_2^-$, $\dot{C}O_3^{3-}$, and $\dot{C}O_2^-$ in the rhyolite of the Yellow Stone of Nevşehir. Therefore, one can expect a similar inclusion from the similar productions of the old active mountains. The EPR parameters of the radicals are very similar to the ones obtained by other authors. The γ-irradiation induced radicals in trona are $\dot{C}O_3^{3-}$ and $\dot{C}O_2^-$, and seem to exhibit similar features as the rhyolite, but they seem to rotate freely, and the Mn^{2+} and Fe^{3+} ions are ubiquitous in the earth crust.

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