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Radiation effects on TL and EPR of sodalite and application to dosimetry

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Abstract. Sodalite, $Na_8Al_6Si_6O_{24}Cl_2$, a natural silicate mineral, has been investigated concerning its thermoluminescence (TL) and electron paramagnetic resonance (EPR) properties. Samples, both natural and heat treated at 500°C for 30min, present an EPR signal at g=2.01132. The irradiation induces two signals at g=2.0008 and a group of 11 lines due to an O^- ion in an intermediate position with respect to two adjacent Al nuclei, that are superimposed on the signal at g=2.0008. An annealing at 500 °C/30min produces a broad signal around g~2.0, probably due to Fe^{3+} magnetic dipole interactions. The samples were annealed at 500 °C/30min and then irradiated with gamma-ray doses varying from 1 Gy to 20 kGy. All the samples have shown TL peaks at 110, 230 and 270 °C. Similar results were obtained for natural samples. The accumulated dose (AD) was determined to be AD~2.5 kGy and the annual dose of (0.595±0.001) mGy/year was obtained from the concentration of U, Th, and K_2O in the sample. Therefore, the age obtained for natural sodalite was $(4.2\pm0.2)10^6$ years.

1. Introduction

A natural sodalite sample from Minas Gerais, Brazil, has been investigated concerning its electronic paramagnetic resonance (EPR) and thermoluminescence (TL) properties and also the effects of the ionizing radiation and annealing at high temperatures.

Sodalite, of chemical formula $Na_8Al_6Si_6O_{24}Cl_2$, is a mineral of the aluminum silicate family (tectosilicates). This mineral has been investigated by many authors due to its color and interesting photochromic and cathodochromic properties [1-3].

The crystal structure of sodalite consists of an ordered framework of AlO_4 and SiO_4 tetrahedra, in such a way that cubo-octahedral cages are formed, where each atom of Al or Si is located at the center of a tetrahedrical cage of oxygens. In each cage there is a Cl ion tetrahedrally coordinated by Na ions, forming a body-centered cubic structure with lattice parameter between 0.0887 and 0.892 nm [4].

Hodgson et al. [5] studied an artificial sodalite with impurities of S using the EPR technique. Its photochromic property was activated by heating the sample in a hydrogen atmosphere and the hyperfine interaction was observed with 13 lines in the spectrum. The lines are separated by 30.6 G and centered at g=2.002 when the sample is exposed to UV irradiation. Under these conditions the sample acquires a magenta color and an absorption band at 530 nm is then observed. The incidence of

visible light produces a loss of the color and the disappearance of the 13 lines of the EPR spectrum and of the optical absorption bands. Hodgson and collaborators [5] proposed that the color center is an electron trapped in a Cl^- vacancy interacting with the nuclear spins (I=3/2) of the four Na ions.

Van den Brom et al. [6] investigated the behavior of electric dipoles and proposed a model where the dipole is associated with the alkali metal ion (in general Na^+) that provides the necessary charge compensation resulting from the substitution of Al^{3+} for Si^{4+} in the SiO_4 tetrahedron. The arising Al-Na complex or $[AlO_4/M^+](M^+=Na^+)$ center is affected by the X-ray irradiation which liberates an alkali ion leaving an aluminum center $[AlO_4/h]$, where h is a hole.

Hassib et al. [7], investigated natural sodalites and verified that samples heat treated at 900 °C in air and X-ray irradiated, show a pink color that is bleached when illuminated with visible light. After some cycles of coloration and bleaching processes the sample presents the characteristic blue color of the natural samples and a growth of the isotropic EPR line around g=2.0112 and ΔH=10 G is observed. The collapse of the F centers at room temperature into colloidal aggregates of Na generates the blue color of the sodalite. The isotropic EPR line (g=2.0112) linked to the blue color disappears with the disappearance of the color. Another EPR signal occurring at g=1.9978 was also observed by Annersten and Hassib [8] on an irradiated blue sodalite single crystal. The spectrum was anisotropic with maximum resolution of a hyperfine structure along the orientation [1 1 0] parallel to the magnetic field. The 11 observed hyperfine lines support the assignment of the O^- ion to a position intermediate with respect to two Al nuclei (I=5/2), one in a lattice site and one replacing a Si^{4+} of the crystal structure breaking the usual alternation of aluminum and silicon that occurs in the perfect lattice.

Hassib [9] analyzed the allowed (Δm=0) and prohibited (Δm=±1) hyperfine Mn^{2+} transitions in the sodalite. The six hyperfine lines of the central transition (m=|+1/2> $\rightarrow$ |-1/2>) were observed. The obtained g-value and hyperfine structure constant were g=2.033 and |A|=83±1 G respectively. EPR spectral investigations of natural sodalite containing Fe^{3+} and Fe^{2+} ions in tetrahedral coordination were performed by Ravikumar et al. [10]. The signal near g=2 was attributed to Fe^{3+} in Al^{3+} sites in the sodalite crystal lattice.

No paper was found in the literature concerning thermoluminescent studies on natural sodalite crystal.

2. Experimental procedure

The natural sample of blue sodalite investigated in our work is from Bahia, Brazil.

A portion of the sample was crushed and sieved and the grains between 0.180 and 0.080 mm in diameter were selected for TL and EPR measurements and the grains smaller than 0.080 mm were used for fluorescence and X-ray diffraction analysis.

The X-ray diffraction measurements have been carried out at the Laboratory of X-Ray Diffraction of the Institute of Physics, University of São Paulo, while the X-Ray Fluorescence analysis at the Institute of Geosciences at the University of São Paulo.

The irradiations were carried out at the center of technology of radiations of the Institute of Nuclear an Energy Research using a ^{60}Co γ-source with a dose rate of 0.37 kGy/h and a Gammacell with a dose rate of 5.50 kGy/h at room temperature and under conditions of electronic equilibrium.

The TL measurements were carried out in a Daybreak TL reader, Model 1100, equipped with a bialkali photomultiplier EMI 9235QA for light detection with filters Corning 7-59 and Schott BG-39 used in front of the PMT. The used heating rate was 4°C/s in nitrogen atmosphere.

EPR measurements were performed in a Bruker EMX spectrometer with a rectangular cavity (ST ER4102) using a microwave frequency of 9.75 GHz (X–band), microwave power of 20 mW and a modulation field of 100 kHz.

3. Results and discussion

Table 1 shows the composition in weight % of the oxide components of the sodalite and the concentration of some impurities in ppm.

Table 1. Composition of natural sodalite using X-ray fluorescence analysis.

Compound	SiO_2	Al_2O_3	Na_2O	CaO	Fe_2O_3	K_2O	MnO	MgO	Ti_2O	P_2O_5
(w.%)	38.93	32.27	25.68	0.21	0.08	0.07	0.035	0.02	0.014	0.01
Elements	U	Th								
(ppm)	0.985	0.54								

The EPR spectra of natural and additionally irradiated with several γ-doses samples are shown in Fig. 1. In Fig. 2 the samples were submitted to a thermal treatment at 500 °C for 30 minutes prior to the irradiation. An intense signal at g=2.01132 (3468 G) was observed in both cases. The irradiation induces two signals at g=2.0008 and a group of 11 lines completely superimposed on the signal at g=2.0008. These lines are associated with an O^- ion in an intermediate position with respect to two adjacent Al nuclei as discussed in the introduction. The behavior of the EPR signal at g=2.01132 for five different γ-doses is presented in Fig. 2(a). In Fig. 2(b) a sublinearly growth starting from 1 kGy of dose is observed and for doses larger than approximately 5 kGy the EPR intensity becomes linear with the dose.

For high irradiation doses, above 10 kGy, 11 hyperfine lines are now observed, due to the fact that high irradiation is able to form a large concentration of O^- centers. On the other hand, in most of the silicate minerals the line at g=2.01132 is due to E'_1 centers, which are oxygen vacancies that have captured electrons.

The fact that we did not observe the 11 hyperfine lines below 5 kGy of irradiation probably means that, in the present case only small concentrations of O^- centers are created.

Fig. 3 presents the changes in the EPR spectra of samples thermally treated for a period of 30 min at temperatures from 200 to 900 °C respectively before being γ-irradiated with a dose of 2 kGy. The signal at g=2.01132 decreases with temperature up to 600 °C, but for T>600 °C the intensity of the signal increases quickly. On the other hand as the annealing temperature increases, the signal around g=2 becomes broad. Furthermore for the 900 °C anneal, the intensity of the signal at g~2 grows in an intense way. This may indicate the oxidation of iron from Fe^{2+} to Fe^{3+} after heat treatment.
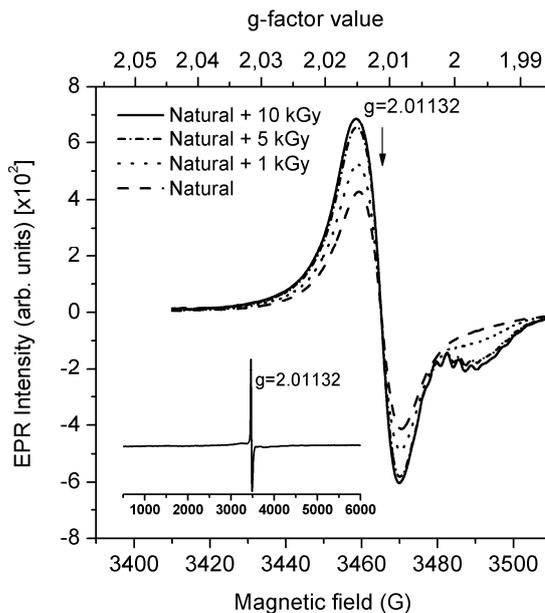

Figure 1. Behavior of the lines at g=2.01132 and g=2.0008 in the EPR spectra of natural and additionally irradiated samples.
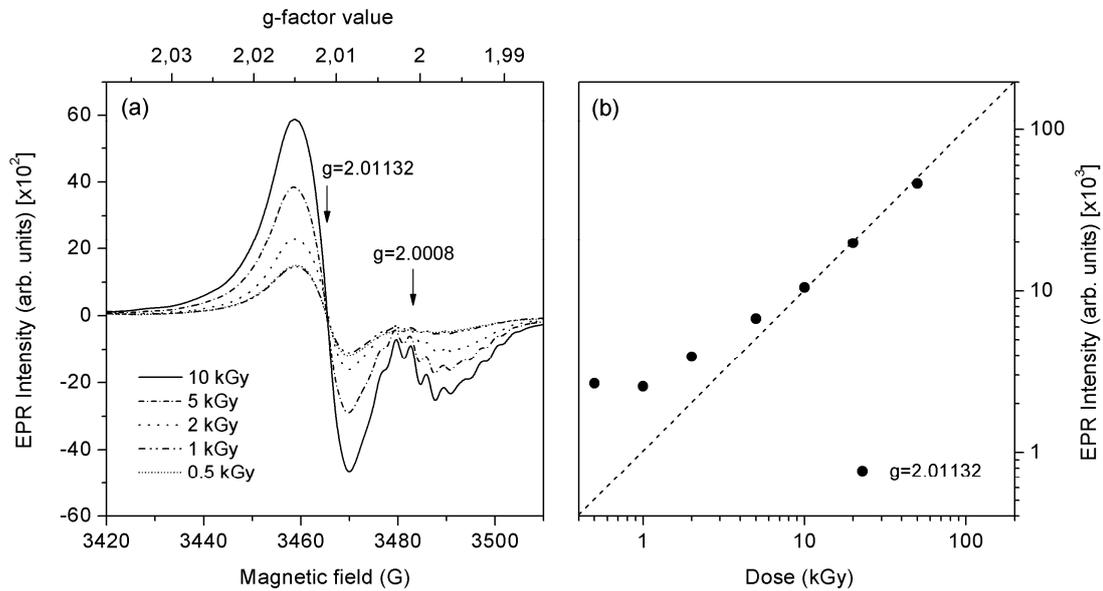
Figure 2. (a) EPR spectra of samples annealed at 500 °C/30min and then irradiated with five gamma doses. (b) EPR intensity vs. dose.

Isochronal annealing results for natural samples and isochronal annealing results for natural samples receiving a prior heat treatment at 500 °C for 30 min being subsequently irradiated with a γ-ray dose of 2 kGy are shown in Fig. 4. The respective thermal stability of the EPR signal at g=2.01132 observed in both types of samples was investigated during these isochronal annealing at temperatures varying from 50 to 390 °C for 15 min periods. The EPR signal intensity at g=2.01132 decrease substantially above 290 °C, for both types of samples indicating that for the samples irradiated at the laboratory the paramagnetic centers are stable at room temperature. Fig. 4 also shows the decay during annealing of the g=2.0008 EPR signal for the sample, in this case the signal decays substantially above 70 °C.
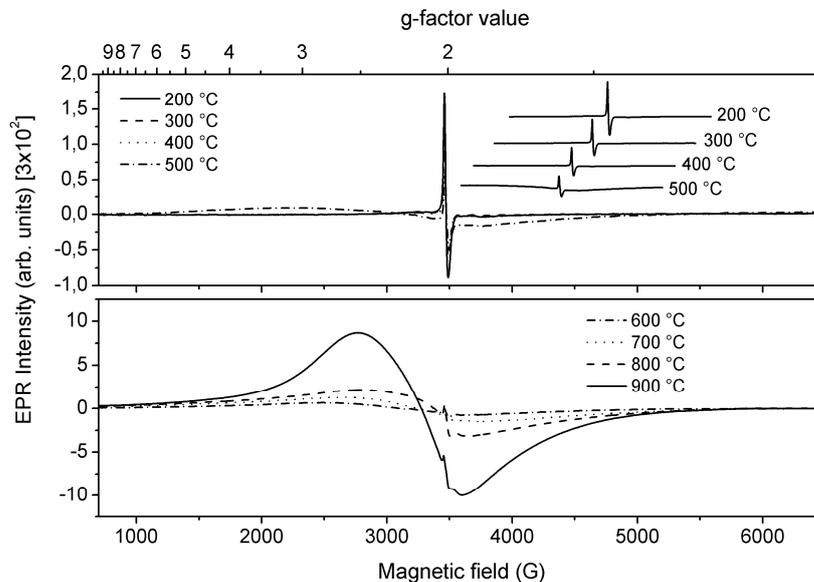

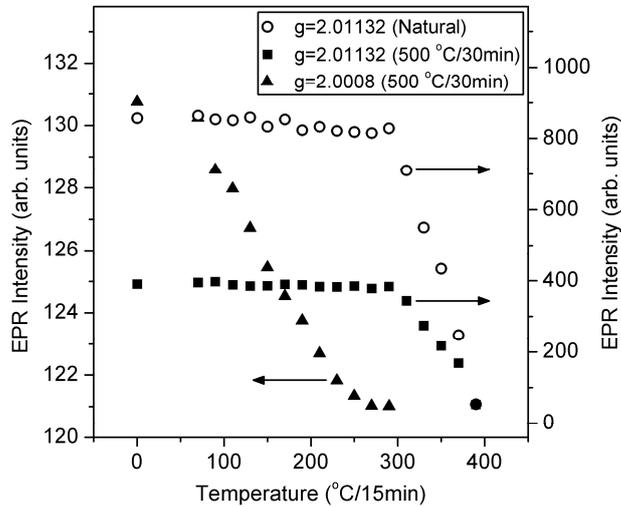**Figure 3.** EPR spectra of natural sodalite annealed from 200 up to 900 °C before the γ-irradiation.

Figure 4. Behavior of the lines at g=2.01132 and g=2.0008 with isochronal annealing for the indicated samples indicated.

Natural sodalite samples were each subjected to thermal treatment at temperatures varying from 300 to 700 °C/30min (see Fig. 5) respectively before being γ-irradiated with a dose of 2 kGy. The inset in Fig. 5 having an enlarged ordinate scale shows the TL glow curves for as-received natural sample as well as those of the samples pre-heated to 300 and 400 °C respectively. The main figure shows the results for all samples and together with the inset illustrates the great increase in the TL intensity with heat treatment. The TL peaks at 365 and 445 °C observed in the as-received natural samples almost disappear with the rapid growth of the peaks at 110, 230 and 270 °C with heat treatment and irradiation.

In Fig. 6(a) the glow curves of as-received natural samples irradiated to additional γ-ray doses varying from 1 Gy to 20 kGy are shown. Fig. 6(b) present the sublinear growth of the 110 °C peak from 100 Gy to 1 kGy. Beyond 1 kGy the peak saturates. The 365 and 445 °C peaks grow much more slowly than the 110 °C peak. However the 365 °C peak can be used for radiation dosimetry and geological dating as will be discussed below. A very weak TL peak around 200 °C becomes noticeable for high doses.
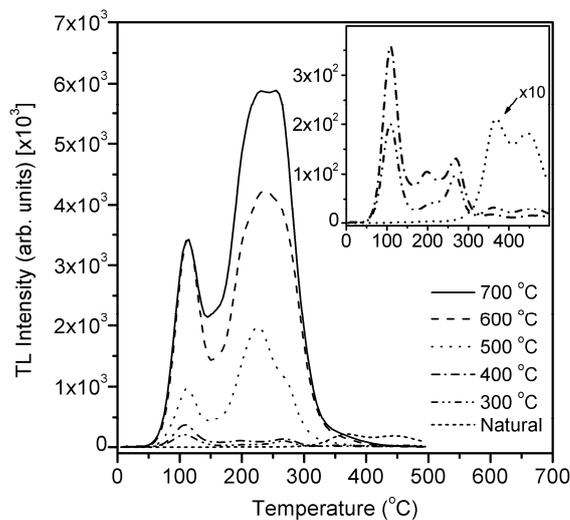

Figure 5. TL glow curves of natural sodalite samples subjected to preheating to the temperature indicated and then gamma irradiated with a dose of 2 kGy. The glow curve of as-received sample is shown. The inset provides results in more detail for the as-received sample and those for the lower temperature preheating.
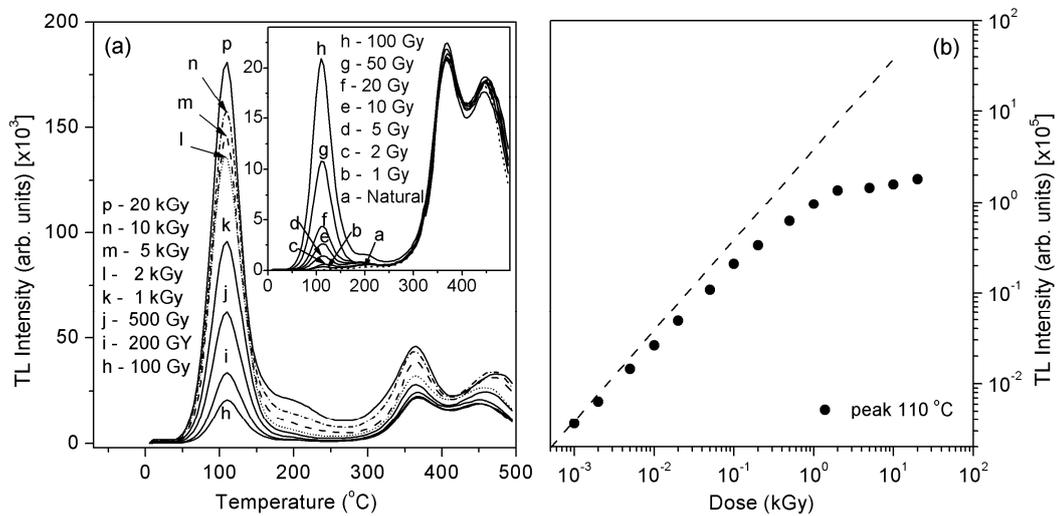
Figure 6. (a) Glow curves of natural sodalite samples plus additional γ-doses up to 20 kGy. (b) TL response curve of 110 °C peak as function of dose.

Fig. 7(a) shows the glow curves of samples previously annealed at 500 °C/30min and irradiated to several doses. Fig. 7(b) presents the TL response curve as a function of dose. It is interesting to notice that the 500 °C annealing brought as a consequence the increase of the 110 °C TL peak by a factor of more than 4 times and furthermore the weak peaks observed in the glow curves shown in Fig. 6(a), now appear very strong, presenting a peak intensity growth of a factor close to 600. It is known that in silicate crystals pre-irradiation annealing at high temperatures (500 - 1000 °C) sensitizes the TL peaks [11, 12]. However in the present case, the peaks around 230-280 °C that are almost invisible in Fig. 6(a), become greatly enhanced as a result of the 500 °C pre-annealing. This fact has not been yet explained. Fig. 7(b) shows that both 110 and 230 °C peaks grow linearly with dose up to about 1 kGy, saturating subsequently.
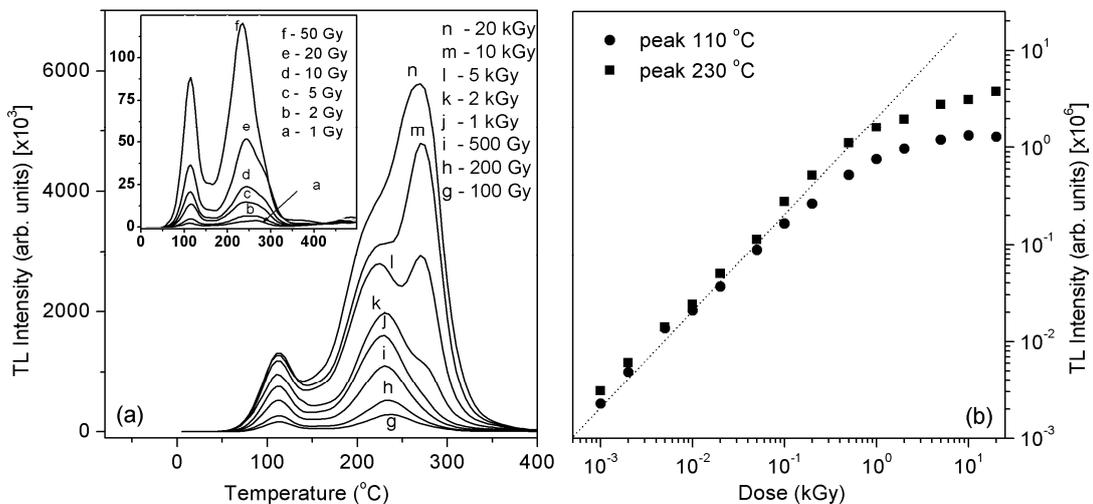

Figure 7 (a) TL glow curves of the natural samples pre-annealed at 500 °C for 30 min and then irradiated at different γ-ray doses. (b) The intensities of the TL peaks at 110 and 230 °C as a function of γ-ray dose.

Fig. 8 shows the isochronal decay of the peaks at 230 (from Fig. 7a) and 365 °C (from Fig. 6a). Both peaks are stable at room temperature allowing us to use the natural sodalite to calculate geological ages as well as the 500 °C/30min thermal treated sample for dosimetry.

Fig. 9(a) shows the obtained activation energies (E) using the E-Tstop method [13, 14]. With these results and applying the equations proposed by Kitis et al. [15] we obtain the deconvolution of the TL glow curve of natural sodalite thermally pre-heated at 500 °C/30min and then γ-irradiated with a dose of 2 kGy. Fig. 9(b) shows the five TL peaks separated using first- and second- order kinetics in the region between 50 and 350 °C. The positions, frequency factors (s), activation energies (E) and lifetimes (τ) are presented in Table 2.
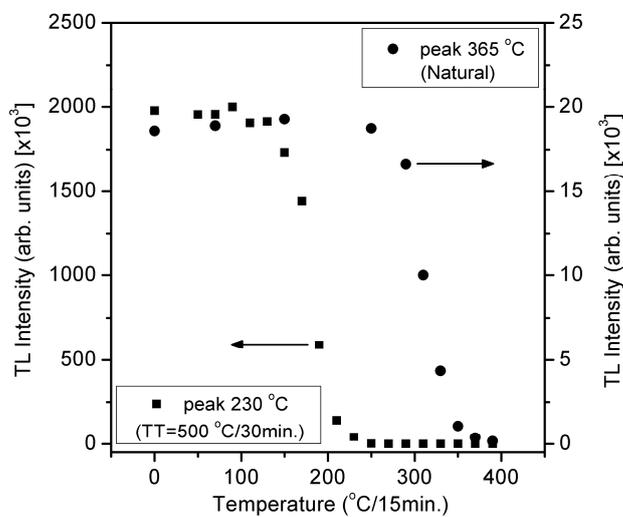

Figure 8. Effect of the isochronal annealing on the TL intensity of the sodalite samples.
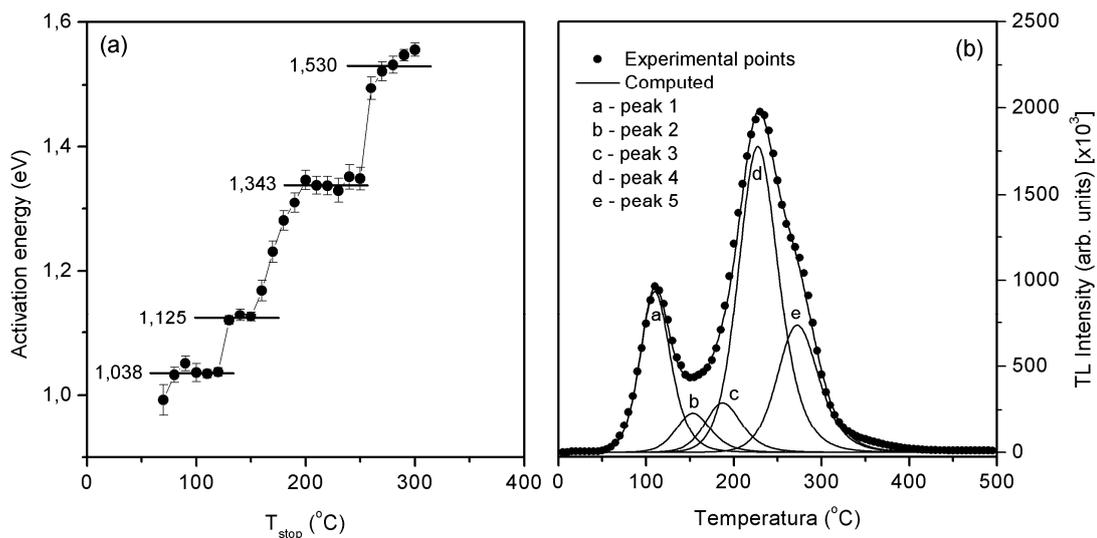

Figure 9. (a) Activation energy vs. T_{stop} obtained by the E-T_{stop} method. (b) TL glow curve from natural sodalite pre-annealed at 500 °C/30min and subsequently receiving a γ-ray dose of 2 kGy. A good fit between the experimental glow curve (circles) and the simulated glow curve (full line) can be achieved by assuming the presence of five peaks.

Table 2. Energy (E), frequency factor (*s*) and lifetime (τ) of TL traps of sodalite.

TL peak (°C)	E (eV)	$s(s^{-1})$	τ(years) (at 15 °C)
110	1.038±0.007	$(1.478\pm0.011)10^3$	$(3.091+0.007)10^{-3}$
153	1.125±0.005	$(5.805\pm0.029)10^{12}$	(0.262 ± 0.002)
*187	1.250	1.558×10^{13}	17.352
227	1.343±0.008	$(8.509\pm0.053)10^{12}$	$(1.162\pm0.010)10^3$
272	1.530±0.024	$(3.337\pm0.052)10^{13}$	$(5.525\pm0.123)10^5$

* In the E-T_{stop} method the error could not be evaluated.

4. Conclusions

The EPR spectra show the g=2.01132 and g=2.0008 lines and 11 hyperfine lines due to an O$^-$ ion in an intermediate position with respect to two Al nuclei (I=5/2), superimposed on the g=2.0008 signal.

The TL glow curve of natural samples shows high temperature peaks at 365 and 445 °C. Samples heat treated at 500 °C/30min and irradiated with different gamma doses present peaks at 110, 230, 270 and very weak TL peaks at 365 and 445 °C. The glow curve deconvolution shows that in fact, in the region varying from 50 to 350 °C, five overlapping TL peaks are observed.

The TL peak at 365 °C and the EPR signal at g=2.01132 probably are due to a same defect center, and they yield ages of $\sim(4.2\pm0.2)10^6$ year for natural sodalite.

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