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Study of paramagnetic and luminescence centers of microcline feldspar

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Abstract

Microcline feldspar crystal has been analyzed in order to determine the centers suitable for use in ESR and luminescence dating. ESR measurements at RT showed the Fe^{3+} line, and at 77 K the Si–O^-..X signal with $g = 2.0052$, 2.0098 and 2.0128. TL glow peak at 157 and 300 °C in UV interval were observed and in the VIS range we noted peaks at 150, 280 and 340 °C. TL growth curve of the 340 °C peak could be fitted by a saturating exponential equation and can be used in TL dating. Emission curves showed band widths 1.95 ± 0.09, 2.73 ± 0.08 and 4.94 ± 0.50 eV. Transitions from $^4T_1 \rightarrow {}^6A_1$ of Fe^{3+} can be associated with the 1.95 eV band and the transition from $^4A_1$ $^4E(G) \rightarrow {}^6A_1(S)$ with 2.73 eV band.

Keywords: ESR; Thermoluminescence; Emission spectrum; Feldspar; Microcline

1. Introduction

Feldspar crystal is in the aluminum silicate series, which may be classified chemically as members of the ternary system $NaAlSi_3O_8$ (albite)–$KAlSi_3O_8$ (orthoclase)–$CaAl_2Si_2O_8$ (anorthite). Therefore, the general composition of feldspar can be expressed by the formula MT4O8, in which T sites are filled by Si, Al and eventually by Fe^{3+}; the M sites are occupied by alkaline metals (K^+ and Na^+) or alkaline-earth metals (in general, Ca^{2+}, Sr^{2+} and Ba^{2+}). They compose 60% of the Earth's crust and can be found in igneous rocks. Although the feldspars are susceptible to alteration and weathering, they are second in abundance to quartz among the arenaceous sediments.

Brazil has more than 50×10^6 ton of feldspar reserves, and granitic pegmatite rocks are the main production source, located in the southern and northeastern parts of the country. Therefore, it will be very interesting if the feldspar can be used routinely in ESR and TL dating methods.

Many efforts have been made to identify and analyze the feldspar centers. Speit and Lehmann (1982) investigated EPR spectra of 15 feldspar samples with widely different compositions and showed Al–O^-–Al, O^-…Al, Si–O^-…X (X is a divalent metal ion, Mg^{2+} or Be^{2+}) and Pb–O^-…X (X is Pb^{2+} and Mg^{2+}) hole centers, detected after X-ray irradiation, and one electron center, Ti^{3+}.

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TL of feldspars has also been studied by many authors (Visocekas, 2000; Hütt et al., 1999; Correcher and García-Guinea, 2001). Kirsh et al. (1987) reported a very complex monochromatic TL glow curve for albite ($NaAlSi_3O_8$) exhibiting eight TL peaks and for microcline ($KAlSi_3O_8$) five. They compared ESR measurements with TL emission spectra and discussed several possibilities to explain the emissions. They associated emissions at 450–480 and at 500–560 nm with radiative recombination between thermally released electrons with Al–O^-–Al and Al–O^- … M^{2+} (M = Zn, Mg, Mn), respectively. Finally, the emissions at 580–660 nm were explained as relaxation of Eu^{3+} ions excited by the blue photons.

Mittani et al. (1999) investigated ESR and TL results after various thermal treatments and γ-ray irradiation experiments on K-feldspar (orthoclase). They suggested a model to explain the emission of the 310 °C TL peak as follows: during irradiation the electron is released from an Al–O^{2-}–Al center, and is trapped in Fe^{3+} ion and Fe^{2+} is formed; subsequently during the reading of the TL the electron is thermally released from Fe^{2+} and recombines with the Al–O^-–Al center emitting TL.

In OSL dating the infrared stimulation (800–900 nm) can be used for most of the feldspar crystals and emissions can occur in a wider wavelength range spanning 250–650 nm. Hütt et al. (1988) proposed a model to explain this emission. They suggested a thermal assistance mechanism, in which photons of the infrared raise electrons from the ground state to the excited state. Then some of them rise thermally into the conduction band and OSL is emitted by recombination of the electron with a hole trapped in a luminescence center.

In the present work, results of measurements of ESR, TL, OSL and emission spectra of microcline feldspar will be presented. Annealing and irradiations experiments were performed in order to verify correlations between the ESR signals and the luminescence centers. TL, OSL and ESR growth curves were analyzed in order to identify the centers suitable for use in dating method.

2. Experimental procedure

The specimen investigated in this work is a microcline with few albite trace contents, verified by X-ray diffraction. The sample was collected from the natural reserve located in Paraná state, Brazil. Impurity contents were determined by neutron activation analysis (NAA). About 100 mg of two portions of the sample and two standards, Buffalo River Sediment (NIST-SRM-2704) and Coal Fly Ash (ICHTJ-CTA-FFA-1), were irradiated in the swimming pool research reactor, IEA-R1 m, at a thermal neutron flux about 5×10^{12} ncm^{-2} s^{-1} for 8 h. γ-radiation spectra were obtained after 7 and 15 days decay time using a Ge-hyperpure detector, model GX 2020, Canberra, FWHM 1.9 keV gamma peak of ^{60}Co and an 8192 channel S-100

Table 1
Chemical composition of microcline feldspar sample obtained by NAA and X-ray fluorescence technique

Element	Sample 1—(NAA) (ng/g)	Sample 2—(NAA) (ng/g)	Sample 3—(XRF) (ng/g)
Sm	41.8 ± 4.2	52.9 ± 4.2	
Lu	14.5 ± 5.0	32.0 ± 5.7	
Yb	196.3 ± 43.6	113.6 ± 38.2	
La	279.6 ± 56.5	232.1 ± 47.1	
Sb	846.2 ± 35.8	931.9 ± 35.7	
Ce	327.4 ± 155.8		
Cr		566.2 ± 269.5	
Sc	52.4 ± 3.6	65.0 ± 3.7	
Na	$(37.0 \pm 0.1) \times 10^6$	$(48.8 \pm 0.2) \times 10^6$	$(16.0 \pm 0.5) \times 10^6$
Ba	$(230.7 \pm 23.2) \times 10^3$	$(316.8 \pm 27.3) \times 10^3$	
Cs	$(59.5 \pm 1.6) \times 10^3$	$(69.3 \pm 1.9) \times 10^3$	
Rb	$(2.03 \pm 0.06) \times 10^6$	$(1.94 \pm 0.06) \times 10^6$	$(3.6 \pm 0.1) \times 10^6$
Fe	$(181.7 \pm 16.0) \times 10^3$	$(123.1 \pm 16.4) \times 10^3$	$(528 \pm 53) \times 10^3$
K	$(19.5 \pm 0.8) \times 10^3$	$(30.6 \pm 1.1) \times 10^3$	$(159 \pm 5) \times 10^6$
O			$(380 \pm 11.4) \times 10^6$
S			$(139 \pm 14) \times 10^3$
Al			$(87 \pm 3) \times 10^6$
Ca			$(370 \pm 37) \times 10^3$
P			$(338 \pm 34) \times 10^3$
Sr			$(130 \pm 13) \times 10^3$
Pb			$(102 \pm 10) \times 10^3$
Ga			$(82 \pm 8) \times 10^3$
Si			$(352 \pm 11) \times 10^6$

Canberra MCA (Munita et al., 2001; Yee et al., 2003). X-ray fluorescence (XRF) analysis (Jenkins, 2003) was also done in one portion of the sample, using a Rigaku spectrometer, model RIX 3000; the measured interval was from 0.1 to 10 Å and the standard material used was Feldspar 70a (NBS). All the results are summarized in Table 1. The results show the inhomogeneity of the sample and the accuracy of the techniques. Rare earth elements could be detected by NAA and these elements can replace Al and Ca in crystalline net; some transition metals like Fe were also found, which replaces the Si or Al in T sites. The chemical components results obtained are similar to those described by Correcher et al. (1999). The mean molecular compositions of orthoclase, albite and anorthite in terms of percentage were calculated using chemical analysis results and we obtained $Or_{85.2}$-$Ab_{14.6}An_{0.2}$.

All the ESR spectra were taken at RT and 77 K, below saturation, by means of the homodyne X-band VARIAN E-4 spectrometer with a 100 kHz magnetic field modulation, a microwave power of 20 mW and a TE_{011} mode cavity. The Modulation amplitude used was 2.5 G peak-to-peak and the scan speed was 4000 G in 480 s for RT measurements and for temperature at 77 K it was 2.0 G and 100 G in 60 s, respectively. TL glow curves were measured in an oxygen-free nitrogen atmosphere using a Daybreak Nuclear and Medical Systems Inc., Model 1100-series and the heating rate was 10 °C/s. Optical filters used for TL detection were Schott BG-39 and Kopp 7–59, and for OSL, Hoya U-340.

For ESR, TL, OSL and emission spectra measurements, the specimen was carefully ground with a mortar and pestle, and the fraction between 88 and 180 μm was selected. The selected grains were treated with 10% HCl for 10 min, in order to reduce spurious TL and to remove the surface layer grain. Then they were washed extensively with water and subsequently with acetone. All the γ-ray irradiation was performed at RT with a ^{60}CO source (0.3091 kGy/h). Emission spectra were measured with a Xe-lamp (300 W) and a Jarrell Alsh monochromator; the excitation was made at 880 nm with an RG 780 filter; signal was detected with a photomultiplier S-20, Spex monochromator and a lock-in amplifier; the sample was placed at 45° between excitation and emission beams (Hütt et al., 1988; Kassab et al., 2002).

3. Results and discussion

Fig. 1 shows typical ESR spectra measured at RT for natural and γ-ray -irradiated samples after annealing at 400, 500 and 600 °C for 40 min. A broad Fe^{3+} signal ($g = 2.2533$, 2.4939 and 4.0385) can be observed in Fig. 1. We observed that heat treatment at high temperatures increased their intensities. Speit and Lehmann (1982)

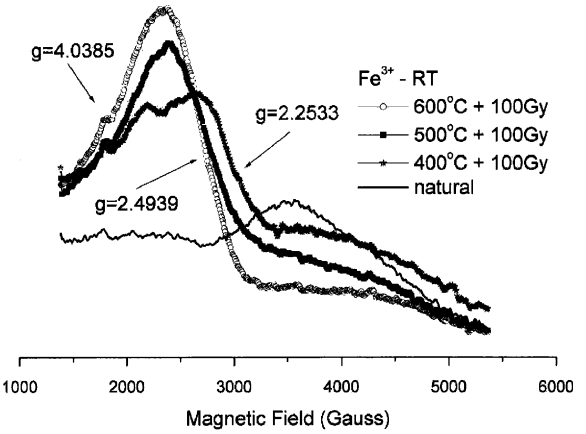

Fig. 1. ESR spectra of Fe^{3+} center in microcline feldspar sample. Natural sample (solid line); sample submitted to γ-ray irradiation (100 Gy) and previously heated at 400 °C (open cicle), 500 °C (dashed line) and 600 °C (triangle), during 10 min.

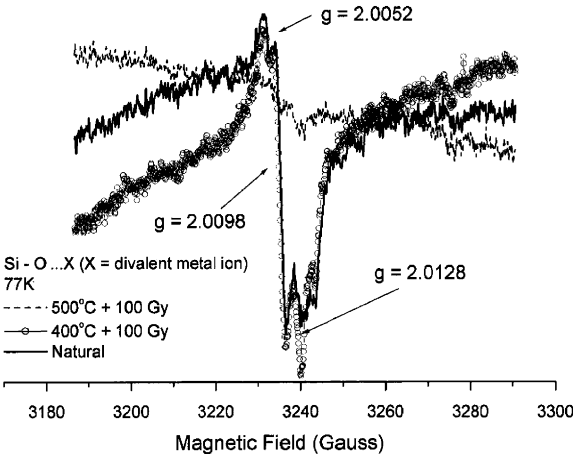

Fig. 2. ESR spectra of Si–O–…X hole center in microcline feldspar sample. Natural sample (solid line); sample submitted to γ-ray irradiation (100 Gy) and previously heated at 400 °C (open square) and 500 °C (dashed line), during 10 min.

and Ikeya (1993) cited a broad Fe^{3+} signal near $g = 2.0$ found in feldspar and they concluded that this signal is due to clusters of magnetically interacting Fe^{3+} ions. Measurement at 77 K revealed the $Si–O^{-}…X$ (X = divalent metal ion, Mg^{2+} or Be^{2+}) hole center with $g =$ 2.0052, 2.0098, and 2.0128. These values are very similar to those found by Speit and Lehmann (1982). Heat treatment at temperatures above 400 °C decreased their intensities, as is shown in Fig. 2. Among the metal elements found in the present sample (Table 1), only Fe^{2+} ion has an ionic radius between 0.065 and 0.074 nm, and was therefore able to occupy the T site (Kirsh et al., 1987). It was observed that $Si–O^{-}…X$ center intensity did not increase with increased γ-ray doses.

Fig. 3 shows the luminescence spectra obtained by exciting the sample at 880 nm. Three broad bands at 251, 455 and 640 nm (1.95±0.09, 2.73±0.08 and 4.94±0.50 eV) were revealed and they could be fitted by Gaussian equations. Some narrow bands are also noted at 316 and 563 nm, probably related to Sm^{3+} ion; this ion was also detected by NAA (Nachimuthu et al., 1997). Poolton et al. (1996) reported some luminescence spectra results for 35 samples of alkali and plagioclase feldspar minerals. They correlated the energy levels of electronic transition for d^5 electrons of the Fe^{3+} ion located in tetrahedral position with emission bands between 400 and 700 nm. In our case, the 455 nm band can be correlated to $^4A_1\ ^4E(G) \rightarrow {}^6A_1(S)$ and the 640 nm one with $^4T_1 \rightarrow {}^6A_1$. The band at 251 nm, which is not reported in previous work, still remains without explanation and may be related to Ce. All the bands increased with additional irradiation and decreased with pre-heating at 200 °C, but not in the same proportion.

OSL measurements were made by exciting the sample with an infrared diode laser at 880 nm and the optical filter for detection was the Hoya U-340 (270–377 nm). Therefore we observed part of the 250 nm band and 316 nm band. OSL growth curves are shown in Fig. 4 and we obtained linear growth up to 10^3 Gy for samples without pre-heating; for samples pre-heated at 200 °C for 5 min, a supralinear behavior is observed for doses higher than 10^2 Gy.

Fig. 5(a) shows two prominent TL peaks at 157 and 300 °C for curves obtained with the UV filter (270–377 nm). The TL growth curve of the 300 °C peak shows a linear increase up to 50 Gy and then a sublinear growth. Fig. 5(b) shows the TL glow curve obtained in the VIS region (327–483 nm). There are peaks at 150, 280 and 340 °C, approximately; the growth of the 340 °C peak could be fitted with a saturating single exponential equation. No significant anomalous fading was observed in 12 months of experiments, keeping the samples at RT.

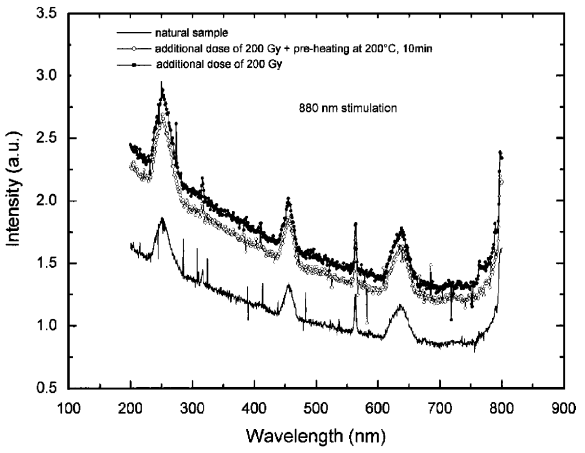

Fig. 3. Emission spectra of microcline feldspar sample. Natural sample (solid line); sample submitted to γ-ray irradiation (200 Gy) and previously heated at 200 °C, during 10 min (open circle); sample submitted to γ-ray irradiation (200 Gy) (full circle).

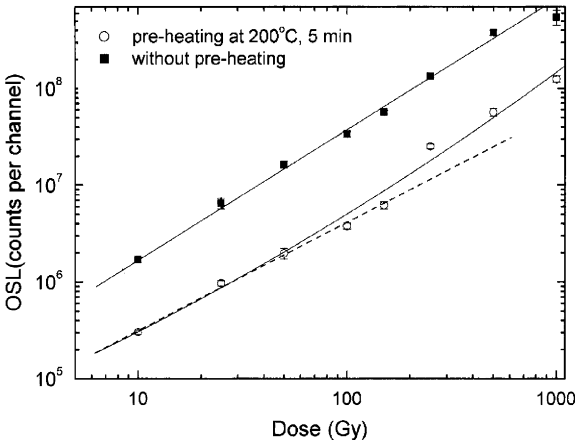

Fig. 4. OSL growth curve for microcline feldspar pre-heated at 200 °C during 5 min (open cicle) and without pre-heating (full square).

4. Conclusions

ESR is a very sensitive means for detecting radiation defects and the incorporation of allovalent impurities in crystal. Using ESR we could identify some radiation-induced defects, which can be assigned to the emission bands in natural crystals of microcline feldspar. The results of our studies on the Fe^{3+} ESR signal showed an increase in their intensity with heat treatment at temperatures above 400 °C. Therefore, high-temperature treatments provide an increase in Fe^{3+} cluster formations. Otherwise, the $Si–O^-\ldots X$ signal decreased with this treatment and did not increase with increased γ-ray doses. Based on our results the X divalent metal ion can be Fe^{2+}. The emission bands results are in agreement with ESR ones, showing the presence of Fe^{3+} too. The prominent bands at 455 and 640 nm could be related to Fe^{3+} transitions $^4A_1\ ^4E(G) \rightarrow {}^6A_1(S)$ and $^4T_1 \rightarrow {}^6A_1$, respectively. Narrow bands at 316 and 563 nm can be correlated to Sm^{3+} emission. The OSL growth curve supplied a supralinear behavior after doses higher than 10^2 Gy. The TL glow curve observed at 270–377 nm revealed peaks at 157 and 300 °C; the growth of the 300 °C peak shows a linear increase up to 50 Gy and then becomes a sublinear one. However, between 327 and 483 nm there are three peaks at 150, 280 and 340 °C. The TL growth of the 340 °C peak could be fitted by a saturating single exponential equation and can be used in TL dating. ESR measurements showed the hole centers $Si–O^-\ldots X$ and Fe^{3+}, which can be correlated with TL in the 327–483 nm range, as in the Mittani et al.

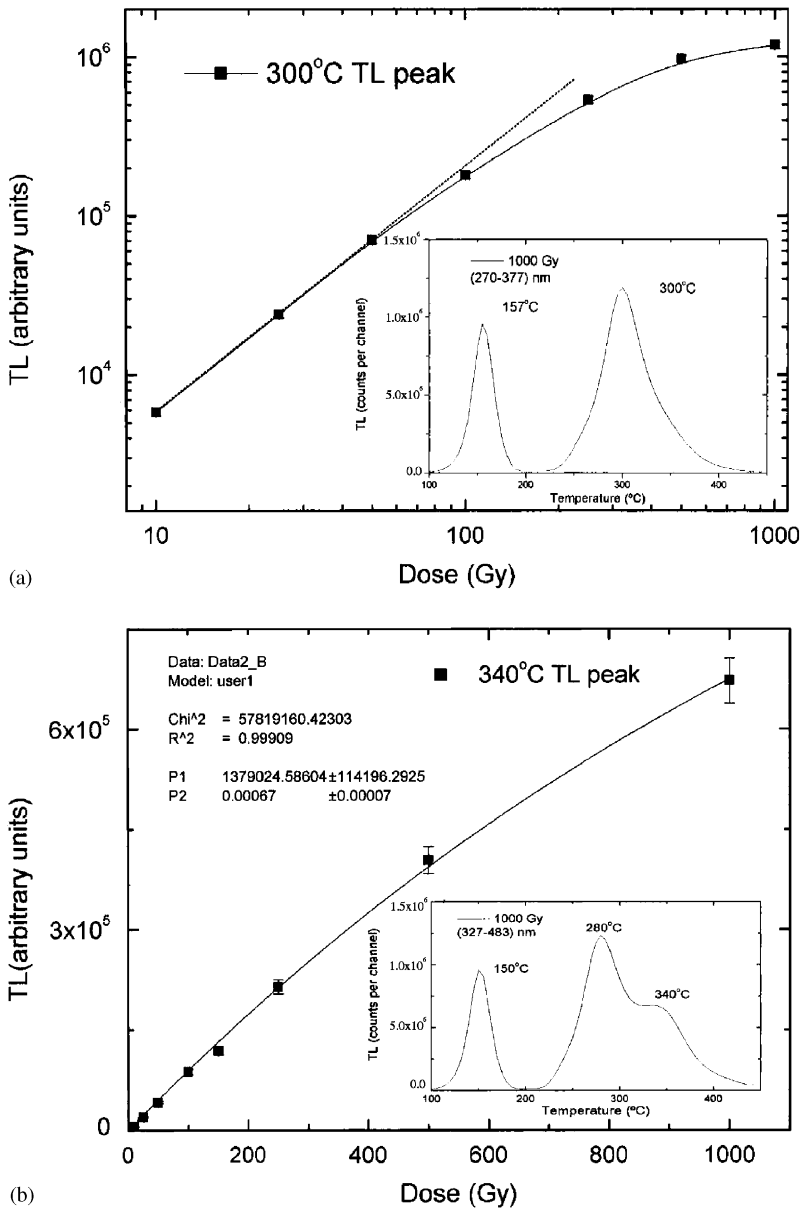

Fig. 5. (a) TL glow curves of microcline feldspar sample with peaks at 157 and 300 °C, obtained at the 270–377 nm wavelength interval, TL growth curve of the 300 °C peak. (b) TL glow curves of microcline feldspar sample with peaks at 150, 280 and 340 °C, obtained at the 327–483 nm wavelength interval, TL growth curve of the 340 °C peak, experimental points (full squares) were fitted by saturating exponential equation (solid line).

(1999) model; in our case the Si–O^-…X substitute the Al–O^-–Al center. In addition, we may have some contribution of Fe^{3+} emission at 455 nm too.

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References

Correcher, V., García-Guinea, J., 2001. On the luminescence properties of adularia feldspar. J. Lumin. 93 (4), 303–312.

Correcher, V., García-Guinea, J., Delgado, A., Sánchez-Munõz, L., 1999. Spectra thermoluminescence emissions and continuous trap distribution of across-hatch twinned low microcline. Radiat. Prot. Dosim. 84 (1–4), 503–506.

Hütt, G., Jaek, I., Tchonka, J., 1988. Optical dating: K-feldspars response stimulation spectra. Quaternary Sci. Rev. 7, 381–385.

Hütt, G., Jaek, I., Brodski, L., Vasilchenko, V., 1999. Optically stimulated luminescence characteristics of natural and doped quartz and alkali feldspars, Appl. Radiat. Isot. 50, 969–974.

Ikeya, M., 1993. New Applications of Electron Spin Resonance. World Scientific Publishing Co. Pte. Ltd, 333–336.

Jenkins, R., 2003. X-ray Fluorescence Spectrometry, Second ed. Willey, New York.

Kassab, R.P.L., Courrol, L.C., Morais, A.S., Tatumi, S.H., Wetter, N., Gomes, L., 2002. Spectroscopic properties of lead fluoroborate glasses codoped with Er3+ and Yb3+. J. Opt. Soc. Am. B 19 (12), 2921–2926.

Kirsh, Y., Shoval, S., Townsend, P.D., 1987. Kinetic and emission spectra of thermoluminescence in the feldspar albite and microcline. Phys. Stat. Sol. (a) 101, 253–262.

Mittani, J.C.R., Matsuoka, M., Watanabe, S., 1999. ESR and TL studies of feldspar. Radiat. Effects Defects Solids 149, 175–181.

Munita, C.S., Paiva, R.P., Oliveira, P.M.S., Momose, E.F., Plá, R., Moreno, M., Andonie, O., Falabella, F., Muñoz, L., Konenkamp, I., 2001. Intercomparison among three activation analysis laboratories in South America. Trace Microprobe Techn 19 (2), 189–197.

Nachimuthu, P., Jagannathan, R., Nirmal Kumar, V., Narayana Rao, D., 1997. Absorption and emission spectral studies of Sm^{3+} and Dy^{3+} ions in PbO-PbF_2 glasses. J. Non-Cryst. Solids 217, 215–223.

Poolton, N.R.J., BØtter-Jensen, L., Johnsen, O., 1996. On the relationship between luminescence excitation spectra and feldspar mineralogy. Radiat. Meas. 26 (1), 93–101.

Speit, B., Lehmann, G., 1982. Radiation defects in feldspar. Phys. Chem. Minerals 8, 77–82.

Visocekas, R., 2000. Monitoring anomalous fading of TL of feldspars by using far-red emission as a gauge. Radiat. Meas. 32, 499–504.

Yee, M., Tatumi, S.H., Suguio, K., Barreto, A.M.F., Munita, C.S., Paiva, R.P., 2003. Thermoluminescence (TL) Dating of Inactive Dunes from the Rio Grande do Norte Coastal, Brazil. J. Coastal Res. 35, 293–299.