Study of the effects of heat treatments in the paramagnetic centers of alkaline feldspars and their implications in the luminescence properties

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Abstract. The present work shows a detailed study of the effects of preheating in ESR signals of four alkaline feldspar samples. ESR results showed Fe³⁺, Al-O⁻Al, Ti³⁺ and [Pb-Pb]³⁺ centers. When the samples were gamma-irradiated, the concentration of the Fe³⁺ centers deceased in all the samples, but the Al-O⁻Al center concentration increased after about 50 Gy while that of the Ti³⁺ and [Pb-Pb]³⁺ centres became almost constant. The effects of preheating were observed in samples previously irradiated with doses of 0.2 and 3 kGy after heating at 100, 200, 300 and 400 °C, respectively for 10 minutes. In the orthoclase sample FELW, the Fe³⁺ signal remained almost constant up to 300 °C and increased at 400 °C, while that of the Al centre decreased slowly between 100 and 300 °C, but increased at 400 °C. In the microcline sample FELG an increase of the Al coupled with [TiO₄]⁻ centres was observed up to 300 °C, while a decrease occurred for higher temperatures. Fe³⁺ center concentration increased up to 200 °C and became nearly constant for higher temperatures. According to our results, even preheating at temperatures as low as 200 °C can change the concentration of Fe, Al and Ti centers in the sample; this fact can modify the luminescence response of the samples with the dose, because all these centers are associated with one or more emission spectra bands.

1. Introduction
It is known that heating occasionally can change the luminescence sensitivity of crystals. A large number of luminescence studies carried out to analyze the origin of the sensitivity change, but few works correlating luminescence with ESR (Electron Spin Resonance) experiments have been done.

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Nowadays, the SAR protocol [1] is largely applied in IRSL (Infrared Stimulated Luminescence) of feldspar for determining accrued radiation doses in unheated and heated samples, both for dating and accident dosimetry purposes. This protocol can correlate the luminescence sensitivity of the sample in regeneration method.

In the regeneration method using a single aliquot, the sample was submitted to several irradiation, optical stimulation and preheating cycles, that can promote changes in luminescence sensitivity. Another example of luminescence sensitivity change occurs in the optical dating of materials previously submitted to heating, such as pottery, bricks and tile.

The main object of this work is to present a detailed study of the effects of preheating in ESR signals of alkaline feldspar samples and its implications with ESR and optical dating results.

2. Experimental Procedure
Natural specimens of microcline and orthoclase, identified by X-rays diffraction, were investigated; Table I shows some characteristics of each sample. The samples named FELW, FELG and FELP were previously analyzed with TL, ESR, X-ray fluorescence and Neutron Activation Analysis; the results were published by Bitencourt et al., 2006 [2].

Table I. Some crystallographic and structure information, colour and origin of the sample.

| Sample | Structure | Compositions | Colour |
|--------|-----------|--------------|--------|
| FELW   | Orthoclase| Or$_{96.99}$Ab$_{12.97}$An$_{0.04}$ | White |
| FELG   | Microcline| Or$_{87.63}$Ab$_{12.33}$An$_{0.04}$ | Gray  |
| FELP   | Microcline| Or$_{81.36}$Ab$_{15.45}$An$_{3.19}$ | Pink  |
| FELAM  | Microcline| Or$_{96.99}$Ab$_{12.97}$An$_{0.04}$ | Green |

The fourth sample named FELAM is an amazonite collected from the southeast region of Brazil (Minas Gerais State). X-ray fluorescence analysis were performed and trace elements of La < 28 ppm, Ce < 35 ppm, TiO$_2$ < 0.007 mol%, Pb = 378 ppm, Fe$_2$O$_3$ = 0.1 mol%, MnO = 0.008 mol% and Al$_2$O$_3$ = 18.35 mol% impurities were found. Similar results were obtained for the three previously cited samples, except for the Pb content, which was not detected in FELW, FELG and FELP samples.

For ESR and emission spectra experiments, the specimens were carefully ground with a mortar and pestle, and the fraction between 88 and 180 $\mu$m was selected. The selected grains were treated with 10% HCl for 10 minutes, in order to reduce the grind effects. After that, they were washed extensively with distilled water and acetone. All the gamma-rays irradiations were performed at RT with $^{60}$Co source (0.3906 kGy.h$^{-1}$).

ESR spectra were taken at 77K, below saturation, by means of the homodyne X-band Varian E-4 spectrometer with a magnetic field modulation of 100 kHz, a microwave power of 20 mW and a TE011 mode cavity. The modulation amplitude used was 2.5 G peak-to-peak and the scan speed was 2.0 and 100 G in 60 seconds. The g-values were determined with a DDPH standard signal.

3. Results and Discussion
Fig. 1 shows the ESR spectrum for the natural FELAM sample and the spectra resulting for gamma irradiation of the sample with various doses. The spectra show the presence of Fe$^{3+}$, Al-O –Al, [Pb-Pb]$^{3+}$ and [TiO$_4$]$^{+}$ centers in all samples. Table II shows the g-values found for the FELAM sample and their related centers. The values g = 2.946 and g = 1.802 can be related to [Pb-Pb]$^{3+}$ centres [3,4], g =2.012 to Al centers and g = 2.946 and g =3.819 to Fe$^{3+}$ centers.

The effects of preheating are observed in samples previously irradiated with doses of 0.2 and 3 kGy and after preheating at 100, 200, 300 and 400 °C, respectively, for 10 minutes (Figure 2). In the orthoclase sample FELW, the Fe$^{3+}$ signal became almost constant up to 300 °C and increased at 400
C, while the Al centers decrease slowly between 100 and 300 °C and increase for the 400 °C preheating.

In the microcline sample FELG an increase in the concentration of the Al coupled with [TiO4]− centres was observed up to 300 °C, while a decrease occurred for higher temperatures (Figure 3). Fe3+ center concentration increased up to 200 °C and became nearly constant for higher temperatures.

![Figure 1. ESR spectra of microcline sample FELAM, irradiated with gamma-rays.](image)

**Table II.** G-values found for FELAM sample and their respective probable relates center.

| Sample | g-values | Probable related center |
|--------|----------|-------------------------|
| FELAM  | 3.819    | Fe3+                   |
|        | 2.946    |                         |
|        | 2.012    | Al-O-Al                 |
|        | 1.802    | [Pb-Pb]3+               |
|        | 1.360    |                         |
White Feldspar

- - 3 kGy 100°C
- - 3 kGy 200°C
- - 3 kGy 300°C
- - 3 kGy 400°C

Figure 2. Effect of preheating in ESR spectra of the Al-O-Al center of FELW sample, irradiated with 3 kGy of gamma-rays.

Gray Feldspar

- - 0.2 kGy 100°C
- - 0.2 kGy 200°C
- - 0.2 kGy 300°C
- - 0.2 kGy 400°C

Figure 3. Effect of preheating in ESR spectra of the Al/Ti<sup>3+</sup> centers of the FELG sample, irradiated with 200 Gy of gamma-rays.

4. Conclusions

According to our results, the concentrations of Fe<sup>3+</sup>, Al-O-Al and [TiO<sub>4</sub>]<sup>-</sup> centers can change, even with the use of low temperature preheating. It is know that these impurities are important luminescence centers [5,6], which are used for sediments optical dating [7,8].

All the centers can be associated with emission bands obtained with infrared stimulation. Thus precautions are advised with heat treatments of dating materials, taking into account the results presented.

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References

[1] Jacobs Z, Wintle A G, Duller G A T 2006 Evaluation of SAR procedures for De determination using single aliquots of quartz from two archaeological sites in South Africa Radiation Measurements vol. 41 issue 5 pp.520-533.

[2] Bitencourt J F S, Silva D M, Silva P H, Kinoshita A, Munita C A and Tatumi S H 2006 Luminescence and ESR properties of Brazilian feldspars Radiation Measurements vol. 41 issues 7-8 pp. 948-953.

[3] Petrov I, Mineeva R M, Bershov L V and Agel A 1993 EPR of [Pb-Pb]$^{3+}$ mixed valence pairs in amazonite-type microcline American Mineralogist vol. 78 pp. 500-510.

[4] Mittani J C R, Cano N F and Watanabe S 2005 Use of [Pb-Pb]$^{3+}$ center of the amazonite for dating Applied Radiation and Isotopes vol. 62 pp. 251-254.

[5] Poolton N R J, Mauz B, Lang A, Jain M and Malins A E R 2006 Optical excitation processes in the near band-edge region of KAlSi$_3$O$_8$ and NaAlSi$_3$O$_8$ feldspar Radiation Measurements vol. 41 pp. 542-548.

[6] Krbetschek M R, Götze J, Dietrich A and Trautmann T 1997 Spectral information from mineral relevant for luminescence dating Radiation Measurements vol. 27 pp. 695-748.

[7] Argyilan E P, Forman S L, Johnston J W and Wilcox D A 2005 Optically stimulated luminescence dating of late Holocene raised strandplain sequences adjacent to lake Michigan and Superior, Upper Peninsula, Michigan, USA Quaternary Research vol. 63 pp. 122-135.

[8] Hashimoto T, Yawata T and Takano M 2005 Comparison of naturally accumulated radiation-doses between RTL, BTL, OSL and IRSL using white minerals from burnt archaeological materials and usefulness of RTL-dating from quartz extracts Geochemical Journal vol. 39 pp. 201-212.