Studies on the physics of the infrared radioluminescence of potassic feldspar and on the methodology of its application to sediment dating

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Abstract

The methodology of the new infrared radiofluorescence (IR-RF) dating technique on K feldspar applied to the age determination of Quaternary sediments overcomes many physical problems, which often occur when luminescence dating methods are used (undefined dose characterists, sensitivity changes, statistical problems due to small number of measured dose points etc.). However, there are unanswered physical questions, which influence can adversely affect the dating precision. This paper summarises ideas to solve problems of the functional dose curve description of the IR-RF. Some new aspects of the physical interpretation of the IR luminescence are reported, together with new results of a luminescence emission band at 910 nm in K feldspars. Furthermore, derived from investigations on Pb doped KCl crystals, we discuss a mechanism of the dissociation of Pb^{2+} to Pb^{+} during interaction with ionising radiation as possible origin of the creation of the electron trap at 1.43 eV in the potassic feldspar lattice.

Key words: feldspar, sediment dating, radioluminescence, luminescence defects

1 Introduction

Feldspar minerals are used as natural dosimeters for sediment dating since Mejdahl (1983) has shown their dosimetric characteristics to be suitable for

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such applications. First measurement protocols based on the thermoluminescence (TL) behaviour of these minerals, but when Hütt et al. (1988) came up with an optical excitation study on potassic feldspar, the optically stimulated luminescence (OSL) on this material became a widely used readout technique used in Quaternary sediment dating. Trautmann et al. (1998) investigated in a first spectral and dosimetrical radiofluorescence (RF) study on crystals of the whole K-Na-Ca ternary feldspar system the characteristics of charge transitions as well as the charge storage mechanisms during interaction with beta and internal conversion radiation from a $^{137}Cs/^{137}Ba^{m}$ source. The results of this study suggested the use of radiofluorescence measurements as a new tool for dosimetry and dating. The dosimetrical conclusions of the continuative work on the radioluminescence (RL) (Trautmann, 1999) pointed out, that the use of this new technique for dating is limited to an emission in the infrared at 865 nm (IR-RF), which only occurs in some potassic feldspars, such as microcline and orthoclase. The process measured (IR-RF) during laboratory irradiation is the same that takes place in the sediment while buried (apart from energy spectra of ionising radiation and dose rates). The methodology and the advantegeous physical background of this new dating technique is completely different from those of TL and OSL techniques and the age determination range is predicted to be arround 250 ka (Trautmann, 1999; Krbetschek et al., 2000).

This paper outlines state-of-the-art knowledge on the physical background of the IR luminescence of potassic feldspar, focussing the methodology for the application to Quaternary sediment dating using the RF method.

2 Experimental

Measurements were taken using a fully automated radioluminescence (RL) reading instrument designed and built by Erfurt et al. (submitted) and a highly sensitive CCD spectrometer system firstly described by Rieser et al. (1994). The basic principle of measuring the radioluminescence with these instruments is described elsewhere (Trautmann et al., 1998). The radiophosphorescence (RP) after electron bombardement was measured using an UV-IR spectrometer connected to an electron accelerator at the Leipzig University, Faculty of Chemistry and Mineralogy. This pulsed accelerator emits 1 MeV electrons and delivers about 100 Gy·pulse^{-1} (pulse length was set to 10 ns). The decaying phosphorescence was measured 16 ns after the pulse and the detection has been performed by an IR sensitive photodiode (+filter for the signal detection and filters to cut out multi-order diffraction light generated by the spectrograph). The potassic feldspar samples were either extracted phases from clastic Quaternary sediments (Mar8, Ros2) or rock-forming minerals (K7) from the Mineralogical and Petrographical Collection at the Freiberg

University of Mining and Technology. All samples measured using the spectrometer or the RL reading system, respectively, were grains size fractionated (100..150 μm) and underwent additional flotation to extract the whole feldspar fraction before the K feldspars and plagioclases of all samples were separated by density using standart procedures. Samples for the measure of the radiophosphorescence were XDA analysed pieces of $10 \times 10 \times 10$ mm of rock-forming K feldspars.

3 Results

3.1 Functional dose curve description

The measured decay of the IR-RF against additive or regenerative dosing, follows an exponential decay function for all sediment extracted and rock-forming K feldspars. Following the results of a modelling approach, Trautmann (1999, 2000) suggested a single-exponential decay function

$$\Phi(D) = \Phi_0 - \Delta\Phi \cdot (1 - e^{-\lambda \cdot D}), \tag{1}$$

where Φ is the IR-RF flux, either depending on the applied dose D, the initial flux at natural dose D_0 or the change $\Delta\Phi$ during irradiation. The factor λ is an exponential parameter. Trautmann (1999); Trautmann et al. (1999); Krbetschek et al. (2000) used a non-automated CCD spectrometer system for all measurements. This resulted in a limited number of 20 to 40 dose points covering the dose range of 800 Gy (distance of dose points 20 to 40 Gy). The automated RL instrument (see section 2) allows the measure of a quasi-unlimited number of dose points (e.g. 760 dose points in figure 2) with a distance of only a few mGy. Due to the small dynamic range (about factor 2, comparing saturated and bleached signals) of the IR-RF process, the data quality or density, respectively, strongly influences the fit precision and the significance of the measured data. Regarding fit residues (figure 3), it becomes clear, that a single-exponential decay does not describe the measured data precisely.

Fitting the data to a single exponential or a two-term exponential function leads to completely different results for the palaeodose determination (additive IR-RF dose curve of an aliquot of sediment sample Mar8 in figure 1). Therefore, a two-term exponential function, as written in equation 2, describes the dose charcteristics perfectly with non-significant residues. However, the physical background of this second term is speculative and we doubt the comparability of the fit results for different dose curves (e.g. due to the low dynamic

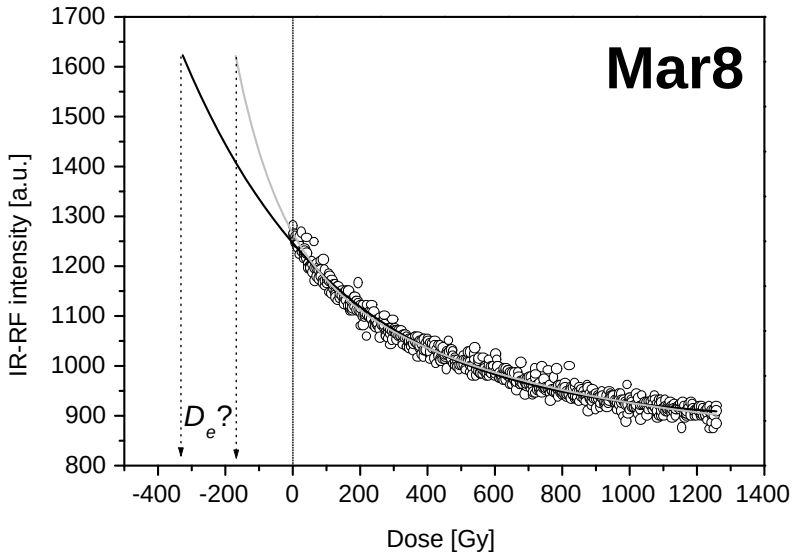

Fig. 1. Additive IR-RF dose curve of a sediment sample Mar8 (open circles) with single-exponential (dark gray) and two-term exponential (light grey) fit. The resulting palaeodose D_e is completely different.

range of the first term signal).

$$\Phi(D) = \Phi_0 - \Delta\Phi_1 \cdot (1 - e^{-\lambda_1 \cdot D}) - \Delta\Phi_2 \cdot (1 - e^{-\lambda_2 \cdot D}) \tag{2}$$

It has been suggested, e.g. by Pavesi and Ceschini (1993), that a stretched exponential function can describe a behaviour which is often encountered in disordered condensed-matter systems. They suggested that the dispersion of charge carrier transition or release rates and trap energies in multiple trapping-detrapping mechanisms can be expressed in the factor β in equation 3, which is the stretched form of equation 1.

$$\Phi(D) = \Phi_0 - \Delta\Phi \cdot (1 - e^{-\lambda \cdot D})^{\beta} \tag{3}$$

Using such an function, the dose curves can also be described yielding residues close to zero, as one can see in figure 2 of a slided dose curve (regenerative+additive) of sample Mar8. Consequences for the model proposed by Trautmann (2000) are discussed in the summary.

Regarding all in our laboratory measured „slided“ dose curves, also considering different sample ages from 10 to 200 ka, we mainly noticed a very good agreement of the IR-RF between regeneration and additive dosing. Significant deviations only occured, if the signal intensity of the samples was insufficient.

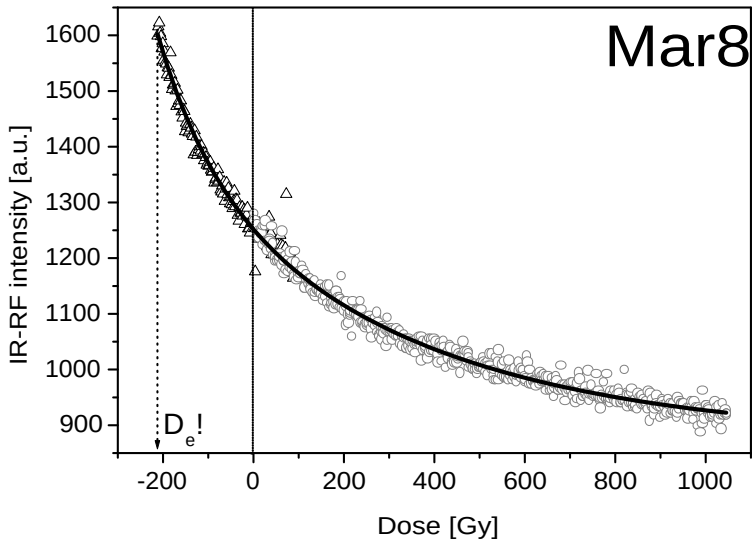

Fig. 2. Slided (regenerative (open triangels)+additive (open circles)) dose curve (see Krbetschek et al. (2000) for IR-RF slide technique) of sediment sample Mar8 with stretched single-exponential fit (black line), Note that this slided dose curve consists of 760 dose points

Thus, reproducibility problems due to low counting rates in the light detection system might be the consequence. Schilles (2002) addressed those effects to sensitivity changes during the IR-RF process and proposed an empirical method to overcome this problem. We suggest to reject samples that do not show an agreement as shown in figure 2.

Bearing in mind, that the radioflurescence is steadily excited by the irradiation source, it becomes clear, that different emission wavebands can be measured at once (Erfurt et al., submitted).

Considering an quasi-equilibrium in the valence and the conduction band during interaction with ionising radiation (McKeever and Chen, 1997), the complex kinetics of different transitions are influenced by the densities of charge carriers in traps or activators (also those which are non-radiative centres). If this density changes in an electronic state due to thermal instabilities or a tunneling probability of the charges, also the kinetics into other, e.g. stable, traps or recombination sites may be disturbed. Measuring all ,,visible" transitions during the dating performance (figure 4) could be a powerful tool to recognise effects which adversely affect the palaeodose determination (e.g. unstable recombination centres).

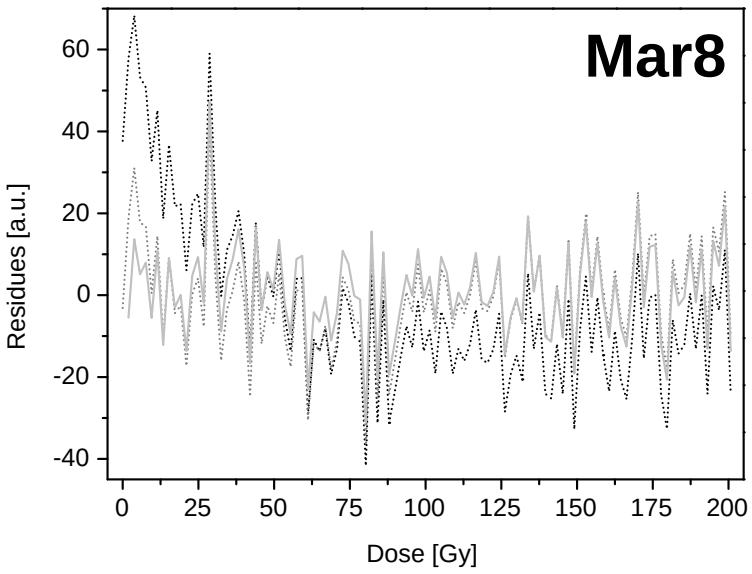

Fig. 3. Fit residues of the single- (dotted black), two-term- (dotted dark grey) and stretched single-exponential (light grey) of sediment sample Mar8 for the first 200 Gy regenerated dose

3.2 Emission waveband $\lambda > 865$ nm

Within the last years, the occurance of a second optical absorption band ($E < 1.44$ eV) in the IR in potassic feldspar was often discussed (Hütt et al., 1988; Bøtter-Jensen et al., 1994; Clark and Sanderson, 1994). If such an absorption energy level does exist and this would also allow the radiative electron transition from the conduction band via an excited state, it must also allow a luminescence emission. We considered such an radiative transition in a shallow trap as explanation of the two-term exponential decay of the dose curves and forced an investigation (spectrometer setup, see section 2). The region 1.2 to 1.9 eV has been cut out and a Gaussian distribution has been determined which clearly shows a second emission band centered at 1.36 eV (figure 5).

Another attempt to measure an radioluminescent emission $\lambda > 865$ nm was carried out on a linear electron accelerator (see section 2). The spectra were measured on a microcline and an orthoclase rock-forming sample (K7 in figure 6) and both showed a second emission band also centered at 1.36 eV. Its intensity is higher than the known emission at 1.43 eV, which is most likely due to different kinetics of the RF and the RP processes (RP measured 16 ns after the electron pulse). Note, that the spectra taken with both system

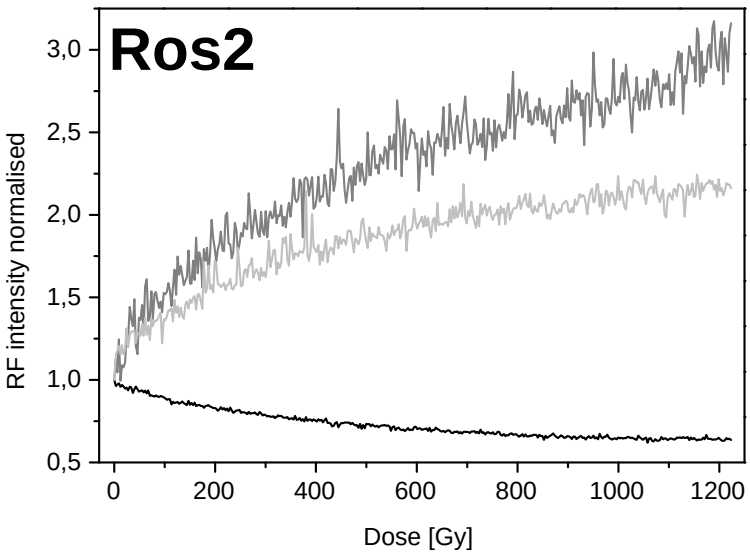

Fig. 4. Typical dose characteristics of a potassic feldspar (sediment sample Ros2) at the emission wave bands 865 nm (black), 700 nm (dark grey) and 415 nm (light gray), Note the small dynamic range, especially for the 865 nm emission

were not corrected for wavelength dependent overall sensitivity. This overall sensitivity of these devices, however, decreases with longer wavelengths, what implies stronger intensities in the IR than measured.

It is yet not known, whether this 910 nm emission band displays a dose dependency. But its existance should generally be taken into account, when IR detection filters are choosen. Attempts to measure the IR luminescence at 865 nm using long pass (e.g. Schilles (2002)) or edge (high pass) filters would allow a significant transmission for the known feldspar emission at around 700 nm (the red RF emission in feldspars is often the most intensive, see 700 nm signal dynamic in figure 4). To measure the IR-RF at 865 nm, we used a special designed Andover interference filter (200FC35-25/8650) with a FWHM of 18.7 nm and 27.9 nm at ten percent of the central wavelength transmission, what complies with all spectroscopic requests mentioned above.

4 Correlation between Pb and the IR waveband at 1.43 eV

Woksmenzev et al. (1989) reported in a spectral luminescence study on amazonites (=microcline) on the occurance of a X ray induced luminescence as

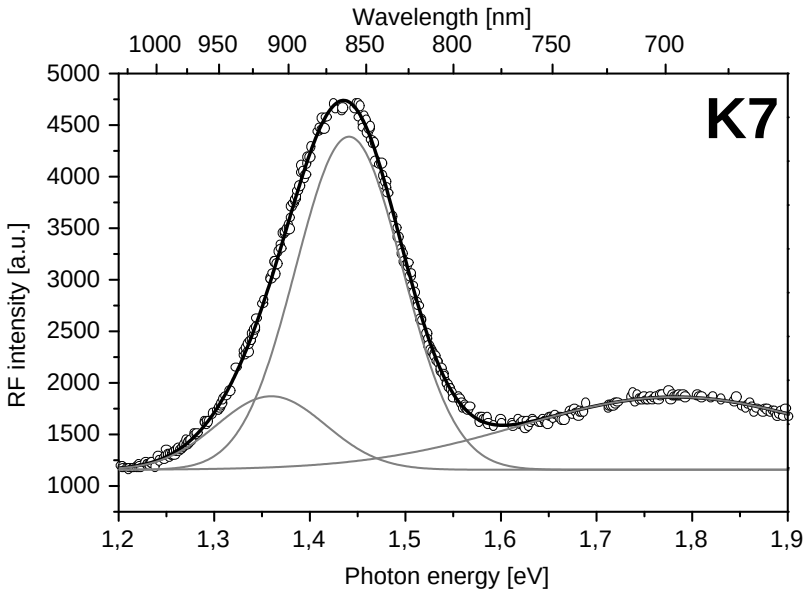

Fig. 5. Typical IR to red spectrum (open circles) of a potassic feldspar (rock-forming sample K7) with two emission bands (1.36 eV, 1.44 eV, grey peaks) in the IR, the envelope (black line) shows perfect agreement with the spectrometer data

well as of a photoluminescence at 1.44 eV (860 nm), which was furthermore reported to be a luminescence effect that is limited to potassic feldspar. The dose response is similar to that measured on our samples under electron irradiation (e.g. figure 2). The following mechanism (4) has been suggested for the creation of this IR luminescence based on a radiative electron trapping intracentre in Pb^+, which was investigated on Pb doped KCl crystals (Nagli and Dyachenko, 1986) ($E \rightarrow$ RL excitation (X ray, γ, electrons, etc.), $e^- \rightarrow$ electron, $e^+ \rightarrow$ hole).

$$Pb^{2+} + E \rightarrow Pb^{2+} + e^- + e^+ \rightarrow (Pb^+)^* + e^+ \rightarrow Pb^+_{\hbar\omega_{860\,nm}} + e^+ \qquad (4)$$

The IR luminescence of amazonites and other K feldspars is assigned to the dissociation of Pb^{2+} to an excited state of monovalent $(Pb^+)^*$, that subsequently relaxes to the ground state of Pb^+, emitting 1.44 eV photons. This mechanism would confirm the general behaviour of charge transitions connected to the IR-OSL trap and IR-RF luminescence center (Trautmann, 2000). It is known that the luminescence behaviour of ions with s^2 configuration (like Pb^+) does strongly depend on the host lattice (Blasse and Grabmeier, 1994), which could be the reason for the shift of the central wavelength to 955 nm compared to that of K feldspar at 865 nm (cubic lattice of KCl and tetrahedral framework of feldspar). The dose characteristic is, however, equal to that

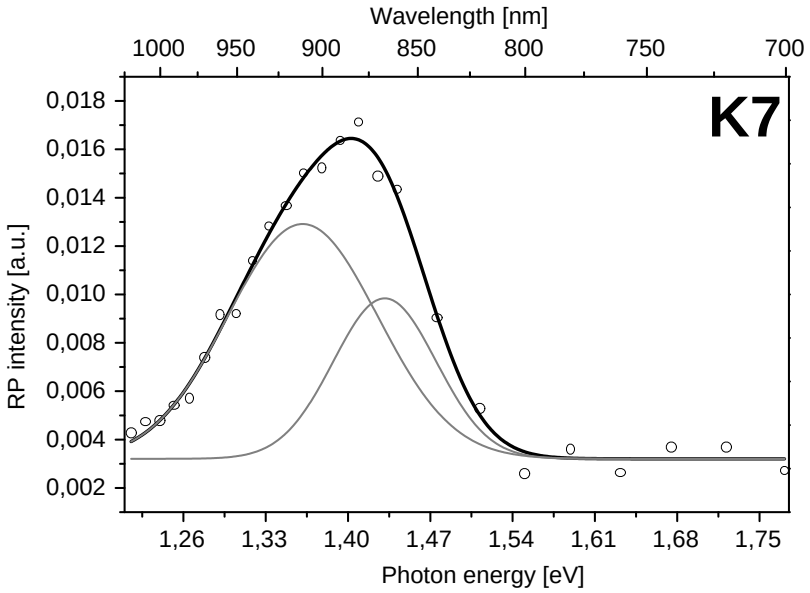

Fig. 6. Radiophosphorescence spectrum (open circles) of a potassic feldspar (rock-forming sample K7) with two emission bands (1.36 eV, 1.43 eV, grey peaks) in the IR after electron bombardement

of the IR-RF emission of K feldspar at 865 nm (figure 7, KCl sample doped with 30 ppm Pb, spectrometer setup described in section 2). Comparing the IR luminescence of K feldspar with that of KCl:Pb is interesting, that Nagli and Dyachenko (1986) detected also a second IR emission band in KCl:Pb at 1.18 eV which is as well caused by an intracentre transitions in Pb^+, but from an other excited state into the same ground level.

In contrast to this, it is believed, that Pb^+ does not occur in other K feldspars than amazonite (Marfunin and Bershov, 1970), that was concluded from results of a EPR study but not from IR luminescence effects. The model suggested above points out, that Pb^+ is only present in irradiated K feldspars. However, to find better correlation between the content of Pb in K feldspars and the intensity of their 1.43 eV band, a spurious ICP-MS analysis of different rock-forming K feldspars is in preparation.

5 Conclusions

- A single stretched-exponential function describes the IR-RF behaviour succesful without significant residues. The dispersion of electronic states and transition rates in the material would then be reflected by the factor β. The

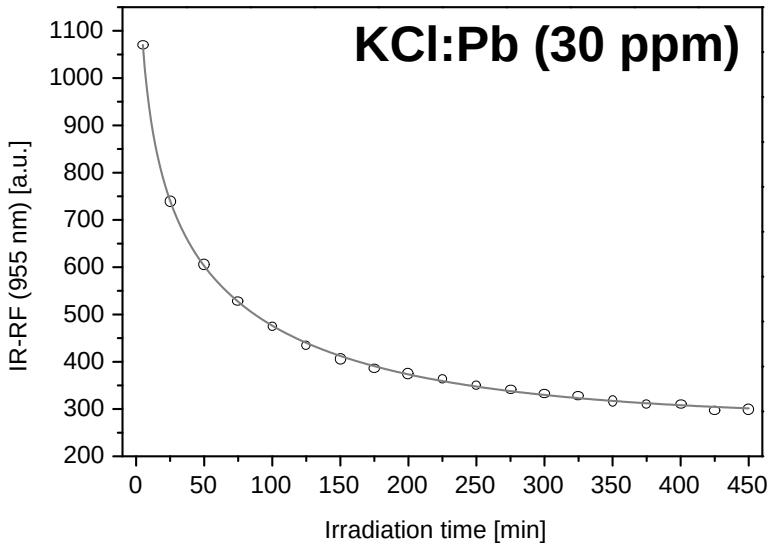

Fig. 7. ,,Potassic feldspar“ IR-RF dose characteristics (open circles) of an annealed KCl:Pb sample at 1.29 eV (955 nm) fitted to a stretched single-exponential function (grey line)

analysis of the fit data, especially the factor β seems to be a good possibility to compare the IR-RF behaviour of different feldspar samples (as parameter of the possible dispersion of the electronic structur) and this should be investigated in future studies. This new fit approach does not affect the conclusions from the model suggested by Trautmann (2000).

- The huge advantage of the IR-RF dating method comparing TL and OSL is the high density of measured dose points, what implies good significance of the data. If a slided dose curve (additive+regeneration) shows no compliance (to be controlled by fit values), the sample should be rejected. We also advise to consider statistical problems, depending on the number of dose points measured (OSL $\rightarrow$ 5..15; IR-RF $\rightarrow$ 500..800).
- An IR detection filter must be chosen carefully. The 700 nm emission in feldspar is often the most intensive. The overlap and the different dynamics of the dose response can cause errors during the palaedose reconstruction, if filters with broad band transmissions are used.
- The measure of all radiative radiofluorescent transitions can help to recognise influences of unstable centres on the precision of the IR-RF dating technique. Due to multi-trapping-detrapping processes in feldspars, the steady measure of the dynamic equilibrium during irradiation is proposed as a powerful tool.
- The proposed theory of a radiativ electron transition into the IR-OSL trap in

K feldspar (Trautmann, 1999) is supported by the most likely mechanism of a radiative electron trapping mechanism in Pb^+ ions, explained by a similar effect in KCl:Pb (main IR emission at 955 nm (1.29 eV)).

- A second IR emission band in K feldspar was measured at about 910 nm (1.36 eV). Also KCl:Pb exhibits a second IR emission band at 1.18 eV (Nagli and Dyachenko, 1986) and the shift of these two emissions is in both materials about 0.08 to 0.10 eV. In KCl:Pb, this is also caused by an intracentre transition from a different excited state of Pb^+ into the same ground level (=electron trap). If both emissions at 1.43 eV and 1.36 eV in feldspar can be attributed to intracentre transitions in Pb^+, electrons are kept in the same trap. This could also be an approach to explain the ,,dispersed" single-exponential decay. The transition from an other excited state into the same ground level does change the density (and straightforwardly the transition probabilities for electrons, transiting from the two excited states into the same ground level).

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