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PALEODOSIMETRICAL PROPERTIES OF SODIUM ALKALI FELDSPARS AND PROBLEMS OF LUMINESCENT DATING OF SEDIMENTS

Summary. Emission spectra of natural alkali feldspars extracted from sediments are studied using CCD camera based high sensitivity spectrometer. Two dominant emission bands – blue (410 nm) and orange (570 nm) are revealed in infrared optically stimulated luminescence (IROSL) spectra obtained using semiconductor laser (860 ± 1 nm) for the most of sediments from Scandinavian profiles. Luminescence and dosimetrical properties of the hole traps, induced orange emission band typical for sodium alkali feldspars are studied. High light bleachability but less stability of the dosimetrical information in sodium alkali feldspars are found. Problems of luminescence dating of sediments on the basis of potassium-sodium alkali feldspars mixture are discussed.

PALEODOZYMETRYCZNE WŁAŚCIWOŚCI SKALENI SODOWYCH A PROBLEM LUMINESCENCYJNEGO DATOWANIA OSADÓW

Streszczenie. Widma emisyjne naturalnych skaleni alkalicznych wydzielonych z osadów badano za pomocą spektrometru o wysokiej czułości z kamerą CCD. W większości próbek z profili skandynawskich wykryto dwa dominujące pasma –niebieskie (410 nm) i pomarańczowe (570 nm) – IROSL luminescencji stymulowanej promieniowaniem podczerwonym lasera półprzewodnikowego (860 ± 1 nm). Badano własności luminescencyjne i dozymetryczne pułapek dziurowych i stymulowanej emisji w paśmie pomarańczowym. Stwierdzono dużą podatność na wybielanie światłem ale mniejszą stabilność informacji dozymetrycznej skaleni alkalicznych sodowych. Przedyskutowano problem datowania luminescencyjnego osadów w przypadku mieszania skaleni alkalicznych potasowo-sodowych.

1. Introduction

Alkali feldspars $K(Na)AlSi_3O_8$ are widely spread natural minerals. During the last decade the attention of scientists focused on the study of the luminescent and dosimetrical properties of minerals in order to elaborate luminescence dating techniques for Quaternary sediments.

The main requirements for minerals serving as palaeodosimeters are:

- 1. high stability of stored age information in the time span actual for the Quaternary sediments,
- 2. high bleachability of minerals by the natural light for zero-point realization,
- stability of dosimetrical and luminescent properties during burrying and all laboratory treatments.

Minerals are extracted usually by heavy liquid with density 2.58 g/cm³, and a mixture of sodium and potassium components is obtained due to the isomorphism of the solid solution of $K(Na)AlSi_3O_8$. It is practically impossible to separate these two components. The only way to study their characteristics independently - optical separation based on the difference of their emission spectra.

The spectral characteristics of sodium and potassium feldspars have been rather well studied (Taraschan et al., 1978; Dalal et al., 1988; Kirsh and Townsend 1988; Prescott et al. 1988; Huntley et al. 1991; Jungner and Huntley et al., 1991; Spooner, 1993). It is shown, that potassium feldspars emission spectra have a maximum at 410 nm (blue) and that sodium feldspars have a very bright luminescence with a maximum at 570 nm (orange), for fine grains extracted from sediments the orange emission band is dominant.

Potassium-component of alkali feldspars (emission about 410 nm) is widely used for dating of Quarternary events up to $150 \div 200$ ka.

The objective of the following investigation is the detailed study of the palaeodosimetrical properties of sodium component of alkali feldspars and its possible application for luminescence dating.

2. Experimental

The samples under study were from Finnish, Swedish and German profiles. Alkali feldspars (100 - 160 m) were extracted from these sediments following the techniques described before (Mejdahl, 1983; Hütt and Smirnov, 1983). Both natural and laboratory-irradiate samples were studied. Laboratory irradiations were performed by γ -source ⁶⁰Co or X-ray at room temperature.

The following characteristics of samples were measured:

- 1. Spectra of phosphorescence,
- 2. Spectra of stimulation,
- Infrared stimulated (860±1 nm) emission (IROSL) spectra of natural and laboratory irradiated samples,
- 4. Bleachability of luminescence induced by blue and orange centra of recombination,
- 5. Dose reconstruction using different emission bands,
- 6. IROSL spectra at low and elevated temperatures.

The phosphorescence and OSL spectral studies were performed using a CCD-camera based high sensitivity spectrometer. The whole spectra from 200 to 800 nm are focused simultaneously on a liquid nitrogen cooled CCD-cell with 115×298 pixels. Because of high efficiency (from 16% in the UV to 40% in the IR) and extremely low background noise of the cell, very weak luminescence may be detected. Depending on the luminous intensity, the signal can be accumulated by the cell for an integration time of 30 ms up to several hours (Rieser et al., 1994). The procedure for measurement of the stimulation spectra was described before (Hütt et al., 1988). Semiconductor laser with pulse and permanent regime of work (860±1 nm) was used as a source of infrared light.

Bleaching was performed by natural diffused light and artificial daylight simulator with or without UV component produced by UVA lamp.

3. Results and discussion

3.1. Phosphorescence spectra and spectra of stimulation

Phosphorescence spectrum (fig. 1) reveals the whole set of centra of recombination of charge carriers released from shallow traps. It was measured 1 min after β -irradiation. Following measurements during one week did not discover any changes in the shape of the spectra.

Spectra of stimulation for the orange emission band were measured (fig. 2). It was shown that the traps which induced the maximum at about 900 nm were the same that for blue emission. The same was also the thermooptical mechanism of OSL (Hütt et al., 1988; Hütt and Jaek, 1990).



- Fig. 1. Spectrum of phosphorescence of alkali feldspars extracted from sediments (sample No. 986). CCD-camera spectrum is uncorrected. Spectrum is measured 1 min after β irradiation
- Rys. 1. Widmo fosforescencji skaleni alkalicznych wydzielonych z osadów (próbka No. 986). Widmo rejestrowano po upływie 1 minuty od napromieniowania promieniowaniem β za pomocą kamery CCD (widmo nie skorygowane)



- Fig. 2. Spectra of stimulation (IR part) of alkali feldspars, extracted from sediments, for emission band 570 nm (filters of USSR production with FWHM 580⁺²⁰₋₃₀nm), sample No. 986
- Rys. 2. Część podczerwona widma stymulacji pasma emisyjnego 570 nm (filtry produkcji ZSRR, FWHM 580⁺²⁰₋₃₀ nm) skaleni alkalicznych wydzielonych z osadów: próbka No. 986

3.2. Infrared stimulated luminescence spectra

IROSL emission spectra consist of two rather well resolved bands at 410 nm and 570 nm (fig. 3).



Fig. 3. IROSL spectra of typical alkali feldspars extracted from Scandinavian profiles.
 1 - sample No. 986, K_{internal} = 10.0%. 2 - sample No. 1022, K_{internal} = 11.8%.
 Semiconductor laser 8601 nm in pulse mode was used

Rys. 3. Widma IROSL typowych skaleni alkalicznych wydzielonych z profili skandynawskich. 1 – próbka No. 986, $K_{internal} = 10,0\%$, 2 – próbka No. 1022 $K_{internal} = 11,8\%$. Wykorzystano laser półprzewodnikowy 860±1 nm, pracujący w reżimie impulsowym

Ultraviolet (UV) and IR parts of the spectra are cut off by filter BG-39, avoiding background signal from stimulated IR light. The differences between IROSL and the spectra of phosphorescence may be explained as follows. In the case of β (γ)-irradiation all hole and electron processes are involved, while IROSL spectra, as it was shown for the blue center of recombination (Jack et al., in press) are caused only by electron recombination. It is worth noting that the above mentioned spectra (fig. 1, 2, 3) are typical for samples from all Scandinavian and German profiles: only the ratio of emission bands differs.

3.3. Bleachability

Light sensitivity of the centra of recombination (blue and orange) or bleachability was studied using different light sources such as natural sunlight, natural diffused light, laboratory natural daylight simulator, with UV and without UV component. The most pronounced effect was revealed using either sunlight or artificial light with added UV component. The orange band is much more quickly quenchable than the blue one, and the residual luminescence is negligibly small (fig. 4). This fact is extremely important for dating because zero-point is realized much quicker for orange emission of sodium component then for blue emission of potassium one.

3.4. Dose response

IROSL spectra show no changes with the dosing up to 2 kGy. This dose is close to the level of saturation for both sodium and potassium components. The ratio of yellow and blue bands in IROSL spectra was stabilized during three weeks after the irradiation and did not change after 1 - 5 years for the most of the samples studied. This proves absence of permanent channels for anomalous fading in sodium component.

3.5. Stability of optical information

A set of 10 samples from the Scandinavia area with geologically predicted ages in the span of 30-120 ky was checked. To compare the stability of orange and blue centra, the accumulated dose was reconstructed using Schott interference filters UV-DAD-15-3 (391,9 nm) and DMZ-20-2 (529,1 nm) as well as combination of filters 3 mm BG-39 with 3 mm OG-530 (Schott glass filters, FWHM 560^{+30}_{-25} nm). The use of orange emission gave systematically younger ages than that of blue emission (fig. 5).

The same results are illustrated by fig. 6. Four samples from German profiles were measured using different interference filters giving separation of sodium and potassium emission. Different accumulated doses were obtained. The only explanation may be different thermal stability of holes at the orange and blue centra of recombination. By the way, well-known underestimation of luminescence ages for loesses may be explained by the dominance of the orange emission for fine- grains used for the dating.

3.6. IROSL spectra at low and elevated temperatures

Complicated IROSL spectra consisting of bands induced by centra of recombination with different half-life of holes needs special precaution with all kinds of laboratory procedures. As one can see (fig. 7), IROSL spectra changed at elevated temperature (about 80°C). Redistribution of the intensity of orange and blue emission is clearly seen in the

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- Fig. 4. Effect of OSL bleaching of natural sample by daylight together with UV component.
 1 light exposure 0 min, 2 light exposure 1 min, 3 light exposure 2 min, 4 light exposure 3 min, 5 light exposure 5 min. 6 light exposure 30 min
- Rys. 4. Wpływ wybielania światłem dziennym z zawartością ultrafioletu na OSL naturalnych próbek. 1 – ekspozycja na światło 0 min, 2 – ekspozycja na światło 1min, 3 – ekspozycja na światło 2 min, 4 – ekspozycja na światło 3 min, 5 – ekspozycja na światło 5 min, 6 – ekspozycja na światło 30 min



Fig. 5. Accumulated dose reconstruction and age calculation for sample No. 1028 using Schott interference filters: a) UV-DAD-15-3 (391.9 nm), b) DMZ 20-2 (529.1 nm)

Rys. 5. Rekonstrukcja dawki zakumulowanej i obliczenie wieku próbki No. 1028 przy użyciu filtrów interferencyjnych Schott'a: a)UV-DDA-15-3 (391,9 nm), b) DMZ-20-2 (529,1 nm)

spectrum. This is the result of dramatic change of the palaeodosimeter. The same effect takes place after the preheating at the same temperature for 1 min. Preheating procedure used in all luminescence dating techniques by the majority of laboratories can not be recommended without special check of TL and IROSL spectra.



Fig. 6. Dose reconstruction using different emission bands for four samples from German profiles. Measurements were made by Rieser and Krbetchek

Rys. 6. Rekonstrukcja dawki przy wykorzystaniu różnych pasm emisji dla czterech próbek z profilów niemieckich. Pomiary wykonane przez Riesera i Krbetcheka



- Fig. 7. 3-dimensional IROSL spectrum of alkali feldspars at low and elevated temperature. Sample No. 986
- Rys. 7. trójwymiarowe widmo IROSL skaleni alkalicznych w niskiej i podwyższonej temperaturze. Próbka No. 986

4. Summary

- Spectral study of alkali feldspars from Scandinavian and German areas was performed. Sodium feldspar components with the orange centra of emission (570 nm) are revealed in the most of cases in IROSL spectra.
- 2. Spectra of stimulation for the orange emission center has the same IR maximum as for blue center (about 900 nm).
- 3. IROSL spectra of alkali feldspars do not change after laboratory dosing up to 2 kGy.
- 4. Orange emission center is much more effectively bleachable by light with UV component than the blue one.
- Dose, reconstructed using the orange emission band, is systematically less (by 30 50%) than in the event of the blue emission band (for samples older 50 ky).
- 6. Special spectral study is necessary when using elevated temperature or preheating for dating on the basis of alkali feldspars.

It is recommended to try to use orange emission (570 nm) of sodium component of alkali feldspars for dating of Holocene sediments. It is possible to suppose that thermal stability of holes would be enough for this time span, while better resolution of the dating can be reached due to better zero-point realization.

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Streszczenie

Wykonano badanie widma skaleni alkalicznych ze Skandynawii i Niemiec. W większości przypadków widm IROSL (luminescencji stymulowanej światłem podczerwonym) stwierdzono komponent skaleni sodowych z pomarańczowym centrum emisji (570 nm).

Widma stymulacji pomarańczowych i niebieskich centrów emisji mają to samo maksimum w podczerwieni (900 nm). Widma IROSL skaleni alkalicznych nie zmieniają się po napromieniowaniu dawkami laboratoryjnymi do 2 kGy.

Światło ze składową ultrafioletową znacznie efektywniej wybiela pomarańczowe centra emisji niż niebieskie.

W przypadku próbek starszych od 50 ka wartości dawki rekonstruowanej przy wykorzystaniu pomarańczowego pasma emisji są systematycznie niższe o 30-50% od wartości uzyskiwanych przy wykorzystaniu pasma niebieskiego.

Przy wykorzystaniu do datowania skaleni alkalicznych konieczne są dodatkowe specjalne badania widm w przypadku przechowywania porcji ziaren w podwyższonej temperaturze lub stosowania procedury grzania wstępnego.

Zaleca się wykorzystanie pomarańczowej emisji (570 nm) składowej sodowej skaleni alkalicznych do datowania osadów holoceńskich. Można założyć, że stabilność termiczna dziur jast wystarczająca dla celów datowania w tym przedziale czasu, a lepsze spełnienie warunków początkowego zerowania OSL zapewni większą precyzję datowania.