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ADVANCED THERMOLUMINESCENCE DATING OF PERMAFROST: A NEW APPROACH

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Precise age determination is an important tool to study frozen ground as it can be used, through extrapolation, to reconstruct the history of permafrost and to predict its future evolution. However, precise dating is difficult because the classical age methods designed for a narrow time span and a limited number of rock types are inapplicable to permafrost. Having compared several recent techniques, we selected advanced thermoluminescence dating as a procedure best appropriate for frozen ground. The present paper concerns with the dating technology, advantages of the new approach, and testing results.

The formation of permafrost was associated with climate change reflected in the sequence of Quaternary events. Deciphering the rhythms of the process is a key research objective which requires good chronological ties. The age ties provide indispensable reference for reconstructing milestone events as an outline for the past history and possible future of permafrost. Yet, getting this data is not so easy for technological limitations in the standard dating methods. With the aim of improving the instrumental facilities for permafrost studies at the Institute of Earth's Cryosphere (Tyumen), recent age methods have been inventoried in order to extend the scope of rocks and related events fit for dating. As a result, advanced thermoluminescence (TL) dating was selected as the best appropriate procedure for frozen ground, which was tested on different objects in Russia and abroad [*Sheinkman et al., 2001, 2011; Sheinkman, 2002a, b; Shlukov and Sheinkman, 2002, 2007*].

The advantages of the new approach become clearer when compared with other methods of permafrost dating analyzed in their specificity. This specificity is often poorly understood, which brings about errors in the inferred chronology and makes interpretations ever more problematic, the available dates of many permafrost complexes being few and controversial. There are several reasons for this situation. Dating implies identifying a physical process the rocks have undergone and, thus, selecting the respective proxy to be plotted in time series. However, people who study the physics of the process may be unaware of permafrost formation details while those who use the age data rarely look into geochronological technologies far enough to update them.

Rocks are commonly dated proceeding from radioactivity, which is employed in different ways in two large groups of age methods based on radiometry or dosimetry. The two differ in the dating principles and in sampling procedures. The *radiometric* techniques stem from radioactive decay of a radionuclide timer in a certain closed system when the concentration of the progeny indicates how long the timer has stayed in the system. For instance, the decay of ^{14}C accumulated in organic matter allows quite exact timing of organic-bearing rocks, but within a limited span of 40–50 kyr by the common procedure or up to 70–75 kyr by accelerator mass spectrometry (AMS) which appeared not long ago. The AMS technique is applicable to other radioactive elements as well but these can provide only implicit evidence for the age of permafrost. Accumulation of ^{10}Be and ^{26}Al on the surface (a few mm layer) of quartz-bearing bedrock, for example, can measure the time when the rock was exposed on the surface and thus record the respective events. Note that these time spans are already as long as hundreds of thousand or millions of years. Yet, the radiometric dating instruments are expensive and sophisticated. That is why, although being highly precise and easy in the required sampling, radiometry is of a limited use for frozen ground where timer radioactive elements are scarce.

The methods of *dosimetry*, among which is the one we describe, make an alternative to radiometry as they employ radioactivity in a reverse way. Instead of the decay products left in rocks, dating is against the amount of radiation dose the minerals have absorbed, i.e., measured is the gain of radioactive energy rather than its loss. Most techniques are based on stimulated luminescence (thermally stimulated luminescence in our case) of ubiquitous timer minerals, commonly silicates, for the age spans of hundreds of kyr. In the case of frozen ground, however, there is a pitfall of climate noise the silicate timers being highly sensitive to environment changes.

After a number of experiments, we have found out how to avoid the negative effects in dating permafrost without loosing the advantages of the thermoluminscence technique. In the TL method, luminescence is stimulated in minerals which can be both dosimeters and luminophors and, when heated, can re-emit as light the previously absorbed energy from external radiation fields. Bearing in mind that the earlier obtained ages of many dosimeter minerals may be wrong, our primary objective was to select the most reliable timer mineral. It was quartz, which stands out against other minerals in its well-defined lattice, chemical stability, high strength, and ubiquitous occurrence in almost any rock. Its pronounced and explicitly documented properties can provide a realistic time reference for most of the objects of our interest.

Quartz shows low luminescence at temperatures about 150–400 °C. The process is as follows. Quartz absorbs radiation at the account of free electrons released upon its bombardment with radiation products, especially gamma quanta. Having gained additional energy from the γ quanta, electrons in the valence shells become excited and some escape from their places leaving a positive hole charge. The escaping electrons wander over the molecule for some time (and this time characterizes the metastable state of the molecule), but there are positively charged sites other than the hole carriers: the capture sites or electron traps. The free electrons tend to recombine according to the tendency of the electron ensemble to return to its stationary state: some move back to the valence shell when they meet holes but others fall into traps to be taken up.

Traps with high capture energy (deep traps) in the timer mineral become at some point emptied and then recharged from the ambient radiation in a newly formed rock. This process can be diagnostic of the time the timer mineral stays in the rock, i.e., can be used in dating the latter. The traps, which are controlled by the lattice structure, may be hard to recognize. Quartz is a good timer mineral as it has been well studied, and traps are easily spotted in its regular lattice. According to our experience [*Sheinkman, 2002a; Shlukov and Sheinkman, 2002, 2007*], electron traps in quartz are stable and appear to arise at vacancies left by oxygen anions. For various reasons, quartz originates with a certain number of oxygen vacancies and, if oxygen anions are absent, positive charges form in their place with a capture energy about that of the hole charges in the valence shells. This is the main type of electron traps in quartz.

On heating to high temperatures, electrons leave the traps with emission of photons (light quanta), and this luminescence shows up clearly as a peak at about 300 °C. (There are also smaller traps in quartz, but they are less important). In other words, the energy the mineral can store in electron traps can release upon heating while the equivalent light sum can be measured and assigned to traps of a certain type.

The following objective consisted in choosing the procedure for estimating the energy stored by the dosimeter mineral. However, before we had to solve the sampling problem because its previous rules could not provide reliable dating.

In our case, the sampling rules were determined empirically and subjected to statistical checks to avoid random signatures. That required dramatic methodological changes, namely, using mass sampling instead of collecting few single samples and developing special techniques for treating large quantities of sampled material.

Note that frozen ground is a particular object, and TL analysis should be applied with regard to all minute details of sedimentation. The exposure time of the timer mineral is commonly estimated from TL peaks corresponding to the amount of energy (radiation dose) the mineral has received and the activity of the radiation field in the analyzed rock. This seeming straightforwardness and the tendency of simplifying the sampling procedure led to controversy, because the rules of TL sampling actually should be very strict. That is what we have found out.

First, sampling and measurements of radioactivity should be performed *in situ*, in a monolith block of rock, at least 1.2–1.5 m below the surface (length of gamma-ray tracks), with regard to possible migration of mobile radionuclides along cracks. The simplified procedure accepted earlier, with sampling near the ground surface, without *in situ* measurements, and calculation from the element abundances in a sample [*Aitken, 1985*] will not do. A sample receives ambient radiation from a piece of rock as a whole (up to several tons), in which radioactive elements are randomly scattered, but the rock block is too big and heavy to be collected as a sample; otherwise, taking into account the scatter of radionuclides in it is unrealistic. Yet, that standard procedure has been still in use, and we held a special experiment to estimate the error it may run. Samples were collected from different depths and the earlier simplified sampling procedure turned out to give tens of percent greater scatter of ages than the one we suggest.

Second, one has to bear in mind that only carefully bleached (quasi-zeroed) sediments containing a timer mineral are fit for dating. It means that the electron traps should be as empty as possible before the timer mineral becomes buried; only since that time on, the absorption of a new radiation dose in the sedimenting material will be the age criterion, and only then the dosimeter mineral can become a timer. There are two main ways of bleaching. One is by heating the timer mineral to above 300 °C, which allows dating to be applied to objects stored in permafrost, such as baked pottery, deposits affected by forest fires or hot lavas before burial, etc. The other way to empty electron traps in quartz is uniform UV radiation, which means a possibility of TL dating on aeolian sand previously exposed to the sunlight or on fine-grained deposits washed in the alluvium of river spits and deltas.

Third, TL dating is applicable to rocks in which the radiation field is stable. This field is produced mostly by U- and Th-series isotopes, as well as by ^{40}K, with their half-lives far longer than the age of the dated rocks (of the order of many hundreds of kyr). Nevertheless, the stability of the radiation source does not necessarily mean the stability of radiation the timer mineral has been exposed to, because some filters may arise from time to time between the mineral and the source. A part of radiation may be intercepted by water films that coat mineral grains and, being either present or absent, can change the dose. On the other hand, one may be positive only about the radioactivity measured at present, i.e., one has to be sure the values may be extrapolated safely to the greatest part of the dated period. Therefore, only the rocks that have not experienced significant changes in ice and water contents are suitable for TL dating, namely, monolith permafrost outside the active layer.

Fourth, no correction can allow for all wrong estimates of radiation received by the timer mineral. Spike dates always occur and can be leveled out only through mass sampling and statistical checks, which, being too cumbersome [*Frechen and Dodonov, 1998*], have been rarely applied in the standard dating procedure [*Aitken, 1985*]. Furthermore, shortcomings have been found also in the basic principles of the latter [*Shlukov et al., 1993*].

Dating implies comparing signals from a sample which has absorbed most of radiation energy with those from test bleached samples. Bleaching (conventional datum) is quite simple: one has to expose a sample to UV light. However, recharging has been commonly done with laboratory high-energy radiation for the sake of rapidity. Our experiments showed that the intense radiation as short as a few days and the slow natural radiation in low fields for thousands of years are quite different in their effect on dosimeter minerals. The reason is that the natural TL kinetics turns out to be second-order, as it was revealed experimentally [*Shlukov and Sheinkman, 2002, 2007*], instead of the theoretically predicted first-order kinetics which was assumed *a priori* in the traditional TL dating technology and biased strongly (up to several times) the dates.

The kinetics of luminescence concerns with laws of its buildup and decay in luminophor minerals. Luminescence is defined by the probability of uptake and release of photons [*Fok, 1964; Antonov-Romanovsky, 1966; Prokhorov, 1990*]. In the simplest case when the duration of the process is neglected, it is an exponential function:

$$I = I_0 \exp(-t/\tau).$$

The decay kinetics of recombination luminescence (as in our case) in a wide time range is approximated by the Becquerel hyperbola:

$$I = I_0/(1 + pt)^{\alpha},$$

where I_0, I are, respectively, the luminescence intensities at the times t_0 and t; τ is the Einstein coefficient corresponding to the mean time while the electron ensemble stays excited; p is the constant responsible for the lattice structure; α is the order of kinetics (1 and 2 for the first and second order, respectively).

In the first-order kinetics, the excitation time is relatively short: luminescence builds up quickly and decays instantaneously, i.e., electrons rapidly leave the traps and return to the valence shells. The TL curve in the first-order model has a sharp peak (Fig. 1, *b*), and most of its rising part is virtually in mirror symmetry with the falling segment. Theoretically this pattern corresponds to the case when repeated capture of electrons is impossible. However, in the second-order kinetics, the electron ensemble remains in the metastable state for a relatively long

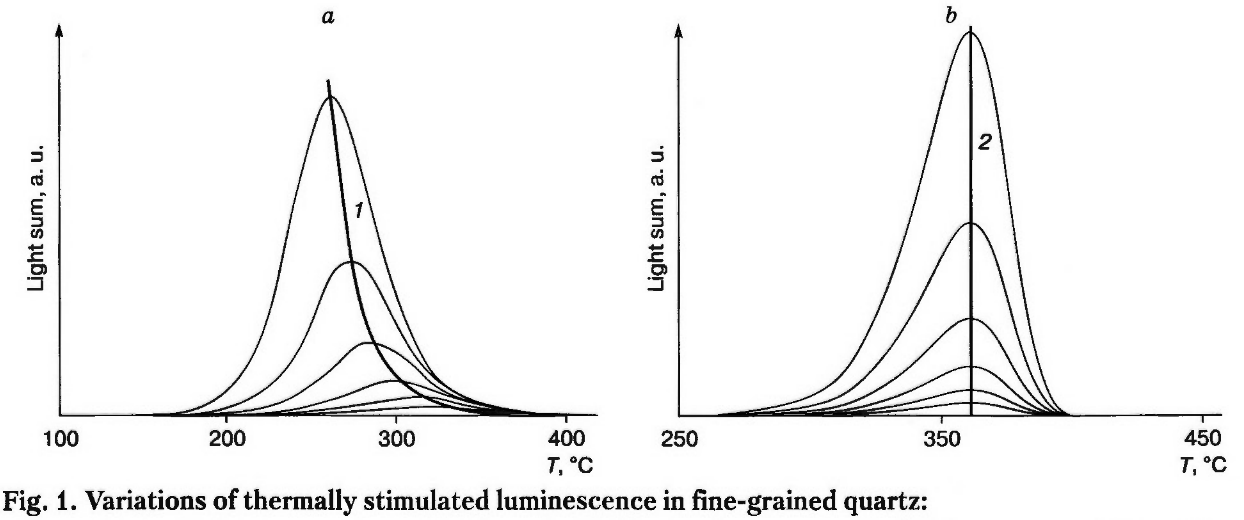

Fig. 1. Variations of thermally stimulated luminescence in fine-grained quartz:

a – second-order TL kinetics: experiment; *b* – first-order TL kinetics: theory; curves *1* and *2* show position of TL peak lines. See text for explanation.

time, and luminescence decays slowly (even though it builds up rapidly) because the once released electrons can be captured again at neighbor traps and escape again. In this case, the TL curve has a low slope in the region of high temperatures (Fig. 1, *a*).

Luminescence in the two cases is estimated in different ways. Namely, luminescence is proportional to electron metastability time (with some factor) at first-order kinetics ($\alpha = 1$) but their relationship is exponential in the second-order case ($\alpha = 2$). Yet, the previous TL dating method has been based on the first-order kinetics model, which became "canonical". The light sum in that model was just fixed instead of being calculated with regard to its slow decay, and that was the cause of dating errors.

The order of kinetics can be identified mainly in a graphic way and required a careful experimental work with the quartz samples in our case. Repeated tests with quartz particles from different sites [*Shlukov and Sheinkman, 2002, 2007*] showed that, when viewed in detail, the TL process is clearly delayed at high temperatures (Fig. 1, *a*). Therefore, the treatment of samples and the data processing had to be different and to proceed from the second-order kinetics, i.e., the basic principle of TL dating needed a major revision.

In the standard procedure, the tested sample is divided into equal aliquots, and each aliquot is irradiated in laboratory at a high intensity increasing progressively for each following aliquot. Then the time dependence of the received dose (dose curve) is extrapolated according to the logarithmic saturation law, and the age of the sample is calculated from its position on the dose curve (Fig. 2, *a*) assuming that the stimulated luminescence reflects a simple TL signal with the first-order kinetics (Fig. 2, *c*).

However, this extrapolation turns out to be wrong [*Shlukov and Sheinkman, 2002, 2007*]. Irradiation in high-energy fields, which are orders of magnitude more intense than those in natural rocks, gives rise to reversals in the state of electron ensemble and reactivates small traps that are dormant in natural conditions. As a result, the TL signal bears peaks associated with those additional traps (dashed line in Fig. 2, *d*), and the dose curve departs strongly from the theoretical one (Fig. 2, *b*). Inasmuch as laboratory irradiation is rather expensive, the aliquots are commonly few, and may bias the ages if correspond to the

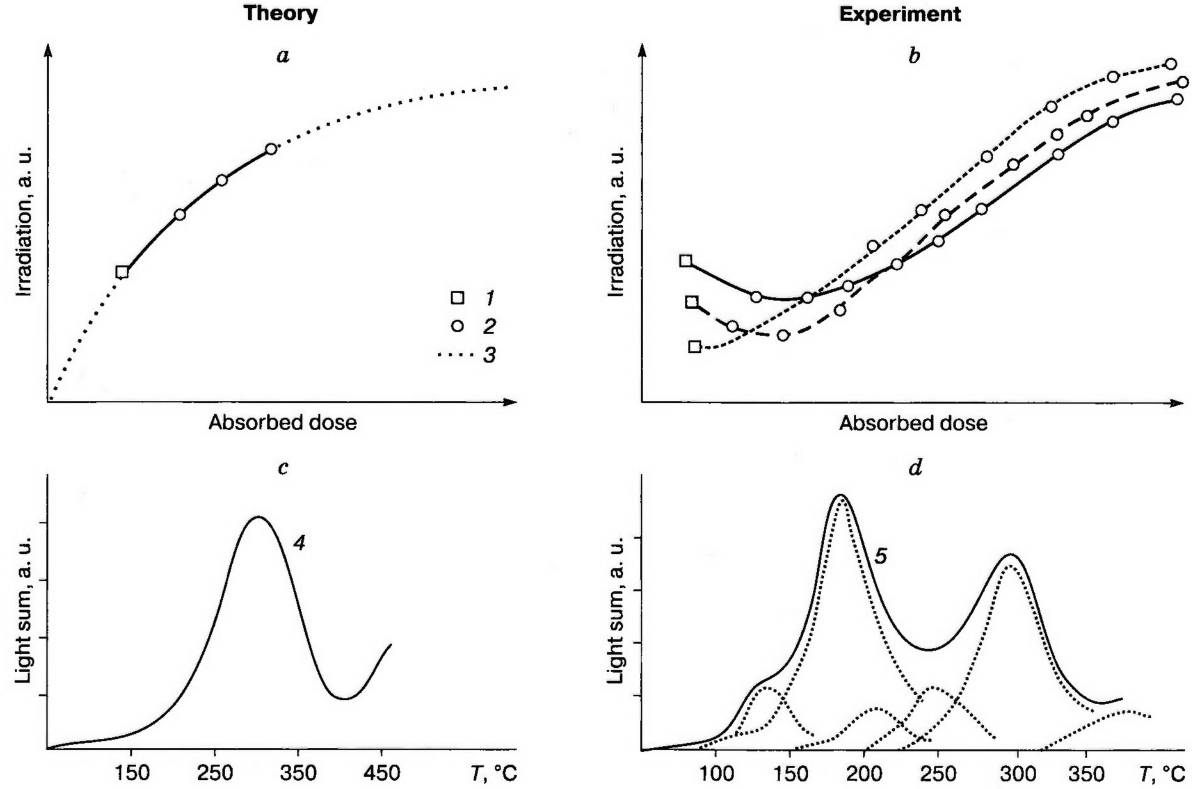

Fig. 2. Theoretical interpretation of data in the standard TL dating approach (*a*, *c*) and its real application (*b*, *d*) in experiment:

1 – radiation dose received by the tested sample *in situ*; *2* – radiation dose received by aliquots of the tested samples after their rapid laboratory irradiation in a high-energy field; *3* – extrapolated time dependence of radiation dose; *4* – TL curve of the tested sample; *5* – TL curve of the laboratory irradiated sample.

distorted segments of the dose curve. Furthermore, the classical procedure estimates the total TL signal while the peaks and troughs are averaged and elevated to the level of a virtual plateau. The main focus being on the averaged luminescence peak, the optical properties of quartz have been neglected but they differ in different quartz varieties, as it was shown in experiments, and likewise influence the output luminescence. Nevertheless, even after our data had been published [*Shlukov and Sheinkman, 2002, 2007*], the followers of the standard procedure took the way of making the dating instruments more sophisticated (and thus more expensive) and applying corrections rather than changing the principles.

With the aim of obtaining a reliable and, if possible, straightforward method which would allow treating a large number of samples, we refused the previous unreliable dating criteria and cumbersome procedures. In the new approach, they are the coordinates of TL peaks in the dose curve, instead of the peak intensity, that make a more reliable age criterion based on second-order TL kinetics. This criterion, which stems from the more stable thermal rather than optical properties of quartz, was missed in the first-order kinetic TL model as its recognition would require a different problem formulation and instrumental background. The validity of the suggested approach has been confirmed in repeated tests: the younger the sample (Fig. 1, *a*) the lower and the higher-temperature its TL peak. The range of these shifts toward high temperatures (over 100 °C) is quite enough to obtain precise dates.

Thus, the new criterion cancels the drawbacks of the standard methods and changes the very approach to TL dating. The suggested technique is an order of magnitude cheaper and much easier to perform than the classical procedures, which makes it a high-quality and accessible tool for investigating permafrost. Its reliability has been validated additionally by checking the new TL dates against radiometric dating [*Shlukov and Sheinkman, 2002, 2007; Sheinkman et al., 2011*].

In conclusion, we note that the background for geoscience applications of TL dating was first developed in the 1960s by G.V. Morozov in the Ukraine and A.I. Shlukov in Russia [*Morozov, 1968; Shlukov et al., 1993*]. The Russian science has laid a solid foundation in this field of research and long remained the leader, but the leadership has been lost lately and alarming tendencies are currently appearing. Some geoscientists (see the review in [*Sheinkman, 2008*]) suggest to refuse TL dating at all referring to its ambiguous results without proper understanding the idea of the method while others praise foreign technologies which try to repair the drawbacks through updating the instruments. Yet, both ways are deadlock.

The suggested approach based on studies in Russia does not claim to be panacea but it allows making good progress in solving the urgent dating problem and, moreover, creates prerequisites for advance in geochronology of permafrost. This is especially important as the chronological constraints of events in geosciences are crucial for synthesis of the existing experience and gaining new knowledge. In this respect the new approach can be used for systematizing all available data with reference to the time scale.

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