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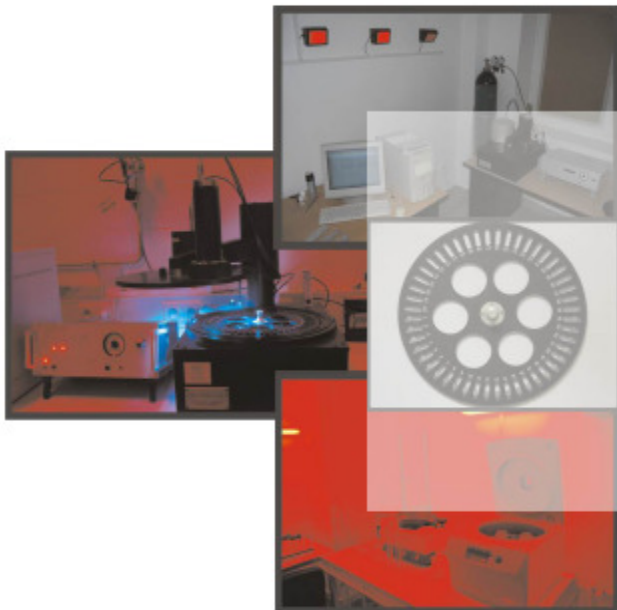
Teză de doctorat

Summary

Retrospective luminescence dosimetry: applications in archaeology, geology and environmental studies

Dozimetrie retrospectivă luminescentă cu aplicaţii în arheologie, geologie şi mediu

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Key words:

- ➢ **retrospective dosimetry**
- ➢ **optically stimulated luminescence (OSL)**
- ➢ **thermoluminescence (TL)**
- ➢ **infrared stimulated luminescence (IRSL)**
- ➢ **natural radioactivity**
- ➢ **high resolution gamma spectrometry**
- ➢ **natural crystals**
- ➢ **quartz**

- ➢ **luminescence dating**
- ➢ **absolute ages**
- ➢ **archaeology**
- ➢ **ceramics**
- ➢ **palaeoclimatology**
- ➢ **loess**
- ➢ **paleosoils**

ABSTRACT

The objective of this thesis was to implement luminescence dating at Babeș-Bolyai University and to apply state-of-the art dating technology to materials that are relevant to archaeology and earth sciences. Chapters I-III present luminescence methods as well as procedural and methodological intrinsic rigor tests. The work on Neolithic ceramics from Lumea Nouă (Chapter IV) represents one of few studies available in international literature that apply SAR-IRSL and OSL luminescence dating technology to ceramics and demonstrate the potential of these modern techniques for establishing chronological frameworks of archaeological sites. In the last chapter, fundamental as well as applied luminescence research of Romanian loess is presented. The results obtained show that luminescence dating of loess is far less straightforward than generally is accepted and thus challenge earth-scientific as well as luminescence dating communities.

1. Retrospective luminescence dosimetry – brief definition of terms

The term retrospective dosimetry refers to techniques used for evaluation of past radiation exposure in media of interest.

Luminescence phenomena encompass a very wide range of processes. Generically, based on the decay times associated with the luminescence emission, these processes are divided into fluorescence (decay times ranging from 10^{-9} to 10^{-3} seconds (*Ropp, 2004*) and phosphorescence (delayed emission, with a decay time of more than 10^{-3} seconds).

For the purpose of retrospective dosimetry only optically stimulated luminescence (OSL) and thermoluminescence (TL) processes are of interest (*Bøtter-Jensen et al., 2003*). OSL and TL is the luminescence emitted from an irradiated insulator or semiconductor during exposure to light or heat, respectively. According to the classification based on the decay times, OSL and TL can be regarded as a fluorescencent process. However, it should be emphasized that OSL and TL are stimulated processes, and they are usually accompanied by photoconductivity phenomena. The luminescence signal emitted is dependent on the irradiation history of the sample. In the case of OSL the wavelength of the emitted signal is shorter than the wavelength of the stimulation. Thus, materials used in retrospective luminescence dosimetry are anti-Stokes phosphors.

Based on luminescence methods, retrospective dosimetry has two main applications: dating and accident dosimetry.

Luminescence dating is based on the property of certain minerals to store the energy of nuclear radiation. A low level of nuclear radiation is omnipresent in nature, and the longer the minerals are exposed, the more energy they store. By stimulation with heat or light, the minerals can release part of this energy by emitting a small amount of light, which is called luminescence. The intensity of this luminescence signal is a function of the total accumulated radiation dose, and hence also to the total acquisition time.

There are two variants of luminescence dating, namely thermoluminescence (TL) and optically stimulated luminescence (OSL) dating, depending on whether the luminescence is stimulated by heat or light, respectively. OSL dating is also simply referred to as optical dating. More specific terms can be used depending on the wavelength of the stimulating light, such as infra-red stimulated luminescence (IRSL), green light stimulated luminescence (GLSL or GSL) or blue light stimulated luminescence (BLSL or BSL).

In all of the cases the latent dating information is carried in the form of trapped electrons. These electrons are produced by the interaction of the nuclear radiations with the atoms of the mineral and then may get trapped in certain defects of the crystalline structure. The number of trapped electrons is a measure for the total dose – **the paleodose** or the **archaeodose** (the total amount of energy absorbed from the ionizing radiation) the mineral has received over a certain period of time. If also the rate is determined by which the mineral has been absorbing the dose – **the annual dose**, this period of time (i.e. an age), can be determined. The paleodose or the archaeodose is a combined dose, resulting from exposure to α, β and γ radiation, it cannot be measured directly. Therefore, it is determined as an **equivalent dose**, i.e. the amount of artificial dose delivered by irradiation in the laboratory that induces a luminescence signal identical to the natural one in the sample. The annual dose is derived by calculation based on the estimation of environmental nuclide concentrations.

The moment that is dated with luminescence techniques is a zeroing event during which all the effects on the mineral of its exposure to radiation are removed. In the case of pottery, the zeroing is caused by the firing, the final part of the manufacturing process. For sediments, the zeroing event is the exposure of the sediment grains to sunlight during transportation, prior to deposition. Once the zeroing agent is removed, for instance when sedimentary minerals are deposited and shielded from sunlight by other grains falling on top of them, the luminescence signal starts to build up again. The signal can also be removed in the laboratory by exposing the mineral grains to the same zeroing agents (heat or light). This time, the luminescence signal is measured and used to determine the time that has elapsed since it was last set to zero.

Thus, the aim of luminescence dating is to determine the total radiation dose absorbed in minerals throughout time from which an age can be derived. In accident dosimetry the goal is to reconstruct the doses absorbed by available materials as a consequence of radiation accidents. These doses are superimposed on the doses determined in dating applications (*Bailiff, 1999; Bailiff et al., 2000; Göksu et al., 2002; Bailiff et al., 2004*). The techniques used in accident dosimetry and dating applications are identical (*Banerjee, 1999; McKeever, 2001; Bøtter-Jensen et al., 2003; Thomsen, 2004*)

2. Aim of our work

Luminescence methods are important analytical techniques for dating worldwide (reference can be made to review works of *Aitken, 1985, 1998, 1999; Roberts, 1997; Stokes, 1999; Duller, 2004; Lian et al., 2006; Wintle, 2008a, b, respectively Cosma et al., 2008b,d and Timar, 2008b, 2009c-in Romanian*). Despite this, the method was not thoroughly applied in Romania up to now. It should be mentioned that some attempts in using thermoluminescence for dating were made in the past by Professor V.V. Moraiu in Cluj in the 1980s and by a group in Bucharest in 1990s (*Labău et al., 1996*) but the research was abruptly ceased for reasons we are not aware of. The interest of the group of Professor Cosma in luminescence dating dates for more than one decade ago (*Văsaru and Cosma, 1999*), and our first applications have been carried out using a Harashaw 2000 dosimetric system (*Cosma et al., 2006; Cosma et al., 2008a,c*). In 2006, the material means necessary to develop a modern luminescence laboratory affiliated to the Faculty

of Environmental Sciences of Babeş-Bolyai University Cluj were finally obtained through a research grant. The work presented in this thesis started in the same year and its structure is undoubtedly linked to the development of the first state of the art luminescence dating laboratory in Romania.

The first aim of our work was to **ensure that the methodology applied in Luminescence Dating Laboratory in Cluj both in the case of gamma spectrometric measurements (for radionuclide specific activity determination in environmental samples) as well as for sample preparation and luminescence measurements are robust in order to be able to obtain accurate values for both annual dose and equivalent doses of samples investigated**. In order to do that, both internal checks and intercomparison exercises with other laboratories have been performed. The second but more important aim of this thesis was **to apply state of the art luminescence methodology in dating archaeological and geological materials of interest.**

For archaeological applications, the Lumea Nouă site was chosen, as this location is considered to be of major importance for reconstructing the Neolithic and Aeneolithic periods in Romania and well known for its Neolithic painted pottery.

Most efforts were conducted into applying luminescence methods for dating geological materials, in particular the famous loess palaeosol sequence of Mircea Vodă. We have chosen this application because it is widely recognized that Romanian loess sequences preserve a significant terrestrial record of Quaternary climate change, but in comparison to similar sequences elsewhere in Central and Eastern Europe, the deposits in Romania have been less extensively studied (*Frechen et al., 2003*). Having an absolute chronology on Romanian loess sequences is of uttermost importance as these sequences are thought to be amongst the thickest and most complete in Europe, and they form the link between the glacial loess deposits of Western and Central Europe and the non-glacial loess deposits that extend all the way to China. Obtaining an absolute chronostratigraphical framework for the Romanian loess deposits is essential to determine (i) the timing of climatic events that are registered in the loess, (ii) the rate of processes such as sedimentation and pedogenesis and (iii) the correlation between the loess sequences that are spread all over Europe.

We point out as well that by reconstructing past climates and the climatic variation throughout time data obtained can be used to test the accuracy of computer models that simulate climatic change. Simulations of the radiative impacts of dust under present climate conditions have been performed and already incorporate the effects of anthropogenically derived dust (*Tegen et al 1996*). However, the impact of the changes in the productivity of natural dust sources over geological time and the incorporation of dust deflation, transport and deposition processes is just beginning as spatially extensive data sets documenting the observed changes in dust accumulation rates during the last interglacial-glacial cycle are required in order to test model simulation of dust cycles (*Harrison et al 2001*). Thus investigation of sediment deposition in relation to palaeoclimatic changes is a major focus in modern earth modeling because having an accurate knowledge of the aeolian sedimentation rates during the Quaternary may help in creating extended models of dust cycles and thus of climate change, with eventually making predictions on future trends possible. Thus, dating sedimentary deposits is important for environmental sciences not only as a matter of reconstructing the past trends but also for predicting future ones.

3. Outline of the thesis

The thesis is structured in five chapters. **Chapter I** presents the basic principles of luminescence processes and how these phenomena can be used for dating, including a discussion on signal growth and lifetime. The general one trap model is presented as well as the more complex model developed by *Bailey (2001)* for optical stimulated luminescence of quartz, and the model proposed by *Hütt et al. (1988)* for IRSL emission of feldspars. Excitation and emission spectra of quartz and feldspars are presented as well as a comparison of their decay curves with more emphasize on quartz signal components under the two stimulation modes used routinely in this work (continuous wave optically stimulated luminescence CW-OSL, respectively linearly modulated luminescence LM-OSL). A presentation of anomalous fading of feldspars is also included along with the method used in this work (*Huntley and Lamothe, 2001*) for correcting for this malign phenomenon. Although this chapter is based on the study of literature it also contains own research in order to illustrate the properties described.

Chapter II briefly presents the techniques and methodologies available for equivalent dose estimation. Emphasize is placed on the SAR protocol as this technique was used throughout the present work. The underlying assumptions of the protocol are presented and their fulfillment is exemplified by showing the behavior of samples investigated in this work. This chapter contains also the description of the sample preparation techniques used throughout this work in order to extract coarse (90-125µm, 63-90µm, 35-50 µm) quartz, polymineral fine grains and respectively fine quartz (4-11µm), along with a short presentation of luminescence measurement facilities used, including the checks routinely performed in order to verify their suitable functioning. The calibration procedure of the radioactive sources used in our study is described to a somehow grater detail.

Chapter III is structured in two parts. The first part presents specific aspects associated with the evaluation of the annual dose. In the following part gamma spectrometric methodologies used for natural radionuclides specific activities measurement implied in our laboratory are presented. These are based our previous experience with environmental radioactivity evaluation (*Begy et al., 2007, 2009a,b; Cosma et al., 2007, 2009a, b, c; Timar et al., 2007, 2008a*). An intercomparison exercise for determining the radionuclides concentration in soil samples performed between our laboratory and two other laboratories using independent methods (-alpha spectrometry carried out in the Laboratory of Radiochemistry Veszprem, Hungary respectively instrumental neutron activation analysis carried out at the Institute for Nuclear Research, Pitesti, Romania) in order to validate our methods is presented.

Chapter IV presents the actual application of luminescence dating in archaeology, work being carried out on four pottery fragments excavated at Lumea Nouă (Alba Iulia, Romania). The application of single-aliquot regenerative-dose (SAR) protocol to both blue (OSL) and infrared stimulated luminescence (IRSL) signals from coarse (90-125 µm) quartz and polymineral fine (4-11 µm) grains, respectively is described in detail, along with a more conventional approach, which used a multiple-aliquot additive-dose (MAAD) protocol and thermoluminescence (TL) signals from polymineral fine grains. Quartz OSL ages obtained are compared to the conventional TL ages and to the fading corrected IRSL ages and the reliability of the investigated protocols is discussed. Data presented are based on a former collaboration of colleagues in

Babeş-Bolyai University of Cluj, Appulum University of Alba Iulia and Gent Luminescence Dating Laboratory (*Benea et al., 2007*) and serve as an example on how luminescence dating, especially by the use of the state-of-the-art techniques can contribute to establishing a complete chronological framework for the ancient cultural development in Neolithic sites.

Chapter V presents the application of optical methods on geological samples. The main part of the chapter presents the detailed description of the application of optical dating using quartz as a dosimeter for the purpose of establishing an accurate chronology of deposition for Mircea Vodă section in South Eastern Romania (*Cosma and Timar 2008e; Timar et al. 2008c; Timar et al., 2009 a, b; Timar et al., 2010a,b,c*). The behavior of both fine (9-11 µm) quartz grains and silt sandy (63-90 µm) quartz grains in the SAR protocol is presented in great detail, along with a comparison of equivalent doses obtained from fine grains in our laboratory and Gent Luminescence Dating Laboratory. A thorough study on the luminescence optical properties (thermal stability tests, LM-OSL analysis, growth curve characteristics, equivalent dose distribution analysis etc.) of the two grain fractions is also presented. The potential and the limitations of applying SAR OSL dating on quartz for dating Romanian loess is discussed in detail. In Section V.2 luminescence techniques are applied for dating soil covers from the forest steppe zone in Transylvanian Basin (*Timar et. al., 2010d*)

The studies presented serve to illustrate the contribution that luminescence dating methods can make to archaeological and paleoclimatic research in Romania and **conclusions** are subsequently summarised.

4. Quality assurance of procedures implemented for equivalent and annual dose estimation

4. 1. Quality control for the equivalent dose measurements

Sample and aliquot preparation

Conventional procedures (*Zimmerman, 1971; Lang et al., 1996; Frechen et al., 1996*) were used to extract coarse sized quartz, fine quartz grains and polymineral fine (4-11µm) grains from the

samples. All sample preparation was carried out under subdued red and orange light (Encapsulite R-10, Ilford 902 safelights). Samples were treated overnight with diluted HCl (10%) to remove carbonates, and then repeatedly washed with distilled water. To remove organic materials, 10% H_2O_2 was added and the mixture was again left overnight. The following day more concentrated 30% H_2O_2 was added. The mixture was left for 24h to assure a complete removal of organic materials, and was subsequently washed several times with distilled water. Following this pretreatment, wet sieving was performed.

After sieving, this fraction consists of an undifferentiated mixture of minerals, including quartz, feldspars and heavy minerals. These minerals have slightly different densities and can be separated in suspension using heavy liquids. The heavy liquids used were solutions of sodium metatungstate $Na_6[H_2W_{12}O_{40}]$ $xH2O$ (a heavy inorganic salt) with distilled water. First the polymineral sample is suspended in a solution with a density of 2.62 g/cm^3. This enables the separation of quartz and plagioclase grains from the lighter minerals such as clay, potassium and sodium feldspars. Subsequently, the mineral grains are suspended in a solution with a density of 2.75 g/cm^3. In this case, quartz and plagioclase feldspars will float while heavy minerals such as zircons and apatite will sink. The floating fraction was kept, washed and dried.

Quartz can no longer be separated from plagioclase by means of difference in density. Therefore, a treatment with 40% hydrofluoric acid (40 min) was performed for coarse grains, respectively, 35 % hidrofluorosilicic acid ($H_2 Si F_6$) (5 days) for quartz fine grains. The feldspars are less chemically resistant and are dissolved. The etching also removes the outer surface of the quartz grains, which reduces the external alpha particle contribution to these grains to a negligible level. A 60 min wash with warm (50°C) dilute HCl was applied after etching to remove any precipitated fluorides. This was followed by repeated washing with distilled water and drying. Finally the product was sieved again sieve.

To extract polymineral fine grains, the fraction < 36μm was first put in beaker and (NH_4OH) was added for deflocculating. The fraction less than 11μm were then isolated by settling in Atterberg cylinders according to Stokes' law. The removal of the grains < 4 μm was carried out in a centrifuge using the method described by *Frechen et al. (1996)*.

For measurement, the quartz grains were sparingly poured through a sieve on stainless steel disks. Silicon oil was used as adhesive. The silicon oil used was tested and it was concluded that it does not give any parasitic signal.

For polymineral fine grains and quartz fine grains aluminum disks were used. Aluminum is advantageous because it has the same scattering characteristics as quartz and feldspars. For measurement, aliquots were made by pipetting a 1 ml suspension of the fine grains (2mg of grains /1 ml acetone) onto each aluminum disc. Prior to pipetting, the solution was homogenized in an ultrasonic bath. The acetone was then allowed to evaporate either at room temperature, or in an oven at ~50°C.

Testing the purity of quartz extracts

Theoretically, complete feldspar removal from samples is desirable. In practice however, it is important to have a negligible contribution from feldspars in the signal analyzed for equivalent dose estimation. Several tests have been used to check the purity of quartz extracts in this work. In most studies, a signal above background in response to IR stimulation is attributed to feldspars, as at room temperature the fast component of quartz OSL is not stimulated by IR (*Aitken, 1998*), whereas a large variety of feldspars respond to IR excitation by emitting in the UV (*Krbetschek and Rieser 1995, Krbetschek 1997*). All samples have been analyzed based on this criterion and yielded negligible IR signal compared to signal collected under blue stimulation (**Figure 1**)

The "IR depletion ratio" test (*Duller, 2003*), uses the ratio of the sensitivity corrected [post-IR]-OSL, ($L_{x\ post-IR}$ / $T_{x\ OSL}$) to the sensitivity corrected OSL (L_x / $T_{x\ OSL}$). This test is based on the assumption that the UV recombination centers in feldspars responsible for IRSL and OSL share the same source traps, as indicated by *Jain and Singhvi (2001)*. This test has been applied to every aliquot analyzed throughout this work by making an additional measurement at the end of each SAR run. It was extremely rare that aliquots were rejected based on this criterion. Average values obtained for this test for samples analyzed are quoted in for all measurements.
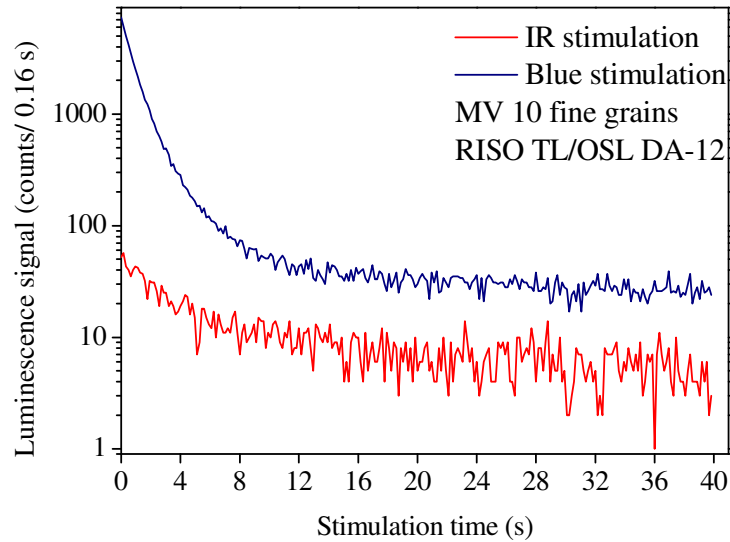
Figure 1: *UV signals stimulated in blue light (@125 ^{o}C), respectively IR (@60 ^{o}C for sample MV10 fine grains (natural)*

A general observation that has been made is that during measurement the OSL signal from quartz tends to decrease rapidly, and to a low residual level (*Smith and Rhodes, 1994; Bailey et al 1997*), while for feldspars the initial decrease is slower and a significant tail is observed even after prolonged stimulation (*Bailiff and Poolton, 1991*). This different behavior potentially provides a mean of differentiation (*Duller, 2003*). It is known as well that pulsed optically stimulated luminescence characteristics of quartz and feldspars are very different, and the use of differences in luminescence lifetimes to discriminate between quartz and feldspar signals under pulsed stimulation has been suggested (*Denby et al, 2006*). As luminescence lifetimes associated to the fast component of quartz OSL are around 30 μs, using a pulse timing of this magnitude leads to virtually recording only the quartz signal during the off time as feldspar signals are dominated by a fast lifetime component which rises and falls with the on-period of the stimulation LEDs. **Figure 2** presents a comparison of decay curves obtained on calibration quartz and fine and coarse grains of quartz extracted from loess analyzed in this work under continous wave stimulation, respectively pulsed stimulation on time: 50 μs, off time 50μs. It can be observed that the decay rates are indistinguishable proving that any feldspar contamination is negligible.
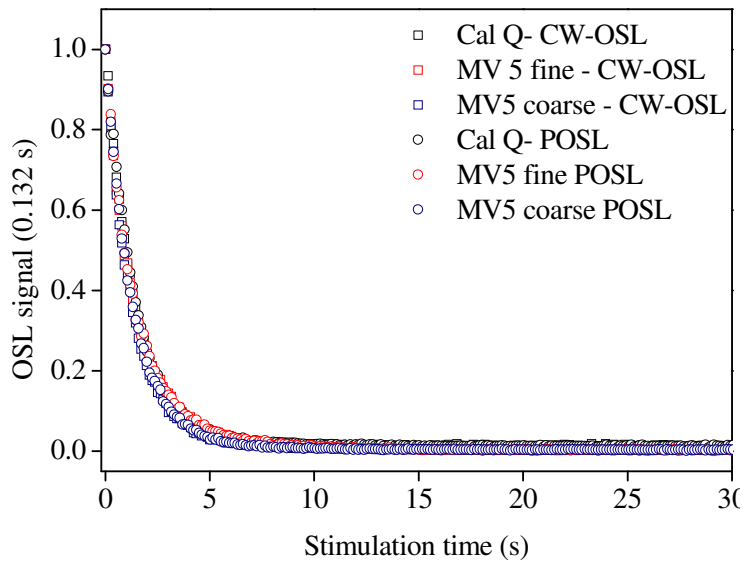
Figure 2: *Comparison of decay curves of calibration quartz and MV5 fine (4-11 µm), respectively coarse (60-90 µm) grains under continous wave stimulation, respectively pulsed (on time: 50 µs, off time 50µs). Signals have been recorded after a preheat of 10 s at 220 °C. Signal is normalized to initial intensities.*

SAR protocol intrinsic rigor tests

All equivalent doses determined in this work are based on a SAR protocol measurement routine. The SAR protocol (*Murray and Wintle 2000, 2003*) truly revolutionized optical dating, and it is nowadays considered as the technique of choice for determining the dose accrued in quartz (*Stokes et al., 2000; Murray and Olley, 2002; Duller, 2004; Vandenberghe, 2004, Wintle and Murray, 2006*).

The basic assumptions for determining the equivalent dose are:

a) The signal selected for dating comes from traps stable in geological time (the signal has to be carefully selected and the unwanted components have to be removed).

- usually this is done by applying a preheat.

b) Any competition for charge during trap filling is the same during laboratory irradiation as during natural irradiation (i.e. trap filling is the same during laboratory and natural irradiation)

- this assumption is difficult to be tested in the laboratory and was empirically showed to be fulfilled by comparing ages luminescence ages obtained by applying the SAR protocol with ages obtained on the same samples by applying other independent methods.

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c) The luminescence per unit of trapped charge is the same during all measurements.

- applying a thermal treatment before measuring regenerated quartz OSL signals is mandatory in order to isolate the stable (in archaeological / geological time) component. A further reason would be the need to redistribute trapped charge in order to prevent thermal transfer to the dosimetric trap during measurement. However, this treatment may also redistribute holes and thus can cause sensitivity changes. For further details, reference is made *to Wintle and Murray (1999), Murray and Wintle (2000; 2003),* and *Vandenberge (2004).*

The main assumption underlying the SAR protocol is that sensitivity changes occurring throughout a measurement cycle can be corrected for by using the luminescence responses to a constant test dose.

The regenerated OSL signals can than be corrected for sensitivity changes by normalizing them to the corresponding test dose responses.

Step	Treatment	Observe
1.	Give dose Di	-
2.	Preheat (at a temp between160 and 300°C for 10s)	-
3.	Optically stimulate for 40s at 125 ^{o}C	**Li**
4.	Give test dose Dt	-
5.	Heat to T < preheat in step 2 (cutheat)	-
6.	Optically stimulate for 40 s at 125 ^{o}C	**Ti**
7.	Optically stimulate for 40 s at T> preheat in step 2 (280 ^{o}C)	-
	(ETOSL)	-

Table 1: Generalized SAR measurement sequence for quartz.

The measurement procedure starts with the measurement of the natural OSL signal after the aliquot has been preheated ($D_{i=1}$=0 Gy). A test dose is then given, followed by another preheat and the measurement of the OSL response to the test dose. The test-dose preheat (cutheat) is meant to empty the shallow traps. This measurement cycle is then repeated after a regenerative dose is given, and this as many times as desired. Various regenerative doses can be used throughout the experiment but the test dose is kept constant. By dividing the regenerated OSL signals by the corresponding test dose signals, a growth curve is obtained, which is corrected for sensitivity changes.

In the SAR protocol, it can be checked for if the sensitivity correction is working properly. This is done by repeating a measurement of the response to a dose that had been previously administrated. If the responses are indistinguishable, this means that sensitivity correction is working properly. The ratio of these two corrected OSL or IRSL signals is called the **"recycling ratio"** and should ideally be equal to 1. The deviation of the recycling ratio from unity can be a criterion for acceptance or rejection of aliquots. A good recycling value can be also considered as evidence that the growth curve patter obtained is real and not a sensitivity artifact (*Wintle and Murray 2006*).
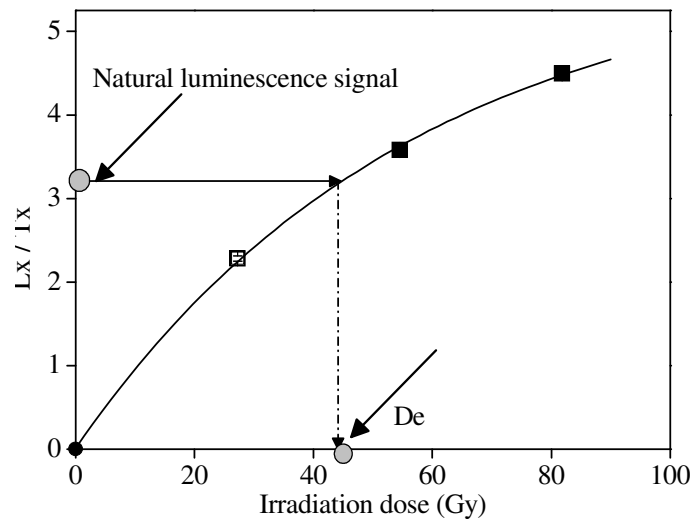
Figure 3: *Typical growth curve for sedimentary quartz constructed in a SAR protocol. The recycling point is represented as an open square while the zero-dose response is shown as solid circle. (Timar A, 2006)*

A second important test is to check whether the dose-response curve starts indeed at the origin. This is accomplished by measuring the response to a zero regenerative dose. Although one would expect this to give a zero signal, in practice a small signal is observed. The **"recuperation"** of the signal arises from thermal transfer of charge inserted by the test dose into thermally shallow but light insensitive traps which are not emptied by the cutheat. These traps are emptied by the preheat and some of this charge can be trapped into the light sensitive traps. In most cases it has been shown that this transfer is mainly not into the main OSL trap (fast component) but into other OSL traps (medium component) (*Jain 2003*). Step 7 at the end of each cycle was later introduced into the SAR protocol in order to reduce recuperation. For more details, reference is made to *Vandenberghe (2004)* and the original works of Murray and Wintle. For a sample that

behaves well in the SAR protocol, recuperation should be negligible. The amount of recuperation that is observed can be used as a criterion for acceptance or rejection of an aliquot.

The ultimate test for checking the performance of the SAR protocol is the **"dose recovery test"**. This test was first suggested for feldspars by *Wallinga et al. (2000)* and was subsequently recommended by *Wintle and Murray (2003)* for quartz as well. The dose recovery test consists of optically zeroing a sample; irradiating it with a known dose and then measuring this given dose using the SAR protocol as if it was an unknown dose.

If De measurement and dose recovery tests are performed for different preheat temperatures and a preheat plateau is obtained this is evidence that:

- *any unwanted thermal transfer is not relevant*
- *sensitivity changes are properly corrected for (as different thermal treatments may lead to a different degree of sensitivity change)*
- *the dosimetric signal investigated comes from traps that are thermally stable*

The measurement protocol is proven to be useful if the given dose can be measured accurately. However, as pointed out by *Murray and Wintle (2003)*, an accurate recovery of the known dose does not necessarily imply an accurate determination of the naturally acquired dose as well. Nevertheless, the dose recovery test does serve to increase confidence in the measurement procedure. *Murray and Wintle (2003)* also showed that the dose recovery test is a more diagnostic than the recycling ratio for evaluating the applicability of the SAR procedure to a given sample.

Recycling ratios and recuperation values have been evaluated for all aliquots investigated in this work. Dose recovery tests have been carried out on all samples.

Measurement and irradiation facilities performance tests

Measurements on quartz were performed using a Risø TL/OSL-DA-12, TL/OSL-DA-15 (in Ghent) readers respectively a Risø TL/OSL-DA-20 device in Cluj.

Calibration of the radioactive sources

Calibration of the beta source is performed by comparing the luminescence induced in a sample by a known dose (usually administrated by a calibrated gamma source) with the luminescence

induced in the same sample by a given duration of irradiation by the beta source of unknown strength. Because of the aforementioned effects of build-up, backscattering and attenuation, the calibration applies only to the precise conditions of the beta irradiation. New calibrations must be carried out for other grain sizes, substrates, etc. (*Armitage and Bailey 2005; Chen S. et al 2009*) For calibrating the beta sources, use was made of the calibration quartz produced by Risø National Laboratory.

This calibration quartz is quartz that had been annealed to a high temperature and subsequently received a known gamma dose. Calibration quartz of different grain sizes is available. The calibration was performed using the SAR protocol. This yields a value in seconds from which the source strength is easily derived. The dose rate for the Da-12 reader (Ghent) for fine grains was 0.057 Gy/s (reference date March 2008), while for the DA-20 machine (Cluj Napoca), values of 0.175 Gy/s for the coarse grains on stainless steel disks, respectively 0.135 Gy/s for the fine grains on aluminium disks (June 2008). For all the irradiations that were carried out after the calibration, allowance was made for the decrease in the strength of the sources owing to the radioactive decay of ^{90}Sr (T½ = 28.74 y).

Testing for thermal stability of the heating plate

The thermal stability and the constancy of the heating rate (5 ºC/s) for the kanthal heater element was constantly monitored making use of the 110 ºC TL peak of quartz, as it is known from the kinetics of the luminescence phenomena that TL peaks will shift to higher temperatures as the heating rate increases.

Testing for stability of the photomultiplier tube

Before each measurement was performed photomultiplier dark counts were registered for 10s. Risø systems also include a blue calibration LED. Measuring the counts using this LED assures that there is no breakthrough of the blue stimulation light into the photomultiplier through the thick Hoya UV filter when performing OSL measurements on quartz.

Intercomparison with Gent Luminescence Dating Laboratory

Several samples of fine grains of quartz extracted from loess have been measured on the

Risø TL/OSL DA-20 reader in Cluj Luminescece Laboratory as well as on the Risø TL/OSL DA-12 machine in Gent Luminescence Dating Laboratory using the same measurement protocol. The results obtained are resented in the following table and show a very good agreement between the data obtained in the two different laboratories.

SAMPLE	DE (Gy)	Recycling	Recuperation (%)	IR depletion ratio	DE UBB/ DE Gent
MV1	25.5 ± 0.4	0.98 ± 0.02	0.07 ± 0.03	0.97 ± 0.01	**1.02 ± 0.02**
MV3	67.2 ± 0.7	1.00 ± 0.01	0.05 ± 0.01	1.00 ± 0.01	**1.04 ± 0.03**
MV7	203 ± 2	1.00 ± 0.01	0.03 ± 0.01	0.99 ± 0.01	**1.03 ± 0.02**
MV9	224 ± 2	0.98 ± 0.01	0.07 ± 0.01	0.99 ± 0.01	**1.01 ± 0.02**
MV10	314 ± 4	1.00 ± 0.01	0.04 ± 0.01	1.00 ± 0.01	**1.01 ± 0.03**
MV12	433 ± 18	1.00 ± 0.01	0.01 ± 0.01	0.99 ± 0.01	**1.01 ± 0.05**

Table 2: Comparison of equivalent doses obtained for different samples in Ghent and Cluj Luminescence Laboratories.

4. 2. Quality control for annual dose estimation

Estimation of environmental radionuclide concentrations in soils, a comparison of methods for the annual radiation dose determination in luminescence dating in archaeology – a case study

The assessment of the annual radiation dose is an important step in the dating process since it influences directly the final result and its uncertainty is linearly transferred to the age.

However, in the determination of the dose rate for luminescent dating it is important to distinguish between the dose absorbed by the soil matrix and by the grain showing luminescence. For example, quartz grains separated from the soil are almost free of internal radioactivity, and the outer layer of large grains can be etched, reducing thus the contribution of alpha radiation to zero. On the contrary, the fine grain technique is concerned only with grains that have received the total matrix dose. In particular, humidity is also an important factor, influencing mostly the alpha dose received by grains (*Aitken, 1985*). Therefore the annual dose rate of radiation has to be divided at least into three contributions to the varied absorption of alpha, beta and gamma radiation. And the age calculated upon the equation:

$$Annual\ dose\ = a \cdot \frac{D_{\alpha(U,Th)}}{1+1.5WF} + \frac{D_{\beta(U,Th,K,Rb)}}{1+1.25WF} + \frac{D_{\gamma(U,Th,K)}}{1+1.14W_lF} + D_{cos}$$

Where:

a – is the alpha efficiency factor

W - is the water saturation level

-W=W_1 in the case of sediment dating

-W refers to the water saturation level of the ceramic shred in the case of pottery dating

- W_1 refers to the water saturation level of the surrounding soil in the case of pottery dating

F- fraction of saturation

Dα, Dβ, Dγ- are the α, β,γ dose rate contribution derived from radioactive elemental concentration or specific activities using conversion factors. And D_{cos} is the cosmic dose rate.

Thus, the determination of the dose rate in luminescent dating implies two steps. Firstly, the activities of the above mentioned isotopes have to be measured and then the relevant activities have to be converted to the energy released per disintegration. This energy has to be related to the alpha, beta and gamma contribution. As usual, Auger and internal conversion electrons are included in the beta part, X-ray and bremsstrahlung radiation in the gamma contribution. Conversion is performed using factors calculated from nuclear data tables, the most recent system being the one proposed by Adamiec and Aitken (*Adamiec and Aitken, 1998*).

In this work three of the most important methods available for natural radioactive isotope concentration measurement are compared, namely: instrumental neutron activation for measuring [238]U, [232]Th and [40]K, high resolution gamma spectrometry for determining the activities of [234]Th, [226]Ra, [214]Pb, [214]Bi, ^{210}Pb, [228]Ac, [208]Tl, as well as [40]K, and, moreover, concentrations of [210]Po, [226]Ra and [238]U were also determined through alpha spectrometry.

It should be mentioned that no special efforts were made to measure the Rb-annual dose rate, which can be derived with sufficient accuracy from an assumed average K: Rb concentration ratio of 200:1 (*Aitken 1985*). Also, our measurement does not yield information on [235]U. This is however of minor importance in view of its small contribution to the total U activity (~4.4%). Nevertheless, its contribution can be taken into account via [238]U, assuming a natural isotopic ratio of [235]U to [238]U. Finally, the contribution from cosmic radiation amounts to a few percent

and can be calculated using the formula developed by Prescott and Hutton (*Prescott and Hutton, 1994*).

The case study chosen was the Neolithic archaeological site of Lumea Nouă, Romania. The analysis was carried out on five soil samples.

High resolution gamma ray spectrometry analysis was carried out on an ORTEC hiperpure germanium detector having the following characteristics: active volume of 181 cm^3, 0.878 keV FWHM at 5.9KeV, 1.92 keV FWHM and 34.2 % relative efficiency at 1332.5 keV in the laboratory of Natural Radioactivity and Nuclear Dating Center.

Alpha spectrometric measurements and neutron activation analysis has been carried out at Radiochemistry Department, University of Veszprém, Hungary, Institute for Nuclear Research, Mioveni, Pitesti Romania, respectively.

The system was calibrated in energy using a standard Eu source. The detector is mounted in a lead castle and has a 0.5mm beryllium window which makes it suited for measuring several U and Th decay products, down to ^{210}Pb with a gamma ray energy of 46.5keV. This is important, because it is an indicator for possible radon escape in archaeological or geological times. In addition to this nuclide, other lines that were investigated are ^{234}Th (63.3keV), ^{226}Ra (186.2keV), ^{214}Pb (295.2 and 351keV), ^{214}Bi (609keV). The line at 609 keV of ^{214}Bi was later on excluded from calculation as it was concluded that suffers consistent sum out effects. This is in agreement with other studies as well (for example *Garcia-Talavera et al 2001*) The lines at 63.3keV and 186.2keV are moderately to heavily interfered by the 63.8 and 185.7keV lines of ^{232}Th and ^{235}U, respectively, thus requiring proper corrections (*Hossain, 2002*). In the ^{232}Th decay chain we measured ^{228}Ac (338.3 and 911keV) and ^{208}Tl (583.2keV). Eventually, also the 1460.8keV gamma ray of ^{40}K can be measured (**Figure 4**).

The activity of each nuclide in the sample was derived from the equation:

$$\Lambda = \frac{N}{t_m \cdot \varepsilon \cdot y}$$

Where N represents the net number of counts (intensity) under the peak of interest, t_m is the spectrum acquisition time, ε is the computed efficiency of the sample-detector and y represents

the absolute intensity (emission probability) of the gamma line. Detection efficiencies were computed for the energies of interest using a Monte Carlo Code (GES-Gamma Electron Efficiency Simulator version 2.7 (*Fulea, 2009*).
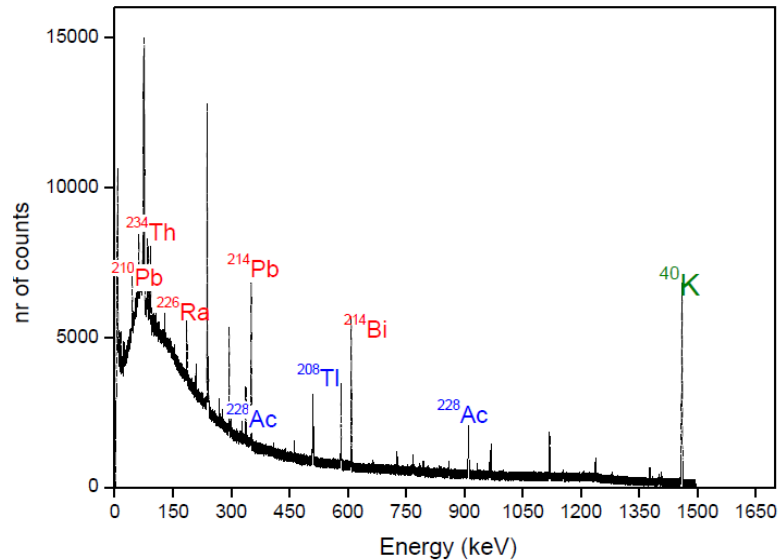

Figure 4: *Typical high resolution gamma spectrum of a soil sample (soil sample number 5). The measurement time was 500000 seconds.*

In order to validate the procedure used we also determined the detection efficiencies experimentally, using radiometric reference materials RGU-1 (400 ± 2 µg/g) and RGTh-1 (800 ± 16 µg/g), issued by the IAEA.

All the samples were measured for at least 150000 seconds the measurement geometry being a cylinder in all cases. Radon loss due to sample preparation was estimated at 15%, thus we stress upon the need for storing the samples for three weeks before measurement in order to for the radioactive equilibrium to be reached again.

As previously mentioned, ^{226}Ra 186.2keV is heavily interfered by the ^{235}U 185.7keV line and a correction for this interference is needed to obtain unambiguous results, directly obtained values for ^{226}Ra being of major importance as usually in soils equilibrium cannot be assumed between ^{238}U and ^{226}Ra the latter being soluble and thus being subjected to transportation by percolating

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groundwater. Correction for the interference was made following a suggestion of *De Corte et al (2005)*. This is based on the calculation of ^{235}U 185.7 peak area from the rather intense ^{234}Th peak at 63.3keV. Two assumptions have to be made in this case: that ^{238}U and ^{235}U are present in their isotopic natural ratio and that ^{238}U and its immediate daughter ^{234}Th are in equilibrium. Moreover 63.3 keV ^{234}Th peak is also spectrally interfered by a ^{232}Th peak at 63.8 keV. The correction for this interference is made using ^{228}Ac peak at 338.1keV, obviously assuming equilibrium between ^{232}Th and ^{228}Ac. (**Figure 5**)

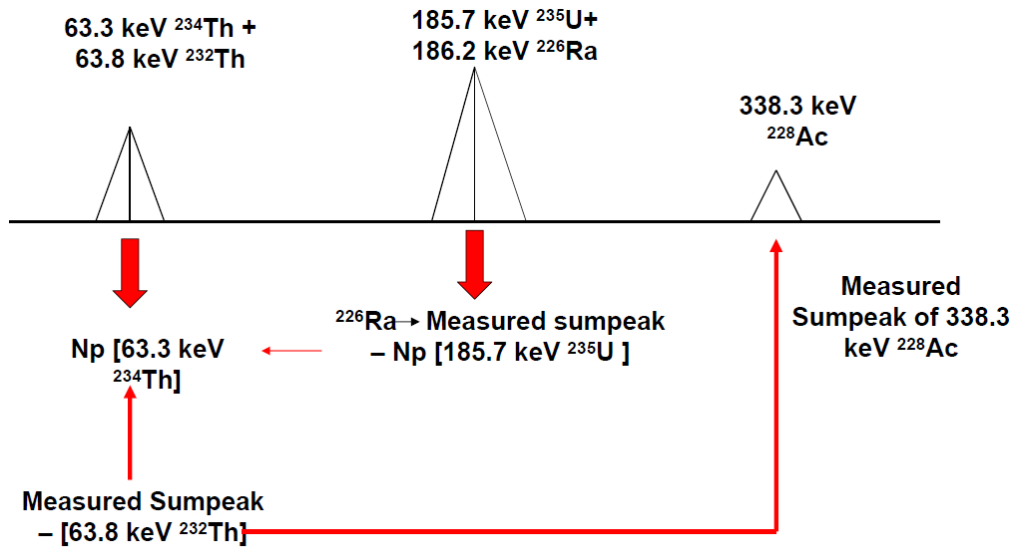*Figure 5: The principle for direct measurement of Ra-226 activity from the 185.7 keV gamma line*

The procedure was validated by measuring IAEA-312 radionuclides in soil standard. Values obtained experimentally and values given by IAEA are plotted in **Figure 6**. It can be seen that a very good agreement within error limits was obtained. Thus the procedure was applied for all measured samples.
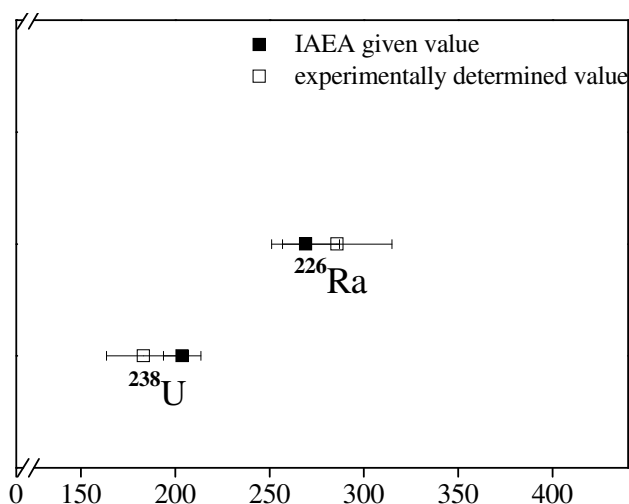
Figure 6*: comparison between the experimentally calculated values and the values given by IAEA for the specific activities for uranium, radium and thorium for standard material "IAEA-312 radionuclides in soil".*

Specific activities of the nuclides of interest measured in the three different laboratories are presented (**Figure 7**). Values obtained for [238]U by instrumental neutron activation are consistent within error limits with the values obtained for [234]Th through high resolution gamma spectrometry. As equilibrium between the above mentioned nuclides can be regarded as a fair assumption in the case of soils, we can conclude that the emission at 63 keV of [234]Th can be used with satisfying accuracy for gamma spectrometric measurement of [238]U. The assumption that radium disequilibrium is not unusual in soils was supported by the results obtained both through gamma spectrometry in the cases of sample 2 and sample 3, where a certain degree of radium enrichment can be noticed.

However, the degree of disequilibrium is not sufficiently severe to have an important influence on the final age of ceramics taking into consideration the overall precision of the luminescence method (see **Figure 8**). Nevertheless, taking into consideration the fact that gamma spectrometric data are supported by alpha spectrometric results for [226]Ra we do stress upon considering the detailed investigation on the concentration of this nuclide as a worthwhile procedure when performing gamma spectroscopic measurements.

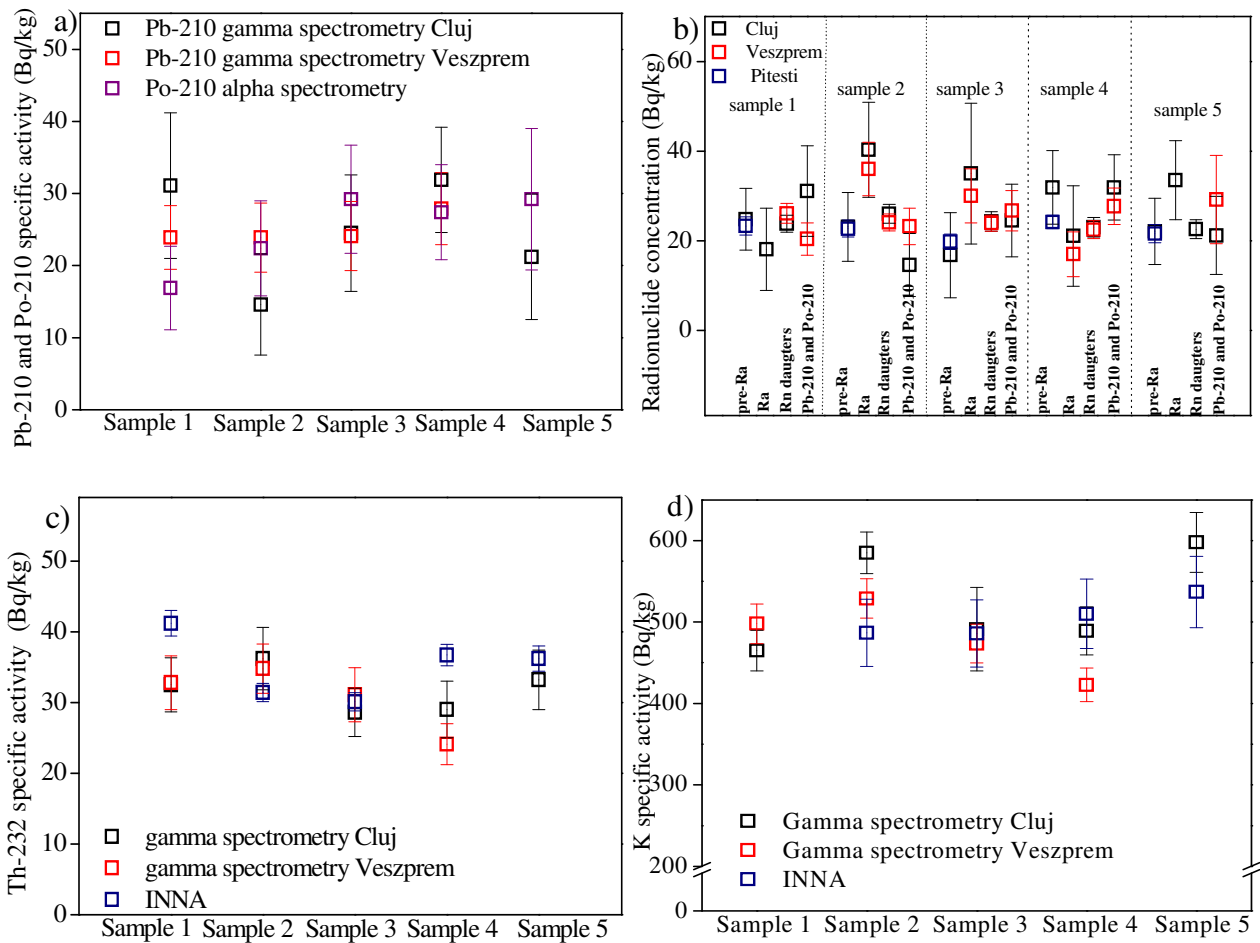***Figure 7:*** *Comparison between specific activities of radionuclides of interest obtained in the three different laboratories.*
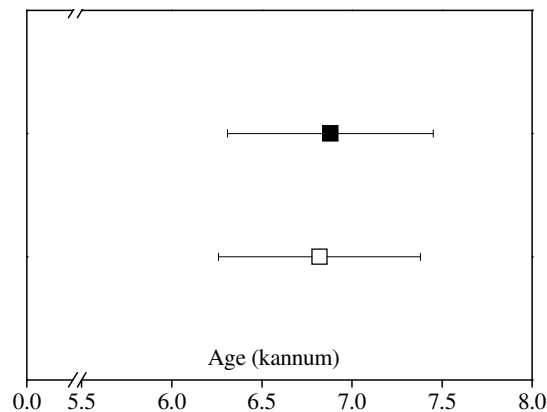

Figure 7: *Calculated ages for an Eneolitic shred collected from Lumea Nouă archaeological site taking into consideration the dosimetric information for soil sample 2 provided by gamma ray spectrometry (□) (taking into consideration radium enrichment) and by neutron activation*

analysis (■) (method that does not take into consideration the possible cases of disequilibrium in uranium series). Internal dose rate was taken from Cosma et al. (2006).

Deriving the activity ^{210}Pb is also of major importance as this nuclide can serve as an indicator of radon loss throughout geological or archaeological time. Due to the low energy emission of this nuclide (46.5 keV) gamma spectrometric measurements are difficult to be performed with sufficient precision unless special detectors in ultra low background conditions are being used. Thus we consider data on ^{210}Po derived through alpha spectrometry to yield more reliable results.

A relatively good agreement between gamma spectrometry and instrumental neutron activation was observed. Nevertheless, it can concluded that despite the better precision of instrumental neutron activation the method of choice for obtaining routine dosimetric information regarding natural nuclides in soils in luminescence dating can be considered to be gamma spectrometry due to the less efforts involved in the experimental procedure and the advantages it offers on the possibility of checking for radioactive disequilibrium in uranium series.

Considering an equivalent dose of 19.97 ± 0.810 and an average of the internal dose rates presented in *Benea et al 2007*, the luminescence ages calculated taking in to consideration the external dose rates determined by elemental radionuclide concentration with the above described methods yield the following ages: CLUJ GAMMA SPECTROMETRY- Age = 6.82 ± 0.57 ka, VESZPREM -Age = 6.79 ± 0.56 Ka, INNA PITESTI- Age = 6.88 ± 0.57 Ka leading us to conclude that annual dose rates necessary in order to calculate luminescence ages can be determined with sufficient confidence using gamma spectrometry measurements in our laboratory.

It should be noted that this study should be taken as intoductory work for the validation of methodologies. All gamma spectrometric measurements have been carried ot in 2007. Research resulted in a BDI publication. At the moment of writing this thesis gamma spectometric measurements in Environmental and Nuclear Dating Center are carried out in much lower background condition due to a new lead shielding enabling higher precision of measurements as well as a lower limit of detection of the system. Other gamma spectometric investigation of environmental samples are presented in Begy et al 2009 a,b, Cosma et al 2007.

5. Applications of luminescence dating in key applications and potential contributions compared to the most recent achievements in mainstream publications

5.1 Applications in archaeology

Luminescence dating of Neolithic ceramics from Romania

Pottery is often the most abundant material found on archaeological sites and is the basis of many chronological frameworks for the Neolithic, especially in Southeast Europe.
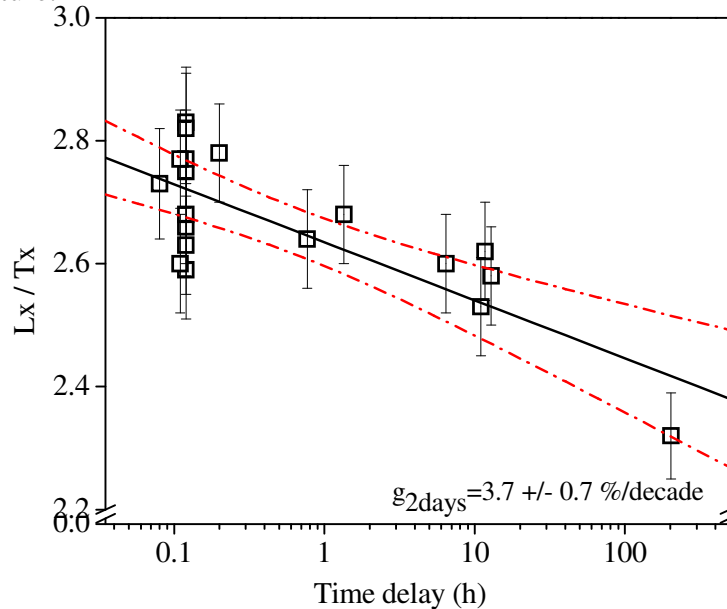
The possibility of dating ceramic objects by the use of their thermoluminescent properties was first proposed by *Grogler et al. (1960) and Kennedy and Knopff (1960)*. Since then, the method has been extensively studied and applied (see e.g. the reviews by *Aitken, 1985* and *Roberts, 1997*). In the last few years, there have been major developments in both luminescence dating instrumentation and measurement methodology. The introduction of optically stimulated luminescence (OSL) signals in combination with single-aliquot measurement protocols has led to a significant increase in precision, while less sample material is required; this makes luminescence dating a potentially much more useful chronometric tool in archaeology. Nevertheless, the application of luminescence to burnt pottery appears to have benefited only little from these advances in dating technology. Only a few studies are available in the literature and some relevant reports include those by *Hong et al. (2001), Takano et al. (2003)* and Lamothe (2004). The latter author applied state-of-the-art luminescence dating procedures (i.e. using the single-aliquot regenerative-dose (SAR) protocol, and both infrared and blue stimulated luminescence signals) to heated artefacts from archaeological sites in Quebec (Canada), and demonstrated that these procedures are able to provide a reliable chronological framework.

In this study, luminescence dating was applied to four pottery fragments excavated at Lumea Nouă (Alba Iulia, Romania). Although the Lumea Nouă settlement has been investigated for over 6 decades now, there is still no accurate and precise chronology available for the excavated Neo-Aeneolithic habitation levels. Therefore, the aim of this study was to apply new approaches in optical dating to improve the chronological framework for the site.

To this purpose, the single-aliquot regenerative-dose (SAR) protocol was applied to both blue (OSL) and infrared stimulated luminescence (IRSL) signals from coarse (90-125 µm) quartz and

polymineral fine (4-11 µm) grains, respectively. For the sake of comparison, a more conventional approach, which uses a multiple-aliquot additive-dose (MAAD) protocol and thermoluminescence (TL) signals from polymineral fine grains, was applied as well. The characteristics of the OSL and IRSL signals were investigate in terms of behavior in the SAR protocol, dose response and dose recovery.

The presence of anomalous fading in the 410 nm IRSL emission as well as blue TL emission indicates that our IRSL and TL ages would underestimate the true ages (**figure 9**). To correct the SAR-IRSL results for fading, we applied correction procedure proposed by *Huntley and Lamothe (2001)*. No correction was applied to the TL results, as it not valid to correct the bulk signal originating from an undifferentiated fine-grained mineral mixture using the fading observed from only part of this mixture.

Figure 9: Anomalous fading data for a representative aliquot of sample A1. Plotted are the measured L_i/T_i ratios versus the logarithm of the time elapsed since the end of the irradiation.

The TL, SAR-OSL and SAR-IRSL ages (both corrected and uncorrected) are plotted in **Figure 10.** In general, the uncorrected TL-ages are consistent with the uncorrected SAR-IRSL ages, and both are lower than the quartz SAR-OSL ages. The uncorrected TL age for sample V2 is higher than the uncorrected SAR-IRSL age, but this might be due to a lack in measurement precision. The fading corrected ages. Compared to the TL method, the IRSL and OSL approaches are based on a more robust dating methodology. Therefore, they are expected to yield the most reliable age

information. As SAR-OSL dating of quartz yields the most precise age estimates, this is considered to be the technique of choice.
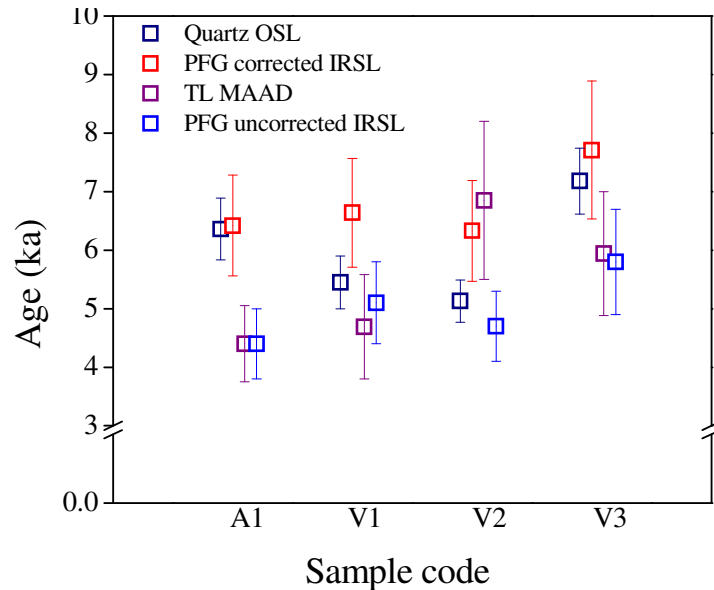

Figure 10: *Illustrative comparison of the ages obtained through the methods used*

As mentioned before, there is no age control for Lumea Nouă site. The average of the four quartz SAR-OSL ages presented above would place the transition from Foeni to Petreşti culture at Lumea Nouă site around 6.2±0.5 ka; taking into consideration the archaeological information, this age seems extremely plausible. Further investigations are needed for establishing a complete chronological framework for the ancient cultural development at Lumea Nouă. Nevertheless the present study clearly illustrates how luminescence dating, especially by the use of state-of-the-art techniques can contribute to this purpose.

It should be noted that the measurements have been carried out in Gent Luminescence Dating Laboratory; fading corrections have been newly developed at the time, and SAR OSL dating of sand sized quartz extracted from heated ceramics was a relatively novel application. The research has been published in an international-peer reviewed journal (Benea et al, 2007).

5.2. Applications in geology and environmental studies

5.2.1. Optical dating of Romanian loess using fine grained quartz

Loess deposits preserve a potentially important and detailed archive of Pleistocene climate change. Although a variety of loess characteristics (such as magnetic susceptibility and grain size) can be studied as proxy record for palaeoclimate and palaeoenvironment, the deposits can only be fully understood, and their significance evaluated, once a robust chronological framework is established. Indeed, it is well known that terrestrial archives may be incomplete, and an increasing body of evidence demonstrates that the rate of loess accumulation may vary considerable both within a stratigraphic unit and between equivalent units at different localities (see e.g. *Frechen et al., 2003; Roberts, 2008*).

Luminescence dating is, at present, the only method that allows establishing an absolute chronology for loess deposits. The method uses grains of quartz and/or feldspar, which are both typically abundant in loess, and the windblown nature of loess ensures that the luminescence clock was completely reset prior to deposition. We have reported the first optically stimulated luminescence (OSL) ages for the loess sequence near Mircea Vodă (Dobrogea, SE Romania). The study focussed on loess from the last four glacial periods and used silt-sized (4-11µm) quartz as dosimeter.

The study site is located near the village of Mircea Vodă, which is situated in the Dobrogea-plateau (SE Romania) at about 15 km from the River Danube. The section is ~26 m thick; it comprises six well-developed palaeosols (stratigraphic nomencelature: S0-S5, with S0 representing the Holocene soil) and intercalated loess layers (L1-L6), with no apparent evidence for remarkable hiatuses.
C. Panaiotu used magnetic susceptibility record to create a time-depth model, which indicated that the first well-developed palaeosol (S1) was formed during MIS 5; the model allocated a weakly developed soil in middle of the uppermost loess unit (L1) to the MIS 3 interstadial.

Fine quartz grains analysed displayed bright fast decaying OSL signals indicating that are dominated by a fast component and thus ammendable to the application of the SAR protocol (**Figure 11**).
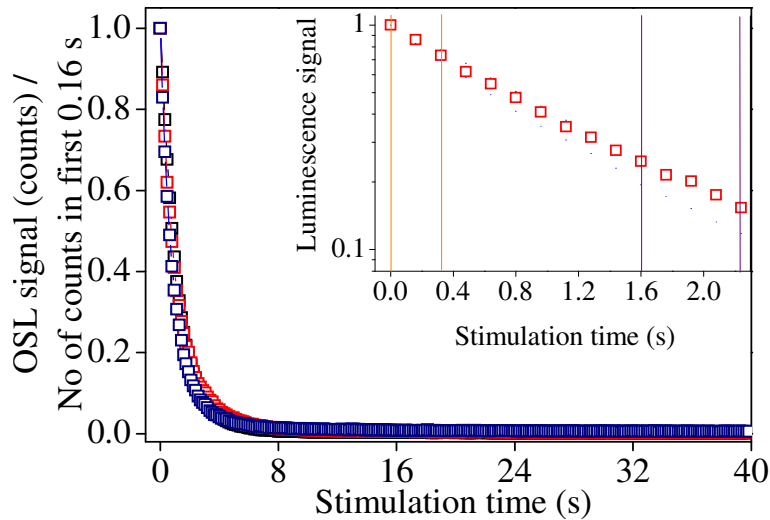

Figure 11: Typical decay curve of natural (red symbols) OSL signal of sample MV10 (fine quartz) compared to the regenerated signal (navy symbols) and the OSL decay of calibration quartz (black symbols). Signal and background integration intervals are indicated in the inset. The measurement was performed on a Risø TL OSL DA-12 machine.

An internally consistent set of optical ages was obtained and the optical ages have been compared with a magnetic time-depth model based on magnetic susceptibility measurements (**Figure 12**).

Based on luminescence ages, evidence was presented for a varying loess accumulation rate during the Last Glacial the optical ages indicate that this unit did not accumulate at a constant rate (**Figure 12 –inset**), with loess being deposited at a significantly lower rate during the past ~50 ka. This illustrates the limitations of proxy records (such as magnetic susceptibility) to interpret and derive a chronology for these deposits. The age results for the L1 unit contrast with the commonly held assumption that loess sedimentation in this region occurred at a constant rate. They are, however, in line with the ideas emerging from the study of *Singhvi et al. (2001),* and the recent insights gained from optical dating of Chinese loess; at several localities in the Chinese loess plateau, loess accumulation rates have been found to vary during the last glacial period (see

e.g. *Stevens et al. 2007; Buylaert et al., 2008*).

While it could be confirmed that the uppermost palaeosol (usually denoted by S1 in stratigraphic nomenclature) formed during the last Interglacial, comparison with independent age control (pedostratigraphy and a newly developed palaeomagnetic time-depth model) also indicated that the dating procedure underestimates the true burial age from the penultimate glacial period onwards.
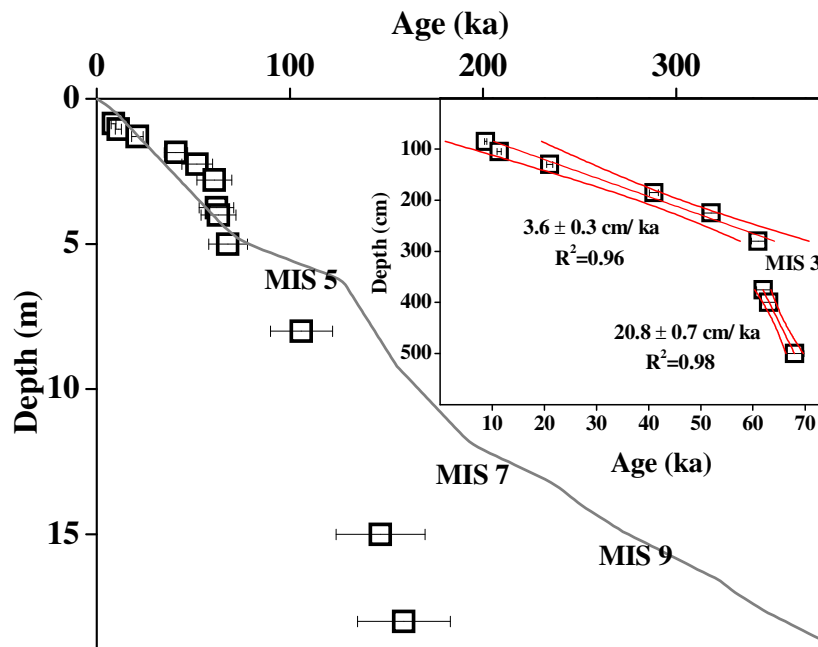
Figure 12: *Plot of optical ages (open squares, 1 sigma total uncertainties) as a function of depth; the results from the palaeomagnetic time-depth modeling are shown by the gray line (C. Panaiotu).The inset shows the optical ages (open squares, 1 sigma random uncertainties) and sedimentation rates obtained for the L1 unit.*

The SAR-OSL ages obtained for the three samples taken below the S1 soil are interpreted as age underestimates, with the degree of age underestimation increasing with depth.

Interestingly, the luminescence characteristics do not indicate such behavior: (i) the dosimetric signal continues to grow to high doses **(Figures 13a, b),** (ii) yields D_e's and recovered doses that are independent of preheat temperature (suggesting that the signal is thermally stable; **Fig. 14, a, b**), (iii) passes the testing of the laboratory measurement procedure (**Figure 15**), and (iv) leads to ages that increase with depth (up to at least 15 m).
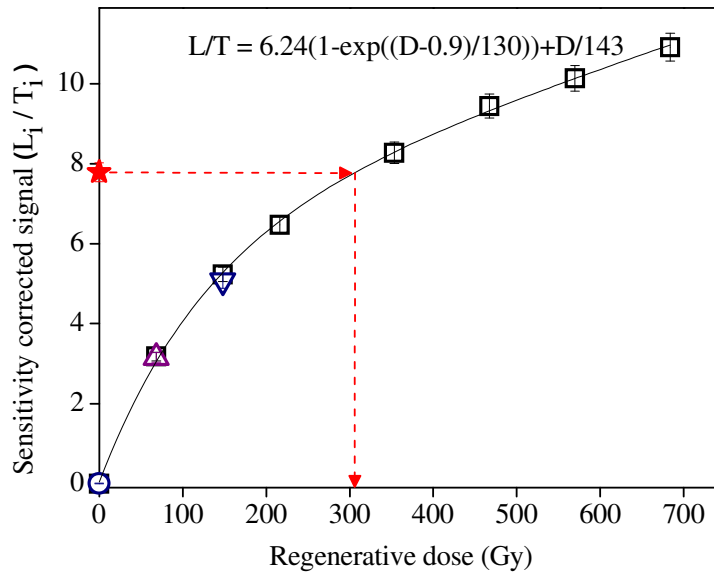
Figure 13a: *Representative SAR growth curve for a single aliquot of fine-grained quartz extracted from sample MV 10. Recycling and recuperation points are shown as an open triangle and open circle.*
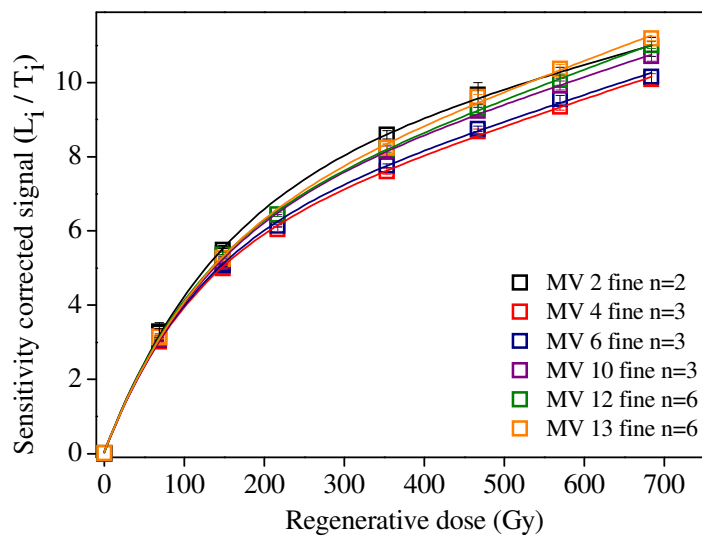
Figure 13b: *Comparison of average SAR-OSL growth curves for fine quartz from 6 samples of different ages.*
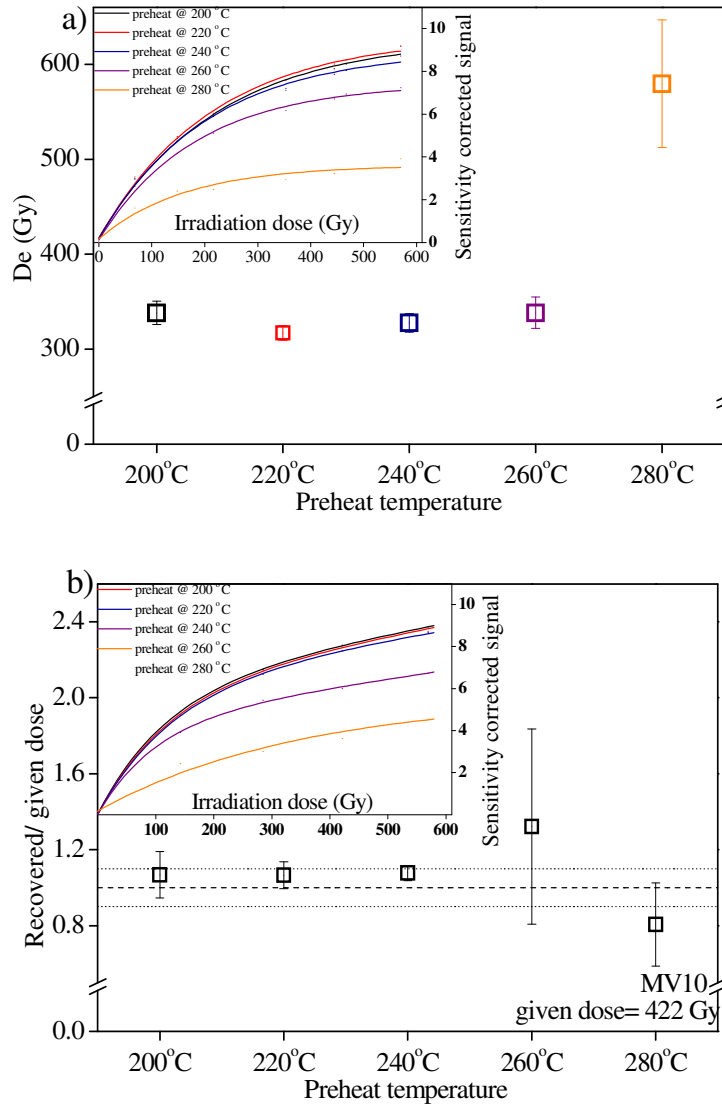
Figure V.14*: a) Dependence of D_e (a) and of the measured to given dose ratio; b) on preheat temperature for sample MV10. Each data point represents the average (± 1 standard error) of at least three replicate measurements. The dashed and dotted lines in (b) are meant as an eye guide and indicate a ratio of 1.0±0.1.*

The dose recovery experiments indicate that our SAR protocol is able to accurately measure a laboratory dose given prior to any heat treatment (**Figure 15**). Note that good dose recoveries were also obtained from the high dose linear region of the growth curve (**Table 2**). Although the results give confidence in the reliability of the laboratory measurement procedure, they do not

necessarily imply that natural doses can be measured accurately as well. For each sample, at least six replicate measurements of the D_e were made. The average values ($\pm$ 1 standard error) are summarized in **Table 3.**
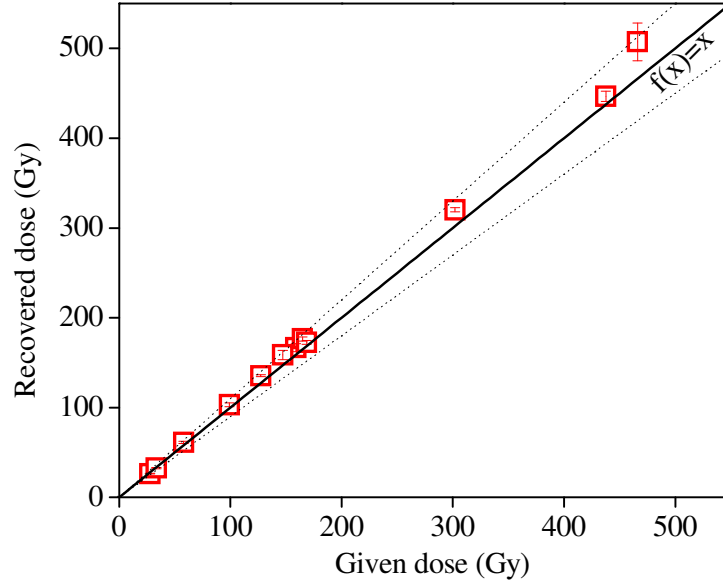
Figure V.15: *Summary of dose recovery data for all samples using a preheat of 10s at 220 °C). The given dose was chosen to approximate the equivalent dose; for sample MV10, the dose recovery test was carried out for given doses of ~300Gy and ~420Gy (data presented in Fig V.12). The solid line (eye guide) represents the 1:1 relation; the dotted lines (eye guide) bracket a 10% deviation from unity.*

Sample code	$\chi 2$ / DOF (exponential fit)	D_0 (Gy)	D_0 error (Gy)	"Practical limit" (Gy)	$\chi 2$ / DOF (exponential + linear fit)	D_0* (Gy)	D_0* error (Gy)
MV2	0.085	225	25	426	0.011	126	12
MV4	0.092	235	27	446	0.014	108	13
MV6	0.091	238	27	452	0.010	110	11
MV10	0.101	241	28	457	0.010	112	10
MV12	0.096	255	29	448	0.017	113	9
MV13	0.134	255	38	484	0.027	116	18

Table 2: *Goodness of fit and values for the characteristic dose (D_0 and D_0*) for SAR growth curves for fine quartz from six samples of different ages. The dose-response curves were measured up to ~ 700 Gy using a constant test dose of 17.1 Gy. The functions used for fitting were a single saturating exponential $I=I_{max}(1-exp(-(D+D_i)/D_0)$, and the sum of a single saturating exponential and a linear component $I=I_{max}^*(1-exp(-(D+D_i*)/D_0*)+D\bullet a$. 85 % of saturation level in the case of a single saturation exponential fit is denoted as "practical limit".*

These results are consistent with those reported for old (>70 ka) Chinese loess (*Buylaert et al., 2007; 2008*), and with the more general suggestion that SAR may underestimate the true age (to some degree) in the older age range (*see e.g. Murray et al., 2007*). Our results are in contrast to the findings by *Murray et al. (2008)* for quartz extracted from a deposit on the Seyda River in northern Russia. In the latter study, natural doses of ~350 Gy were obtained using the high dose linear region of the growth curve, which resulted in optical ages that were in excellent agreement with the independent age controls.

We concluded that optical dating of fine-grained quartz can be used to establish a reliable chronology for Romanian loess up to ~70 ka. This age values correspond to equivalent doses of ~ 200Gy. Up to this value an exponential function and an exponential plus a linear term function give the same goodness of fit to experimental data. At least for our samples, the results obtained from the high dose linear region of the growth curve do not appear to be accurate. The procedure underestimates the true burial age when applied to loess that was deposited before the last climatic cycle; further research is necessary to establish what causes the age underestimation. Our results illustrated that an apparently reliable OSL laboratory measurement procedure not necessarily guarantees an accurate determination of the true burial.

It should be noted that a substantial part of the measurements performed on quartz fine grains have been carried out in Gent Luminescence Dating Laboratory; the results have been published in a highly ranked peer reviewed journal (Timar et al. 2010a) and have already been referenced to.

5.2.2. A comparison of luminescence properties and optical ages obtained on different grain sizes of quartz extracted from loess

Introduction

Loess is generally considered as an ideal material for luminescence dating. The first luminescence methods that have been applied to loess used thermoluminescence (TL) signals from polymineral fine (4-11 µm) grains (see e.g. *Wintle 1981, Van den haute et al. 1998, 2003*). This was followed by stimulation of the polymineral fine grains with infrared light (infrared stimulated luminescence; IRSL), which became increasingly used for dating loess (*Forman,*

1991; Frechen and Dodonov, 1998; Frechen, 1999; Tsukamoto et al., 2001). More recent developments in dating technology allowed exploring the potential of quartz. Optically stimulated luminescence (OSL) dating has been applied to silt-sized (4-11 µm) quartz (*Watanuki et al. 2003; Wang et al. 2006; Lu et al. 2007; Timar et al., 2010a*), middle-sized (35-63 µm) quartz (*Roberts, 2006; Stevens et al. 2007; Lai et al., 2007*) and sand-sized (63-90 µm) quartz (*Buylaert et al., 2007; 2008*). While it seems logic to assume that for a windblown material (such as loess) grains from several fractions are suitable for optical dating, this has not been explicitly demonstrated. At least to our knowledge, no studies are available that compare the luminescence characteristics and age of quartz grains of different granulometric fractions extracted from loess. This study reports on such an investigation for samples collected from the loess sequence near Mircea Vodă (Dobrogea, SE Romania). *Timar et al. (2010)a* previously dated this sequence using OSL signals from 4-11 µm quartz grains. Here, we investigate the luminescence properties and age of the fine sandy (63-90 µm) quartz fraction from exactly these same samples; additional investigations on the silt-sized fraction are included.

Luminescence characteristics

Investigations were performed on the same samples as used by Timar et al. (2010a). Samples MV1 to -MV9 come from the first loess layer (L1), while samples MV10, -12 and -13 were taken from the L2, L3 and L4 loess units, respectively.

Luminescence investigations were carried out using automated Risø readers (TL/OSL-DA-12 and TL/OSL-DA-20) equipped with blue (470±30 nm) LED's. Stimulation with infrared light was through an IR laser diode (830 nm; TL/OSL-DA-12) or IR diodes (875 nm; TL/OSL-DA-20). All luminescence emissions were detected through a 7.5 mm thick Hoya U-340 UV filter.

The luminescence characteristics of both the fine and coarse grains were investigated using a single-aliquot regenerative-dose (SAR) protocol (*Murray and Wintle, 2000*). Stimulation with the blue diodes was for 40 s at 125°C. The initial 0.32 s of the decay curve was used, less a background evaluated from the 1.60 to 2.24 s interval. A constant test dose of 17 Gy was used in all experiments. Unless stated otherwise, a preheat of 10 s at 220°C preceded the measurement of natural and regenerative signals and a cutheat to 180°C that of test dose signals, respectively.

After the measurement of each test dose signal, a high-temperature bleach was performed by stimulating with the blue diodes for 40 s at 280°C (*Murray and Wintle, 2003*).

The OSL signals of both the fine and the coarse quartz grains exhibit a fast decay with stimulation time. The natural and regenerated signals have the same shape, and all are indistinguishable from the signals observed from calibration quartz. As it is generally accepted that the quartz OSL signal of calibration quartz is dominated by a fast component, it is deduced that the signals from the samples are as well. This is confirmed by examination of the LM-OSL signal. The natural and regenerated LM-OSL signals show a well-defined peak early in the curve; the position of this peak matches the signal observed for calibration quartz **(Figure 16)** and is not dependent on prior heating between 180°C and 360°C **(Figure 17)**. The same observation was made for the other samples as well.
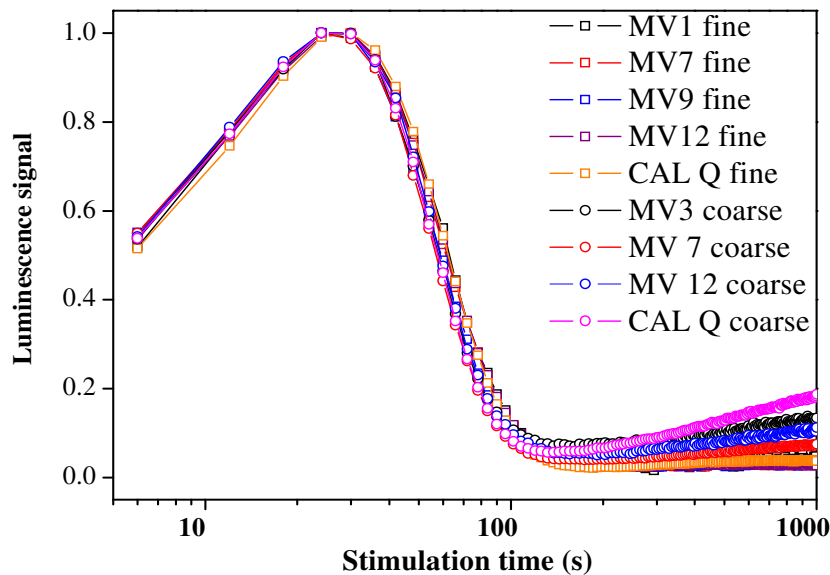
Figure 16: *LM-OSL natural signals of fine (4-11µm) and fine sand (63-90 µm) sedimentary quartz extracted from Mircea Vodă section compared to calibration quartz. Stimulation was performed at 125 °C ramping the stimulation power from 0-100% in 3000s. One data channel represents 6 seconds of stimulation. For a better visual comparison values collected in all data channels have been normalized to the maximum value obtained in a data channel.*
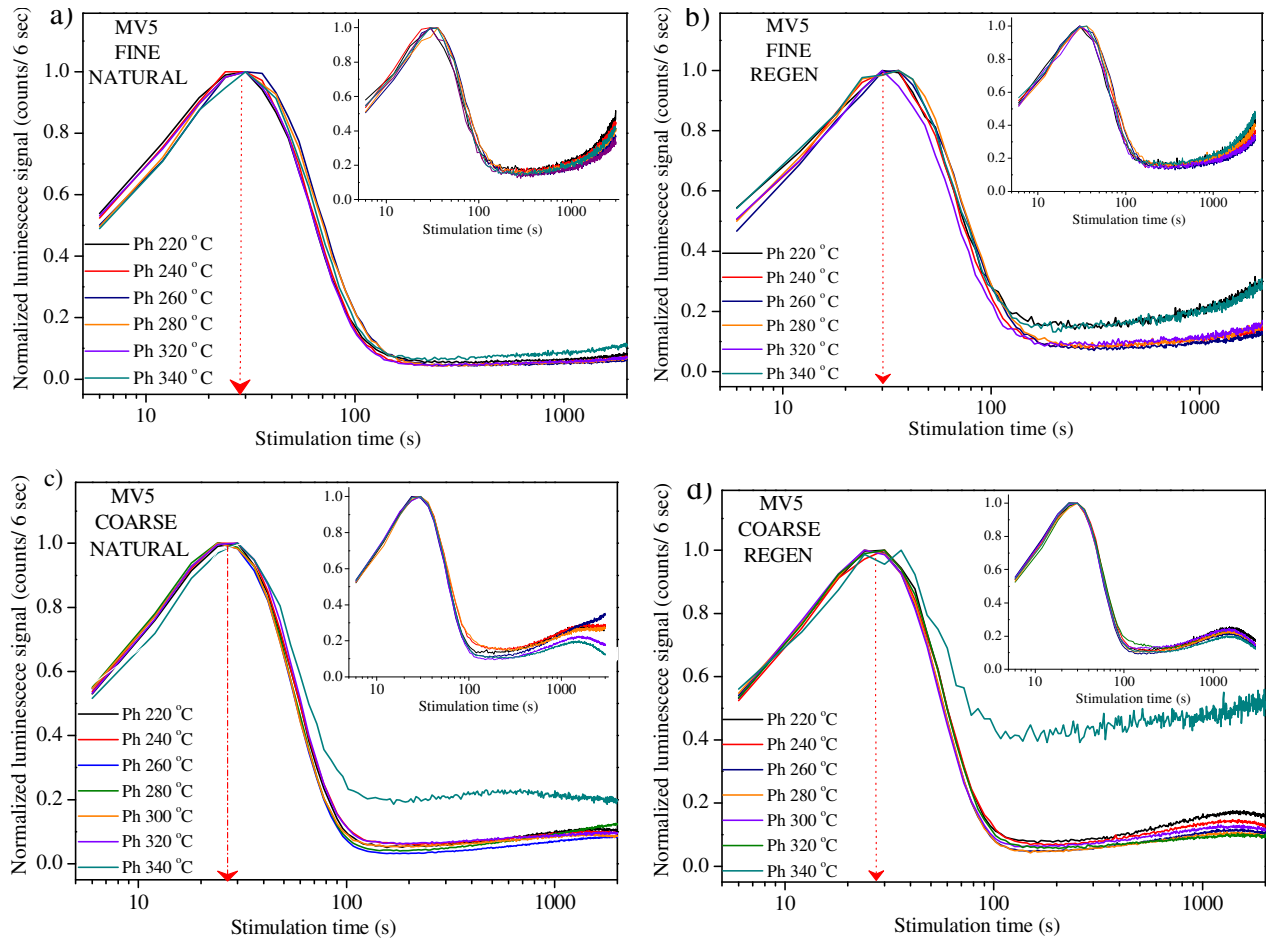
Figure 17: *LM-OSL natural signals of fine and coarse sedimentary quartz extracted from Mircea Vodă section following preheats of 2 seconds at temperature ranging from 220 °C to 360°. The inserts present the corresponding test dose signals (recorded after a cutheat to 180 °C) For a better visual comparison values collected in all data channels have been normalized to the maximum value obtained in a data channel.*

It has been previously showed that the SAR protocol is applicable to the OSL signals from the 4-11 µm quartz extracts: sensitivity changes occurring throughout a SAR measurement sequence are accurately corrected for (as indicated by recycling ratios indistinguishable from unity), recuperation is negligible (< 0.2% of the sensitivity corrected natural signal), and a known dose given to a bleached and unheated sample can be accurately measured.

The 63-90 µm quartz grains exhibit a similar behavior. The response to a zero dose (recuperation) amounts to less then 0.3% of the corrected natural signal and sensitivity changes occurring throughout a SAR measurement cycle are accurately corrected for. The latter is illustrated in **Figure 18.** The response of fine and silt-sandy quartz aliquots of sample MV9 was

analyzed in a SAR protocol, the response to a regenerative dose (220 Gy) being repeatedly measured. It can bee seen that the sensitivity corrected signals are indistinguishable.

The applicability of a SAR protocol to the sand-sized quartz grains was also tested through a dose recovery test. In this test, natural aliquots were bleached twice for 250s at room temperature using the blue diodes; the two bleaching treatments were separated by a 10ks pause. The aliquots were then given a known dose chosen to be equal to the estimated natural dose, and measured using the SAR protocol. The results are shown in **Figure 19** (circles). The given dose can be recovered reasonably accurately over the entire dose range (i.e. from ~28Gy to ~ 480Gy) and the overall average measured to given dose ratio is 1.04 ± 0.02 (n = 12). For the sake of comparison, the results from the dose recovery test on the fine grains are included in **Figure 19** (squares; from Timar et al., 2010); in this case, the overall average measured to given dose ratio is 1.04 ± 0.04. The results from the dose recovery test indicate that the SAR protocol is able to measure laboratory doses given prior to any heat treatment both accurately and reasonably precisely, for both the coarse and the fine quartz grains. This does not necessarily imply, however, that natural doses can be measured equally precise and accurate for one or both grains size fractions.
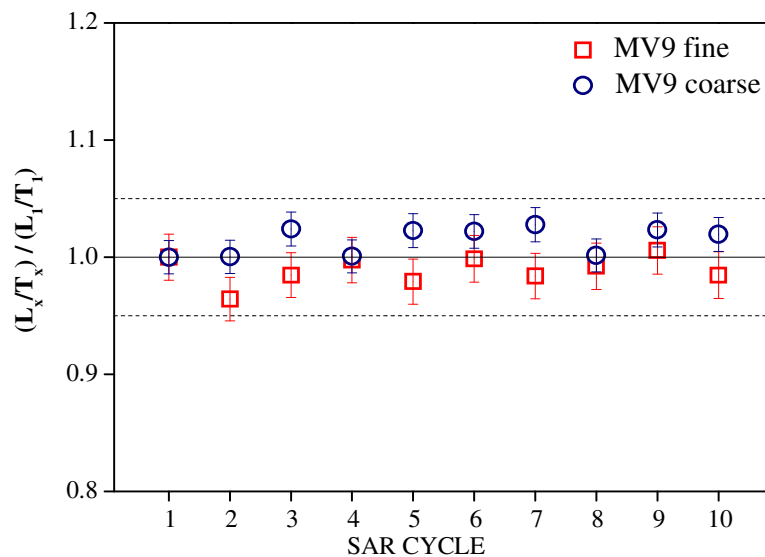
Figure 18: Sensitivity corrected signals obtained using a constant regenerative dose of 220 Gy over 10 SAR measurement cycles. All values are normalized to data obtained in the first measurement cycle. Lines are meant as eye-guides. Dashed lines represent 5% deviation from unity.

The SAR protocol has been designed for use with the fast component of the quartz OSL signal; the above-mentioned test are intended to detect the effects of faster and/or slower components

(*Murray and Wintle 2000; 2003*). Application of these tests to our samples thus indicates that the signal selected for analysis is dominated, if not composed exclusively, of the fast component, which confirms the observations made.
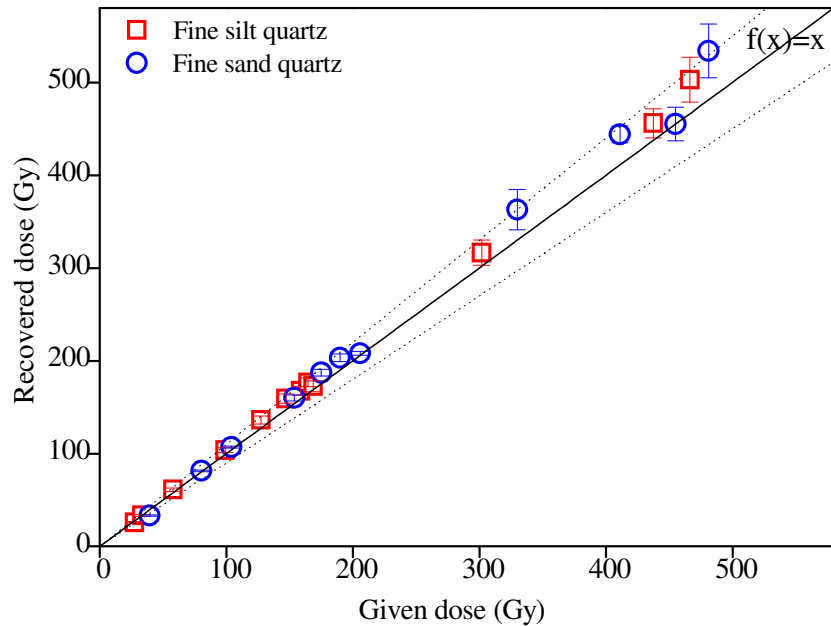
Figure 19: Summary of dose recovery data for all silt-sized (open squares; data from Timar et al., 2010) and sand-sized (open circles) quartz samples. The given dose was chosen to approximate the equivalent dose. The solid line (eye guide) represents the 1:1 relation; the dotted lines (eye guide) bracket a 10% deviation from unity.

Thermal stability

Although the majority of studies concerning OSL signal components *(Singarayer and Bailey 2003, Jain 2003)* report long term stability of the medium OSL component (with a thermal lifetime at ambient temperature of an order of magnitude of 10^5 MA), several studies have highlighted that a contamination of the OSL dosimetric signal (fast component) with a medium components can cause significant underestimation of optical ages *(Choi et al 2003, Li and Li 2006, Steffen et al 2009)*. These studies argue that the long thermal lifetime quoted above does not ubiquitously apply and the characteristics of this signal component may be related to the geological origin and history of quartz.

Signal deconvolution in CW-OSL measurements was not performed as after several fitting attempts we have concluded that in many cases the procedure may be unreliable, the results

depending strongly on the choice of initial parameters, number of components and background. Deconvolution of signals composed of a sum of exponential factors is not a straightforward matter, the problem being termed ill posed *(Istratov and Vyvenko 1999).* Nevertheless, we are confident that the OSL dosimetric signal of our fine grains is not contaminated with an unstable medium component and in the following we will present the evidence that led us to conclude this.

i) Contamination with a thermally less stable slow component is unlikely to be significant considering the background subtraction (signal: 0-0.32s; background: 1.6-2.24s) and the shape of the decay curves. For all samples, the regenerated signals are identical in shape to that of the natural and to the CW- OSL signal of calibration quartz. This is further substantiated by the shape of the LM-OSL signals.

ii) The preheat plateau is specifically intended to isolate a thermally stable signal; we observed a lack of dependence of D_e on preheat temperature

iii) In order to compare the behavior of our signals to the finds of *Choi et al 2003, Li and Li, 2006, Steffen et al 2009;* we constructed D_e (t) plots for samples of different ages. We observed no dependence of D_e with stimulation time. In our case, contrary to the finds of *Li and Li (2006),* there is no falling trend in De (t) plots of natural signals, just the same degree of scatter in both the natural and laboratory induced signals (data nor shown).

iv) We used a pulse anneal experiment to confirm the thermal stability of the OSL signals from the fine quartz extracts; for the sake of comparison, this experiment was also performed for sand-sized quartz, and for fine and coarse-grained calibration quartz.

The results are shown in **Figure 20**. The pulse anneal curves for both the coarse and the fine grains are very similar to those measured using calibration quartz. In all cases, there's little signal loss when heated to 250°C for 10s and the signal is removed after preheating at temperatures > 325°C. The pulse anneal data do not indicate that the regenerated OSL signals are significantly contaminated by a thermally less stable component. The derivatives of the data (see inset to Figure 20) show a minimum in the range of 300-330°C; this might arise because of the depletion of the 325 ^{0}C TL trap *(Murray and Wintle, 1999)*.
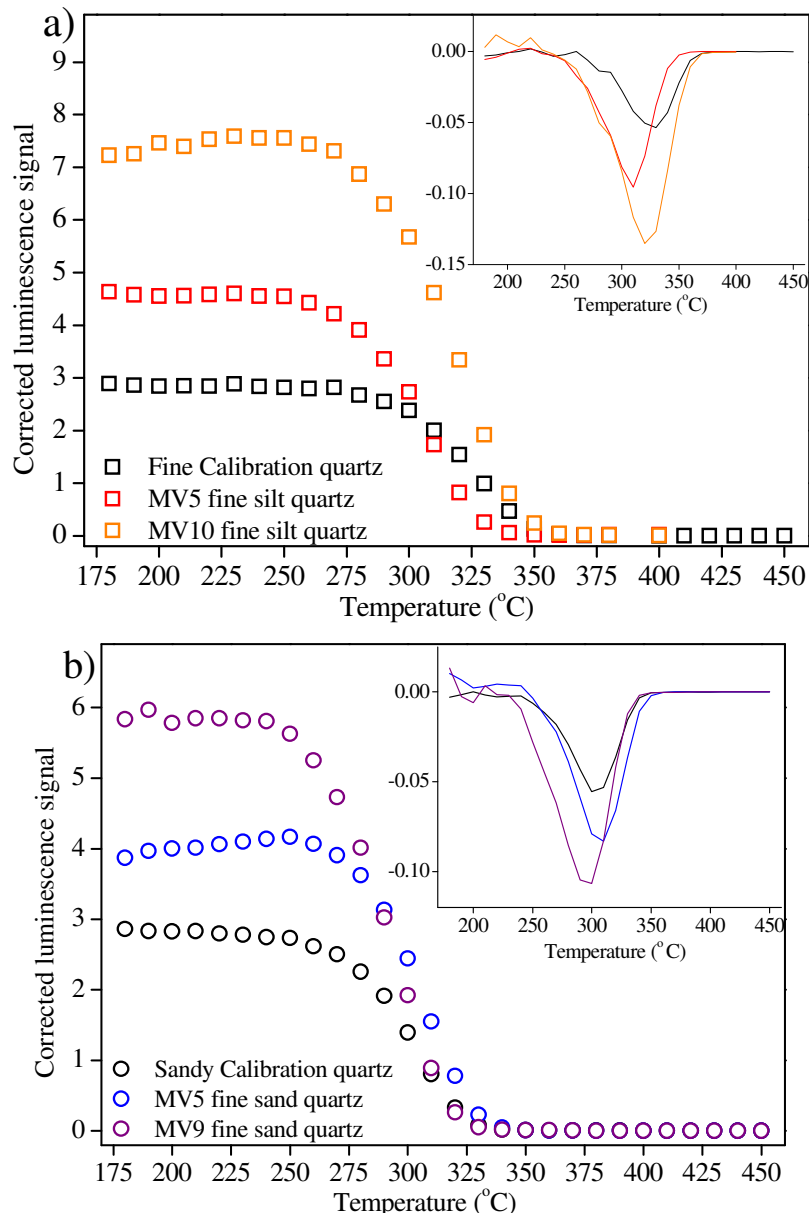
Figure 20: *Pulse anneal curves for the OSL signals from an aliquot of silt-sized (a) and sand-sized (b) quartz grains from samplesMV5, 9 and calibration quartz. The analyzed aliquots have been bleached, given a dose approximately equal to the equivalent dose, the OSL signal being measured at 125 ^{o}C following different preheat (10 s) temperatures, each value being normalized to the response to a constant test dose of 17 Gy (cutheat to 180°C). The suitability of the sensitivity change correction has been monitored by at six repeat points (data not shown).The inset shows the first order derivative of the curves.*

Growth curve characteristics

For both the fine and the coarse quartz grains, sensitivity-corrected growth curves extending up to ~ 700Gy were constructed using the SAR protocol. A very different pattern of growth was noticed for the two quartz grain fractions analyzed. Based on a single saturation exponential fit ($I=I_{max}^*(1-\exp(-(D+D_i^*)/D_0))$), the OSL signal shows much higher saturation characteristics (Do ~ 250 Gy) in the case of fine quartz than in the case of coarser grains (Do ~ 155 Gy). Although the growth curves could be fitted acceptably to a single saturating exponential, the growth to high doses is represented best by the sum of a single saturating exponential and a linear component ($I=I_{max}^*(1-\exp(-(D+D_i^*)/D_0^*)+D\cdot a)$). For each grain size fraction, the dose response curve exhibits little variation in saturation characteristics as a function of depth. The average characteristic dose D_0^* obtained using at least three aliquots per sample on 6 samples of different ages is 120 Gy in the case of fine grains, respectively 80 Gy in the case of fine sandy quartz grains.

As good dose recoveries were also obtained from the high-dose linear region of the growth curve, the difference in saturation characteristics would suggest that the signal from fine-grained quartz could be useful for D_e determination over a larger dose range.

Equivalent dose (D_e) determination

Equivalent dose determination used a SAR protocol with a preheat of 10 s at 220°C and a cutheat to 180°C. Aliquots were accepted if both the recycling and depletion ratio were within 10 % from unity and if recuperation did not exceed 5 % of the natural corrected signal; no aliquots had to be rejected on the basis of these criteria.

Optical ages

Table 3 summarizes the information relevant to the age and uncertainty calculation. Uncertainties on the ages were calculated following the error assessment system formalized by *Aitken and Alldred (1972) and Aitken (1976).*

It can be seen that the systematic uncertainty is dominant in the overall uncertainty on the ages.

Sampling Depth (m)	Laboratory code	Grains Size (μm)	Equivalent Dose (Gy)	Recycling ratio	Recup. (%)	IR depletion ratio	Total dose rate (Gy/ka)	Cosmic dose rate (Gy/ka)	Age (ka)	Random error (%)	Systematic error (%)
0.85	MV 1	4-11	24.9 ± 0.4 $_{n=11}$	0.95 ± 0.01	0.06 ± 0.02	0.94 ± 0.01	2.84 ± 0.05	0.19 ± 0.03	8.7 ± 1.3	2.2	14.2
		63-90	37 ± 2 $_{n=11}$	1.01 ± 0.01	0.27 ± 0.07	0.98 ± 0.01	2.40 ± 0.04		16 ± 2	7.1	12.4
105	MV 2	4-11	32.3 ± 0.9 $_{n=11}$	0.94 ± 0.01	0.05 ± 0.02	0.95 ± 0.01	2.86 ± 0.05	0.19 ± 0.03	11.3 ± 1.6	3.3	14.2
		63-90	46 ± 4 $_{n=8}$	1.03 ± 0.01	0.06 ± 0.02	0.99 ± 0.01	2.42 ± 0.04		20 ± 3	8.5	12.5
130	MV 3	4-11	64 ± 2 $_{n=11}$	0.96 ± 0.01	0.05 ± 0.02	0.96 ± 0.01	3.07 ± 0.05	0.19 ± 0.03	21 ± 3	2.7	14.3
		63-90	87 ± 4 $_{n=12}$	1.00 ± 0.01	0.15 ± 0.03	1.00 ± 0.01	2.58 ± 0.04		32 ± 4	4.4	12.5
185	MV 4	4-11	114 ± 2 $_{n=11}$	0.99 ± 0.01	0.04 ± 0.01	1.00 ± 0.01	2.78 ± 0.04	0.17 ± 0.03	41 ± 6	2.0	14.4
		63-90	118 ± 3 $_{n=10}$	0.99 ± 0.01	0.09 ± 0.02	1.01 ± 0.01	2.33 ± 0.03		51 ± 7	2.8	12.6
225	MV 5	4-11	156 ± 3 $_{n=11}$	1.00 ± 0.01	0.07 ± 0.03	0.98 ± 0.01	3.00 ± 0.06	0.17 ± 0.03	52 ± 8	2.6	14.5
		63-90	157 ± 5 $_{n=11}$	1.02 ± 0.01	0.08 ± 0.01	1.01 ± 0.01	2.51 ± 0.05		63 ± 8	3.5	12.6
280	MV 6	4-11	190 ± 3 $_{n=11}$	0.98 ± 0.01	0.05 ± 0.02	0.99 ± 0.01	3.09 ± 0.04	0.16 ± 0.03	61 ± 9	2.0	14.6
		63-90	210 ± 4 $_{n=40}$	1.01 ± 0.01	0.08 ± 0.01	1.01 ± 0.01	2.58 ± 0.03		82 ± 11	2.5	12.6
375	MV 7	4-11	197 ± 0.4 $_{n=11}$	1.01 ± 0.01	0.05 ± 0.01	1.01 ± 0.01	3.15 ± 0.05	0.15 ± 0.02	62 ± 9	2.1	14.7
		63-90	217 ± 3 $_{n=61}$	1.00 ± 0.01	0.09 ± 0.01	1.00 ± 0.01	2.62 ± 0.04		83 ± 11	2.1	12.7
400	MV 8	4-11	209 ± 3 $_{n=11}$	1.00 ± 0.01	0.06 ± 0.01	0.97 ± 0.01	3.30 ± 0.05	0.14 ± 0.02	63 ± 9	2.0	14.6
		63-90	247 ± 8 $_{n=20}$	1.01 ± 0.01	0.07 ± 0.01	1.01 ± 0.01	2.76 ± 0.04		89 ± 12	3.4	12.8
500	MV 9	4-11	221 ± 5 $_{n=11}$	0.97 ± 0.01	0.06 ± 0.01	0.91 ± 0.01	3.27 ± 0.03	0.13 ± 0.02	68 ± 10	2.4	14.5
		63-90	237 ± 6 $_{n=30}$	0.99 ± 0.01	0.14 ± 0.01	1.00 ± 0.01	2.74 ± 0.03		86 ± 11	2.5	12.8
800	MV 10	4-11	310 ± 9 $_{n=11}$	0.98 ± 0.02	0.05 ± 0.01	1.00 ± 0.01	2.91 ± 0.04	0.10 ± 0.02	106 ± 16	3.1	14.7
		63-90	319 ± 15 $_{n=12}$	0.98 ± 0.01	0.12 ± 0.02	0.98 ± 0.01	2.44 ± 0.03		132 ± 18	4.9	12.9
1500	MV 12	4-11	430 ± 13 $_{n=6}$	1.00 ± 0.01	0.07 ± 0.01	1.01 ± 0.02	2.91 ± 0.05	0.06 ± 0.01	147 ± 23	3.3	14.8
		63-90	438 ± 6 $_{n=5}$	1.00 ± 0.01	0.17 ± 0.05	1.02 ± 0.01	2.43 ± 0.04		200 ± 27	2.1	13.6
1800	MV 13	4-11	467 ± 11 $_{n=6}$	1.01 ± 0.02	0.06 ± 0.02	1.01 ± 0.01	2.91 ± 0.03	0.05 ± 0.01	159 ± 24	2.6	14.9
		63-90	554 ± 11 $_{n=4}$	0.99 ± 0.01	0.11 ± 0.01	1.00 ± 0.01	2.43 ± 0.03		230 ± 31	2.3	13.2

Table 3: Summary of equivalent doses (D_e), recycling ratios, recuperation values, IR depletion ratios, calculated dose rates, optical ages, and random and systematic uncertainties. The uncertainties mentioned with the luminescence and dosimetry data are random; the uncertainties mentioned with the optical ages are the overall uncertainty. All uncertainties represent 1 sigma. The number of replicate D_e measurements is given between brackets. Measurements have been performed on large (9mm diameter aliquots). The total dose rate includes the contribution from cosmic rays, and allowance was made for both the effect of moisture (assuming water content of 20±5%) and the beta attenuation factor (assuming a value of 0.94 ± 0.045 in the case of 63-90 μm quartz grains) as well as for the lower efficiency of alpha radiation in inducing luminescence in fine silt (4-11 μm) grains (assuming an a value of 0.04 ± 0.02). An internal dose rate of 0.010 ± 0.002 Gy/ ka was assumed in the case of the coarser fraction based on Vandenberghe et al (2008). Equivalent dose values determined interpolating on a single saturation exponential plus a linear term fit.

We previously reported the ages for the silt-sized quartz extracts. Their data set shows no clear outliers and increases with depth; optical ages in between 8.7 ± 1.3 ka and 68 ± 10 ka were obtained for the L1 unit, while samples taken from below the S3, S2 and S1 palaeosols yield optical ages of ~160 ka, ~150 ka, and ~110 ka, respectively.

The ages obtained using sand-sized quartz are as consistent with the stratigraphic position of the samples as the ages for the fine grains. They are, however, significantly and systematically older: the L1 unit range is dated in between 16 ± 2ka and 86 ± ka, and optical ages of ~230 ka, ~180 ka, and ~130 ka are obtained for samples from below the S3, S2 and S1 palaeosols. The age difference varies from ~20 to ~70%; apart from perhaps for the two uppermost samples, there is no clear dependence on the age of the samples.

Discussion

Figure 21 compares the OSL ages obtained using sand-sized (63-90 µm) quartz to the age information that was previously obtained by Timar et al. (2010) through optical dating of silt-sized quartz and time-depth modeling of magnetic susceptibility data. Given that no confidence limits can be defined for the time-depth model, we conclude that it is broadly consistent with both sets of optical ages for the L1 unit. The inset to **Figure 21** shows the optical ages obtained for the L1 unit as a function of depth to greater detail. The optical ages indicate a clear change in the rate of loess accumulation during the last Interglacial/Glacial cycle.

Although the sedimentation rates obtained using the fine and coarse-grained quartz are reasonable consistent, they cover different absolute time-ranges and, by consequence, conflict on the precise timing of the change in sedimentation rate. Indeed, the ages obtained using fine-grained quartz suggests that the rate of loess accumulation varied during the last glacial period. The change in sedimentation rate occurred at ~60 ka, which coincides with the transition of MIS 4 to MIS 3. The fine-grained optical age chronology also allocates a weakly-developed palaeosol in the middle of the L1 unit to MIS 3; this is consistent with the prediction from the magnetic time-depth model. The fine grains do seem to underestimate the true burial age from the penultimate glacial periods onwards, but confirm that the S1 unit must have formed during MIS5.
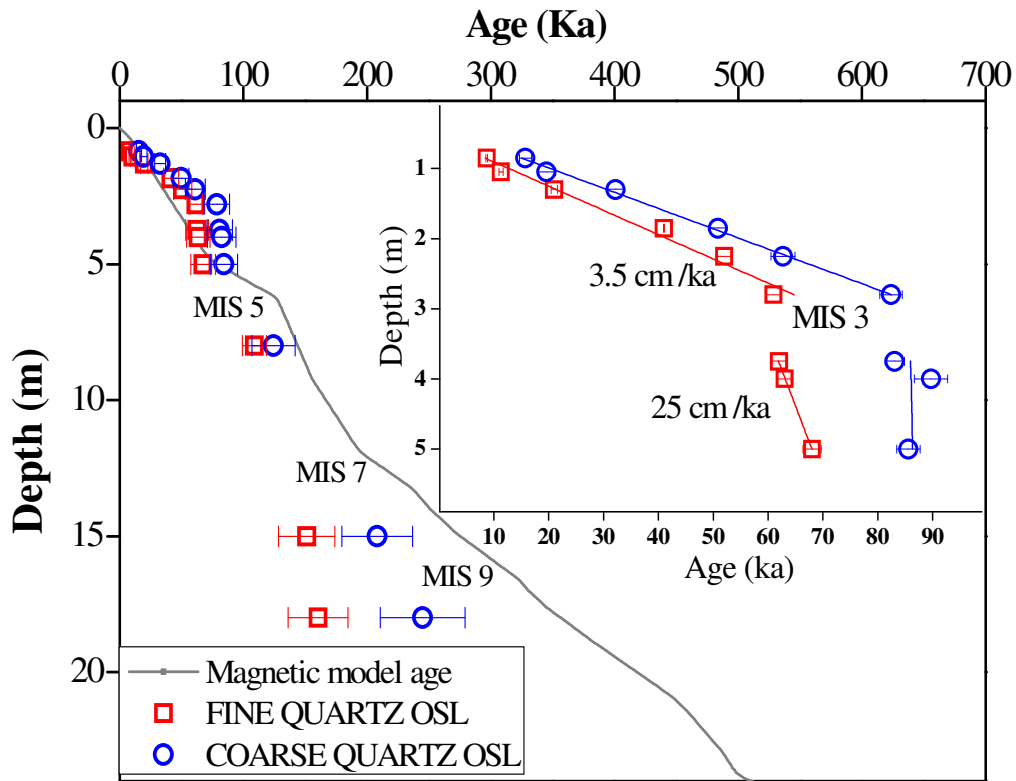
Figure 21: *Plot of optical ages obtained on fine sand quartz grains (open circles, 1 sigma total uncertainties) as a function of depth compared to fine silt optical ages (open squares, 1 sigma total uncertainties) and the results from the palaeomagnetic time-depth modeling (shown by the gray line. The inset shows the optical ages (1 sigma random uncertainties) and sedimentation rates obtained for the L1 unit.*

The optical ages obtained using sand-sized quartz, on the other hand, suggest that loess accumulated at a constant rate during the Last Glacial Stage (MIS 4-2). Furthermore, the dataset indicates that the weak palaeosol, the uppermost well-developed palaeosol (S1) and the intercalated loess unit (the lower part of L1) belong to one complex that formed during MIS5. It is only for significantly older loess units (L3 onwards) that optical dating of coarse quartz grains appears to underestimate the true burial age.

Quartz from both grain-size fractions behaves in the SAR protocol in a similar manner, and procedural tests (recuperation, recycling ratio, and dose recovery) suggest that their OSL signals should be suitable for equivalent dose determination. All signals are dominated by a thermally stable fast component. The cause for the difference in age is, therefore, not understood. One could argue that incomplete resetting may account for age overestimation in the optical dating of

coarse grains. This remains to be investigated, but is considered unlikely to be the only cause for the observed age discrepancy. Indeed, it would require residual doses of the order of at least tens of Gy to explain the age offset for all samples. Even in fluvial environments, where exposure to sunlight is usually more restricted, dose offsets in samples older than a few ka are rarely significant (*Jain, 2004*). An other source of inaccuracy may be the a-value. The alfa efficiency in inducing luminescence in fine grains could not be measured directly in our study and a value of 0.04 ± 0.02 was adopted from other studies (*Rees Jones et al 1995*). Adopting a lower value would slightly increase the fine grain OSL ages. However, the values obtained on sand -sized quartz are always higher than the De's in the silt-sized quartz and in the case of the younger samples not even using a nil value for the alpha efficiency would not overcome the age discrepancy. Furthermore, in the case of older samples the alpha efficiency values could be even higher than 0.04 (*Mauz et al 2006*), thus leading to a more pronounced age difference.

Conclusions

Loess is generally considered as an ideal material for luminescence dating. It is a windblown deposit, which should ensure that the constituent mineral grains received sufficient light-exposure to fully reset the luminescence clock. In recent years, quartz has become the dosimeter of choice and modern optical dating technology is increasingly applied to various grain-size fractions of quartz that have been extracted from loess. In these studies, it is implicitly assumed that the age for each grain-size fraction is indeed identical and accurately reflects the time of burial.

This study demonstrates that luminescence dating of loess may be more complicated. For samples collected from the loess sequence near Mircea Voda (SE Romania), it is observed that OSL signals from silt-sized and sand-sized quartz yield ages that differ significantly. The OSL characteristics of both fractions, however, appear just as suitable for dating the deposits. The signals are dominated by a fast component and they are thermally stable. The OSL signals from the two fractions behave well in the SAR protocol (in terms of recycling, recuperation and dose recovery), indicating that the SAR protocol should be suitable for determining the equivalent dose in both. As such, there would be no cause to doubt the data generated by analysis of a single grain-size fraction of quartz (at least from a pure laboratory-methodological perspective).

For now, it is concluded that optical dating of quartz is a powerful tool for recognizing variations in loess sedimentation rate that occurred during the last Glacial/Interglacial cycle. At least for the loess record near Mircea Voda, it also allows establishing the chronostratigraphic position (MIS 5) of the uppermost well-developed palaeosol (S1).

The apparent controversy arises upon comparison of the age results obtained for quartz grains from different fractions and this observation is of relevance to both past and future studies. Indeed, although this study focussed on samples from a single section, there is evidence that the phenomenon may be more ubiquitous (*Vandenberghe et al., 2009*). At present, this age discrepancy is not understood and further work is underway that aims at resolving the issue.

The research presented has been carried out in the Luminescence Dating Laboratory of Environmental Radioactivity and Nuclear Dating Centre of Babes-Bolyai University Cluj Napoca and have been presented to several international meetings (Timar et al. 2009b, 2010b) and submitted to a highly ranked peer reviewed publication (Timar et al. 2010a)

5.2.3. Further investigation into the luminescence properties of silt sandy (63-90 μm) and fine (4-11 μm) quartz

An examination of the equivalent dose distributions of fine and silt-sandy quartz grains

Analyzing the random variability of equivalent doses can give information on partial bleaching, microdosimetric variations or post depositional mixing

If an analysed sample was well bleached at deposition, has gone no significant post-depositional alteration or translocation and has been subjected to a uniform radiation field the De values obtained should form a narrow Gaussian distribution.

Figure 22 presents the equivalent dose distribution (represented as a histogram and as a radial plot) obtained for sample MV2 using small (2 mm diameter) aliquots. It can be observed that despite the fact that the uncertainty in each individual equivalent dose due to counting statistics is typically 3-6 % the distribution obtained on 49 disks though, is very broad, having a relative standard deviation of almost 50 %. The distribution obtained in the case of the dose recovery test (recovered dose approximating the natural dose) is symmetric and has a relative standard deviation of 10 % (**figure 22 b)**).

This clearly indicates that an additional source of scatter is present in the natural data which is not related to analytical or instrumental uncertainties.

We do not exclude that partial bleaching might be a cause for the age oversitmation of the coarser quartz fraction compared to the fine grains; this is unlikely though to be the case due to the windblown nature of the of the deposits analyzed; it is also unlikely to account alone for the difference observed for the older samples in which the De's differences amount from tens to hundreds of Gy.
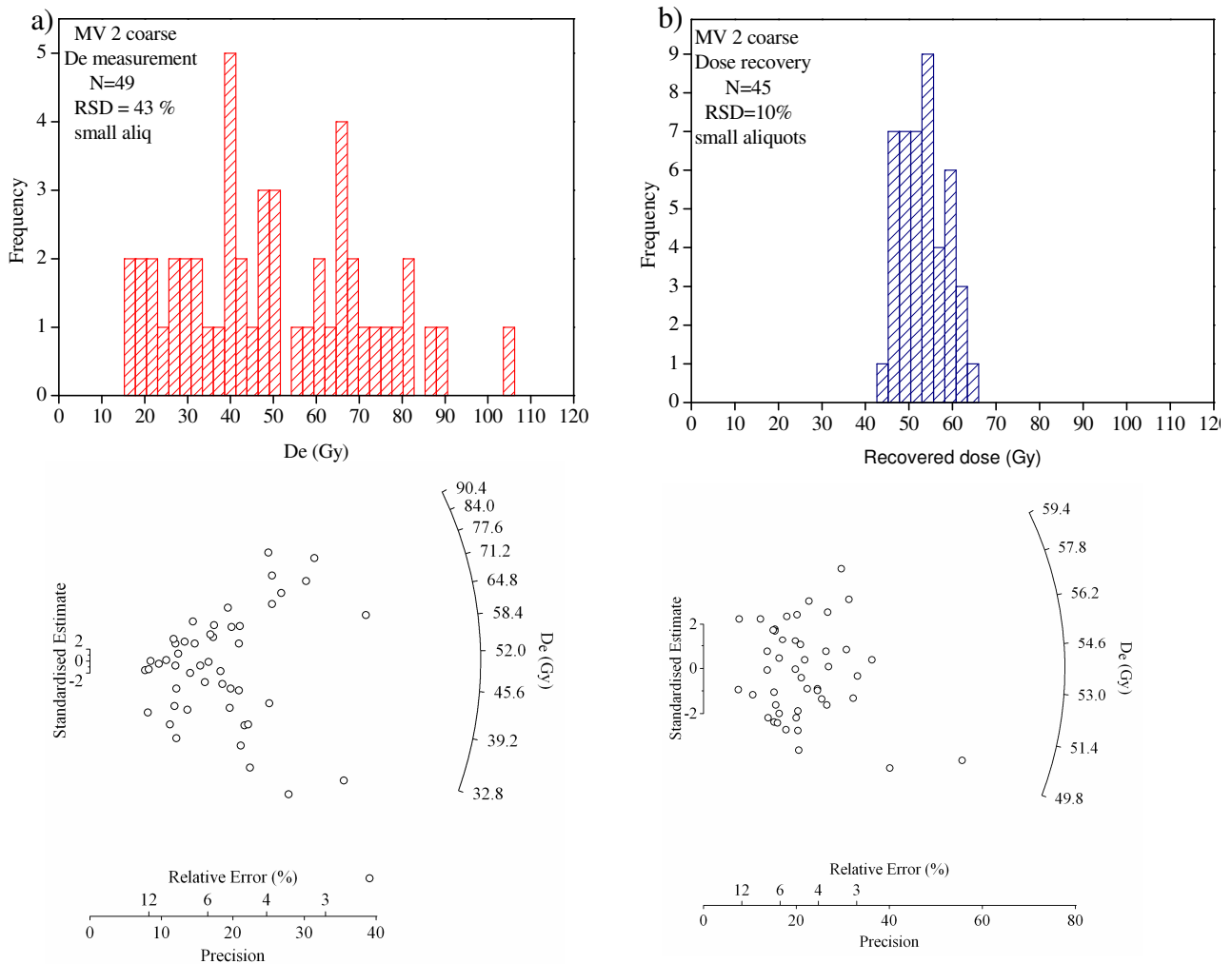
*Figure 22: Distribution of equivalent doses for natural signals obtained on 49 small aliquots (2 mm diameter) of sample MV 2 coarse grains represented as a histogram and as a radial plot. **b):** Distribution of equivalent doses obtained in a dose recovery test on 45 small aliquots (2 mm diameter) of sample MV2 represented as a histogram and as a radial plot. The given dose was chosen to be approximately equal to the equivalent dose. The average recovered to given dose ratio obtained was 1.04 ± 0.02.*

Testing the possibility of the existence of thermally unstable recombination centers in coarse (silt-sandy) quartz

A question that has to be addressed is whether it is possible for different quartz types to yield different equivalent doses following common palaeodoses. A fundamental requirement of luminescence dating procedures is that natural and artificial irradiation are equivalent in terms of the luminescence produced. This assumption basically means that the growth curve constructed in the laboratory matches signal growth in nature. This assumption is impossible though to be tested directly as natural dose rates of our samples are $\approx 8*10^{-11}$ Gy /s while the dose rates used in laboratory are ≈ 0.1 Gy /s.

Based on the model developed in 2001 Bailey *(Bailey, 2004)* suggested that dose rate effects in quartz may cause systematic overestimation of absorbed doses (and therefore age estimates). Based on numerical simulations he argued that this effect can be caused by competition from the relatively thermally unstable R1 recombination centre. Later on Bailey et al., (2005) investigated pulsed-irradiation regeneration of quartz OSL and showed that in the case of certain samples this technique can correct for equivalent dose overestimation. *Bailey, (2004)* suggested that performing the irradiations at high temperature (200 ^{o}C) would remove this unwanted effect, as the holes would be detrapped from R1 centre due to the thermal treatment. We have carried out elevated temperature irradiation on 3 aliquots of silt sandy quartz of sample MV8. An average equivalent dose of 240 ± 20 Gy was obtained; this value is consistent within error limits to the one obtained using normal irradiation (248 ± 8 Gy). There was no difference noticed in the case of growth curve shape.

Pulsed irradiation (as recommended by *Wallinga (2002))* had also been investigated. A small (~ 6%) decrease in the average measured equivalent doses is obtained in the case of pulsed irradiation for samples MV5 and MV8, while the average equivalent doses obtained for sample MV6 are consistent. At a first look, the decrease observed both in the case of pulsed irradiation and elevated temperature irradiation might suggest the possibility of competition effects of R1 centers. However, this was not substantiated by a change in growth curve shape.

Unfortunately, older samples could not have been investigated due to the lack of material.

Further dose response investigations

We have taken out investigation one step further and constructed much extended growth curves up to 10000Gy. In **figure 23**, we are showing the dose response of one aliquot of fine grains extracted from sample MV10. In this case the dose response could not be fitted satisfactory with a single saturating exponential, the behavior being described by the sum of two such functions.
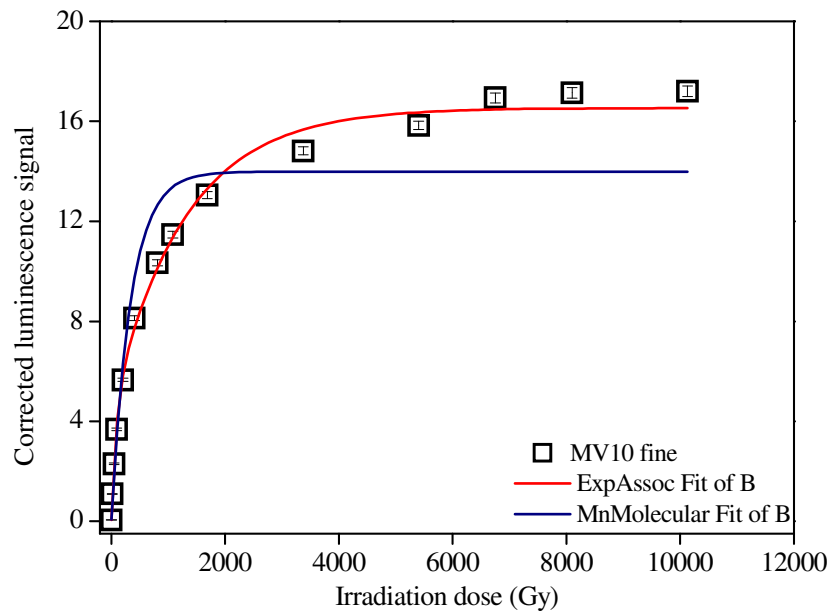
Figure 23: Dose response curve of fine grains constructed up to 10000 Gy.

The dose response up to 10000 Gy of an aliquot of coarse grains was compared to the response of fine grains as well as the dose response of an aliquot of coarse grains after subjecting it to repeated cycles of dosing and bleaching. It was observed that the fine grains have higher saturation characteristics than the coarse grains. Upon subjecting the coarse grains to repeated cycles of bleaching and irradiation (thus simulating transport in nature) the growth pattern obtained resembles fine quart behaviour may imply that the high saturation characteristics of fine quartz might be a consequence of changes generated by weathering.

It should be noted that no difference was observed in the growth pattern in the lower region of the dose response curve. As differences exist only for the non-linear part of the response, we infer that the mechanism is dose dependent. A possible mechanism for this behavior was proposed. However it need further investigations in order to be confirmed.

5.2.4. Testing the potential of optically stimulated luminescence dating methods for dating soil covers from the forest steppe zone in Transylvanian Basin

The drier colder climatic period of the Holocene known as the Subboreal favored the expansion of the Boreal forests and steppes / forest-steppes in Western Eurasia. In the late Holocene a climatic transition from this climate to milder wetter conditions (Subatlantic) has taken place.

In the area of the expositional forest-steppe in the Transylvanian Basin there are many larger or smaller islands of Clinostagnic Phaeozems and Chernozems (named formerly "Black Clinohydromorph Soils" by the Romanian Pedologists) covered by Luvisols. These are gradually diminishing with increasing of the precipitations until they completely disappear as actual soils.

The C-14 dating of the dark forest-steppe soils from such areas revealed ages in between 14.000-20.000 ka BP proving that in such drier regions the forest-steppe type of landscape and its associated soils (not necessarily also the strict vegetational types) are stable structures since the upper Pleistocene (*Pendea et al., 2002; Pendea, 2005*).

Unfortunately, though intuitively posed in connection with the climate change associated with the Subboreal-Subatlantic climatic transition (*Badarau, 2005*) no such a pedological structure was dated until now in Transylvania.

Luminescence analysis were performed on a sample of Albic Luvisol –LABORATORY CODE: 3A (LU), and a sample of Clinostagnic Phaeozem –LABORATORY CODE: 4B (PHZ). Linearly modulated-OSL measurements (*Bulur et al 2001*) indicated that the luminescence signal of interest is dominated by a fast component (**Figure 24**), and thus amendable to be analysed through the single aliquot regeneration protocol (*Murray and Wintle 2003, Wintle and Murray 2006*)

Equivalent doses were determined for both samples performing 30 replicate measurements. An average value of 28.3 Gy was obtained for sample 4B clinostagnic phaeozem while for sample 3A albic luvisol we have obtained an average value of 12.6 Gy.

Overdispersion can be observed in the data. This is not an experimental artifact or a result of quartz OSL signal intrinsic characteristics, as it was demonstrated that our measurement protocol is robust. From radial plots, it can be seen that the precision in individual equivalent doses obtained is always better than 3%. The observed scatter is probably an effect quartz grain mixing

in the soil layer due to pedo or bioturbation. The scatter might be also caused by the low resolution that is achieved when sampling soils for luminescence dating (7 cm in our case).

In order to find the best estimate for the true value of the burial dose measurements have to be repeated using smaller amount of grains and by applying statistical analysis of the dataset. However minimum and maximum ages based on a selected limited number of analysed aliquots are presented in **Table 4.**

SAMPLE	De average (Gy)	De minimum (Gy)	De maximum (Gy)	AVERAGE AGE (ka)	MINIMUM Age (ka)	MAXIMUM Age (ka)
4B (PHZ)	28.8 ± 0.8 (n=30)	24.0 ± 0.8 (n=6)	35.1 ± 0.8 (n=7)	10.9 ± 1.4	9.2 ± 1.2	13.4 ± 1.8
3A (LUV)	12.6 ± 0.3 (n=30)	11.8 ± 0.2 (n=20)	14.4 ± 0.3 (n=10)	4.3 ± 0.6	4.0 ± 0.5	4.9 ± 0.5

Table 4: *Average, respectively maximum and minimum assumed equivalent doses derived from a selected number of aliquots denoted by n. Uncertainties quoted represent only random errors. For the age calculation a total moisture content of 20 ± 5 % was assumed and a beta attenuation factor of 0.94 ± 0.45. Systematic uncertainties of 5% concerning the calibration of the gamma spectrometer, respectively 3% for the calibration of the radioactive source. The last columns presents the ages and the corresponding overall uncertainties calculated using the system of Aitken (1976).*

The ages obtained can be regarded as evidence that the dark soil cover was a stable feature in the Subboreal in most of the area of Transylvania and their replacement with Luvisols reflects a climatic transition from a drier climate (Subboreal) that have favored the extension of the Boreal forests and steppic grasslands to a wetter milder one (the Subatlantic) that favored the expansion of the nemoral and subtropical forests in the Holocene. Thus the paleo-pedological structures from Transylvania and presumably from other areas of Romania which consists of a fossil mollic horizon of a Phaeozem covered by an albic horizon of an actual Luvisol can be considered as a climatic marker which resumes the climatic changes which are associated with the Subboreal-Subatlantic transition which began around 4ka BP.

These results have been accepted for publication in a peer reviewed journal (Timar et al., 2010d).

Summary and conclusions

Luminescence phenomena encompass a very wide range of processes. For the purpose of retrospective dosimetry only optically stimulated luminescence (OSL) and thermoluminescence (TL) processes are of interest. OSL and TL is the luminescence emitted from an irradiated insulator or semiconductor during exposure to light or respectively heat; thus OSL and TL are stimulated processes. The luminescence signal emitted is dependent on the irradiation history of the sample.

Although the processes giving rise to luminescence phenomena in natural wide-gap crystals such as quartz and feldspars are complicated and not fully understood this phenomenon can be exploited for dating.

In the past ten years luminescence dating has undergone extreme technological and methodological advances and at the moment is characterized by a degree of quality control seldom seen with other dating techniques. Despite this however, modern luminescence dating techniques have not been applied in a Romanian laboratory up to now. In this thesis quality control of procedures concerning sample preparation, paleodose and annual dose estimation in Luminescence Dating Laboratory, Environmental Radioactivity and Nuclear Dating Centre of Babeş-Boyai University of Cluj Napoca, Romania have been presented. State-of-the-art luminescence dating techniques have applied in key applications.

For equivalent dose measurement, the extraction of quartz and polymineral fine grains from samples using conventional luminescence dating sample preparation techniques was implemented in our laboratory. The purity of OSL signals from the extracted quartz grains was tested and confirmed by the absence of IR signals following irradiation, through the measurement of IR depletion ratios, by recording TL glow curves, and by performing pulsed OSL measurements. The dose rate delivered on different substrates and for different grains sizes by the ^{90}Sr-Y beta source mounted on the Risø TL/OSL DA-20 luminescence reader was determined by making use of gamma dosed calibration quartz supplied by Risø and equivalent

dose measurement procedures were validated through an intercomparison exercise with Gent Luminescence Dating Laboratory, Belgium.

Annual dose was determined based on radionuclide concentrations determined in our laboratory by means of high resolution gamma ray spectrometry using an ORTEC hiperpure germanium detector (active volume of 181 cm^3, 0.878 keV FWHM at 5.9KeV, 1.92 keV FWHM and 34.2 % relative efficiency at 1332.5 keV). The system was calibrated in energy using an europium source while the efficiency calibration was performed using a Monte Carlo routine which was validated using IAEA standards. A method for determining ^{226}Ra concentrations directly by making use of the interfered line at 186.2keV was implemented. ^{234}Th, ^{214}Pb, ^{214}Bi, ^{214}Bi, ^{210}Pb, ^{228}Ac, ^{208}Tl, and ^{40}K can be routinely measured in environmental samples. The procedures have been validated through an intercomparison exercise with two other different methods - alpha spectrometry (The Radiochemistry Laboratory from Veszprem), respectively instrumental neutron activation (Institute for Nuclear Research, Pitesti, Romania), and with Gent Luminescence Dating Laboratory where the same techniques are being used (high resolution gamma spectrometry with relative efficiency calibration).

Luminescence dating was applied to four pottery fragments excavated at Lumea Nouă (Alba Iulia, Romania). The aim of this study was to apply new approaches in optical dating to improve the chronological framework for the site. To this purpose, the SAR protocol was applied to both blue (OSL) and infrared stimulated luminescence (IRSL) signals from coarse (90-125 µm) quartz and polymineral fine (4-11 µm) grains, respectively. For the sake of comparison, a more conventional approach, which MAAD protocol and thermoluminescence TL signals from polymineral fine grains, was applied as well. The presence of anomalous fading in the 410 nm IRSL emission as well as blue TL emission indicated that our IRSL and TL ages would underestimate the true ages. To correct the SAR-IRSL results for fading, we applied the correction procedure proposed by Huntley and Lamothe. No correction was applied to the TL results, as it is not valid to correct the bulk signal originating from an undifferentiated fine-grained mineral mixture using the fading observed from only part of this mixture. It was concluded that **c**ompared to the TL method, the IRSL and OSL approaches are based on a more robust dating methodology. As SAR-OSL dating of quartz yielded the most precise age

estimates, this was considered to be the technique of choice. The average of the four quartz SAR-OSL ages presented above placed the transition from Foeni to Petreşti culture at Lumea Nouă site around 6.2 ± 0.5 ka an extremely plausible age taking into consideration the archaeological information. Further investigations are needed for establishing a complete chronological framework for the ancient cultural development at Lumea Nouă. Nevertheless our study is a clear illustration of how luminescence dating, especially by the use of state-of-the-art techniques can contribute to this purpose.

The Romanian loess-palaeosol sequences preserve a significant terrestrial record of Quaternary climate change during at least five Glacial / Interglacial cycles. We have reported the first high resolution optically stimulated luminescence (OSL) dating study for the loess sequence near Mircea Vodă (Dobrogea, SE Romania). The study focussed on loess from the last four glacial periods and used silt-sized (4-11µm) quartz as dosimeter.

An internally consistent set of optical ages was obtained and the optical ages have been compared with a magnetic time-depth model ellaborated by Conf. Dr. Cristian Panaiotu and Conf. Dr. Cristina Panaiotu (University of Bucharest) based on magnetic susceptibility measurements. Based on luminescence ages, evidence was presented for a varying loess accumulation rate during the Last Glacial. The optical ages indicated that this unit did not accumulate at a constant rate, with loess being deposited at a significantly lower rate during the past ~50 ka. This illustrates the limitations of proxy records (such as magnetic susceptibility) to interpret and derive a chronology for these deposits.

While it could be confirmed that the uppermost palaeosol (usually denoted by S1 in stratigraphic nomenclature) formed during the last Interglacial, comparison with independent age control (pedostratigraphy and a newly developed palaeomagnetic time-depth model) also indicated that the dating procedure underestimates the true burial age from the penultimate glacial period onwards. The SAR-OSL ages obtained for the three samples taken below the S1 soil were interpreted as age underestimates, with the degree of age underestimation increasing with depth. Interestingly, the luminescence characteristics did not indicate such behavior: the signal continues to grow to high doses, the laboratory measurement procedure is accurate, and the ages increase with depth.

In that study we concluded that optical dating of fine-grained quartz can be used to establish a reliable chronology for Romanian loess up to ~70 ka. This age values correspond to equivalent doses of ~ 200Gy. Up to this value an exponential function and an exponential plus a linear term function give the same goodness of fit to experimental data. At least for our samples, the results obtained from the high dose linear region of the growth curve do not appear to be accurate. The procedure underestimates the true burial age when applied to loess that was deposited before the last climatic cycle; further research is necessary to establish what causes the age underestimation. Our results illustrated that an apparently reliable OSL laboratory measurement procedure not necessarily guarantees an accurate determination of the true burial.

In recent years, quartz has become the dosimeter of choice and modern optical dating technology is increasingly applied to various grain-size fractions of quartz that have been extracted from loess. While it seems logic to assume that for a windblown material (such as loess) grains from several fractions are suitable for optical dating, this has not been explicitly demonstrated. At least to our knowledge, no studies are available that compare the luminescence characteristics and age of quartz grains of different granulometric fractions extracted from loess. We have conducted such a study.

Our results indicate luminescence dating of loess may be more complicated. For samples collected from the loess sequence near Mircea Vodă (SE Romania), it was observed that the optical ages obtained on silt-sandy grains (63-90 μm) are in between ~20 and 70% higher than those obtained on the fine silt fraction (4-11 μm). Optical ages obtained on several samples of different ages using the coarse silt fraction (35-50 μm) fraction are in agreement with the ages obtained on the silt sandy fraction. The apparent controversy is of relevance to both past and future studies worldwide.

It was observed that the equivalent doses obtained for sand -sized quartz are always higher than the De's in the silt-sized quartz, with the relative difference being more pronounced in the case of the younger samples. Not even considering a nil value for the alpha efficiency would overcome the age discrepancy. As such, we conducted our investigation for determining the cause for the observed age controversy focusing on luminescence emissions.

Based on LM-OSL analysis it was concluded that all samples analysed have signals dominated by the fast component and thus are suitable for equivalent dose measurement using the SAR

protocol. It was also shown that the signal used for optical dating is thermally stable. The OSL signals from all fractions behaved well in the SAR protocol (in terms of recycling, recuperation and dose recovery), indicating that the SAR protocol should be suitable for determining the equivalent dose in both. As such, there would be no cause to doubt the data generated by analysis of a single grain-size fraction of quartz (at least from a pure laboratory-methodological perspective).

Both coarser fractions show overdispersion in equivalent dose distributions. Partial bleaching can be considered as a possible cause as grains size distributions in the investigated loess are bi-modal or even three-modal distributions, reflecting multiple sources of the clastic material. The coarse silt and fine sand material could have proximal source, while the silt could have a distant source.

However, partial bleaching could not account alone for the age discrepancy observed in the case of older samples where residual doses of the order of at least tens of Gy would be required. Thus, we concluded that at least in the case of older samples a second mechanism should interfere.

By constructing dose response curves to high dose (up to ~700 Gy) a very similar pattern of growth was observed for samples of different ages in the case of both fractions. It was also observed that the growth can be best represented by a function of the form of a single saturating exponential plus a linear term. Growth curve characteristics of the two fractions investigated were found to be very different though, with coarse grains saturating at much lower doses. The average characteristic dose (D_0^*; obtained using a single saturation exponential plus a linear term) was 120 Gy in the case of fine silt quartz grains, and 80 Gy in the case of the coarse silt and fine-sandy grains.

It should be noted that the existence of a linear component in dose response curves constructed at high doses has been identified in other studies as well. However, the intrinsic mechanism of this behavior is far from being understood and the reliability of using this part of the growth curve has yet to be investigated. Very little is known empirically on the possible dose rate dependence of OSL while different simulation studies infer that this kind of effects is prone to occur. For our investigated samples the possibility of existence of dose and/ or dose rate effects could not be excluded, and a speculative mechanism was proposed. We infer that the fundamental requirement of luminescence dating that the natural (low dose rate) and artificial irradiation (very

high dose rate) are equivalent in terms of luminescence produced might not be fulfilled for high doses, at least in the case of certain samples.

The results obtained show that luminescence dating of loess is far less straightforward than generally is accepted and thus challenge earth-scientific as well as luminescence dating communities. Further work should refine our knowledge of the origin of luminescence signals in quartz. The upper dating limit of quartz OSL signals and particularly the cause of the observed linear plus-exponential shape of the dose response curves at higher doses are issues that remain to be addressed. Optical dating of old sediments remains thus a difficult task.

Selected References:

Adamiec G. and Aitken M. (1998)
Dose-rate conversion factors: update.
Ancient TL 16, 37-50.

Aitken M.J. and Alldred J.C. (1972)
The assessment of error limits in thermoluminescent dating.
Archaeometry 14, 257-267.

Aitken M.J. (1976)
Thermoluminescent age evaluation and assessment of error limits: revised system.
Archaeometry 18, 233-238.

Aitken M.J. (1985)
Thermoluminescent Dating.
Academic Press, London, 359p. ISBN: 0-12-046380-6.

Aitken M.J. (1998)
An introduction to optical dating. The dating of Quaternary Sediments by the use of Photon-Stimulated Luminescence.
Oxford University Press, Oxford, 267p, ISBN: 0-19-854092.

 Aitken M.J. (1999)
Archaeological dating using physical phenomena.
Rep. Prog. Phys. 62, 1333-1376.

Armitage S.J., Bailey R.M. (2005)
The measured dependence of laboratory beta dose rates on sample grain size.
Radiation Measuremets 39, 123-127.

Bădărau Al. S. (2005)
Landscape Transformation in the Transylvanian Basin, with special focus upon the biogeographical aspects.
Phd. Thesis, Babeş-Bolyai University Cluj Napoca .

Bailey R.M., Smith B.W., Rhodes E.J. (1997)
Partial bleaching and the decay form characteristics of quartz OSL.
Radiation Measurements 27, 123-126.

Bailey R.M. (2001)
Towards a general kinetic model for optically and thermally stimulated luminescence of quartz.
Radiation Measurements 33, 17-45.

Bailey R.M. (2004)
Paper I- simulation of dose absorption in quartz over geological timescales and its implications for the precision and accuracy of optical dating.
Radiation Measurements 38, 299-310.

Bailey R.M., Armitage S.J., Stokes S. (2005)
An investigation of pulsed irradiation regeneration of quartz OSL and its implications for the precision and accuracy of optical dating. (Paper II)
Radiation Measurements 39, 347-359.

Bailiff I.K., and Poolton, N.R.J. (1991)
Studies of charge transfer mechanisms in feldspars.
Nuclear tracks and radiation measurements 18, 111-118.

Bailiff I.K. (1999)
The Development of Retrospective Luminescence Dosimetry for Dose Reconstruction in Areas Downwind of Chernobyl.
Radiation Protection Dosimetry 84 (1-4), 411-419.

Bailiff I.K., Bøtter-Jensen L., Correcher V., Delgado A., Göksu H.Y., Jungner H., Petrov A.S. (2000)
Absorbed dose evaluations in retrospective dosimetry: methodological developments using quartz.
Radiation Measurements, 32, 609-613.

Bailiff I K., Stepanenko V F., Göksu H Y., Jungner H., Balmukhanov S B., Balmukhanov T. S., Khamidova L. G., Kisilev V. I., Kolyado I. B., Kolizshenkov T.V., Shoikhet Y. N., Tsyb A F. (2004)
The Application of Retrospective Luminescence Dosimetry in Areas Affected By Fallout from the Semipalatinsk Nuclear Test Site: An Evaluation of Potential.
Health Physics, 87 (6), 625-641

Banerjee D., Bøtter-Jensen L., Murray A.S. (1999)
Retrospective Dosimetry: Preliminary Use of the Single Aliquot Regeneration (SAR) Protocol for the Measurement of Quartz Dose in Young House Bricks.
Radiation Protection Dosimetry 84 (1-4), 421-426.

Begy R., Cosma C., **Timar A.,** Fulea D. (2007)
A study on Cs-137 contamination of soils from certain regions of Transylvania
Environment and Progress 9, 73-76.

Begy R.C., Cosma C., **Timar A**., Fulea D. (2009a)
The Determination of Absolute Intensity of ^{234m}Pa's 1001 keV Gamma Emission Using Monte Carlo Simulation.
Journal of Radiation Research 50, 277-279.

Begy R., Cosma C., **Timar A**., (2009b)
Recent changes in Red Lake (Romania) sedimentation rate determined from depth profiles of ^{210}Pb and ^{137}Cs radioisotopes"
Journal of Environmental Radioactivity 100, 644-648.

Benea V., Vandenberge D., **Timar A**., Van den Haute P., Cosma C., Gligor M., Florescu C. (2007)
Luminescent dating of Neolithic ceramics from Lumea Nouă, Romania.
Geochronometria 28, 9-16.

Bøtter-Jensen L, McKeever S.W.S, Wintle A. G. (2003)
Optically Stimulated Luminescence Dosimetry
Elsevier, 355 p, ISBN 0 444 50684 5

Bulur E., Bøtter-Jensen L. and Murray A.S. (2001)
Optically stimulated luminescence from quartz measured using the linear modulation technique.
Radiation Measurements 32, 407-411.

Buylaert J.P., Vandenberge D., Murray A.S., Huot S., De Corte F. and Van den Haute P. (2007)
Luminescence dating of old (>70ka) Chinese loess: a comparison of single aliquot OSL and IRSL techniques.
Quaternary Geochronology 2, 9-14.

Buylaert, J.P., Murray, A.S., Vandenberghe, D., Vried, M., De Corte, F., Van den haute, P., (2008)
Optical dating of Chinese loess using sand-sized quartz: Establishing a time frame for Late Pleistocene climate changes in the western part of the Chinese Loess Plateau.
Quaternary Geochronology 3, 99-113.

Chen S., Liu X., Zhang C., Tang Q. (2009)
The Monte Carlo simulation of the absorbed dose in quartz.
Radiation Measuremets 44, 626-628.

Choi J.H., Murray A.S., Cheong C.S., Hong D.G., Chang H.W. (2003)
The resolution of stratigrafic inconsistency in the luminescence ages of marine terraces sedimets from Korea.
Quaternary science Reviews 22,1201-1206.

Cosma C., Benea V., **Timar A.,** Barbos D., Paunoiu C. (2006)
Preliminary dating results on ancient ceramics from Romania by means of thermoluminescence.
Radiation Measurements 41, 987-990.

Cosma C., Petrescu I, Meilescu C., **Timar A.** (2007)
Properties of lignite from Oltenia and their influence on the environment
Studia Universitatis Babes-Bolyai, Ambientum, I, 1—2, 65-75.

Cosma C. **Timar A.,** Benea V., Pop I., Jurcut T., Ciorba D. (2008a)
Using natural luminescent materials and highly sensitive sintered dosimeters MCP-N (LiF: Mg, Cu, P) in radiation dosimetry.
Journal of optoelectronics and advanced materials vol. 10, nr 3, 573-577.

Cosma C., **Timar A.,** Benea V., Somlai J. (2008b)
Applications of nuclear dating methods in archaeology, geology and environmental science" *ECOTERRA, nr 19, an V*, p.: 28-30.

Cosma C., Benea V., **Timar A.,** Gligor M., Varvara S. (2008c)
Datarea prin luminescenta stimulate termic (TL) si optic (OSL). Aplicatii in arheologie.
ACTA MVSEI APVLENSIS, Apulum, XLV, 579-598

Cosma, C., **Timar, A.,** Benea, V., Begy, R., (2008d)
Nuclear and Seminuclear Dating Methods: Application in Archeology, Geology and Environmental Science.
Terrestrial radionuclides in the Environment, Environmental Conferences Veszprem, ISBN 978 963 9696 488, pp. 23-35.

Cosma C., **Timar A.,** (2008e)
Testarea potentialului metodelor luminiscente in datarea unei sectiuni de loess din Dobrogea, *MENER, Universitatea Politehnica - Bucuresti*, 643-650.

Cosma C., Ciorba D., **Timar A.,** Szacsvai K., Dinu A. (2009a)
Radon exposure and lung cancer risk in Romania.
Journal of Environmental Protection and Ecology, nr 1-2009, 94-104.

Cosma C., Petrescu I., Meilescu C., **Timar A.** (2009b)
Studies on the radioactivity of lignite from the area between the Danube and Motru (South-West Romania) and the incidence on the environment.
Journal of Environmental Protection and Ecology, nr 1-2009, 192-201.

Cosma C., **Timar A.,** Benea V., Pop I., Moldovan M. (2009c)
Carbon Molecular Sieve for Radon and Thoron Monitoring"
Romanian Journal of Physics, nr. 3-4, vol. 54, 401-405.

De Corte F., Umans H., Vandenberghe D., De Wispelaere A. and Van den Haute P. (2005)
Direct gamma-spectrometric measurement of the Ra-226 186.2 keV line for detecting U-238/Ra-226 disequilibrium in determining the environmental dose rate for the luminescence dating of sediments.
Applied Radiation and Isotopes 63, 589-598.

Denby, P.M., Bøtter-Jensen L., Murray A.S., Thomsen K.J., Moska P. (2006)
Application of pulsed OSL to the separation of the luminescence components from a mixet quartz/ feldspar sample.
Radiation Measurements 41, 774-779.

Duller, G.A.T. (2003)
Distinguishing quartz and feldspar in single grain luminescence measurements.
Radiation Measurements 37, 161-165.

Duller G.A.T. (2004)
Luminescence dating of Quaternary sediments: recent advances.
Journal of Quaternary Science 19, 183-192.

Frechen M., Schweitzer U. and Zander A (1996)
Improvements in sample preparation for fine grain technique.
Ancient TL 14, 15-17.

Frechen M., Dodonov A.E., (1998)
Loess chronology of the Middle and Upper Pleistocene in Tadjikistan.
Geologische Rundschau 87, 2-20.

Frechen M. (1999)
Luminescence dating of loessic sediments from the Loess plateau, China.
International Journal of Earth Sciences 87, 4, 675-684.

Frechen, M., Oches, E.A., Kohfeld, K.E., (2003)
Loess in Europe – mass accumulation rates during the Last Glacial Period.
Quaternary Science Reviews 22, 1835-1857.

Forman S. (1991)
Late Pleistocene Chronology of loess Deposition near Louchuan, China.
Quaternary Research 36, 19-28.

Fulea D. Cosma C. (2009)
Monte Carlo sampling for gamma and beta detectors using a general purpose PC program.
Radiation Measurements 44, 278–282.

Garcia-Talavera M, Laedermann J.P., Decombas M., Daza M.J., Quintana B. (2001)
Coincidence summing corrections for the natural decay series in γ ray spectrometry.
Journal of Radiation and Isotopes 54, 769-776.

Göksu, H. Y.; Degteva, M. O.; Bougrov, G.; Meckbach, R.; Haskell, E. H.; Bailiff, I. K.; Bøtter-Jensen, L.; Jungner, H.; Jacob, P. (2002)
First International Intercomparison of Luminescence Techniques Using Samples From the Techa River Valley.
Health Physics, 82, 94-101

Grogler N, Houtermans FG and Stauffer H. (1960).
Ueber die datierung von Keramik und Ziegel durch Thermolumineszenz.
Helvetica Physica Acta 33, 595-596.

Harrison S., Kohfeld K., Roelandt C., Claquin T. (2001)
The role of dust in climate changes today, at the last glacial maximum and in the future.
Earth Science Reviews 54, 43-48.

Hong DG, Yi SB, Galloway RB and Tsuboi T. (2001).
Optical dating of archaeological samples using a single aliquot of quartz stimulated by blue light.
Journal of Radioanalytical and Nuclear Chemistry 247, 179-184.

Hossain S.M., De Corte F., Vandenberge D., Van den Haute P. (2002)
A comparison of methods for annual radiation dose determination in the luminescence dating of loess sediments.
Nuclear Instruments and Methods in Physics Research A 490, 598-613.

Huntley D.J. and Lamothe M. (2001)
Ubiquity of anomalous fading in K-feldspars and the measurement and correction for it in optical dating.
Canadian Journal of Earth Science 38, 1093-1106.

Hütt G., Jaek I. and Tchonka J. (1988)
Optical dating: K-feldspars optical response stimulation spectra.
Quaternary Science Reviews 7, 381-385.

Istratov A.A., Vyvenko O.F. (1999)
Exponential analysis in physical phenomena.
Review of scientific instruments, vol 70, no 2, 1233-1257.

Jain M. and Singhvi A. (2001)
Limits of depletion of blue-green light stimulated luminescence in feldspars: implications for quartz dating.
Radiation Measurements 24, 883-892.

Jain M., Murray A.S., Bøtter-Jensen L. (2003)
Characterization of blue-light stimulated luminescence components in different quartz samples: implications for dose measurement.
Radiation Measurements 37, 441-449.

Jain M., Murray A.S., Bøtter-Jensen L. (2004)
Optically stimulated luminescence dating: How significant is incomplete light exposure in fluvial environments?
Quaternaire 15 (1-2), 143-157.

Kennedy GC and Knopff L. (1960)
Dating by thermoluminescence.
Archaeology 13, 147-148.

Krbetschek M.R. and Reiser U. (1995)
Luminescence spectra of alkali feldspars and plagioclase.
Radiation Measurements 24, 473-477.

Krbetschek M.R., Götze J., Dietrich A. and Trautman T. (1997)
Spectral information for minerals relevant to luminescent dating.
Radiation Measurements 27, 695-748.

Labau, V., Gaspar, E., Paunica, T. (1996)
Speleothems dating using the thermoluminescence method.
Theoret. Appl. Karstology 9, 29–34.

Lai ZP, Wintle A.G., Thomas S. G. (2007)
Rates of dust deposition between 50 ka and 20 ka revealed by OSL dating at Yuanbao on the Chinese Loess Plateau.
Palaeogeography, Palaeoclimatology, Palaeoecology 248, 431-439.

Lamothe M. (2004)
Optical dating of pottery, burnt stones, and sediments from selected Quebec archaeological sites.
Canadian Journal of Earth Sciences 41, 659-667.

Lang A., Lindauer S., Kuhn R. and Wagner G.A.T (1996)
Procedures used for Optically and Infrared Stimulated Luminescence Dating of Sediments in Heidelberg.
Ancient TL 14, 7-11.

Li B, Li S-H. (2006)
Comparison of De estimates using the fast component and the medium component of quartz OSL.
Radiation Measurements 41, 125-136.

Lian O.B., Roberts R., G., (2006)
Dating the Quaternary: progress in luminescence dating of sediments.
Quaternary Science Reviews 25, 2449-2468.

Mauz B., Packman S., Lang A. (2006)
The alfa effectiveness in silt size quartz: New data obtained by single and multiple aliquot protocols.
Ancient TL, vol 24, No 2, 47-52.

McKeever S.W.S. (2001)
Optically stimulated luminescence dosimetry.
Nuclear Instruments and Methods in Physics Research B, 184, 29-54.

Murray A.S. and Wintle A.G. (1999)
Isothermal decay of optically stimulated luminescence in quartz.
Radiation Measurements 30, 119-125.

Murray A.S. and Wintle A.G. (2000)
Luminescence dating using an improved single-aliquot regenerative dose protocol.
Radiation Measurements 32, 57-73.

Murray A.S. and Olley J.M. (2002)
Precision and accuracy in the optically stimulated luminescent dating of sedimentary quartz: a status review.
Geochronometria 21, 1-16.

Murray A.S. and Wintle A.G. (2003)
The single aliquot regenerative dose protocol: potentials for improvement in reliability.
Radiation Measurements 37, 377-381.

Murray A.S., Svendsen J.I., Mangerud J., Astakhov V.I. (2007)
Testing the accuracy of quartz OSL dating using a known-age Eemian site on the river Sula, northern Russia.
Quaternary Geochronology 2, 102-109.

Murray, A.S., Buylaert, J.-P., Henriksen, M., Svendsen, J.-I, Mangerud, J. (2008)
Testing the reliability of quartz OSL ages beyond the Eemian.
Radiation Measurements 43, 776-780.

Pendea, I.F., Szanto, Zs, Badarau, Al. S., Dezsi, S. (2002)
Age and pedogenic reconstruction of a paleo-relict chernozem soil from Central Transylvanian Basin.
Geologica Carpathica, 53, 37-38.

Pendea, F. (2005)
Late Quaternary geomorphic paleoenvironments in the Transylvanian Basin, Romania.
Phd Thesis, Babeş-Bolyai University Cluj Napoca.

Prescott J.R. and Hutton J.T. (1994)
Cosmic ray contributions to dose rates for luminescence and ESR dating: large depths and long –term variations.
Radiation Measurements 23, 497-500.

Rees-Jones, J, Tite, M.S. (1995)
Optical dating results for British archaeological sediments.
Archaeometry 36, 177-187.

Roberts R.G. (1997)
Luminescence dating in archaeology: from origins to optical.
Radiation Measurements 27, 819-892.

Roberts H.M. (2006)
Optical dating of coarse-silt quartz from loess: Evaluation of equivalent dose determination and SAR procedural checks.
Radiation Measuremets 41, 923-929.

Roberts H.M. (2008)
The development and application of luminescence dating to loess deposits: a perspective on the past, present and future.
Boreas, 37, 483–507.

Ropp R.C. (2004)
Luminescence and the solid state.
Elsevier 2004, 711p. ISBN: 0-444-51661-1.

Singarayer J.S. and Bailey R.M. (2003)
Further investigations of the quartz optically stimulated luminescent components using linear modulation.
Radiation Measurements 37, 451-458.

Singhvi, A.K., Bluszcz, A., Bateman, M.D., Someshwar Rao, M. (2001)
Luminescence dating of loess- palaeosol sequences and coversands: methodological aspects and palaeoclimatic implications.
Earth-Science Reviews 54, 193-211.

Smith B.W. and Rhodes E.J. (1994)
Charge movements in quartz and their relevance to optical dating.
Radiation Measurements 23, 329-333.

Stevens, T., Armitage, S.J., Huayu, L., Thomas, D.S.G. (2007)
Examining the potential of high resolution OSL dating of Chinese loess.
Quaternary Geochronology 2, 15-22.

Steffen D., Preusser F., Schlunegger F. (2009)
OSL quartz age underestimation due to unstable signal components.
Quaternary Geochronology 4, 353-362.

Stokes S. (1999)
Luminescence dating applications in geomorphological research.
Geomorphology 29, 153-171.

Takano M, Yawata T and Hahimoto T. (2003)
Luminescence dosimetry of archaeological and ceramic samples using a single- aliquot regenerative dose method.
Journal of Radioanalytical and Nuclear Chemistry 255, 365-368.

Tegen, I., Lacis A.A., Fung I. (1996)
The influence of climate forcing of mineral aerosols from disturbed soils.
Nature 280, 419-422.

Timar A. (2006)
Comparing quartz OSL and polymineral IRSL ages for Chinese loess: a case study.
MsD Thesis, Universitatea Babes Bolyai -Gent University.

Timar A., Cosma C., Benea V., Begy R., Jobagy V., Szeiler G., Barbos D., Fulea D.
(2007)
Estimation of environmental radionuclide concentration in soils, a comparison of methods for the annual radiation dose determination in luminescence dating.
Studia Universitatis, Babes-Bolyai, Geologia, 52 (1), 80-81.

Timar A., Cosma C., Benea V., Begy R.C., Jobaggy V., Szeiler G., Fulea D. (2008a)
A comparison of methods for external dose rate determinatin in luminescence dating of archaeological materials
Foldkergi Radioizotopok a Kornyezetunnkben, Pannon Egyetemi Kiado, Egyhazy Tiborne- Editor, p. 35-44.

Timar A. (2008b)
Fenomenul de termoluminescenta si luminescenta stimulata optic si aplicatiile sale in datare*, Varste absolute prin metode nucleare cu aplicatii in arheologie, geologie si mediu.
Masa Rotunda. Alba-Iulia, Quantum, Editor: Cosma C., Varvara S., Gligor, M., p.: 33-43.

Timar A., Cosma C, van den Haute P., Vandenberghe D. (2008c)
Datarea secventelor de loess-palaeosol prin luminescenta stimulata optic.
Varste absolute prin metode nucleare cu aplicatii in arheologie, geologie si mediu. *Masa Rotunda. Alba-Iulia, Quantum*, Editor: Cosma C, Varvara S., Gligor, M., p.: 66-78

Timar A., Vandenberghe D., Vasiliniuc S., Cosma C. (2009a)
Optical dating of Romanian loess: A comparison between sand-sized and silt-sized quartz.
Book of Abstracts Loessfest '09 – International conference on loess research, 31 [st] August – 1 [st] September 2009, Novi Sad, Serbia, p. 77-78

Timar A., Vandenberghe D., Vasiliniuc S., Cosma C. (2009b)
On the optical age of sand-sized and silt-sized quartz grains extracted from Romanian loess.
Book of Abstracts - UK Luminescence and ESR Meeting, Royal Holloway, University of London, 26th-28th August 2009.

Timar A., Vasiliniuc S., Vandenberge D., Cosma C. (2009c)
Absolute dating of Romanian loess using luminescence techniques: palaeoclimatic implications.
Ecoterra 22-23, 45-47.

Timar A., Vandenberghe D., Panaiotu E.C., Panaiotu C.G., Necula C., Cosma C. and Van den haute P. (2010a)
Optical dating of Romanian loess using fine-grained quartz.
Quaternary Geochronology, 5, 143-148.

Timar Gabor A., Vandenberghe D.A.G., Vasiliniuc, S., Panaoitu, C. E., Panaiotu, C. G., Dimofte, D., Cosma, C. (2010b)
Optical dating of Romanian Loess a comparison between silt-sized and sand-sized quartz. *Quaternary International* (QUATINT - S-10- 00155).

Timar Gabor A., Vandenberghe D.A.G., Vasiliniuc, S., Panaoitu, C. E., Panaiotu, C. G., Cosma, C. (2010c)
Further investigations on the optical age of fine silt (4-11 μm), coarse silt (35-50 μm) and fine sand (63-90μm) quartz grains extracted from Romanian loess.
X[th] international conferecence *"Methods of Absolute Chronology"-Book of abstracts*, page 29.

Timar Gabor, A., Vasiliniuc, Ş., Bădărau, A.S., Begy, R., Cosma C. (2010d)
Testing the potential of optically stimulated luminescence dating methods for dating soil covers from the forest steppe zone in Transylvanian basin.
Carpathian Journal of Earth and Environmental Sciences- in press.

Thomsen K. (2004)
Optically Stimulated Luminescence Techniques in Retrospective Dosimetry using Single Grains of Quartz extracted from Unheated Materials
PhD thesis Risø National Laboratory, Roskilde, Denmark, 176p.

Tsukamoto S., Fukuasawa H., Ono Y.and Fang X. (2001)
Infrared Stimulated Luminescence and Thermoluminescence Dating of loess from Lanzhou, China.
Quaternary Research 40, 385-392.

Vandenberghe D. (2004)
Investigation of the optically stimulated luminescence dating method for applications to young geological sediments.
PhD thesis, Gent University, Gent, Belgium, 289p.

Vandenberge D., De Corte F., Buylaert J-P., Kučera J., Van den haute P. (2008)
On the internal radioactivity in quartz.
Radiation Measurements 43, 771-775.

Vandenberghe D.A.G., De Meester E., Velghe G., Zöller L., Van den haute P. (2009)
A chronological study of the loess deposits over- and underlying the Eltville tephra using the newest luminescence techniques applied to sand-sized quartz: results from two Late-Weichselian type localities.
Abstract book Loessfest '09 – International Conference on Loess Research, 31 August – 1 September, 2009, Novi Sad, Serbia, 31.

Van den haute P., Vancraeynest L. and de Corte F. (1998)
The Late Pleistocene loess deposits of eastern Belgium New TL age determinations.
Journal of Quaternary Science 13, 487-497.

Van den haute P., Frechen M., Buylaert J.-P., Vandenberghe D. and De Corte F. (2003)
The last Interglacial palaeosol in the Belgian loess belt: TL age record.
Quaternary Science Reviews 22, 985-990.

Văsaru G, Cosma C (1998)
Geocronologie Nucleară.
Editura Dacia, Cluj Napoca, 346p, ISBN:973-35-0650-8.

Wallinga J., Murray A.S. and Wintle A.G. (2000)
The single-aliquot regenerative –dose (SAR) protocol applied to coarse-grain feldspar.
Radiation Measurements 32, 691-695.

Wallinga J., Murray A.S., Wintle A.G., Bøtter-Jensen L (2002)
Electron trapping probability in natural dosemeters as function of irradiation temperature.
Radiation Protection Dosimetry 101, 339-344.

Wang X, Lu Y and Zhao H. (2006)
On the performance of single-aliquot regenerative –dose (SAR) protocol for Chinese loess: fine quartz and polymineral grains.
Radiation Measurements 41, 1-8.

Watanuki T., Murray A.S., Tsukamoto S. (2003)
A comparison of OSL ages derived from silt- sized quartz and polymineral grains from Chinese loess.
Quaternary Science Reviews 22, 991-997

Wintle, A. G. (1981)
Thermoluminescence dating of Late Devensian loesses in southern England.
Nature 289, 479–480.

Wintle A.G. and Murray A.S. (1999)
Luminescence sensitivity changes in quartz.
Radiation Measurements 30, 107-118.

Wintle A.G. and Murray A.S. (2006)
A review of quartz optically stimulated luminescence characteristics and their relevance in single-aliquot regeneration dating protocols.
Radiation Measurements 41, 369-391.

Wintle A.G. (2008a)
Luminescence dating: where it has been and where it is going
Boreas, 37, 471–482.

Wintle A.G. (2008b)
Fifty years of luminescence dating.
Archaeometry 50, 2, 276–312

Zimmerman D.W. (1967)
Thermoluminescence from fine grains from ancient pottery.
Archaeometry 10, 26-28.