Babeş-Bolyai University, Cluj-Napoca
Faculty of Physics

OPTICALLY STIMULATED LUMINESCENCE AND ELECTRON SPIN RESONANCE DATING OF SEDIMENTARY QUARTZ

Doctoral Thesis Summary

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Keywords: natural quartz, optically stimulated luminescence, electron spin resonance, luminescence dating

1 Introduction

1.1 Introduction

Luminescence dating is a chronological method that is based on the property of common minerals such as quartz and feldspars to record the amount of radiation to which they have been exposed in the natural environment by storing trapped charge. This energy stored in the form of trapped charge can be released as light (luminescence) upon stimulation with heat (thermoluminescence – TL) or light (optically stimulated luminescence - OSL) and quantified. The age is equal to the paleodose (Gy) that the sample has received since a resetting event occurred divided by its annual dose rate (Gy/a). In the case of sediments, the resetting event is represented by exposure to light and the dated event is the deposition of the sediment. As all solid state dosimetric methods, luminescence dating relies on a calibration procedure. The paleodose is determined as an equivalent dose (D_e) by comparing the natural luminescence signal with that of artificially applied known doses delivered by a laboratory source. Most often this is performed by using the single-aliquot regenerative-dose (SAR) procedure developed by Murray and Wintle (2000, 2003); Wintle and Murray (2006).

Loess (windblown dust deposit) is generally considered an ideal material for the application of luminescence dating and is part of loess-paleosol sequences that serve as a high-resolution and quasi-continuous continental record of Quaternary paleoclimates.

Problems are also encountered in the use of OSL for dating and recent studies have shown that both age discrepancy between different quartz grain sizes (fine and coarse), and age underestimations are important issues in the high dose range. More precisely, age underestimations have been repeatedly reported for samples of either silt or sand size over ca. 70 ka, even though younger samples had ages in agreement with independent controls. Recent studies on quartz extracted from Romanian, Serbian and Chinese loess reported optical ages obtained on coarse quartz (63-90 μm) to be systematically higher than those on fine quartz (4-11 μm), when the ages correspond to equivalent doses larger than ~100 Gy. At the moment, the source of the age discrepancy is thought to reside, at least partly, in the different saturation characteristics of fine grains compared to the coarse grains, and in the differences reported between the laboratory and the natural dose response curves.

Electron spin resonance (ESR) can also be used as a dating tool, in a similar manner as luminescence, both methods being classified as trapped charge dating techniques. ESR measures trapped electron concentrations directly by exposing a sample to a magnetic field

and measuring the microwave absorption by unpaired electrons. Moreover, ESR is a sensitive enough method to monitor defects in quartz and thus an approach that integrates both ESR and luminescence has the potential to be a key tool that leads to new information concerning the charge storage, movement and recombination in quartz.

1.2 Aims of this thesis and contents overview

This thesis is comprised of 4 main chapters, each addressing a specific aim. Chapter 2 lays the groundwork for the subsequent studies reported in this thesis. The current methodology used for OSL dating of quartz and the models which explain the physical basis of this application are described. Chapter 3 presents an OSL dating study of quartz of different grain sizes extracted from an archaeological site on the Bistrița Valley in north-eastern Romania. In addition, radiocarbon dating was applied to the archaeological layers identified in the section. Chapter 4 presents an investigation into the impact of muscovite (a mineral commonly found as a contaminant mineral phase in some of our samples of quartz extracted from sediments) on the OSL dating of quartz samples contaminated with muscovite. Keeping in mind that luminescence investigations have not yet provided a satisfactory explanation for the discrepancies observed between the 4-11 μm quartz grains and the coarser fractions, we conduct in chapter 5 preliminary ESR investigations on two grain sizes of sedimentary quartz, namely 4-11 μm and 63-90 μm, focusing on qualitative differences in ESR signals between the two fractions.

This thesis is a piece in a bigger puzzle represented by the quest to unravel the mechanism responsible for the observed discrepancies and develop innovative trapped charge dating measurement protocols based on quartz that will yield reliable ages for and beyond the last interglacial glacial cycle.

2 Physical basis of optically stimulated luminescence phenomena in quartz

2.1 Introduction

Luminescence has been widely used over the past 30 years in dating applications. Luminescence methods are based on stimulated phenomena, and out of the different stimulation options available, the optically stimulated luminescence (OSL) (i.e. stimulation carried out in the visible region of the electromagnetic spectrum) signal has been the mainstream choice when obtaining depositional ages of sediments.

2.2 Luminescence models

2.2.1 Background

The understanding of luminescence production generally makes use of the band theory of solids. The defects formed in the forbidden energy gap either by intrusion of impurity atoms or by structural defects in real crystals are localised energy states. The interaction of nuclear radiation with matter ultimately results in the liberation of a large number of free electrons and holes respectively within the target mineral and it is the accumulation of such electrons in crystal defects that may eventually lead to the formation of the signal used in luminescence dating.

2.2.2 The simplest model: One-trap/One-center

The simplest model that explains the mechanism of OSL production involves only one electron trap and one hole trap that acts as a radiative recombination center. This is an oversimplification which allows basic understanding of the mechanism of OSL formation, but in real crystals, more than one type of traps and recombination centers compete for charge.

2.2.3 The energy-band-model for quartz

Bailey (2001) developed a model illustrating how TL and OSL are produced in quartz and this model served as a basis for future improvements provided by Bailey (2001, 2002, 2004) and Pagonis et al. (2007; 2008) by applying this model with modified parameters to address more specific issues. A summary of these models, as combined by Friedrich et al. (2016) is presented in the energy level diagram in **Figure 2.1**.

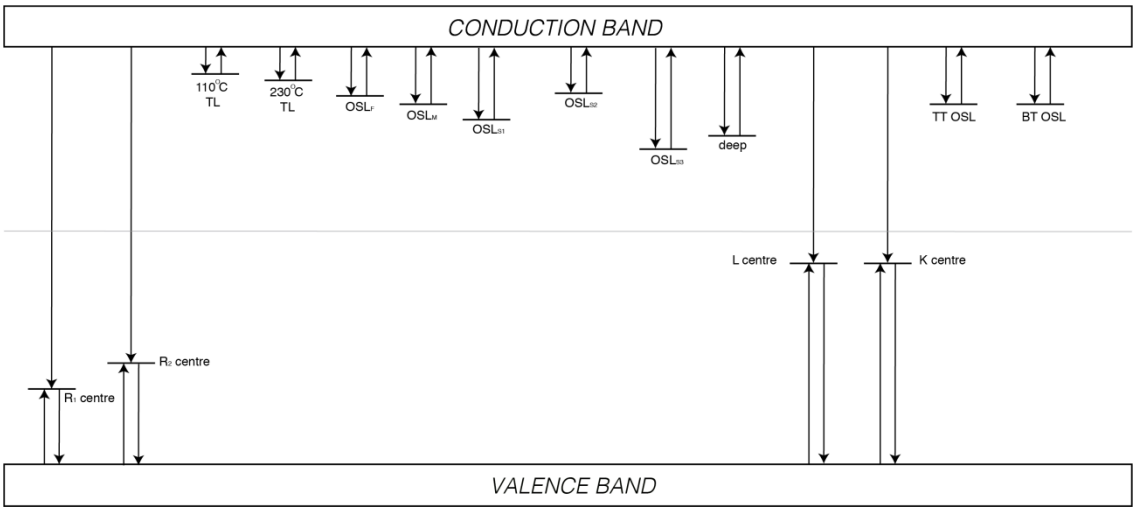

Figure 2.1 Comprehensive energy band model for quartz showing different traps and recombination centers and possible charge transitions. Redrawn after Friedrich et al. (2016).

2.2.4 Other models

Other models such as the defect pair model (Itoh et al., 2001, 2002) or the statistical simplified Monte Carlo method (Pagonis et al., 2014) were proposed. However, the energy-band-model remains for now the model mostly used in the luminescence dating community as a basis for explaining the phenomenon.

2.3 Application of quartz in optically stimulated luminescence dating

The depositional age of a sediment is equal to the paleodose (Gy) of the sample divided by its annual dose rate (Gy/a). Several different techniques can be used for determining the annual dose, but for the samples analysed in the Luminescence Dating Laboratory of Babeș-Bolyai University, the radionuclide (U-238/Ra-226, Th-232, K-40) specific activities are measured using high-resolution gamma-ray spectrometry and the dose rates are derived using the conversion factors of Adamiec and Aitken (1998). The paleodose is the combined dose (from α, β, γ and cosmic radiation) absorbed by the mineral grains since their last exposure to light (last deposition) and is determined as an equivalent dose (D_e). The most commonly used method for quartz equivalent dose determination is the single-aliquot regenerative-dose (SAR) protocol (Murray and Wintle, 2000, 2003; Wintle and Murray, 2006).

2.3.1 The single-aliquot regenerative-dose (SAR) procedure

By applying the SAR protocol to a quartz aliquot (steps shown in **Figure 2.2**), a dose response curve is constructed using the sensitivity corrected OSL signals (L_x/T_x) registered as

response to laboratory given regenerative doses. The natural sensitivity corrected OSL response of the aliquot is interpolated on this curve to determine the equivalent dose. Several tests are used to check the performance of the SAR protocol and include recycling, recuperation, dose recovery, preheat plateau. The recycling test confirms whether sensitivity correction has worked. It is done by measuring the OSL response to the same regenerative dose at the beginning and again at the end of the SAR cycle and calculating the ratio between these two sensitivity corrected signals, which should be close to unity. The recuperation test examines the response to a zero regenerative dose, for which L_0/T_0 should be close to 0 if thermal transfer induced in the preheating step is insignificant. A preheat test can be used to investigate the effect of preheat temperature on equivalent dose, by plotting the De as function of preheat temperature. The dose recovery test is used to check if a known dose given in the laboratory can be accurately recovered in the SAR protocol.

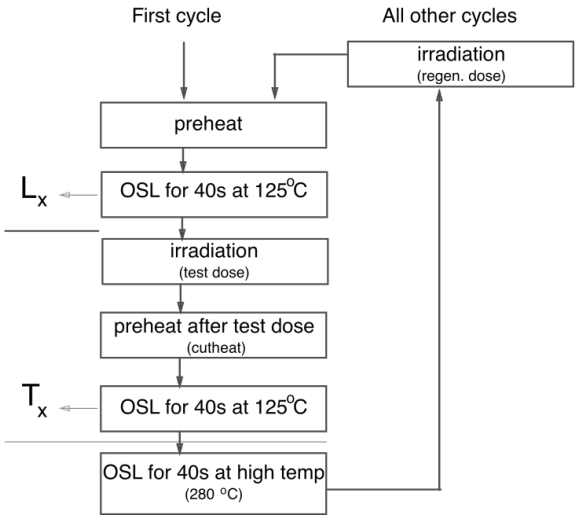

Figure 2.2 General steps in the single-aliquot regenerative-dose (SAR) protocol (redrawn after Murray and Wintle (2000)). L_x represents the natural or regenerated signal and T_x is the test dose signal.

2.3.2 Sample and aliquot preparation

Sample preparation for luminescence measurements is usually performed under low intensity red light conditions to avoid eviction of charge from light sensitive dosimetric traps. The conventional preparation protocol for extraction of quartz includes a combination of acid treatments, sieving and density separation (Aitken, 1985).

2.4 Problems with the use of OSL for dating quartz – the importance of grain size

Limitations of the use of OSL in dating have been noted and include age underestimations for older samples (>70 ka) (Buylaert et al., 2007; Lowick et al., 2010; Timar et al., 2010), age discrepancies between silt and sand sized quartz (Timar-Gabor et al., 2011;

Timar-Gabor and Wintle, 2013; Constantin et al., 2014, 2015; Timar-Gabor et al., 2015b; 2017). It was hypothesised that the cause for this differences resides in the different saturation characteristics of the dose response curves, and different growth pattern of the laboratory dose response curve when compared to the natural dose response curve, for either fine or coarse quartz, as shown in **Figure 2.3** (Timar-Gabor et al., 2015).

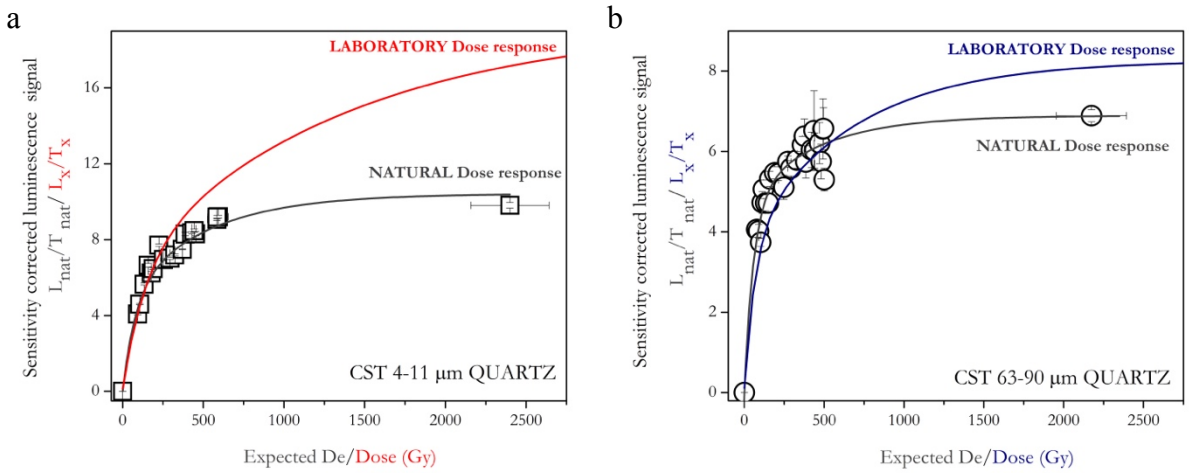

Figure 2.3 From Timar-Gabor et al. (2015). The average sensitivity-corrected natural signal for 26 samples from Costinesti (a) fine and (b) coarse grains plotted as function of their expected equivalent dose. The average laboratory dose response curve (based on data taken up to 5000 Gy) is displayed for each grain size.

2.5 Thermal lifetime of a dosimetric trap – results reported in Timar-Gabor et al. (2017)

One of the possible causes for age underestimation in luminescence dating is the thermal loss of the signal during its build-up (Christodoulides et al., 1971). Although thermal instability is typically addressed through routine preheat plateau tests, the thermal lifetime of the target OSL dosimetric trap used for dating is seldom explicitly determined.

Isothermal luminescence decay experiments were carried out in order to quantify the thermal stability of the dosimetric trap for quartz samples of different grain sizes extracted from loess from the Costinesti section (SE Romania). The time-evolution of the OSL signal L(t) [a.u.] at a temperature T [K] is illustrated in **Figure 2.4** and was found to be best described by a single decaying exponential function of the form:

$$L(t) = L_{max}\exp\left(-\mathrm{s}\exp\left(-\frac{\mathrm{E}}{\mathrm{k_B\,T}}\right)\mathrm{t}\right) \quad (2.1)$$

Where L_{max} is the initial OSL light sum, E [eV] and s [s^{-1}] are the Arrhenius parameters (activation energy and frequency factor, respectively), k_B [eV K^{-1}] is Boltzmann's constant and t [s] is the holding time at temperature T. Trap lifetime was derived using the equation:

$$\tau = s^{-1} \exp(\frac{E}{k_B T}) \quad (2.2)$$

Trap lifetimes for both investigated samples are well beyond the age of interest for dating purposes: 230 Ma for fine quartz and 14750 Ma for coarse quartz.

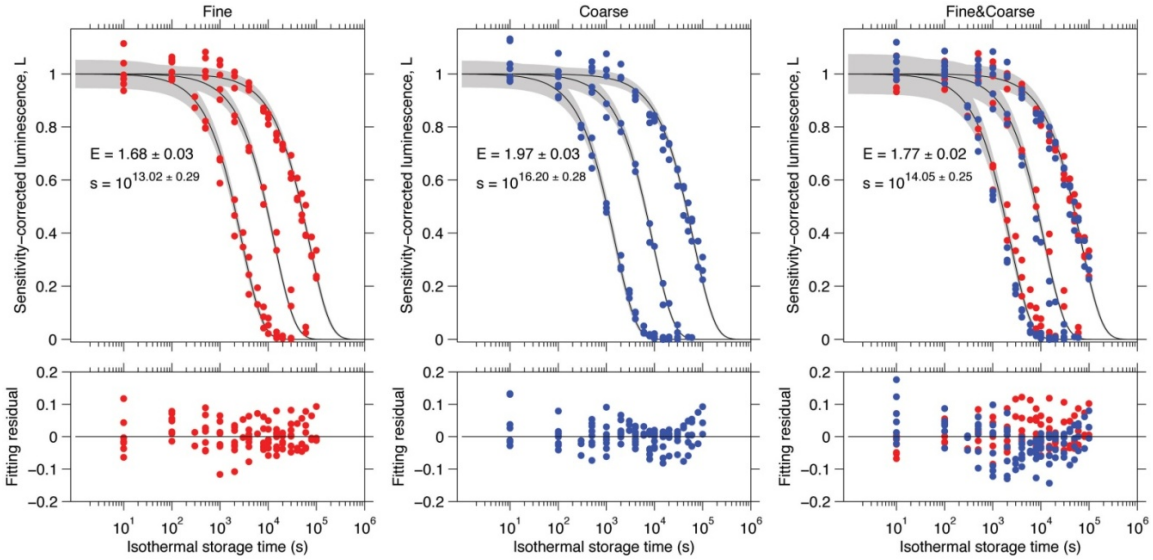

Figure 2.4 Isothermal decay of the fine (4-11 µm; sample CST 2) and coarse (63-90 µm; sample CST 22) quartz OSL signal with best-fitting curves (95% confidence intervals shaded) and fitting residuals shown below. Combining the data for fine and coarse data (right panel) is also inadequate, as seen by segregation of the residuals by dataset; hence the different best-fit parameters for each grain size fraction are considered as genuine.

2.6 The influence of pulsed irradiation on the OSL dose response of fine and coarse quartz extracted from loess

A condition for accurate D_e determination is that competition for charge during trap filling is the same during laboratory irradiation as during natural irradiation. However, the difference in dose rates between nature and laboratory environments (~ 9 orders of magnitude higher dose rate in laboratory conditions) leads to a difference in filling of shallow traps (traps with a short retention time at ambient temperatures): they remain empty at low-dose rates in nature because of thermal decay, acting as a competitor for the dosimetric trap, but they might saturate at the high dose rates usually employed in the laboratory. This would lead to a higher density of charge trapped at the dosimetric trap in the artificial irradiation scenario, which translates to an extended growth of the laboratory dose response curve compared to the natural dose response curve, a behaviour previously observed (Timar-Gabor and Wintle, 2013). Pulsed irradiation mimics the circumstances in nature, keeping the shallow traps

mostly empty during irradiation. Measurements were carried out to investigate the influence of pulsed irradiation on the OSL dose response curve for both fine and coarse quartz.

2.7 Conclusion

Our results show that thermal instability of the OSL signal is not an issue for any of the quartz fractions investigated. Regarding the extended growth of the laboratory dose response curve at high doses compared to the natural dose response curve, our pulsed irradiation experiment rules out a possible trap competition between shallow traps and the dosimetric trap as the culprit.

3 OSL dating of fine and coarse quartz from a Palaeolithic sequence in north-eastern Romania – based on Trandafir et al. (2015)

3.1 Introduction

This study was aimed at (i) extending our previous area of investigation in order to see whether the differences between fine and coarse quartz ages are a more general feature, or are restricted to typical loess sections in South East Europe and (ii) discussing the luminescence ages obtained on different grain size fractions in a more general chronological frame, obtained by applying radiocarbon dating on the archaeological layers. To increase the confidence of the results, luminescent investigations have been independently carried out in two laboratories in Romania (Cluj-Napoca) and Germany (Bayreuth).

3.2 Study site

The archaeological site at Bistricioara-Lutărie III (BL III) is located nearby the better known Bistricioara Lutărie I and II settlements, on the 16-18 m high terrace of the river (around 500 m in altitude), covered with loess derivates accumulated on a gentle slope

3.3 Radiocarbon dating

Radiocarbon ages of 3 samples from BL III profile were obtained by accelerator mass spectrometry (AMS) ^{14}C dating on wood charcoal using facilities at Hertelendi AMS Lab (Debrecen, Hungary) and Erlangen.

3.4 Optical dating

3.4.1 Samples and analytical facilities

One set consisting 5 samples was processed to extract fine (4–11 μm) and coarse (63–90 μm) quartz and measured at the Luminescence Dating Laboratory of Babeș-Bolyai University and a second set of 4 samples was processed at the Luminescence Laboratory at Bayreuth University to extract quartz of 3 different grain sizes: 4–11 μm, 63–90 μm and 90–200 μm. Both laboratories used automated Risø TL/OSL readers for luminescence measurements.

3.4.2 Luminescence characteristics

The OSL signals for all samples (both grain sizes) displayed a rapid decay during optical stimulation, with indistinguishable natural and regenerated signals. Recycling, IR depletion and recuperation tests have been employed to check for the suitability of these samples for D_e

determination using the SAR protocol. Dose recovery and preheat plateau tests were also employed. Due to a significant feldspathic contribution on the coarse grain fractions, a double-SAR protocol (Roberts and Wintle, 2001; Banerjee et al., 2001) was also employed for both grain sizes, meaning that IR stimulation was performed for 100 s at 125ºC (IR bleach) prior to the blue LED OSL stimulations, and the [post-IR] OSL signal was used for D_e calculation. A good reproducibility was observed between SAR and double-SAR equivalent doses estimated for the same grain size of each sample, the values being the same within 95% confidence limits. As such, equivalent doses estimated both with SAR and with double-SAR protocols (where applicable) were considered when calculating the OSL ages.

Apart from the youngest sample (BL3 1.6), the other samples measured in Cluj presented systematically higher D_e values for coarse (63-90 µm) quartz than for fine quartz. This is counter-intuitive when considering the alpha-particle contribution to the annual dose rates of finer grains, which should result in higher D_e values for this material. The 4 samples extracted from The Cube show a similar behaviour. However, despite the fact that the 63-90 µm equivalent doses are consistently higher than the 4-11 µm D_e, there is no systematic trend observable for the 90-200 µm fraction.

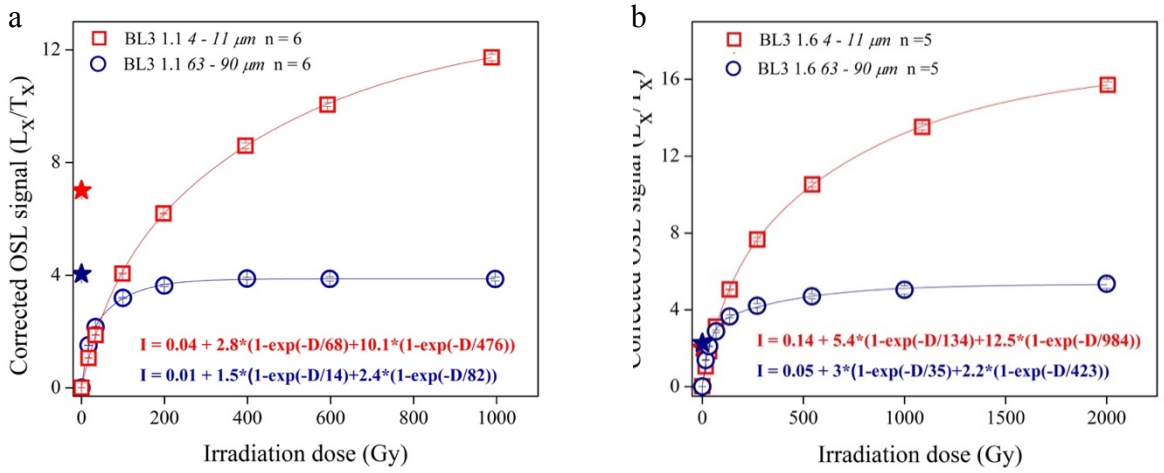

Figure 3.1. Comparison between averaged sensitivity-corrected dose responses constructed for fine and coarse quartz extracted from sample (a) BL3 1.1 and (b) BL3 1.6. In all cases, each data point represents the average value of at least 5 replicate measurements. The data are best fitted with a double saturating exponential function. Natural signals are shown as stars.

Dose response for high doses was investigated for each grain size of the oldest (BL3 1.1 – **Figure 3.1.a** and BL3 1.2) and youngest (BL3 1.6 – **Figure 3.1.b**) samples, respectively. The sensitivity corrected growth curves extending up to 2 kGy are best fitted by a sum of two

saturating exponential functions. Fundamentally different growth patterns were observed between the fine (4-11 µm) and coarse (63-90 µm) quartz for all samples analysed, similar to the findings reported on quartz extracted from loess (Timar-Gabor et al., 2011; 2012; 2015).

3.4.3 Dose rate determination

Radionuclide (U-238/Ra-226, Th-232, K-40) specific activities were measured using high-resolution gamma-ray spectrometry and the dose rates were derived using the conversion factors of Adamiec and Aitken (1998). In the case of the samples extracted from The Cube, sediment from the same layer as the samples was analysed by alpha-counting for determination of U and Th concentrations and by ICP-OES for K concentration.

3.4.4 Optical ages

Athough each grain size fraction yielded a set of ages consistent with the stratigraphic position of the samples (**Figure 3.2**), significant discrepancies were obtained between grain fractions. Optical ages ranging from 8.0 ± 1.1 ka to 76.3 ± 8.4 ka were obtained for fine (4-11 µm) grains, whereas for the coarse (63-90 µm) quartz dates between 8.6 ± 1.1 ka and 50.7 ± 6.7 ka were found.

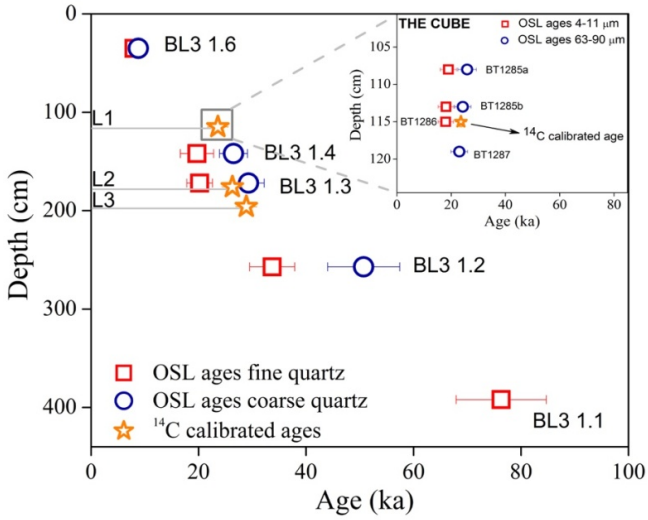

Figure 3.2. Optical ages of fine and coarse quartz grains from all samples studied compared with radiocarbon ages for the topmost three cultural layers. Ages for the 63-90 µm fractions of BL3 1.1 and BT1286 could not be obtained, since the samples were in dose saturation. The fine fraction of BT1287 was affected by heavy feldspar contamination. The errors quoted for luminescence ages represent 1σ and for the calibrated radiocarbon ages (yr BP) 2σ, respectively.

3.5 Discussion and conclusions

3.5.1 Methodological

Discrepant ages were obtained between fine (4-11 μm) and coarse (63-90 and 90-200 μm, respectively) quartz for equivalent doses higher than ~80-100 Gy, while agreement is reached fot the youngest sample (~8 ka). Comparison of optical ages with independent control provided by ^{14}C dating shows better agreement for the coarse grain ages. The very different dose response characteristics of coarse and fine grained quartz to high laboratory beta dose rates ask for further systematic investigations and question the general equivalence of luminescence production in nature and in the laboratory for silt-sized quartz.

3.5.2 Chronological

The OSL ages on coarse quartz show a good agreement with the calibrated radiocarbon dates. They point to the existence of some older, likely Gravettian occupation layers, as already identified in the neighbouring settlements at Bistricioara I-II (Steguweit et al., 2009), but also and more importantly to a possibly earlier presence of the Upper Palaeolithic in the area.

4 Luminescence properties of natural muscovite relevant to optical dating of contaminated quartz samples – based on Antohi-Trandafir et al. (2018)

4.1 Introduction

Significant amounts of mica commonly found in sediments are not removed during sample preparation for the extraction of quartz and the question arises whether they can influence the luminescence properties of contaminated quartz separates. We investigated the luminescence properties of hand-picked muscovite grains from a contaminated quartz sample extracted from loess. Furthermore, as it is fair to assume that different types of muscovite may have different properties, we present luminescence investigations of other muscovite samples in order to evaluate their potential implication in OSL dating of impure quartz samples.

4.2 Samples and experimental facilities

The sedimentary quartz sample CST 18 is extracted from a loess sample previously dated by Constantin et al. (2014) that belongs to the L2 loess unit from the Costinesti section in SE Romania. Using scanning electron microscopy (SEM) and X-ray diffraction (XRD), muscovite grains were identified in the 63-90 μm fraction of sample CST 18. The muscovite grains were picked by hand under the stereomicroscope and one aliquot was thus formed called muCST 18.

Four museum specimens of muscovite (laboratory codes: MM, CS, VL and MR) were provided by the Mineralogical Museum of Babes-Bolyai University, Cluj-Napoca for analysis. Their geochemistry was analysed using energy dispersive X-Ray fluorescence spectroscopy (EDXRF).

A quartz sample (180-250 μm quartz from aeolian sand dunes, Denmark) provided by Risø National Laboratory (Hansen et al., 2015) and called hereafter RQ was used for a comparative dose recovery experiment and was chosen due to its chemical purity and the availability of high amounts of sample.

Luminescence measurements were performed using an automated Risø TL/OSL-DA-20 reader.

4.3 Results and discussions

4.3.1 Evaluation of minerals

SEM images show a high contamination of sample CST 18 with an Al-rich mineral (**Figure 4.1**). XRD confirms that besides quartz, muscovite is clearly detectable in the sample.

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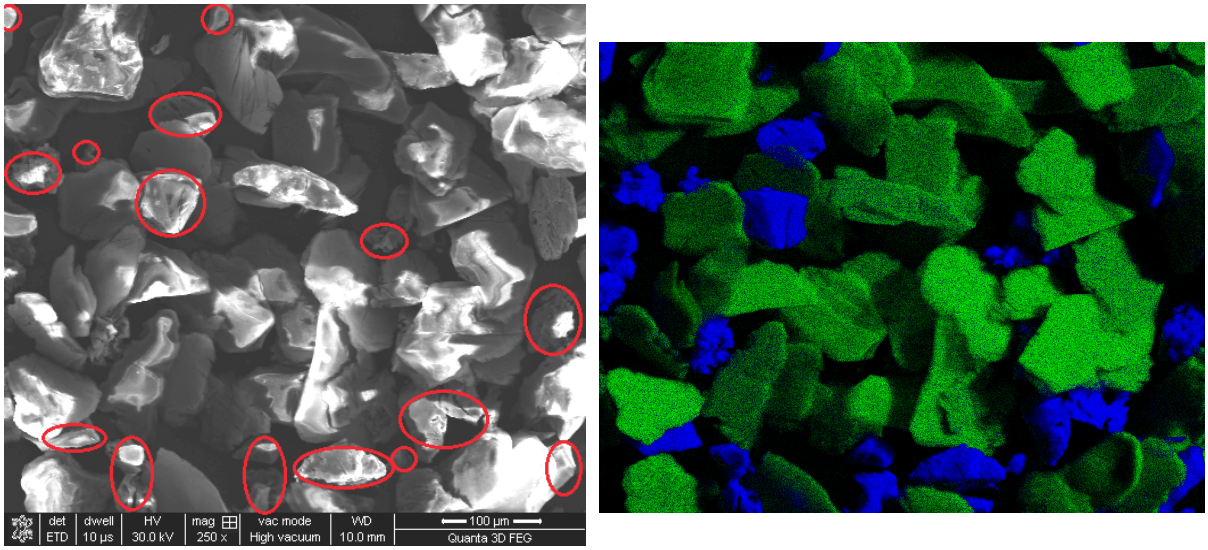

Figure 4.1 (a) Scanning electron microscopy image of a contaminated quartz sample (CST 18, 63-90 µm). The open red circles indicate the quartz grains. (b) Compositional image of Si (blue) and Al (green) of the same aliquot obtained using the EDX attachment. Both panels show the same field of view.

4.3.2 Luminescence investigations

The regenerated OSL signals of all muscovite aliquots (hand-picked grains and museum muscovite samples) were recorded using the SAR protocol (Murray and Wintle, 2000, 2003) with a preheat of 220°C and a cutheat of 180°C and a test dose of 68 Gy for sensitivity correction. A modified SAR protocol was employed to record the IR stimulated luminescence (IRSL) of muscovite, in order to resemble standard IR protocols (Blair et al., 2005).

Sample muCST18 has no OSL or IRSL responses for a dose of 136 Gy, but it produces low OSL (**Figure 4.2a**) and IRSL (**Figure 4.2b**) signals for very high doses of 5000 Gy. When compared to the OSL signal produced by 10 mg of CST 18 (see inset in **Figure 4.2a**), the muscovite OSL signal is negligible, amounting to no more than 5% of the OSL signal of CST 18. Nonetheless, other studies report blue light and IR sensitivity of muscovite mineral for lower doses (Clark and Sandersons, 1994; Kortekaas and Murray, 2005), which is why we

looked into the luminescence properties of other muscovite specimens, to see whether they present different characteristics.

Samples MM and CS are bright and display a steep OSL decay (**Figure 4.3a**), comparable to that of quartz. This is similar to the OSL decay shape reported in Kortekaas and Murray (2005). Samples VL and MR are characterised by a very weak blue light sensitivity. MM and CS show similar IR brightness, while MR and VL present no response after the IR stimulation (**Figure 4.3b**).

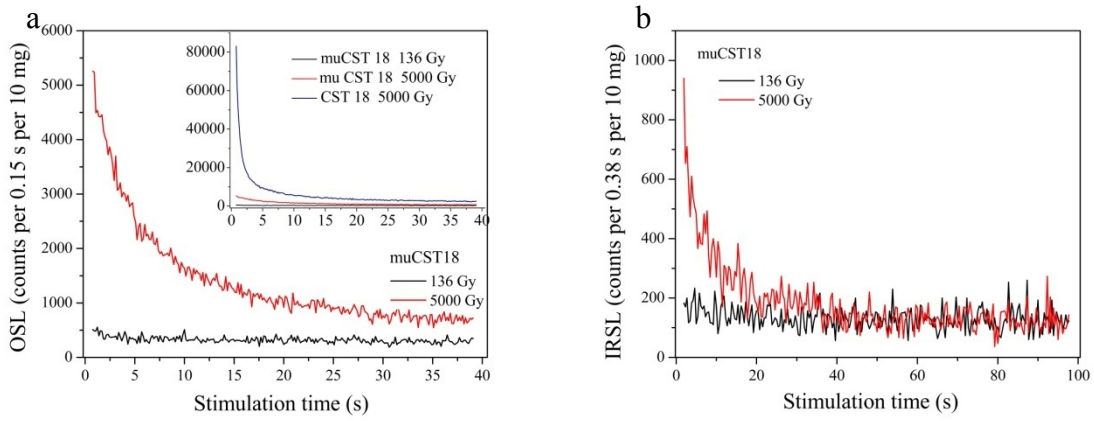

Figure 4.2 (a) OSL and (b) IRSL decay curves for muCST 18 after irradiation doses of 136 Gy and 5000 Gy. A preheat of 220°C was employed prior to the optical stimulations. (a) The inset shows in addition an OSL decay curve obtained after a dose of 5000 Gy on CST18 (63-90 μm).

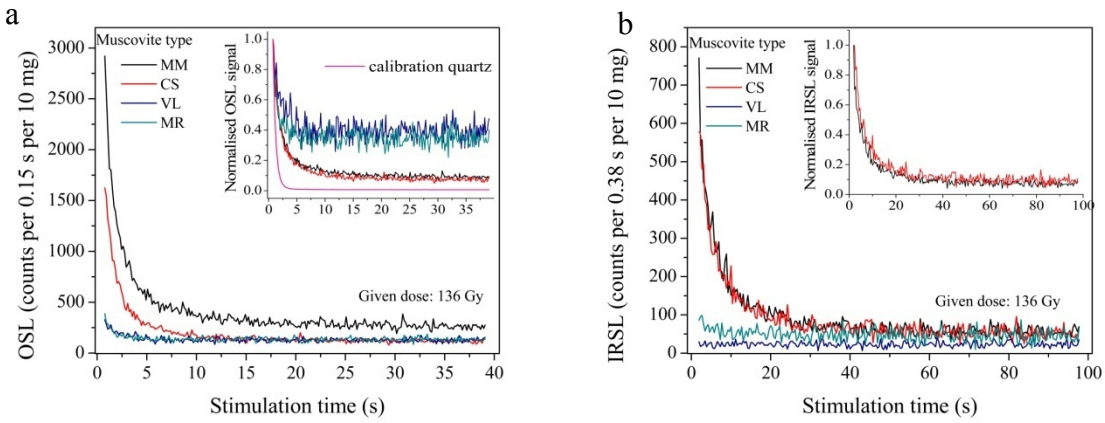

Figure 4.3 The (a) OSL and (b) IRSL decay curves for the four museum muscovite specimens show varying sensitivity to blue light and to infrared light respectively after irradiation with a dose of 136 Gy. The insets show: (a) the OSL decay curves normalised to the signal recorded in the first channel for muscovite and calibration quartz - a preheat of 220°C for 10 s was employed prior to the optical stimulations; (b) the IRSL decay curves normalised to the signal recorded in the first channel for the 2 samples that are IR sensitive - a preheat of 220°C for 600 s was employed prior to the IR stimulations.

To identify quartz samples contaminated with muscovite minerals similar to MM and CS (OSL and IR sensitive), a simple purity check can be performed by monitoring the IRSL response to a large beta dose, as proposed by Vandenberghe et al (2003) and earlier by Smith et al. (1990) and Stokes (1992). In addition to checking the magnitude of the IRSL signal (if any), an IRSL depletion ratio can also be employed as described by Duller (2003).

The OSL and IRSL growth curves up to 5000 Gy for samples MM and CS (**Figure 4.4**) were measured and the OSL signals start to saturate only after 2 kGy but are fully saturated around 5 kGy (values higher than in the case of quartz).

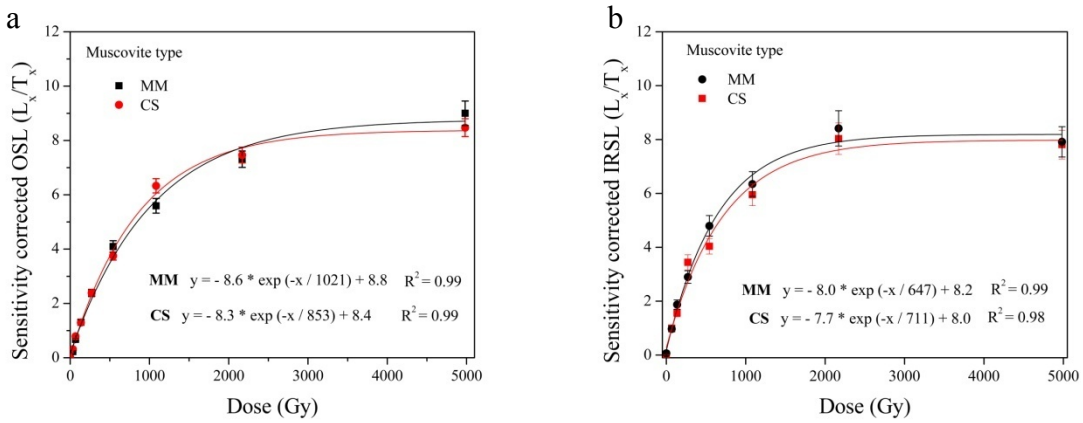

Figure 4.4 Typical (a) OSL and (b) IRSL growth curves up to 5000 Gy for muscovite specimens CS and MM (1 aliquot for each curve). A test dose of 68 Gy was employed for sensitivity correction in all cases. All response curves were best fitted by an exponential function. (a) A preheat of 220°C and a cutheat to 180°C were used. (b) The IR stimulation was performed at 40°C for 100 s and both the preheat and the cutheat (both 220°C) were maintained for 600 s.

In order to evaluate the influence that screening for muscovite using an IR purity check has on D_e determination, a dose recovery experiment was constructed and applied on samples composed by mixing quartz (RQ) and muscovite (MM) minerals by hand in different proportions. While for the samples dominated by quartz (100% and 80% RQ) the IR depletion ratio average was 0.96 ± 0.003, with no aliquots being rejected, for the sample made up of only 20% RQ and 80% MM, only half of the aliquots (24 out of 48) had an IR depletion ratio within 10% of unity. Overall the IR depletion ratio test is successful in indicating a potential muscovite contamination in a quartz extract.

4.4 Conclusion

The luminescence properties of muscovite vary greatly among naturally occurring minerals so that generally applicable characteristics cannot be described in terms of their optical luminescence response. Our results show that at least in the case of bright quartz, muscovite minerals are not an issue in luminescence measurements and do not influence the determination of equivalent doses. Furthermore, the application of IR recycling ratio test routinely applied for screening feldspar contamination is also effective in indicating significant muscovite contamination.

5 Electron spin resonance spectroscopy characterisation of quartz extracted from sediments

5.1 ESR – Basic concepts

Electron spin resonance (ESR - the acronym mostly used in the dating field), also known as electron paramagnetic resonance (EPR) is a spectroscopic technique used to detect, identify and measure the concentration of paramagnetic species.

5.2 ESR dating

ESR is a trapped charge dating technique (same as TL and OSL). In the case of minerals like quartz, feldspar, apatite or calcite, the accumulation of trapped unpaired electrons and positively charged holes takes place as long as natural radiation (α, β, γ, cosmic radiation) interacts with the minerals. The trapped electrons and holes may form paramagnetic centres, which produce characteristic ESR signals. The radiation-sensitive ESR signal intensity can be reliably converted into an equivalent dose if it satisfies a series of criteria (Rink, 1997; Grün, 2007; Blackwell et al., 2016). The upper age limit for ESR dating is determined by saturation and thermal stability of the signal, which depend on the specific paramagnetic centre and the environment of the sample. Ages as old as 2 million years have been obtained using ESR (Han et al., 2017; Rink et al., 2007).

Figure 5.1 compares the age ranges for different dating methods used to date quaternary materials. ESR has clear advantages from this respect, covering a wider time range than luminescence (TL, OSL) and the $^{230}Th/^{234}U$ method. ESR can date much older fossils than the ^{14}C dating limit and younger materials than the U-Pb methods or the $^{39}Ar/^{40}Ar$ method (Blackwell et al., 2016). However, these age limits may vary considerably depending on specific sample type and so each situation should be considered individually.

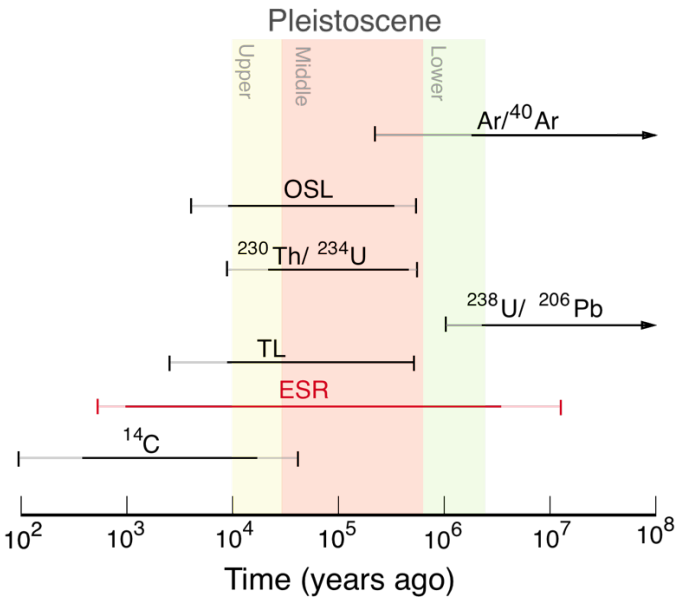

Figure 5.1 Age ranges of several dating methods applicable to the Quaternary. Redrawn from Blackwell et al. (2016).

5.2.1 ESR dating on quartz

While there are many paramagnetic defects reported in quartz, the E_1', Al, Ti and Ge centres are the ones relevant for dating. The E_1' centre is an oxygen vacancy defect characterised by an unpaired electron on one of the 2 Si atoms, which relaxes towards the vacancy, while the other Si, positively charged, relaxes away from the vacancy into a nearby plane configuration of its neighbouring oxygen atoms (Preusser et al., 2009; Toyoda, 2015). The g values for E_1'centre known from single crystal studies are 2.0018, 2.0005 and 2.0003 (Jani et al., 1983). Al^{3+} is one of the most common substitutional ions replacing Si^{4+} in quartz and it achieves charge compensation in the presence of an ion^+ (mostly Li^+, Na^+ or H^+) (Preusser et al., 2009). The powder spectrum generated by the Al center is characterised by a hyperfine structure and is made up of 16 peaks, but it also corresponds to an anisotropic powder spectrum with g factors 2.060, 2.009 and 2.002 (Nuttal and Weil, 1981). Ti^{4+} may substitute Si^{4+} in quartz with no charge compensation, creating $[TiO_4]^o$, the precursor for the Ti center (Weil, 1984). Upon room temperature irradiation, Ti^{4+} may trap an electron together with a cation M^+ for charge compensation, thus forming $[TiO_4/M^+]^o$, where M^+ can be either Li^+, H^+ or Na^+ (Toyoda, 2015). The resulting Ti centers have different ESR signals. An important advantage of the Ti centers over the Al center is represented by the fact that Ti centers are more easily bleached by artificial lighting and sunlight, making them an ideal tool for dating sedimentary deposits. Al and Ti centers require low temperature (<120 K)

measurements. ESR signals of the Ge center are observed usually only in irradiated quartz samples (Toyoda, 2015), and are rarely reported in natural quartz (Toyoda et al., 2000).

No generally accepted single protocol for the determination of the equivalent dose exists, similar to the SAR-OSL protocol (Murray and Wintle, 2000) extensively used in luminescence dating. A first point of variation with the different protocols employed regards the choice of the center used the Al and/or the Ti centers. A multiple center approach is recommend and implies considering an ESR age to be accurate only if D_e estimates based on Al and Ti signals agree. Most ESR dating studies estimate equivalent doses using the multiple aliquot additive dose (MAAD) method, but a regeneration method has the main advantage that the equivalent doses are obtained by interpolation onto the dose response curve, thus this approach is less dependent on the function used for fitting and its use has been attempted in recent studies using multiple (Asagoe et al., 2011) or single aliquots (Tsukamoto et al., 2015).

5.2.2 Applications

The first notable ESR application to dating is the work of Ikeya (1975) on dating speleothems from the Akiyoshi cavern of Japan. Since then, periodic reviews (Grün, 1989; Ikeya, 1993; Rink, 1997; Skinner, 2000; Blackwell et al., 2016) have shown the constant development of the method and the growth of the number of uses for ESR. Despite continuous advancement over the past 30 years of ESR dating applications, Blackwell et al. (2016) warns against using ESR as the sole chronometer in a situation where other methods are also applicable to ensure the accuracy of the ages.

5.3 Equipment and measurements

ESR measurements were carried out at the Luminescence Dating Laboratory of the Interdisciplinary Research Institute on Bio-Nano-Sciences (Babeș-Bolyai University, Cluj-Napoca) with a Bruker X-band ESR spectrometer fitted with a high sensitivity cavity and 100 kHz field modulation.

The parameters listed in **Table 5.1** were selected as optimum for measuring the most common paramagnetic centers observed in quartz and relevant to ESR dating, namely E_1', $[AlO_4]^0$ and $[TiO_4/Li^+]^0$.

Table 5.1 Acquisition parameters used in this study to measure the ESR signals for the 3 main centers observed in quartz and used for ESR dating.

Parameter \ Paramagnetic center	E_1'	$[AlO_4]^0$	$[TiO_4/Li^+]^0$
Temperature	290 K	90 K	90 K
Center field	3500 G	3350 G	3490 G
Sweep width	50 G	300 G	220 G
Microwave power	0.02 mW	2 mW	5 mW
Modulation amplitude	0.1 G	1 G	1 G
Conversion time	100 ms	100 ms	100 ms
Time constant	81.92 ms	81.92 ms	20.48 ms
Sweep time	500 s	300 s	330 s
Number of sweeps	1	3	10

5.4 Samples

In addition to calibration quartz (CQ) provided by Risø National Laboratory (Hansen et al., 2015), quartz extracted from loess sections in Romania (CST 22) and Ukraine (STY 1.10) was used for ESR investigations.

5.5 Observed ESR signals

Based on measurements in which parameters such as modulation amplitude or power were varied, a set of optimum parameters was chosen for the acquisition of the main signals present in quartz, relevant for dating.

A power saturation experiment was conducted for the E_1' signal of CQ (180-250 μm) and CST 22 (63-90 μm), collecting spectra at 18 microwave powers with values ranging from $3.17 \cdot 10^{-4}$ to 40 mW. The spectrum acquired using the parameters chosen based on this experiment (modulation amplitude 0.1 G and microwave power 0.02 mW) is shown in **Figure 5.2**, where the peak-to-peak height of the signal taken as its intensity is also highlighted.

The complex spectrum defined by the Al center in quartz can be measured at liquid nitrogen temperatures (~90K). A comparison between the signal of sample CQ recorded at 90K and at higher temperatures up to room temperature is shown in **Figure 5.3**.

No Ti-H center signals were identified in the samples studied in this work. The microwave power is varied for the acquisition of the Ti-Li center signal in **Figure 5.4**.

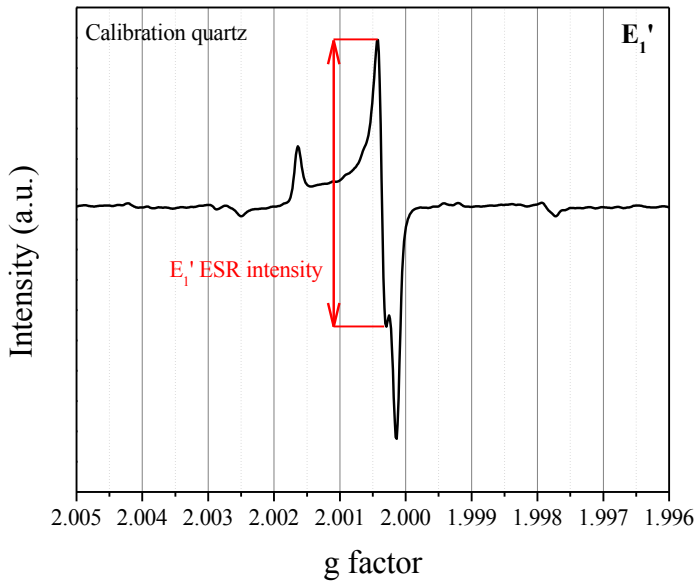

Figure 5.2 ESR signal corresponding to the E_1' center in calibration quartz, recorded at 0.02 mW microwave power and 0.1 G modulation amplitude.

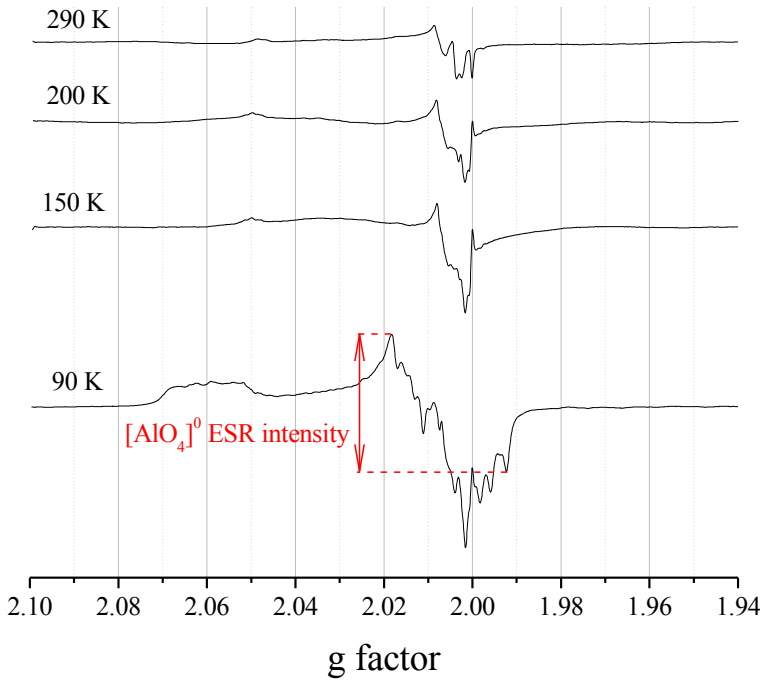

Figure 5.3 ESR spectra recorded at different temperatures (from 290K (room temperature) to 90 K) for calibration quartz, using a modulation amplitude of 1G and microwave power of 2 mW. The region between 3200 and 3500 G is swept.

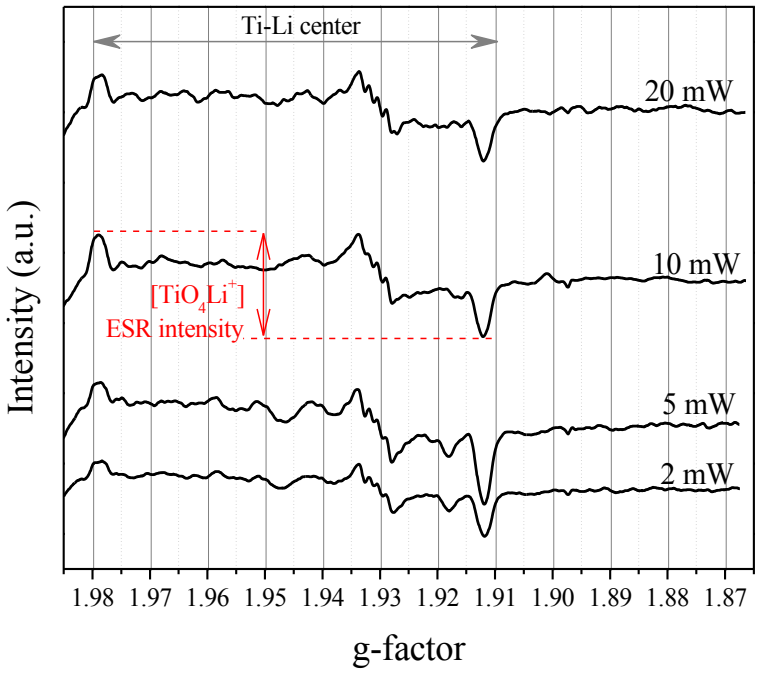

Figure 5.4 ESR signals corresponding to the Ti-Li center recorded for calibration quartz at 90K for 1G modulation amplitude and at different powers.

5.6 Effect of heating and etching of quartz on ESR signals

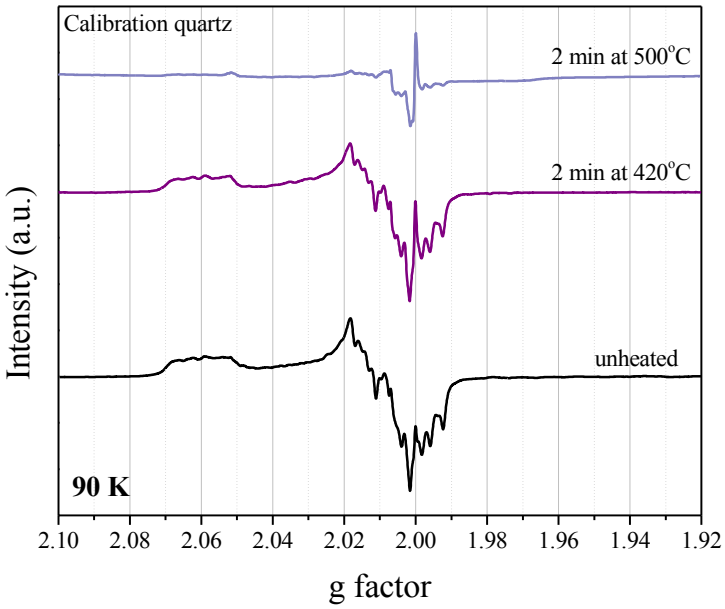

Figure 5.5 Effect of heating on the ESR signals of calibration quartz measured at 2 mW microwave power and 1G modulation amplitude at low temperature (90K).

It was shown in this work that the Al-center is interfered by other signals visible at room temperature (**Figure 5.3**). An annealing experiment was thus conducted with the aim of better resolving the signal of interest. Three heat treatments were applied and ESR measurements were performed using the resulting material (CQ 2 min at 280ºC, at 420ºC and at 500ºC, respectively). The spectral patterns of the E_1' center remain the same after heating, but the intensity of the signal increases up to 420ºC and then decreases at 500ºC. The variation of the Al center is shown in **Figure 5.5** and it can be seen that the signal intensity decreases after heating 2 minutes at 420ºC and after 2 minutes at 500ºC, the Al center signal is gone. In the same time, a signal around g = 2.0006 – 1.9986 overlapping the Al center signal is revealed.

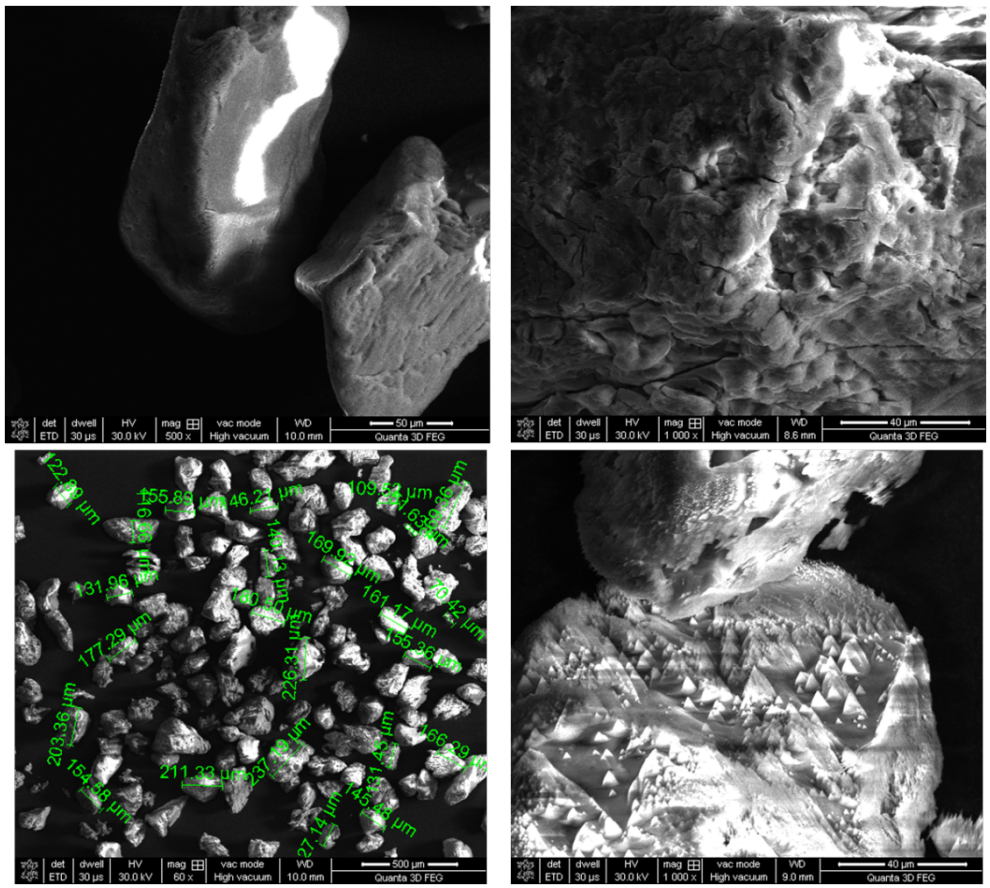

Figure 5.6 Scanning electron microscopy images of calibration quartz sample (CQ, 180-250 µm) (a), (b) after standard laboratory preparation, including HF etching for 40 min and (c), (d) after an extra 5 h of HF etching.

Extensive etching experiments are useful for identifying if certain defects are concentrated on the surface of the grains. If so, it would be expected that smaller grains display a higher concentration of such defects, due to surface to volume effects. A portion of quartz (180-250 µm) from sample CQ (calibration quartz) was etched an extra 5 hours in

hydrofluoric acid (HF) in order to analyse the effect of etching on the ESR signals. **Figure 5.6** shows SEM images of quartz grains before (a,b) and after (c,d) this step was performed. The size of the quartz grains was not significantly decreased by etching (**Figure 5.5.c**) because the acid seems to have preferentially etched certain amorphous areas of the grains. No significant effect of the 5h-etching is observed on the Al center signal.

5.7 ESR signals of fine and coarse quartz

The qualitative differences in ESR signals between fine (4-11 μm) and coarse (63-90 μm) quartz fractions are reported in this section on sample STY 1.10. **Figure 5.7** shows wide spectra for both grain size fractions. While the signals are overlapping around the interval 3400-3500 G, the 63-90 μm quartz is characterised by several additional signals that are not present for the 4-11 μm quartz.

Indistinguishable spectral patterns are observed for the E_1' center of both fine and coarse quartz (**Figure 5.8**). The sharp lines that form the powder spectrum of $[AlO_4]^0$ center are shown in **Figure 5.9** for fine and coarse quartz. The overlapping peroxy signal at g = 2.0074, although observable in both size fractions, is more pronounced in the fine fraction and it represents the highest intensity of the spectrum, while for the coarse fraction, the top of the first peak of the Al spectrum at g = 2.018 has the highest intensity. A significant difference between fine and coarse quartz is noted for the Ti paramagnetic centers. The ESR signal of $[TiO_4Li^+]^0$ in coarse quartz is shown in **Figure 5.10.a**. In the same time, no $[TiO_4M^+]^0$ signal could be detected in fine quartz (**Figure 5.10.b**).

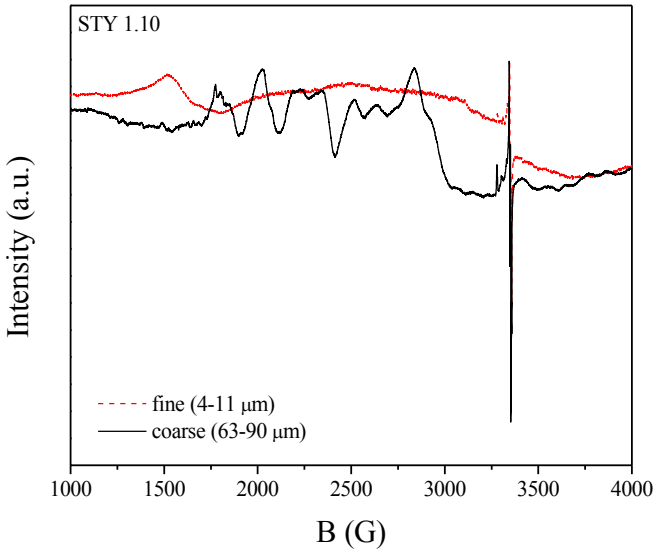

Figure 5.7 ESR spectra of fine (4-11 μm) and coarse (63-90 μm) quartz fractions of sample STY 1.10 obtained at room temperature, for 1G modulation amplitude and 2 mW microwave power.

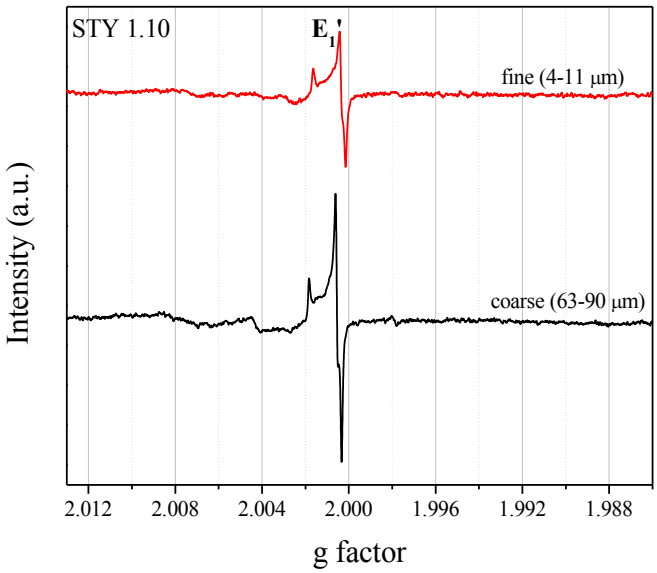

Figure 5.8 Comparison of ESR signals corresponding to the E_1' center in fine (4-11 μm) and coarse (63-90 μm) quartz fractions of sample STY 1.10 recorded at 0.02 mW microwave power and 0.1 G modulation amplitude. The spectra were recorded at room temperature.

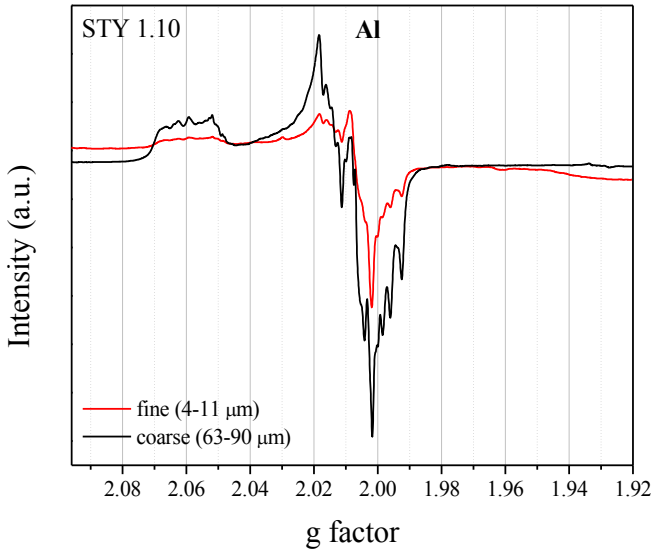

Figure 5.9 Comparison of ESR signals corresponding to the Al center in fine (4-11 µm) and coarse (63-90 µm) quartz fractions of sample STY 1.10 recorded at 2 mW microwave power and 1 G modulation amplitude. The spectra were recorded at low temperature (90K).

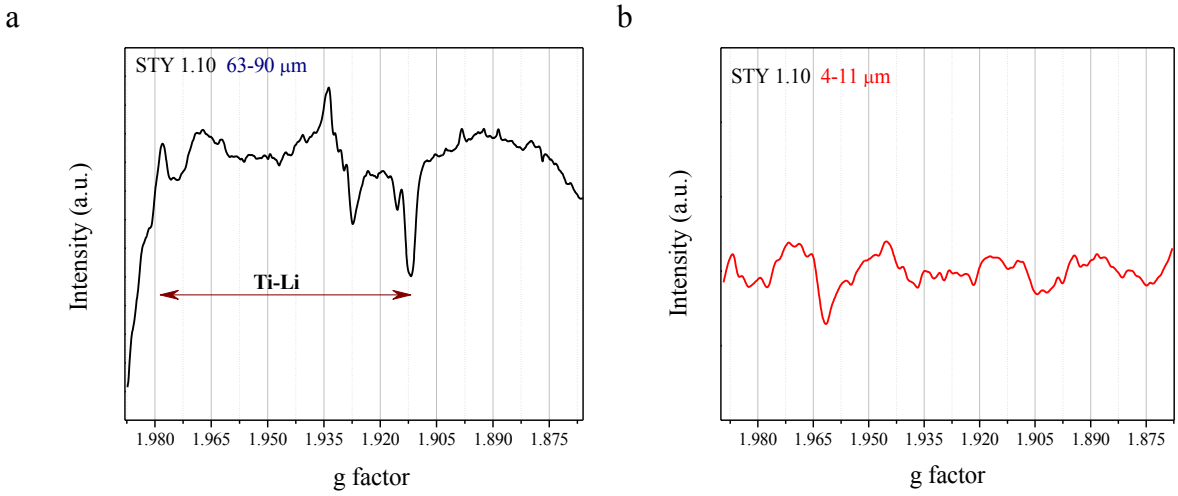

Figure 5.10 Comparison of ESR signals corresponding to the Ti-Li center in (a) coarse (63-90 µm) and (b) fine (4-11 µm) quartz fractions of sample STY 1.10 recorded at 5 mW microwave power and 1 G modulation amplitude. The spectra were recorded at low temperature (90K).

5.8 Discussion and future investigations

A recent study (Liu et al., 2015) analysed the effect that grain size has on quartz ESR dating of the Ti-Li center looking at 5 grain size fraction in the interval 50 - 450 μm. To our knowledge, nowhere in the literature is the 4-11 μm quartz fraction analysed in an ESR dating context. The trend observed by Liu et al. (2015) regarding the Ti-Li signal intensity seems to apply to some extent to our results. They show gradually decreasing ESR signal intensity with decreasing grain size, with significantly lower intensity for the 50-100 μm quartz fraction compared to the 300-450 μm fraction of the natural sample (~10 times lower). Our measurements show no Ti-Li signal for the 4-11 μm grain size, implying that the decreasing trend is continued down to very small grain sizes, until no signal is detected. Given these results, it can be assumed that the $[TiO_4M^+]^0$ centers are not the electron traps involved in OSL production, since no signal is present in the fine grain fraction.

While the E_1'center induces the same ESR spectral pattern in both 4-11 μm and 63-90 μm quartz, the signature of $[AlO_4]^0$ seems to be stronger in coarse quartz and the interference by peroxy signals is more pronounced in the 4-11 μm grain fraction. The E_1'and $[AlO_4]^0$ paramagnetic centers could serve as possible candidates for either OSL recombination centers or OSL recombination center competitors. Further quantitative measurements are needed for clear conclusions to be drawn.

5.9 Conclusion

The results presented in this chapter are preliminary and while further measurements are needed, a few conclusions can be drawn. The ESR signals of both fine (4-11 μm) and coarse (63-90 μm) quartz were measured and some differences in behaviour were noticed, most notable being the absence of Ti center signals in fine quartz, while present in coarse quartz. Overlapping peroxy signals were detected in the $[AlO_4]^0$ signals and care is recommended when using these interfering signals in ESR dating. Our preliminary results indicate $[AlO_4]^0$ and E_1' as possible candidates for either OSL recombination centers, or OSL recombination center competitors. $[TiO_4/Li^+]^0$ does not seem to play a role as an OSL electron trap.

Summary and Conclusions

Optically stimulated luminescence (OSL) dating of quartz has become one of the most significant chronological tools currently used in Quaternary research. Models have been created to explain the physical mechanism that permits natural quartz to be used as a dosimeter, but many phenomena still remain subject for further research. Problems are also encountered in the use of OSL for dating and recent studies have shown that both age discrepancy between different grain sizes (fine and coarse), and age underestimations are important issues in the high dose range. More precisely, age underestimations have been repeatedly reported for samples of either silt or sand size over ca. 70 ka, even though younger samples had ages in agreement with independent controls (Buylaert et al., 2007; Lowick et al., 2010; Timar et al., 2010). Recent studies on quartz extracted from Romanian, Serbian and Chinese loess reported optical ages obtained on coarse quartz (63-90 μm) to be systematically higher than those on fine quartz (4-11 μm), when the ages correspond to equivalent doses larger than ~100 Gy. At the moment, the source of the age discrepancy is thought to reside, at least partly, in the different saturation characteristics of fine grains compared to the coarse grains, and in the differences reported between the laboratory and the natural dose response curves (Timar-Gabor et al., 2015).

A case study applied on quartz samples extracted from loess demonstrated that thermal instability is not at fault for the age underestimations previously reported. The trap lifetimes were calculated for fine (230 Ma) and coarse (14750 Ma) quartz and the values obtained are well beyond the age of interest for dating purposes, indicating that a possible age underestimation for one or both fractions is not related to their thermal stability (Timar-Gabor et al, 2017). An experiment that evaluated the influence of pulsed irradiation on the OSL dose response of fine and coarse quartz was performed in order to test whether a possible trap competition between shallow traps and the dosimetric trap is responsible for the extended growth of the laboratory dose response curve at high doses compared to the natural dose response curve and this hypothesis was not confirmed by the results obtained.

Previous works focused on optically stimulated luminescence dating of quartz extracted from Romanian and Serbian loess reported significant discrepancies between ages obtained on fine (4-11 μm) and coarse (63-90 μm) quartz (Timar-Gabor et al., 2011, 2012; Timar-Gabor and Wintle 2013; Constantin et al., 2014, Timar-Gabor et al., 2015b). We aimed at expanding these investigations by applying the SAR-OSL and double SAR-OSL protocols on

quartz of different grain sizes belonging to 9 samples extracted from a newly identified archaeological site at Bistricioara-Lutărie III on the Bistrița Valley (NE Romania). Radiocarbon ages were also obtained for the 3 uppermost cultural layers hosted in the loess-like deposit.

Discrepant ages were obtained between fine (4-11 μm) and coarse (63-90 and 90-200 μm, respectively) quartz for equivalent doses higher than ~80-100 Gy. However, a very good agreement was achieved for the youngest sample, with an age of ~8 ka (with a De of 38 Gy for fine and 35 Gy for coarse grains, respectively). The comparison with independent control provided by radiocarbon dating suggests better agreement of ages calculated for coarse quartz (Trandafir et al., 2015). Our results are once again proof that concerns should be raised regarding the reliability of the equivalent doses obtained in the high dose range on quartz samples for which the laboratory dose response cannot be fitted by a single saturating exponential function. Further systematic investigations are required regarding the very different saturation characteristics of fine and coarse grained quartz.

Muscovite is a mineral commonly found along quartz in sediments, where the latter is the mineral of choice in numerous OSL dating studies. Since muscovite cannot be efficiently eliminated following standard laboratory treatments, it is important to assess its luminescence properties. Our focus was to investigate muscovite hand-picked from a quartz sample extracted from loess and museum specimens of muscovite in order to evaluate their potential implication in the OSL dating of quartz samples contaminated with muscovite grains. The obtained results show that generally applicable luminescence characteristics cannot be described for muscovite. In terms of the thermoluminescence (TL) response, all samples investigated display the same wide peak at 200ºC. The blue light and infrared (IR) sensitivities differ between the samples: 3 out of 5 samples present no or negligible level of OSL and IRSL response, while the other 2 samples are characterised by both blue light (2000 – 3400 counts in 0.31 s of stimulation for 10 mg of muscovite after irradiation with a dose of 136 Gy) and IR sensitivity (265 –320 counts in 0.31 s of stimulation for 10 mg of muscovite after irradiation with a dose of 136 Gy). Based on the samples anaylsed in this study, aliquots of quartz contaminated with optically (blue light) sensitive muscovite would also be IR sensitive. Hence, potentially problematic aliquots can be identified via the IRSL purity test usually used in the OSL dating of quartz samples for detection of feldspar contamination. The impact of muscovite on dose determination for quartz was also tested and it was concluded that at least in the case of bright quartz, muscovite minerals do not influence the OSL measurements (Antohi-Trandafir et al., 2018).

Electron spin resonance (ESR) is not only a promising dating technique for Quaternary quartz, but it can also provide valuable structural and dynamic information about the system being studied. Our long-term aim is to carry out fundamental studies of the ESR signal behaviour of both fine and coarse quartz extracts, in an attempt to draw a correlation between these signals and the luminescence (TL and OSL) signals recorded for the same samples. In this thesis, the first ESR measurements performed in our laboratory for this goal were presented, along with a literature overview of ESR dating, with a focus on applications on quartz from sediments.

The ESR signals given by the E_1', peroxy, Al and Ti centres in a calibration quartz sample and in quartz extracted from loess samples from Romania and Ukraine were identified and the optimum parameters needed for measurement were determined. The effects on the ESR signals of heating and prolonged hydrofluoric acid etching of quartz were investigated for the calibration quartz sample (180-250 μm).

Qualitative differences between the ESR spectra of fine (4-11 μm) and coarse (63-90 μm) quartz were reported and include variations between the signals of the wide spectra (2500 G centerfield, 3000 G sweep width) of the two fractions and the absence of Ti center signals in fine quartz, while present in coarse quartz. Aluminium-hole ($[AlO_4]^0$) signals are observed in all investigated samples when spectra are recorded at low temperature (90K). To our knowledge, this is the first time that ESR spectra are studied for quartz fraction 4-11 μm. Our preliminary results indicate $[AlO_4]^0$ and E_1' as possible candidates for either OSL recombination centers, or OSL recombination center competitors. $[TiO_4/Li^+]^0$ does not seem to play a role as an OSL electron trap.

Our results indicate once again that the optical ages for loess beyond 30 – 40 ka are most likely inaccurate and new approaches are necessary in order to overcome this issue. An intense focus on ESR investigations, combined with detailed OSL and TL observations may lead to an improvement of the understanding of the mechanism that is responsible for luminescence production in quartz.

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