Luminescence properties of natural muscovite relevant to optical dating of contaminated quartz samples


Interdisciplinary Research Institute on Bio-Nano-Sciences, Babeș-Bolyai University, Treboniu Laurian 42, 400271 Cluj-Napoca, Romania
Faculty of Physics, Babeș-Bolyai University, M. Kogălniceanu 1, 400084 Cluj-Napoca, Romania
Faculty of Environmental Science and Engineering, Babeș-Bolyai University, Filandrului 30, 400294 Cluj-Napoca, Romania
Department of Geography, Northumbria University, Newcastle-upon-Tyne, United Kingdom
Institute of Speology, Romanian Academy, Clinicilor 5, 400006 Cluj-Napoca, Romania

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ABSTRACT

Muscovite is a mineral commonly found among quartz in sediments, where the latter is the mineral of choice in numerous optically stimulated luminescence (OSL) dating studies. Since muscovite cannot be efficiently eliminated following standard laboratory treatments, it is important to assess its luminescence properties. This study is focused on the investigation of muscovite hand-picked from a quartz sample extracted from loess and of 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 200 °C. 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 analysed 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.

1. Introduction

Geological dating of sediments using TL and OSL is a well-established and reliable technique, widely used in Quaternary research. Either quartz or feldspars are extracted from sediments for this purpose following standard laboratory steps consisting of a combination of acid treatments, sieving and density separation (Aitken, 1985). However, significant amounts of mica commonly found in sediments are not removed during sample preparation and the question arises whether they can influence the luminescence properties of contaminated quartz separates. This issue is especially important in the context of OSL dating of low sensitivity quartz samples, which can be found all around the world in alpine environments such as the Himalayas (Owen et al., 1997; Richards, 2000) or the European Alps (Klasen et al., 2006; Preusser et al., 2007). Compared to the dim OSL signal of alpine quartz, a potential luminescence contribution from mica minerals could become significant.

Within the mica group, muscovite is one of the most common minerals, characterised by extremely good cleavage due to the layered crystal structure. It is a light-coloured phyllosilicate, predominantly of metamorphic origin, but it can also be found in igneous and sedimentary rocks. The idealized chemical formula of muscovite is KAl₂(Si₃Al)O₁₀(OH)₂ and its density ranges from 2.77 to 2.88 g/cm³ (Blume et al., 2016). Despite its high density, muscovite is not easily separated from quartz using heavy liquids because of its high surface energy (Bailey, 2013), which makes it float. Hydrofluoric acid (HF) etching, routinely done for 40–60 min for the removal of any remaining feldspars and the outer layer of quartz grains is not effective in dissolving muscovite.
minerals. Muscovite is etched in HF for 500 min in nuclear track applications (L’Annunziata, 2003), so a much longer etching time than 500 min would be necessary for its removal, which would lead to excessive etching of the quartz minerals.

The presence of mica was reported in OSL dating studies either as a contaminant mineral phase (Lomax et al., 2014) or as mineral inclusion in quartz or feldspar grains (Meyer et al., 2013). However, only a few studies have focused on investigating TL properties of various phyllosilicates and muscovite in particular (Kalita and Wary, 2016 and references therein) with the main purpose of assessing their potential application in TL dating and dosimetry. Li and Yin (2006) studied the luminescence properties (TL, OSL and IR stimulated luminescence - IRSL) of biotite, another member of the mica group. For the investigated sample, they report beta-induced TL and OSL signals, linear growth to large doses and high thermal stabilities, but also anomalous fading of both TL and OSL signals. To our knowledge, only Kortekaas and Murray (2005) have looked into the OSL characteristics of muscovite, especially with regard to its possible contribution to the luminescence signals recorded from quartz in dating studies. They propose a method for the removal of mica from quartz samples using a detergent solution as a prudent measure. The suggestion comes after observing a measureable but low blue light sensitivity from the manually selected mica after a 60 Gy dose, with a similar rate of optical evi- dence between the mica and quartz samples. The authors conclude that further investigations are needed to assess the applicability of their observations and the potential of mica as a luminescence dosimeter.

In this paper, we investigate 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.

2. Samples and experimental details

The sedimentary quartz sample CST 18 is extracted from a loess sample from the archive of the Luminescence Dating Laboratory of Babes-Bolyai University, previously dated by Constantin et al. (2014) that belongs to the 1.2 loess unit from the Costinesti section in SE Romania. For more details regarding the geological context of the sample, please refer to Constantin et al., 2014. An HCl (10%) treatment was employed for carbonate removal followed by H₂O₂ (10% followed by 30%) treatment for organic matter removal. The coarse grain fraction (63–90μm) was obtained by sieving and etching with HF (40%). Sample CST 18 has an equivalent dose of 425 ± 27 Gy, an OSL brightness of ~7000 counts in the first 0.31 s of the 40 s of blue stimulation for a beta dose of 17 Gy and displays good behaviour in the single aliquot regenerative (SAR) protocol, with a recycling ratio of 0.98 ± 0.01, an IR depletion ratio of 1.00 ± 0.01 and negligible recuperation of 0.10 ± 0.01% (Constantin et al., 2014).

Using scanning electron microscopy (SEM) and X-ray diffraction (XRD), muscovite grains were identified in the 63–90μm fraction of sample CST 18. SEM and chemical analysis of local area by energy dispersive X-ray spectroscopy (EDXRF) were carried out with a FEI Quanta 2D FEG dual beam microscope. The crystal structure of the sample was determined by X-ray diffraction (XRD) analysis using a four-circle Bruker D8 Discover diffractometer. The muscovite grains were picked by hand under the stereomicroscope and placed in a stainless-steel cup. One aliquot of ~3 mg was thus obtained for luminescence investigations and is hereafter 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. They all originate from pegmatites from Romania, in Southern and Eastern Carpathians respectively and an image of one of the samples as it is found in the museum collection is presented in Fig. S1. The material of each of the museum muscovite sample was washed with alcohol and distilled water and ground in a ball mill for 5 min at a frequency of 30 s⁻¹ and the resulting powder was used for luminescence analysis.

The geochemistry of the four museum muscovites was analysed using energy dispersive X-Ray fluorescence spectroscopy (EDXRF). EDXRF was applied to the muscovite samples upon powdering and placing into aluminium cuvettes. Analysis was performed at Northumbria University on a Spectro Analytical X-Lab 2000 fitted with a Gresham Si (Li) detector. Three Barkla scatterer targets were used: boron carbide for elements from Mo to Mn; aluminium oxide for elements from Mo to Ce, and HOPG (highly ordered pyrolytic graphite) for other elements (Dean et al., 2004). Results were calibrated using internal calibration data, developed from 71 reference materials and expressed in mg/kg. Calibration data considered the given concentration against count intensity for each element after correction for background and matrix effects (Dean et al. 2004 and references therein).

A quartz sample (180–250 μm quartz from aeolian sand dunes, Rømø, Jutland, Denmark, lab code H33052) provided by Risø National Laboratory (Hansen et al., 2015) and called hereafter RQ was used for a comparative dose recovery experiment (described in Section 3.2.3). The material received in our laboratory is the 180–250 μm quartz fraction separated from aeolian sand through conventional sample preparation techniques (described in Hansen et al., 2015). This quartz has only undergone physico-chemical preparation, without the sensitisation (annealing, dosing, annealing) described in Hansen et al. (2015). Thus, this is the natural material that was later on used to prepare calibration quartz and not the material termed as calibration quartz. This sample 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 equipped with blue and IR light diodes emitting at 470 ± 30 nm and 875 ± 80 nm, respectively. The emitted luminescence signals were detected by an EMI 9235QA photomultiplier tube through a 7.5 mm thick Hoya U-340 UV filter. Irradiations were carried out using the incorporated ⁸⁶³Sr-⁹⁰Y radioactive source calibrated against gamma dosed calibration quartz supplied by Risø National Laboratory, with a dose rate of 0.141 Gy/s for quartz samples placed in stainless steel cups. Each muscovite aliquot consisted of about 2–7 mg of material.

3. Results and discussions

3.1. Evaluation of minerals

SEM images show a high contamination of sample CST 18 with an Al-rich mineral (Fig. 1). The X-ray diffractogram confirms that besides quartz, muscovite is clearly detectable in the sample (Fig. 2). Fig. 3 shows the SEM image and compositional map of the hand-picked muscovite minerals (muCST 18), where a very low quartz contamination can be observed.

SEM and EDX images of all four museum muscovite samples can be examined in Fig. S2. The geochemical analysis of these samples (Fig. S3) shows elevated concentrations of Al and Si, as well as K, albeit in varying amounts. The EDXRF data indicate that the analysed samples are phyllosilicate minerals of Al and K, but with significant concentrations of Fe in all samples, as well as Mg in sample VL (Table S1). Biotite (K(Mg,Fe)₃Al₃Si₃O₁₀(F,OH)₂) and or phlogopite (K(Mg,Al)₃Al₃Si₃O₁₀(F,OH)₂), common phyllosilicate minerals within the mica group both contain Fe and Mg too, however, the physical appearance (whitish to grayish laminae, with a slight brown tinting and perfect cleavage) suggest that the analysed minerals are muscovite (KAl₂₂(AlSi₃O₁₀)(OH)₂). It is therefore likely that Fe and Mg, as well as other elements found within all samples in minor and trace concentrations (e.g., Ti, Cl, and Ca in all samples, the rest of elements in negligible concentrations) reflect the natural variance of the host rocks, or weathering.
3.2. Luminescence investigations

All aliquots used for luminescence measurements were weighted and the signals obtained were normalised to an average weight of 10 mg. To investigate the possible influence of muscovite on quartz luminescence measurements, 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, as this combination was used for dating quartz sample CST 18 (Constantin et al., 2014). A test dose of 68 Gy was used for sensitivity correction. This large test dose was used because of the better counting statistics, as lower doses (such as 17 Gy) yielded a very weak OSL signal in the case of muscovite. No natural OSL signals were recorded for any of the muscovite samples due to the fact that the muCST 18 sample was exposed to daylight during sample preparation and the museum specimens were kept in daylight conditions in the museum. TL glow curves were measured up to 400 °C at a heating rate of 5 °C/s. No background subtraction was performed. The reproducibility of the TL response was tested by giving a dose of 400 Gy to an aliquot and measuring the resulting signal. This was repeated at least 3 times on each aliquot investigated.

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). 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. An elevated temperature IR clean-out of 40 s at 220 °C was inserted after each measurement cycle. The net continuous wave OSL (CW-OSL) signal of the aliquots was evaluated from the first 0.31 s of the decay curve and the IRSL signal was evaluated from the first 0.76 s of the decay curve and were both corrected with an early background subtraction (Ballarini et al., 2007). The reproducibility was assessed for OSL and IRSL signals by repeating the same regeneration SAR cycle (the same regeneration dose) several times in a row and comparing the sensitivity corrected signals obtained in each cycle. A good reproducibility of the luminescence signals would allow us to make comparisons between measurements on the same aliquot, since the quantity of material is limited. In addition, the OSL signal reproducibility was checked in order to see whether the signal

Fig. 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. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 2. X-ray powder diffractogram of a contaminated quartz sample (CST 18, 63–90 μm) indicating the crystallographic peaks of minerals present i.e. muscovite and quartz.

Fig. 3. (a) Scanning electron microscopy image of the minerals hand-picked from CST18. The open red circles indicate the quartz grains. (b) Compositional image of Si (turquoise) and Al (magenta). Both panels show the same field of view. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
contribution from muscovite could increase through the SAR cycle.

3.2.1. Hand-picked muscovite (muCST18)

The luminescence properties of a muscovite aliquot of muCST 18 were investigated to verify if it had any influence on the measurements performed on the quartz sample (CST 18) from which it was selected. The TL glow curve shown in Fig. 4 illustrates a wide peak at ∼200 °C, but there appears to also be a second peak still growing at 400 °C. No clear 110 °C peak is distinguishable, as reported by Kortekaas and Murray (2005).

The mineral has no OSL or IRSL responses for a dose of 136 Gy, but it produces low OSL (Fig. 5a) and IRSL (Fig. 5b) signals for very high doses of 5000 Gy. Note that these signals are representative for a cup filled with muscovite (10 mg), whereas in a contaminated quartz aliquot, the amount of muscovite would be much smaller. When compared to the OSL signal produced by 10 mg of CST 18 (see inset in Fig. 5a), 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 Sanderson, 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.

3.2.2. Museum muscovite

The TL glow curves of 400 Gy irradiated museum muscovite samples are shown in Fig. 6. All specimens display a very wide TL peak at ∼200 °C, albeit of significantly different sensitivities. Total signal outputs vary from ∼3000 counts/mg for sample MR to ∼80 000 counts/mg for sample CS. The TL signal of hand-picked muCST 18 falls in this interval, with ∼30 000 counts/mg, similar to sample MM. The TL glow curves presented here differ from others reported in literature. Kortekaas and Murray (2005) note a TL peak for a museum muscovite irradiated with a dose of 60 Gy that is visually indistinguishable from the 110 °C TL peak from a quartz sample, while Kalita and Wary (2016) observe a stable TL peak at around 73 °C and an additional peak at 135 °C after annealing the muscovite sample. The TL responses of muscovite samples vary among different studies and even within the same study – Ige et al. (2006) examine the TL of muscovite specimens from two different deposits and report that their TL responses are deposit dependent, whereas the results reported in this study show the same TL peak regardless of the origin or geochemistry of the minerals. The TL signals presented here show good reproducibility, as assessed using the protocol described in the previous section (Fig. S4). Fig. 7a shows mass-normalised OSL decay curves from aliquots of all museum muscovite samples after a dose of 136 Gy. The signal outputs of the 4 aliquots are displayed in this graph, while the inset allows a comparison between the shapes of the decay curves of the mica minerals and that of a calibration quartz aliquot. A separation can be made at this point between the samples, according to their blue light
sensitivity. Samples MM and CS are bright and display a steep OSL decay, comparable to that of quartz. This is similar to the OSL decay shape reported in Kortekaas and Murray (2005) (see aliquots 2 and 3 in their Fig. 2c). Samples VL and MR are characterised by a very weak blue light sensitivity. The investigation into the reproducibility of the OSL signal was thus performed only on the minerals belonging to samples with significant blue light sensitivity (MM and CS) and the results are shown in the supplementary material, Fig. S5. Within error limits, all the sensitivity corrected OSL responses normalised to the signal in the first cycle are spread within 10% deviation of unity.

Regarding the IR stimulated luminescence response, there are again divergent results reported in other studies: while Clark and Sanderson (1994) detect luminescence signal of mica under IR stimulation, Kortekaas and Murray (2005) show no IR sensitivity for mica minerals manually selected from a contaminated quartz sample. Fig. 7b shows the IR stimulated luminescence decay curves following a dose of 136 Gy for all 4 museum muscovite specimens analysed in this study. As was the case for the OSL decay curves, the samples present different IR sensitivities: MM and CS show similar brightness, while MR and VL present no response after the IR stimulation. Further on, the inset shows the shape of the decay curves for the samples MM and CS, which are indistinguishable from one another. According to these observations, muCST 18 is similar to samples MR and VL, based on the fact that they also present IRSL sensitivity.

In order to evaluate the influence of muscovite screening on D_t determination

In order to evaluate the influence of screening for muscovite using an IR purity check has on D_t 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. MM is the brightest of the museum muscovite samples analysed in this study. As was the case for the OSL decay curves, the samples present different IR sensitivities: MM and CS show similar brightness, while MR and VL present no response after the IR stimulation. Further on, the inset shows the shape of the decay curves for the samples MM and CS, which are indistinguishable from one another. According to these observations, muCST 18 is similar to samples MR and VL, based on the fact that they all present no or insignificant OSL and IRSL responses to a relatively low dose of 136 Gy. The reproducibility test results for IRSL are shown in Fig. S6 and although variations from cycle to cycle are more pronounced than in the case of the OSL signals, this is mainly due to the lower counting statistics obtained in this case. No correlation can be drawn between the geochemical properties (see Section 3.1) of the museum muscovite samples and their luminescence properties. Namely, no cross correlation was found between low luminescence sensitivity samples (VL and MR – low TL, OSL and IRSL sensitivity) and elemental concentrations of their most abundant elements (Si, Al, K, Fe).

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) and performed in Section 3.2.3.

3.2.3. Influence of muscovite screening on D_t determination

In order to evaluate the influence that screening for muscovite using an IR purity check has on D_t 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. MM is the brightest of the museum muscovite samples analysed in this study, with an OSL response of 3467 counts in 0.31 s/10 mg and an IRSL response of 781 counts in 0.76 s/10 mg for a given dose of 136 Gy. A dose recovery test (Murray and Wintle, 2003) employed on 6 aliquots of sample MM showed that for a given dose of 100 Gy, the recovered/given dose ratio was consistent with unity (1.00 ± 0.07). Similar results have been obtained on sample CS.

Three batches, each consisting of 48 aliquots, were prepared by mixing grains of RQ and MM in different weight proportions (Table 1). Muscovite (MM) was added in 2 different proportions (80% and 20%) to the quartz sample RQ in order to resemble real situations after sample preparation of dating samples, when muscovite remains as a contaminant in quartz samples. Each aliquot consisted of ~10 mg of material.

Aliquots were irradiated with a known dose (100 Gy) and measured in the SAR protocol. The responses to 5 regenerative doses were used to construct the dose response growth curve up to 200 Gy onto which the sensitivity corrected signal corresponding to the initial given dose was interpolated. The recycling ratio was also checked for each aliquot by
repeating a measurement of the response to a dose of 100 Gy and the ratio of the two corrected OSL signals was consistent with unity for all aliquots. The IRSL response to a regenerative dose of 100 Gy measured at 60 °C for 100 s was used to evaluate the contribution to the OSL signal of the muscovite grains, which was done by calculating the ratio of the sensitivity corrected (post-IR)-OSL, \( (L_{\text{post-IR}}/T_{\text{OSL}}) \) to the sensitivity corrected OSL, \( (L_{\text{IR}}/T_{\text{OSL}}) \). The IR depletion ratio average for 100% RQ and for 20% MM is 0.96 ± 0.003, with no aliquots being rejected, while for 80% MM, only half of the aliquots (24 out of 48) had an IR depletion ratio within 10% of unity. These results, along with the recovered average doses are shown in Table 1.

The recovered dose does not improve after rejecting the aliquots with IR depletion ratio < 0.90, remaining the same within error limits: 99.4 ± 1.5 Gy when all aliquots are taken into account compared to 97.6 ± 1.7 Gy for only the accepted aliquots. This is to be expected, considering the very good dose recovery of MM.

While this quartz sample (RQ) is very bright (~130,000 counts in 0.31 s for 10 mg of quartz for a test dose of 17 Gy), it is worth mentioning that the rejected aliquots of sample 80% MM are characterised by a much dimmer OSL signal (~3 times less than the accepted aliquots). This can be caused by more quartz grains with little or no useful signal being present in the rejected aliquots. In any case, overall the IR depletion ratio test is successful in indicating a potential muscovite contamination in a quartz extract.

**4. Conclusion**

Based on the results of the present study, 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. 3 out of 5 of the muscovite samples investigated here present no or negligible levels of OSL and IRSL response, while the other 2 samples are characterised by both blue light and IR sensitivity. Given the results of energy dispersive X-Ray fluorescence spectroscopy analysis this difference does not stem from a major differentiation in geochemical composition between the muscovite samples.

For the 2 samples that present blue light and IR signals, we also investigated the reproducibility of the signals, conducted dose recovery tests and constructed dose response curves up to 5000 Gy. While testing the applicability of this mineral for dating falls beyond the scope of this study, the good dose recovery, reproducibility and growth of the signal up to doses of ~2000 Gy indicate that in the circumstance when other more suitable minerals are not available for OSL dating, certain types of muscovite might be taken into consideration. However, further measurements are needed to confirm this possibility, including the investigation of OSL fading characteristics of muscovite.

Concerning the main goal of our investigation, namely checking the possible influence of muscovite on potentially contaminated quartz extracts from sedimentary samples, 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.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.radmeas.2017.12.004.

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