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

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ABSTRACT

Muscovite is a mineral commonly found along 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 $KAl_2(Si_3Al)O_{10}(OH)_2$ and its density ranges from 2.77 to 2.88 g/cm^3 (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

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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 eviction 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 L2 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 H_2O_2 (10% followed by 30%) treatment for organic matter removal. The coarse grain fraction (63–90 μm) 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 63–90 μm fraction of sample CST 18. SEM and chemical analysis of local area by energy dispersive X-ray spectroscopy (EDX) were carried out with a FEI Quanta 3D 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 muscovite 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 ^{90}Sr-^{90}Y 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 $(K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2)$ and/or phlogopite $(KMg_3AlSi_3O_{10}(F,OH)_2)$, 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 $(KAl_2(AlSi_3O_{10})(OH)_2)$. 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.