Supplementary Material

Application of geochemical weathering indices to loess-paleosol sequences from Central Asia (Tajikistan)

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# Luminescence dating

## Sample preparation and instrumentation

12 samples for luminescence dating were collected from a c. 15 m deep loess-palaeosol section at Karamaidan (KAR), Tajikistan. These samples were processed under filtered red-light conditions at the Johannes Gutenberg University and Max Planck Institute for Chemistry, Mainz. All the samples were wet-sieved to grains of different size fractions. Of these, <63 µm fraction, being in abundance was further processed to obtain fine-grained (4-11 µm) quartz and polyminerals for luminescence dating. The <63 µm was treated with 10% HCl and 10% H2O2 to remove carbonates and organics respectively. Following which, it was treated with 0.1 N sodium oxalate to remove clays. Every successive chemical pre-treatment step was followed by multiple-wash steps with deionised water. The separation of the fine-grained (4-11 µm) polyminerals from the bulk (<63 µm) was done using Stokes law. A portion of the 4-11 µm polyminerals was treated with 37 % hexafluorosilicic acid for 7 days, followed by a wash with 10% HCl to remove feldspars and fluoride precipitates respectively, to obtain fine grain quartz.

All luminescence measurements were performed on an automated Risø TL-DA-20 reader equipped with a 90Sr/90Y beta source (Thomsen et al., 2006). The sample was stimulated using IR LED (870 ± 30 nm, 300 mW/cm2) and blue LED (470±30 nm, 80 mW/cm2) and the emitted luminescence signal was detected by EMI 9235QA photomultiplier tube fitted with a 7.5 mm Hoya U-340 and a combination of Schott BG-39 and BG-3 filters to detect quartz and feldspar emissions respectively. In order to avoid stimulation cross-talk, aliquots were placed at alternate positions in the sample carousel. All luminescence measurements were conducted on aliquots prepared by suspending 4-11 µm quartz or polymineral grains on stainless steel cups.

## Methodology

Optically stimulated luminescence (OSL) dating technique allows us to measure the time elapsed since grains of quartz and feldspar were last exposed to sunlight, and is obtained by taking the ratio of the equivalent dose in the sample to the total environmental dose received by the sample during burial (Aitken, 1998). We measured the equivalent dose (De) for fine-grained quartz samples using the Double - Single aliquot regenerative (DSAR) protocol (Banerjee et al 2001; Jain and Singhvi, 2005; Table S1a), which includes an additional IR stimulation prior to all blue stimulation steps within the SAR (Murray and Wintle, 2000; 2003) protocol. The De for polymineral fine-grained samples was obtained by applying the elevated temperature post-infrared - Infrared stimulated luminescence (pIRIR) dating protocol (Thiel et al., 2011; Table S1(b)).

The environmental dose rate for the samples was calculated from radioelemental concentrations using published conversion factors (Guerin et al., 2011), combined with moisture content (10 ± 5 %, typical for loess deposits) and published equations for cosmic-ray dose rate contributions (Prescott and Hutton, 1994). The radioelemental concentrations in the samples were measured using high-resolution germanium gamma spectrometry, analysed at the Felsenkeller, VKTA Dresden. An alpha efficiency value of 0.038 ± 0.002 for fine-grained quartz and 0.086 ± 0.004 for polymineral fine grains was used for all dose rate calculations (Rees-Jones, 1995). The dose rates were calculated using the Dose Rate and Age Calculator (DRAC ver 1.2) by Durcan et al (2015).

**1.3. Results**

Prior to De measurements on fine grained quartz, preheat tests were performed on representative sample (A0226) to determine the optimal preheat temperature for application of the DSAR protocol. A DSAR protocol was applied to 3 aliquots each of sample A0226 with preheat temperatures of 180, 200, 220, 240, 260, 280 and 300oC respectively. Figure S1 shows, an acceptable preheat temperature at 280 oC, and hence a preheat of 280oC for 10s was chosen for all De measurements.

De was determined for 15-24 aliquots each, for all the 12 fine grained quartz samples from the KAR sequence. The DSAR protocol employed for measurements is presented in Table S1. The IR wash prior to OSL measurement (Table S1) showed no feldspar signal, suggesting no feldspar contamination in the samples. The recycling ratio was found to be within 10% of unity, while the recuperation ratio was less than 5% of the natural signal for all aliquots, thus suggesting the robustness of the DSAR protocol and its suitability for De determination. Th net OSL signal from each aliquot was determined from the first 0.8 s after subtraction of the average from the last 8 s of the background OSL signal. The average dose model was used for calculation of De’s for all samples. 0. The De distribution of the fine-grained quartz sample A0240 showed a high dispersion in its De distribution (c. 75%), particularly due to one aliquot with suspiciously low De. After the removal of this aliquot, the dispersion in De distribution is c. 30%. The reason for this over-dispersion in the sample, especially in fine grained sample, remains unknown. The De from all the samples are presented in Table 1

From recent studies (Timar-Gabor et al, 2017) it is known that unlike coarse grain quartz, fine-grained quartz does not show saturation of the quartz signal even at high doses, yet is known to underestimate true depositional ages (after > 40 ka). In our samples, after a depth of c. 9m, for sample A0240 (at a depth of 9m) we observe a high dispersion in the fine-grained quartz, while for the subsequent samples A0242, A0243 and A0245 at depths 10, 10.5 and 11.5 respectively, we suspect a case of possible underestimation of the true depositional age. Therefore, for samples below 9 m (A0240, A0242, A0243 and A0245), we also evaluated the elevated pIRIR ages from fine-grained polymineral samples using the pIRIR protocol as described in Table S2 (after Thiel et al, 2011). Studies based on application of elevated temperature pIRIR protocol on feldspar have shown low fading rates for the resulting IRSL signal (Thomsen et al, 2008; Buylaert et al, 2008; Thiel et al, 2011) and therefore we consider fading to be minimum for our samples. Nonetheless, since the K-feldspar ages presented in this paper have not been corrected for residual dose and fading, we consider these as maximum ages for our samples. The robust ages for the top 8 m of the section based on quartz OSL and the preliminary uncorrected pIRIR ages from below 9 m, provides us with a preliminary chronology for our site. Further work based on high-resolution multi-method luminescence dating at the site is currently in preparation and will be presented elsewhere.



**Figure S1.** Variation of equivalent dose in representative sample A0226 with different preheat temperatures. Aliquots that did not meet the recycling and recuperation criteria were rejected from the analysis.

**Table S1. (a)** DSAR protocol (modified Banerjee et al, 2001) and **(b)** pIRIR protocol (Thiel et al, 2011) used in this study for determination of the equivalent dose from the quartz and polymineral samples respectively.

1. **DSAR protocol (modified from Banerjee et al, 2001)**

|  |  |
| --- | --- |
| Step | Treatment |
| 1 | Dose (Natural or laboratory) |
| 2 | Preheat 10s at 280 oC |
| 3 | IRSL wash, 60oC for 10s |
| 4 | Blue OSL, 125 oC for 25 s |
| 5 | Test dose |
| 6 | Cut heat, 260 oC for 10s |
| 7 | IRSL wash, 60oC at 10s |
| 8 | Blue OSL, 125 oC for 25s |
| 9 | Blue OSL, 280 oC for 40s |
| 10 | Return to step 1 |

1. **pIR50IR290 protocol (after Thiel et al, 2011)**

|  |  |
| --- | --- |
| Step | Treatment |
| 1 | Dose (Natural or laboratory) |
| 2 | Preheat, 320 oC for 60s |
| 3 | IRSL, 50oC for 200s |
| 4 | IRSL, 290 oC for 200s |
| 5 | Test dose |
| 6 | Preheat, 320 oC for 60s |
| 7 | IRSL, 50oC for 200s |
| 8 | IRSL, 290 oC for 200s |
| 9 | IRSL, 325 oC for 200s |
| 10 | Return to step 1 |

## References

Aitken, M. J. (1998). An introduction to optical dating. Oxford University Press.

Banerjee, D., Murray, A. S., Bøtter-Jensen, L., & Lang, A. (2001). Equivalent dose estimation using a single aliquot of polymineral fine grains. Radiation Measurements, 33(1), 73–94. doi: 10.1016/S1350-4487(00)00101-3

Guerin, G., Mercier, N., Adamiec, G., 2011. Dose-rate conversion factors: update. Ancient TL, 29, 5-8.

Murray, A. S., & Wintle, A. G. (2000). Luminescence dating of quartz using an improved single-aliquot regenerative-dose protocol. Radiation Measurements, 32(1), 57–73. https://doi.org/10.1016/S1350-4487(99)00253-X

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

Thomsen, K. J., Bøtter-Jensen, L., Denby, P. M., Moska, P., & Murray, A. S. (2006). Developments in luminescence measurement techniques. Radiation Measurements, 41(7), 768–773. doi: 10.1016/j.radmeas.2006.06.010

Buylaert, J. P., Murray, A. S., Vandenberghe, D., Vriend, M., Corte, F. D., & haute, P. V. den. (2008). Optical dating of Chinese loess using sand-sized quartz: Establishing a time frame for Late Pleistocene climate changes in the western part of the Chinese Loess Plateau. Quaternary Geochronology, 3(1), 99–113. doi: https://doi.org/10.1016/j.quageo.2007.05.003

Durcan, J.A., King, G.E., Duller, G.A.T., 2015. DRAC: Dose rate and age calculator for trapped charge dating. Quaternary Geochronology, 28, 54-61.

Thomsen, K. J., Murray, A. S., Jain, M., & Bøtter-Jensen, L. (2008). Laboratory fading rates of various luminescence signals from feldspar-rich sediment extracts. Radiation Measurements, 43(9), 1474–1486. https://doi.org/10.1016/j.radmeas.2008.06.002

Thiel, C., Buylaert, J.-P., Murray, A., Terhorst, B., Hofer, I., Tsukamoto, S., & Frechen, M. (2011). Luminescence dating of the Stratzing loess profile (Austria) – Testing the potential of an elevated temperature post-IR IRSL protocol. Quaternary International, 234(1), 23–31. doi: https://doi.org/10.1016/j.quaint.2010.05.018

Galbraith, R. F., Roberts, R. G., Laslett, G. M., Yoshida, H., & Olley, J. M. (1999). Optical dating of single and multiple grains of quartz from Jinmium rock shelter, northern Australia: Part I, experimental design and statistical models. Archaeometry, 41(2), 339–364. Scopus. doi: 10.1111/j.1475-4754.1999.tb00987.x

Timar-Gabor, A., J.-P. Buylaert, B. Guralnik, O. Trandafir-Antohi, D. Constantin, V. Anechitei-Deacu, M. Jain, et al (2017) On the Importance of Grain Size in Luminescence Dating Using Quartz. Radiation Measurements 106, 464–71. https://doi.org/10.1016/j.radmeas.2017.01.009.