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# Luminescence dating at Cueva de Covalejos (Cantabria, Spain): preliminary results.

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## INTRODUCTION.

Luminescence dating is an appropriate method to determine the age of sediments (Aitken, 1985; 1998). Ubiquitous minerals such as quartz and feldspar store radiation energy delivered by natural radionuclides (mainly potassium and the uranium and thorium decay series). This energy can then be released by optical stimulation in the form of luminescence signal: this phenomenon is called Optically Stimulated Luminescence (OSL). By dividing the dose received by the mineral (through OSL measurements) by the dose rate it has been exposed to (through gamma spectrometry and/or *in situ* gamma dosimetry), one can estimate the time elapsed since the last exposure to light and subsequent burial (age).

This age is derived using the following equation:

$$\text{Age (in ka)} = P \text{ (in Gy)} / DR \text{ (in Gy/ka)}, \quad (1)$$

where  $P$  is the palaeodose (the total amount of dose absorbed by the mineral); an equivalent of this dose ( $D_e$ ) is estimated in the laboratory and called equivalent dose.  $DR$  is the dose rate (the rate of the radiation energy received per unit time). Fig. 1 shows sampling in the upper Layers of Cueva de Covalejos; in total, 13 sediment samples were collected, spanning Layers 1-15.

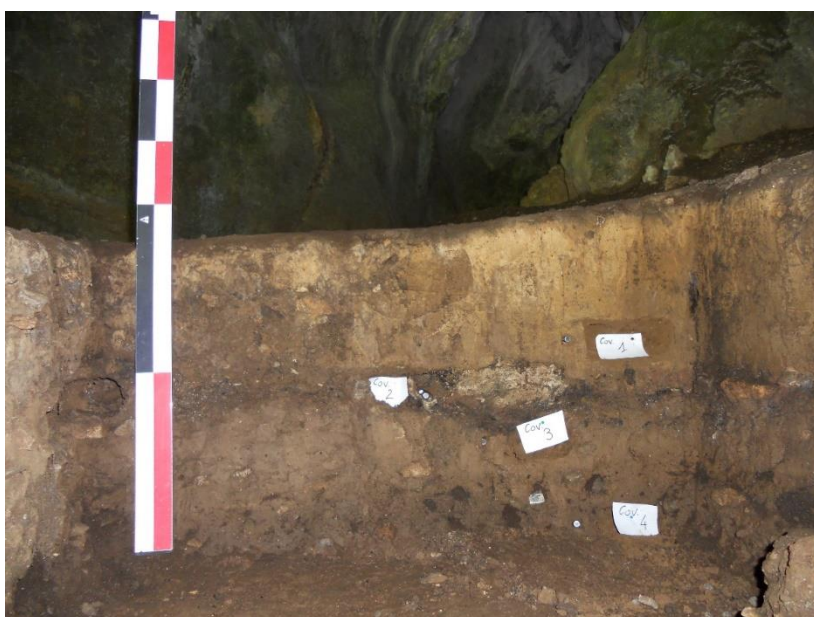


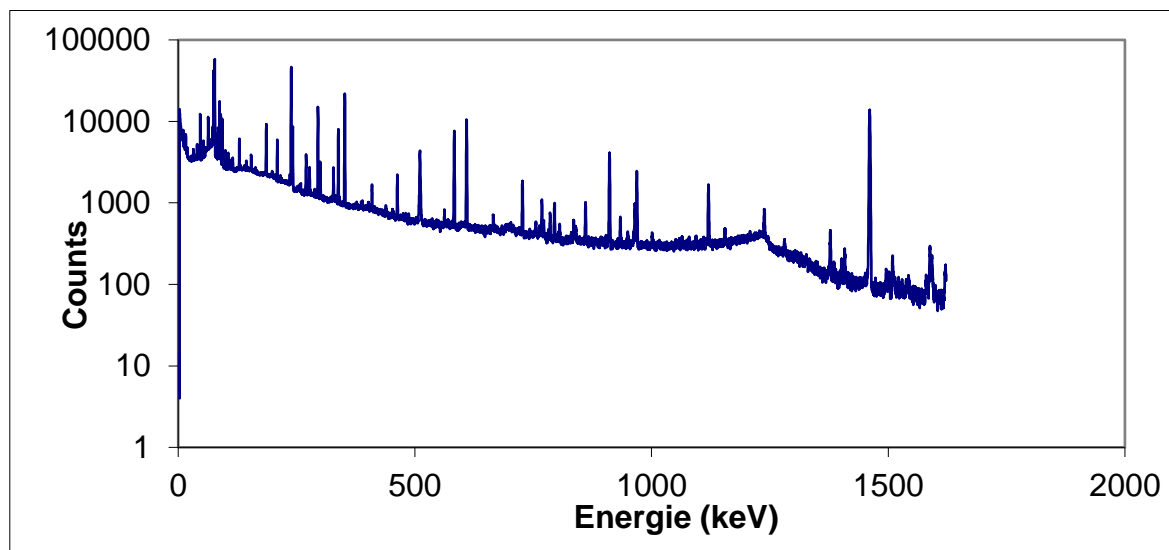
Fig. 1. Sampling in the upper Layers of Cueva de Covalejos (May 6, 2015).

## 1. Sample preparation and dose rate determination

Samples were prepared using standard luminescence dating preparation procedures (e.g., Wintle, 2008).

1. Sediments were wet sieved to extract the 180-250 grain size fraction, to allow single grain OSL measurements if needed (see below).
2. The samples were subsequently treated with HCl (10%) for 30 min to remove carbonates, H<sub>2</sub>O<sub>2</sub> (15%) for 2 days to remove organic materials.
3. The mineral quartz was extracted from the polymineral sample through density separation using a heavy liquid solution (density 2.62 g/cm<sup>3</sup>).
4. The fraction with a density > 2.62 g/cm<sup>3</sup> was etched with HF (40%) for 40 min to remove the alpha-irradiated outer layer (~ 20 µm) of the grains. The etched quartz grains were then treated with 10% HCl for 30 min to remove any fluorine that could have been produced during HF etching, and then further rinsed in purified water.

On the other hand, the fraction of the sediment samples that had been exposed to sunlight was crushed and sealed for gamma spectrometry measurements. Fig. 2 shows an example of gamma spectrum to determine beta dose rates. To measure gamma dose rates, Al<sub>2</sub>O<sub>3</sub>:C dosimeters were inserted on May 6, 2015, retrieved on July 5, 2016, and subsequently measured at the IRAMAT-CRP2A (Bordeaux; Richter *et al.*, 2010).



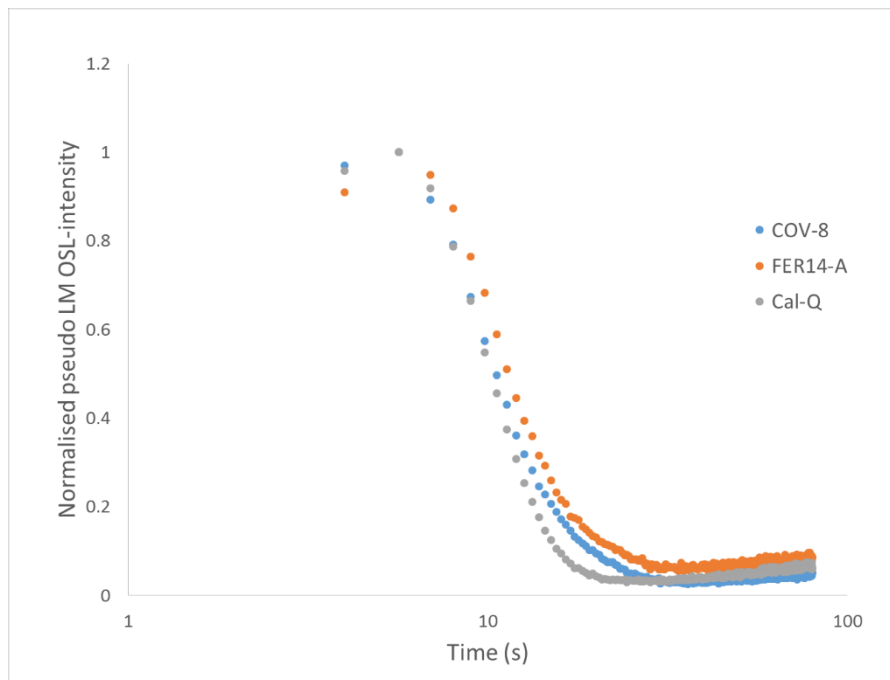
**Figure 2.** Example of gamma Spectrum measured with a High Purity germanium (HPGe) detector at IRAMAT-CRP2A.

## 2. Luminescence measurements

### Multi-grain OSL: performance tests

To determine the palaeodose of a sample, the SAR protocol (Murray and Wintle, 2000) is generally used. However, the performance of this protocol must be tested to check that the studied samples verify a number of necessary conditions to be dated. The first condition is

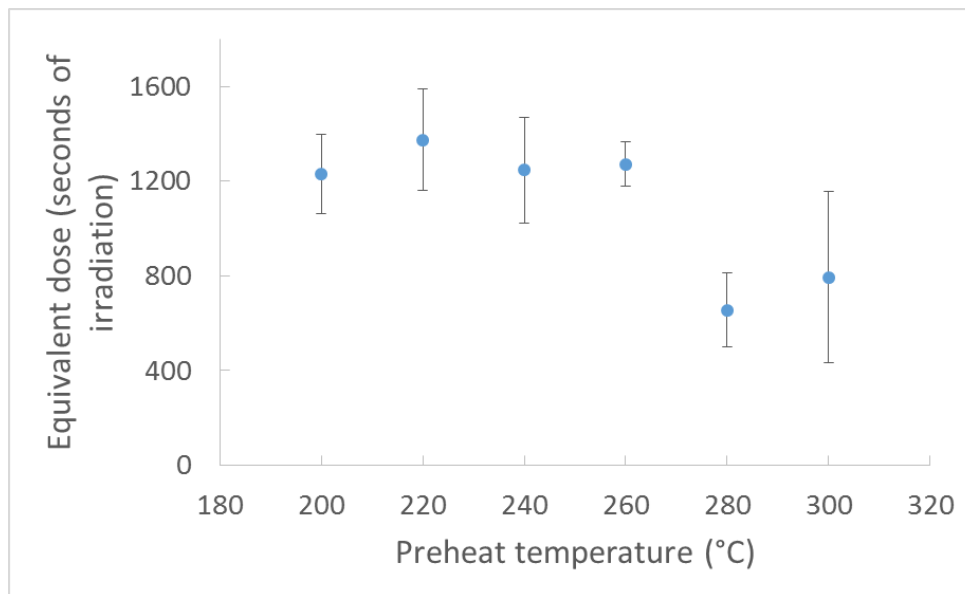
that their OSL signal must be dominated by the fast component. Fig. 3 shows a ‘pseudo LM-OSL’ curve (Bos and Wallinga, 2012), on which the data from sample COV-8 are compared with two reference samples: calibration quartz (Hansen *et al.*, 2015) and a sample from the La Ferrassie rockshelter (Dordogne, France; Guérin *et al.*, 2015a).



**Figure 3.** Pseudo LM-OSL curves showing that the OSL signal from sample COV-8 is dominated by the fast component, like calibration quartz.

It appears that sample COV-8 displays a peaked curve similar to the two reference samples and, as such, is suitable for dating with OSL.

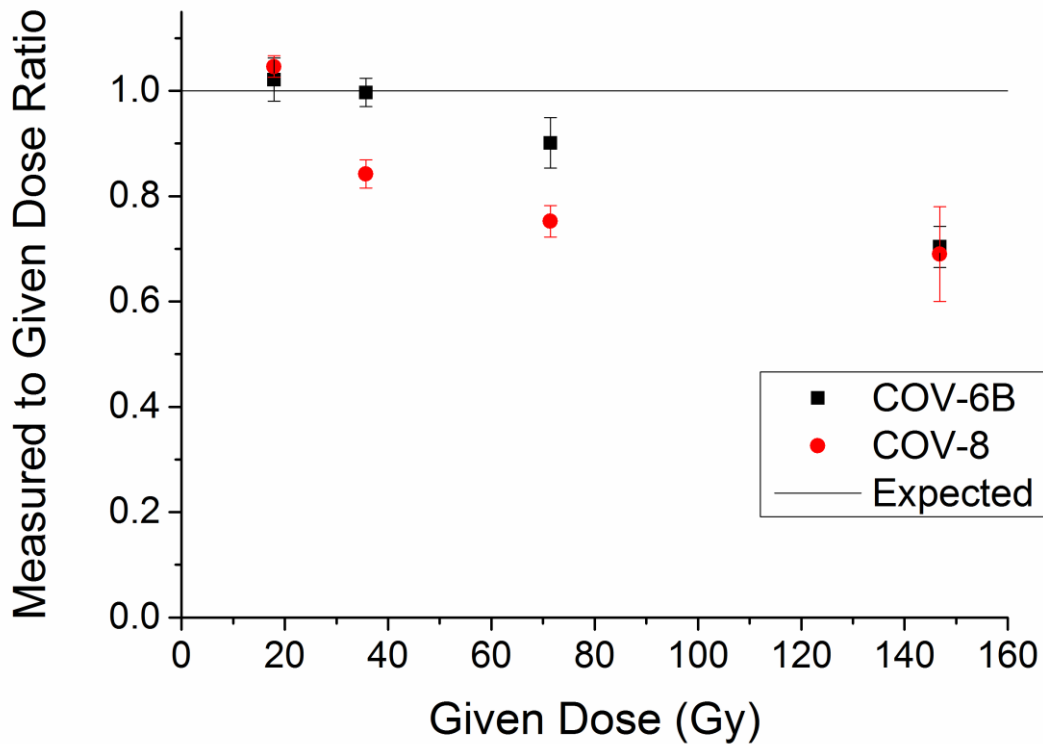
The next test that we conducted was a preheat plateau test aimed at studying the dependency of the measured equivalent dose (used as a proxy for the palaeodose) as a function of temperature (Fig. 4). Below 260 °C the curve is flat, so any temperature in the range 200-260°C will give identical results, which shows (i) that the SAR protocol is robust and (ii) the sample is well-behaved (there is a ‘plateau’).



**Figure 4.** Results of a preheat plateau experiment on multi-grain aliquots (each point corresponds to the average of 5 aliquots).

However, the dispersion in the results (as shown by the standard errors on the mean in Fig. 4) is important ; in addition, a number of aliquots (13%) were found to be in saturation.

This led us to conduct a series of dose recovery experiments, which consist of first removing the OSL signal by optical stimulation, then delivering the sample a know dose and finally measuring it using the SAR protocol. Fig. 5 shows the measured to given ratio, for sample COV-8, for a series of increasing doses. The test is satisfactory if the ratio is equal to one, within uncertainties (or at least does not deviate from unity by more than ~10%).



**Figure 5.** Results of multi-grain OSL dose recovery tests as a function of dose. The measured dose systematically underestimates the given dose as dose is increased.

Fig. 5 clearly shows that saturation of the OSL signal is of significant concern for the Covalejos samples. To put it simply, it means that in the multi-grain aliquots, a significant fraction of the grains are in saturation for doses of several tens of Gy. To try and overcome this, we decided to conduct the same dose recovery for the highest dose, but in single grain mode (Duller *et al.*, 1999).



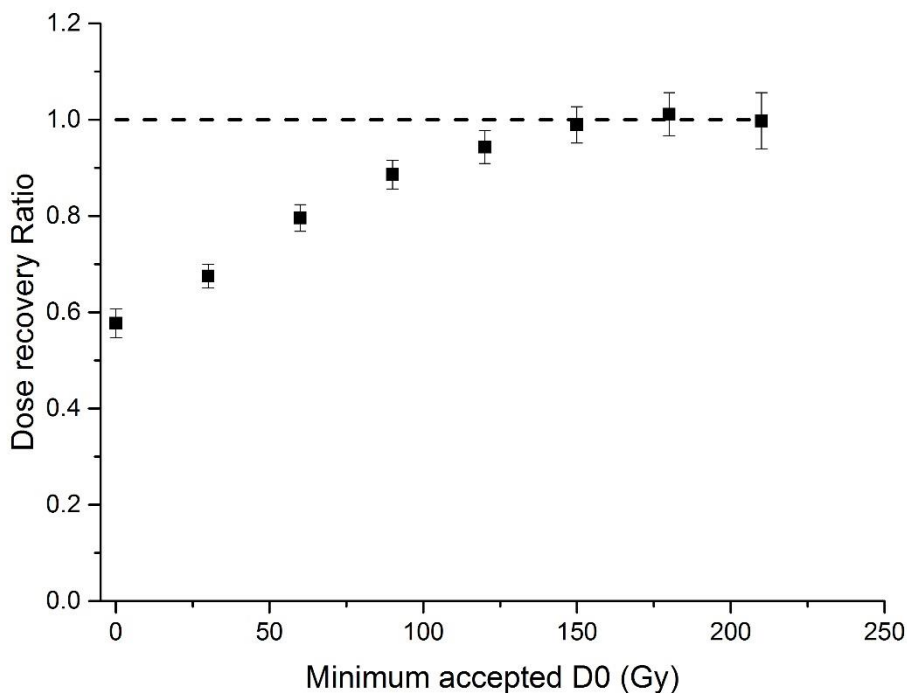
**Photo: G. Guerin retrieving the dosimeters.**



**Photo: Final aspect of Covalejos' profiles**

### Single grain luminescence tests.

Fig. 6 shows the results of a single grain OSL dose recovery test, for a given dose of 166 Gy given to sample COV-6B. The  $D_0$  parameter mentioned in the x-axis title corresponds to the curvature parameter of the dose response curves (see Singh et al., 2017; Guérin et al., 2015a): the higher this parameter, the larger the dynamic range in dose for a given grain. As can be seen, removal of early saturating grains (*i.e.* grains with low  $D_0$  values) gives satisfying results and a plateau is reached for  $D_0$  values greater than 150 Gy, which is perfectly consistent with the results of Thomsen *et al.* (2016) who advocated this analysis technique. As a result, all samples were measured in single grains.



**Figure 6.** Results of a single grain, high dose (166 Gy) dose recovery test. Unlike with multi-grain aliquots, adequate selection of the grains at the single grain scale allows recovering a large given dose.

### Summary and preliminary ages

The tests that we conducted on samples from Covalejos revealed that the extracted quartz presents adequate characteristics for dating with OSL: the signal is dominated by the fast component and the SAR protocol is applicable, yielding results that are independent of preheat treatment. Furthermore, low doses can be measured accurately; however, as the dose to recover is increased to levels corresponding to the palaeodoses of the samples, multi-grain aliquots are significantly affected by early saturation, thus leading to underestimates in equivalent dose measurements. To overcome this problem, Thomsen *et al.* (2016) recently proposed to select, at the single grain level, only the grains showing an important dynamic range in their dose response curve. The adequacy of this approach was validated for samples

from Covalejos (Fig. 6); as a result, we defined an appropriate protocol and well-suited analytical treatment for the dating of the entire sequence of Covalejos. 2000 grains were measured for each sample, and a first set of preliminary ages may be proposed.

Statistical analysis has quite significantly evolved over the past few years; a complete study should compare the ages calculated with the commonly employed Central Age Model (Galbraith *et al.*, 1999), the more accurate Average Dose Model (Guérin *et al.*, 2017) – both of which are well-suited for well-bleached samples – the Minimum Age Model (Galbraith *et al.*, 1999) and the Finite Mixture model (Roberts *et al.*, 2000) for poorly-bleached and mixed samples, respectively.

However, a suite of Bayesian models was developed recently (Combès *et al.*, 2015; Guérin *et al.*, 2015b; Combès and Philippe, 2017; Philippe *et al.*, 2019) for the analysis of OSL data. The corresponding software, called BayLum (Christophe *et al.*, 2018) allows calculating ages using stratigraphic constraints, modelling systematic uncertainties and including independent ages (typically radiocarbon ages) that do not suffer from the luminescence measurement uncertainties. Unfortunately, such detailed analyses require the users to critically examines all independent ages with close scrutiny before applying chronological models; this modelling will be conducted in future work. As a result, below sets of obtained ages were obtained as follows: BayLum was ran (i) on all grains for which the  $D_0$  parameter is greater than 90 Gy (this choice remaining arbitrary at this stage); (ii) assuming dose response curves passing through the origin; and (iii) assuming a Gaussian distribution of equivalent doses around the central dose (see Heydari and Guérin, 2018, for the justification of this choice). All samples were considered independent from each other, *i.e.* the effect of systematic errors is not taken into account – which corresponds to classical OSL age calculation – and no stratigraphic constraints were used for age calculation. In other words, the set of ages presented in Table 1 must be viewed as only preliminary.

Sample	Bayes estimate	68% C.I. (ka)		95% C.I. (ka)	
		lower boundary	upper boundary	lower boundary	upper boundary
COV 1	31.1	29.4	32.5	28.2	33.9
COV 2	23.2	21.9	24.4	21.0	25.8
COV 3	42.2	39.4	44.6	37.1	47.8
COV 4	35.7	33.3	37.5	31.8	39.6
COV 5	43.8	41.2	46.2	38.7	48.7
COV 6B	49.2	46.5	51.4	44.8	54.3
COV 7	52.5	48.9	55.1	46.6	59.5
COV 8	49.0	45.4	53.2	42.0	56.7
COV 9	64.1	59.7	67.8	55.9	72.5
COV11	93.0	83.5	99.7	76.7	110.1
COV 15	84.3	79.0	88.3	74.6	93.7

**Table 1. Preliminary OSL ages (in ka). The sample number corresponds to the layer number. ‘C.I.’ denotes the credibility intervals; the Bayes estimates correspond to the most likely ages.**

## **Concluding remarks**

These preliminary ages show relatively good consistency, *i.e.* the ages generally increase with depth. However, sample COV 2 is in stratigraphic inversion with sample COV 1; given the available independent ages, COV 2 likely underestimates the true age of Layer 2. Similarly, it appears that samples COV 3 and 4 are also in stratigraphic inversion, but in the present state of our knowledge it is difficult to explain these apparently inconsistent results. One observation that could explain these problems is the surprisingly large concentration values of uranium obtained for samples COV 2, 3 and 4 (greater than 20 ppm for the top part of the U chain for sample COV 3); in addition, these samples also show strong disequilibrium in the U-series. Additional measurements and/or analyses will be required for a better understanding of these surprising values, and for the luminescence-based chronology of Covalejos as a whole.

## **Bibliography**

- Aitken, M. J., 1985. Thermoluminescence dating. Academic Press, London, 359 p.
- Aitken M.J., 1998. An introduction to optical dating. Oxford University press, Oxford, 267 p.
- Bos, A. J., & Wallinga, J. (2012). How to visualize quartz OSL signal components. Radiation Measurements, 47(9), 752-758.

- Christophe, C., Philippe, A., Kreutzer, S., Guérin, G., 2018: 'BayLum': Chronological Bayesian Models Integrating Optically Stimulated Luminescence and Radiocarbon Age Dating. R package, version 0.1.3. <https://CRAN.R-project.org/package=BayLum>
- Combès, B., & Philippe, A. (2017). Bayesian analysis of individual and systematic multiplicative errors for estimating ages with stratigraphic constraints in optically stimulated luminescence dating. *Quaternary Geochronology*, 39, 24-34.
- Combès, B., Lanos, P., Philippe, A., Mercier, N., Tribolo, C., Guérin, G., Guibert, P., Lahaye, C., 2015. A Bayesian central equivalent dose model for optically stimulated luminescence dating. *Quaternary Geochronology*, 28, 62-70.
- Duller, G.A.T., Bøtter-Jensen, L., Murray, A.S., Truscott, A.J., 1999. Single grain laser luminescence (SGLL) measurements using a novel automated reader. *Nuclear Instruments and Methods B* 155, 506–514.
- 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, 339–364.
- Guérin, G., Frouin, M., Talamo, S., Aldeias, V., Bruxelles, L., Chiotti, L., Dibble, H. L., Goldberg, P., Hublin, J.-J., Jain, M., Lahaye, C., Madelaine, S., Maureille, B., McPherron, S. P., Mercier, N., Murray, A. S., Sandgathe, D., Steele, T. E., Thomsen, K. J., Turq, A., 2015a. A Multi-method Luminescence Dating of the Palaeolithic Sequence of La Ferrassie Based on New Excavations Adjacent to the La Ferrassie 1 and 2 Skeletons, *Journal of Archaeological Science* 58, 147-166.
- Guérin, G., Combès, B., Lahaye, C., Thomsen, K. J., Tribolo, C., Urbanova, P., Guibert, P., Mercier, N., Valladas, H., 2015b. Testing the accuracy of a single grain OSL Bayesian central dose model with known-age samples. *Radiation Measurements* 81, 62-70.
- Guérin, G., Christophe, C., Philippe, A., Murray, A.S., Thomsen, K.J., Tribolo, C., Urbanova, P., Jain, M., Guibert, P., Mercier, N., Kreutzer, S., Lahaye, C., 2017. Absorbed dose, equivalent dose, measured dose rates, and implications for OSL age estimates: Introducing the Average Dose Model. *Quaternary Geochronology* 41, 163-173.
- Hansen, V., Murray, A.S., Buylaert, J.-P., Yeo, E.-Y., Thomsen, K.J., 2015. A new irradiated quartz for beta source calibration. *Radiation Measurements* 81, 123-127.
- Heydari, M., Guérin, G., 2018. OSL signal saturation and dose rate variability: investigating the behaviour of different statistical models. *Radiation Measurements* 120, 96-103.
- Murray, A. S., Wintle, A. G., 2000. Luminescence dating of quartz using an improved single-aliquot regenerative-dose protocol. *Radiation Measurements* 32, 57-73.
- Philippe, A., Guérin, G., Kreutzer, S., 2019 "BayLum" an R package for Bayesian Analysis of OSL Ages & Chronological Modelling. *Quaternary Geochronology* 49, 16-24.
- Richter, D., Dombrowski, H., Neumaier, S., Guibert, P., Zink, A., 2010. Environmental gamma dosimetry for in-situ sediment measurements by OSL of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:C. *Radiation Protection*

Dosimetry 141, 27-35.

Roberts, R. G., Galbraith, R. F., Yoshida, H., Laslett, G. M., & Olley, J. M. (2000). Distinguishing dose populations in sediment mixtures: a test of single-grain optical dating procedures using mixtures of laboratory-dosed quartz. *Radiation Measurements*, 32(5-6), 459-465.

Singh, A., Thomsen, K.J., Sinha, R., Buylaert, J.-P., Carter, A., Mark, D.F., Mason, P.J., Densmore, A.L., Murray, A.S., Jain, M., Paul, D., Gupta, S., 2017. Counter-intuitive influence of Himalayan river morphodynamics on Indus Civilisation urban settlements. *Nature Communications* 8, 1671. doi:10.1038/s41467-017-01643-9.

Thomsen, K.J., Murray, A.S., Buylaert, J.-P., Jain, M., Helt-Hansen, J., Aubry, T., 2016. Testing single-grain quartz OSL methods using known age samples from the Bordes-Fitte rockshelter (Roches d'Abilly site, Central France). *Quaternary Geochronology* 31, 77-96.

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