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Supplemental Materials to "Timing of the last sequence boundary in a fluvial setting near the highstand shoreline – Insights from optical dating", by T.E. Törnqvist, J. Wallinga, and F.S. Busschers

QUARTZ OPTICAL AGES

SAMPLE COLLECTION AND PREPARATION

Drilling was performed with a mechanized bailer drilling unit (Oele et al., 1983) of the Netherlands Institute of Applied Geoscience TNO, yielding undisturbed cores with 10 cm diameter. The cores were opened in subdued red light, after which samples for optical dating were taken. All samples were water washed and treated with 10% HCl and 30% H_2O_2 to remove carbonates and organic matter. After drying, the samples were sieved and subsequently density separated using an aqueous solution of sodium polytungstate to extract the potassium-rich feldspar fraction (<2.58 g cm^{-3}). The denser fraction was treated with concentrated (40%) hydrofluoric acid for 40 minutes to obtain clean quartz samples and to etch away the outer 10 μm of the quartz grains.

EQUIVALENT-DOSE DETERMINATION

Measurements were made with an automated Risø TL/OSL reader, using an internal $^{90}Sr/^{90}Y$ beta-source (Bøtter-Jensen et al., 2000). The quartz grains were mounted on stainless-steel discs using silicone spray. For the Leidschendam samples the entire disc was covered with grains, whereas for the Delft and Wassenaar samples only the center of the disc (3 mm diameter) was covered, corresponding to 14 mg (~1400 grains) and 3 mg (~300 grains) of sample material per disc, respectively.

Blue light emitting diodes (LEDs) were used for stimulation and the resulting luminescence signal was detected through 9 mm of Schott U-340 filters (detection window 250-390 nm). The single-aliquot regenerative-dose (SAR) procedure (Murray and Wintle, 2000) was used for estimation of the equivalent dose. Parameters used in the SAR procedure are shown in Table 1. To check whether significant sensitivity changes took place during the first preheating, a dose-recovery test (Wallinga et al., 2000, 2001) was carried out. During this test, the samples were bleached for 20 seconds at room temperature with blue LEDs and subsequently given a laboratory dose in the same range as the natural dose. The resulting test-dose corrected OSL signal was then compared to that obtained in two subsequent SAR cycles using the same dose. For all samples the laboratory dose was retrieved correctly (ratio of given dose to obtained dose was equal or close to unity). We checked whether feldspar grains were present in our samples by measuring the response to infrared (IR) stimulation; no significant feldspar contamination was detected.

A range of preheat temperatures (between 120ºC and 280ºC for 10 s) was used for the Delft and Wassenaar samples. The test dose was heated to a relatively low temperature (120ºC) prior to measurement to enable the use of low preheat temperatures for the natural and regeneration doses while still applying a more stringent preheat to the

regeneration dose than to the test dose (following Murray and Wintle, 2000). For the majority of samples there was no dependency of the equivalent dose on the preheat temperature used for the preheat temperature range from 160ºC to 280ºC. Results obtained with a preheat of 120ºC were scattered and therefore discarded. The preheat range used for calculating the equivalent dose of samples from the Delft and Wassenaar cores is indicated in Table 2. Dependence of equivalent dose on preheat temperature was also investigated for the Leidschendam samples. No dependence was found for the 180ºC–280ºC, 10 s preheat range (Wallinga et al., 2001); we chose to routinely use a 10 s preheat at 260ºC for the Leidschendam samples.

DOSE-RATE ESTIMATION

The natural dose rate was estimated in the laboratory using high-resolution gamma spectrometry (Murray et al., 1987) on bulk samples that were taken from around the sample used for equivalent-dose determination. All our samples have been saturated with water throughout their lifetimes, which diminishes the dose rate (Aitken, 1985).

RESULTS AND DISCUSSION

The quartz optical dating results are presented in Table 2. The calculated optical ages are reported with 95% (2σ) confidence intervals, which include systematic and random errors in equivalent dose and dose-rate estimations. Although most optical ages are in stratigraphic order and in agreement with the stratigraphic interpretation, there are some reversals within the Leidschendam and the Wassenaar cores at what we interpreted as the OIS 5 to OIS 4 interval. We discuss these inconsistencies here.

Based on compelling stratigraphic evidence (notably biostratigraphic and paleoecologic data; discussed at length by Törnqvist et al., 2000), we conclude that sample Leidschendam VI must be of OIS 5 age. The optical age of this sample is thus most likely underestimated by some 20 k.y. (30%). There are two possible explanations for this, namely (1) underestimation of the equivalent dose, or (2) overestimation of the dose rate. We are inclined to believe that the age underestimation most likely arises from the dose-rate determination. This is primarily based on the observation that similar trends as for quartz OSL were found in IR-OSL equivalent-dose determinations (and resulting ages) on feldspar samples from the Leidschendam core (Wallinga et al., 2001). As equivalent dose determination of both minerals is independent, the most likely source of error in both quartz and feldspar optical ages is the external dose rate which is similar for both. If the age underestimation is indeed caused by an overestimation of the dose rate, this must imply that the radioactivity of material at the sample depth at present is higher than that experienced by the sample during its geologic past. This could be caused by recent precipitation of radionuclides, for instance during draining of the core tubes. Another possibility is that the radionuclide concentration in mud drapes in the Leidschendam core is much higher than that in adjacent sandy layers. Oversampling of these mud drapes for dose-rate estimation may have resulted in an overestimation of the dose rate.

For the Wassenaar core there is no unequivocal stratigraphic evidence of an OIS 5 age for any of the samples. Hence, it is not clear whether the age reversal is a consequence of age overestimation (for samples Wassenaar IV and V) or age

underestimation (for sample Wassenaar VI). We investigated whether the age of samples Wassenaar IV and V could be overestimated due to incomplete resetting of the OSL signal prior to deposition and burial. No clear indications for poor bleaching were found in the dose distribution obtained from 20 small aliquots (~100 grains) of each sample. Moreover, offsets in age of the order of 20 k.y. (needed to explain the age reversal) are very unlikely in view of optical dating results on young fluvial deposits reported in the literature (reviewed by Wallinga, 2002). Therefore, we deduce that the optical age obtained on sample Wassenaar VI underestimates the true age of this sample, likely for the same (unidentified) reasons as for sample Leidschendam VI at the same stratigraphic level.

Despite these problems, comparison of the chronological data as a whole with independent stratigraphic evidence lends support to our interpretation of optical ages in terms of oxygen isotope stages. Specifically, the lower, essentially non-fossiliferous, coarse-grained unit that is sedimentologically distinct from overlying facies has been widely interpreted as a fluvial deposit from the penultimate glacial (OIS 6), related to a sudden shift of the Rhine-Meuse system into our study area due to the advance of the Fennoscandian ice sheet to a position immediately to the north (e.g., Zagwijn, 1974). This is consistent with optical ages in each of the dated cores, indicating the overall robustness of our chronology for the past 150-200 k.y.

REFERENCES CITED

Aitken, M.J., 1985, Thermoluminescence dating: London, Acadamic Press, 359 p.

Bøtter-Jensen, L., Bulur, E., Duller, G.A.T., and Murray, A.S., 2000, Advances in luminescence instrument systems: Radiation Measurements, v. 32, p. 57-73.

Mejdahl, V., 1979, Thermoluminescence dating: beta dose attenuation in quartz grains: Archaeometry, v. 21, p. 61-72.

Murray, A.S., and Olley, J.M, 2002. Precision and accuracy in the optically stimulated luminescence dating of sedimentary quartz: a status review: Geochronometria, v. 21, p. 1-16.

Murray, A.S., and Wintle, A.G., 2000, Luminescence dating of quartz using an improved single-aliquot regenerative-dose protocol: Radiation Measurements, v. 32, p. 57-73.

Murray, A.S., Marten, R., Johnston, A., and Martin, P., 1987, Analysis for naturally occurring radionuclides at environmental concentrations by gamma spectrometry: Journal of Radioanalytical and Nuclear Chemistry, v. 115, p. 263-288.

Oele, E., Apon, W., Fischer, M.M., Hoogendoorn, R., Mesdag, C.S., De Mulder, E.F.J., Overzee, B., Sesören, A., and Westerhoff, W.E., 1983, Surveying The Netherlands: sampling techniques, maps and their applications, *in* Van den Berg, M.W., and Felix, R., eds., Special issue in the honour of J.D. de Jong: Geologie en Mijnbouw, v. 62, p. 355-372.

Olley, J.M., Murray, A.S., and Roberts, R.G. 1996, The effects of disequilibria in the uranium and thorium decay chains on burial dose rates in fluvial sediments: Quaternary Science Reviews, v. 15, p. 751-760.

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 v. 23, p. 497-500.

Törnqvist, T.E., Wallinga, J., Murray, A.S., De Wolf, H., Cleveringa, P., and De Gans, W., 2000, Response of the Rhine-Meuse system (west-central Netherlands) to the last Quaternary glacio-eustatic cycles: a first assessment: Global and Planetary Change, v. 27, p. 89-111.

Wallinga, J., 2002, Optically stimulated luminescence dating of fluvial deposits: a review: Boreas, v. 31, in press.

Wallinga, J., Murray, A.S., and Duller, G.A.T., 2000, Underestimation of equivalent dose in single-aliquot optical dating of feldspars caused by preheating: Radiation Measurements, v. 32, p. 691-695.

Wallinga, J., Murray, A.S., Duller, G.A.T., and Törnqvist, T.E., 2001, Testing optically stimulated luminescence dating of sand-sized quartz and feldspar from fluvial deposits: Earth and Planetary Science Letters, v. 193, p. 617-630.

Weerts, H.J.T., 1996, Complex confining layers. Architecture and hydraulic properties of Holocene and Late Weichselian deposits in the fluvial Rhine-Meuse delta, The Netherlands: Nederlandse Geografische Studies, v. 213, p. 1-189.

Zagwijn, W.H., 1974, The palaeogeographic evolution of The Netherlands during the Quaternary: Geologie en Mijnbouw, v. 53, p. 369-385.

Zimmerman, D.W., 1971, Thermoluminescent dating using fine grains from pottery: Archaeometry, v. 13, p. 29-52.

TABLE 1. SAR PARAMETERS

Step	Leidschendam samples	Delft and Wassenaar samples	Observed[c]
1	Give dose[a], D_i	Give dose[a], D_i	-
2	Preheat, 10 s @ 260ºC	Preheat, 10 s @ 120–280ºC[b]	-
3	Stimulate with blue LEDs, 40 s @ 125ºC	Stimulate with blue LEDs, 20 s @ 110ºC	L_i
4	Give test dose, D_t	Give test dose, D_t	-
5	Heat to 160ºC	Heat to 120ºC	-
6	Stimulate with blue LEDs, 40 s @ 125ºC	Stimulate with blue LEDs, 20 s @ 110ºC	T_i
7	Repeat step 1 to 6 for a range of D_i	Repeat step 1 to 6 for a range of D_i	-

(a) For the natural sample no dose is administered.

(b) Preheat temperatures of 120, 160, 200, 240 and 280ºC were used, with 3 aliquots measured for each temperature.

(c) The observed L_i (OSL signal resulting from natural or regenerative dose) and T_i (OSL signal resulting from the test dose) are derived from the initial OSL signal (Leidschendam: 0.16 s, Delft and Wassenaar: 0.08 s) minus a background estimated from the last part of the stimulation curve (Leidschendam: 4 s, Delft and Wassenaar: 2 s). For T_i the background from the previous signal was used, as suggested by Murray and Wintle (2000).

TABLE 2. QUARTZ OPTICAL DATING RESULTS

Sample	Depth (m –OD)	Grain size (μm)	Radionuclide concentration[a] (Bq kg^{-1}) ^{238}U	^{226}Ra	^{232}Th	^{40}K	Dose rate[a,b] (Gy k.y.$^{-1}$)	Equivalent dose[c] (Gy)	10 s preheat[d] (ºC)	Optical age[e] (ka)
Delft I	17.29	90-180	33 ± 5	35.8 ± 0.5	39.1 ± 0.5	483 ± 10	2.19 ± 0.07	24.6 ± 1.0	160-280	11.2 ± 1.2
Delft II	18.29	180-212	13 ± 2	8.8 ± 0.2	9.1 ± 0.2	316 ± 5	1.05 ± 0.03	15.5 ± 0.9	160-280	14.8 ± 1.8
Delft III	22.04	212-250	8 ± 2	8.8 ± 0.2	10.1 ± 0.2	318 ± 6	1.17 ± 0.03	22 ± 2	160-240	18.5 ± 2.8
Delft IV	25.09	212-250	11 ± 4	9.1 ± 0.3	9.9 ± 0.3	357 ± 7	1.12 ± 0.03	25 ± 2	160-280	22 ± 4
Delft V	26.09	212-250	9 ± 4	6.9 ± 0.3	7.7 ± 0.2	212 ± 5	0.74 ± 0.02	43 ± 3	160-280	59 ± 8
Delft VI	27.29	212-250	5 ± 3	5.8 ± 0.2	6.3 ± 0.2	177 ± 5	0.62 ± 0.02	41 ± 3	160-280	66 ± 12
Delft VII	30.29	250-300	9 ± 2	5.6 ± 0.2	6.6 ± 0.2	212 ± 4	0.69 ± 0.02	117 ± 9	160-280	169 ± 28
Delft VIII	31.29	212-250	14 ± 4	7.5 ± 0.3	8.3 ± 0.2	249 ± 6	0.84 ± 0.03	152 ± 29	160-280	183 ± 70
Leidschendam I	19.12	180-212	10 ± 3	9.5 ± 0.5	9.6 ± 0.4	297 ± 13	1.11 ± 0.06	54 ± 3	260	48 ± 8
Leidschendam II	21.17	180-212	6 ± 3	9.5 ± 0.3	10.8 ± 0.3	249 ± 7	0.99 ± 0.05	54 ± 5	260	55 ± 12
Leidschendam III	23.62	180-212	6 ± 2	9.5 ± 0.4	7.5 ± 0.3	200 ± 10	0.78 ± 0.05	64 ± 6	260	82 ± 18
Leidschendam IV	25.52	180-212	12 ± 3	12.8 ± 0.3	14.1 ± 0.3	341 ± 7	1.29 ± 0.06	92 ± 7	260	71 ± 12
Leidschendam V	26.52	180-212	6 ± 3	6.9 ± 0.5	8.2 ± 0.4	253 ± 13	0.92 ± 0.05	56 ± 3	260	61 ± 10
Leidschendam VI	29.22	180-212	8 ± 3	9.8 ± 0.2	10.7 ± 0.2	314 ± 7	1.13 ± 0.05	66 ± 3	260	58 ± 8
Leidschendam VII	30.12	180-250	12 ± 3	6.8 ± 0.3	6.7 ± 0.2	237 ± 6	0.86 ± 0.04	104 ± 6	260	120 ± 18
Leidschendam VIII	31.02	180-250	10 ± 2	6.5 ± 0.4	8.2 ± 0.4	201 ± 10	0.79 ± 0.05	124 ± 7	260	158 ± 26
Leidschendam IX	32.57	180-212	11 ± 2	5.5 ± 0.3	7.4 ± 0.2	190 ± 7	0.74 ± 0.04	107 ± 10	260	145 ± 32
Leidschendam X	35.77	180-212	7 ± 3	6.9 ± 0.3	8.2 ± 0.2	240 ± 6	0.87 ± 0.04	156 ± 23	260	180 ± 56
Wassenaar I	15.45	180-212	11 ± 4	7.3 ± 0.3	8.3 ± 0.3	329 ± 7	1.05 ± 0.03	7.4 ± 0.4	160-280	7.1 ± 0.8
Wassenaar II	18.50	180-212	9 ± 4	9.8 ± 0.3	12.5 ± 0.3	257 ± 6	1.04 ± 0.03	35 ± 2	160-280	34 ± 4
Wassenaar III	21.00	180-212	13 ± 4	11.1 ± 0.3	11.5 ± 0.3	323 ± 8	1.10 ± 0.03	41 ± 4	160-280	37 ± 8
Wassenaar IV	23.70	250-300	6 ± 3	5.1 ± 0.2	5.4 ± 0.2	148 ± 4	0.53 ± 0.02	40 ± 3	160-280	76 ± 12
Wassenaar V	25.65	212-250	5 ± 3	5.0 ± 0.2	5.9 ± 0.2	180 ± 5	0.61 ± 0.02	46 ± 2	160-280	76 ± 8
Wassenaar VI	26.80	180-212	11 ± 3	8.6 ± 0.2	9.7 ± 0.2	247 ± 5	0.87 ± 0.02	51 ± 4	160-280	59 ± 8
Wassenaar VII	30.90	180-212	13 ± 4	7.7 ± 0.3	8.9 ± 0.3	294 ± 7	0.95 ± 0.03	96 ± 9	160-240	102 ± 20
Wassenaar VIII	32.00	250-300	9 ± 3	5.9 ± 0.2	7.0 ± 0.2	176 ± 5	0.61 ± 0.02	75 ± 12	160-240	122 ± 40
Wassenaar IX	35.85	250-300	9 ± 4	5.1 ± 0.2	6.5 ± 0.2	184 ± 5	0.61 ± 0.02	141 ± 14	160-280	231 ± 50
Wassenaar X	38.00	212-250	13 ± 4	5.2 ± 0.2	6.6 ± 0.2	236 ± 6	0.74 ± 0.02	164 ± 14	160-280	220 ± 40

(a) Spectral data from high-resolution gamma spectrometry (Murray et al., 1987) converted to activity concentrations and infinite matrix dose rates using the conversion data given by Olley et al. (1996).

(b) The natural dose rate was calculated from the infinite matrix dose rate using attenuation factors given by Mejdahl (1979) and includes a contribution from cosmic rays (Prescott and Hutton, 1994). All dose rates calculated for a water content of 20 ± 2% (based on a porosity of 34 ± 3%; Weerts, 1996) using attenuation factors given by Zimmerman (1971).

(c) Mean equivalent dose obtained on 8 to 15 aliquots and the standard error of the mean.

(d) Range of preheat temperatures used for equivalent-dose determination. See main text for explanation.

(e) Uncertainties (in k.y.) are reported as 95% confidence intervals.