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OPTIMISATION OF PREPARATION AND MEASUREMENT PROTOCOLS FOR LUMINESCENCE DATING OF SMALL SAMPLES FROM A SUITE OF PORCELAINS AND FAIENCES

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ABSTRACT

Experiments designed to evaluate protocols for preparation and luminescence measurement of small samples (<100 mg) from high fired ceramics are described. These include: additive TL of untreated material; multiple stimulation (Predose TL, OSL, TL) of hydrofluoric washed fragments; Simplified Predose and SAR OSL of silicate powders from hydrochloric and fluorosilicic acid treatment.

The 110°C TL signal in the Simplified Predose technique minimised required sample size, but growth with cumulative predose was sub-linear. For exponential extrapolations 11/26 faience samples yielded results within 1σ of typological expectations, but substantial scatter was interpreted as relating to radiation quenching effects. Extrapolation errors were investigated by deactivating samples and regenerating their predose responses. Acid treatment of cores drilled from sherds enabled preparation of mineral and grain-size fractions while avoiding crushing effects, and damage to or contamination by the glaze and decoration.

Results of luminescence measurements indicate that future work should focus on the use of open detection filter combinations to increase signal levels, to enable quenching corrections in predose measurements and the use of high temperature TL signals.

KEYWORDS: TL, OSL, High fired ceramic, Core, Simplified predose, Additive-regenerative

INTRODUCTION

As part of a study into the production and importation of porcelain and faience in Portugal, luminescence dating is being used to test typology-based chronologies for ceramics from various archaeological sites in Lisbon.

Luminescence dating measurements are ideally conducted on specific mineral and grain-size fractions isolated from large samples (e.g. entire sherds ~20 g, Aitken, 1985). This allows the measurements to be tailored to a particular mineral's behaviour, and reduces uncertainty in estimates of dose rate to the fraction being measured. Conventional approaches to luminescence measurement of small samples from structurally weaker ceramic fabrics use powder obtained directly by drilling using a tungsten bit (e.g. Zink and Porto, 2005). Drilling or crushing of compact fabrics can remove signals and alter a sample's behaviour, so they are conventionally measured in slices cut from a core drilled through the sherd (e.g. Göksu et al., 1996). Both approaches produce a polymineral sample and hence variations in luminescence behaviour depending on sample composition. A grain-size fraction may be separated from the powder by Stokes settling, but results from slices represent the range of doses absorbed by all grain sizes in the ceramic's fabric.

The absorbed dose can be evaluated using a range of techniques. Thermoluminescence (TL) measurement using the Multiple Aliquot Additive Dose (MAAD) technique is relatively robust to a variety of behaviours and has therefore been widely applied for measurement of polymineral samples (Aitken, 1985). It requires at least 2 subsamples, but is ideally conducted on more to improve accuracy and precision. Optically Stimulated Luminescence measurement (OSL) using the Single Aliquot Regenerative (SAR) technique enables precise determination of the dose absorbed by a single subsample of quartz since it was last exposed to light or heating (Murray and Wintle, 2000). OSL signals from quartz are often higher than TL because they are measured at lower temperature and so avoid thermal quenching (Wintle, 1975). However, in thin or translucent ceramics sufficient light may enter the sherd to bleach OSL signals. Low temperature TL signals measured using the Predose technique (Bailiff, 1994) are highly sensitive to radiation, but are thermally unstable and so do not provide a direct register of absorbed dose. Instead, their sensitivity to radiation following thermal activation is compared for natural and laboratory doses. This is thought to be little affected by exposure to daylight.

The present study aimed to develop protocols for luminescence testing of small samples (<100 mg) from porcelains and faiences in a uniform manner. Specifically:

1. Extract core samples of ceramic fabric from already broken faces of sherds, to minimise damage to the sherds and contamination of the samples by the glazes.
2. Test the MAAD TL measurement procedure with crushed but otherwise unprepared material.
3. Prepare coarse ceramic fragments with acid etched surfaces to remove crushing effects, and test for available luminescence signals (TL, OSL, Predose TL).
4. Weaken cores in HCl prior to disaggregation to avoid crushing effects, then prepare quartz enriched grain-size separates for Predose TL and SAR OSL measurement.

METHODS

Cores were drilled from the broken faces of sherds (Figure 1) using hollow diamond tipped bits, 2-6 mm diameter, then split for luminescence, and geochemical and mineralogical analyses by INAA (Dias and Prudêncio, 2007) and XRD. For initial luminescence measurements, parts of some larger cores were coarsely crushed in a hydraulic press, disaggregated in an agate pestle and mortar, dispensed onto stainless steel cups and measured by dose-normalised MAAD TL (3 aliquots: N, N+1.7 Gy, N+3.3 Gy). Other crushed sub-samples were treated briefly in HCl and HF to remove carbonates and surfaces affected by crushing, and single aliquots measured using a combined initial test sequence (CIT) designed to indicate the signal levels and behaviour of Predose TL and regenerative TL and OSL (Table 1). Subsequent work focussed on the isolation of grains of

quartz. Cleaned cores were treated in 1M HCl for 3 days to weaken the ceramic by removing carbonates. Where necessary these were crushed and disaggregated. The >60 μm fraction was isolated by settling in acetone and treated in 25% fluorosilicic acid for 3 days to reduce aluminosilicate content. This quartz enriched material was measured using the Simplified Predose TL technique (Table 4) and SAR OSL where sufficient was obtained (Galli et al., 2006; Murray and Wintle, 2000).

Measurements were made using a Risø DA-15 TL-OSL reader with $^{90}Sr/^{90}Y$ β irradiator giving 0.081 Gys^{-1} to coarse grains on steel cups. BG25+HA30 detection filters (50% T_{max} 350-460 nm) were used for MAAD TL measurements; all others were made using 7.5 mm of Hoya U-340 (50% T_{max} 280-370 nm).

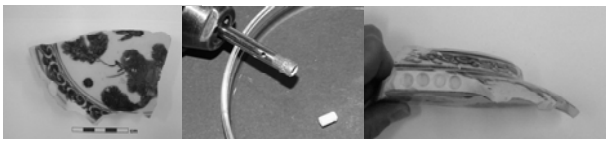

Figure 1. Drilling of core sample: d.= 3 mm, l.= 5 mm.

Table 1. CIT measurement sequence (see Figure 2 e-h).

Measurement Cycle:	Natural	Regen.1	Regen.2	Regen.3
Operation	Irradiation/Preheat/Measurement			
Dose (4.15 Gy)	-	1	2	3
TL (160 °C, 5 °C/s)	Preheat	S1	S2	Preheat
TL (260 °C, 5 °C/s)	LN	L1/S1	Preheat/S2	Preheat
OSL / IRSL	LN, OSL	L1, OSL	L2, IRSL	-
Dose (0.83 Gy)	D_TN	D_T1	-	-
TL (160 °C, 5 °C/s)	S0	Preheat	-	-
TL (260 °C, 5 °C/s)	TN/S0	T1	-	-
OSL	TN	T1	-	-
TL (500 °C, 5 °C/s)	LN(+D_TN)	L1(+D_T1)	L2	L3

RESULTS

Drilling cores from the broken edges of sherds using hollow diamond tipped drill bits avoided damage to the decoration and glaze of the diagnostic sherds sampled, and produced samples of 0.06 - 1.35 g. Porcelains were often very thin and produced the least material. XRD indicated that all samples were quartz-rich and contained carbonates in varying amounts. Gehlenite and Diopside in faiences indicated firing above ~900 °C, Mullite in porcelains indicated firing above 1050 °C.

Crushed but otherwise untreated samples produced optimal material yield, and MAAD TL measurements yielded usable natural signals (Figure 2) with maxima between 250 and 300 °C. However, no response to the normalisation dose was observed in this region, and no clear plateau in natural/additive dose response was observed. Absorbed dose estimates obtained for different temperature integrals were not in agreement, with or without normalisation.

Brief treatment of crushed samples in HF produced very high material losses. In the CIT measurements applied to this material, 210 °C TL and 300-400 °C TL signals exhibited very low sensitivity and highly variable absorbed dose estimates (Table 2). OSL yielded variable sensitivity and higher absorbed doses than the other measurements. The 110 °C TL signal exhibited the highest sensitivity and least variable estimates of absorbed dose, based on its increase in sensitivity with cumulative predose.

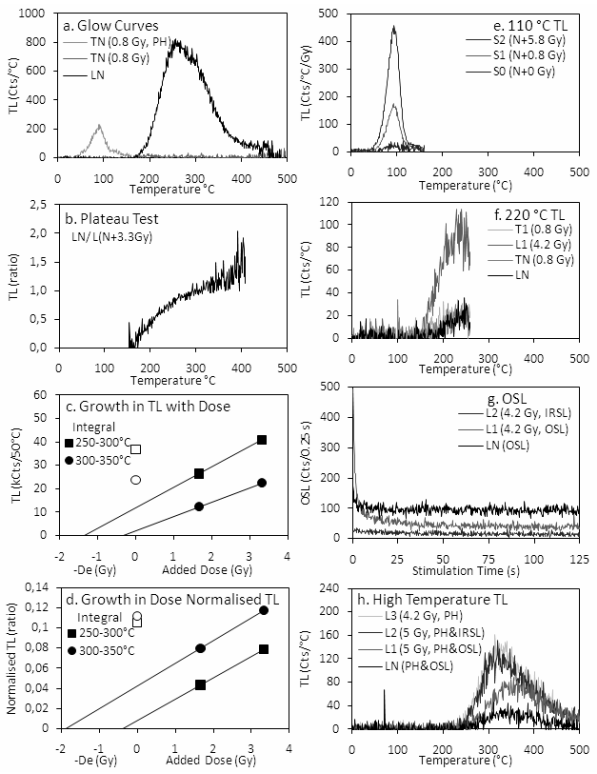

Figure 2. a-d: MAAD TL results for a crushed but untreated sample of faience. e-h: CIT results for a faience sample exhibiting all signals at usable levels.

Table 2. Results of the combined initial test (CIT)

Signal	110 °C TL	210 °C TL	OSL	TL
Integral	50-150 °C	160-260 °C	0-25 s	300-400 °C
Method	Predose	Regenerative		
	(2 point)	(test response corrected)		(post OSL)
N	15	15	21	21
Sensitivity (cts/Gy)				
Median	166	10	94	11
Mean	1272	168	2815	965
Equivalent Dose (Gy)				
Median	2.15	1.04	5.20	2.31
Mean	2.62	47.8	8.78	3.18
% s.d.	73	325	158	318

Prolonged treatment of whole cores in HCl weakened the ceramic fabric so that crushing produced powder rather than shards: many of the faiences were already reduced to powder. Fluorosilicic acid treatment increased the ratio of 110 °C TL to high temperature TL in both porcelains and faiences. It also increased the initial sensitisation in the Predose measurement sequence (S1/S0), but did not alter the saturation characteristics of the 110 °C signal. Porcelains yielded lower signals than faiences, but growth was initially more linear (Figure 3).

Dose rates of 2.5 to 3.7 $mGya^{-1}$ were estimated for >60 μm quartz grains from the faience samples, and 4.9 to 5.5 $mGya^{-1}$ for the porcelains. Maximum grain size was assumed to be 90 μm based on observed settling rates. Calculations were based on Aitken (1985) and references therein, taking account of grain size, sherd geometries and radionuclide concentrations (from INAA), and the average (±s.d.) of gamma dose rates for a selection of contrasting Portuguese soils and sediments.

Estimates for the date of manufacture of the sherds based on linear extrapolation from the initial simplified predose measurement cycles, ranged from 0 to 1700 AD with estimated uncertainties of on average 300 years (Figure 3; Table 3). Similar estimates based on extrapolation from double saturating exponential fits to all the measured data for each sample ranged from 1100 to 1960 AD, with average uncertainties of 200 years. Estimates based on SAR OSL for a limited number of samples ranged from 1600 to 2000 AD, with average uncertainties of 90 years. When compared to the dates based on typological interpretation, the linear predose estimates were on average older by 440±90 years (mean ± $sd.n^{-0.5}$), the exponential predose estimates were younger by 20±50 years, and the SAR OSL estimates were younger by 130±50 years.

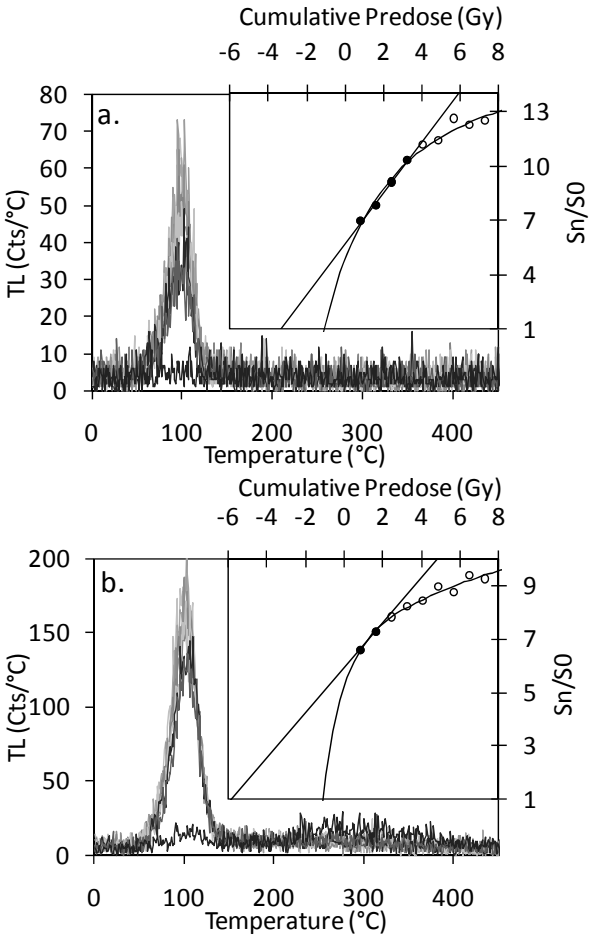

Figure 3. TL response of porcelain (a, ITN_LUM_549) and faience (b, ITN_LUM_550) to repeated 0.8 Gy β irradiations, following prolonged HCl and fluorosilicic acid treatment. Inset is the growth in "110 °C" TL response with cumulative predose, with un-weighted linear fits to initial data points (filled symbols), and un-weighted double saturating exponential fits to all the data (full growth curves in Figure 5). Propagated errors on individual values were 18%(a.) and 5%(b.); RMS residuals for the double exponential fits were <1%.

Table 3. Date estimates based on typological interpretation, and luminescence measurements of absorbed dose. F= faience, P = porcelain.

Sample (ITN_ LUM_)	F / P	Date Estimate (AD) Typological	Simplified Predose Linear	Predose Exponential	SAR OSL
506	F	1650 ± 50	1500 ±200	1780± 70	1700 ±100
508	F	1550 ± 50	1500 ±200	1900± 70	1700 ±100
509	F	1630 ± 15	1400 ±200	1770± 70	
510	F	1630 ± 15	1000 ±500	1800± 100	
511	F	1675 ± 25	1400 ±200	1700± 100	1800 ±100
512	F	1675 ± 25	1300 ±200	1700± 100	
513	F	1635 ± 15	1500 ±200	1780± 90	1780 ±90
514	F	1700 ± 100	1200 ±300	1710± 90	
515	F	1625 ± 25	1500 ±200	1700± 900	
516	F	1700 ± 20	300 ±600	1500± 200	1600 ±200
517	F	1700 ± 20	0 ±700	1300± 300	1700 ±100
519	F	1635 ± 15	1300 ±300	1800± 200	
521	F	1660 ± 50	1300 ±200	1600± 200	
522	F	1625 ± 25	1500 ±100	1700± 100	
524	F	1675 ± 25	1400 ±200	1600± 300	
527	F	1675 ± 75	1400 ±200	1960± 20	
528	P	1550 ± 25	1600 ±90	1910± 50	2000 ±4
530	F	1625 ± 25	1600 ±100	1920± 30	
531	F	1625 ± 25	1500 ±200	1300± 700	
532	P	1600 ± 100	1500 ±300	1800± 80	1860 ±40
535	F	1650 ± 50	1700 ±70	1710± 70	1720 ±70
537	P	1525 ± 25	1600 ±200	1790± 90	
538	F	1675 ± 25	700 ±400	1500± 200	
539	F	1725 ± 25	1400 ±200	1600± 200	
542	F	1635 ± 15	1200 ±200	1740± 80	
543	F	1725 ± 25	1200 ±300	1700± 100	
549	P	1500 ± 25	500 ±500	1930± 70	
550	F	1675 ± 25	300 ±800	1700± 100	
551	F	1675 ± 15	1600 ±10	1100± 300	
552	F	1725 ± 25	200 ±800	1200± 300	

DISCUSSION

The dominant grain-size fraction obtained following acid treatment was relatively large and hence convenient for the constraint of dose rate values, which could be improved by etching the grains in HF. However, high material losses in the initial experiment with HF indicate that the grains obtained following fluorosilicic treatment may still contain substantial phases with high susceptibility to HF attack, e.g. glassy quartz.

The 110°C TL response was identified as the signal most commonly available at usable levels in prepared material, but sensitivity was not high enough to use small test doses (e.g. Bailiff, 1994). U340 filters were used in the present study to detect the ~380 nm emission from quartz, but a more open combination could be used to detect additional signals (Adamiec, 2005).

The Simplified Predose technique of Galli et al. (2006) is a multiple activation predose procedure (Fleming, 1973, procedure 2), which treats the activation dose as a (large) test dose and thus eliminates the possibility of correction for radiation quenching. Uncorrected radiation quenching induces sub-linearity in growth in sensitivity with cumulative predose (Aitken and Murray (1976). Chen (1979) found that quenching does not affect absorbed predose determinations where growth is linear (e.g. Galli et al., 2006), but that for saturating growth (e.g. Figure 3) a correct result is only obtained when the laboratory dose increment equals the natural dose, even after correction for quenching: for natural doses greater than the laboratory dose increment the natural dose is underestimated, and vice versa.

In the present study, the dose increment chosen for simplified predose measurement was 0.8 Gy, which was similar to or slightly lower than the dose expected in the faience samples, but ~1/3 of that expected in the porcelains. The majority of linear extrapolations from the lowest dose points produced overestimates of dose and hence age (Table 3; Figure 4; Grün, 1996). High expected natural doses in porcelains were underestimated using exponential extrapolation: the results of linear extrapolation were better for 3 of the 4 samples. For expected natural doses similar to the dose increment, 11/26 of the exponential extrapolations were within 1σ of expected values, but the remainder were scattered to both higher and lower values (Figure 4).

Chen (1979) noted that the different growth curves obtained using quenching-corrected and -uncorrected data sometimes extrapolate to the same values. This would not be surprising if radiation quenching were proportional to sensitivity, i.e. that while the total number of holes increased following each irradiation-activation cycle, the ratio of those in luminescent:non-luminescent centres remained constant, along with the proportion of electrons trapped in the source trap during each irradiation.

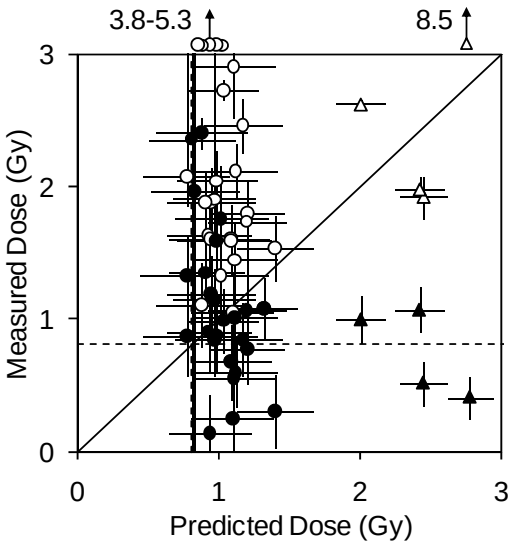

Figure 4. Measured doses vs. doses predicted from typological ages and dose rate estimates: circle = faience; triangle = porcelain; open = linear extrapolation; closed = double saturating exponential extrapolation. Dashed lines = laboratory dose increment.

The results of exponential extrapolation for the faiences in the present study indicate that these conditions may commonly be approximated, but that deviations from them might be responsible for the significant levels of observed scatter. However, this scatter could also relate simply to the sensitivity of the fits to the precise form of growth and/or scatter in the measurements.

With the aim of enabling the absorbed dose to be interpolated, the Simplified Predose measurement sequence was adjusted to include a 600°C/1hr anneal, followed by a repeat of the sequence to regenerate the sample's response (Table 4). All data were normalised to the initial sensitivity (SA0), and the regenerated data were transformed to the additive data by minimising the square of residuals in Sn/S0 for the overlapping range of doses. This was tested on one sample each of porcelain and faience.

Table 4. Simplified Predose Additive-Regenerative (SPAR) sequence (Simplified Predose = Steps 1-3).

Step	Operation	Details	Signal
1	Irradiation	0.8 Gy β	
2	TL Measurement	500 °C @ 10 °C/s	SA0
3	Repeat Steps 1 & 2	x 33	SAn {n = 1 - 33}
4	TL Measurement	500 °C @ 10 °C/s	Background
5	Anneal	600 °C/1 hr	
6	Repeat Steps 1-4		SRn {n = 1 - 33}

Annealing affected the samples differently, so two types of transformation were applied (Figure 5). In the porcelain sample the maximum sensitivity increased, but saturation rate with cumulative predose remained unchanged. In the faience, maximum sensitivity increased and was accompanied by a proportional reduction in saturation rate.

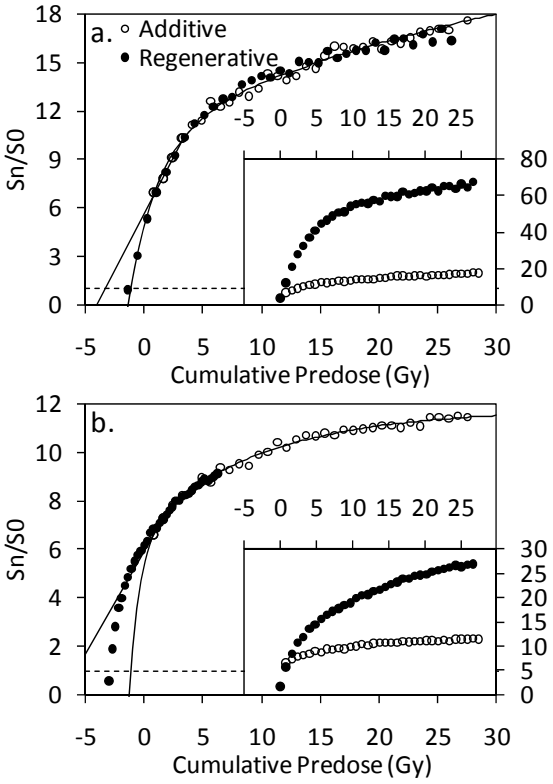

Figure 5. SPAR growth curves for samples of porcelain (a. ITN_LUM_549) and faience (b. ITN_LUM_550). Main plots show measured additive data with extrapolations (enlarged in Figure 3), and transformed regenerative data. Insets show as-measured values.

These changes in sensitivity to predose sensitisation of quartz from the porcelain and faience samples can be explained by considering small changes in the electronic environments of defects in the quartz with annealing. The change observed in the porcelain could result from an increase in the proportion of luminescent-type hole centres (Yang and McKeever, 1990) able to emit in the wavelengths measured, with the total number of centres available remaining the same. That observed in the faience could be explained if additional luminescent-type hole centres were brought into spatial association with the electron trap (Martini et al., 2009).

The changes do not appear to relate directly to the firing temperatures of the ceramics. For the porcelain sample the transformed regenerative data corroborated the exponential extrapolation from the additive data, which had underestimated the expected dose and age for the sample (Table 3). For the faience the transformed regenerative data lay in between the linear and exponential extrapolations from the additive data, whereas for this sample the exponential extrapolation had produced dose and age estimates in agreement with expectations.

These results indicate that even the moderate apparent success obtained using exponential extrapolations from simplified predose data, with a dose increment similar to the expected natural dose, may be subject to additional analytical uncertainties. Inclusion of correction for radiation quenching would not only address variations in the effects of irradiation and activation through a multiple activation sequence, but would also improve fitting and extrapolation by increasing the rate of growth in Sn/S0 with cumulative predose, and ultimately facilitate the use of simpler linear fits.

CONCLUSIONS

Prolonged HCl treatment of cores drilled from porcelains and faiences avoids (further) damage to and contamination by the glaze and decoration, reduces the potential for removal of natural signals or production of spurious signals by crushing or polishing, and enables the uniform preparation of similar mineral and grain-size fractions for luminescence measurement.

The sensitivity of the 110 °C TL signal, combined with Gy-level doses in the Simplified Predose technique, minimises the sample size required to obtain usable signal levels. Despite a moderate apparent success rate in predicting dates (expected on typological grounds) for samples of faience (11/26 within 1σ), the applicability of this technique is limited by its inability to correct for radiation quenching.

A uniform preparation protocol has been developed, but precise and accurate dating results have yet to be obtained for small samples from the present suite of porcelains and faiences. A priority for future investigation of quartz from these samples is therefore exploration of its luminescence behaviour using open filter combinations to obtain more signal per sample mass. This may enable the use of small test doses for quenching correction in multiple activation predose measurements, and the use of high temperature TL signals for MAAD absorbed dose determinations. Other important aspects are a wider evaluation of the thermal activation and deactivation characteristics of these samples, the effects of using different dose increments, and testing of the utility of regenerated predose growth curves for reducing extrapolation uncertainties.

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