Luminescence dating of archaeometallurgical slag: use of the SAR technique for determination of the burial dose

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Abstract

The potential of using luminescence techniques to date metallurgical slag of archaeological origin has been investigated. Slag is an important residue from the metal smelting process and there is no technique currently available to directly date it. An attempt has been made to apply an optically stimulated luminescence (OSL) single-aliquot technique using quartz extracted from the slag matrix. A single-aliquot regeneration technique was used and preliminary results are encouraging in spite of problems encountered in the determination of the equivalent dose ($D_e$) and apparent underestimation of the preliminary dates obtained. The results presented here were obtained from measurements on copper and iron slag from archaeological sites in Britain and Greece. © 2000 Elsevier Science Ltd. All rights reserved.

1. Metallurgical slag and luminescent mineral

There is currently no technique available to directly date slag, a metallurgical residue commonly found in archaeometallurgical sites. Associated material (such as furnaces) is not always present, while slag may accumulate on the site in quantities of up a several tons, sometimes in the form of slag heaps. Metallurgical slag makes up an important part in ancient metallurgy studies and a dating technique would constitute a valuable tool for research in that field.

Slag forms as a by-product of metal smelting, a process that allows the recovery of the metal from the ore by separating it from the gangue, i.e. the unwanted minerals. The resulting slag is essentially made up of potassium and aluminium silicates that constitute a "glassy" matrix, in which a number of mineral grains are embedded, including some potential luminescence emitters. Quartz may occur (Fig. 1) as sand was sometimes added as a flux during smelting. Any residual (geological) signal would be erased at the high temperatures (at least $1000^\circ$C for several hours) reached during smelting. Previous studies (Elitzsch et al., 1983) that looked at using thermoluminescence (TL) showed that, as in ceramic, radioactivity seems to be located within the matrix while the mineral inclusions are relatively radioactive-free. However, attempts at dating the slag using TL had limited success (Lorenz, 1988; Elitzsch et al., 1983).

Preliminary experiments using an imaging photon detector (IPD) in combination with a scanning electron microscope allowed us to identify the quartz as the probable main luminescence emitter.

2. Determination of the equivalent dose ($D_e$) from extracted quartz

Initial attempts at using thermoluminescence on polymineral fine grains were successful for only a small number of samples. Chemical extraction of clean quartz from the slag matrix became a necessary step in sample preparation. However, since yields were usually quite small, single-aliquot OSL techniques appeared an interesting path to explore (TL techniques usually require at least 24 aliquots). Also, quartz was extracted in the form of coarse grains, for which TL normalisation (between aliquots) turns out problematic. This and the recent development of a single-aliquot OSL technique (e.g. Murray and Wintle, 2000) that apparently overcome sensitivity changes problems further encouraged us to investigate the use of OSL.

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2.1. Material and sample preparation

The slag studied came from copper and ironworking sites, most of which were dated independently using associated material (Stos-Gale, 1987), so that the accuracy of the techniques used could be checked. Samples were coarsely crushed with a metal crusher to allow a greater reaction rate and dissolved in fluorosilicic acid (H₂S,F₆), which removed virtually all non-quartz material. After dissolution samples were rinsed in distilled water, dried and coarse grain fractions were separated out by sieving. The quartz grains obtained were then etched at room temperature for 40 min using HF (48%), thus removing approximately a 10 µm layer. Grains were then deposited homogeneously as a monolayer onto aluminium or stainless-steel discs, each disc carrying about 5 mg of material. Various grain fractions were used, depending on availability (e.g. 90–125 or 125–180 µm); this was taken into account for the calculation of the beta attenuation in the quartz grains, in order to determine the actual dose received (based on calculations by Mejdahl, 1979).

2.2. Optically stimulated luminescence

2.2.1. Use of the SAR technique

Since many samples yield small amounts of quartz — in some cases, only a few aliquots can be prepared — single-aliquot techniques seemed particularly suited. Other advantages of using a single-aliquot for the measurements are the higher precision obtained and the fact that no inter-aliquot normalisation is required.

The recently developed SAR technique (latest developments in Murray and Wintle, 2000) was applied. Repeated measurements on a single aliquot of quartz quite often induce changes in sensitivity of the main OSL peak with each cycle of regenerative dose (usually an increase). The SAR protocol includes a correction for these sensitivity changes and is now being routinely used by researchers, mainly to date sedimentary material but also with heated quartz from archaeological samples (Mejdahl and Botter-Jensen, 1994).

Experimental details: Measurements were made with an automated Risø reader (TL-DA-12). Stimulation was by blue–green light from a fitted 75 W halogen lamp delivering light at a power of 16 mW cm⁻² (Botter-Jensen and Duller, 1992). The filtered stimulating light (HA-3 heat absorbing, CG420 and broad band interference filters were used) spanned a band between 420 and 560 nm. The emitted light was detected (by means of an EMI9635QA photomultiplier) between 270 and 370 nm after filtering with two Hoya U340 glass filters.

The results presented here were obtained from measurements made at elevated temperature (usually 130°C) in order to optimise the signal output by thermal assistance (a desirable effect that is counter-balanced by thermal quenching when the temperature is further increased) and prevent the re-trapping of charge in the 110°C TL peak trap. The heating rate used was 2 °C s⁻¹.

The SAR procedure (based on Murray and Roberts, 1998 but using different preheats) is outlined below.

1. Natural/regeneration dose + preheat (220°C, 300 s).
2. 100 s blue–green light: natural or regenerated OSL.
4. 100 s blue–green light.

Steps 3 and 4 are used to correct for possible sensitivity changes. The “sensitivity corrected OSL” or “normalised OSL” refers to the ratio of the OSL measured in step 2 to that measured following a test dose (sensitivity), measured in step 4.

Prior to the SAR measurements, quartz purity was tested using IRSL 10s illumination (on natural and dosed samples) to check for the presence of feldspars. No IRSL signals were observed.

2.2.2. Quartz OSL signal in slag and its characteristics

Quartz properties may vary greatly from one sample to another, depending on its (geological) origin and its thermal history. Quartz that was embedded in slag (at the time of slag formation) and heated to high temperatures seems to exhibit some characteristics that differ from those usually observed in sedimentary or archaeological material.

It should be borne in mind that quartz grains within slag were submitted to quite severe thermal treatments,
reaching temperatures around 1000°C or more during the smelting process, while ceramics get heated to about 900°C only. Observations with the electronic microscope also showed that large grains of quartz were sometimes heat-shattered within the slag matrix; they often present a large number of little cracks (Fig. 1). Such a severe treatment could account for some of the different characteristics observed. For example, the dependence of quartz sensitivity on past thermal treatments, especially repeated heating, is well known (e.g. McKeever et al., 1996). The results presented here were obtained on nine samples from three different archaeological sites.

- **Decay form and growth characteristics:** In most of the samples studied, the decay of the shine-down curve seems quite slow compared to that of “typical” sedimentary quartz, for which the initial sensitivity is reduced to about 2–5% in 20 s (in similar experimental conditions, i.e. at the same stimulation power — see experimental details — and at a measurement temperature of 130°C). For the samples measured, 100 s of stimulation only reduce the signal to about 10% of its initial sensitivity. A typical shine-down curve is shown in Fig. 2. This could be due to the presence of the slow component (Bailey et al., 1997) in a proportion higher than that normally observed. The possibility that minerals other than quartz are present in the extracted material was discounted by FTIR measurements on the separated grains, confirming that the material measured was pure quartz.

Sensitivity and brightness vary between samples, and often from aliquot to aliquot. However, all samples except one showed sufficiently good growth characteristics to allow \( D_\alpha \) determination. Two representative OSL signals and their corresponding growth curve are shown in Figs. 3 and 4.

- **OSL signal following preheat:** In all samples examined, a signal is observed after optical bleaching (for 100 s) followed by preheating at 220°C for 300 s (one example is shown Fig. 5). It amounts to about 10–20% of the natural signal in many samples, up to 40% in some cases. Although this was observed in sedimentary samples by other researchers (Rhodes and Bailey, 1997), it was neither as systematic, nor as intense as for the samples investigated here. This is thought to be due, at least partially, to the transfer of charge from shallower traps to the main OSL dating trap/traps during preheat. It might also reflect the presence of a slow component in a larger proportion than that usually observed, “typically” 2–3% in sedimentary samples (Bailey et al., 1997). Further evidence for this is the frequent observation of a “build-up” phenomenon at the very beginning of the stimulation, which also constitutes a characteristic of the slow component (Bailey, 2000a). Examples are shown for three different samples in Fig. 6 to illustrate the diversity of behaviour of the signal with respect to its amplitude and variation with each cycle of regenerative dose.

- **Saturation:** Some samples from one particular site (Kythnos, Greece) seem to show an early onset of saturation. Their growth curves can be well fitted with a single saturating exponential. However, this did not seem to be a general feature in slags, and was not observed for samples from other sites.
2.2.3. Problems encountered in the determination of equivalent doses

$D_e$’s were calculated for the nine samples mentioned above (Section 2.2.2). A minimum of three dose points was measured, in order to bracket the natural signal, and linear interpolation was used for $D_e$ determination. The errors indicated are based on a combination of statistical errors (in the OSL measurement) and on the goodness of the linear fit (for the interpolation).

For most, only a small number of aliquots ($< 6$) could be measured and problems of discrepancy between $D_e$ values were encountered. To illustrate this, results obtained on quartz from two copper slag samples (KYT30a, KYT70a) from Kythnos, Greece, are presented (Table 1). Owing to sample size limitations, different grain size fractions had to be used and this would probably account for some of the differences observed. The grain sizes were actually taken into account in the age calculation. However, this does not explain the discrepancy between the two samples that were thought to be the same age, according to the archaeological context. Also, there is some scatter between $D_e$ values obtained on aliquots from the same sample.

The presence of thermal transfer ranging from 10 to about 20% of the signal is worth noting (Fig. 7(3)). The
Table 1

$D_e$ values obtained on different quartz aliquots from copper slag samples (KYT30a, KYT70a1, Kythnos, Greece). Both samples were assumed to be of the same age. There is a problem of discrepancy between $D_e$'s from the two samples and to a lesser extent, between aliquots from the same sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain size (µm)</th>
<th>$D_e$ (Gy)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>KYT30a</td>
<td>90–125</td>
<td>2.19</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>90–125</td>
<td>2.52</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>53–90</td>
<td>2.22</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>38–53</td>
<td>2.09</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>125–180</td>
<td>1.85</td>
<td>0.11</td>
</tr>
<tr>
<td>KYT70a1</td>
<td>125–180</td>
<td>5.8</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>&gt; 180</td>
<td>3.7</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>&gt; 180</td>
<td>5.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Fig. 7. Quartz extracted from copper slag (KYT30a). Dependence on preheat temperature of (1) equivalent dose, (2) recycling ratio and (3) thermal transfer is discussed in the main text.

The general trend is an increase with preheat temperature. To check whether the preheat temperature used (220°C, 300 s) was appropriate, aliquots from sample KYT30a were preheated to different temperatures ranging from 160 to 260°C with 20°C increments, for a duration of 60 s. The $D_e$ values were then plotted against preheat temperature. Fig. 7(1) shows an apparent stabilisation of the $D_e$ between about 200 and 260°C, a range that encompasses the 220°C temperature used. Caution must be exerted, however, in the extrapolation of these results to previous measurements, since longer (300 s) preheats were used.

Also, the recycling ratio, i.e. the ratio of the sensitivity corrected OSL measured for a given dose point (for example after the last generated cycle) to that measured for the same dose point, provides a good way of checking whether the sensitivity correction works. It was measured for KYT30a and, although not equal to unity, seemed however to be constrained within acceptable limits (Fig. 7(2)).

Therefore, the experimental conditions do not seem to have been a cause for the differences in $D_e$ values observed. To further investigate possible causes to this problem, we conducted a series of experiments on annealed quartz extracts.

2.2.4. Testing of the SAR technique

Aliquots of quartz were heated up to either 500 or to 680°C (for 100 s) and were artificially irradiated in the laboratory with a beta dose to mimic the natural dose. The equivalent dose was then determined using the SAR technique, the first cycle starting with a preheat (without any regeneration dose), followed by measurement of the sensitivity to test dose, as would be done for the measurement of a natural dose. Annealed samples showed characteristics similar to those observed in “natural” quartz extracted from the slag. A representative growth curve is shown in Fig. 8. They also showed strong thermal transfer.

For most of the samples measured, the $D_e$ determined using the SAR technique matched the known dose quite closely. Values obtained on coarse-grained quartz from KYT30a (Table 2 and Fig. 9) seem quite satisfactory, in spite of a slight overestimation. It should be noted that for this sample, the signal following optical bleaching and preheat (without dosing) amounted to about 40% of the natural signal.

- **Effect of thermal transfer.** In order to investigate the possible effects of thermal transfer on the $D_e$ values, a SAR cycle in which no dose was given (except for the test dose) was inserted after the first cycle (measuring the natural) and after each subsequent SAR regenerative cycle. Four samples were investigated using such a procedure. Thermal transfer variations with dose cycle were very similar to the patterns observed in the corresponding natural samples (see Fig. 6) (the same sub-samples were re-used). For most of the samples measured, it represented a significant fraction of the natural signal (at least 10%). Since it potentially
Fig. 8. Typical SAR growth curves obtained from a copper slag (KYT30a). A single “zero dose point” (empty square) was measured at the end of the SAR measurement and was always found to represent a significant fraction of the natural signal. The (sensitivity corrected) natural signal is represented by the empty diamond.

Table 2

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>( D_e ) (Gy)</th>
<th>Error</th>
<th>Rel. error (%)</th>
<th>Thermal transfer (% of nat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KYT30a #2</td>
<td>5.0</td>
<td>0.4</td>
<td>9</td>
<td>43</td>
</tr>
<tr>
<td>KYT30a #3</td>
<td>5.5</td>
<td>0.2</td>
<td>4</td>
<td>46</td>
</tr>
<tr>
<td>KYT30a #9</td>
<td>5.5</td>
<td>0.4</td>
<td>7</td>
<td>42</td>
</tr>
<tr>
<td>KYT30a #25</td>
<td>5.5</td>
<td>0.3</td>
<td>7</td>
<td>43</td>
</tr>
<tr>
<td>KYT30a #38</td>
<td>5.2</td>
<td>0.2</td>
<td>6</td>
<td>40</td>
</tr>
</tbody>
</table>

Fig. 9. Equivalent doses (in Gy) obtained by the SAR technique on annealed (680°C, 100 s) and dosed (~ 5 Gy beta) quartz extracted from a copper slag (KYT30a). The five aliquots were preheated before measurement of the pseudo-natural OSL, and a normal SAR procedure applied. The dotted line indicates the level of the laboratory beta dose given to the samples.

Fig. 10. Annealed and dosed quartz (2 Gy beta) extracted from a slagged furnace lining (CAS1). The dependence on preheat temperature of (1) equivalent dose (2) recycling ratio and (3) thermal transfer is discussed in the main text.

● Effect of preheat temperature: It was also thought that the preheat treatment used may be too severe (220°C for 300 s) and could induce large transfers of charge. As was previously done on a natural sample, \( D_e \) values were measured on aliquots from a iron slag (CAS1) and plotted for different preheat temperatures between 160 and 260°C for 60 s. Results are shown for one sample (Fig. 10(1)) for which, after an initial overestimation of the \( D_e \) for temperatures below about 200°C, after which the \( D_e \) seems to level off at the correct dose between 200 and 260°C, which encompasses the preheat temperature used in the measurements previously described. Here again, one must be cautious when extrapolating these results to previous measurements made with longer (300 s) preheats.

The thermal transfer, as would be expected, does increase with preheat temperature, but interestingly, it does not seem to affect the \( D_e \) values. In the 200–260°C temperature range the thermal transfer signal increases by nearly 100% (Fig. 10(3)) while the \( D_e \) value remains constant. It might be the case that if thermal transfer...
3. Dating of samples

3.1. Calculation of the annual dose rate

Since coarse-grain techniques were used, annual dose consists mainly of the beta contribution from the slag (internal dose) and of the gamma contribution of the environment (soil + cosmic rays). The alpha contribution was removed by HF etching. Determination of U, Th, and K contents in the slag was done by ICPMS analysis. Because the samples investigated here originated from old excavations, no soil was available for the determination of the environmental dose rate, which had to be assumed. The values used were taken from Fleming et al. (1970) and correspond to the upper and lower limits that were measured on archaeological sites.

3.2. Age estimates (preliminary results)

Preliminary dates are presented in Table 3, obtained on a limited number of aliquots (sometimes only one) owing to the material scarcity. Samples originate from the same site (Kythnos island, Greece). As aliquots from different grain size ranges were used, ages were calculated separately for each size, in order to account for the beta attenuation in bigger grains, and then combined to give a mean age. Two 14C dates were obtained for associated material which agreed with the age expected from the typology of pottery fragments (Stos-Gale, 1987). The OSL (Table 3) ages show clear underestimation. However, the maximum ages (calculated assuming a very low environmental dose) fall within the expected ages for four samples out of seven. It is interesting to note the age obtained on sample KYT30a (calculated from five aliquots) falls well outside the expected range, considering that it had been quite thoroughly investigated; experimental conditions appeared to be appropriate and the robustness of the SAR technique for this sample was demonstrated by the measurement of the recycling ratio, although one should not rely on a single measurement of a “repeat point” at the end of the procedure, as discussed above. However, it must be noted experimental conditions for this site were far from ideal. Apart from the lack of information about the dosimetry of the site, the depth from which the samples were taken is unknown (they were collected with lead isotope analysis in mind). It may be also be that some of the samples were re-heated at

Table 3

Preliminary ages obtained from 7 samples of copper slag from the Cycladic Islands. Two extreme values were taken for the environmental dose, leading to the calculation of a minimal and a maximal age. The values given are either mean values and the corresponding standard deviation when several aliquots could be measured or a D value from a single aliquot and its error. The 14C dates are taken from Stos-Gale (1987)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age min (years)</th>
<th>Stdev or error</th>
<th>Age max (years)</th>
<th>Stdev or error</th>
<th>Expected age range in years (14C dates)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KYT30a</td>
<td>921</td>
<td>153</td>
<td>2095</td>
<td>331</td>
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</tr>
<tr>
<td>KYT70a</td>
<td>1100</td>
<td>177</td>
<td>2637</td>
<td>574</td>
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<tr>
<td>KYT45</td>
<td>1801</td>
<td>102</td>
<td>3919</td>
<td>386</td>
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<tr>
<td>KYTY0</td>
<td>2745</td>
<td>324</td>
<td>5235</td>
<td>705</td>
<td>Min = 4140</td>
</tr>
<tr>
<td>KYTX2</td>
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<td>78</td>
<td>2139</td>
<td>223</td>
<td>Max = 5092</td>
</tr>
<tr>
<td>KYT80d</td>
<td>1701</td>
<td>101</td>
<td>3905</td>
<td>408</td>
<td></td>
</tr>
<tr>
<td>KYT70a</td>
<td>1926</td>
<td>302</td>
<td>4449</td>
<td>799</td>
<td></td>
</tr>
</tbody>
</table>
a later date, or that they are actually younger. At this stage of our experiments, it is difficult to ascertain the causes of this underestimation. More testing of the SAR technique is underway on samples from better-defined contexts and will hopefully help us shed some light on this problem.

4. Conclusion

In order to develop a dating technique for archaeometallurgical slag, a new approach using optically stimulated luminescence has been adopted where previously only thermoluminescence had been used, with limited success. Experiments using OSL on clean quartz grains chemically extracted from the slag matrix were encouraging. Restrictions imposed by the small amounts of quartz obtained and new developments in the field of OSL research prompted us to test the suitability of the SAR technique for quartz that had been heated to high temperatures within the slag. Most of our effort so far has been put into testing the robustness of the SAR technique for quartz originating in heated slag samples. The presence of an important thermal transfer signal did not seem to represent an obstacle to the correct determination of the burial dose. Moreover, experiments carried out more recently showed that the magnitude of the thermal transfer is actually much less than was thought and results will be published elsewhere. Preliminary dates obtained on seven samples from the same site show underestimation of the known age. In spite of this, the single aliquot regenerative technique still appears a suitable method to date slag, although its application must be exercised with caution, and its validity checked for each sample. We are hopeful that current investigation on a wider range of samples from different, well-defined contexts will be successful.

Acknowledgements

The author would like to thank the National Environmental Research Council for help in funding this project as well as Z. Stos-Gale for providing some of the copper slag samples used in this study. Discussions with Dr. R.M Bailey, G. Adamiec and Dr. E.J. Rhodes are also gratefully acknowledged.

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