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TL-DATING OF VITRIFIED MATERIAL

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Abstract: While attempting to date material from the vitrified ramparts of various hill-forts in central and western Europe by thermoluminescence (TL) methods, obviously erroneous results appeared. Searching for possible reasons, an investigation into the upper temperature limit of TL-dating was started. It is well known that insufficient heating causes far too old erroneous TL-ages. Less well known and yet unexplored is the temperature region where vitrification commences. From a hill-fort near Uppsala, samples were taken along a trench through the vitrified rampart. Firing temperatures were determined for each sample by petrographic methods within ±50°C, and TL-measurements were carried out. The results show that the ages determined become successively younger with increasing firing temperatures, for samples heated to temperatures exceeding 900°C. The younger the apparent age, the higher the glass content of the sample. Although most of our data are from vitrified ramparts – somewhat exotic to the majority of archaeologists – our findings apply to all strongly heated materials. Examples are archaeometallurgic remains (slags, furnaces, hearths), tempered ceramics (stoneware, porcelain), or molten bricks. The paper also presents clearly erroneous TL-dates for several of these materials, along with an explanation of the phenomenon.

1. INTRODUCTION

While dating the vitrified ramparts of various hill-forts in Sweden, and other parts of Europe, by thermoluminescence (TL) techniques (Kresten and Goedicke, 1996), some peculiar results were obtained. Similar results were also found in the literature. The suspicion arose from a plot of all TL-dates on vitrified ramparts available at present (**Fig. 1**), showing a maximum of ages between 1000 and 1500 years BP. While many of the older ages, i.e., those >3000 years BP may be explained by remnant geologic luminescence, there are surprisingly many dates <1000 years BP.

Plotting apparent TL-dates <1500 years BP versus available ^{14}C age determinations (**Fig. 2**), it becomes evident that the correlation is rather poor indeed. Even when taking into account tree-ring calibration, and the possible ages of the trees (in most cases, wood-type analyses are lacking), it still seems that TL-dating yields far too young results. One may argue that this discrepancy reflects the age difference between construction of a timber-laced rampart as dated by ^{14}C, and its firing as dated by TL. However, very old timber would in most cases be a rather poor fuel, insufficient to supply the heat required for melting substantial amounts of rock.

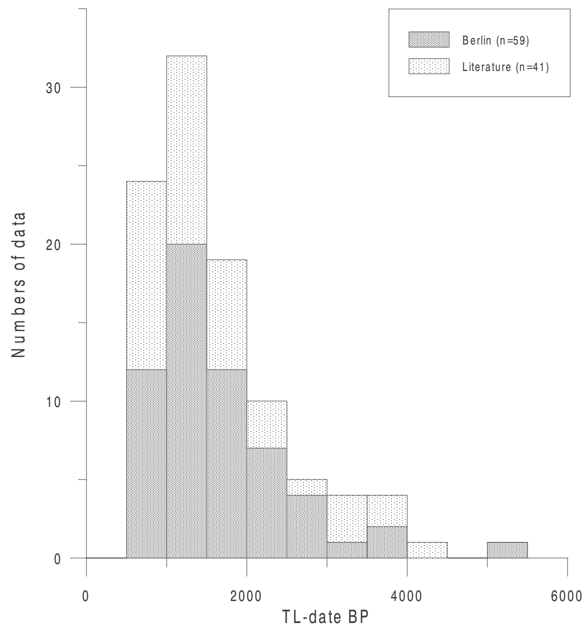

Fig. 1. *Histogram showing the distribution of TL-dates for vitrified ramparts in Europe. Determinations by Rathgen-Forschungslabor, Berlin, and data from the literature (Engström, 1984; Mejdahl, 1983, 1986, 1989, and unpublished data 1993-5; Sanderson et al., 1988; Strickertsson et al., 1989a, 1989b).*

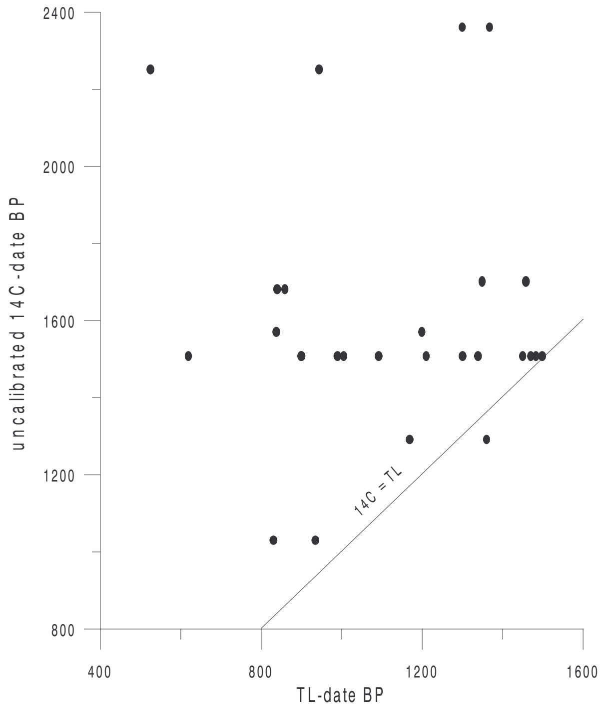

Fig. 2. *TL-dates of <1500 years BP for vitrified ramparts versus corresponding [14]C-ages (literature data as for Fig. 1, and Cunliffe, 1974; Damell and Kresten, 1994; Longley, 1982; Lorin, 1985; MacKie, 1969; Nicolardot et al.).*

2. SYSTEMATIC UNDERESTIMATION OF TL-AGES: EXAMPLES

During 1992, the vitrified inner rampart at Broborg, a hill-fort near Uppsala, Sweden (Kresten *et al.*, 1993), was excavated by the first author. A series of samples was taken from the trench, ranging from apparently unheated rock (granitic gneiss) to partially molten samples (**Fig. 3**). A preliminary estimate on the temperature distribution was based upon the stability of biotite (Hjärthner-Holdar and Kresten, 1996), resulting in isotherms at about 500°C (decomposition) and 1000°C (melting). Further refinement was performed using the stability of various minerals, as well as fission track healing (Kresten, 2000). The temperatures within the vitrified mass were determined using differential thermal techniques, as well as olivine-liquid equilibria (Kresten *et al.*, 1993; Kresten *et al.*, 1996). Precise temperatures cannot be given for the whole section, as one may expect chimney effects, blocking effects, dry distillation (i.e., formation of hydrocarbons), as well as fluctuations in oxygen and water partial pressures to occur. Thus, the accuracy of the temperature determinations is about ±50° at any given point within the section.

Several of the samples taken were used for TL-dating. A fine grain fraction was used for the analyses which was obtained by sedimentation of crushed material in aceton (Zimmerman, 1971). During this process quartz and feldspar grains between 2-11 μm are preferentially settled out, but also clay minerals are deposited which, however, do not contribute to the TL-signal as their sensitivity is low compared to quartz and feldspar. The fine grain technique allows the preparation of sets of multiple and indistinguishable samples, thus avoiding normalisation procedures. The results, (**Fig. 4**) show that samples that were heated to temperatures below 550°C yield ages that are (far) too old. This is expected, as the quartz had not been completely annealed and a smaller or larger geologic component remains. Between 600 and 900°C, TL-dates that are comparable to (calibrated) [14]C age determinations (UA3065, 3066) are obtained. Above the latter temperature, samples become apparently younger with increased firing temperature (**Fig. 4**). Of the samples analysed by Mejdahl (1983, and unpublished data), the two most high-temperature samples could be placed correctly according to temperature (as the first author performed the sampling), while the firing temperature of the third sample is more uncertain.

The inner rampart at Broborg has been regarded as an example of constructive vitrification (Kresten and Ambrosiani, 1992; Kresten *et al.*, 1993), i.e., the date of construction would be the date of firing. Therefore, TL-dates and [14]C-dates would be equivalent, taking the biological age of the timber into account. This is verified by the TL-dates within the "safe" temperature interval.

In general, TL-dates are regarded as being safe if several samples yield the same age. **Fig. 4** may serve as yet another example for this opinion. Unfortunately, even if TL-ages are consistent, systematic age underestimation may occur as shown in the next example. **Fig. 5** shows

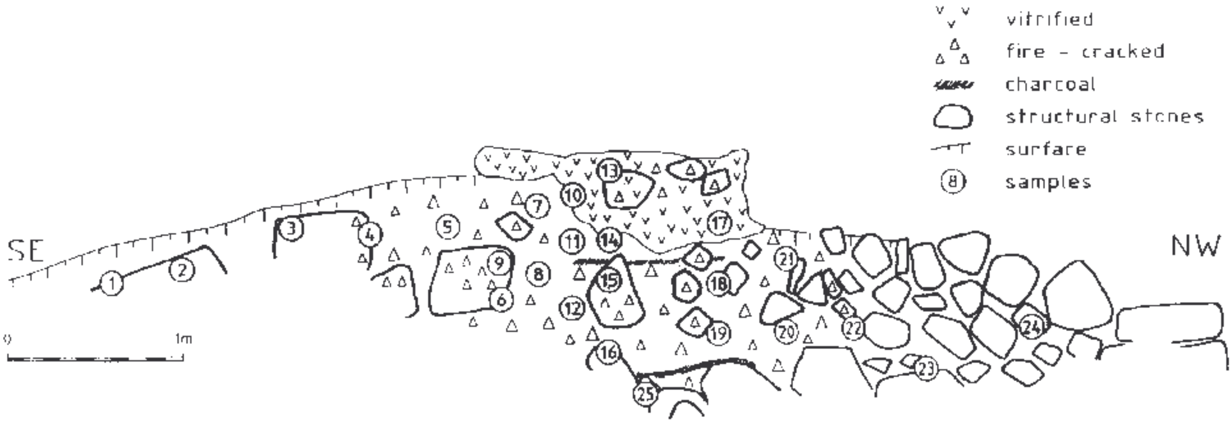

Fig. 3. *Section through the vitrified rampart of Broborg, showing sample locations (in circles).*

a series of TL-dates from the vitrified rampart (again mainly granitic gneiss) of Vällnora hill-fort in Uppland. Apparently, most determinations cluster around AD 1150. They do so only because they were sampled within the same horizon, i.e., within a narrow (but too high) temperature interval, involving partial melting of the granite. The correct date appears to be about AD 600 (**Fig. 5**), obtained for a sample that had been heated to about 700°C (as the hill-fort has not been excavated, no ^{14}C dates are available). The example emphasises the need for geothermometric determinations prior to TL-dating.

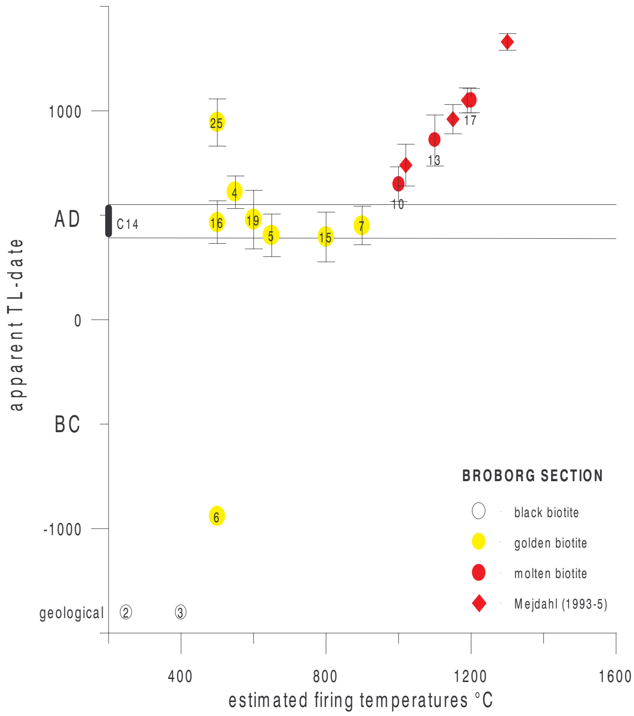

Fig. 4. Apparent TL-dates versus firing temperatures for samples from the Broborg section. For sample locations, see Fig. 3.

Another example of obviously erroneous results are from Bernstorf, a fortified Bronze Age settlement north of Munich, Bavaria (Moosauer and Bachmaier, 2000). Here, archaeological finds are in accordance with ^{14}C-dates, at about 1500 BC. Three potsherds yielded a context age (TL) of 1560±230 BC. In contrast, TL-dating of vitrified silt found outside of the rampart yields a very much younger age: six samples resulted in a mean age of 510±85 BC, i.e., apparently about 1000 years younger. Investigations by the first author and others (quoted by Moosauer and Bachmaier, 2000) have shown that the vitrified material had been heated to 1300-1350°C, resulting in a glass-quartz-mixture.

3. RESULTS AND DISCUSSION

The cause of these erroneous determinations for samples that had been fired to temperatures above 950-1000°C must be (at least, in part) due to ongoing vitrification. Experiments have shown that we are about the solidus (i.e., beginning of melting) temperature for granites and gneisses, major building materials for many ramparts. In other words, the formation of quartz-feldspathic glass commences at about 950-1000°C. In order to check that assumption, planimetric analyses of the most high-temperature samples from Broborg that were analysed in Berlin were carried out. Sample T10 had only traces of glass, while sample T13 showed 3.8% and sample T17 36.3% glass by volume. **Fig. 6** shows a log-normal relationship between time (or temperature) and glass content, as is expected. Unfortunately, the sample heated beyond

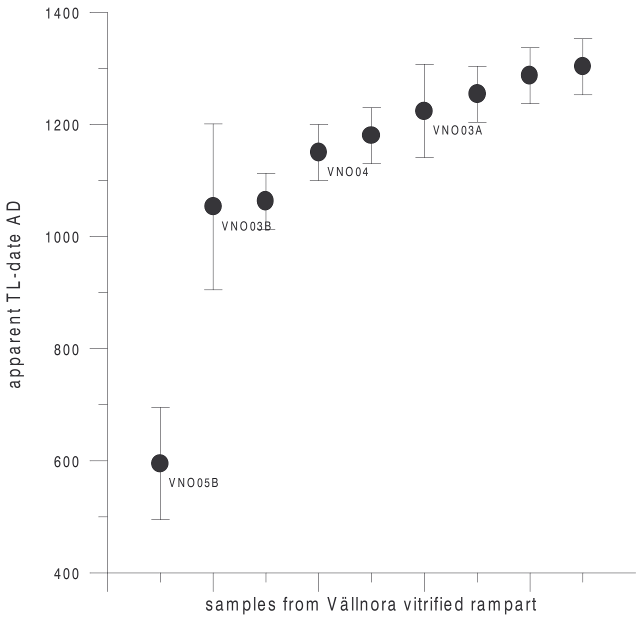

Fig. 5. Apparent TL-dates for samples from the vitrified rampart at Vällnora borg, Uppland. The correct date is most likely about AD 600.

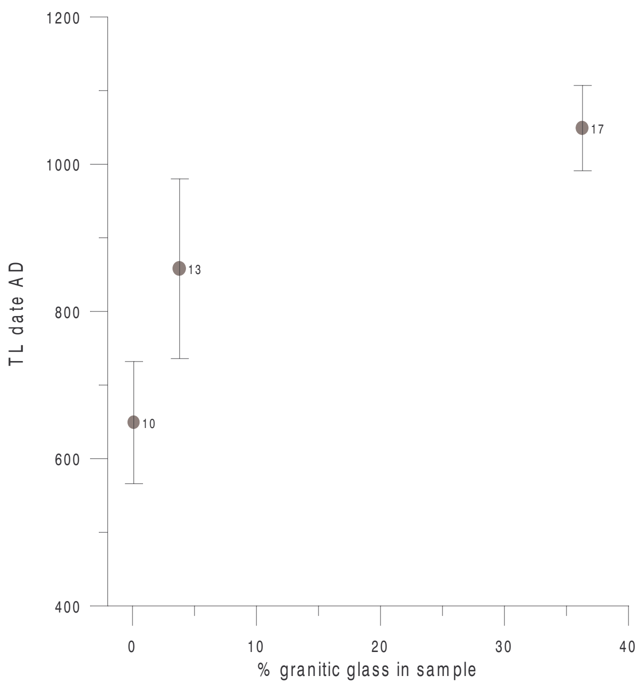

Fig. 6. Apparent TL-date versus glass content for the three most high-temperature samples of the Broborg section.

1200°C of **Fig. 4** could not be measured. On the basis of the observations, we may thus suggest that the formation of quartz-feldspatic glass is the reason for TL-dating to fail, giving rise to results that are too young.

It must be emphasised that in the present context, the term "glass" applies to quartz-feldspathic glass only and not to the basaltic glass found at many sites (Kresten and Ambrosiani, 1992; Kresten *et al.*, 1993). While the former is the melting product of the main building material (granite, gneiss, arkose, sandstone, etc.), the latter is an admixed component (dolerite or amphibolite) that is quartz-free, not interfering with TL-dating.

TL-dating of glass has often been attempted, but has never proven to be successful on a broad scale (Müller and Schvoerer, 1990). The thermodynamic disorder of glass causes the energy difference between traps and the conduction band to decrease and enhances the probability of spontaneous recombinations of charge carriers among energy levels within the band-gap which are almost continuously distributed. In consequence, the luminescence storage potential of glass is greatly reduced and this explains why glass shows extremely low TL-sensitivities. If natural TL-emission can be observed from glass, it has no significance for dating since it lacks reproducibility.

These preliminary data on the glass content versus time/temperature suggest that it might be possible to correct erroneous TL-dates provided that temperature or glass content are known. Nevertheless, the most straightforward method would be to select samples for dating following geothermometric methods, thus avoiding any later corrections that just might add another error.

4. IMPLICATIONS TO ARCHAEOLOGICAL DATING

Having arrived at the conclusion that TL-dating of high-temperature samples from vitrified ramparts are unsafe, the question arises whether or not these findings have any bearing on other material from archaeological sites. Unfortunately, this seems to be the case.

Possibly the most perfect example (although the originators might disagree) is the TL-dating of a copper-smelting site in north-eastern China (Chen Tiemei *et al.*, 1998a). It is worthwhile quoting the abstract:

"Niuheliang is a Neolithic site of Hongshan Culture. At this site copper-smelting crucibles with attached slag were found and also a copper ear-ring was found in a tomb. Some archaeologists think that these copper smelting related objects are related to Hongshan Culture which would push the copper smelting in North-East China back to as early as 4500 BP. However thermoluminescence dating on the crucibles gives an age of 3000-3500 years BP, younger than that of Hongshan Culture. Very likely they are related to the early stage of Xiajiadian Culture".

In essence, pottery yielded ages of 3899±555 to 4928±345 years BP, while crucibles gave dates of 3000±330 to 3494±340 years BP. Considering that red ware has firing temperatures of about 750°C, while crucibles would have been heated to a minimum of 1100°C (somewhat above the melting point of pure copper), the apparent age difference could readily be explained as a difference in firing temperatures! Thus, there is no need to invoke arguments such as "an older culture, eating but not smelting" as opposed to "a younger culture, smelting but not eating" - it is really a difference in firing temperatures!

Yet another example is provided by the tomb of pharaoh AHA ("Hor-aha", first king of the first Egyptian dynasty). The pharaoh died about 2925 BC, and his tomb was looted some thousand years later. On this occasion, the cedar wood interior of the burial chamber was set afire causing the mud bricks of the walls to melt. Unsurprisingly, these bricks yielded TL-dates that not only are far too young, but inconsistent as well, 1560±280 BC, and 450±270 BC. A partially molten vine jar belonging to the burial inventory shows a still younger apparent date, AD 700±100. In this extreme case, the dating error is almost three thousand calendar years!

In consequence, similar arguments must hold true with respect to differences between TL-dates for red or black ware (low-temperature) versus stone-ware or porcelain (high temperature), or all remains from metallurgic activities (slags, furnaces, hearths, moulds, crucibles). We agree with Chen Tiemei *et al.* (1998b) that "meticulous care should be taken in TL dating of furnace of iron metallurgy". However, we may add "never date a sample without having established the firing temperature".

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