110 °C TL peak records the ancient heat treatment of flint

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In recent years there has been an increased interest among archaeologists in the firing temperature of flints for two reasons. Firstly, in connection with the practise of heating flints before shaping them into tools in prehistoric times. Secondly, for those flints which were heated, there is the question of whether the heating temperature was adequate for zeroing the geological signal in order to obtain reliable ages by the thermoluminescence dating method. It has been found that the thermally activated sensitivity change of the 110 °C thermoluminescence (TL) peak of flints can be used to provide a simple, reliable test for the temperature determination of ancient heat treatment. The method has several advantages over other methods developed earlier. It does not require the source material for comparison. It is simple and quick, and TL dating laboratories may use it without the need for extra equipment.

In early work the most common test was based on the examination of the visual appearance. The change in colour, vitreous lustre, cracks and potlids are often taken as evidence of heat treatment. Many forms of flint exhibit these characteristics. However, they are not always clearly visible and they may even result from non-thermal effects like frost and weathering.
More sophisticated techniques have recently been developed. Weymouth and Mandeville (1975) have studied heat treated cherts by x-ray diffraction and have observed broadening of diffraction lines. Robins et al. (1978, 1981) and Wieser et al. (1986) used electron spin resonance spectroscopy for detecting former heat treatment in flint. A number of signals are reported that are associated and could be altered by the heat treatment in the temperature range 200 - 800 °C. Johnes et al. (1979) studied the effect of heat treatment on the Mössbauer spectrum. It was shown that iron compounds which are present as impurities in flints are altered by heat treatment above 275 °C and this can be revealed by the iron-57 spectrum.
All of these methods require additional equipment and facilities which may not be easily accessible by TL dating laboratories. Some of the above mentioned methods require geologically identical unheated material in order to be certain about the heating temperature. Apart from these, two more methods were developed which make use of the TL properties. The first method was developed by Melcher and Zimmerman (1977). For samples which were heated at some point during the last 8000 years, the equivalent radiation dose was at least 100 times less than that observed for the raw flint, in which the TL signal was in saturation. By comparing the equivalent dose of a particular sample with the dose needed to saturate the TL signal, it was possible to determine heating temperatures. However, this method has certain drawbacks because for certain types of flint the TL signal saturates at relatively low levels of doses (20 Gy) which are comparable with archaeological doses (Göksu, 1973). Furthermore, possible partial annealing of the geological thermoluminscence may cause further difficulties in the interpretation of the results.
The second TL method, developed by Valladas (1983), is based on the thermally activated sensitivity change of the 380 °C TL peak of flint. However, if the archaeological heat treatment was below 500 °C, this method is not sensitive enough to indicate the firing temperature.

Results

In this work we have observed that the sensitivity of the 110 °C peak increases in a similar fashion to the 380 °C TL peak and that it can be used for the assessment of archaeological heat treatment. In this experiment, 5 flints of different geological origins from the eastern part of Turkey were used. The samples were broken into small pieces and each piece was heated to different temperatures from 200 °C to 700 °C for 1 hour. One was kept unheated for control measurement. After grinding and sieving, grains between 75 and 175 microns were selected, washed with acetone to eliminate the very fine grains sticking to the surface. Then 6 mg aliquots were spread evenly on aluminium trays and irradiated with a Sr90/Yr90 beta source with a dose of 1.40 Gy. The TL area under the 110 °C peak was recorded between 50-150 °C using a Harshaw 2000 B automatic integrating picoammeter, similar to that used in TL dosimetry. The sample was heated on a graphite heating planchet in a dry nitrogen atmosphere, using a constant heating rate of 8 °C/sec. The TL intensity of the 110 °C peak increased approximately by a factor of 20 after 700 °C preheating (Figure 1).

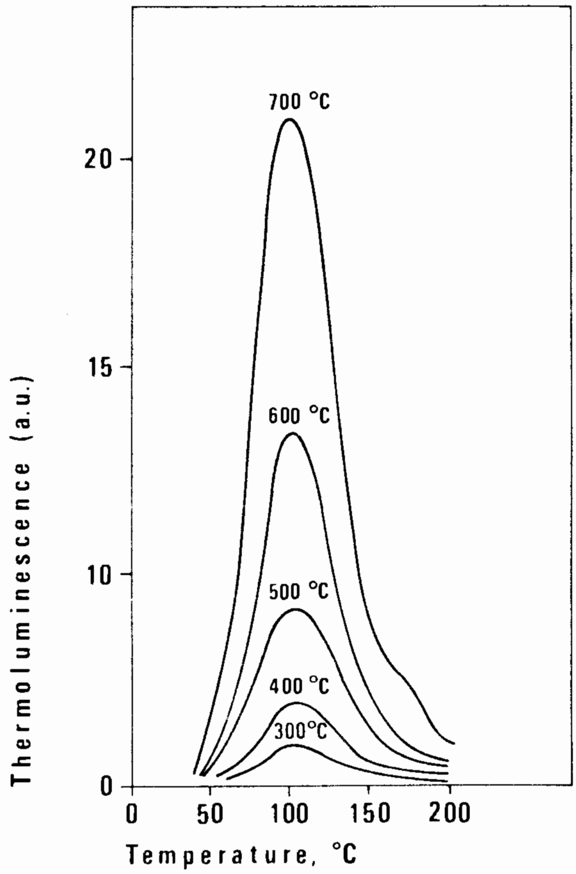

Figure 1 *Thermally activated sensitivity change of the 110 °C TL peak. Aliquots of a geological sample exposed to the same radiation dose after they had been heated to various temperatures for one hour.*

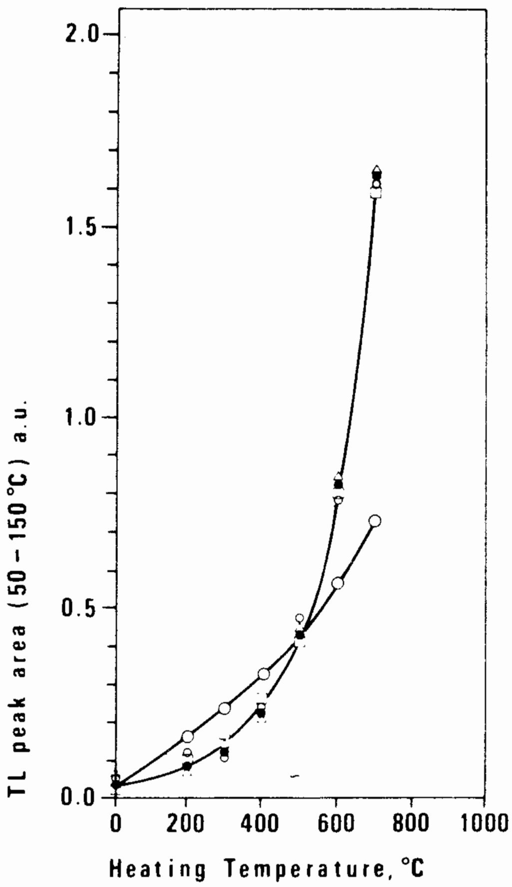

Figure 2 *Geological flints; Annealing temperatures versus TL glow area (50 - 150 °C) for samples exposed to the same test dose. The samples originated from the following sites. O - Hasek Höyük(red), • - Hasek Höyük (grey), ❑ -Degirmentepe, Δ - Tepecik, o - unknown source.*

Figure 3

Flints from the burned layers of Hasek Hoyuk were found to be heated to different temperatures. From the marked change of the slope of the sensitivity curves the archaeological heating temperatures are determined.

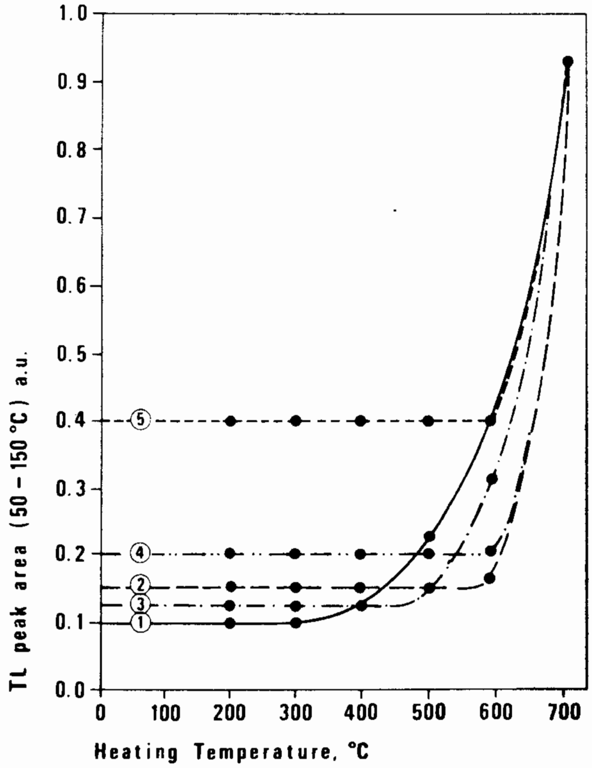

Figure 2 illustrates the thermally activated sensitivity change of the 110 °C peak for five different geological samples from different origins. As can be seen, under laboratory heat treatment, four samples have a very similar increase in TL, while one sample behaved differently.

To test the method, samples from the burned layers of Hasek Hoyuk are used. To simplify the test further, fine grains were deposited on 6mm diameter stainless steel discs and 8 discs were prepared from each sample. The sensitivity of 110 °C peak was measured by exposing the samples to 1.40 Gy after they had been annealed at different temperatures. From the rise of the sensitivity curves the heating temperatures were determined. As can be seen in figure 3., sample 1 was heated to 400 °C, sample 3 below 500 °C, and the other three samples were heated above 500 °C.

Conclusion

The use of the 110 °C peak has several advantages over other methods. The 110 °C peak does not exist in natural samples and can only be regenerated after the administration of radiation doses; it therefore offers the possibility of detecting previous annealing below 400 °C. The 110 °C peak is less prone to spurious signals which may arise due to grinding or heating, so that even small changes in sensitivity can be detected. Additionally, the TL sensitivity of the 110 °C peak to radiation is high enough to be observed with low doses (below 1Gy); therefore the irradiations and measurements are shorter than when the high temperature peak is used.

Further studies on the effect of duration of annealing and cooling are needed in order to understand better the effect of thermally induced sensitivity change of the 110 °C TL peak in flint.

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PR Reviewer's comments (Steve Sutton)

Pre-dose dating of quartz is complicated by natural activation of the 110 °C peak sensitivity under ambient conditions. Exploiting this effect to estimate the degree of heat treatment experienced by flints is an interesting idea. the basic premise is that the activation curve of an ancient heat treated flint will show a plateau until the heating temperature is reached at which point additional sensitization occurs. the reliability and accuracy of this method remain to be demonstrated. Much work has been done in attempting to understand sensitization phenomena in quartz and analagous experiments on flint need to be conducted, as suggested by the authors. Such work should include studies of grinding effects, test dose activation and reproducibility within individual specimens, all of which are likely to be different for each flint. Most crucial are simulation experiments, ie if one preheats a geologic (naturally unheated) flint in the laboratory to some known temperature and then applies this technique, is the correct result obtained? The stability of flint sensitivity over long timescales should also be explored.

Reply:

Our experiments were primarily based on simulation, ie geological samples were heated in the laboratory (first five samples). Therefore correct results were obtained. However, I agree with the Reviewer that the method has to be tested for long term stability of the sensitivity. We have not observed any effect of grinding on 110 °C peak in flint. Therefore we believe this is the main advantage over the method developed by Dr H. Valladas. Concerning the duration of heating, our recent experiments had showed that the effect is the same whether they are heated for 15 mins or one hour.