Reports

Age Determination of Burned Flint by a Thermoluminescent Method

Abstract. *Interference by tribothermoluminescence and by regeneration thermoluminescence can be eliminated for burned flint if thin polished slices are used instead of the powders conventionally used in thermoluminescent measurements. Measurement of the internal and external radiation dose rates then makes possible the absolute determination of the date of pyrolization of small fragments of chert or chalcedony to an accuracy of about 10 to 15 percent. The method may be usable to ages in the range from 200,000 to 300,000 years before the present (B.P.). For samples from the archeological site at Carigüela in southern Spain dates from 12,000 to 50,000 years B.P. have been determined, covering deposits ranging from Late Paleolithic–Epipaleolithic to Mousterian. One Bronze Age specimen gave an age of 4,300 years B.P., in excellent agreement with the age determined by other methods.*

The last serious technical obstacle to the use of thermoluminescence (TL) for obtaining quantitative dates from burned flints appears solved by methods reported here, which provide a feasible and potentially inexpensive means of dating archeological materials older than the limits of the ^{14}C method and younger than the minimum range of the potassium-argon method. The technique of TL dating of burned flints, like the dating of bones or teeth (*1*), has the advantage of dealing directly with archeological material. Burned flints are virtually imperishable and are ubiquitous at Paleolithic sites where the use of ^{14}C dating often is limited by the lack of suitable material or by the antiquity of the site, or both. Thus the potential value of TL dating is obvious.

Random errors of measurement, usually a few hundred years, set a lower limit on the usefulness of the technique. An upper limit is fixed by the onset of saturation because for each material there is a limit to the amount of energy that can be stored in a form that can be determined. Thus, if the maximum amount which can be stored corresponds to 100,000 rads, saturation would be reached after 100,000 years of exposure at a dose rate of 1 rad per year. Any further dose can add nothing more. A sample which had been exposed for millions of years would still give an apparent age of only 100,000 years. For each flint to be investigated, the dose that would produce saturation must be measured.

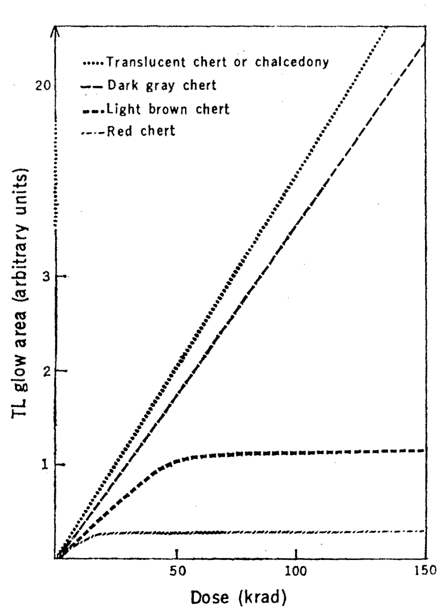


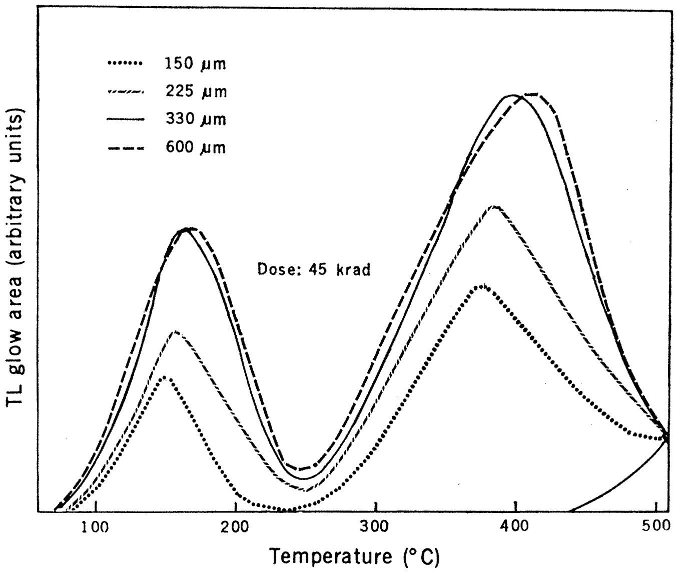
Fig. 1. Variation of glow area with dose for various types of flints.

As can be seen from Fig. 1, the relation between glow area and dose becomes nonlinear well below saturation, so that the accuracy may be expected to diminish for doses exceeding approximately half the saturation value. In practice we find that, although some types of flint such as red cherts will saturate at a few tens of thousands of rads, some chalcedonies may not saturate until 300,000 rads or more (see Table 1). Because typical dose rates rarely exceed 1 rad per year and are usually considerably less, we may determine the burning date of such chalcedonies to a maximum age of about 300,000 years.

The TL dating of younger materials, such as fired potsherds, has been demonstrated with success (*2*). Earlier procedures for dating burned flints have not yielded reliable results (*3*). We have found that it is impossible to date burned flints through the use of samples that have been powdered in the conventional manner, because of complication by two factors: tribothermoluminescence and regeneration thermoluminescence.

Tribothermoluminescence (TTL) is a well-known effect (*4*) which is produced by friction during the grinding of a substance but which cannot be distinguished from the radiation TL. As a result, samples appear to reflect an older age than is correct. Regeneration TL (RTL) (*5*) is another type of spurious glow which builds up in the absence of radioactivity, even in the dark, and seems to be accelerated by the presence of water. The combination of the two effects yields a light output equivalent to that produced by a radiation dose of some tens of kilorads, comparable with the low saturation dose of some of the flints upon which chronological estimates depend. Furthermore, it is not possible to reduce the TTL by etching the outer surface of the grains with HF, by eliminating the small grains less than 10 μm in diameter, or by crushing the grains under water or liquid nitrogen. Nevertheless, both TTL and RTL originate as surface effects. Thus, an effective way to reduce the TTL and to eliminate the RTL is to use thin slices, rather than crushed flint, for measurement. In this way a linear response with variations of dose can be obtained.

Thin slices of flint were cut with a diamond wheel. The structural weakness of the flints made it difficult to cut thinner than 2 to 3 mm with equipment available. The thickness of the slices was then reduced, first with wet



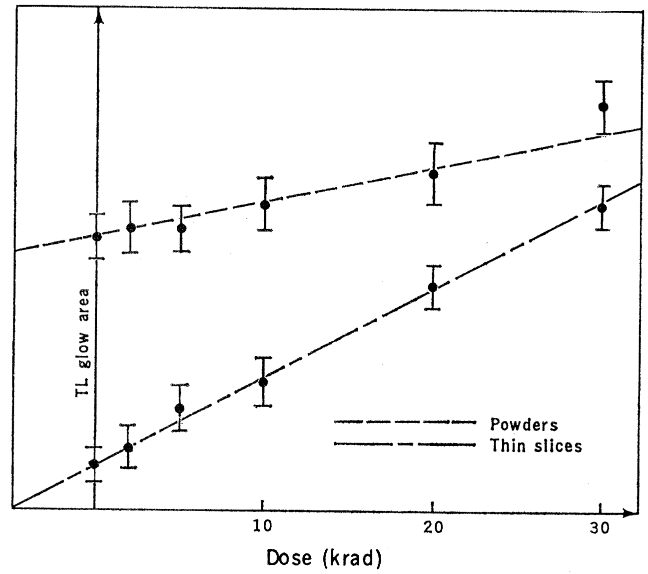


Fig. 2 (left). Glow of flint sections irradiated to 45 krad for various section thicknesses. Fig. 3 (right). Variation of glow area with dose for thin slices and powders (45 μm).

and dry emery paper, grades 400 to 600 in sequence, resulting in a final thickness of approximately 300 μm. Samples were then polished with fine diamond dust on microcloth moistened with Dialap fluid. During the polishing first 4/8-μm and then 0/1-μm Diadust was used. Slices then were annealed to 500°C, cut into small squares (3 by 3 mm), and irradiated with different doses of beta particles. All samples were heated on a tantalum strip, and a small conical stop (having an aperture of 5 mm) was placed between the sample and the photomultiplier. A filter (Ilford 622 blue bright spectrum) and a silica window were used to reduce the thermal radiation during heating. All heating was done in oxygen-free nitrogen at the rate of 20°C per second. We also studied the effect of the thickness of the slice: sections cut from the same piece of flint were ground to various thicknesses (600, 330, 225, and 150 μm) and were processed similarly. These flints were all irradiated at the same position and distance from a ^{90}Sr/^{90}Yr (0.5 c) beta source to a dose of 45 krad. The glow from each slice was measured, and the resulting curves are reproduced in Fig. 2. In making quantitative measurements we used only the glow above 350°C, since some of the glow released at lower temperatures would have been lost by thermal annealing during the thousands of years of storage underground. The high-temperature peak increases to a maximum for slices up to a thickness of 300 μm and then levels off to a constant value. This result suggests that most of the glow is derived from the first 300 μm on the surface of the flint, so that this thickness will be sufficient for glow determinations. More transparent flint would give a larger optimum thickness, but the temperature lag between the lower and upper parts of the section would become too great for much thicker sections to be measured properly.

Finally, to determine the extent to which TTL and RTL have been eliminated by the new technique, another experiment was carried out. Two slices (2 to 3 mm thick) of annealed flint were irradiated to surface beta radiation doses of 5 krad. One was then crushed to a powder $\leqq 45$ μm in par-

Table 1. List of samples from Carigüela.

Sample	Material	Total dose (krad)	TL age (years B.P.)	Cultural association	Saturation dose (krad)
		Well-burned samples			
TB-1	Brown chalcedony, burned	21	32,000	Mousterian	60
TB-2	Gray chert, burned	18	28,000	Mousterian	> 260
TB-3	Dark gray chert, burned	28	46,000	Mousterian	Measurement unreliable
TB-4	Light (translucent) chert, burned	3	4,300 ± 400	Bronze Age	220
TB-5	Reddish-brown chert, burned	15–18	31,000–35,000	Mousterian	100
TB-6	Light brown chert, burned	8.5–11.5	20,000 ± 3,000	Late Paleolithic	150
TB-7	Brown chalcedony, burned	7–8	12,000–14,000	Late Paleolithic–Epipaleolithic	192
TB-8b	Gray-white oolite, burned	14–15	20,000–21,000	Late Paleolithic	130
TB-9a	Gray chalcedony, burned	30	48,000	Mousterian	> 270
TB-12	Gray chalcedony, burned (?)	27	39,000	Mousterian	> 270
		Unburned or inadequately burned samples			
TB-8a	Red chert, burned (saturated)	50	80,000*	Late Paleolithic	58
TB-9b	Dark brown chert, unburned	70	140,000*	Mousterian	75
TB-10	Dark brown chert, unburned	54	100,000*	Mousterian	60
TB-11	Grayish white chert, unburned	20–50	30,000–70,000	Mousterian	40
TB-13	Gray chalcedony, unburned	100	180,000*	Mousterian	< 270
TB-14	Gray chalcedony, unburned	200	300,000*	Mousterian	< 270

* Apparent TL age.

ticle size; the other was ground away on the unirradiated side and polished to a thickness of 300 μm. Subsequently both samples were exposed to various doses of beta radiation.

Figure 3 shows the variation of glow area with variation of dose for both types of samples. The line for thin slices extrapolates to 5 krad within the experimental error, but the line for the powder extrapolates to a much higher value with a much greater error, although, owing to the thickness of the original slice, the effective average initial dose would have been less.

Because our use of thin slices appears to have removed the last major problems associated with the use of TL for obtaining absolute dates from burned flints, we have tested the technique on a stratigraphically controlled sequence of such flints from the archeological site of Carigüela in Spain (described briefly below). In this experiment the following measurements were made:

1) Measurement of the irradiation of the samples from outside by cosmic rays and gamma rays from the surrounding soil. The cosmic-ray dose has not been directly measured but by calculation is small. The soil gamma-ray dose has been found by measuring the gamma activity of 1-kg samples of soil with the help of small pellets of $CaSO_4$ (dysprosium catalyst) which store enough energy for accurate TL measurement in a month's exposure.

2) Measurement of the internal irradiation derived from potassium, uranium, and thorium in the sample itself. The amounts of the first two elements have been determined by chemical and activation analysis, respectively, and the maximum possible thorium content was determined by activation analysis. The K factor (the ratio of the thermoluminescent efficiency of alpha particles to that for beta or gamma rays) also has to be measured on each sample. The contribution of internal alpha-particle activity is small enough by comparison with the soil gamma-ray dose that the accuracy is not a question.

3) Measurement of the natural glow area G_n and the artificial glow area G_a produced after a known artificial irradiation dose D with beta rays from a 0.5-c $^{90}Sr/^{90}Yr$ source. (The range of beta particles from ^{90}Yr is some seven to eight times the thickness of the slices used. Only a small correction is necessary for nonuniformity of irradiation.) The number of years to which this artificial glow corresponds is the known artificial dose divided by the dose per year received by the sample as recorded.

The age T of the sample (in years) is then found by proportion from the measured natural and artificial glows to be

$$T = \frac{G_n}{G_a} \times \frac{D}{d}$$

where d is the total irradiation dose per year received by the sample from all sources since it was last burned in a campfire.

The main source of error lies in the TL measurements of the glow area. This error can be materially reduced if several repetitive measurements are made. In the work reported here we believed that it was more important to cover a range of examples than to make a number of measurements on each.

Measurements were made on flint collected in stratigraphic sequence from sediments within Carigüela, a limestone solution cavern approximately 35 km north-northeast of Granada, Spain. Excavations made at Carigüela more than a decade ago showed it to contain artifacts of Mousterian and Bronze Age occupations (*6*), and our own work at the site since 1968 (*7*) has shown materials of intermediate ages to be present also.

The validity of the method may be assessed on the following criteria: (i) stratigraphic position, (ii) comparison of associated cultural materials of known age, (iii) geological estimation of age, and (iv) microscopic study affirming pyrolization and composition affecting saturation.

Flints treated experimentally comprise two groups: those actually burned during primitive times and otherwise identical flints not subjected to burning. The TL properties of both groups were measured without prior knowledge on the part of the laboratory staff as to which were pyrolized. A microscopic study was subsequently carried out.

The easiest of the measurements obtained to evaluate is that determined from sample TB-4, from Bronze Age deposits, for numerous radiocarbon dates associated with Bronze Age materials in the Mediterranean region place the period between 4,000 and 4,500 years before the present (B.P.) (*8*). The calculated age of 4,500 ± 400 years B.P. since the burning of flint TB-4 obviously is in agreement, although it represents only a single sample.

The apparent age of 12,000 to 14,000 years B.P. measured for sample TB-7 was more difficult to assess as the associated culture has not been reported. No radiocarbon dates are therefore available for comparison. A somewhat later assemblage, lying just above the level from which this flint was removed, contains small backed bladelets and points loosely termed "gravettes" in Spain. The stratigraphic sequence is correct, and the age is in the expected range. Samples TB-6 and TB-8b come from closely similar strata falling between that containing sample TB-7 and the main suite of samples from the underlying Mousterian occupations. This is a transitional industry reflecting a developed Mousterian technology. The age of 20,000 years B.P. is stratigraphically appropriate as well as culturally acceptable.

Eleven samples are from lower sediments, all in association with Late Mousterian cultural materials. Specimens TB-1, TB-2, and TB-5 yield measurements suggesting a span of 28,000 to 35,000 years B.P. for the sediments from which they were removed. (The measurements for the earliest of these, sample TB-3, may be unreliable because of abnormal saturation characteristics.) Radiocarbon dates for the Late Mousterian of France (*9*) are comparable, ranging from 30,000 to 35,000 years B.P. for the close of the Mousterian. Thus, the Carigüela dates are in the range expected.

Finally, data obtained from the unburned set of "control" flints indicate not only that certain specimens possess storage capacity sufficient to have allowed valid age determinations well beyond 200,000 years had they been burned that long ago, but also that the characteristic nature of their glow curves is consistent enough to serve as a double-check against spurious dates obtained through inadvertent measurement of a flint which had not been pyrolized or which had been heated incompletely. Sample TB-8a is an example of this: The surface showed clear evidence of some burning but the glow was saturated.

Thus, we consider experimental work now completed adequate to demonstrate the feasibility of obtaining TL age determinations from burned flint, which are of the correct order of magnitude and have a potential range of use of greater than 100,000 years.

H. Y. Göksu, J. H. Fremlin
Birmingham University,
Birmingham, England
H. T. Irwin, R. Fryxell
Washington State University,
Pullman 99163

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10. Laboratory measurements were made at Birmingham University by H.Y.G. and J.H.F.; archeological and geological stratigraphic control and the collection of specimens were undertaken by H.T.I. and R.F. We thank Prof. M. Almagro, Museo Arquelogica Nacional de España, for collaboration in the fieldwork in Spain. Support for the TL measuring equipment was provided by the Wenner-Gren Foundation. This work was made possible through grants GS-2536 and GS-3005 from the National Science Foundation.

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Carbon Dioxide Hydrate and Floods on Mars

Abstract. *Ground ice on Mars probably consists largely of carbon dioxide hydrate,* $CO_2 \cdot 6H_2O$. *This hydrate dissociates upon release of pressure at temperatures between 0° and 10°C. The heat capacity of the ground would be sufficient to produce up to 4 percent (by volume) of water at a rate equal to that at which it can be drained away. Catastrophic dissociation of carbon dioxide hydrate during some past epoch when the near surface temperature was in this range would have produced chaotic terrain and flood channels.*

None of the features revealed by the 1971 Mariner 9 Mars orbiter has evoked more surprise than the huge channels in the equatorial zone, some as much as 40 km wide and hundreds of kilometers long. Accordant junctions, teardrop-shaped islands, braided reaches, and meandering courses indicate that these channels were shaped by running water (*1*). The widths and apparent depths of many channels indicate discharges much greater than that of the Amazon. Such discharges could only have been maintained for short periods. Indeed, the channels appear immature by comparison with river systems on Earth which evolved over geologic time and instead resemble catastrophic flood channels. The channeled scablands of Washington, a complex of deep channels carved in basalt in a few days or at most weeks by water released on the failure of an ice dam retaining glacial Lake Missoula (*2*), offer a particularly close analog, and landforms that in the scablands indicate extraordinary volumes and velocities of flow can be recognized in narrow-angle frames of martian channels (*3*). The scablands are the one terrestrial feature that approaches the martian channel systems in magnitude. Although the Lake Missoula flood was an exceptional and perhaps unique event in the geologic record, comparable floods appear to have been normal phenomena in the history of Mars.

Two of the conditions listed below are implied by any fluvial activity; the third is required by its catastrophic nature:

1) Surface temperatures and atmospheric pressures allowed the stability or at least the persistence of water on or near the surface at one or more epochs in martian history.

2) A source for the water existed.

3) A mechanism for generating or releasing liquid water at a rate rarely if ever matched on Earth operated repeatedly.

Explanations for the first two conditions have been advanced; the third is the principal concern of this report.

The mean surface temperature of Mars is well below the melting point of ice, and, although midday temperatures in the equatorial region may reach 25°C, diurnal warming affects only a shallow near-surface layer (*4*). The total atmospheric pressure is insufficient or barely sufficient to prevent water from boiling, and the water content of the atmosphere is extremely low. Various hypotheses have been proposed, however, which indicate that more clement epochs have occurred in the past. Recent studies (*5*) suggest that advective instability in the atmosphere permits the martian climate to be driven by changes in the planetary obliquity, the solar luminosity, or the albedo of the polar caps from one to the other of two stable states, one close to present conditions and one with higher pressures and temperatures that would allow liquid water at the surface in the equatorial zone.

Although evidence for its existence is only inferential, ground ice is widely believed to exist on Mars (*6–8*) and its melting would be the obvious source of water. The decay of ground ice was proposed as the cause of the massively fractured and slumped "chaotic terrain" revealed in 1969 by the Mariner 6 Mars orbiter (*6*). Although alternative origins for chaotic terrain have been advanced, the decay of ground ice

Fig. 1. Chaotic terrain apparently drained northward by flood channels. The arrow points to the feature interpreted by Maxwell *et al.* (*11*) as an impact crater drained southeastward. Chryse region of Mars; frame center, 27.9°W, 3.4°N; frame width, 500 km. Mariner 9 photograph 7758698.