

Thermoluminescence (TL) dating of burnt flints: problems, perspectives and some examples of application

Marco Martini^a, Emanuela Sibilìa^{a*}, Silvia Croci^a, Mauro Cremaschi^b

^aIstituto Nazionale di Fisica della Materia (INFN) e Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, via Cozzi 53, I-20125 Milan, Italy

^bDipartimento di Scienze della Terra, Università degli Studi di Milano, via Mangiagalli 34, I-20133 Milan, Italy

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Abstract – Thermoluminescence (TL) dating is a powerful tool in archaeology, and its reliability has been checked since the early 1970s. It is, in principle, specific for ceramic, but it can also be successfully applied to other materials of archaeological interest, provided that they have been submitted in the past to some kind of heating up to several hundreds of degrees centigrade. This is the case of prehistoric flint deliberately or accidentally burnt by ancient man. Illustrating the specific aspects of this application, we report the TL dating results of a group of burnt flints from three prehistoric sites in northern Italy. The first two, Ghiardo and Ghiardello, are open-air sites close to Reggio Emilia, at the fringe of the Apennine on Middle Pleistocene terraces. The third, Fumane, is a large cave system in the Venetian Pre-Alps, in the Lessini plateau, close to Verona. It includes a thick Palaeolithic sequence, spanning the whole first Pleniglacial period. © 2001 Éditions scientifiques et médicales Elsevier SAS

archaeometry / thermoluminescence / flint / palaeolithic

1. Introduction

TL dating techniques are complementary to radiocarbon dating: while the latter is applied to organic materials, the former are specific for materials containing insulating crystals submitted to some kind of heating in the past. The application of TL dating to archaeological and historical ceramics is now well assessed; uncertainties in the calculated ages in the order of 5–10% can be reached.

The possibility of applying TL to other fields and materials has also been explored. In particular, good results have been obtained in dating burnt flints, burnt stones, metallurgical slags, clay-cores of bronzes, volcanic lava, stalagmitic calcite and geological sediments [1, 2]. Among these applications, burnt flint dating is surely of great interest, particularly in palaeolithic geo-archaeological sites whose age is beyond the upper limit of radiocarbon (generally about 40 000 years).

Despite the problems encountered in this application, which we are going to discuss here, flint dating is widely used. There are many published results, extending from flints burnt only 2 000 years ago [3] to flints burnt about 2 500 000 years ago [4, 5]. The works of Valladas and co-workers [6–8] give good examples of the importance of TL dating of Palaeolithic sites. Their results played in fact a primary role in the revision of the chronology of the presence of Neanderthal man and of modern humans in the Middle-East [9].

2. Basics of thermoluminescence dating

The principles and procedures that are at the basis of TL dating have been presented in depth in various papers and books: a thorough discussion can be found in reference [1]. We will restrict ourselves here to a simplified description of the standard methods developed for ceramics, briefly summarising the main experimental sources of uncertainty. The specific problems connected with flints will be widely discussed later.

*Correspondence and reprints.

E-mail addresses: emanuela.sibilìa@unimib.it (E. Sibilìa), m.martini@unimib.it (M. Martini), mauro.cremaschi@unimi.it (M. Cremaschi).

Most clay constituents are thermoluminescent, i.e. they ‘store’ electrons in deep traps when alpha, beta and gamma radiation passes through them. A heating of the clay releases electrons from the traps and the recombination energy is delivered in the form of light: the thermoluminescence. The act of firing erases any previous geological TL due to the natural irradiation experienced by the constituent minerals; since then, the TL signal grows again with the age, the rate of growth being dependent on the natural radioactivity content of both pottery and burial soil.

Once the total dose absorbed by the sample since its last heating is measured, through the measure of its TL, and the rate of absorbed dose due to the radioactivity content of ceramic and soil is measured, the basic age equation for TL dating is:

$$\text{Age (years)} = \text{Total Absorbed Dose (Gy)} / \text{Annual Dose Rate (Gy/year)}$$

where Gy stands for Gray, the IS unit for the absorbed dose: 1 Gy = 1 J/kg.

There are two main techniques developed for TL dating: the fine-grain technique [10], which uses the polymineral fraction of the ceramics with sizes between 1 and 8 μm , and the inclusion technique [11], which uses only the grains of quartz of about 100–200 μm . Sampling is made with a low-speed drill (fine-grain) or by crushing in an agate mortar (inclusion).

The total absorbed dose is obtained from the measure of the TL of the sample, calibrated by artificial irradiation. Its evaluation can be difficult or even impossible in the presence of spurious thermoluminescence, an intrinsic non-dose-dependent emission [12]. Another disturbing effect is the anomalous fading, a leakage of trapped electrons during antiquity due to the instability of high temperature peaks [13]. Specific experimental tests must be routinely performed to check if both effects are absent.

In order to obtain the annual dose-rate, three main quantities have to be determined: alpha, beta and gamma dose-rates. The first two derive mainly from the radioactive content of the ceramics, while the last is essentially due to the radioactivity of the burial soil. Because alpha particles produce, for the same dose, a lower amount of TL than beta, their contribution must be weighted by a correction factor, the so-called *a*-value [1] that has to be evaluated for each sample. Additional correction factors take into account possible radioactive disequilibria and environmental situations: namely the precise contribution of thorium vs uranium (Th/U ratio), the extent of radon escape and the water content of the sherd (water absorbs radiation, reducing the effective dose). The difficulty in calculating or estimating this last quantity is one of

the main sources of uncertainty in TL dating and in the resulting final date that otherwise can be calculated with an error of $\pm 5\text{--}9\%$ [14].

3. Archaeological flints

Chert and flints are dense siliceous sedimentary rocks, present in nature as nodules or layers. From the geological point of view, they are not synonyms, and the discussion about their precise definition is open: the difference is related to the kind of geological formation [15]. Flints are compact silica nodules in Cretaceous chalk beds, while cherts are massive silica deposits formed by diagenesis of biogenic sea floor sediments or abiogenic saline lakes. From the TL dating point of view, we will consider them, however, as synonyms according to literature [1]: their basic component is in fact SiO_2 , occurring as opal-A (silica), opal-CT (cristobalite/tridymite with strong stacking disorder) and α -quartz. In particular, α -quartz is present in three crystalline varieties: mega-quartz (well-defined crystals of any size authigenic α -quartz, ordered over the long range), chalcedony (fibrous SiO_2 containing water in submicroscopic pores: the fibres are polycrystalline α -quartz with twinned crystals) and microquartz, which represents the prevailing phase in flints, and is an intergrowth of twinned hydrous granular α -quartz, ranging in size from less than 1 μm to 50 μm [16, 17]. Flints can form in different ways: for instance, bedded flints originate when diatom oozes change in opal-CT and α -quartz via a series of solution re-precipitation steps, while nodular flints derive from silicification of carbonates or direct precipitation of microquartz. The most common archaeological flints come from deposits formed in layers of limestone [17].

Flint was in widespread use by prehistoric humans: due to its hardness and conchoidal fracturing properties it was largely employed in manufacturing a large number of implements. Some of these artefacts were accidentally heated by falling into fire, some were deliberately heated in order to improve their properties. The burning, fortuitous or intentional, is obviously essential for the erasure of any previous geological signal.

4. Burnt flint dating

Goksu and co-workers [18] highlighted the possibility of burnt flint dating, presenting at the same time the limits and the specific problems relative to such materials. Beside the difficulties in sample prepara-

tion, TL measurements are complicated by very low TL sensitivity and sensitivity changes after irradiation and heating, regeneration TL [19], bleaching of the signal due to sunlight exposure, fading, spurious emission in case of presence of carbonates and incomplete erasure of geological TL due to insufficient heating. Moreover, the often very low concentration of radioactive elements in flints requires very sensitive measuring systems, and confers great relevance to the contribution of the ambiental gamma dose-rate.

While for pottery the sample preparation has been successfully assessed [10, 11], this is not the same for flints. In fact, the standard procedures are not applicable to flints, a serious problem being the modification of the signal as a consequence of the experimental operations.

The glow-curves of burnt flints are characterised by a short-living peak at 90–120 °C, which is then observed only after artificial irradiation, and by a stable broad high temperature peak centred at about 370–390 °C. *Figure 1* shows a typical natural TL glow-curve of a flint and the TL induced by two different doses of artificial β irradiation after preheating at 200 °C for 1 min. The lifetime of electrons in the high temperature traps has been estimated to be in the order of 50 million years for storage at 20 °C [20]. The intensity of the TL emission can vary by orders of magnitude from flint to flint, depending on the kind and concentration of traps in the sample, on its age and on the radioactivity field. The upper limit of flint dating is therefore not defined by the thermal stability of traps, but by their saturation level. In flints, TL growth vs dose is usually linear up to 100 Gy, reaching the saturation in the range 100–700 Gy, depending on the sample. Attempts to date flints with natural TL at the onset of saturation have also been done [21, 22].

4.1. Sample preparation and chemical treatments

The difficulty in sample preparation appears to be a major problem, due to the hardness of flints. Goksu and co-workers [18] used thin slices of samples to avoid spurious TL, regeneration TL and signal loss effects induced by the crushing in mortar. It was found, however, that with slices, allowance had to be made for transparency effects, except in the cases in which the alpha contribution to the annual dose-rate is negligible [20]. The need of signal normalisation from slice to slice has also been pointed out [23]. Other methods using coarse grains (100–150 μm) turned out to be applicable, after demonstrating [24] that both regeneration and spurious TL could be eliminated by washing with diluted HCl, being in most cases related to the presence of carbonates [12].

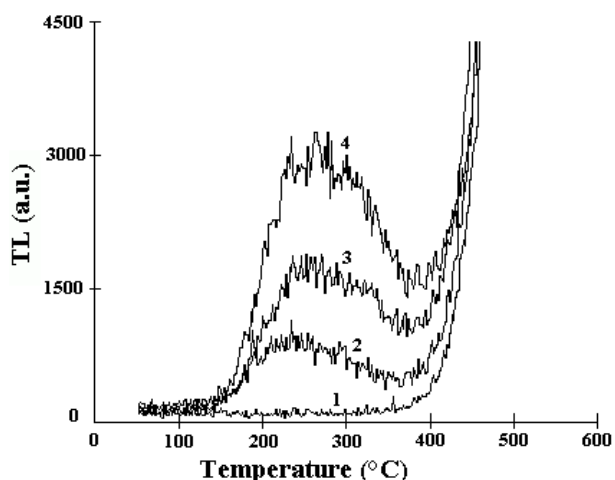


Figure 1. Some typical glow-curves of a flint. 1) Black body emission; 2) Natural TL; 3) Natural TL+ 52 Gy β ; 4) Natural TL+104 Gy β (preheating at 200 °C for 1 min).

Even the fine-grain technique, slightly modified, appeared to be a valid method [25]. In both techniques, the desired size was obtained by crushing in agate mortar. This system has, however, the disadvantages that only a small amount of fine grains (1–8 μm) can be obtained and that the mechanical shocks can be extremely strong. Moreover, the use of agate mortars can lead to sample contamination, having the agate almost the same hardness of flint. We found that the use of a steel hydraulic press for fracturing the sample presents interesting advantages: with gradual compression, intense shock can be avoided and a comparative higher amount of fine-grain material can be quickly and effortlessly obtained.

As mentioned, chemical treatments for the removal of any undesirable spurious emission are necessary: diluted HCl, HF or acetic acid are recommended, depending on the type of carbonates present, if any, and on the type of flint. The effect of the elimination of carbonates by acetic acid washing is presented in *figure 2*. An intense spurious TL is evident in the untreated sample, and completely disappears after the chemical attack.

Nevertheless, we believe that great care should be used even with slight acid treatments: sometimes we observed, beside the spurious TL elimination, other changes in the TL behaviour of the attacked aliquots. If in most cases the acetic acid wash improves the TL properties, eliminating the unstable and non-dose-dependent components in the glow-curves, in a few cases we found undesirable effects, like decrease in the linearity of TL growth vs dose, or variation in TL

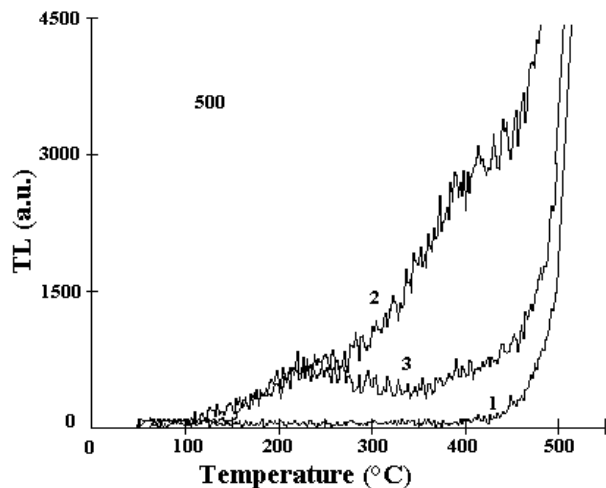


Figure 2. Flint BR11: effectiveness of acetic acid washing in the elimination of carbonates. 1) Black body emission; 2) Natural TL+198 Gy β , as received; 3) Natural TL+198 Gy β , pre-washed in diluted acetic acid (1:1) for 30 min at room temperature.

sensitivity to alpha irradiation. It appears to be odd, because acetic acid should not affect α -quartz. In certain flints, however, being the microcrystals intensely deformed by the intergrowth, some kind of modifications of surface defects induced by acid cannot be excluded.

Concluding, a standard method for sample preparation and treatment has not been established yet, and perhaps does not exist, reflecting the great variability of TL characteristics from flint to flint: for each sample, the most suitable treatment has to be found.

4.2. Detection of heating

Determining whether a flint has been burnt or not is essential for the suitability of TL dating: a well burnt flint should have been heated, depending on the duration of the treatment, at a temperature in the range of 300–400 °C according to Aitken [1], or at 450 °C at least, according to Valladas [26]. The morphological appearance (crackling, reddening, vitreous luster) is not a secure indication of heating, being sometimes absent in surely burnt flints, or caused by non-thermal effects in raw materials [27]. However, many physical properties of flints change after thermal treatment, causing, for instance, a broadening of X-ray diffraction lines [28], changes in the Mossbauer spectrum [29] and in the ESR signal [30]. Unfortunately, these differences can be appreciated only by comparison with the signal of unheated aliquots. Alternative

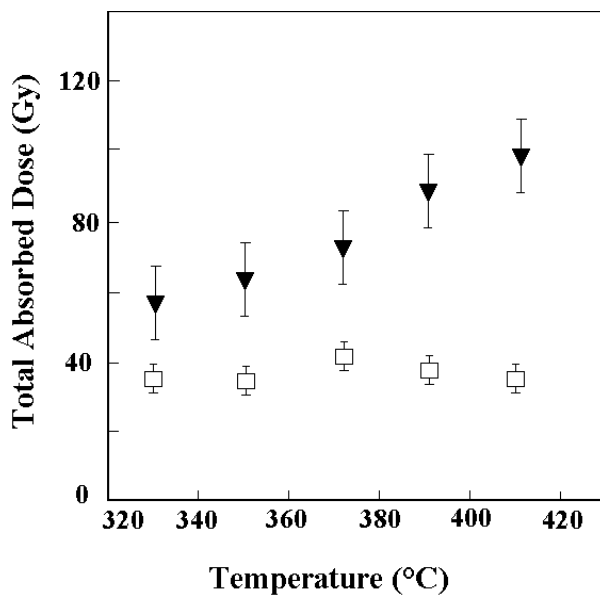


Figure 3. Total absorbed dose versus temperature for a well burnt flint (squares) and for a not well burnt flint (triangles). Each point represents the total absorbed dose obtained in a temperature interval of 20 °C centred at the corresponding abscissa.

methods, based on TL properties, have been developed. Melcher and Zimmermann [31] suggested that the heating could be detected by comparison of the total absorbed dose with the dose needed to saturate the natural TL signal. Low saturation doses and partial annealing cause problems in the interpretation of the results. Valladas [32] and Goksu [27] proposed tests based on the temperature dependent sensitivity changes of the 380 °C and 110 °C peaks, respectively. The first method is not sensitive enough for thermal treatments below 500 °C, and the second is complicated by the lack of knowledge about long term stability of the low temperature peak.

The plateau test [31] is the safest way to ascertain if a sufficient temperature has been reached: it can be performed plotting the total absorbed doses obtained in different temperature intervals as a function of the temperature. For well burnt flints, a plateau is obtained, otherwise the dose steadily grows with temperature, as shown in *figure 3*. The analysis of the glow-curve shape can also give indication of burning [26]: in non-heated flints a peak at about 450 °C is observed in the natural TL glow-curve, disappearing in the curve obtained after artificial irradiation on the same aliquot, characterised by the usual peak at about 380 °C (*figure 4*).

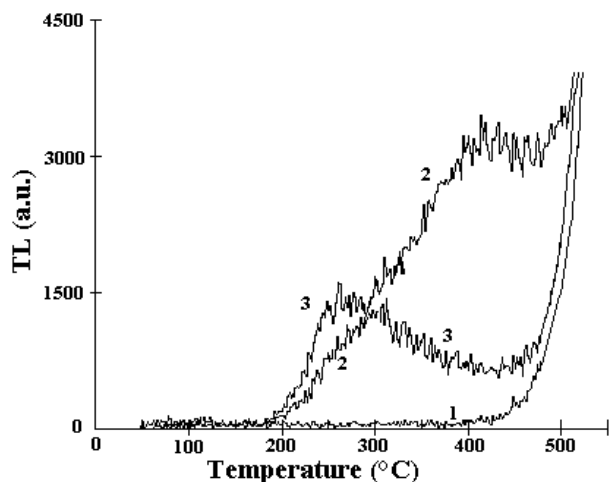


Figure 4. TL behaviour of a not well burnt flint. 1) Black body emission; 2) Natural TL; 3) TL induced by 98 Gy β irradiation, same aliquot, after 20 s at 200 °C. The 480 °C peak is present only in the natural signal, as a consequence of insufficient heating.

4.3. Optical bleaching, anomalous fading, sensitivity and sensitivity changes

Solar light can affect the TL of a sample, inducing trap depletion or transfer of trapped electrons [33], causing incorrect evaluations of the total absorbed dose. The effect of solar and UV exposure on the TL of flints was the subject of several studies [20, 31, 34, 35], leading to dissimilar results, hence again underlining the great variability in the TL behaviour of these materials. Exposure to sunlight must always be avoided, implying that the samples have to be transferred to black containers as soon as excavated and handled and treated only under safe red laboratory light. The removal of the outer 2 mm surface layer is prescribed: the inner part was found, in almost all cases, free from bleaching and other undesirable effects.

Another phenomenon that can affect the TL of a sample is the anomalous fading [13], which is fundamentally a non-thermal emission of trapped electrons, leading to an underestimate of the total absorbed dose. To verify the absence of this effect, specific tests have to be performed, consisting of the comparison of the TL of irradiated samples measured after different times from the irradiation. Experiments completed on different samples, at different storage temperature and for different times [36, 37] showed the absence of short term fading. Flints seem to be free from such effect, but it is nevertheless recommended to verify it for each sample.

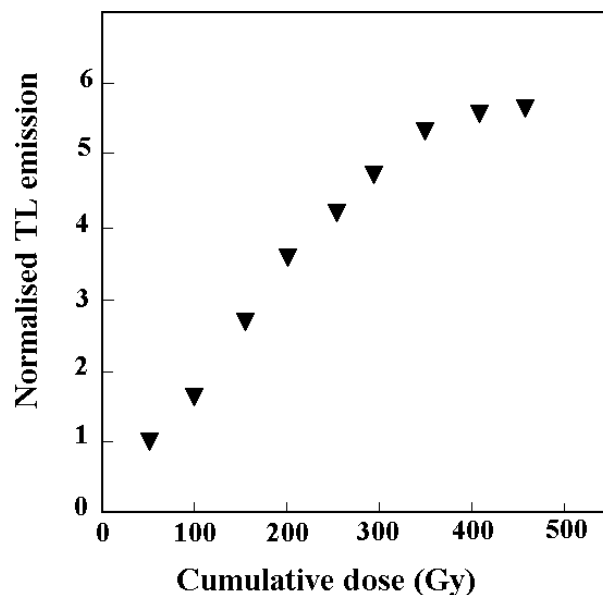


Figure 5. Variation of the TL emission of the 380 °C peak of a single sample, repeatedly irradiated with the same dose (50 Gy β).

The TL sensitivity of flints is normally low compared to that of ceramics. It implies that relatively high radiation doses are necessary to get a TL signal measurable with sufficient accuracy, and therefore young flints (burnt more recently than several thousand years ago) are difficult to be dated. This is not normally a problem, because in historical settlements TL dating can be alternatively performed on ceramics.

TL sensitivity depends on the heat treatments experienced: sensitivity changes are possibly correlated to variations in the optical absorption coefficient [20, 23]. Since TL measurements imply heating, sensitivity changes can be induced in a sample submitted to more than one reading. Huxtable and Jacobi [38] found an enhancement of more than 40% in the TL emission of a single aliquot. In some cases, therefore, all techniques requiring repeated measurements on a single fraction of sample, like the supralinearity correction [39] and the single-aliquot method [40], must be used with extreme attention. Dealing with flints characterised by strong sensitivity changes is usual. An example is reported in *figure 5*, showing the variation of the TL intensity of a single fine-grain disc repeatedly irradiated with the same dose.

4.4. Dose-rate evaluation

The annual dose-rate is the sum of two contributions: the internal dose-rate, due to the concentrations

of radioactive elements of the sample, and the external dose-rate, due to the radioactivity of the burial site. In both cases, the main radioisotopes involved are ^{232}Th , ^{238}U and ^{40}K . The decay of the uranium and thorium chains determines an irradiation of α and β particles and γ -rays, while potassium is a β and γ emitter.

Flints usually contain 0.5–1 part per million (ppm) of uranium, 0.3–2.0 ppm of thorium and 100–1 000 ppm of potassium. Uranium and thorium concentrations can be obtained using ZnS(Ag) scintillators for thick source total alpha counting or by high resolution gamma spectroscopy. The ratio between thorium and uranium concentrations (Th/U ratio) can be estimated using the pairs counting method [1]. In most flints, contrary to ceramics, uranium is more abundant than thorium. Potassium content is usually measured by flame photometry.

The spatial distribution of radioisotopes in flints, examined by fission track mapping [35], image intensifier photography of TL [37] and neutron activation analysis [1], was found to be homogeneous in almost all studied cases. In the archaeological flints studied by Mercier [41], the uranium series was in secular equilibrium, indicating the absence of migration of radioisotopes between environment and sample.

Due to the different ranges of α -, β - and γ -rays (tens of microns, a few millimetres and about a metre respectively), their contribution to the internal dose-rate is different. As a consequence of the small size of archaeological flints, γ emission contributes less than 1% to the dose. The evaluation of the dominant α and β components is complicated by their different efficiency in inducing TL. Alpha efficiency is about 1/10 of beta and gamma [1], but can vary by a factor of three from flint to flint [8]. Considering that in some cases the α radiation accounts for 50% of the internal dose-rate, high precision in evaluating the relative alpha efficiency (a -factor) is essential. Internal annual dose-rate usually ranges from 0.05 to 1.50 mGy/year.

Environmental radioactivity is responsible for the external contribution to the annual dose-rate. It is due to the radioisotope content of the burial soil (uranium, thorium and potassium), and to cosmic rays. The short range of α and β rays prevent them from penetrating more than 1–2 mm inside the flint, while γ and cosmic rays cross it completely. The elimination of the outside layer of the sample circumvents the problem of taking into account the first two contributions.

Several techniques are used to evaluate the average external dose-rate relative to the burial period of a flint, mainly in-situ dosimetry techniques [42], γ -ray spectrometry with portable detector and direct dose-

rate evaluation with ionisation chamber for environmental dosimetry [1]. The first technique consists of burying synthetic dosimeters (CaF_2 , CaSO_4 , LiF , Al_2O_3) at the flint burial site for a period of about 1 year: in such a way the average attenuation due to water content and its seasonal fluctuations are taken into account. External dose-rate usually ranges from 0.5 to 1.50 mGy/year.

As a consequence of the natural spread of both internal and external dose-rates, we can deal with flints for which the internal apportion is dominant, while for others it is practically negligible. In the first case, the uniformity of radioactivity distribution in the sample becomes particularly important. The comparison of the total absorbed doses is obtained in the same sample using both fine and coarse grains and can give an easily achievable indication about significant inhomogeneity in the spatial distribution of radioactive elements [1].

Due to the very low level of internal radioactivity of flints in most cases, however, the external contribution is dominant, being sometimes more than 80% of the total [6, 7]: precision and accuracy in its evaluation become essential for the precision and accuracy of the calculated age. Water content of flints is usually negligible, due to their compactness.

4.5. Data uncertainties

TL dating techniques require quite a large number of experimental evaluations to obtain the age of a sample: each of them is accompanied, like every physical measurement, by experimental uncertainties. The procedure for error-limit assessment [14] is to calculate the percentage error in the date corresponding to a given error in each quantity or parameter evaluated, and to obtain the overall error as the square root of the sum of the squares of individual errors. This implies a Gaussian distribution of the scatter of the measured values, using the standard deviation σ as a measure of the error limit. There will be a 68% probability that the true age lies within this limit, and a 95.5% probability that it lies within limits twice as wide.

If TL dating is performed on more than three supposed coeval samples another error is quoted, which corresponds to the standard error on the average age. It is normally less than the first one and gives an indication of the precision of the context dating. For ceramics, the present accuracy of TL dating is between $\pm 5\%$ and $\pm 10\%$ of the age. For flints, due to the described experimental problems, and to the characteristics of the material, the error is normally higher, ranging from $\pm 10\%$ to more than $\pm 20\%$ of the age.

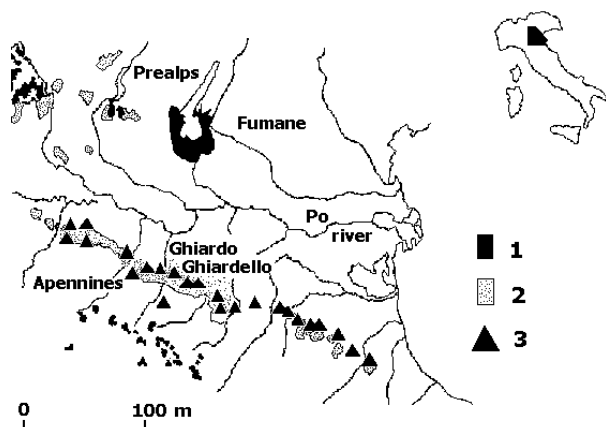


Figure 6. Location map of the palaeolithic sites dated. 1) Moraine systems; 2) Main loess deposits; 3) Palaeolithic sites at the Apennine fringe.

5. TL dating of flints: some examples

We report the results obtained from the study of the TL properties of 20 apparently burnt flints from three Palaeolithic archaeological sites in northern Italy, namely Ghiardo, Ghiardello and Fumane (figure 6). The first two are open-air sites close to Reggio Emilia, located at the fringe of the Apennine on Middle Pleistocene terraces [43]. Fumane is a large cave system in the Venetian Pre-Alps, in the Lessini plateau, close to Verona. It includes a thick Palaeolithic sequence, spanning the whole first Pleniglacial period [44].

The TL studies were aimed not only at dating the samples, but also at understanding their TL behaviour and the effects of acid treatments. Measurements have been carried out using both a conventional 2-D system and a highly sensitive 3-D system to detect the emitted wavelengths.

The flints were also analysed to determine their composition through X-ray diffraction and scanning electron microscopy with microprobe.

5.1. The Ghiardo and Ghiardello sites

The top of the Pleistocene terraces at Ghiardo is covered by Pleistocene loess, which was dated to the late Middle Pleistocene on the basis of the palaeopedological characteristics of the soils. The loess includes archaeological sites consisting of clusters of Palaeolithic artefacts (figure 7) which were attributed to late Acheulean on the basis of their typological characteristics. The archaeological context of this site

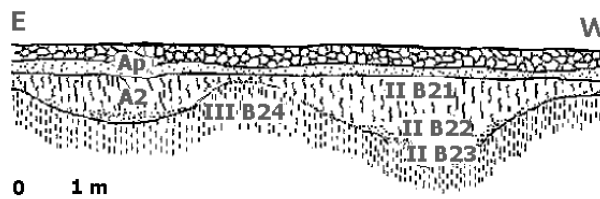


Figure 7. Stratigraphic sequence of the Ghiardo site; the palaeolithic artefacts are concentrated inside the II B23 horizon.

is quite poor, as the soil-forming processes affecting the loess in which they are included destroyed most of the organic remnants. A systematic excavation conducted at Ghiardo in the 1980s [43, 45] gave consistent information on the stratigraphic position of the lithics and on the intersite organisation. From the stratigraphic point of view, the artefacts lie at the base of the loess layer, at the interface between it and the buried vertisol developed in clay (figure 8). Vertical dispersion of the artefacts is poor, and they have to be regarded as strictly in situ on a palaeosurface covered by loess deposit. From the topographic point of view, the artefacts are concentrated in a few clusters, one of which has been systematically investigated. It consists

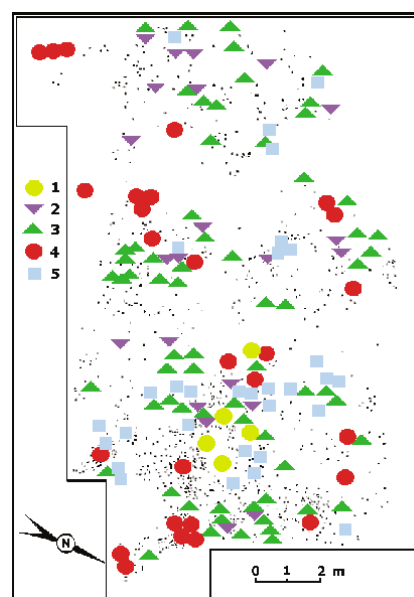


Figure 8. Ghiardo site: distribution of artefacts in the excavated area. 1) Artefacts with fire damage; 2) Levallois flakes with damages due to use; 3) Tools; 4) Cores; 5) Broken stones.

of a lithic workshop in which some flakes are refitted together. There is a hearth indicated by stones, charcoal and a burnt bone, wrapped by Fe-Mn concretions and by burnt flint artefacts, one of which was later devoted to TL measurements.

The Ghiardello site is located about 10 km south-east of Ghiardo, and displays the same stratigraphic sequence. Artefacts with typological characteristics and a stratigraphic position similar to those from Ghiardo were collected from a pit exposed by quarrying. One of them had evidence of exposure to fire.

As far as lithic industry and stratigraphic position is concerned [46], some hundreds of sites similar to Ghiardo and Ghiardello exist on the loess-covered terraces at the northern fringe of the Apennine from Piacenza to Rimini. Before TL results discussed in this paper, these sites were attributed to the Acheulean culture and the loess including them was dated to the Middle Pleistocene.

5.2. The Fumane shelter

Archaeological excavations in the Fumane shelter started in the 1950s thanks to a team of the Museo di Storia Naturale di Verona, and are now going on under the direction of A. Broglio (Istituto di Geologia e Paleontologia, Università di Ferrara) and one of the authors (M.C.). The sedimentary fill of the atrial part of the cave has been exposed in full. It is about 12 m thick and includes, from the very base, Middle and Upper Palaeolithic living floors quite rich in artefacts, fauna remains and archaeological structures such as structured hearths and stone wind breaks (*figure 9*).

From the stratigraphic point of view, these main units can be distinguished as follows:

- Sand Unit (S). At the base of the sequence, colluvial sand, intercalated to small circular hearths and Middle Palaeolithic artefacts, were found;
- Breccia Unit (BR). It is composed of angular stone deposits, mainly originated from frost shattering of the shelter. Some layers include an important loess fraction. Archaeological evidence consists of Mousterian artefacts associated with living floors with structured hearths, separated by levels poor in artefacts;
- Anthropogenic Unit (A). It consists of layers strongly affected by human activity. Structured hearths and several structures connected to dwelling are present. This unit is attributed to Mousterian and Aurignacian;
- Landslide Unit (D). It is a large block due to a vault collapse. The archaeological evidences are scarce, among them a Gravettian backed point.

The environmental changes of the late stage 5 to the stage 2 of the glacial Pleistocene are fully represented

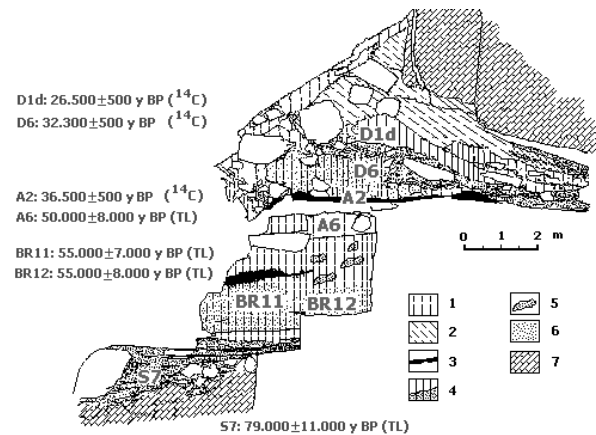


Figure 9. Stratigraphic sequence of the Fumane shelter. 1) Soils; 2) Landslide unit; 3) Living floors; 4) Loess and sandy loess; 5) Concretions; 6) Sand; 7) Bedrock.

in the sequence. Wet and moderately cold conditions dominate in the Sand Unit. The Breccia Unit is indicative of a full glacial period and, after returning to a dry and cold condition, is conducive to loess sedimentation. Periglacial features represent several cold spells. In Unit A, interstadial features and soil formation are better represented, and the return to severe cold conditions is indicated by the upper rock-fall, which sealed the entrance of the cave during stage 2.

Several radiocarbon dating results [47] refer the A Unit, including Aurignacian, to the final stage 3. Up to now, no absolute data were obtained for the lower units as they exceed the limit of radiocarbon techniques. Their attribution was based upon climatostratigraphy.

5.3. Experimental details and results

The standard procedure for sample preparation adopted in the laboratory consists of the elimination of the outer layer of the flint (2 mm) with a diamond saw, followed by crushing with a steel hydraulic press with slow and gradual compression [48]. As mentioned before, this procedure was found to be advantageous in minimising both the mechanical shocks and the waste of sample. The powder obtained is then selected in size, depending on the technique to be used, and eventually submitted to chemical treatments. The fraction $1 < \phi < 8 \mu\text{m}$ was used for both conventional and wavelength resolved TL measurements, as well as for X-ray diffractometry. The fraction $10 < \phi < 64 \mu\text{m}$ was utilised for electron micros

copy with microprobe. At any stage of preparation, flints are never exposed to solar or white light, but only to red laboratory light.

TL measurements have been carried out using the fine-grain technique. The system used for conventional TL measurements is home-made, consisting of an oven for controlled heating, where the glow-curves are measured in ultra pure N₂ atmosphere, at a heating rate of 8 °C/s, using a photon counting technique with an EMI 9635QB photomultiplier tube coupled to Corning BG12 blue filters. (PC-interfaced system and software by AeDI-Milano). Artificial irradiations were performed using a 1 400 MBq ⁹⁰Sr-⁹⁰Y beta source (Dose-rate: 1.62 Gy/min), an X-ray tube (operating conditions: 80 kV, 5 mA; Dose-rate 1.1 Gy/s), and a 37 MBq ²⁴¹Am alpha source (Dose-rate: 14.8 Gy/min). Radioactivity analyses were made using ZnS (Ag) scintillators for thick source total alpha counting, and flame photometry for potassium concentration measurements.

To study the wavelengths of TL emission a high sensitivity homemade apparatus has been used, with a detector consisting of a two-stage micro-channel plate (MCP) with a 512-photodiode array. The whole system, cooled by a Peltier control unit, reaches a signal-to-noise ratio comparable with that of a photomultiplier. The spectra are corrected for the wavelength response of the detection system. Detailed information are reported elsewhere [49].

X-ray diffractometry was performed with a PW1719BASED system, detection limit 0.5%, while for SEM analyses a Cambridge Stetoscan 250 with Link AN10000 microprobe (detection limit 0.2%) was used.

For all flints, complete sets of measurements were performed on untreated samples as well as on samples submitted to 1 h wash in acetic acid (dilution 1:1 at room temperature) and to 30 min wash in HCl 1 N at room temperature.

X-ray diffraction and microscopy analyses showed that, beyond the microcrystalline SiO₂ matrix, carbonates were present in almost all flints. Megaquartz, calcite and aragonite were found only in a few samples. Neither magnesite nor dolomite was detected. Through SEM analyses, we observed that both acid treatments were effective in the elimination of carbonates: for TL dating measurements, we used therefore the samples treated in acetic acid, less susceptible than HCl to induce undesirable effects on the TL characteristics of the samples. The presence of carbonates is in almost all cases associated to an intense spurious TL emission. Its elimination was often, but not always, obtained after chemical treatment (such a case is illustrated in *figure 2*). The TL

behaviour of treated samples usually improved, but in two cases definitely got worse. These observations suggest that carbonates alone cannot always be considered responsible of non-regular TL characteristics, as previously noted on archaeological ceramics [12].

The verification of the complete erasure of the TL signal as a consequence of the heating in the past was made following Melcher and Zimmermann [31] and Valladas [26]. Samples exhibiting the peak at 450 °C in the natural TL, like that shown in *figure 4*, were rejected.

The cases in which burning was not enough to fully erase the TL signal are not evident from the observation of the glow-curve shapes, but they were detected from the study of the stability of the signal vs temperature, as previously mentioned and illustrated in *figure 3*. Owing to the impossibility of determining the total absorbed dose, such flints could not be dated.

After this screening, we found that only six flints were well burnt: all of them showed a good TL behaviour and the total absorbed doses could be obtained with an accuracy of 10–13%. Anyway, it must be noted that almost all samples were characterised by strong sensitivity changes after irradiation and heating.

Wavelength resolved TL measurements have been carried out on fine-grain samples, previously washed in acetic acid. The very weak emission did not allow precise spectral measurements of natural TL. A rough estimate of the TL spectral distribution gave, however, results very similar to the spectral distribution observed after artificial irradiations at various doses.

As an example, in *figure 10* is reported a contour plot obtained from a 3-D spectrum of a sample X-irradiated with 1.5×10^4 Gy. The spectral data have been smoothed and corrected for the spectrometer response. The spectrum shows the main emission regions that have been detected, with different relative intensities, in all the samples measured: a first UV region at 260–330 nm, a second UV-blue region at 350–450 nm and a third red region at 580–640 nm. They are not always contemporarily present, and appear to be due to a superposition of different peaks, whose relative intensities vary from flint to flint. The UV-blue emission is commonly found in quartz and is selected by the photomultiplier response plus filter cut-off combination typical of the 2-D TL measurements; its characteristics have been fully investigated [50]. The red emission has already been observed by Wintle and Aitken [20] and by Huntley and co-workers [51], who used a red-sensitive photomultiplier and appropriate filters.

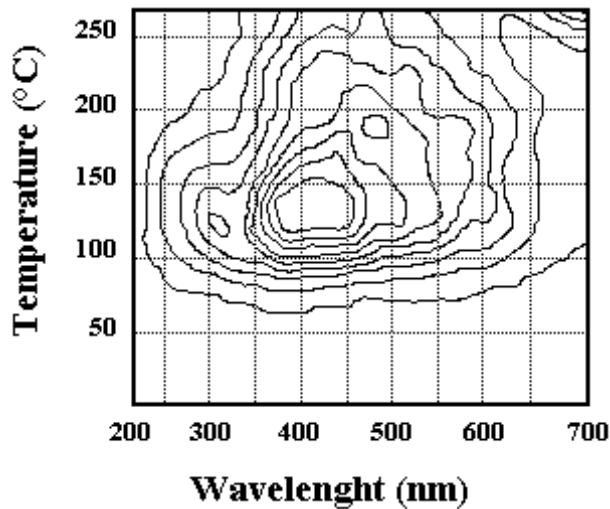


Figure 10. Wavelength resolved TL emission of flint 6, after 1.5×10^4 Gy X-ray irradiation. Contour plot.

The further UV emission has not been reported so far. It seems to have good dosimetric properties, even if our results are not conclusive yet, needing further study.

The effect of pre-heating at 100 °C for 1 min was investigated, as well as possible changes in the emission wavelengths in the spectra of the second and third glows. Measurements have also been made on surely unburnt flints. Only preliminary results have been obtained till now, but it seems that, for these samples, heating treatments do not affect the emission spectra.

From the 20 flints we started with, 14 had to be rejected: eight because they were not burnt and six because they were incompletely burnt. Only six were dated (four from Fumane, and one each for the other sites), and the results are summarised in *tables I and II*. Water content of flints was negligible. For two samples the external contribution to the annual dose-rate, obtained through radioactivity measurements on the excavation soils, was predominant, even if the concentrations of radioactivity were unusually low. It was impossible to perform any measurement of the seasonal variations in the humidity of the site. The quoted overall errors take into account therefore a fluctuation from 25% to 100% of saturation water in soils, and are consequently higher than expected with the recommended procedures.

6. Conclusions

Being aware that our data, obtained from a single sample per stratum, cannot be regarded as ultimate

Table I. Radioactivity data.

Sample	Layer	^{238}U (ppm)	^{232}Th (ppm)	Th/U ratio	K_2O (%)	<i>a</i> factor
6	A6	0.6	0.5	0.8	0.09	0.25
Soil		2.2	7.0	3.2	0.48	
11	BR11	0.2	0.2	1.0	0.01	0.15
Soil		2.4	7.2	3.0	0.24	
12	BR12	0.7	0.7	1.0	0.12	0.11
Soil		1.9	6.1	3.0		
7	S7	0.2	0.2	1.0	0.01	0.18
Soil		1.6	4.9	3.0	0.32	
GH	IVB23t	0.25	0.20	0.8	0.30	0.13
Soil		3.33	10.6	3.2	1.2	
GHL	IIB22t	0.26	0.23	0.9	0.29	0.10
Soil		3.80	11.8	3.1	1.1	

Table II. TL dating results.

Sample	ED (Gy)	Dose-rate (Gy/ka)	External dose-rate (%)	Age (ka)
Fumane				
A6	90 ± 10	1.78 ± 0.12	41	50 ± 8
BR11	72 ± 7	1.31 ± 0.10	35	55 ± 7
BR12	45 ± 7	0.79 ± 0.09	85	57 ± 8
S7	61 ± 7	0.77 ± 0.08	77	79 ± 11
Ghiardo				
GH	95 ± 10	1.57 ± 0.13	61	61 ± 9
Ghiardello				
GHL	114.0 ± 16	1.57 ± 0.16	64	73 ± 11

dating results, their consistency with the stratigraphy is at least encouraging: if confirmed by further work, they could add useful information to the archaeological and palaeoenvironmental history of a key Pleistocene period, up to now poorly dated. In fact, these results could have relevant consequences on both archaeological and geological fields. From the archaeological point of view, they could suggest the attribution of many loess sites of the Apennine fringe to the Mousterian culture, indicating an intensive occupation of loess area along both sides of the Po plain by the Mousterian hunter. In the perspective of Quaternary geology, these data would indicate that the bulk of loess sedimentation in the Po basin dates back to the glacial Upper Pleistocene, and that the later argilluviation processes which acted on the loess covers were very effective.

Moreover, the data from the Fumane shelter would allow the correlation of the base of the Sand Unit with the stage 4 and the Breccia unit with the stage 3, and would largely improve the quality of the palaeoenvi-

ronmental information on the site. They would furthermore represent the oldest datings for Mousterian deposits in northern Italy.

It is worth mentioning that the data here reported are in good agreement with other TL results obtained for the site of Bagaggera, near Lecco, in northern Italy, (OXTL-750f, $60\,500 \pm 7\,500$ years B.P. [52]). This site, similarly to Ghiardo, was uncovered at the base of a loess deposit.

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