THERMOLUMINESCENCE DATING OF ART OBJECTS

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Speaking before the Royal Society on October 28, 1663, the English chemist Robert Boyle described the phenomenon of thermoluminescence (TL) for the first time. He had studied a remarkable diamond that gave a faint glow when placed on the warmest part of his body. We now know that what Boyle observed was the result of millions of years' exposure to radiation from small quantities of uranium and thorium and radioactive potassium present in the diamond and its geological matrix. Many minerals are thermoluminescent to some degree, but most of these require sensitive instruments to detect and measure the glow.

The atoms in crystalline materials are arranged in regular arrays, but natural crystals, such as minerals, usually have defects (impurity ions, stress dislocations, and the like) which interrupt this regularity and when present give rise to the phenomenon of thermoluminescence in the following way. Some of these defect sites are attractive to electrons and when ionizing radiation --alpha and beta particles and gamma rays--passes through the crystal, some of the electrons knocked loose from atoms are trapped there. When the crystal is subsequently heated, the electrons are freed, and in the process of recombining with an atom, each electron emits a photon--light measurable in the laboratory as thermoluminescence (TL). The amount of light released is proportional to the dose of radiation absorbed by the crystal. After heating, no TL is measurable until a further radiation dose is given to the material, as the electron traps have been emptied.

This "zeroing" is the basis for thermoluminescence dating of ceramics (which are made of small grains of clay and other minerals such as quartz and feldspars), as the accumulation of thermoluminescence is set to zero when the object is fired. If the thermoluminescence of a clay pot were measured before firing, the light accumulated by the clay minerals over perhaps millions of years would be detected, but the firing heats the clay to a temperature of 600-1000C, and releases that TL. Immediately after firing, if the TL were then measured by heating a sample of the pot, there would be no light observed (except for the thermal, or red-hot, glow) even by the extremely sensitive light detector, a photomultiplier tube, used in the laboratory. Once the fired clay cools down, the radioactive materials present in the clay and in the environment start the accumulation of trapped electrons again. If the TL acquired since the c lay was fired is compared to that resulting from known calibration doses, the radiation dose acquired since firing can be determined. The rate at which this dose builds up is then computed from measurements of the radioactivity of the clay and its environment, and the number of years since the pot's last firing can be found by dividing the accumulated dose (rads) by the dose rate (rads/year). The fundamental assumption in TL dating is that the dose rate has been constant since the clay was fired. Except for a very few sites thus far studied where uranium is moved by acidic groundwater, this assumption has proven to be valid within experimental errors by dating programs at Oxford University using known age material. TL is an absolute method for determining age, not relying on other, similar-aged material, or material from the same region, for comparison. This seemingly simple calculation, though, is complicated by the large number of quantities which must be measured to obtain the most accurate figure for the dose rate, and is subject to a number of pitfalls that are properties of particular clays or sites and which limit the precision of the age calculation. Under the most ideal circumstances, the best dates so far obtained have error limits of about +-15 per cent of the age for single samples, +-5-7 per cent when the average age of several samples from the same archaeological context is used. As discussed below, the error limits for art objects are usually greater.

Under ideal conditions, an archaeological context is dated using many sherds, each weighing several grams, which are partially or wholly destroyed in the process. Ideally, each sherd would have been packed in a waterproof container along with its surrounding soil so that the moisture content of pottery and soil could be evaluated. A highly sensitive thermoluminescent dosimeter may be placed in the hole from which the sherd was taken and left for a year so that the environmental dose rate may be mesured. (Sensitive gamma radioactivity counters are now often used at the site to make the measurement in a matter of hours.) The large size of the samples permits making the battery of test measurements that are necessary.

In dating art objects, one is limited both in the amount of sample that can be obtained and in the information available about the environment, and these limitations affect the precision in the TL age that can be attained. Usually only a few tens of milligrams (the powder from a hole the size of a grain of rice to that of a large pea) can be drilled from an inconspicuous place on the object, so that the number of measurements that can be made is limited to the most essential ones, at a reduced level of precision. Most pieces are thoroughly cleaned of burial soil by the time they are submitted for dating, and of course no dosimeters can be buried at the generally unknown discovery site, so that it becomes necessary to take a range of possible environmental dose rates into the calculation rather than actual measurements. Because of these limitations, the error limits on the TL age for art objects are seldom better than +-20 per cent and may sometimes be 30-50 per cent if the internal radioactivity of the sample is low and one has to assume possible ranges of major parameters. This level of precision is adequate for the purposes of authentication: either the object is old (and of the approximately correct age), or it has been fired recently. In part, this relatively poor precision is due to constraints on time. When all measurements are made on the ideal sherds above, no more than two samples per week can be dated, so that it may take a month's work to date a context. For authenticity testing, the lack of some important data makes unworthwhile some measurements which are time-consuming but could lead to somewhat better precision. Sometimes one sees better precision claimed for TL dates, but the error limits may not include all known sources of error, especially systematic errors inherent in a particular clay or site, but only the random errors of measurement. (In some circumstances where there is a large body of known age material and very uniform geology, as on the great Loess Plateau in central China, some of the internal and environmental parameters can be determined to fall in a narrow range by "reverse dating". This is very helpful in obtaining more precise dates for these objects, although some objects may fall outside the general range of parameters and the TL age may then be slightly in error.) There are some additional considerations with respect to pieces which have been restored. Samples from a number of areas on the piece may be necessary if there is extensive skillful restoration, since parts of the object may be of different ages. Further complicating the situation is the refiring of objects -- at one time occasionally part of the restoration process, but fortunately extremely rare. If the piece were x-rayed at some point, the TL age could be invalidated unless the conditions of exposure were known, and a correction made. Fortunately, techniques for determining whether an object has been x-rayed have been developed and it is unlikely that such treatment, if it accounted for a sizable fraction of the TL signal, would go unobserved.

Before going on to a description of the process of obtaining a date, it would be worthwhile to discuss the types of material amenable to dating by TL. Generally speaking, any mineral material that has been heated above 500C at the time in which you are interested is a possible candidate. Terra cottas are the most straightforward to analyze, as clay must be heated at least to 600C to hold together as all. In the area of Asian ceramics, the early terra cottas, from China and India, present a variety of different clays, the majority of which are quite well behaved. By "well behaved", we mean a clay which has a good TL sensitivity (high light output for a given dose of radiation), is free from spurious, or chemi-, luminescence, which can make TL measurements difficult or impossible in some cases, and has a light output proportional to the radiation dose. Another problem often found in clays from the Near East, Cyprus, and occasionally from Italy, is anomalous fading, where part of the TL signal is not stable with time, leading to underestimates of age by up to 50 per cent. It is possible to correct for this up to a point, but the measurements involve long waiting periods for irradiated samples held at elevated temperatures to accelerate the fading effect. Some of the nearly white clays from the Chinese T'ang dynasty are marginal for TL dating, but most of these are at least sufficiently good to determine whether the object was fired in antiquity or not. Ceramics from Indonesia and much of Oceania are not suitable for TL dating (and virtually all objects from West Mexico in the New World share this unfortunate problem). As first stoneware, and then porcelain, became the preferred ware, TL dating begins to run into difficulty. Usually Chinese proto-porcelains prior to T'ang can be dated conventionally, porcelains cannot. Suwankalok highfired wares from Thailand have too low a signal for measurements. There are two problems that may appear with these materials. First, the white kaolinite clay that the potters used has a very low TL sensitivity and radioactivity, makingit very difficult to obtain measurements good enough even for a basic "old or new" authenticity result. Porcelains are really almost a glass, with tiny islands of quartz often

present, and are extremely hard as well, making sampling without overheating difficult. If the friction of drilling heats the sample above 400C, the TL of the sample will begin to drain away, affecting the date obtained, or the pressure may cause a spurious signal (piezoluminescence and triboluminescence) that masks the TL. A diamond core drill is instead used for this material to remove a plug of ceramic. This is then cut with a diamond saw into very thin slices for analysis. When the material does contain quartz, a good TL mineral added as a temper to improve workability of the clay, this technique has shown excellent results. Unfortunately, as we move into these highfired wares, the problem of destructive testing -- and this is what TL dating is (although we try to minimize the damage to a piece) -- becomes more pronounced, as pieces without restoration are especially prized and sample holes are not tolerable.

Other materials that are suitable for TL dating include the cores from lost wax metal castings. The wax model for the object is made around a core, a mixture of clay and rice hulls or charcoal, and then an "investment" of the same material is put around the model. When the wax model is burnt out to leave a hollow mold, and the molten metal poured in, the core material is fired. Quite a good deal of work has been done on Shang bronzes at Oxford, and at Daybreak we have tested a considerable number of Tibetan and Nepalese bronzes and found their cores to be an excellent material because of their high TL sensitivity and high internal radioactivity. Burnt stones are another material which can be dated by TL, and in fact promise to be the most rewarding field of endeavor for TL dating in archaeology (for example, the dating of 100,000 year old burnt flints from Neanderthal and Cromagnon cave sites in the Near East). The precision limitations on TL dating of ceramics make it no competitor to radiocarbon dating when organic material is present in the archaeological context. Radiocarbon dating is fundamentally a much simpler technique and capable of precision in the 1-3 per cent range, but of course cannot be used to date inorganic objects, such as ceramics. Radiocarbon is not usable beyond about 30,000 years ago, when its precision becomes too poor to be useful and organic material is uncommon, so that if fired stone or a baked hearth is found, TL dating finds important use. (There is sometimes old carbon present in clay deposits, so that attempts to radiocarbon-date pottery from soot left from firing or from cooking fires generally yields ages much too great.)

In authenticity testing, the usual sample is 20-100 mg of powder drilled out of the submitted object with a carbide dental bur. The drilling breaks up some of the larger sandy grains and introduces additional uncertainty in the TL age, so that when the best precision possible is required, or when the minimum age if authentic is less than twice the maximum age if a forgery, a fragment the size of a large pea rather than a drilled sample is necessary. The problem here is that pottery is very inhomogenous, with differing amounts of radioactivity and therefore different radiation dose in the fine and coarse grains. Sampling is carried out in subdued incandescent light, as ultraviolet radiation from the sun or from fluorescent lamps can cause some of the natural TL to fade away. The sample is stored in a light-tight container and all work with it is performed in a laboratory lit with safelights.

There are two major TL measurement techniques: the more commonly used additive dose method, whereby radiation doses are added to the pre-existing natural TL dose to obtain the "growth curve" of the TL signal versus radiation dose; and the pre-dose method which uses the increase in sensitivity of a low temperature (125C) TL peak of quartz to measure radiation dose. The pre-dose method is more difficult and time-consuming, but finds considerable application in those cases where the additive dose method is not feasible because of a spurous signal or low signal levels in the high temperature range (300-500C), and also for recent (the last 500 years) objects that contain quartz. Since this method is not used for Indian ceramics, which have excellent high temperature TL characteristics, we will simply note the availability of pre-dose for certain difficult cases. The techniques are further divided into two, depending on the clay grain size used for measurements: "fine grain", using the silty component of the clay (particles 1-10 microns diameter), and "inclusion", which uses the larger sandy component (80-120 micons across). Inclusion dating yields somewhat more precise dates than fine grain, but requires a much larger sample and is more difficult. The following discussion of dating technique will describe fine grain additive dose TL dating.

The fine grains used for the TL measurements are selected by their settling time in acetone. The bulk drilled sample is shaken with 6 cm of acetone in a test tube and allowed to settle for two minutes: this leaves particles less than 10 microns diameter still suspended in the acetone. The suspension is poured off into another test tube, where it is allowed to settle for 20 minutes, leaving the grains less than 1 micron diameter in suspension. This suspension is then poured off and discarded leaving the 1-10 micron fraction of the sample behind in the second tube. Acetone is added and agitated and then pipetted into ten vials each having a 1 cm aluminum disk on the bottom. The sample material settles onto the disks and the acetone is evaporated, leaving about 1 mg of sample per disk, so that a number of measurements on identical samples can be made. The remainder of the original sample left in the first tube is dried and is used for radioactive assay

measurements. For TL measurements, a sample disk is placed in what is called the glow oven on a heating plate and raised in temperature to 500C at a rate of about 20C/sec. The faint light signal emitted by the sample is counted photon by photon using a photomultiplier tube. This thermoluminescence signal is recorded against temperature to give what is called a "glow curve." In order to reduce the spurious luminescence signals due to oxygen and water vapor in the glow oven reacting with the sample during heating, the glow oven is evacuated and then purged with highly purified gas, either nitrogen or argon, before heating the sample for measurement. After the natural TL (the TL accumulated since firing) is read out from a number of sample disks, other disks are given known doses of beta and alpha radiation to determine the beta dose equivalent to the natural dose accumulated and the alpha/beta relative efficiency, as the sensitivity of clays to these radiations is different. The calibration doses are given before reading out the natural TL (hence the technique is called "additive dose") because the sensitivity will usually change after heating. Figure 2 shows as example glow curves from a Chandrakhetagarh plaque from West Bengal, India (lab. reference 84A41, shown in figure 1). The clay from this area, in fact from all of India, is excellent for TL measurements, and the contrast between the TL from authentic objects and recent forgeries is great. For example, a Chandrakhetagarh mold for plaques (lab. reference 84A5) was found to have a maximum TL age of 7 years, and with only a bit more effort, the actual TL age could be found. An additional series of beta doses is given to the sample disks used for natural TL measurements to determine whether the TL intensity is a straight-line function of radiation dose or is non-linear, thus necessitating a correction to the equivalent dose. Figure 3 shows the beta equivalent dose as a function of measurement temperature. Starting at about 330C there is a plateau of constant dose where the values may be used to obtain the TL age. Once this set of measurements is made, we are halfway to having a TL age.

The next step is radioactive assay. The radiation dose is due to the minute quantities of uranium and thorium and radioactive potassium present in the sample and in to surround soil. Figure 4 shows this schematically for a typical pottery having 12 ppm thorium, 3 ppm uranium, and 1 per cent potassium oxide (radioactive potassium-40 is a relatively scarce isotope). The amounts of these vary considerably worldwide, but are fairly constant within a region. If a large number of objects from a particular area are dated, radioactivity measurements are made usually on only a few to determine the range of values. The remainder of the original sample is placed on a disk covered with zinc sulfide scintillator, which produces a flash of light when an alpha particle hits it. A photomultiplier tube detects this, and the scintillation pulses are counted for a period of time varying between two hours and a week depending on the precision needed. If a burial soil sample is available, it is counted as well. Sometimes, when the increase in precision warrants the effort, the sample used for alpha counting is re-used for a potassium measurement. By making certain assumptions about the relative abundances of the radioactive isotopes contributing to the alpha count, loss of radon (a radioactive gas in the uranium decay chain), and moisture content during burial, the alpha, beta, and gamma dose rate components may be computed from the alpha countrates and the potassium content. For the ideal sherd sample, more direct measurement techniques requiring fewer assumptions can be used. When no soil sample is available, a range of observed values of the environmental dose rate must be used, and in materials where the internal radioactivity is low, this results in considerable uncertainty in the total dose rate. Now, taking the accumulated dose and the dose rate, with their uncertainties, we can divide them to find the age of the object and its error limits.

In the example plaque shown in figures 1 through 3, the beta equivalent dose is 750 +/- 40 rads, and the effective dose rate is 0.35 rad/year. The TL age is 2150 +/- 400 years. The uncertainty in the TL age includes systematic errors in addition to the random errors of measurement.

Thermoluminescence dating is an absolute method of determining the time elapsed since pottery was fired. While obtaining ages with sufficient precision to be useful to the archaeologist is extremely difficult, the technique has proven to be important to the art historian, and to collectors and dealers in ancient art. Most materials will allow measurements yielding TL ages that will at least permit an unambiguous discrimination between authentic objects and recently fired copies. Uncertainties about questionable objects can be resolved, and the authenticity of objects believed genuine can be demonstrated in a manner independent of art historical expertise. TL dating cannot replace the art historian's eye: It is rather one of many techniques available to understand an object.

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Note: most references below are from the journal *Archaeometry*, published by the Research Laboratory for Archaeology and the History of Art, Oxford University. They mostly date from the 1970's. Since that time the technique has become fairly routine, and most authenticity studies have been confidential commercial work, hence not publishable. TL is scarcely used at all in archaeology now, except for work on burnt flints, where it really is the only possible technique available. Most recent work in TL is concentrated in geology, on sediments where exposure to sunlight is the zeroing mechanism.

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Victor J. Bortolot earned his Ph.D. in astrophysics at Columbia University, studying the cosmic background radiation. He measured the rotational excitation temperture of diatomic molecules in interstellar clouds as a means of supporting the 'big bang' theory and established many elemental and molecular abundances, but has since 1971 been active in thermoluminescence research, first at Mt. Sinai School of Medicine in New York City, then in 1977 founding Daybreak Nuclear and Medical Systems, Inc. Daybreak Nuclear is one of the foremost manufacturers of TL and OSL apparatus for archaeology and geology in the world, and is the only commercial laboratory for TL authenticity testing of art objects in the Americas. In 1994, the Bortolot Daybreak Corporation was split off from Daybreak Nuclear to take over Daybreak's authenticity testing services. Dr. Bortolot resides in Guilford, CT .

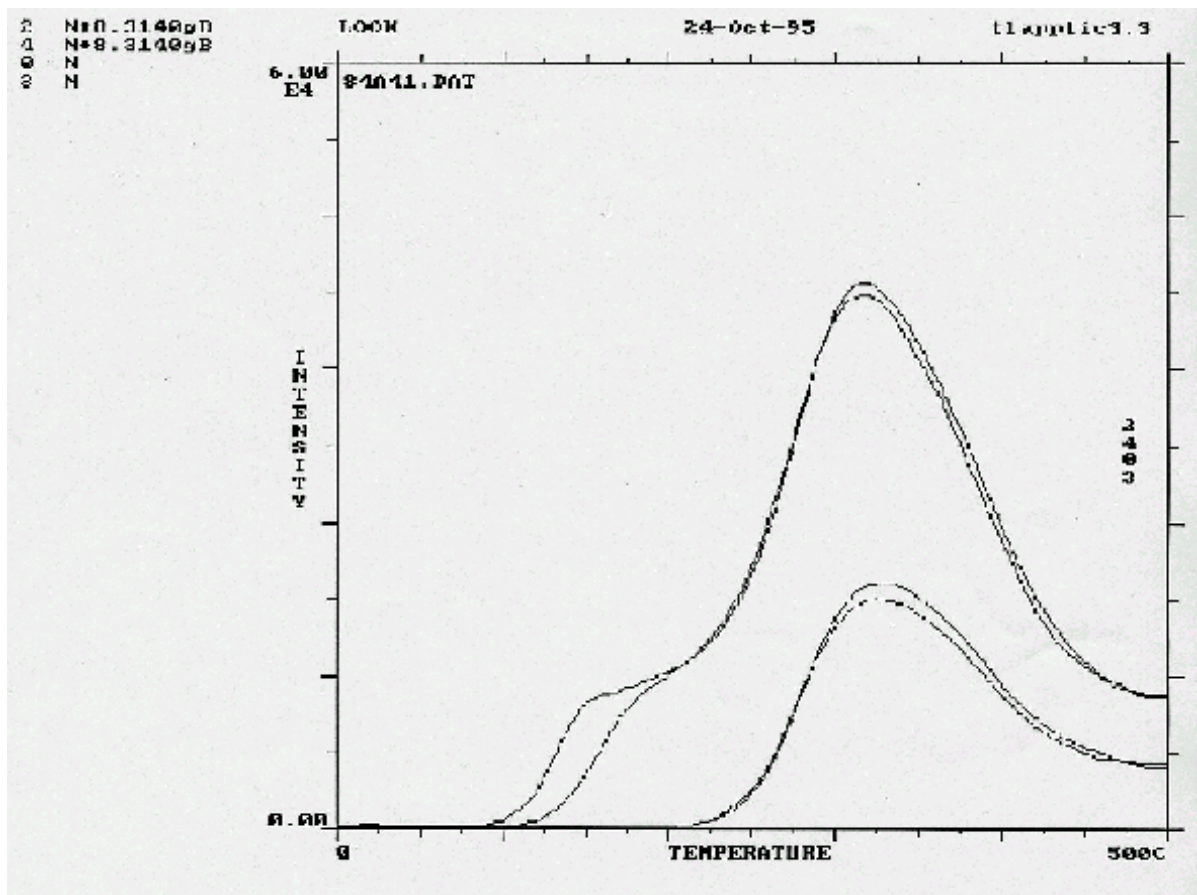**Figure 1.** A votive plaque from Chandrakhetagarh, West Bengal, India, circa 200 BC

Figure 2. TL glow curves from a Chandraketagarh plaque (lab. reference 84A41). The lower curves are replicate measurements of the natural TL signal, while the upper curves show the measurements of the natural TL plus an added 831 rad dose of beta radiation. In all cases, the thermal background ("redhot glow") due solely to the sample temperature has been subtracted. The area between the two sets of curves is the TL due to the added dose. Since the low temperature part of the TL glow curve is subject to decay at normal environmental temperatures, its shape will be markedly different for a calibration dose read out immediately and for a natural dose accumulated over centuries. It is necessary therefore to use data only from a temperature range where the curves have the same shape. This may be found simply by dividing a natural glow curve by the added dose glow curve, the so-called "plateau test".
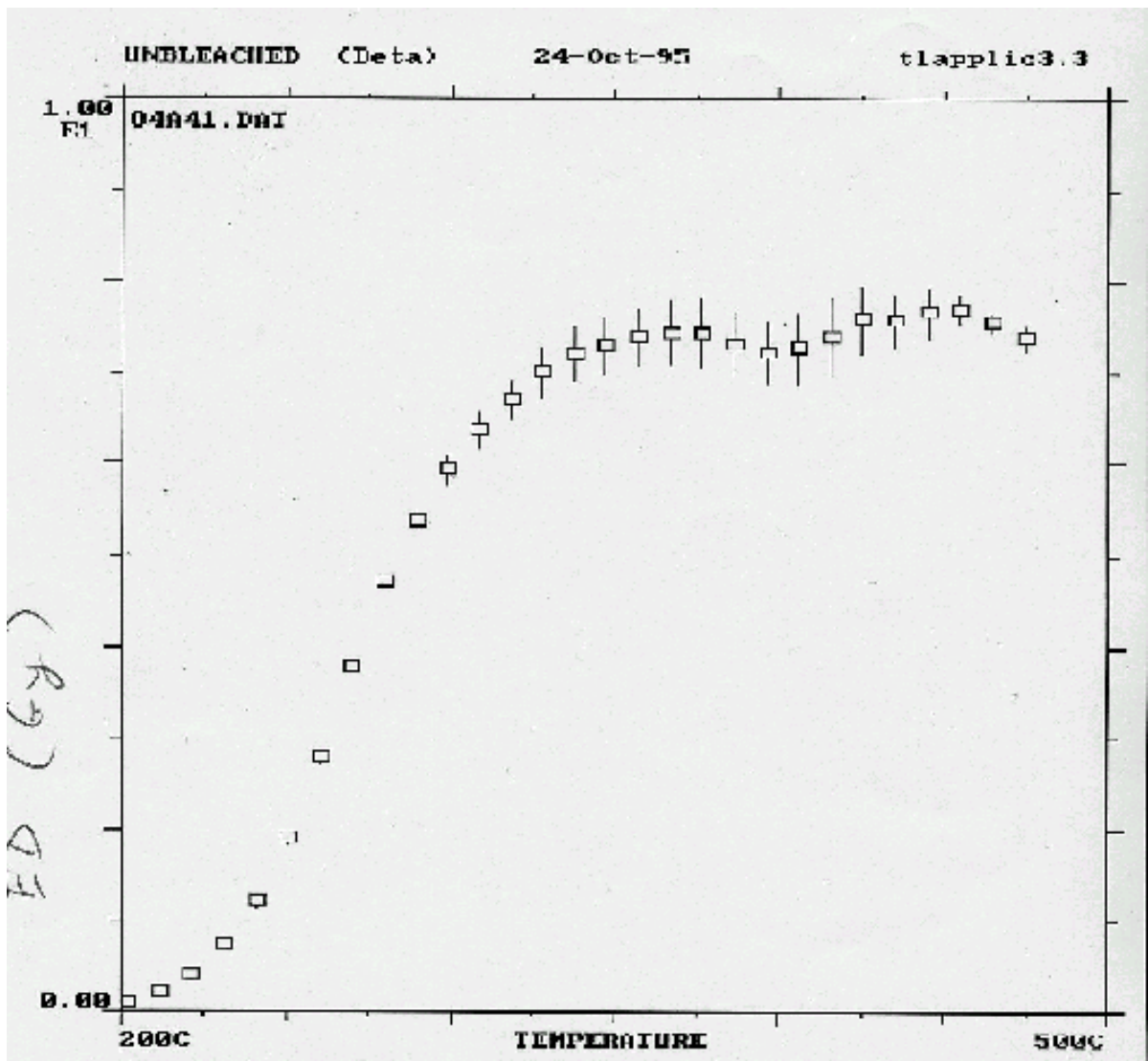
Figure 3. From the TL growth curve determined over a range of measurement temperatures, the beta equivalent dose is computed with its errors. This is shown here for the plaque (84A41), a more sophisticated way of finding the plateau than the simple plateau test made possible by the introduction of computers into the TL measurement apparatus. Here, the equivalent dose is nearly constant above 330C.
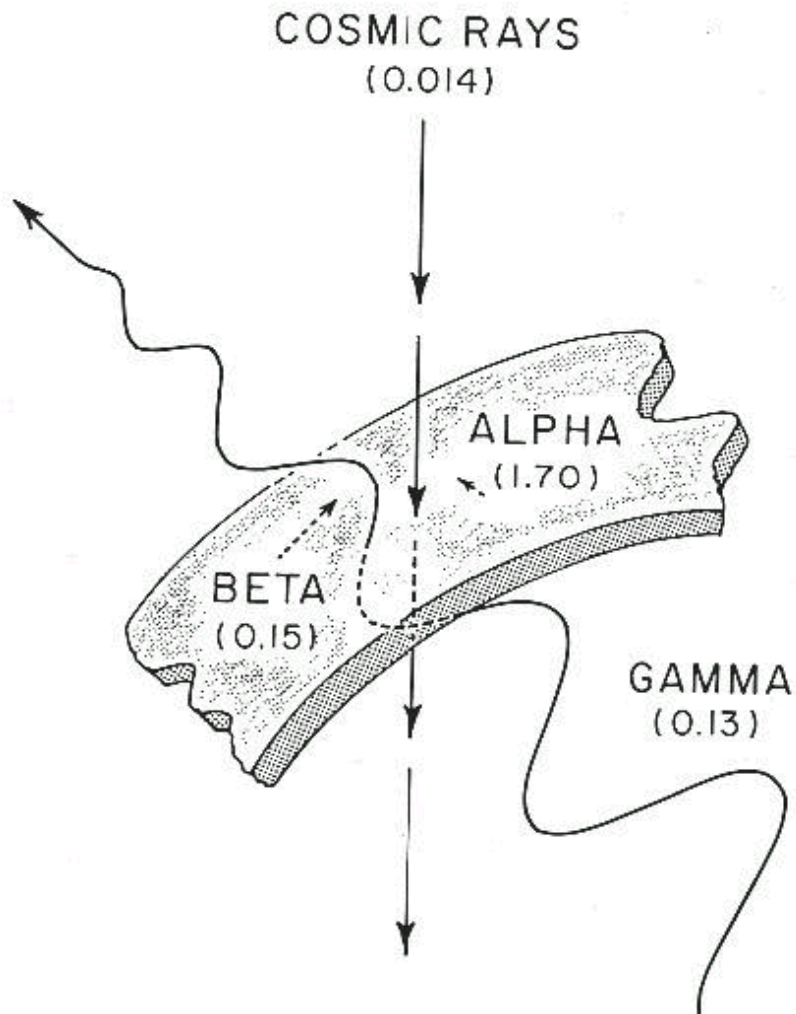
Figure 4. Typical annual radiation dose (in rads) of a potsherd buried in soil. Both pottery and soil have uranium 3 ppm, thorium 12 ppm, and potassium oxide 1 per cent. Actual concentrations of these constituents vary by more than a factor of ten worldwide. The ranges (length of travel before stopping) of the different components of the radiation are indicated by the length of the arrows: alpha particles (20-50 microns), beta particles (1-3 mm), gamma rays (tens of centimeters), and cosmic rays (meters). The total dose to the fine grains is close to 2 rads/year, but as the TL efficiency of alpha particles is typically 6-30 per cent that of betas and gammas, the *effective* dose rate is 0.40-0.80 rad/year. The fine grains have a much higher concentration of alpha-emitters than do the larger grains: since the range of alpha particles is smaller than the dimensions of the larger grains, the effective dose delivered to the larger grains is smaller.