GS/1028

UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA 4, PENNSYLVANIA

Title of Proposal
Continuation of Dating Pottery
by Thermoluminescence

Submitted to
National Science Foundation
Washington 25, D. C.

August 1, 1965

Principal Investigators: Froelich Rainey, Director, University Museum & ASCA
Elizabeth Ralph, Associate Director of ASCA

School: Graduate School of Arts & Sciences   Department: University Museum

Starting Date: 1 October 1965   Duration: 1 year

FUNDS REQUESTED

$16,826.

Corporate Name of University: THE TRUSTEES OF THE UNIVERSITY OF PENNSYLVANIA
(A Pennsylvania non-profit corporation)

Contracting Office: OFFICE OF PROJECT RESEARCH AND GRANTS
3400 Walnut Street, Philadelphia 4, Penna.

Date:________________________   Approved________________________
Roy F. Nichols, V.Provost

Approved:________________________
Froelich Rainey, Principal Investigator
Director, University Museum

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Otto Springer, Dean of the College

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Alfred Kidder II, Associate Director, University Museum
(For Froelich Rainey)

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Elizabeth K. Ralph, Principal Investigator
Assoc. Dir. of ASCA, University Museum

CONTINUATION OF DATING OF POTTERY BY THERMOLUMINESCENCE

ABSTRACT

A brief description of the method of dating pottery by thermoluminescence, a review of our previous progress, the significant advance made during the past year, and plans for the future are included.

I. Description of Research

As one of the projects of the Applied Science Center for Archaeology (abbreviated ASCA), experiments with thermoluminescence, a possible technique for the dating of pottery, have been pursued actively for the past three years.

The suggestion that thermoluminescence might provide a means of dating pottery was made by Farrington Daniels[(1)] and also by F. G. Houtermans.[(2)] The technique was investigated further by George Kennedy[(3)] and is now being engaged in actively at the Research Laboratory for Archaeology and the History of Art, Oxford University[(4)] as well as in our ASCA and other laboratories.

Thermoluminescence in pottery is due to the fact that radiations from the traces of radioactive elements in pottery bombard the other constituents of the clays and raise electrons to metastable levels. When the pottery is heated, such as in firing, each electron falls back to its stable position and emits a photon of light. On being reheated, the amount of thermoluminescence observed is, therefore, representative of the accumulated radiation damage and hence of the time elapsed since the original firing of the pottery.

Once an object has been heated to a temperature of 400°C to 500°C and its electrons have emitted their thermoluminescent light, no further light may be obtained by reheating after a relatively short time. Consequently, recently fired ceramic ware or freshly cooled lava, which have all electrons in stable sites, should show no thermoluminescence.

The basic principle is, therefore, straightforward, but there are a number of uncertainties which must be investigated or circumvented before one may say definitely that thermoluminescence will provide a means of dating pottery. Some of the major uncertainties are as follows:

1) Is the radiation damage caused primarily by alpha bombardment, or is it a combination of alphas, gammas, and betas?

2) How many metastable electrons are lost, especially near the surface, during the passage of time?

3) How, and how much do the susceptibilities of clay to radiation damage vary?

4) How do the differing transparencies of clays affect the detection of the photons emitted upon heating?

5) Does the bombardment from radioactivities in soils cause significant radiation damage to potsherds from external sources?

6) What is the effect of the grinding of the pieces of pottery, a necessary preliminary to thermoluminescent detection?

By means of various experiments most, or all, of these questions may be answered, but in order to start, the preliminary concern has been to assemble apparatus sufficiently sensitive and reliable to make some measurements. We have proceeded, therefore, in a direct way, over-simplified at first, but which has now enabled us to make quantitative measurements with adequate sensitivity.

First of all, for the rate of bombardment, we have assumed that the major damage is caused by alpha bombardment or is proportional to it, and have, therefore, constructed special low-background ZnS screens and associated components for this low-level detection of alpha bombardment. The samples are counted in "infinitely" thick layers with the result that comparative values only are obtained.

For the detection of the photons emitted upon heating, our numerous preliminary experiments indicated that very rapid heating rates and, of necessity, thin layers of powdered potsherds, would allow detection of the maximum light output. This is somewhat of a dual problem. First of all, the accumulation of metastable electrons is very small compared with geological samples that were last heated millions of years ago. In our case, the elapsed times are measured in thousands of years or less. Therefore, very high sensitivity is required to detect the light output, presumably in the visible range, but this sensitivity enables the apparatus to detect also the longer wavelengths of the heat radiation even at temperatures considered usually well below the emission of visible light. These are the reasons why rapid heating (now 16°C per second) is essential - namely, to drive out all of the photons before the surrounding materials get too "hot". The problem therefore, is quite different from that of the detection of thermoluminescence from crystals such as alkali halides for which the experiments are usually carried out between room and liquid nitrogen temperatures.

The apparatus for detection of thermoluminescence is shown in Figs. 1, 2, and 3. Samples are heated in a nitrogen atmosphere to prevent possible combustion of organic particles and also to prevent detection of spurious changes in intensity due to oxygen. A light shutter (see fig. 1) has been installed and other slight improvements have been made during the past year in order to maintain more stable temperature and detection conditions. To obtain very thin uniform layers of powdered pottery, the pottery is ground in a ball mill to less than 200 mesh. Separate pre-baking experiments have shown that the grinding induces negligible thermoluminescence. Then the powder is mixed with silicone oil and applied to aluminum foil on a 3/4 inch diameter "spot" by means of a #10 silk screen. This produces a uniform, thin, and stable coating of pottery on the foil. The size of the "spot" of powdered pottery was dictated by the area that could be heated uniformly by the furnace.

One of the important unknown factors, is the quantitative relationship between the bombardment and the resultant metastable electron accumulation in ancient pottery. It may be determined empirically, however, with series of pottery of known ages. From our small quantity of data accumulated so far, we find that the resultant light output is roughly proportional to age when corrected for alpha rate. The results for a series of fourteen samples from the Solduz Valley, Iran, are listed in Table 1 and plotted in Fig. 4. They have been plotted as integrated light output divided by the alpha rate versus age. The archaeological layers from which these samples were excavated were dated by C-14 from associated charcoal samples (5). Even though C-14 dating is not so precise as tree-ring or historical dating, this series affords a long range in time, from 5500 to 900 B.C. The obvious advantage of this is that the older samples give more light output, but additionally, a long range should afford more information about the possible loss or decay of metastable electrons with time, one of the basic uncertainties.

The determination of potassium contents affords an indirect measure of the relative bombardment rate from beta radiations (due to K^{40}) within the pottery. The results of eight measurements (see Table 1) indicate that this factor is not the cause of the discrepancies in age correspondence for the series of pottery from Iran.

The lack of better consistency in Fig. 4 is thought to imply different susceptibilities. The obvious way to obtain a measure of the susceptibility of a potsherd to radiation damage is by the application of an external dose, from a source with much greater intensity than the natural bombardment in order to duplicate the original radiation damage in a short time. On the basis of the low rates of alpha bombardment in this series of pottery, we estimate that the natural thermoluminescence is caused primarily by the filling of lattice imperfections with metastable electrons rather than by the creation of new "holes". Therefore, with a relatively small artificial dose, it should be possible to repopulate the lattice vacancies. If the dose is increased, then it might be possible to note when the dose becomes sufficient to create new radiation damage.

Our initial susceptibility experiments were carried out with low voltage x-rays. Duplicate samples of pottery were prebaked for one hour at 600°C, and then mounted on aluminum foil in the usual manner for irradiation with x-rays. After several experiments made at various energies and intensities, the effects of these variables appeared to be linear. Subsequent tests were made at 30 Kv and 12.7 ma (GE model XRD-5 x-ray unit) and the times of bombardment were varied. From these measurements, the amount of irradiation required (measured in seconds) to produce the same amount of light output as that obtained naturally was determined. If these times of irradiation are then used as correction factors for varying susceptibilities, the results obtained, if anything, are slightly worse than in Fig. 4.

At first, experiments with longer times of irradiation and applications of these results in various ways as correction factors for susceptibilities did not improve the age correspondence significantly over that obtained in Fig. 4 with no correction for this factor. Then, during the past year, two important observations were made. First, it was found that even though replicate samples were taken from a single piece of pottery that had been ground and mixed thoroughly, there were large variations in susceptibilities among the replicate samples from the one piece. This indicated that the correction by artificial bombardment should be applied to the identical samples that were measured for natural thermoluminescence. Fortunately, our mounting technique with silicone oil on aluminum foil (as opposed to dusting directly on a plate which many workers use) allows this to be done easily. Therefore, when each sample was heated and measured for natural thermoluminescence, bombarded with x-rays (for 60 seconds at 30 Kv and 12.7 ma), and then reheated, the area of the artificial glow curve, applied as a correction factor gave some improvement toward consistent results. The reduction of the overall uncertainty in a series of replicate runs is shown in Table 2. For this particular sample, the statistical deviation of the ratio of natural divided by artificial thermoluminescence is only $\pm 5\%$ whereas the individual spreads were 20 and 17%.

More important, however, is the second observation made within the last six months - namely, that the low temperature peak or peaks in the glow curves induced by x-ray bombardment are unstable and decay within a period of one to two weeks. In the natural glow curves these unstable low peaks have already disappeared due to thermal environment, and possibly decay. Therefore, one must wait for these to decay after the artificial bombardment in order to obtain a reliable correction factor. Alternatively, ideally, one could measure only the area under the high temperature peaks, but with the rapid heating rates which we have found necessary to use for this weak thermoluminescence, the peaks become integrated together into one single peak. A week or two after x-ray bombardment, however, the low temperature part of the integrated peak does decay and a small discernible second peak appears (see Fig. 5). When the area of the latter is used as the correction factor in the formula $(A_{nat.}/A_{art.})/\alpha$, significant improvement in age correspondence is achieved. This is shown in Table 3 and Fig. 6.

Recently several examples of thermoluminescent decay have been reported. E. J. Zeller and L. B. Ronca[6] mentioned that workers engaged in thermoluminescence research have had the impression that inconsistent results were obtained if glow curves were run immediately after samples were irradiated. They suggested that this was the result of the thermal decay of the lowest temperature peak. This effect was reported also by J. M. McNellis[7]. B. E. Sabels[8], in studies of basaltic lava flows, has estimated a hypothetical half-life of thermoluminescent decay for these lavas to be 20,000 years. After various experiments, Sabels concluded that the loss in thermoluminescent output was due to natural decay rather than limitations of storage capacity for excited electrons. Unfortunately, this limits the dating range for basaltic lavas, but should not be a serious obstacle for pottery, most of which was fired much more recently than the lavas studied. However, some evidence of decay in pottery has been observed by Y. Ichikawa(9). Decay of the high temperature peaks in pottery has not been observed in our laboratory as evidenced by the linear correspondence of age with time (Fig. 6) and it has been reported to be insignificant in a recent article by M. J. Aitken(10).

We are encouraged by our recent improvement obtained in age correspondence and we propose to continue these experiments with thermoluminescence. During the next year (for which funds are requested) efforts will be concentrated on the measurement of more series from various parts of the world. A series from Pecos (south-western U.S.A.) on which extensive petrological studies have been done by A. O. Shepard(11) may also be helpful in elucidating the causes of inconsistencies in thermoluminescent output. Other series contemplated in the near future are from Gordion, Turkey and from various sites in Egypt.

At the same time efforts will be made to find the causes of the uncertainties (as exhibited by the spreads for each measurement in Fig. 6) that still exist. More experiments to determine the effect of particle size will be carried out. In regard to the apparatus, changes anticipated will be directed toward better control and linearity in heating rates.

If, after the completion of several different series of pottery, it is found that the time-scale derived from the series now completed (based on sherds from Iran and Italy) is applicable for all, there will be no question that thermoluminescence will provide a reliable means of dating pottery. Additionally, if the consistency of the measurements is improved, the precision may be comparable to C-14 dating. It affords the extra advantage that the pottery itself (abundant and primary) may be dated rather something, such as charcoal, associated with it.

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10. M. J. Aitken, Science Journal 1, 32-38 (1965).
11. A. O. Shepard, The Technology of Pecos Pottery, Part 2 of The Pottery of Pecos 2, 388-628 (Yale Univ. Press, 1936).

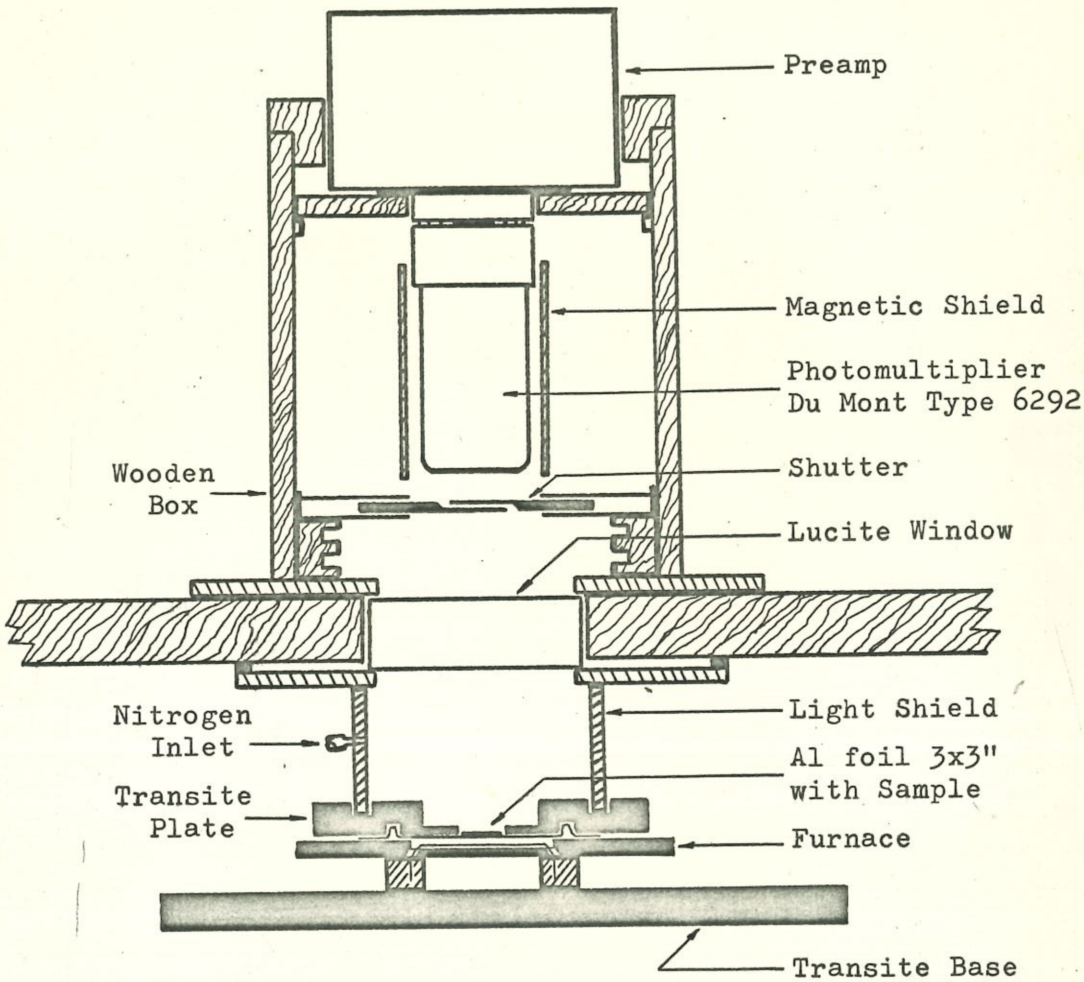

Fig. 1. Cross-section of Photomultiplier, Window, Shutter, and Furnace.

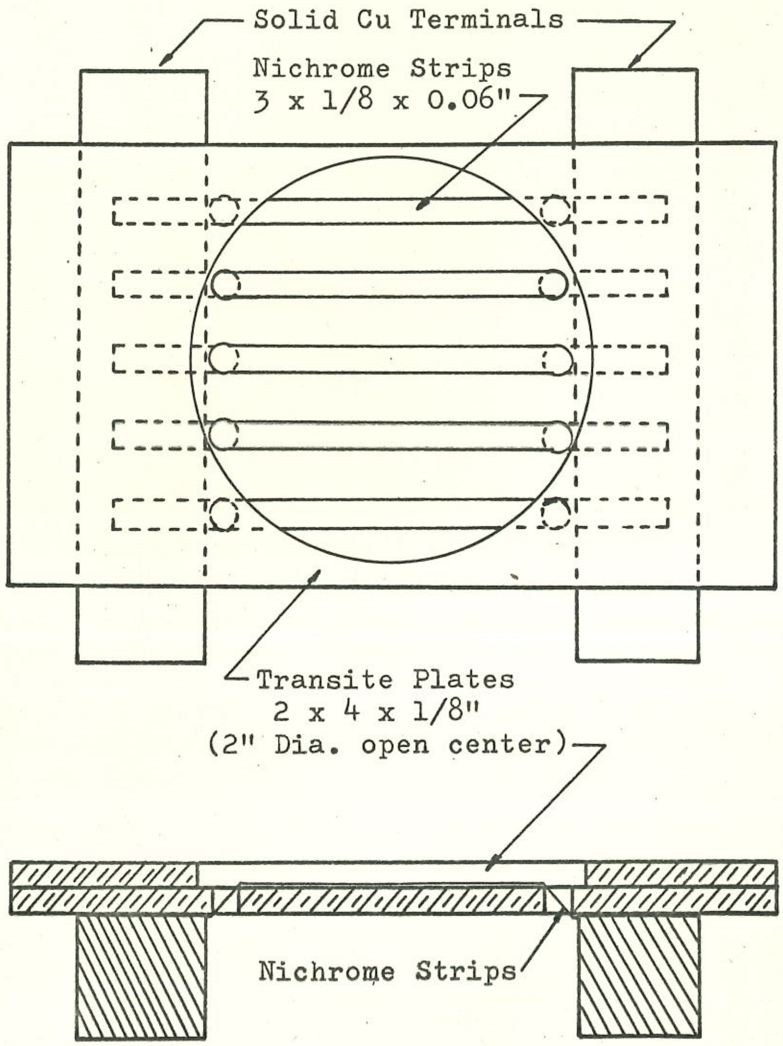

Fig. 2. Top View and Vertical Cross-section of the Furnace.

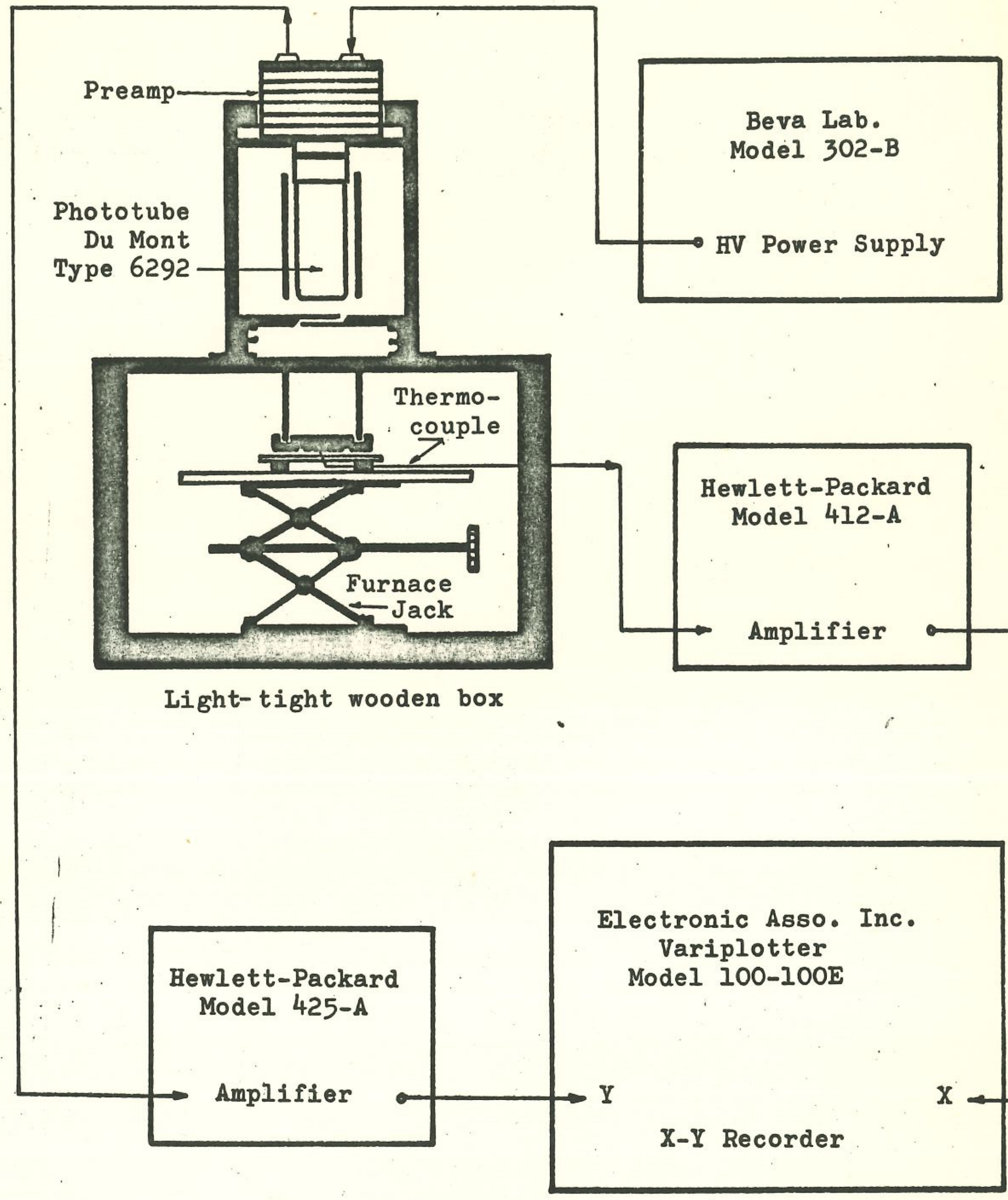

Fig. 3 Block diagram of the glow curve apparatus

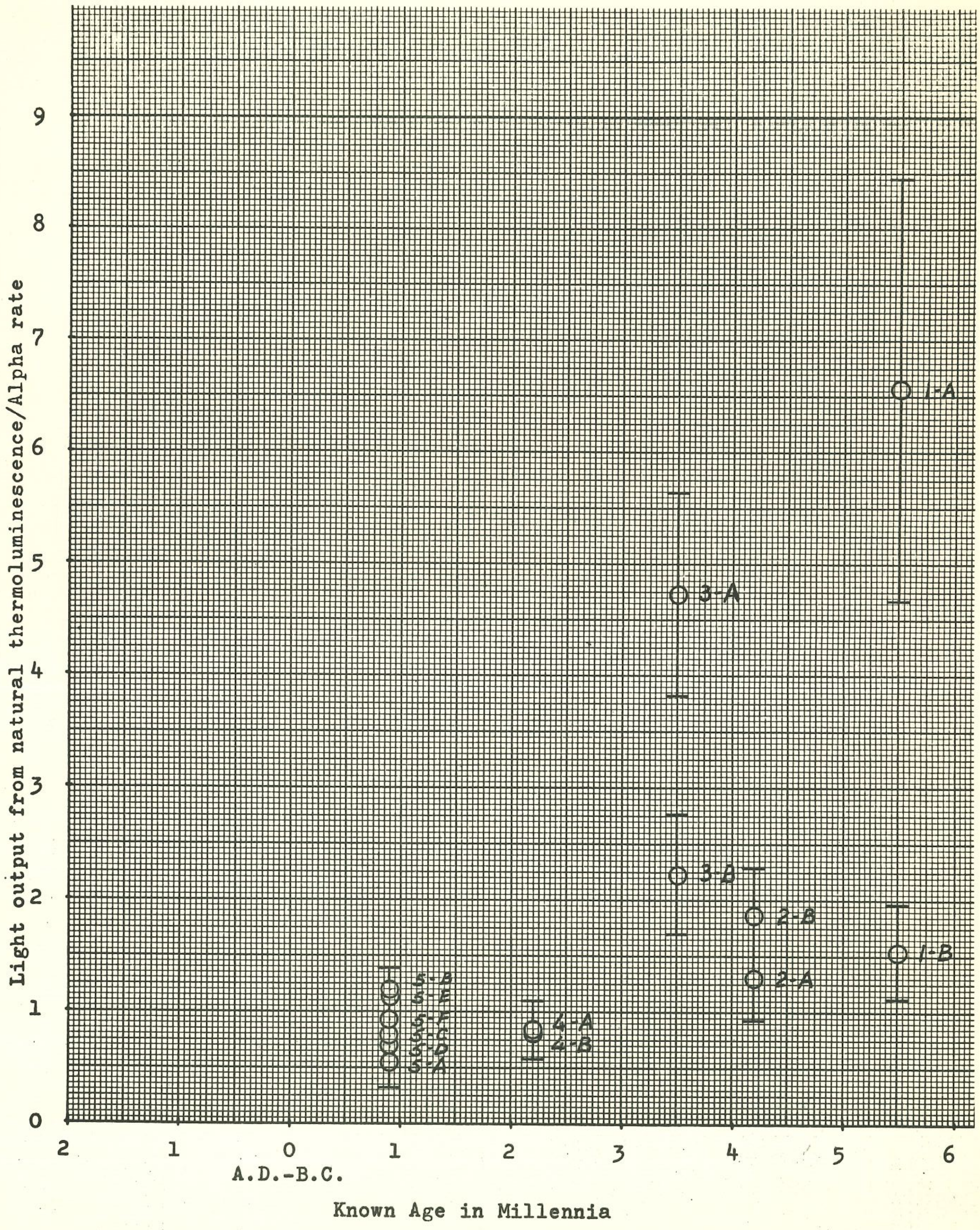

Fig. 4. Plot of light output from natural thermoluminescence divided by alpha rate versus known ages for samples listed in Table 1.

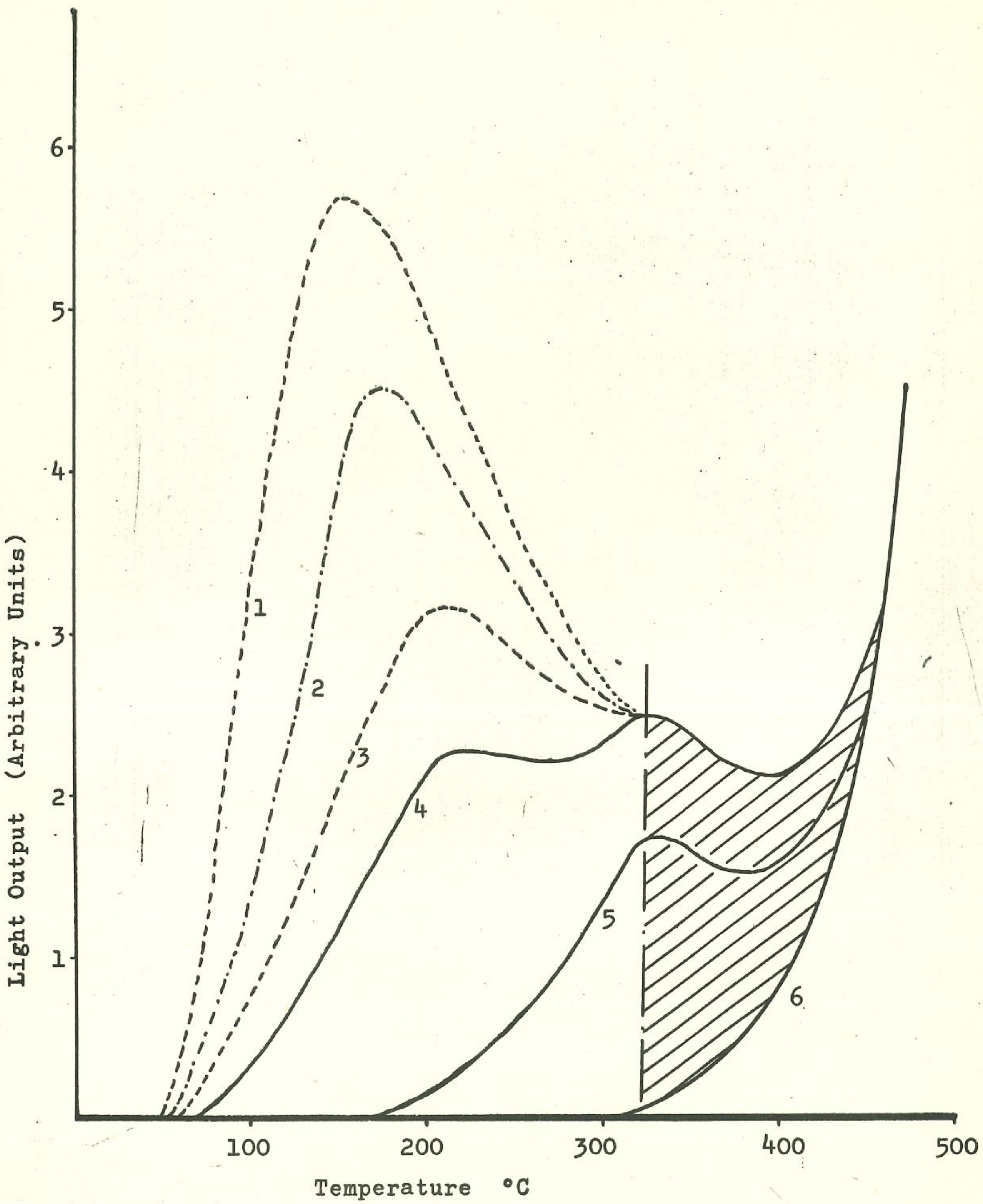

Fig. 5. Typical glow curves.

1. Artificial glow immediately after irradiation with X-Rays.
2. Artificial glow 24 hours after irradiation with X-Rays.
3. Artificial glow one week after irradiation with X-Rays.
4. Artificial glow two weeks after irradiation with X-Rays.
5. Natural glow curve.
6. Background (heat radiation only) curve.

The hatched regions are the significant areas for both the natural and artificial thermoluminescence.

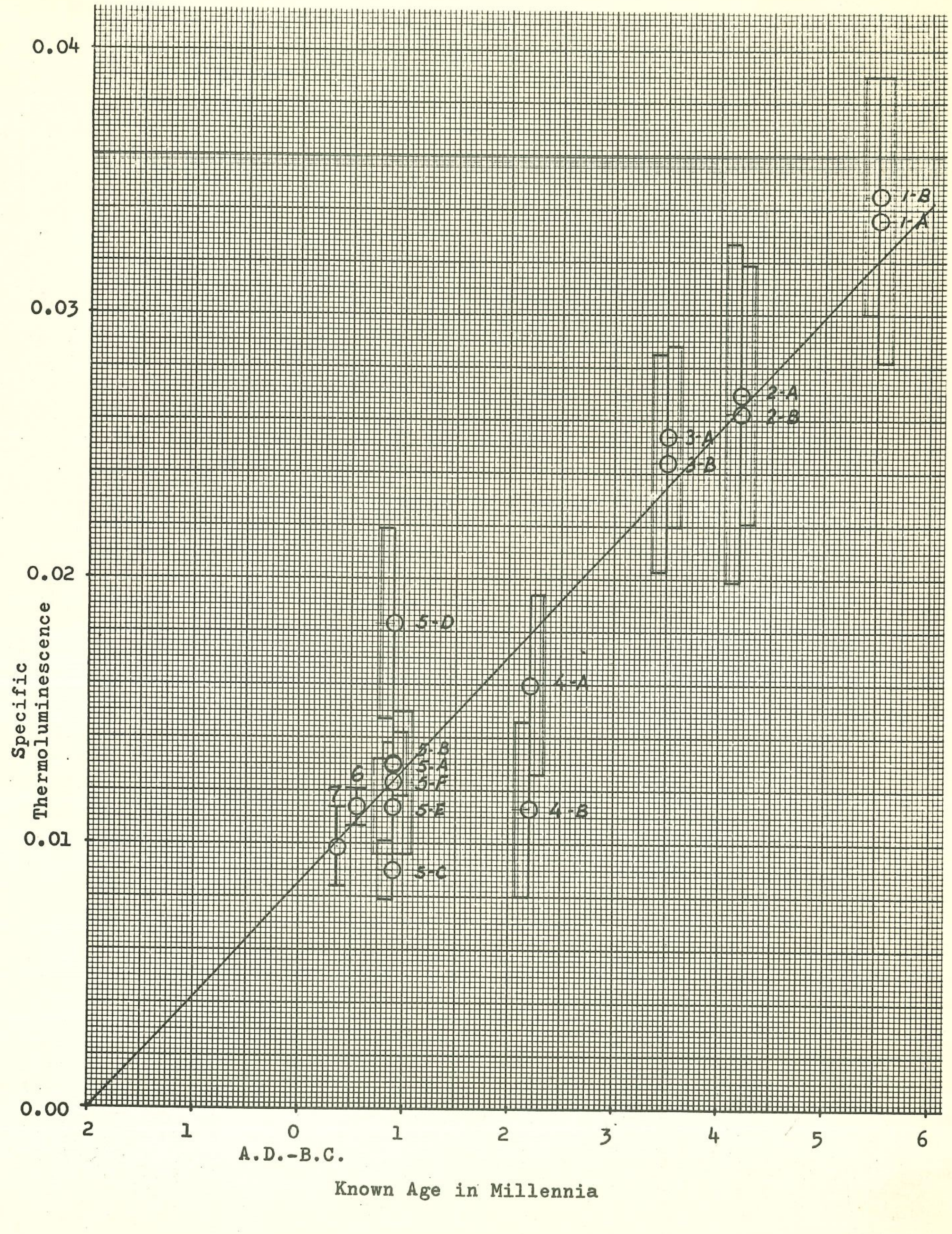

Fig. 6. Plot of Specific Thermoluminescence versus known ages for samples listed in Table 3.

Sample No.	Age B.C.	Relative Alpha Activity in cts/hr. $\alpha \pm \sigma_1$	% K Fusion Extraction	Average Area of Natural Glow in cm^2 Nat.Th-L$\pm \sigma_2$	$\frac{\text{Nat. Th-L}}{\text{Alpha cts/hr.}} \pm \sigma_3$
1-A	5500	11.7 ± 0.3	2.43	76.7 ±22.0	6.56 ± 1.89
1-B		11.3 ± 0.4	2.51	17.4 ± 4.7	1.54 ± 0.42
2-A	4200	11.4 ± 0.6	2.66	14.9 ± 4.2	1.31 ± 0.38
2-B		11.0 ± 0.4	2.34	20.5 ± 6.9	1.86 ± 0.43
3-A	3500	16.9 ± 0.8	3.29	80.0 ±15.0	4.73 ± 0.91
3-B		13.1 ± 0.4	2.80	29.2 ± 6.9	2.23 ± 0.53
4-A	2200	17.1 ± 0.5	N.D.	14.4 ± 4.4	0.842± 0.258
4-B		18.0 ± 0.5	N.D.	14.6 ± 3.3	0.811± 0.185
5-A	900	17.6 ± 0.5	2.47	9.60± 4.11	0.545± 0.233
5-B		8.8 ± 0.5	2.14	10.6 ± 1.6	1.20 ± 0.19
5-C		9.1 ± 0.3	N.D.	7.07± 1.02	0.777± 0.115
5-D		16.1 ± 0.4	N.D.	11.0 ± 1.7	0.683± 0.107
5-E		10.2 ± 0.5	N.D.	11.4 ± 1.7	1.12 ± 0.18
5-F		11.2 ± 0.3	N.D.	10.3 ± 1.2	0.920± 0.107

Table 1. Alpha and natural glow curve measurements of samples from Solduz Valley, Iran. The postscripts A, B, etc. (column 1) represent different sherds of the same age for each number listed.

Abbreviations: Nat. = Natural
Th-L = Thermoluminescence
N.D. = Not determined

σ_3 is the percentage deviation based on the square root of the sum of the squares of σ_1 and σ_2

Sample No. 6.	From: Plain of Sybaris, Italy		
Age: 550 B.C.	Alpha activity: 32.5 ± 1.2 cts/hr. ±(3.7%)		
Run No.	Area of Natural Glow in cm^2 Nat. Th-L ± σ_2	Area of Artificial Glow in cm^2 Art. Th-L ± σ_4	Area Ratio $\frac{\text{Nat. Th-L}}{\text{Art. Th-L}} \pm \sigma_5$
1	17.3	46.5	0.372
2	14.0	37.5	0.373
3	14.9	43.5	0.343
4	17.8	51.0	0.349
5	17.0	48.0	0.354
6	20.3	57.0	0.356
7	21.5	54.0	0.398
8	13.0	39.0	0.333
9	18.8	49.5	0.380
10	22.0	57.0	0.386
11	16.0	44.4	0.360
12	26.0	69.0	0.377
13	16.1	46.5	0.346
14	20.3	51.0	0.398
15	25.0	63.0	0.397
16	23.5	61.5	0.382
17	23.0	60.0	0.383
18	16.5	45.0	0.367
Average	19.1 ± 3.8 ±(20%)	51.3 ± 8.6 ±(17%)	0.370 ± 0.019 ±(5.1%)

Calculation:

Specific Thermoluminescence = 0.370/32.5 = 0.0114

Percentage deviation of the Specific Thermoluminescence = $\sqrt{(5.1)^2 + (3.7)^2}$ = 6.3%

6.3% of 0.0114 = ±0.0007

Result: Specific Thermoluminescence = 0.0114 ± 0.0007

Table 2. Example of replicate runs and calculation of deviations for one sample. The uncertainties for each column represent $\sqrt{\frac{\sum(n_i-\bar{n})^2}{N-1}}$

Sample No.	Age B.C.	Relative Alpha Activity in cts/hr. $\alpha \pm \sigma_1$	Average Area Ratios $\frac{\text{Nat.Th-L}}{\text{Art.Th-L}} \pm \sigma_5$	Specific Thermoluminescence $\frac{\text{Area Ratio}}{\text{Alpha cts/hr.}} \pm \sigma_6$
1-A	5500	11.7 ± 0.3	0.393 ± 0.063	0.0336 ± 0.0054
1-B		11.3 ± 0.4	0.390 ± 0.050	0.0345 ± 0.0045
2-A	4200	11.4 ± 0.6	0.308 ± 0.053	0.0270 ± 0.0049
2-B		11.0 ± 0.4	0.289 ± 0.070	0.0263 ± 0.0064
3-A	3500	16.9 ± 0.8	0.429 ± 0.053	0.0254 ± 0.0034
3-B		13.1 ± 0.4	0.320 ± 0.053	0.0244 ± 0.0041
4-A	2200	17.1 ± 0.5	0.274 ± 0.057	0.0160 ± 0.0034
4-B		18.0 ± 0.5	0.204 ± 0.060	0.0113 ± 0.0033
5-A	900	17.6 ± 0.5	0.227 ± 0.015	0.0129 ± 0.0009
5-B		8.8 ± 0.5	0.114 ± 0.009	0.0130 ± 0.0012
5-C		9.1 ± 0.3	0.0823± 0.0101	0.0090 ± 0.0011
5-D		16.1 ± 0.4	0.294 ± 0.058	0.0183 ± 0.0036
5-E		10.2 ± 0.5	0.116 ± 0.017	0.0114 ± 0.0018
5-F		11.2 ± 0.3	0.138 ± 0.030	0.0123 ± 0.0027
6	550	32.5 ± 1.2	0.370 ± 0.019	0.0114 ± 0.0007
7	360	23.0 ± 0.6	0.227 ± 0.035	0.0099 ± 0.0015

Table 3. Alpha rates, area ratios, and Specific Thermoluminescence for samples from Solduz Valley, Iran, (nos. 1 to 5) and Plain of Sybaris, Italy (nos. 6 and 7). The postscripts A, B, etc. (column 1) represent different sherds of the same age for each number listed.

Abbreviations: Nat. = Natural
Art. = Artificial
Th-L = Thermoluminescence

II. Facilities

During the past three years the work with thermoluminescence dating has been carried out in the laboratories of the Applied Science Center for Archaeology, University Museum, by Mark Han under the direction of Elizabeth Ralph. The equipment, however, except for specialized items constructed by M. Han and a few units purchased with NSF funds, has been temporarily borrowed. Therefore, funds are requested for the purchase of the requisite equipment which may not be borrowed indefinitely, and for the salary of the research chemist.

III. Personnel

Curriculae vitae of the following persons who are engaged actively in this program are attached:

Dr. Froelich Rainey, Principal Investigator, Director of ASCA

Miss Elizabeth K. Ralph, Principal Investigator, Associate Director of ASCA

Mr. Mark C. Han, Research Chemist in ASCA

IV. Budget, Thermoluminescent Dating

Salary		
Research Chemist (12 months)	$8,000	
Employee Benefits (8.4% of salaries)	672	
Equipment		
Replacement of borrowed components		
High Voltage Supply	1,200	
D. C. Amplifier	750	
Scaler	650	
Expendable supplies and materials	2,000	
		$4,600
Travel - conferences, other research centers		750
Total - direct costs		14,022
Univ. of Penna overhead (20% of direct costs)		2,804
TOTAL		$16,826

V. Current Support and Pending Applications

A. Current Support

1. Field Expeditions

   a. Onion Portage, Alaska, 1965 Season, NSF Grant to Brown University, approximately $30,000. (F. Rainey, Principal Investigator for summer 1965).

   b. F. Rainey - directs the expeditions to Sybaris which are supported by privately raised funds.

2. Radiocarbon Laboratory

   a. Univ. of Penna. annual support = $28,000. This includes salary of E. K. Ralph.

   b. C-14 measurements of Known Age Samples, Dec. 1964 to 1966, NSF GP-3778, $24,950 annually (E. Ralph, Principal Investigator).

3. ASCA

   Dating of Pottery by Thermoluminescence, Sept. 1964-1965, NSF GS-566, $20,000. (F. Rainey, Principal Investigator, E. Ralph, Faculty Associate, M. Han, Research Chemist).

4. Dept. of Metallurgy in collaboration with ASCA.

   Research in Metallurgy and Archaeology, Aug. 1965-1967, NSF P-17186, $12,800 annually (R. Maddin, Principal Investigator, E. Ralph, Faculty Associate).

B. Pending Applications

1. Continuation of Dating of Pottery by Thermoluminescence, Sept. 1965-1966, to be submitted to NSF, $16,826 requested, (F. Rainey and E. Ralph, Principal Investigators, M. Han, Research Chemist). (present proposal)

2. Development of Rubidium (or Alkali Vapor) Magnetometer for Archaeological Prospecting, Oct. 1965-1966, to be submitted to NSF, $24,000 requested (F. Rainey, principal investigator, E. Ralph, Faculty Associate).

3. Information Center and ASCA Newsletter, Oct. 1965-1966, to be submitted to NSF, $13,132 requested, (F. Rainey, Principal Investigator, E. Ralph, Faculty Associate, J. Flamm, Research Assistant).

These proposals are not being considered nor will they be submitted to other possible sponsors while they are being considered by the NSF.

Beth — please return Dir. Off.
Techniques

NATIONAL SCIENCE FOUNDATION

WASHINGTON, D.C. 20550

December 8, 1965

Dr. Froelich Rainey
University Museum
University of Pennsylvania
Philadelphia, Pennsylvania, 19104

Dear Dr. Rainey:

In our review of your proposal for support of a "Continuation of Dating Pottery by Thermoluminescence," questions were raised with regard to your group's awareness of the advances being made by physical scientists in this field and, in particular, of Dr. Aitken's work at Oxford. Our referee felt that your group was not profitting as much or as quickly as it might from the work of Aitken and others. For example, on page 7 of the proposal you mention the discovery that the low temperature peak or peaks in the x-ray generated glow curves are unstable. According to our referee this is discussed at some length by Aitken, Tite, and Reid in their work cited as reference 4 in the proposal. Furthermore, the referee asks why after its discovery of this effect, your group still apparently relies on a week or two waiting period after x-ray exposure, instead of getting rid of the low-temperature peaks promptly by post-exposure heating for a few minutes at, say, 150°C.

Our physicist reviewers felt that your project would be much strengthened by informal collaboration with those engaged in more basic research in physics on your own campus.

At this juncture of our review process, it would be very helpful to us if we could have your comments on these questions. The title page of the official copy does not bear your signature so, as in the case of your other proposal, we need a brief note indicating your concurrence.

Sincerely,

Richard W. Lieban

Richard W. Lieban
Program Director for
Anthropology

THE UNIVERSITY MUSEUM
UNIVERSITY OF PENNSYLVANIA
THIRTY-THIRD AND SPRUCE STREETS
PHILADELPHIA, PA. 19104
CABLE ADDRESS "ANTIQUE"
TELEPHONE: EVERGREEN 6-7400
(AREA CODE 215)

December 16, 1965

Dear Dr. Lieban:

In regard to our awareness of Martin Aitken's work at Oxford, we regret that we did not make this clear in our grant proposal. Never before have we collaborated so closely with another organization in another country, than we have in the course of our experiments with thermoluminescence. In addition to approximately monthly correspondence and the exchange of all progress reports, the time table of visits is roughly as follows:

1962, July - Beth Ralph visited Oxford laboratory, spent one week with Aitken there and in the course of the Radiocarbon Dating Conference, Cambridge, England.

1963, July - Beth Ralph visited Oxford, for approximately five days.

1964, April 1-10 - Beth Ralph had discussions with Aitken in the course of NATO Paleomagnetic Institute meeting, in Newcastle, England.

1964, November 6 & 7 - Martin Aitken visited United States and us.

1965, September 14 - Ralph conferred with E. T. Hall (Director of Oxford Laboratory) in Boston.
September 21 - E. T. Hall visited us.
December 2 - S. J. Fleming, graduate student now working with thermoluminescence at Oxford, visited us.

We should like to point out that Miss Ralph started experiments in thermoluminescence in September 1958, three years before Oxford began their work. Copies of three letters dated 1961 are enclosed in which some of our initial contacts and progress are described. A year after our Applied Science Center for Archaeology was initiated (supported by N. S. F. grants, G -13256, 1961; G-1857, 1962; GS-16, 1963; GS-294, 1964; GS-566, 1965) Mark Han was employed to work full-time on thermoluminescence under the direction of Miss Ralph.

Because of our headstart, many of the pitfalls and difficulties described by Tite & Waine (Archaeometry, 1962) had been tried, eliminated or by-passed in our laboratory. The " Note added in proof", p. 79, supports this statement - we both discovered at this time that it was necessary to make all glow curve measurements in an inert atmosphere and that consequently most of our previous determinations and conclusions drawn therefrom were meaningless.

In regard to a few specific aspects of the technique, our comments are as follows:

Grinding: Han constructed a simple ball mill grinder (made with roller skate wheels, string, cardboard, etc.) which enables samples to be ground slowly with a minimum of friction and heating. None of the difficulties nor problems experienced at Oxford have been encountered and no luminescence is enduced.

Alpha Counting: We use a more standard method with ZnS applied to a specially shaped plexiglas holder. The same screen is used for all measurements and we have found that it can readily be decontaminated in an ultrasonic cleaner. Oxford uses ZnS on scotch tape supported by a plexiglas ring. This has the advantage that no counts are lost due to absorption by a plexiglas window, but reproduceability varies by 5%. When Miss Ralph saw the difficulty and uncertainty that this method offered while visiting Oxford, she decided that our technique was more reliable.

Various experiments, initially suggested by Miss Ralph have been carried out at Oxford. Among these are the use of blue and $CuCl_2$

solution filters for the reduction of heat radiation; and the use of an alpha source for artificially-induced thermoluminescence.

In the Oxford reports frequent reference is made to the difficulty of obtaining uniform heating of the samples. It is for this and other reasons that our technique of mounting samples on thin aluminum foils suspended above (and not part of the heating element) was developed. Advantages are as follows:

1) Heating rate over the entire "spot" of thin powdered pottery is uniform. This has been determined with melting point lacquers of equivalent thickness.

2) Heating rate is more rapid and the whole glow curve peak (not just the upward slope) is recorded before the onset of heat radiation.

3) Since the sample is mounted firmly on the aluminum foil with silicone oil, the exact same sample may be used for the measurement of artificial as for the natural thermoluminescence. The advantages of this are pointed out in our grant proposal.

In regard to the referee's comment about decay, we find that Aitken, Tite and Reid (reference 4) are discussing a different type of decay. From p. 66 in the section labeled "Optical Bleaching" they wrote: "Measurement of the natural thermoluminescence of one sample, repeated over several weeks, showed a tendency for the glow to decrease." Then follows a discussion of the effect of exposure to sunlight, etc. This disturbing effect of sunlight has not been detected at all in our laboratory. Perhaps, our silicone oil inhibits this. Some mention is made of experiments with fluorescent light after alpha irradiation, and the following sentence is quoted (p. 70) "When stored in darkness, thermal annealing occurs in the 100-175°C region but is absent in the 250-325°C region." We find this difficult to interpret and possibly contrary to their previous and to our experimental evidence. In the section entitled "Thermal Bleaching," pp. 71-73, after a discussion of curious effects and the problems of heating samples uniformly, Atiken, Tite and Reid state (p. 73) " Consequently light emitted in the 300-500 °C temperature range results from traps both in this range and in lower temperature ranges; emptying of the latter therefore reduces the thermoluminescence observed in the high temperature region."

It is for this reason that we wait two weeks after x-ray irradiation before measuring the glow curves. During this time the unstable induced luminescence decays but without loss of any stable components. Naturally, we experimented with preheating at low temperatures, but we found also that the heating times, rates and temperatures were too critical for this to be a safe means of eliminating the unstable component. A glance at Fig. 9, ref. 4, Tite and Waine, Archaeometry, vol. 5, p. 59, helps to verify this. The individual peaks of curve A obtained with slow heating occur at 87°C, 159°C, 223°C, and 290°C. Each peak may be thought of as a steep hill, separated one from another by deep ravines. Therefore, if one preheats a sample at 150°, one is on a very steep slope of the 159°C peak. It is seen that there is no safe plateau where one could select a temperature without extremely critical control.

In regard to collaboration with those engaged in more basic research in physics on our own campus, we were negligent again in not mentioning the contribution of William E. Stephens, Chairman of our Department of Physics. Miss Ralph's initial experiments were begun at the suggestion of and under the guidance of Stephens and his help and advice have been generously given ever since. At various times, Stephens has called in other appropriate members of the department for informal discussions. Among the most helpful was A. A. Braner who was a member of the department during 1963-1964. At his suggestion, Han and John Gruninger (a graduate student in theoretical chemistry and a member of our Carbon-14 and A. S. C. A. staff) visited Mordechai Schlesinger, Department of Physics, University of Pittsburgh. Both Braner and Schlesinger have been leaders in basic physical studies of thermoluminescence for many years. Among other leaders in basic research, quoted by D. R. Lewis, N. Whitaker and C. Chapman in "Thermoluminescence of Rocks & Minerals," American Mineralogist, Vol. 44, 1959, are Braner, Daniels, Houtermans, Zeller - all of whom have been consulted at least by correspondence. In addition, Takenobu Higashimura, Department of Physics, Kyoto University, spent two days here in

July 1965 and exchange visits are planned with E. J. Zeller, Brookhaven National Laboratory in January.

It is easy to understand why a reviewed of our grant proposal might quote the work accomplished at Oxford and wonder why we, if we have made as much or more progress, have not published more articles (one has recently been submitted to Nature) , especially of a more technical nature. Perhaps, the best answer is that our purposes and approaches are entirely different. At Oxford, the work has been carried on as thesis projects for graduate students - first for M. J. Tite and others, and now for S. J. Fleming. As projects for theses in physics, it has been essential for them to investigate every fundamental aspect of the process even before many of these could be measured, identified, or explained adequately. Our goal has been to develop a workable method of dating pottery to facilitate fundamental archaeological research with the hope that when accurate determinations can be made, many of the basic questions and uncertainties may be resolved. Since the Carbon-14 laboratory is an integral part of our Applied Science Center for Archaeology and since Miss Ralph has been pursuing methodological studies relatedly to the past changes in the inventory of atmospheric C-14 and their basic causes for six years, the ultimate applications of the results of thermoluminescence dating are not being overlooked. For example, we are now obtaining the first indications that this new method of dating may provide a means of assessing the change in C-14 inventory in periods prior to the range of dendrochronology.

Most sincerely yours,

Froelich Rainey
Director

Dr. Richard W. Lieban
Program Director for Anthropology
National Science Foundation
Washington 25, D. C.

FGR/vg

1028

Ralph
ASCH

NATIONAL SCIENCE FOUNDATION
WASHINGTON, D.C. 20550

December 20, 1965

Dr. Froelich Rainey
University Museum
University of Pennsylvania
Philadelphia, Pennsylvania

Dear Dr. Rainey:

We appreciated your prompt and responsive answer to our inquiry concerning the thermoluminescence research. We hope that you will have the Foundation's decision on both this project and the magnetometer project in the very near future.

With best wishes for the holiday season.

Sincerely,

Richard W. Lieban

Richard W. Lieban
Program Director for
Anthropology

NATIONAL SCIENCE FOUNDATION

WASHINGTON, D. C. 20550

DEC 2 3 1965

Dr. Gaylord P. Harnwell, President
University of Pennsylvania
Philadelphia, Pennsylvania 19104 GS-1028

Dear Dr. Harnwell:

It is a pleasure to inform you that a grant of $16,200 is awarded to the University of Pennsylvania for the support of research entitled "Dating of Archaeological Evidence by Thermoluminescence." This research is to be under the direction of Froelich Rainey, University Museum. It is effective January 1, 1966, for a period of approximately one year.

The amount granted includes an indirect cost allowance of up to 20% of total direct costs.

The Foundation requires that this grant be administered in accordance with the conditions, policies, and procedures stated in "Grants for Scientific Research," June 1963 (as amended December 1963), Enclosure R-6, and the attached budget summary.

Please acknowledge acceptance of this grant under the above terms and include in your acknowledgment a reference to the grant number.

Sincerely yours,

JOHN T. WILSON
Deputy Director

Enclosures

NATIONAL SCIENCE FOUNDATION
WASHINGTON, D.C. 20550

DEC 23 1965

Ralph
ASCA

Dr. Froelich Rainey
University Museum
University of Pennsylvania
Philadelphia, Pennsylvania

Dear Dr. Rainey:

This will inform you that your proposal has been approved for support by the National Science Foundation under the title "Dating of Archaeological Evidence by Thermoluminescence" in the amount of $16,200 for a period of approximately twelve months.

I am attaching some materials relating to the conditions of the grant and our administrative requirements. Please review them carefully; if you have any questions about them, or if any questions arise during the course of the grant, do not hesitate to get in touch with us.

May we wish you the best of success in your research program.

Sincerely yours,

Richard W. Lieban

Richard W. Lieban
Program Director for
Anthropology

Enclosures

202 - 343 - 6511
Winter '67 - mid-January

not Monday

THE UNIVERSITY MUSEUM
UNIVERSITY OF PENNSYLVANIA
THIRTY-THIRD AND SPRUCE STREETS
PHILADELPHIA, PA. 19104
CABLE ADDRESS "ANTIQUE"
TELEPHONE: EVERGREEN 6-7400
(AREA CODE 215)

December 13, 1966

Dear Dr. Lieban:

Attached is the final report on grant GS-1028 on the dating of pottery by the thermoluminescence method.

For you and me, the technical problems reported here may be rather thick going, but from the anthropological-archaeological viewpoint, I think it would be clear that the method has worked out and that there are very good possibilities for perfecting it. Already, we are being bombarded from all over the world for more information about the method, for requests to date pottery and for information about how the equipment could be installed in other institutions.

In this connection, I am happy to say that Beth Ralph has been out to Palo Alto, talking with the Varian people and they now want to make use of our research on thermoluminescence to produce equipment for measuring the amount of radioactivity absorbed by people in hospitals who are now using linear accelerators. Apparently, this would be a much more effective way for measuring radioactivity absorbed in any one day. If or when they do this, we will then have instruments which can be purchased by museums and universities for thermoluminescence dating at about $6,000 per instrument. I may also add that the Defense Department, experimenting with our cesium magnetometer, is now developing a simpler and much less expensive recording apparatus which we think can be purchased by the archaeologist at a much more reasonable price.

So, it looks as if this is a two-way street where equipment developed by the archaeologist can be used in industry, which then produces equipment within a price range feasible for the archaeologist. This kind of thing has also worked out for our little two-man submarine since it has been adapted for all kinds of purposes. Somehow, this is a development in archaeology I never expected, and I know it will interest you.

All the very best wishes,

Froelich Rainey
Director

Dr. Richard W. Lieban
Program Director for Anthropology
National Science Foundation
Washington, D. C. 20550

FGR/vg

Ralph
ASCA

NATIONAL SCIENCE FOUNDATION

WASHINGTON, D.C. 20550

December 21, 1966

Dr. Froelich Rainey
The University Museum
University of Pennsylvania
Thirty-Third and Spruce Streets
Philadelphia, Pennsylvania 19104

Dear Dr. Rainey:

We were delighted to receive your final report on GS-1028 and to have the reprints of your articles for the files. I had already read, with considerable interest, the article by you and Beth Ralph in Science.

With best regards.

Sincerely,

Dick Lieban

Richard W. Lieban
Program Director for
Anthropology

Gs 1028

UNIVERSITY OF PENNSYLVANIA

SOCIAL SCIENCES

RAINEY

ANTHROPOLOGICAL SCIENCES

BUDGET

TWELVE MONTH BUDGET

A. SALARIES

Senior Personnel: Principal Investigator	$ -----
Other Personnel: Research Associate (1 calendar year, full time)	8,000
Fringe Benefits	672
	$ 8,672
B. PERMANENT EQUIPMENT	2,600
C. EXPENDABLE EQUIPMENT AND SUPPLIES	2,000
D. TRAVEL	
Domestic	200
TOTAL DIRECT COSTS	$13,472
Indirect Costs (20% of Direct)	2,694
TOTAL	$16,166
ROUNDED TO	$16,200

86-0025

Ralph

UNIVERSITY OF PENNSYLVANIA
OFFICE OF PROJECT RESEARCH AND GRANTS
Digest of Terms of Contract or Grant for Research Project

GRANT NO: GS-1028
ACCOUNT CODE NO: 4-10100-3-6426
SPONSOR: National Science Foundation
TITLE: Dating of Archaeological Evidence by Thermoluminescence
DURATION: 1/1/66 - 12/31/66

PRINCIPAL INVESTIGATOR: Dr. F. Rainey
UNIVERSITY DEPARTMENT: Museum
TYPE OF CONTRACT: Grant
AMOUNT OF CONTRACT: $16,200
OVERHEAD: 20% ($2,694)

REPORTS: Financial- Annual and final to be submitted 90 days after termination. Scientific - Annual report and final 90 days after termination.

TRAVEL: To be authorized by Dr. Rainey (If included in above budget.) Allowance to cover transportation plus subsistence if support receipts accompany claim. Automobile reimbursement at rate of ten cents a mile. Foreign Travel requires prior approval.

BUDGET: A University budget covering these funds should be prepared and submitted through regular channels. 8.4% of salaries and wages should be budgeted for Employee Benefits.

REBUDGETING OF FUNDS: Funds may not be transferred from other categories and used for the following purposes without prior approval of the National Science Foundation:

1. Purchase of office equipment, furniture, air conditioners and motor vehicles.
2. Purchase of equipment in excess of the amount listed in the approved budget.
3. Purchase of major equipment not listed in the proposal.
4. Foreign travel when not listed in the proposal.
5. Salary of Principal Investigator or other senior personnel in excess of that provided in the approved budget.

USE OF UNEXPENDED FUNDS: Unexpended balance reverts to the Foundation.

PUBLICATIONS: Copyrighted material shall carry byline acknowledging sponsor's support and shall grant to the Government royalty-free right to reproduction.

Four (4) reprints of each publication to be forwarded to the sponsor.

PATENTS: Any patentable invention or discovery shall be reported to the National Science Foundation.

PROPERTY: Title to property purchased with grant funds rests with the University.

OTHER:

DISTRIBUTION: Comptroller, Attn: Mrs. Shoemaker, w/cy award
Principal Investigator Dr. Rainey
~~Dean~~
Purchasing
File

AAB:mg 1/12/66

NATIONAL SCIENCE FOUNDATION GRANT GS-1028

CONTINUATION OF DATING POTTERY BY THERMOLUMINESCENCE

FINAL REPORT

by

Froelich Rainey, Principal Investigator
Elizabeth K. Ralph, Faculty Associate
Mark C. Han, Research Chemist

Our progress with thermoluminescent dating of pottery through 1965 is summarized by Ralph and Han in Nature, Vol. 210, No. 5033, pp. 245-247 (April 16, 1966) and also by Rainey and Ralph in Science, Vol. 153, pp. 1481-1491 (Sept. 23, 1966). Four reprints of these articles are enclosed. More recent results were reported by Ralph and Han at the NATO-USAF Advanced Research Institute on Applications of Thermoluminescence to Geological Problems held in Spoleto, Italy from September 5th-16th, 1966.

Other activities include the following experiments:

1) Replacement of the D.C. Power Supply Unit and the Light-Output Amplifier with one of higher sensitivity and with a current suppressor to cancel out the dark-current from the photomultiplier.

2) Dating of a series of Black Glaze sherds from the Agora which range between 2nd and 5th century B.C. Results show the samples are younger than the dates given. This may be due to the fact that this is a city site and the sherds were subjected to subsequent heating.

3) Attempts were made to measure the glow curves of some Roman glasses. In these, no light output was detected, but with glasses which have higher uranium contents (provided by Dr. R. Brill, Corning Glass Center) the glow curves were positive. Further study of ancient

glass is planned.

4) Six samples from three different levels excavated at Torre Mordillo, above the plain of Sybaris, Italy, were dated as unknowns. Results were compared with one C-14 dated charcoal from the lower level; three samples showed agreement, while the other three samples appeared to be much older then they should be.

5) Calcined limestone (provided by Dr. Brill) from the cistern which was used to melt the large glass slab from Beth She'arim, Israel was compared with the natural limestone as well as with some fragments of pottery found beneath the slab and one in contact with the bottom of the furnace foundation. Due to the small amount of pottery available, precise dating was not possible. A comparative study was made of the different types of calcined limestone. Results show that natural limestones have much greater light output than that from the cistern which had been subjected to heating during the process of melting the glass slab. An attempt is being made to date the time when the melting process took place.

6) The dating of unknown samples (submitted by Dr. Carlton Coon) was carried out at ASCA. The samples are from Yengema Cave, Yengema, Sierra Leone. The dates of 1,500 B.C. and 2,200 B.C. are in good agreement with the estimated chronology.

7) Experiments on the sensitivity of chemicals,e.g., $CaSO_4$, $CaCO_3$, and Al_2O_3 were made to determine the possibility of using them as standards, in addition to using their sensitivity as a measure of the radioactive content in samples. Further study is needed to define their possibilities.

8) Installation of a new heating control system to program a linear heating rate is being completed at ASCA. With the increasing

need for analization of glow curve in regard to its shape and the location of peaks, it is necessary to know the exact temperature at which shifts of certain peaks occur. This will provide information about the compositions of pottery as well as previous treatment by heating and/or irradiation with X-rays. Another advantage of programmed linear heating is that the cut-off point can also be controlled. If, for example, heating above 500 ^{o}C causes changes in lattice defects, the heating can be cut-off precisely below this temperature. Subsequent heating after artifical irradiation would then provide a more reliable correction factor.

9) Several objects have been tested to find out whether or not they are modern fakes. In the course of these tests it was suggested that three controversial Etruscan objects which exhibited glow curves and, therefore, were not of recent manufacture, may have been copied in the 1st century B.C. Complete dating of these is now in process and it may shed some light upon copying practices of the Greeks and Romans.

eters of all these interactions between mean and fluctuating motions by means of an eddy viscosity relating local "eddy" stress to local rate of strain, the coefficient may well be negative; it may be meaningless.

The author seeks to interpret many fascinating examples of flow in the earth's atmosphere, the solar atmosphere, ocean circulation, and laboratory experiments in terms of an eddy viscosity. The viscosity is, of course, found to be negative whenever concentrations of flow exist or whenever energy is transferred from smaller to larger scales. For one who understands some fluid dynamics a description of these effects in terms of a negative viscosity is entertaining to read; for others it will surely make them even more mysterious than they are.

O. M. PHILLIPS
Department of Mechanics, Johns Hopkins University, Baltimore, Maryland

A Method for Dating

Thermoluminescence of Geological Materials. Proceedings of a NATO Advanced Research Institute, Spoleto, Italy, 1966. D. J. McDOUGALL, Ed. Academic Press, New York, 1968. xvi + 680 pp., illus. $25.

The papers in this volume stem from a 10-day conference at which 62 papers by 72 authors were presented. As is the case with many symposium volumes, the contributions range from trivial to important, and fully half of the papers could have been omitted with no loss to total information content of the volume. The papers can be grouped under the general headings of theory, instrumentation, and applications.

Unfortunately, thermoluminescence theory is today at best a palimpsest, thinly embracing a relatively rich phenomenology and supplying little guide to the successful application of thermoluminescence to geological and archeological problems. Theory seems to provide little explanation for such phenomena as the initially rapid change with time in the rate of depopulation of high-temperature traps, the effectiveness of radiation at high energy levels in the creation of new traps, the relationship between triboluminescence and thermoluminescence, or grinding glow, nor does theory predict that thermoluminescent glow curves should only be measured in an oxygen-free environment. A measure of the lack of theoretical guidance is that many of the authors of the book dismiss portions of signals that are not understood as "spurious."

Unfortunately, the chapters on design and instrumentation are particularly unenlightening. One is cautioned to have an instrument "able to record with high fidelity," that design of the apparatus should be "considered in its broadest overall aspects," and that "properly designed equipment will provide operational convenience"; one is warned to "avoid the expense of overdesigned functional sections and inadequacies of underdesigned functional sections." In this section one is also informed that "manual control is a method of operation in which the rate is controlled by the operator." We are also told that "a detector is a device which responds to the phenomena being investigated," we are instructed to select a "suitable device," and finally we are told that "the design should accurately tailor the equipment to the measurement needs in every respect."

A substantial number of papers appear under the general heading Applications of Thermoluminescence. A series of papers on geological age determination could be summarized by the single sentence, It can't be done. Thermoluminescence of a mineral is determined not only by its total radiation dose but by saturation of traps, production of new traps with time as a result of radiation damage, drainage of traps, which is a function of thermal history, and the creation and drainage of traps as a function of stress history. It is clear that because of the uncertain history of the average mineral in a geological environment thermoluminescence can give relatively little age information. Even in ideal situations where the thermal history of material is known and most of the variables that can affect thermoluminescence are not operative, such as in recent lava flows, age dating results are not very encouraging. Aitken *et al.* show that the feldspars of the Mount Etna lavas range in thermoluminescence from 0.1 to 90 times the expected glow. Therefore this reviewer cannot agree with the enthusiastic remark of one contributor to this volume that "thermoluminescence can furnish much valuable information about the age of igneous intrusions, faults and metamorphic events."

Dating of archeological artifacts by thermoluminescence seems to be far more promising and on far better ground. Papers by Ralph *et al.* and Aitken *et al.* describe the techniques of archeological age measurements on pottery sherds. In both precision and accuracy, their results do not compare unfavorably with carbon-14 results. It seems likely that in the not too distant future thermoluminescence may become a routine archeological tool.

Unfortunately, it seems likely that many of the other attempted applications of thermoluminescence, such as the determination of paleotemperatures and the determination of geological temperatures, will fail, for the thermoluminescence clock or dosimeter is not sharply set by the event in question, as is the case with the firing of a ceramic pot.

In particular, in this volume the contributions from Oxford by Aitken and his co-workers stand out as of exceptional quality, and they should particularly be read by anyone interested in the application of thermoluminescence to archeological or geological problems.

G. KENNEDY
Institute of Geophysics and Planetary Physics, University of California, Los Angeles

Nucleases and Substrates

Enzymes in Nucleic Acid Research. MICHEL PRIVAT DE GARILHE. Hermann, Paris; Holden-Day, San Francisco, 1968. xiv + 393 pp., illus. $16.25. Chemistry of Natural Products.

This volume naturally falls into two separate parts. The first half serves as an introduction to the structure and origin of nucleic acids and analytical methods for studying them, whereas the second half is apparently a revision of the author's earlier book, *Les Nucléases*.

The first part, evidently written so as to make the book conform to the natural products theme of the series, discusses the nomenclature, basic concepts, synthesis, and isolation of nucleic acids. These chapters tend to be written in a confusing style, which often leads to self-contradictory statements and half-truths. To cite only a few examples, on page 29 we are told that there exist three classes of RNA and on page 37 that there are four, and on page 38 a fifth type is discussed. On page 30 we are told that the messenger RNA's are "unstable, since as soon as they have delivered their message, they should

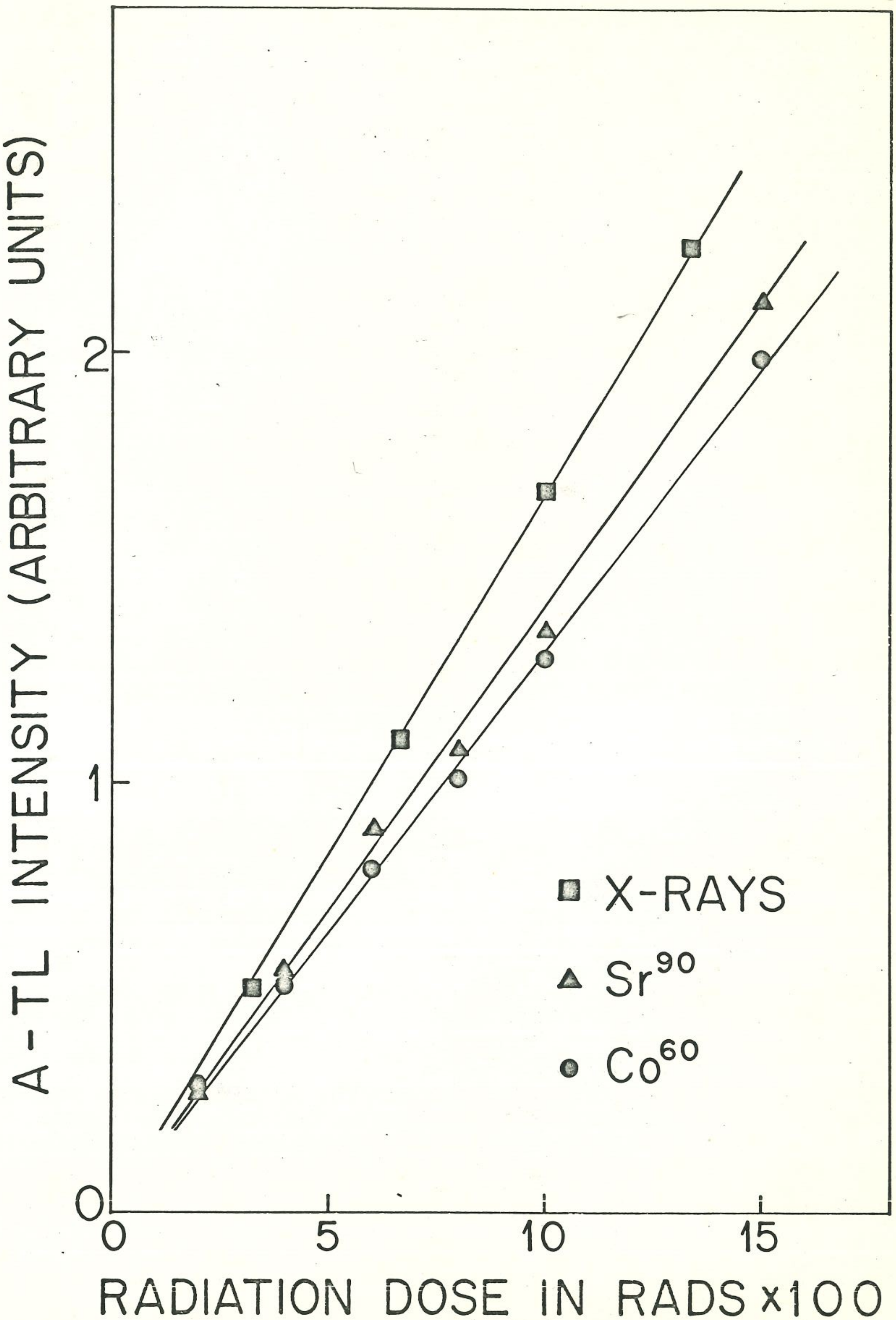

Figure 4. Thermoluminescence from Pottery after X, Beta and Gamma irradiation.