Arch — Techniques

April 25, 1964

Dear Mr. Morgan:

Twenty-one copies of a research proposal entitled "Dating of Pottery by Thermoluminescence" are enclosed.

With your approval, we should like to submit this proposal to the Program Director for Anthropology, National Science Foundation, by May 1st, 1964.

Sincerely yours,

Froelich Rainey
Principal Investigator

Mr. F. Hayden Morgan
Director, Project Research & Grants
3400 Walnut Street

UNIVERSITY of PENNSYLVANIA
PHILADELPHIA 19104

OFFICE OF PROJECT RESEARCH AND GRANTS

~~Technique~~
Techniques

April 29, 1964

National Science Foundation
Washington, D. C. 20550

Gentlemen:

Submitted herewith are twenty (20) copies of a proposal for support of a research project entitled "Dating of Pottery by Thermoluminescence" to be conducted under the direction of Dr. Froelich Rainey, Director, University Museum, Graduate School of Arts and Sciences, University of Pennsylvania.

The proposal has been approved by appropriate University officials and signed on behalf of the University by Dr. David R. Goddard, Provost.

If any further information is needed, please let us know.

Yours very truly,

James L. Malone
Contracts Administrator

JLM:msg
Enclosures 20

cc: Dr. Rainey

December 18, 1964

Dr. Alvin Van Valkenburg
Program Director for Geochemistry
National Science Foundation
Washington, D. C. 20550

Dear Dr. Valkenburg:

Thank you very much for your letter of December 14th with the good news of the grant (GP-3778) approval.

I hope that you will be able to visit us this winter.

Sincerely yours,

Elizabeth K. Ralph

EKR:ek

1964

Title of Proposal

Dating of Pottery by Thermoluminescence

Submitted to

National Science Foundation
Washington 25, D. C.

April 25, 1964

Principal Investigator:	Froelich Rainey	Position:	Director, University Museum
School:	Graduate School of Arts and Sciences	Department:	Museum
Starting Date:	1 September 1964	Duration:	2 years

FUNDS REQUESTED

First Year:	$26,004.00	Total:	$51,336.00

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, Pennsylvania 19104

Date:

APPROVED: ______________________
David R. Goddard, Provost
University of Pennsylvania

APPROVED: Froelich Rainey
Froelich Rainey, Principal Investigator
Director, University Museum
University of Pennsylvania

DATING OF POTTERY BY THERMOLUMINESCENCE

I. DESCRIPTION OF RESEARCH

As one of the projects of the Applied Science Center for Archaeology (abbreviated ASCA), experiments with the thermoluminescence technique of dating pottery have been pursued actively for the past year and a half by Mr. Mark Han, research chemist, supported partly by NSF Grants GS-16 and GS-294. This work at the University of Pennsylvania was initiated originally by E. K. Ralph in 1958, but the early progress was intermittent depending upon time available.

The suggestion that thermoluminescence might provide a means of dating pottery was made by Prof. Farrington Daniels and others (1953) and also by Dr. E. Houtermans. The technique was investigated further by Dr. G. Kennedy (1960) and is now being engaged in actively at the Research Laboratory for Archaeology and the History of Art, Oxford University by Mr. M. S. Tite under the direction of Dr. M. J. Aitken as well as in our ASCA laboratories. The progress at Oxford and discussions of the multiple problems involved are described by Tite and Waine (1962). The basic principles of the technique, as described in condensed form by Kennedy, are quoted here (1960, p 147):

"Radiation, either by alpha, beta or gamma rays, may displace certain electrons or groups of electrons from their stable orbits. These electrons may take up metastable positions among the atoms, in electron traps or f centers. There they may remain, trapped indefinitely, or fall back to their stable positions due to thermal agitation of the atom. As each electron falls back into a stable position, it emits a photon of light. This phenomenon is called thermoluminescence. Thus, when an object is heated to a temperature of 400°C or 500°C, all electrons in traps fall back into their stable sites and thermoluminescent glow is emitted.

"Once an object has been heated 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."

In other words, with the passage of time, naturally radioactive impurities, usually present in the clay, emit alpha particles which excite electrons. Some of these electrons may remain trapped and their number accumulates. On being reheated, the amount of thermoluminescence observed is representative of the accumulated damage and hence of time since original firing of the pottery.

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. These are due mostly to the present lack of knowledge of the basic mechanism of this very weak, natural radiation damage and additionally, in the case of pottery, to the inhomogeneity and variability of the materials. 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, oversimplified 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 if by gammas also, their rate if roughly proportional to that of the alphas, and have, therefore, constructed special low-background ZnS screens and associated components for this low-level detection of alpha bombardment. A block diagram of the apparatus and detail of the screen is included (fig. 3).

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 (detection of 10^{-9} microamps output of the photomultiplier) 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 $16^{\circ}C$ per second) is essential--namely, to drive out all of the photons before the surrounding materials get too "hot."

The important elements of the apparatus were shown in the Final Report, September 1963 for NSF grant GS-16 and copies of fig. 1 with slight revisions and of fig. 2 are included now, and a block diagram (fig. 4).

Since September 1963, additional "tricks" have been developed. Samples are heated in a nitrogen atmosphere to prevent possible combustion of organic particles, etc. The photomultiplier is cooled in dry ice to reduce the dark current and enable higher amplication to be used. To obtain very thin uniform layers of powdered pottery, the pottery is ground in a ball mill. Then it is dusted on a thin coating of silicone oil on aluminum foil. The thin uniform coating of oil on the foil is achieved by means of a #14 silk screen. An alternative procedure is to mix the oil and powdered pottery first and then apply them to the foil with a #10 silk screen. This results, however, in a heavier coating which reduces the heating rate. The additional advantage of a coating only a few particles thick is that the shiny surface of the aluminum foil reflects some of the photons which are not emitted in the upward direction, whereas a thicker layer of pottery tends to absorb them.

With these and other minor problems overcome, we are now (April 1964) getting results from measurements of photons emitted with heating and rates of alpha bombardment, that begin to show some consistency. A typical glow curve is shown in fig. 5.

One of the unknown factors, of course, is the relationship between the bombardment and the resultant metastable electron accumulation. Since there is no way to calculate it at present with these heterogeneous materials, it must be determined empirically and this may be accomplished with series of pottery of known ages. From our small quantity of data accumulated so far, we see that the resultant light output is roughly proportional to the logarithm of the height of the glow curve peak (or its area). Before a definite statement may be made, more measurements both of series from one site and from various regions are required. The latter will indicate also how serious the basic uncertainties may be and whether procedures to overcome these factors are necessary.

The results at the moment, however, are encouraging and it is now anticipated with greater sureness that thermoluminescence will afford a means of dating pottery, and hence, be an invaluable tool for archaeologists. In addition the measurements of these very low rates of bombardment and the consequent effects may furnish some information about the basic mechanisms of this type of radiation damage.

Eventually, also, apparatus with this great sensitivity may be used for other purposes. One possibility is the determination of whether or not there is detectable thermoluminescence from tektites. Theoretically, tektites should have minute metastable electron accumulations due to cosmic ray bombardment. This technique may now be used without question to distinguish between ancient pottery and recently fired modern fakes.

II. FACILITIES

During the past year and one-half 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 all been borrowed from the Department of Physics and from the Radiocarbon Laboratory. 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 and a student assistant.

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, Associate Director of ASCA

Mr. Mark C. Han, Research Chemist in ASCA

IV. REFERENCES

Daniels, F., Boyd, C. A., and Saunders, D. F., 1953. Thermoluminescence as a Research Tool. Science, Vol. 117, p 349.

Kennedy, G., and Knopff, L., 1960. Dating by Thermoluminescence. Archaeology, Vol. 13, pp 147-148.

Tite, M. S. and Waine, J., 1962. Thermoluminescent Dating: A Re-appraisal. Archaeometry, Vol. 5, pp 53-79.

V. BUDGET

FIRST YEAR

Salaries			
Research Chemist (12 months)	$8 000		
Research Assistant (12 months)	5 000		
Total Salaries		$13 000	
Employee Benefits (9.0% of salaries)		1 170	
Equipment			
X - Y Recorder	2 000		
Two D. C. Amplifiers	1 000		
Calculating Machine	1 000		
Expendable Supplies and Materials including replacement photo-multipliers	2 500		
Total Equipment		6 500	
Travel			
Conferences, collaboration with Oxford University, etc.	1 000		
Total Travel		1 000	
Sub-Total			$21 670
University of Pennsylvania Overhead (20% of direct costs)			4 334
Total First Year			$26 004

V. BUDGET (continued)

SECOND YEAR

Salaries			
Research Chemist (12 months)	$8 500		
Research Assistant (12 months)	5 500		
Total Salaries		$14 000	
Employee Benefits (9.0% of salaries)		1 260	
Equipment			
Replacement of obsolete components borrowed from Radiocarbon Laboratory			
High Voltage Supply	1 200		
D. C. Amplifier	750		
Scaler	650		
Expendable Supples and Materials	2 500		
Total Equipment		5 100	
Travel			
Conferences, etc.	750		
Total Travel		750	
Sub-Total Direct Costs			$21 110
University of Pennsylvania Overhead (20% of Direct Costs)			4 222
Total Second year			25 332
TOTAL TWO YEARS			$51 336

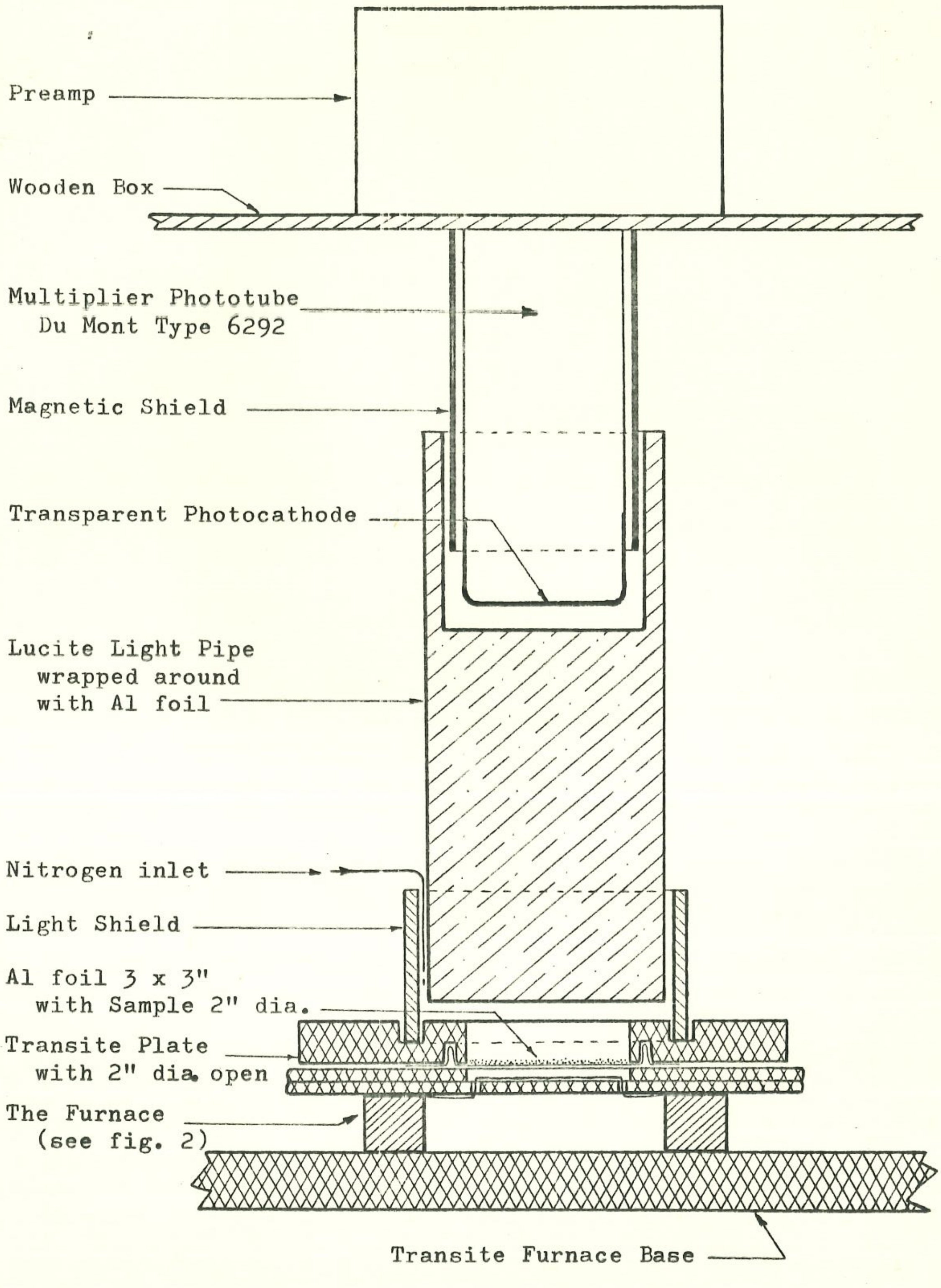


Figure 1 Cross section of Photomultiplier, Light Pipe and Furnace

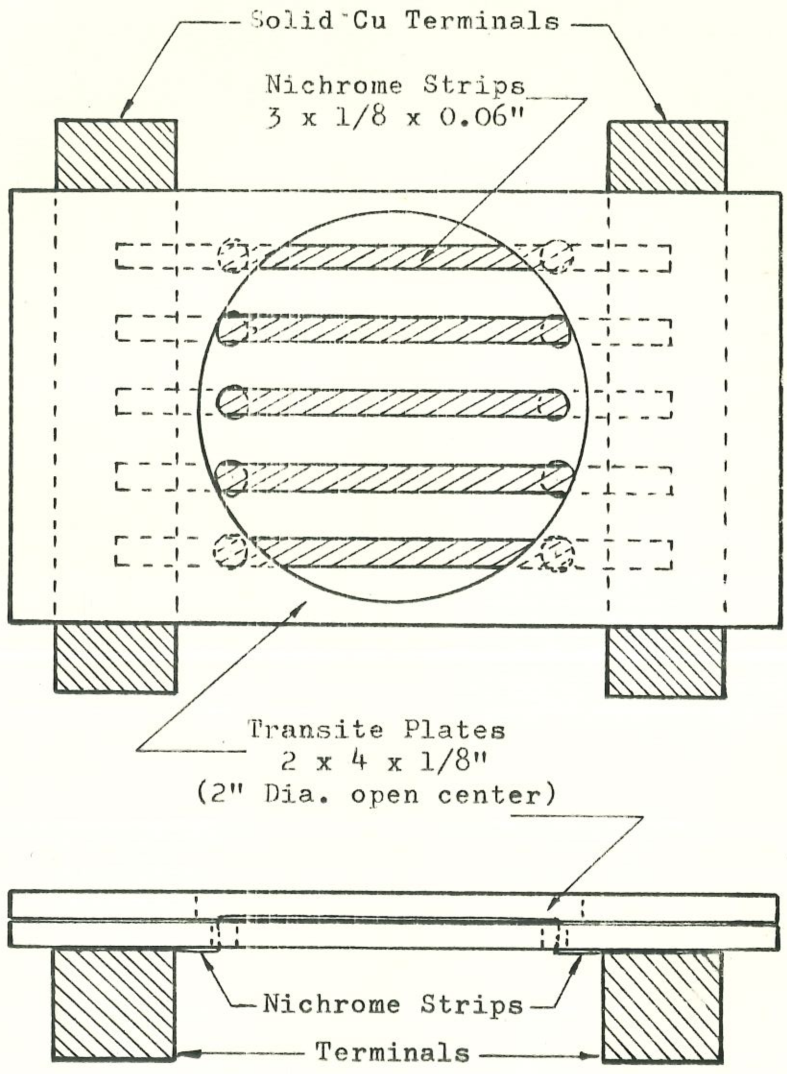


Figure 2 Top and Front view of the Furnace

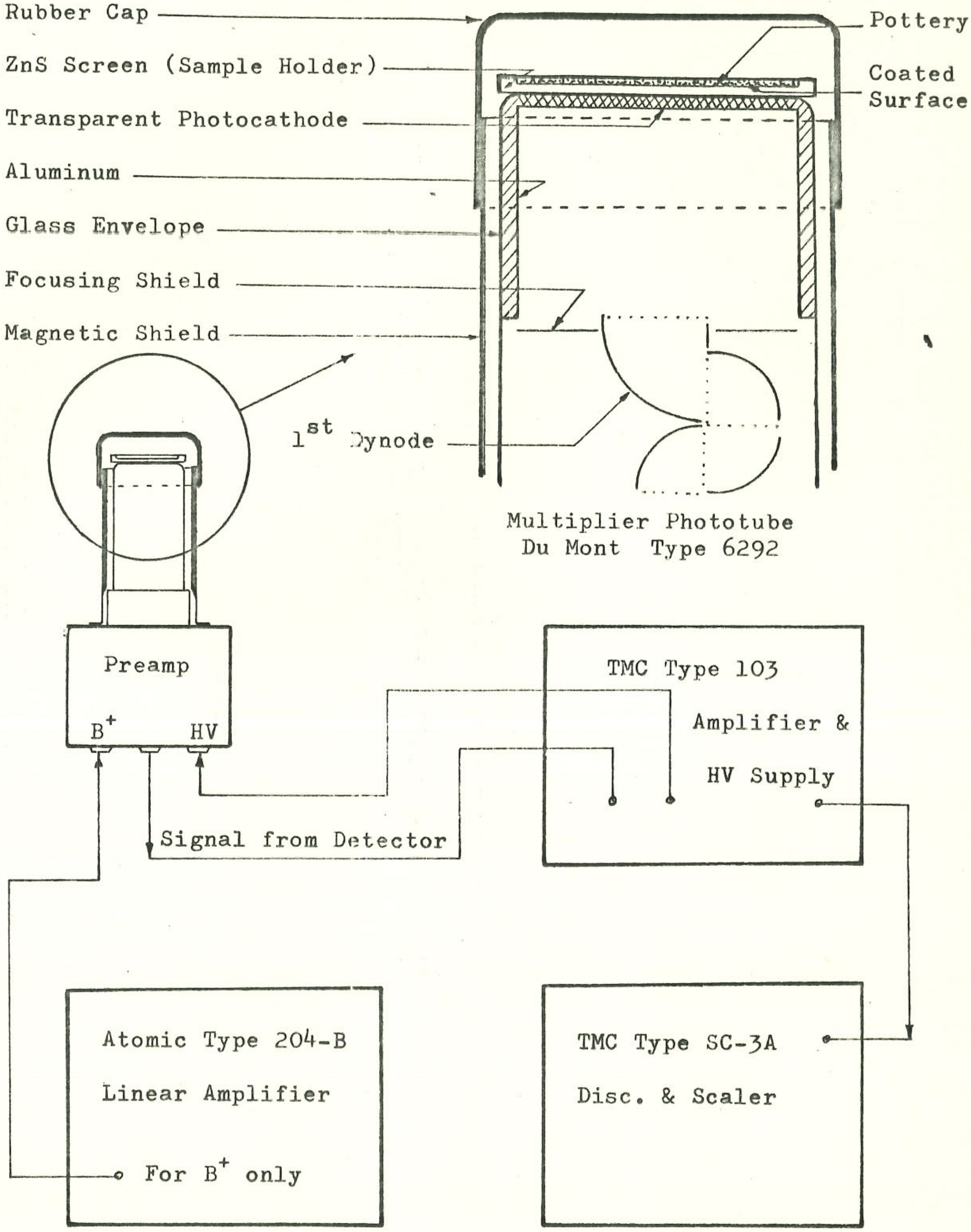


Figure 3 Block diagram of alpha detection apparatus and detail of the ZnS screen

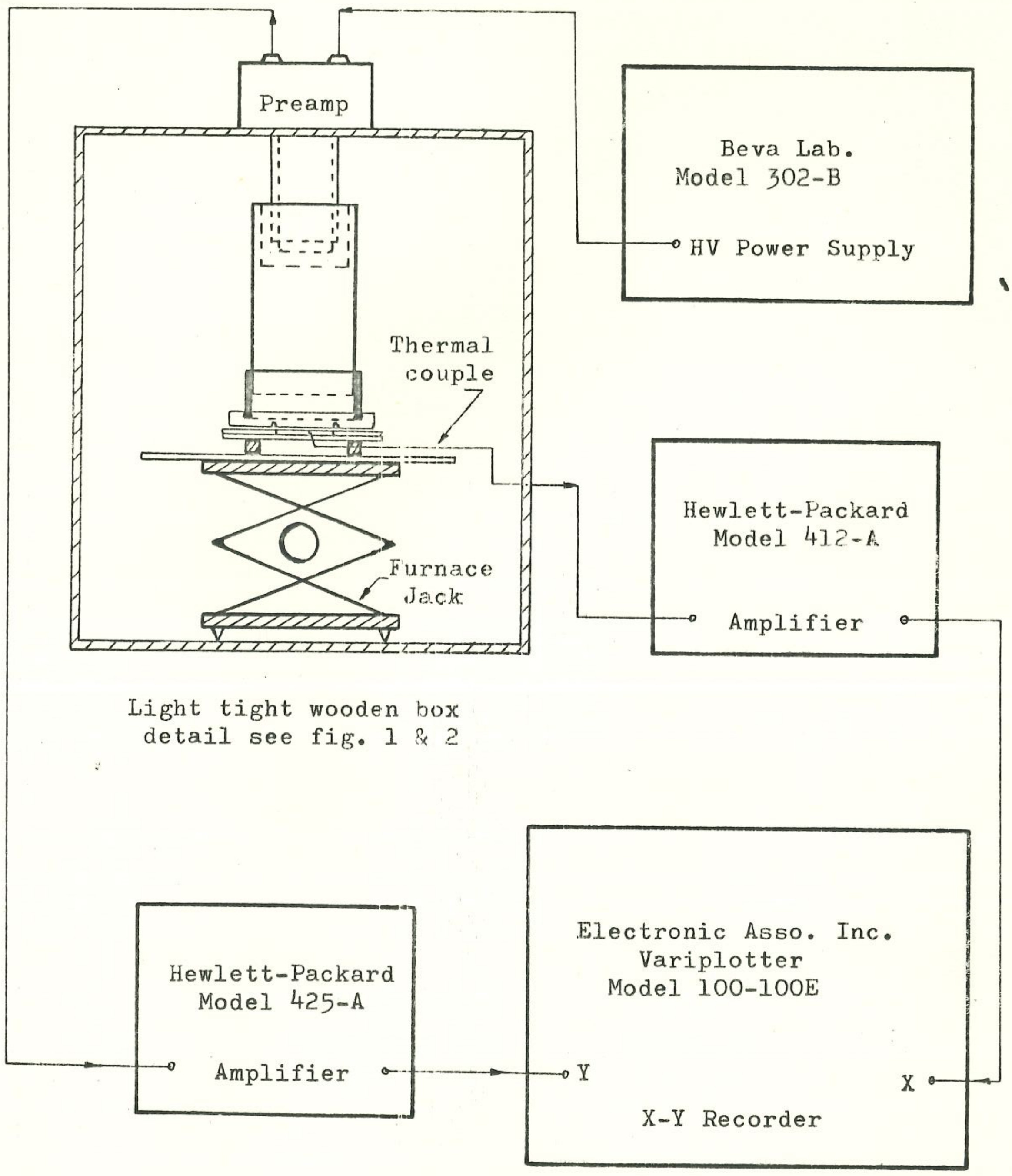
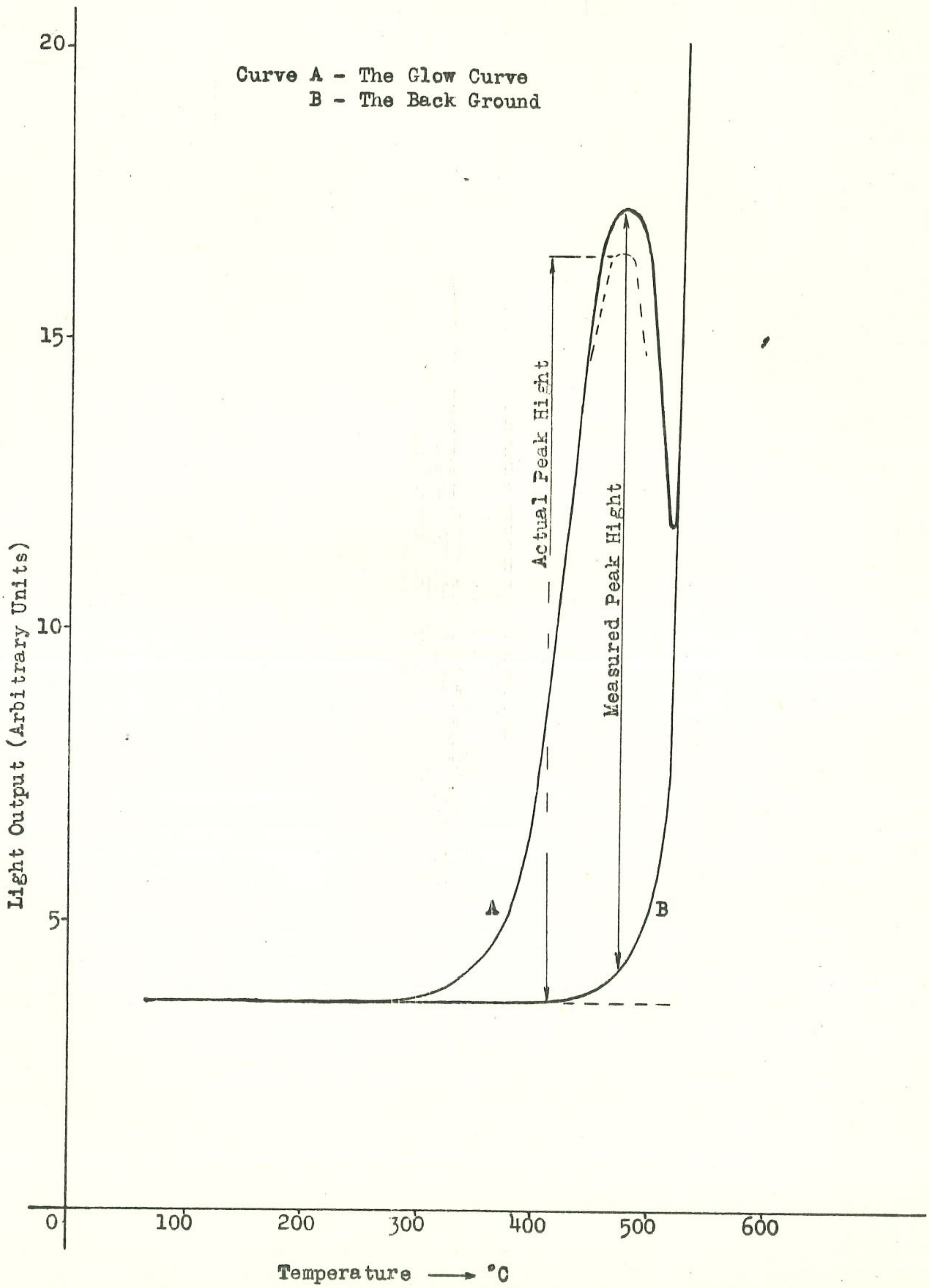


Figure 4 Block diagram of the glow curve measurement equipment

Figure 5 The Glow Curve (Light Output vs. Temperature)



(Temperatures represent those of the thermocouple. Subtract approximately 150° C for the true temperature of the powdered pottery.)

Miss Ralph

6-53778

Progress Report Sept. 1964

DATING OF POTTERY BY THERMOLUMINESCENCE

By
Elizabeth K. Ralph and Mark C. Han
University Museum
University of Pennsylvania
Philadelphia 4, Pennsylvania

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 for the past two 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 our ASCA 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. The photomultiplier is cooled in dry ice to reduce the dark current and enable higher amplification to be used. 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 dusted on a 3/4 inch diameter "spot" of a thin coating of silicone oil on aluminum foil. The thin uniform coating of oil on the foil is achieved by means of a #16 silk screen. An alternative procedure is to mix the oil and powdered pottery first and then apply them to the foil with a #10 silk screen. This results, however, in a heavier coating which reduces the heating rate. The additional advantage of a coating only a few particles thick is that the shiny surface of the aluminum foil reflects some of the photons which are not emitted in the upward direction, whereas a thicker layer of pottery tends to absorb them. The size of the "spot" of powdered pottery was dictated by the area that could be heated uniformly by the furnace. When an attempt was made to enlarge the furnace, the nichrome strips tended to buckle. Before measurement of the glow curves, samples are preheated for 45 seconds at 150°C to remove the less reliable low temperature peaks which might be present.

With these and other minor problems overcome, we are now getting results from measurements of photons emitted with heating and rates of alpha bombardment, that begin to show some age correspondence. Two glow curves are shown in Fig. 4. Curve A is typical of that obtained from pottery which is dark in color and curve B, from that which is light. It is noticed that the "background" (obtained from a second heating of the "spot" of pottery) tends to rise at a lower temperature with light pottery. Since color variations are indicative of variations of the constituents of the pottery, the measurements of contemporaneous samples of varying colors may provide some useful information.

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 eleven samples from the Solduz Valley, Iran are listed in Table 1 and plotted in Fig. 5. They have been plotted as 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 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 this series of pottery.

The lack of better consistency in fig. 5 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, intensities indicated linear effects of these variables. 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 are as shown in fig. 6. It is seen here that age correspondence is not significantly better.

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. 5 with no correction for this factor. There are still, therefore, unclarities in the mechanism and proper ways of taking account of the variations in samples.

Before a definite statement may be made in regard to the optimum means of correcting for varying susceptibilities, many more series must be measured. The results at the moment, however, are encouraging and it is now anticipated with greater sureness that thermoluminescence will afford a means of dating pottery, and, hence, be a valuable tool for archaeologists.

REFERENCES

1. F. Daniels, C.A. Boyd, D.F. Saunders, Science, 117, 349 (1953).
2. F.G. Houtermans, E. Jäger, M. Schön, H. Stauffer, Ann. d. Physik, 20, 283-92 (1957).
3. G. Kennedy, L. Knopff, Archaeology, 13, 147-148 (1960).
4. M.S. Tite, J. Waine, Archaeometry, 5, 53-79 (1962); M.J. Aitken, M.S. Tite, J. Reid, Archaeometry, 6, 65-75 (1963).
5. E.K. Ralph, Amer. J. Sci. Radiocarbon Supplement, 1, 49-50, (1959). R. Stuckenrath, Radiocarbon, 5, 85-90 (1963).

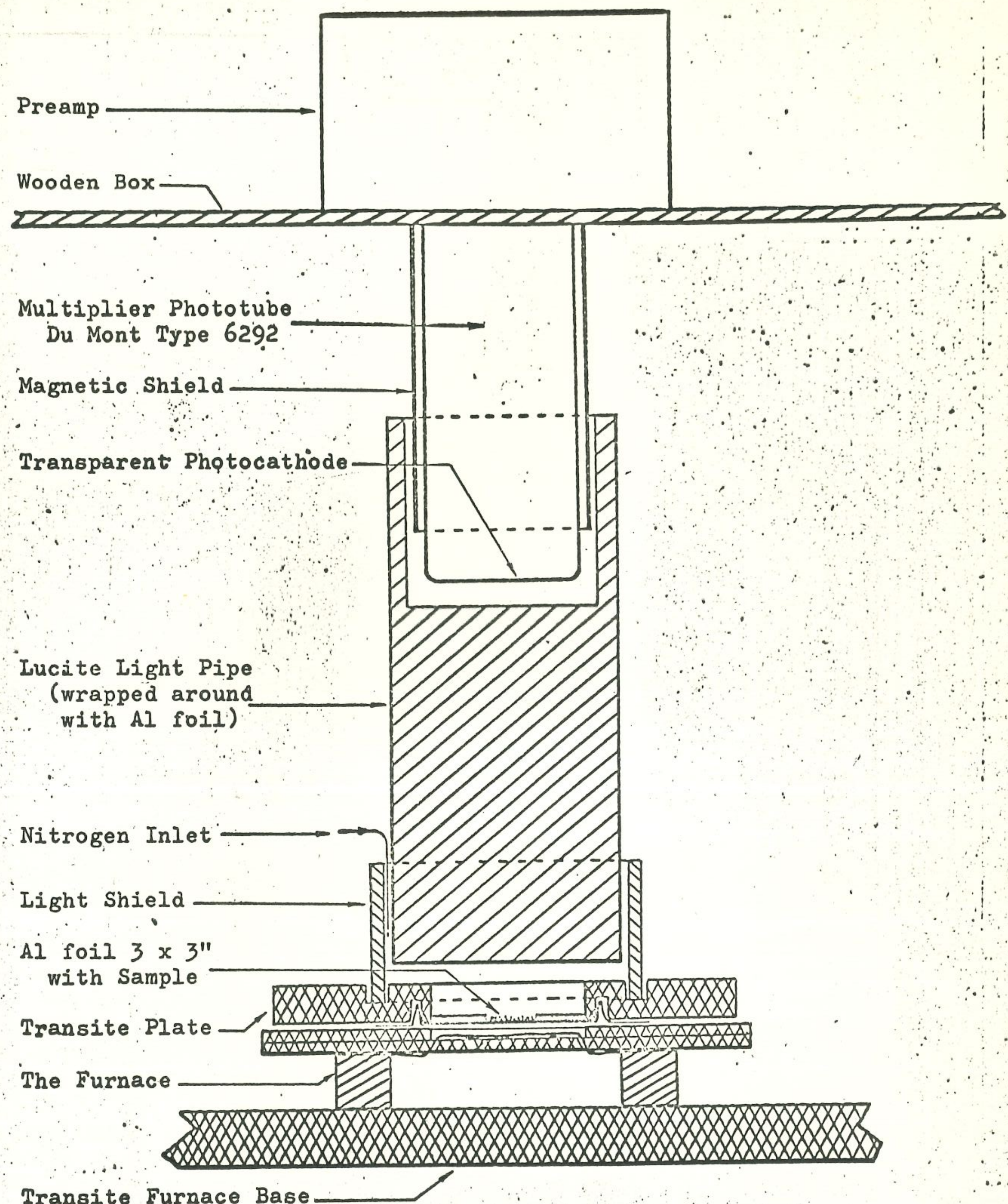


Fig. 1 Cross-section of Photomultiplier, Light Pipe and Furnace

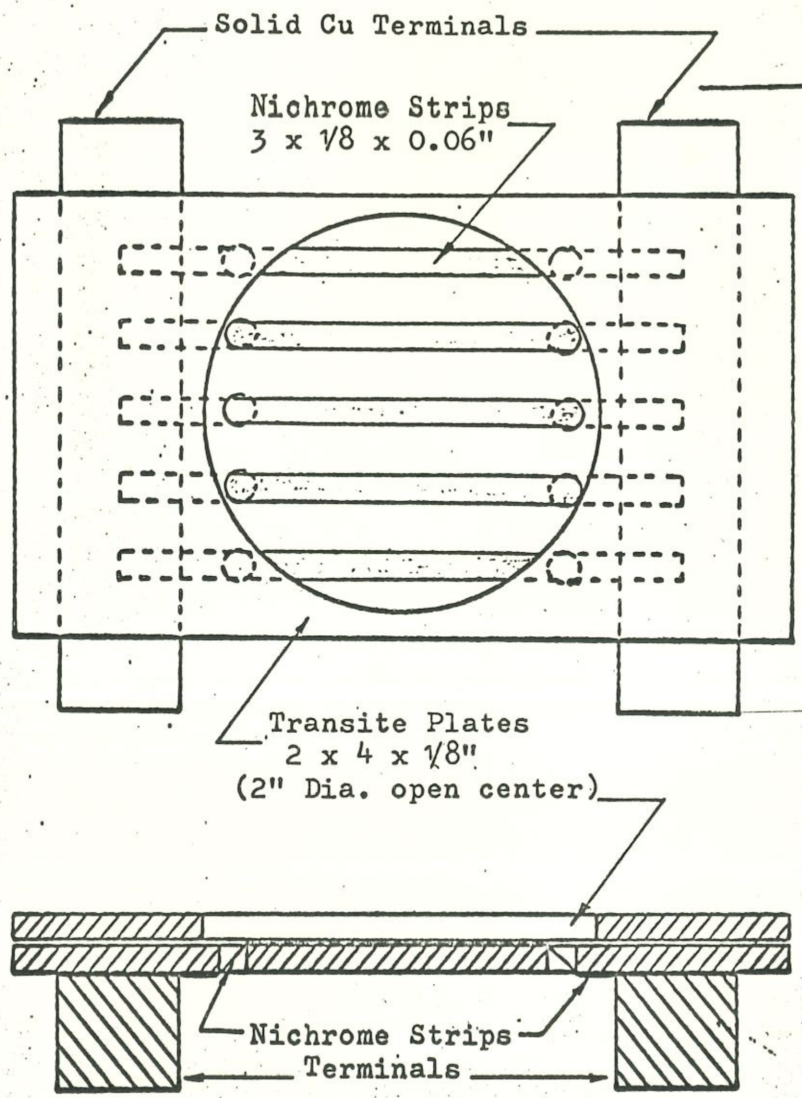


Fig. 2 Top and Front (cross-section) view of the Furnace

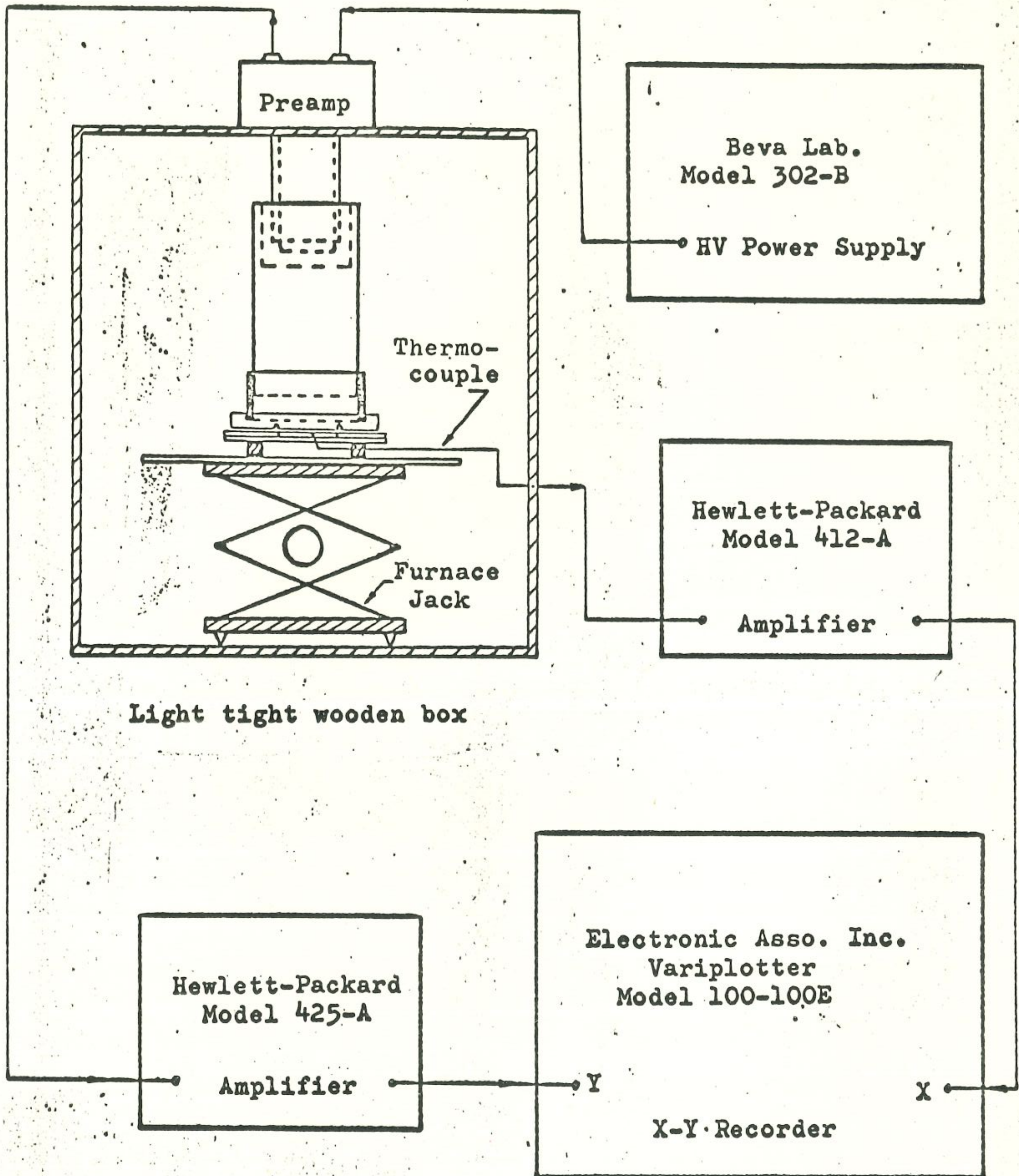
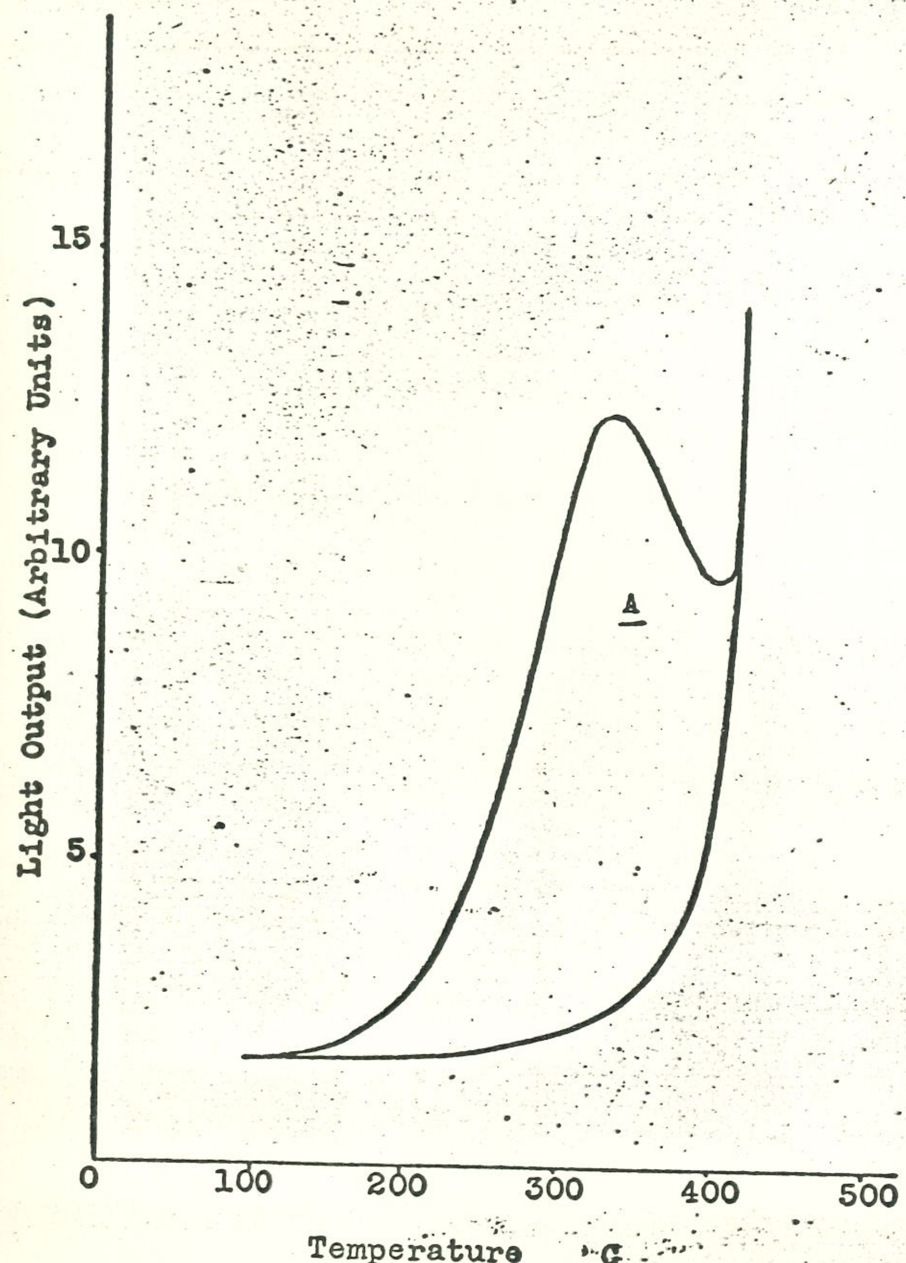


Fig. 3 Block diagram of the glow curve apparatus



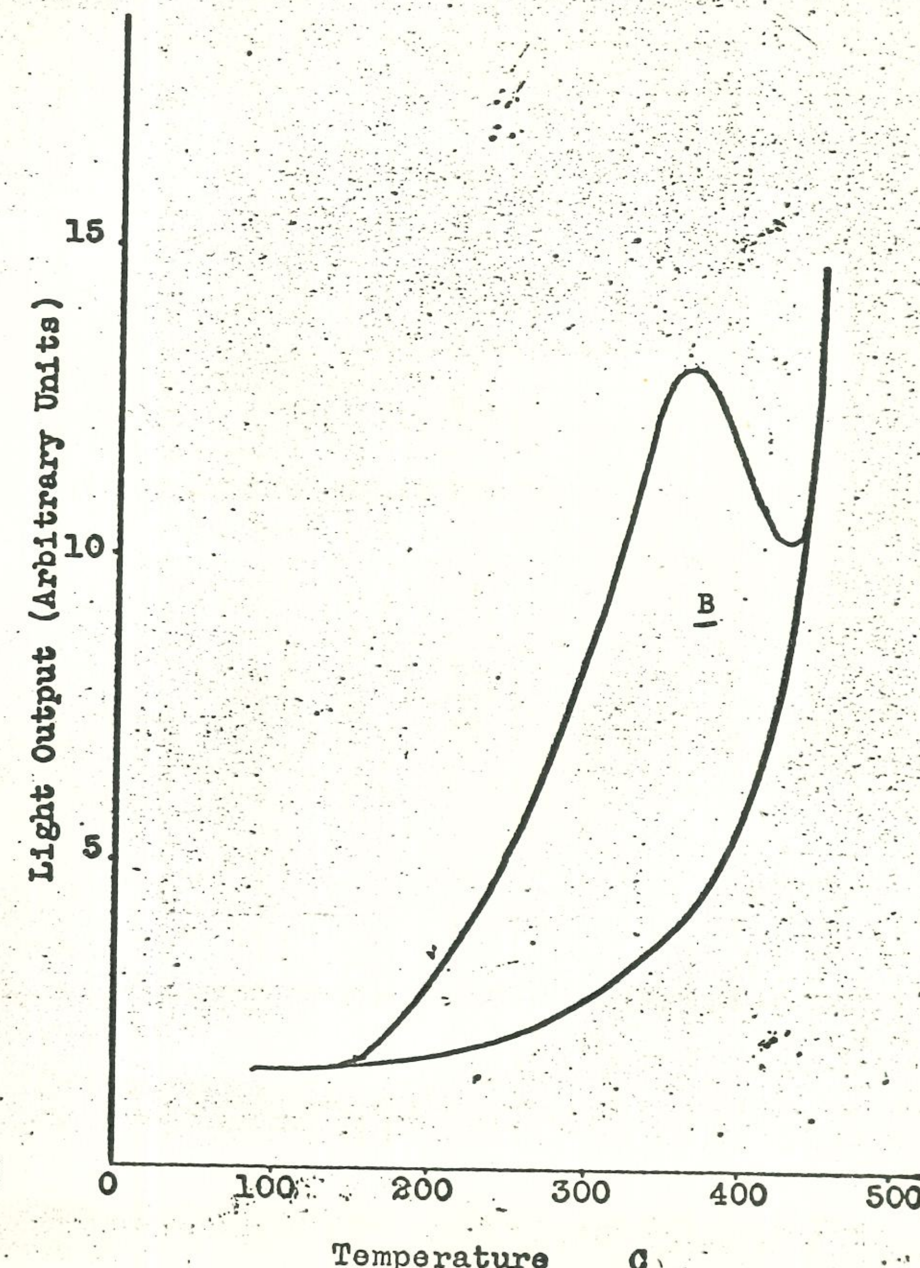


Fig. 4 A represents shapes of curves obtained with dark-colored pottery and B with light-colored

Sample No. & Age (BC)	Relative Alpha rate α C/hr.	Fusion extration K%	Average Light Output (I) μa & Statistical deviation of 20 runs ($\pm\sigma$)	$\frac{I \pm \sigma}{\alpha}$	Time (sec.) to match equal am't Thermoluminescince by X-Rays	$(\frac{I \pm \sigma}{\alpha})$(X-Rays)
1-A 5500	11.7±0.3	2.43	0.271±0.039	0.0232±0.0033	8	0.186±0.026
1-B	11.3±0.4	2.51	0.334±0.069	0.0296±0.0061	12	0.355±0.073
2-A 4200	11.4±0.6	2.66	0.103±0.014	0.0090±0.0013	10	0.090±0.013
2-B	11.0±0.4	2.34	0.265±0.027	0.0241±0.0024	18	0.434±0.043
3-A 3500	16.9±0.8	3.29	0.266±0.028	0.0157±0.0016	29.5	0.463±0.047
3-B	13.1±0.4	2.80	0.326±0.043	0.0249±0.0033	27	0.672±0.089
4-A 2200	17.1±0.5	N.D.*	0.080±0.032	0.0047±0.0019	15	0.071±0.028
4-B	18.0±0.5	N.D.	0.120±0.018	0.0067±0.0010	20.5	0.137±0.021
5-A 900	17.6±0.5	2.47	0.074±0.016	0.0042±0.0009	7	0.029±0.006
5-B	8.8±0.5	2.14	0.029±0.006	0.0033±0.0007	5	0.017±0.004
5-F	11.2±0.3	N.D.	0.084±0.014	0.0075±0.0012	N.D.	N.D.

Table 1   * Not Determined   SERIES OF POTTERY FROM SOLDUZ, IRAN

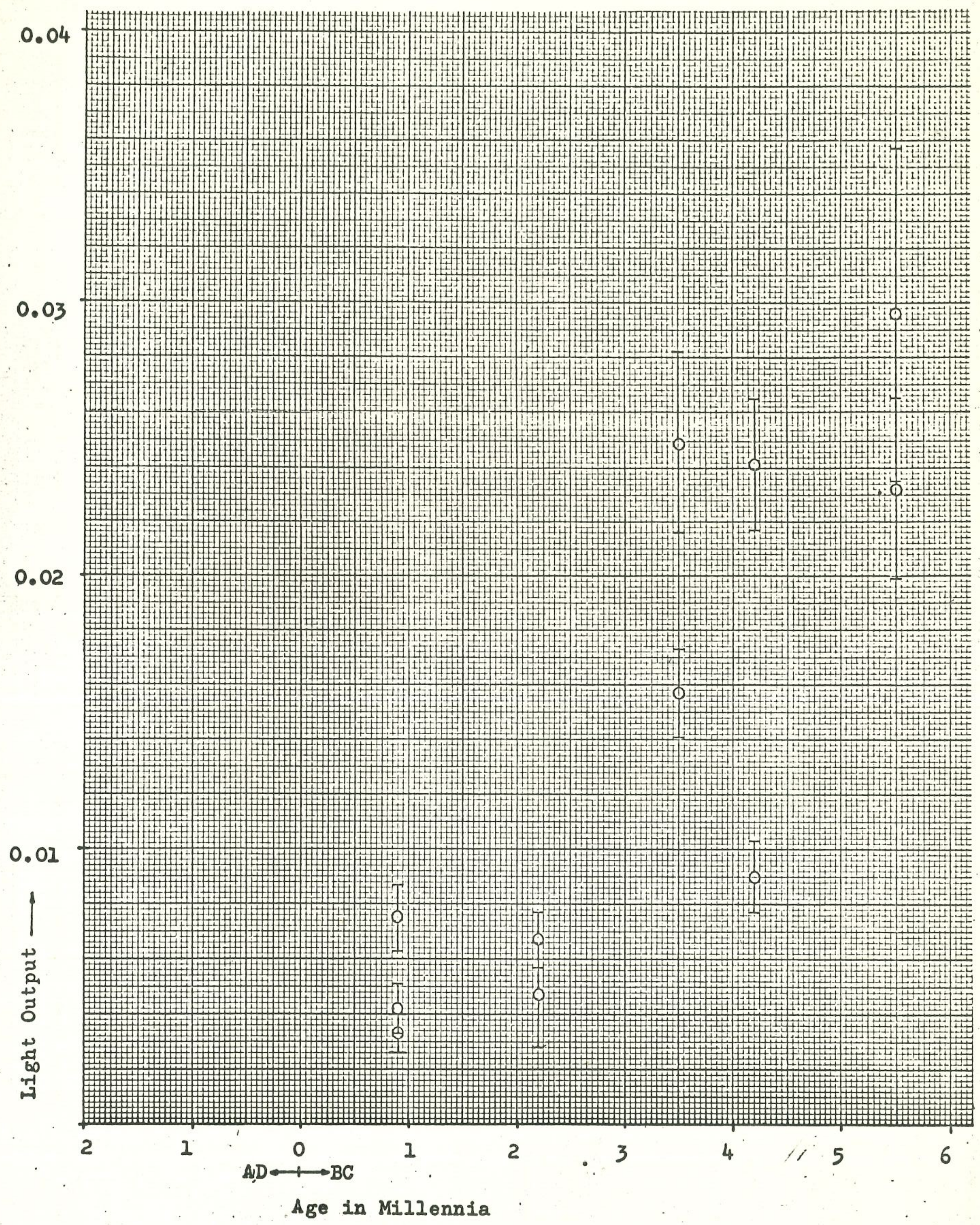


Fig. 5 Light Output with Alpha rate Correction versus Age.

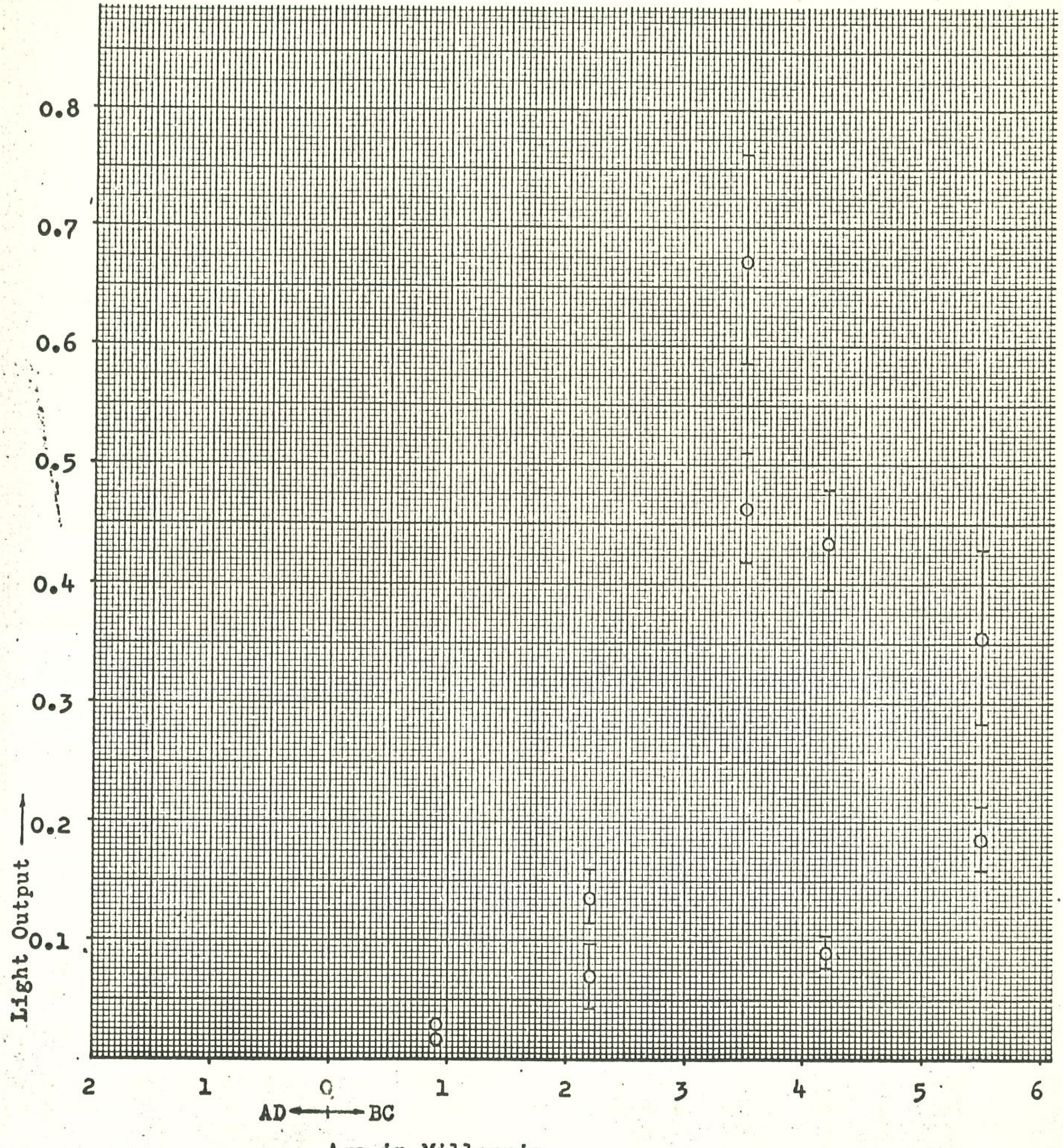


Fig. 6 Light Output vs Age with Alpha Bombardment Rate and X-ray Correction Factors Applied

NATIONAL SCIENCE FOUNDATION

WASHINGTON, D.C. 20550

File
Techniques

November 21, 1966

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

Dear Dr. Rainey:

Your proposal for support of the research named below has been received by the Division of Social Sciences and assigned to the Anthropology Program for study and evaluation.

It will be reviewed by our Advisory Panel at its next meeting. Processing normally requires three to six months from the time of receipt. You will be advised as early as possible regarding the Foundation's ability to support your work.

Sincerely yours,

Richard W. Lieban

Richard W. Lieban
Program Director for
Anthropology

Thermoluminescent Dating of Pottery.

NSF GRANT GP-3778

C-14 Measurements of Known Age Samples

FINAL REPORT

by

Elizabeth K. Ralph, Principal Investigator

April 17, 1967

Carbon-14 dates obtained prior to 1965 for dendrochronologically-dated samples were reported by Ralph, Michael, and Grunninger in "University of Pennsylvania Dates VII" (Radiocarbon, V.7, pp.179-185, 1965). In this Date List the results of dating fifty-four samples of *Sequoia gigantea* were included. In the plot of these (Fig. 1, Date List) one sees evidence of the oscillations in atmospheric C-14 inventory in the period A.D. 1700 to 1400 while C-14 contents from A.D. 1100 to 100 B.C. are found consistently just below the 5730 half-life line. In fact, they are in closer agreement with the Libby half-life (5568) as pointed out by Ralph in "Review of Radiocarbon Dates from Tikal and the Maya Calendar Correlation Problem" (American Antiquity, V.30, pp.421-427, 1965), and in previous publications on this subject. Going back in time beyond 100 B.C., a divergence which seems to increase with age is then apparent from the sequoia results. The average deviations of the samples representative of the period 650 B.C. to 1150 B.C. represents a difference of more than 100 years in ages calculated with the 5730 half-life.

At the time of publication of Date List VII, the dates for samples of bristlecone pines (*Pinus aristata*) were of necessity treated as unknowns.

Unfortunately, the tree sections, collected both by H. Michael (University of Pennsylvania) and by the University of Arizona, for which C-14 dates are reported in Date List VII, happen to be among the most difficult for tree-ring dating. Therefore, most of these have not yet been pin-pointed precisely in time even though the C-14 dating was useful in placing them within a bracketed span of time. Since then, however, C. W. Ferguson at the Laboratory of Tree-Ring Research, University of Arizona, has made significant progress in the collection and in the dendrochronological dating of other sections of bristlecone pines. By the end of 1965, we had received and dated samples extending back to 1625 B.C. These and previous results are summarized by Rainey and Ralph in an article entitled "Archaeology and its New Technology" (Science, V.153, pp.1481-1491, 1966).

In the period January 1966 to March 1967 we received several shipments of samples which cover, at 25 to 50 year intervals, the following time-spans:

1430 B.C. to 1700 B.C.;
2020 B.C. to 2280 B.C.;
2400 B.C. to 3500 B.C.;
4130 B.C. to 4400 B.C.

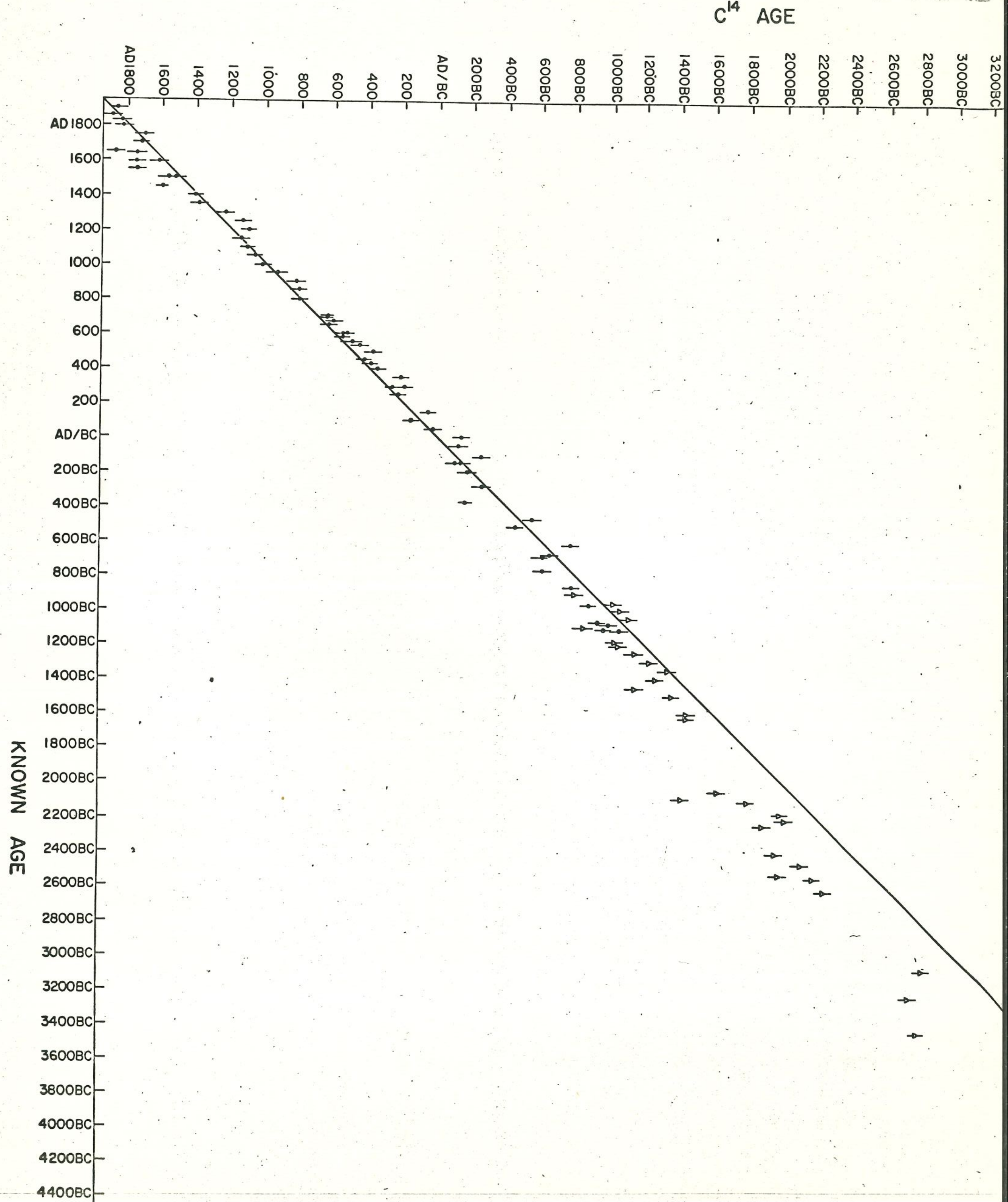
Additionally, two "floaters" (loose pieces of wood) were received and dated 4250 ± 66 B.C. and 4469 ± 68 B.C. respectively. With the expected fluctuation error at this time-distance these dates indicate an antiquity for the woods greater than 4400 B.C., probably by several hundred years. As of this writing the C-14 dating of these samples has not been completed. This is due partly to the late arrival of the older samples and more recently, to numerous technical difficulties in our C-14 laboratory.

The C-14 dates which have been completed are shown in Fig. 1. We see again the general trends of deviations and also a few short-term fluctuations which seem to be significant. For example, in the period from 600 B.C. now extending to 1600 B.C. the C-14 dates are quite consistently younger than known ages by 100 to 200 years (5730 half-life), but there are a few exceptions such as the group of samples in the range of 950 to 1050 B.C. and the extremely deviant one at 2050 B.C. We plan to repeat some of these measurements, but if real, it may be that these have been short-term deviations, possibly associated with climatic changes such as suggested by de Vries for the period A.D. 1600 to 1400. In the range of 1000 to 1200 B.C. there is the possibility of correlation with the 3rd Little Ice Age suggested by Schove and others.

Beyond 1625 B.C. our data at this moment are too scarce and incomplete to suggest possible correlations with one or more of the possible basic causes of changes in the atmospheric C-14 inventory, or even to provide reliable correction factors for the dating of samples of unknown age. One may say tentatively that C-14 dates in the period of 2000 B.C. to 2650 B.C. may be 400 years too young, and from 3100 B.C. to 3450 B.C., 500 years.

In regard to possible correlations with basic causes, there is now new evidence from the work of V. Bucha (J. of Geomagnetism and Geoelectricity, V.17, pp.407-412, 1965 and personal communication, 1966) that changes in the intensity of the earth's magnetic field are cyclic and that sometime before 3600 B.C. the earth's

Fig. 1. Carbon-14 dates from the University of Pennsylvania plotted against known ages for tree-ring-dated sequoia (solid dots) and bristlecone pine (open triangles) samples. Carbon-14 dates were calculated with the 5730 half-life, and are corrected for possible fractionation errors by C^{13}/C^{12} measurements.



field was similar or slightly less intense than in the 20th century. It is hoped that the present range of tree-ring-dated bristlecone pines (back to 4400 B.C.) will be adequate to evaluate this possible correlation.

Other work conducted in connection with NSF GP-3778 included the coring of beams in the pyramids at Meidum and Dashur and the collection of a "floater" in the upper chamber of the pyramids at Dashur. Also corings from the living cedars of Lebanon were collected. Thus far, the only definite result is the dating of the "floater" from Dashur. The date proves the antiquity of the beams as integral parts of the pyramid.

Preliminary work done by B. Bannister (University of Arizona) on the corings from Meidum and Dashur was inconclusive because of the presence in the corings of extremely difficult double rings. The corings from the cedars of Lebanon have been cross-dated within the two groves from which they had been obtained and form a valuable chronology, extending from the present to 450 years ago, which will prove useful for future studies.

Two additional activities, which took place in 1964, should be mentioned. The first was the acquisition of a cross-section from a once-buried trunk of a cedar of Lebanon. It was hoped that it would be possible to correlate its ring pattern with wood from Egyptian pyramids. Although the C-14 age of the wood indicates this possibility, it proved inapplicable because of the complacency of the ring pattern in the cross-section. The second activity was the presentation at the VIIth International Congress of Anthropological and Ethnological Sciences in Moscow, August 1964, by

B. Bannister of a report dealing with his establishment of an 800-year floating chronology for the Anatolian plateau of Turkey.

List of Publications Pertinent to

Grant NSF GP-3778

Ralph, E. K., Michael, H. N., and Grunninger, Jr., J., University of Pennsylvania Dates VII. Radiocarbon, V.7, pp.179-186, 1965. (Reprints of this article were submitted with the annual report, January 1966).

Rainey, F. and Ralph, E. K., Archaeology and its New Technology. Science, V. 153, pp. 1481-1491, 1966. (Reprints are enclosed).

Ralph, E. K., Review of Radiocarbon Dates from Tikal and the Maya Calendar Correlation Problem. American Antiquity, V. 30, pp. 421-427, 1965. (This article is on a related subject for which use of the known age dating program was made. Reprints are enclosed).

Bannister, B., Dendrochronology in the Near East: Current Research and Future Possibilities. Paper delivered at the VII International Congress of Anthropological and Ethnological Sciences, Moscow, August 3-10, 1964. (Abstract only has been published; copies enclosed).

List of Personnel who have Participated in
Grant NSF GP-3778

Elizabeth K. Ralph, Associate in Department of Physics and Associate Director of the Applied Science Center for Archaeology, University Museum.

Henry N. Michael, Research Associate, Department of Physics.

Robert Stuckenrath, Jr., Research Specialist, Department of Physics.

John Grunninger, Jr., Graduate Student in Chemistry.

R. John McHugh, Chemical Electronics Technician, Department of Physics.

Barbara Lawn, Chemical Electronics Technician, Department of Physics.

Temporary students on hourly basis.