COVER SHEET
RESEARCH INITIATION AND SUPPORT

1. Type of Proposal (Check One): Departmental ✓ Interdepartmental Institutional Interinstitutional (Consortium)

2. Highest Degree Awarded in Science Ph. D.

3. Name of Institution or Consortium: University of Pennsylvania
   Address: 101 College Hall/CO
   Philadelphia, Pa. Zip Code: 19174

4. Name and Title of Chief Executive Officer:
   Martin Meyerson, President
   University of Pennsylvania

5. Grant To (If Different from 3. above): Same
   Address:
   Zip Code:

6. Scientific Disciplines in Project:
   Physical, Social, and Earth Sciences

7. Project Director: Name: Elizabeth K. Ralph
   Title & Academic Address: Associate Director of MASCA, Dept. of Physics DRL/E1
   Telephone Number (include area code): 215-243-8168

8. Length of Proposed Project (months): 36 months

9. Total Requested from NSF: $ 249,962 Total Contributed by Grantee: $ 64,112

10. If funds for parts of the project proposed are being requested in another proposal to NSF or another Federal agency, indicate agency, proposal number(s), and date submitted:

    NSF, Proposal No. EAR7614258, January 1976
    (This request will be withdrawn unless awarded before word about this proposal is received, in which case it could be deducted from this budget)

11. Signature of Project Director named in (7) above: Elizabeth K. Ralph

12. Signature of Chief Executive Officer named in (4) above:

13. Date Submitted: March 15, 1976

(SAMPLE)

RESEARCH INITIATION AND SUPPORT

Budget Summary

	REQUESTED FROM NSF	CONTRIBUTION OF HOST INSTITUTION
SALARIES, WAGES, BENEFITS		
11. Director	$ —	$ 22,890
12. Professional Staff	16,000	11,392
13. Assistants	27,308	16,579
14.		
15. Secretarial and Clerical	4,024	2,543
16. TOTAL: SALARIES & WAGES	47,332	53,404
17. Staff Benefits (when charged as direct costs)	10,578	10,708
18. TOTAL: SALARIES, WAGES & BENEFITS (16&17)	57,910	64,112
OTHER DIRECT COSTS		
19. Guest Lecturers	450	Scheduled seminars, ~~etc.~~
20. Staff Travel	3,000	
21. Field Trips		
22. Laboratory and Instructional Materials	11,500	
23. Office Supplies, Communications	700	
24. Fees		
25.		
26. Services, Machine Shop & Glassblowing	3,700	
27. Equipment	133,300	
28. TOTAL DIRECT OPERATING COSTS (18 thru 27)	210,560	64,112
29. INDIRECT COSTS	39,402	
30. TOTAL OPERATING COSTS (28 & 29)	$ 249,962	64,112

RESEARCH INITIATION AND SUPPORT

DETAILED BUDGET

Name of Institution University of Pennsylvania

AMOUNT REQUESTED (In Thousands of Dollars)

ACTIVITIES	Refer to narrative page no.	FIRST YEAR			SECOND YEAR			THIRD YEAR			FOURTH YEAR			TOTAL		
		NSF	OTHER	TOTAL	NSF	OTHER	TOTAL	NSF	OTHER	TOTAL	NSF	OTHER	TOTAL	NSF	OTHER	TOTAL
See more	27 - 34	152	20	172	39	21	60	59	23	82				250	64	314
detailed																
budgets,																
pp. 4 - 11																

B. Budget for First Year

	Requested from NSF	Contribution of Univ. of Penna.
1. Salaries, Wages and Benefits		
a. Elizabeth K. Ralph, Prin. Invest. (A-2) FTE 4 person months		$ 7,190
b. Barbara Lawn, Res. Specialist (A-1) FTE 3 person months		3,578
c. Research Fellows, Grad Students (A-2) 3 summer months - full-time Academic year - ½ time FTE 8 person months		
(1) Jeffrey Klein, Grad Student in Physics		5,208
(2) Two additional ones in Physics, Chemistry, Geology, Anthropology, etc.	$ 10,416	
d. Administrative (A-1), Secretarial and Clerical (A-3), Part-time	120 1,078	799
For this year and the following two years, Secretarial and Clerical Salaries have been calculated as 4.5% of proposed funds for all items except Equipment, and Administrative as 0.5%		
Sub-Total for (d)	1,198	
e. Staff Benefits		
A-1 15.5%	19	555
A-2 21.1%	2,198	2,616
A-3 20.0%	216	
Sub-Total for Staff Benefits	2,433	3,171
2. Guest Lecturers	150	
3. Staff Travel Domestic Examining of new equipment in Calif. and attending meetings and conferences	1,000	
4. Laboratory Materials - Chemical Supplies, Expendable Electronic Components, etc.	5,000	
5. Office Supplies including Printing, Duplicating and Communications	200	

Budget for First Year - Continued

	Requested from NSF	Contribution of Univ. of Penna.
6. Services		
Machine Shop	$ 700	
Glassblowing	1,000	
Total Services	1,700	
7. Equipment (See itemized equipment budget following this 3-year budget for proposed NSF funds)		For University Contribution of Equipment see "Facilities Statement"
Laser and Optics	60,000	
Mass Spectrometer	45,800	
Chemical Processing Train	5,000	
Flow system for gaseous isotope separation	7,500	
Total Equipment	118,300	
Note: If there are delays in the initial experiments, designing, and the delivery of components, some of this budget for Equipment might be applied in the second year of the grant.		
8. Total Direct Operating Costs	140,397	
9. Indirect Costs (51% of all costs except Equipment)	11,269	
10. Total Operating Costs - First Year	$151,666	$ 19,946

C. Budget for Second Year

	Requested from NSF	Contribution of Univ. of Penna.
1. Salaries, Wages and Benefits		
a. Elizabeth K. Ralph, Prin. Invest. (A-2) FTE 4 person months		$ 7,621
b. Barbara Lawn, Res. Specialist (A-1) FTE 3 person months		3,793
c. Research Fellows, Grad Students (A-2) 3 summer months - full-time Academic year - ½ time FTE 8 person months		
(1) Jeffrey Klein, Grad Student in Physics		5,520
(2) Two additional ones in Physics, Chemistry, Geology, Anthropology, etc.	$ 11,041	
d. Administrative (A-1), Secretarial and Clerical (A-3), Part-Time	114	847
For this year and the following year, Secretarial and Clerical Salaries have been calculated as 4.5% of proposed funds for all items except Equipment and Administrative as 0.5%	1,030	
Sub-Total	1,144	
e. Staff Benefits		
A-1 17.0%	19	645
A-2 22.6%	2,495	2,970
A-3 21.5%	221	
Sub-Total for Staff Benefits	2,735	3,615
2. Guest Lecturers	150	
3. Staff Travel Foreign To attend International Conferences	1,200	
4. Laboratory Materials - Chemical Supplies, Expendable Electronic Components, etc.	3,500	
5. Office Supplies including Printing and Duplicating and Communications	200	

Budget for Second Year - Continued

		Requested from NSF	Contribution of Univ. of Penna.
6.	Services		
	Machine Shop	$ 600	
	Glassblowing	500	
	Total Services	1,100	
7.	Equipment Replacements - optical components such as mirrors, dyes, thyristors, etc.	7,500	
8.	Total Direct Operating Costs	28,570	
9.	Indirect Costs (51% of all costs except Equipment)	10,746	
10.	Total Operating Costs - Second Year	$39,316	$21,396

D. Budget for Third Year

	Requested from NSF	Contribution of Univ. of Penna.
1. Salaries, Wages and Benefits		
a. Elizabeth K. Ralph, Prin. Invest. (A-2) FTE 4 person months		$ 8,078
b. Barbara Lawn, Res. Specialist (A-1) FTE 3 person months		4,021
c. Postdoctoral Fellow (A-2) FTE 12 person months	$ 16,000	
d. Research Fellows, Grad Students (A-2) 3 summer months - full-time Academic year - ½ time FTE 8 person months		
(1) Grad Student in Physics		5,851
(2) One additional one in Physics, Chemistry, Geology, Anthropology, etc.	5,851	
e. Administrative (A-1), Secretarial and Clerical (A-3), Part-time	168	
For this year Secretarial and Clerical Salaries have been calculated as 4.5% of proposed funds for all items except Equipment and Administrative as 0.5%	1,514	898
Sub-Total	1,682	
f. Staff Benefits		
A-1 17.5%	29	704
A-2 23.1%	5,048	3,218
A-3 22.0%	333	
Sub-Total for Staff Benefits	5,410	3,922
2. Guest Lecturers	150	
3. Staff Travel Domestic For attending meetings and conferences	800	
4. Laboratory Materials - Chemical Supplies, Expendable Electronic Components, etc.	3,000	
5. Office Supplies including Printing and Duplicating, and Communications	300	

Budget for Third Year - Continued

		Requested from NSF	Contribution of Univ. of Penna.
6.	Services		
	Machine Shop	$ 500	
	Glassblowing	400	
	Total Services	900	
7.	Equipment Replacements - optical components such as mirrors, dyes, thyristors, etc.	7,500	
8.	Total Direct Operating Costs	41,593	
9.	Indirect Costs (51% of all costs except Equipment)	17,387	
10.	Total Operating Costs - Third Year	$58,980	$22,770
11.	Total Costs - Three Years	$249,962	$64,112

Itemized First Year Equipment Budget for Tentative Laser Photolysis

Laser:	Molectron Corp., Sunnyvale, Calif 94086	
	N_2(Nitrogen gas) laser UV-1000	20,000
	Tunable Dye Laser DL-300	13,600
	Frequency Doubler DL-070	5,000
	Spectroscan -10, frequency scan control	13,000
	Additional Fabrey-Perot etalon	2,400
	Scanning interferometer-beam purity check-DL-031A	1,300
	High sensitivity spectrophotometer LP-20	3,000
	Beam Telescope DL-030	1,000
	Lock in-amplifier for feedback system	700
		$60,000

Chemical Processing Train		
	Vacuum pump-Edwards ED 50	475
	Diffusion pump- Edwards EO2	430
	Thermistor Gauge-Bendix GT-348	395
	Vacuum coupling components-Edwards	350
	Glass components-high vacuum stopcocks, tubing, vessels, etc	1,000
	Trap cooler-Neslab Model CC100F	1,050
	Flowmeter -Datametrics	
	Valves and fittings	500
		$5,000

Flow System		
	Optics	1,895
	Beam splitters	
	First surface mirrors	
	Photolysis cells -2	
	Optics for conducting fluorescence to spectrophotometer	
	Manometer Control Systems-2 Datametric type 571	4,200
	Vacuum Pump-Edwards- EB50	475
	Glassware, high vacuum stopcocks, etec	500
	Diffusion Pump-Edwards EO2	430
		$7,500

Itemized First Year Equipment Budget for tentative Mass Spectrometer

Mass Spectometer-Finnegan 3100F-100, deleting items D-0074D, D-0116D, D-042, and D-052 $45,800.

Possible alternate choice

CVC(Bendix) TOF MAss Spectrometer MA-2
Memory And Display 160A
Strip Chart Recorder A51105

LOCAL REVIEW STATEMENT

GOALS AND OBJECTIVES FOR THE UNIVERSITY OF PENNSYLVANIA

From its beginnings in Colonial days the University of Pennsylvania has been distinguished by a respect for the practical as well as the theoretical, for the sciences and the professions as well as the humanities. Benjamin Franklin wished his Academy to teach "those things most likely to be useful," in addition to those things he called "ornamental."

Today, the prescription is more timely than ever. The complexity of society, and its problems, call for men and women versed in the liberal arts and sciences but with experience in the practical applications.

To this mission, Pennsylvania brings assets other than tradition. It is marked by a physical and intellectual unity not commonly found in a large and diverse university, and it has taken advantage of its oneness to enrich the experience of the students and faculty in all its schools. In the view of a visiting team of scholars, the University of Pennsylvania already has achieved "freedom of students to move across faculties."

Now the University is engaged in a program for the years leading to the 1980's, building on these and other strengths. It is a design for marshalling the varied resources of its many schools and departments for the common benefit of all its students and faculty. It is a plan which recognizes that fiscal integrity must underlie any aspirations to excellence. It aims to bring the University of Pennsylvania to the next decade as "One University," and as one whose academic structure rests on a sound financial base. This is the heart of the University of Pennsylvania's goals and objectives for the next decade.

The genesis of goals definition lay in the work of the Development Commission, a broadly-based, prestigious group of faculty, administrators, students, and extra-University persons appointed by the President of the University in 1972 to study Pennsylvania's academic and financial positions with a view toward putting both on higher, firmer ground. The Commission reported in 1973 that it found Pennsylvania:

> A private, urban, residential university of considerable distinction...noted for its professional schools...strong also in many areas of the arts and sciences...committed to research as well as teaching...with close relationships among its schools fostered by their proximity on one campus.

To bring the University to the full measure of its promise, the Commission prescribed a qualitative buildup of Pennsylvania's many academic strengths. As its central theme, it envisioned a joining together of the University's varied talents and programs at all levels--from freshman year through post-doctoral study--in new combinations that would correlate one specialty with another, theory with practice, and the perceptions of the liberal arts with the sense of social purpose and application of the professions. To emphasize its theme of building upon strengths and upon linkages of strengths, the Commission entitled its report "One University," and symbolized the integrating structure they envisioned by the hexagonal interrelationships of its parts as shown on the next page.

Note in the hexagonal design that at the core of the University is the FAS, faculty of Arts and Sciences, encompassing 35 academic disciplines in its four quadrants of basic human learning--Languages, Literature, and Cultures...Social Sciences... Life Sciences...and Physical Sciences. Reaching out from this central Faculty are programmatic links with the professional schools.

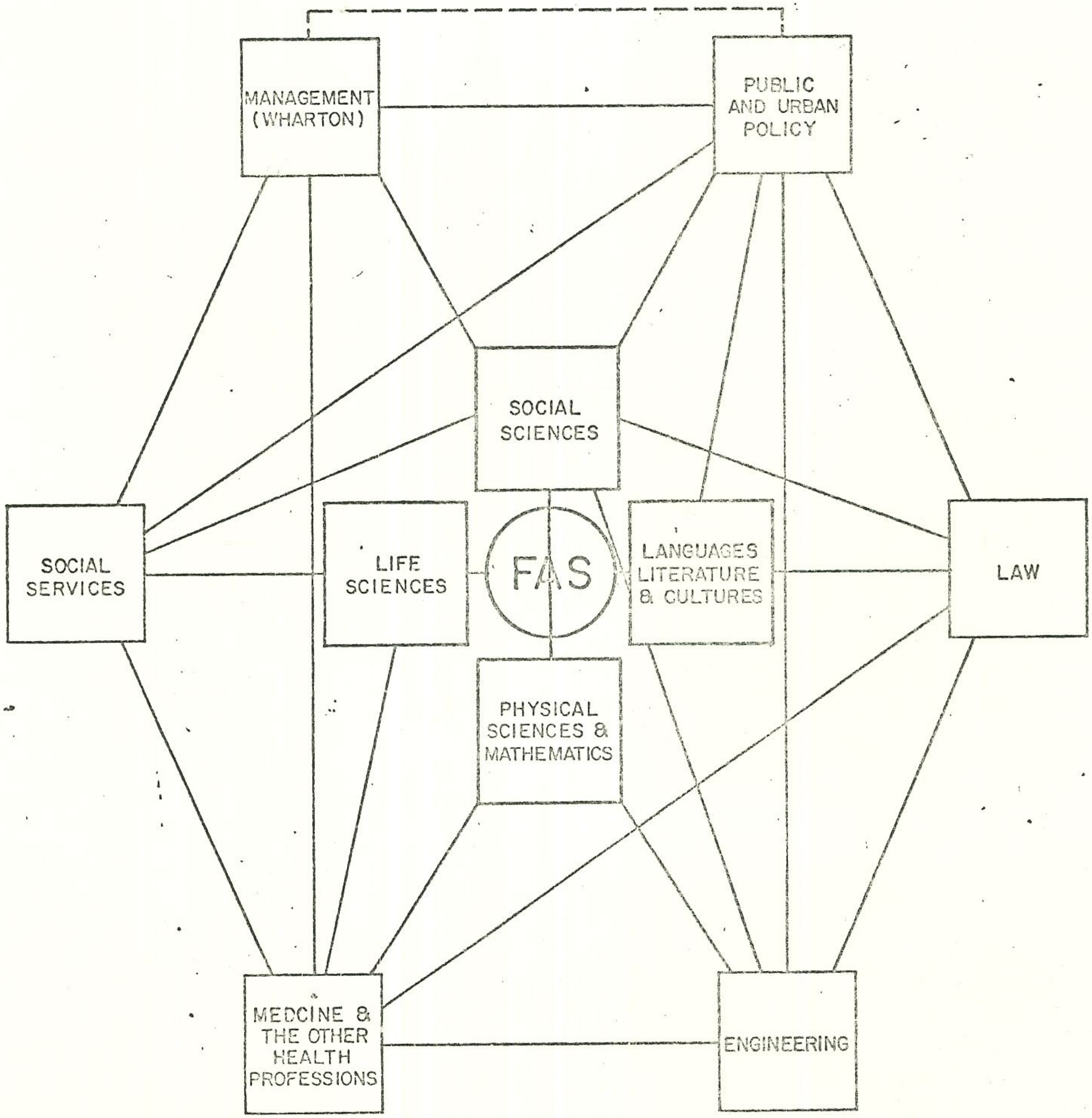
In the central core of the One University the specific objectives include building upon existing strength within the departments in the arts and sciences--the bases of all learning and emphasizing those particular programs that encourage interaction among different areas.

The improvement in quality of present training and research activities for young scientists afforded by the program described on the following pages is in consonance with the institutional objectives of One University. The implementation of this program will serve to strengthen the mutually constructive ties among many of the scientifically-based disciplines purposely built into the compact design of the University of Pennsylvania's academic plan for the next decade. The University of Pennsylvania is committed to maintaining the groups involved in the proposed program and in ensuring that the improvement achieved through this grant will be preserved and sustained.

The diagram on the next page symbolizes the goals for the University of Pennsylvania for the next decade. The diagram's network of lines denotes the web of collaborative relationships that ties together the arts, the sciences, and the professions--all of the fields of learning, theoretical and practical, to be found on Pennsylvania's unified campus. Each junction point represents an area of study as denoted specifically in the diagram. The major goal of academic planning is to strengthen these mutually constructive ties, so that the University may serve its students and society as a total institution greater than the sum of its parts.

The research and educational program proposed here has been conceived as a specific vehicle for strengthening mutually constructive ties particularly between the physical sciences and social sciences.

Martin Meyerson


MANAGEMENT (WHARTON)
PUBLIC AND URBAN POLICY
SOCIAL SCIENCES
SOCIAL SERVICES
LIFE SCIENCES
FAS
LANGUAGES LITERATURE & CULTURES
LAW
PHYSICAL SCIENCES & MATHEMATICS
MEDCINE & THE OTHER HEALTH PROFESSIONS
ENGINEERING

NATIONAL SCIENCE FOUNDATION

PROJECT
SUMMARY
RESEARCH INITIATION AND SUPPORT

NAME OF INSTITUTION	ADDRESS OF INSTITUTION (INCLUDE BRANCH/CAMPUS & COMPONENT)
University of Pennsylvania	Department of Physics David Rittenhouse Laboratory/E1 209 S. 33rd St. Philadelphia, Pa. 19174
PRINCIPAL INVESTIGATOR Elizabeth K. Ralph	

TITLE OF PROJECT

Research Initiation and Education in Application of Physical Sciences to Archaeology, Anthropology, and Geology.

SUMMARY OF PROPOSED WORK

The opening of a broadly based research & training area in laser isotope separation is proposed. The specific purpose is to enrich natural ^{14}C with new equipment. In line with University objectives of cross cultural interactions, these experiments will provide increased opportunities in diverse techniques for graduate and post-doctoral students in the areas of the Physical, Social, and Earth Sciences.

RESEARCH INITIATION AND EDUCATION IN APPLICATION OF PHYSICAL SCIENCES TO ARCHAEOLOGY, ANTHROPOLOGY, AND GEOLOGY

Table of Contents

RESEARCH INITIATION AND EDUCATION IN APPLICATION OF PHYSICAL SCIENCES TO ARCHAEOLOGY, ANTHROPOLOGY, AND GEOLOGY

NARRATIVE

The Radiocarbon (C-14) Laboratory and the Museum Applied Science Center for Archaeology (MASCA) are truly interdepartmental. The C-14 lab was initiated in 1951 through the cooperation of the Department of Anthropology, the University Museum, and the Department of Physics and was located in the Museum and in the Department of Chemistry. In 1956, the C-14 lab was moved to the new Physics building (1800 sq ft in the Rittenhouse Laboratory), MASCA was initiated in 1961 and provided with 2350 sq ft of space in the University Museum. (Both labs have independent air conditioning).

MASCA and C-14 projects are now involved with the following departments in the University: - namely,

Physics

Chemistry

Geology and Geophysics

Anthropology

Classical Archaeology

Metallurgy

Laboratory for Research in the Structure of Matter

Electrical Engineering

Museum

Equipment and facilities in both MASCA and C-14 are available to all students in these and other disciplines, and we offer at least 4 graduate research fellowships each year to qualified students from these departments.

With this grant we hope to make available two additional graduate fellowships for students for two years and one for the third plus a post-doctoral position to be involved in the proposed research and all will be instructed and guided by postdoctoral scientists in the above listed departments.

At present instruction is embodied formally in at least two courses (Anthropology 600 given by Prof. Bernard Wailes, and Metallurgy and Materials Science 585 given by Prof. Robert Maddin). In addition to lecturing in these courses and giving demonstrations in the laboratories, we instruct numerous other classes from the high school level up through advanced graduate students in our various techniques and their applications.

Additionally, members of our staff are called upon frequently to lecture to undergraduate and graduate classes whose professors wish them to learn about our dating and geophysical techniques.

Also, in MASCA we maintain an information center to which the students, faculty, and the public have free access. The MASCA Information Center maintains a catalogue of scientific techniques of value to archaeology and anthropology, consisting of abstracts of articles, references, and information on new developments culled from many publications in diverse fields, as well as unpublished material gathered from correspondence and experimental notes. The files contain about 8000 abstracts collected over the past 15 years. Many of the articles which we abstract are kept in our library files either in the original or xerox copy, so that for most inquiries all necessary material can be found in our library. The Center also has a number of reference books on various techniques and subscribes to about 15 journals directly. Both books and periodicals can be perused by members of the faculty and students in the Information Center or they can be signed out for short periods. Students and faculty from universities and colleges in the Philadelphia area use the facilities frequently as well as visiting scholars and students from the U.S.A. and abroad.

In addition to continuing the development of the information service by abstracting and cataloging, the staff of the Information Center is available to assist users of the Center in the selection of references. They suggest avenues of investigation for specific problems and will conduct library searches in response to specific requests.

A MASCA Newsletter is published periodically to interchange ideas, techniques and information on the applications of science to archaeology. It furnishes an additional medium for the dissemination of the developments which are accomplished.

Our laboratories are increasingly centers for the training of young scientists - undergraduates, graduate students, and recent post-doctoral fellows.

For example, in our own group, as shown on the block diagram (Fig. 2.), Barbara Lawn, Mark Han and Bruce Bevan are studying for Ph. D's in Geology as well as working in their respective laboratories. Raymond Costa, Jr. and John Carpenter expect to receive their Ph. D's in Anthropology in May 1976 and both have contributed valuable services in the ^{14}C and TL labs during the past three years. Jeffrey Klein has just completed his first year of graduate studies in Physics, and is contributing his know-how and practical experience to the development of new techniques such as the laser experiment outlined in this proposal. Kathleen Ryan, while working as Research Bibliographer, has pursued courses in Anthropology and Archaeology, and excavates in Ireland each summer. Gail Weinstein is a candidate for a degree in Classical Archaeology in May, 1977 and has contributed her expertise to the interpretation of ^{14}C dates from Aegean sites. In the same manner, James Weinstein (Ph. D. 1973, in Oriental Studies) is analyzing more than 240 ^{14}C dates of samples from Egypt.

Concerning senior scientists in MASCA, some abbreviated information follows:

Froelich Rainey, Ph. D. in Anthropology, Director of the University Museum.

William E. Stephens, Ph. D. in Physics, Professor of Physics (formerly Chairman of Physics and Dean of the College)

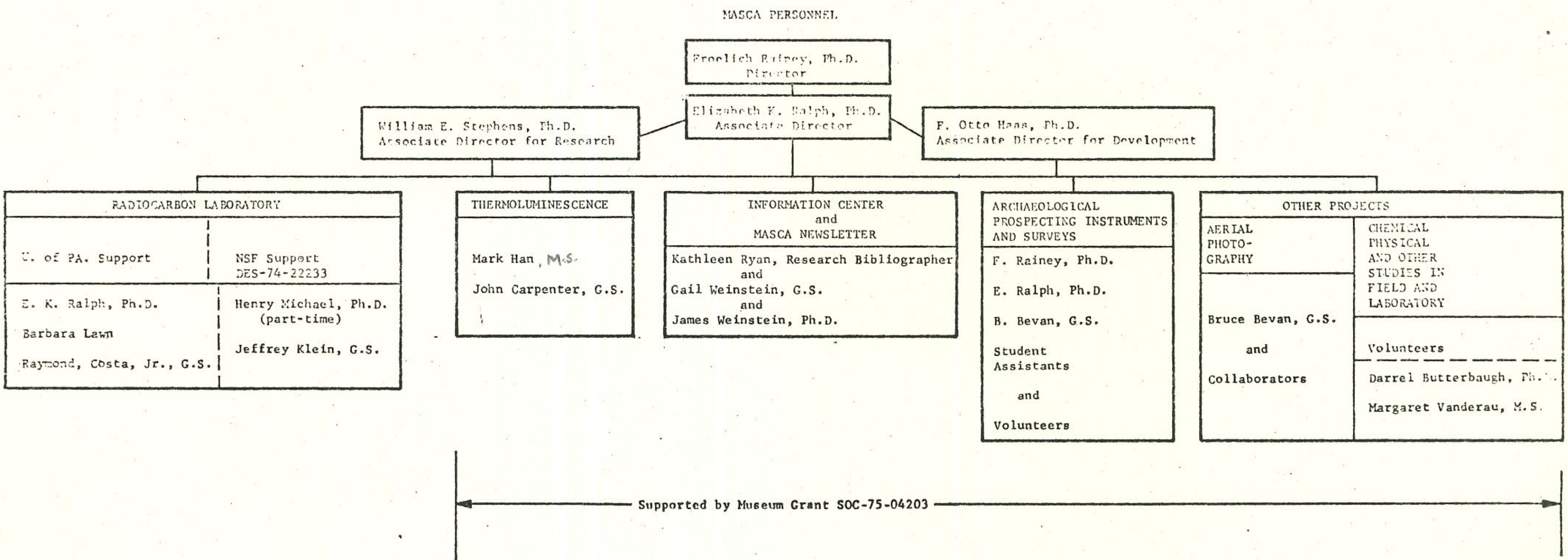
F. Otto Haas, Ph. D. in Chemistry

Elizabeth K. Ralph, Ph. D. in Geology, M. S. in Physics

Henry N. Michael, Ph. D. in Anthropology

Darrel Butterbaugh, Ph. D. in Chemistry

Margaret Vanderau, M. S. in Chemistry



March 1976

G.S. - Graduate Student
1/2-time in academic year
Full-time for 3 summer months

FIG. 2. Block Diagram of MASCA Personnel

Two of the candidates for Ph. D.'s in Geology have already obtained other degrees-namely,

Mark Han, M. S. in Chemistry and M. S. in Chemical Engineering

Bruce Bevan, M. S. in Electrical Engineering

Barbara Lawn, B. A. in Chemistry.

In regard to undergraduates, we have recently instructed three students in all of the routine techniques of our laboratories - David Wood, Physics; Julia Handy, Geology; and Anne Meulengracht - Madsen, visiting scholar in Classics from Denmark. Specialized instruction in TL dating has been given to James Watson, a visiting student in Anthropology from Florida State University.

During the past 25 years, more than 20 other graduate students have been trained and have contributed their expertise in the ^{14}C laboratory. Among these, eight have or are about to receive Ph. D.'s, mostly in Chemistry and Anthropology.

In MASCA, for TL dating, 6 summer students and 3 graduate students have assisted since 1968.

In the Information Center in MASCA 5 graduate students preceeded Kathleen Ryan as Research Bibliographer. Two continue to be candidates for Ph. D.'s and one received his in Oriental Studies in 1974.

MASCA has conducted surveys with geophysical prospecting instruments at archaeological sites in many parts of the world. Notable was the search for ancient Sybaris in southern Italy from 1961 to 1968. For the detection of the remains of the city at depths of 4 to 5 meters and below the ground water table, we developed a cesium magnetometer in collaboration with Varian Associates. This new magnetometer has the capability of 100-fold greater sensitivity than conventional proton magnetometers. With it, we detected roof tiles, etc. (parts of archaic Sybaris) that are now being excavated by the Italian Department of Antiquities.

At archaeological sites abroad and in the U. S. A., we have had the collaboration of scientists and volunteers, also from many parts of the world.

Some examples of additional recent educational and instructional activities are as follows:

Dr. Henry Michael instructed Peter Kuniholm (graduate student in Classical Archaeology at University of Pennsylvania and presently Director of The American Research Institute in Turkey,(Ankara Branch) in the techniques of dendrochronology. As a result, Mr. Kuniholm has now established several floating tree-ring chronologies for Anatolia and has hopes of pinpointing their ages precisely as more wood is found. With his contacts and knowledge of Turkish and the European languages Mr. Kuniholm is receiving excellent support from many scientists in Turkey and also those from neighboring countries: Germany and Russia.

During this spring term (1976), we taught Mr. Kenneth Yu (a graduate student, taking Nuclear Geophysics, Geology 520), in the basic techniques of ^{14}C dating, including the calculation and statistical analyses of the results.

Various students in Metallurgy and Materials Science 585 (mentioned on page 14), are now doing experiments under our guidance. Two specific examples are as follows:

1) Harry Hance (Laboratory Curator at U. of Pa.) - mass spectrographic measurements of C^{13}/C^{12} and K/A ratios.

2) Susan Goldman (visiting student in Chemistry from Swarthmore College) - specific experiments in TL dating.

In addition to these specific examples, a variety of classes periodically visit our laboratories. They come from all of the departments mentioned on page 17 as well as others from both inside and outside of the University and from colleges and universities in New Jersey, Delaware, New York and all parts of Pennsylvania.

PLANNING/ASSESSMENT

The objective is to improve significantly the facilities and educational opportunities available to the education of graduate students and postdoctoral persons in the areas of application of development in the physical sciences to the archaeological, anthropological and geologic sciences.

This will be achieved by a planned program of acquiring appropriate equipment and developing a research effort into the specific area of isotopic enrichment by means of lasers with the objective of achieving methods to extend the time span of dating by the enriched radiocarbon method. These specific objectives will undoubtedly be broadened as the facilities are utilized in interesting ramifications and branching of the original research thereby furnishing an increasing range of research and educational opportunities for later generations of students.

PROPOSED PLAN/STRATEGIES AND ACTIVITIES

Laser spectroscopy and mass spectrometry are valuable aids in increasing the accuracy and range of archaeometric studies. Laser enrichment of isotopes may provide a means for extending the range of radiocarbon dating, and allow reduced statistical counting uncertainties associated with random decay, by increasing the specific activity of the samples (being dated). Potentially it may also be useful as a means for detecting natural ^{14}C directly by highly selective absorption of very narrow linewidth laser pulses and the subsequent observation of low intensity fluorescence.

Mass spectrometry remains the principal means of determining isotopic ratios with good accuracy. These measurements are essential for calibrating enrichment procedures. Isotopic ratios also provide a means of sensing temperature variation from archaeological and geological samples and determining sources of raw materials composing artifacts (Libby 1972, Pandolfi, et al., 1975). Finally, they are vital in quantifying fractionation from natural and chemical processes, an important consideration in accurate dating.

In the past, enrichment of ^{14}C in archaeological samples, as a means of extending the radiocarbon dating range, has been done a few times by thermal diffusion. The technique is of limited practicality due to the slowness of the process (an average of about two months is required per sample) and its expense. (Haring, De Vries and De Vries, 1958; Kretner and Dickel, 1975). Yet, there is a definite need to increase the range of radiocarbon dating from 40,000 to 80,000 years. This would double the portion of the Pleistocene that is datable by ^{14}C and provide a nearly continuous dating system with a range of several hundred to almost a million years by bridging the gap between ^{14}C ($\leq$ 40,000 yrs.) and K-Ar ($\geq$ 100,000 yrs). As a consequence, archaeologists geologists and anthropologists would be provided with vital information.

Remarkable successes in isotope separating in molecules has been reported. Enrichments for just a few percent to several thousandfold can currently be found in the literature. (Walther, H. 1975, Abmartsuman et al. 1975)

Recent demonstrations have shown that it is possible to enrich ^{12}C over ^{13}C by ca. 80 fold using laser induced separation of isotopes. (Clark, et al. 1975) A dye laser is tuned to excite selectively and dissociate CH_2O by rotational and vibrational relaxation of uv absorption to form ultimately $H_2 + {}^{12}CO$. The CO is trapped and the isotopic ratio is measured with a mass spectrometer. While high resolute absorption spectra for ^{12}C and ^{13}C in formaldehyde have been measured, such a spectrum has not been obtained for ^{14}C. Consequently, the feasibility of a similar laser induced isotopic separation has not been assessed.

In cooperation with the Departmentof Chemistry, where tuneable dye lasers are in operation for analytical purposes, we plan to measure the frequencies of molecular absorption in formaldehyde enriched in ^{14}C. Other compounds will also be investigated as to their suitability for use in laser induced separation of carbon isotopes. On the basis of these data it seems likely that a practical enrichment scheme could be developed.

The application of lasers to isotope separation is conditional upon satisfying several requirements. Of primary importance is that there exist at least one absorption frequency for a given isotope that does not overlap any absorptions of the other isotopic species. The degree of overlap which is tolerable, is dependent upon the relative initial concentrations of the isotopes and the final ratio which is the goal. Assuming that radical scrambling and energy transfer from collision are not important (see second consideration), the final ratio is a function of the product of the initial concentration and the relative probability of photon absorption by the reactants. Thus in the event that this product is the most important factor, the relative absorption in a given frequency band (determined by linewidth of laser) is the ultimate limit of enrichment.

The second requirement is that once excited, the molecule undergoes an irreversible chemical reaction, such as dissociation, or reaction with a radical quench within a period of a nano-second to a micro-second (Letokhov, 1972). The lower limit is imposed by consideration of bandwidth of the absorption resonance (a crude measure of selectivity since it determines the tailing of one peak into another);the upper limit is imposed by the requirement that there is a high probability that the molecule undergoes reaction before collision. The upper bound is particularly pertinent in the case of reactions occurring in the gaseous state and might possibly be relaxed in the case of photopredissociation produced in solids. (see further considerations). Furthermore, the upper limit set on the lifetime of the excited molecule depends on the pressure at which the reactions are occurring. Hence it is advantageous to use chemical compounds whose excited states have liftimes as short as is consistent with the lower limit, since this allows the highest pressure to be used in the absorption cell, and therefore the greatest utilization of the available laser energy.

The third requirement is that there exist a practical laser for the frequency required by the first two considerations. For a laser system to be practical it is ncessary that it produce a high flux of photons with a narrow linewidth. Currently 200 nanometers is a lower working limit, below which one is limited by atmospheric absorption. In order to obtain wave lengths shorter than 450 nanometers (or 540 nm with most commercial dyes), it is necessary to use frequency doubling crystals. Current technology limits

ADP (ammonium dihydrogen phosphate) crystal frequency doubling to about 255 nm and although KDP (potassium dihydrogen phosphate) can be used below this, there is a frequency gap of about 20 nannometers in which high photon fluxes are just not readily available. (Schäfer, 1973). In order for there to be an overall efficiency in the absorption process, it is not only necessary that the laser have a large output, but also that the cross-section of the molecule, or extinction coefficient, be large. In general, extinction coefficients are larger in the short UV than in the long, making this region a prime candidate for spectral investigation to assess the feasibility of photo-induced isotope separation. Linewidths of the mandated width are readily producible with careful control of the physical and electrical environment and multiple etalon systems using Fabry-Perot interferometers and intracavity interference filters. In addition, "cold" isotope filters may be used to attenuate emissions at unwanted absorptions in the unselected isotope. Present linewidths of a few MHz to a few GHz are possible, and there is reason to believe that this is more than adequate for most practical separation procedures. (Greenstein and Bates 1975).

Actual selection of a molecular species for isotope enrichment involves several factors other than its spectral properties. For example, the molecule used in the enrichment should have only one atom of the element to be concentrated, or in the case of multiple occurrences, the atoms should appear in equivalent sites throughout the molecule. In this way, desired isotopes are not "hidden away" in bonds of different character than those being excited, thereby reducing the enrichment in proportion to the probability of the atom occurring at a site other than that of interest. Another approach is to synthesize molecules in which the location of the desired element is easily arranged, such as esterification of acids. It should be remembered that since discrete rotational and vibrational states are required, one is limited either to the gas phase and therefore in general small molecules, or crystals at low temperatures.

Similarly, unless one is willing to work in vacuum, or in N_2 flushed systems, bonds labile from rotational and vibrational energies transferred from electron uv absorption above 200 nm are necessary. There must be a means for either an internal irreversible conversion, or intermolecular reaction, which must occur within a mean free path limited time (at least in the gas phase). These conversions and reactions almost always involve free radicals and excited vibrational states. The products so formed must be easily separable from the reactants. When enrichment is motivated by a desire to extend a dating sequence, or measure temperature changes recorded by isotopic fractionation, it is ultimately necessary that the products formed in the photo induced chemical reactions be convertible to a form usable by the technology of the particular field. As an example, consider ^{14}C-dating. The most successful counting methods currently in use involve β-decay measurements made either from gases in proportional counters, or liquids in scintillation counters. The final goal of isotope separation therefore would be either a gas suitable for use in a proportional counter or a liquid compatible with one of the common scintillators such as POP. If enrichments of several orders of magnitude become feasible, then molecules forming ions stable long enough for use in a mass spectrometer would also become reasonable candidates. Consequently, selection of a molecule to be used in a separation scheme is a complex and difficult process, requiring high resolution spectral measurements and careful consideration of the chemistry envolved in converting the original sample to the photo-chemical reactant, and ultimately to a molecule suitable for a radiocarbon dating.

Design of the photolysis apparatus must result from a consideration of the ultimate ends of the enriched species. Unlike most industrial applications where the object is simply maximal enrichment, in the case of isotopic enrichment of archaeological and geological samples, the goal is to improve, or make possible, measurements of the original isotopic ratio. Therefore, it is necessary to monitor the enrichment process carefully in order that the relationships of the final concentrations to the initial concentrations are precisely known. It appears that this can be done by making two types of measurements.

First, it is necessary to determine the functional dependence of the isotopic ratio in the enriched sample to the original ratio. This dependence could be determined by enriching a set of standard samples. In the case of ^{14}C, a set of known age samples, namely, the bristlecone pines are available in our laboratory extending back to 8000 B.P. These provide a range of $^{14}C/^{12}C$ from about 10^{-13} to 10^{-12}. Dilution of these samples with carbon from anthracite, would extend the range to arbitrarily small ratios which might be encountered in much older samples (of the order of 80,000 years).

In addition to correcting for enrichment variations resulting from different starting ratios, it is also necessary to have some continuous monitor of variables affecting each individual separation. Since isotope separation depends so critically on absorption selectivity, enrichment efficiences will undoubtedly be sensitive to small changes in laser linewidth and fundamental frequency. Although an effort will be made to make these fluctuations as small as possible by use of various linewidth narrowing and feedback controls, it is still essential to have some integrating enrichment monitor for every sample. One way of doing this is by inserting a reference cell in the beam of the laser along with the sample cell. The initial concentration of the reference will be from a calibrated source, and at a level measurable with a mass spectrometer. If enrichment is done in the gas phase, the products of photolysis can be monitored continuously on the mass spectrometer and then integrated for the whole period of enrichment, or the final isotopic ratio of the products can be determined at the end of the run. Quantitative stability of the order of $1:10^6$ would be necessary in the mass spec. used in this application. On the other hand, mass resolution will not be a problem for most gases likely to be used. The use of such a monitor for the enrichment would enhance the precision for the measurement of samples of known age and subsequent unknowns, since variations due to natural causes often are of the order of only a couple of parts per thousand. It is unlikely that photometric information alone will be sufficient to supply enrichment data to this precision. Because of the rapid sampling rates of TOF (time of flight) and quadrupole mass specs, both are ideal for this application either as "on-line" machines or as stable quantitative devices.

Due to the successes in enrichment of ^{12}C - ^{13}C in the form of formaldehyde, it is not unreasonable to model a ^{14}C enrichment process for radiocarbon dating using formaldehyde as the photo-predissociating species. A possible method to be investigated might involve the following. A test sample would undergo the standard pretreatment and conversion to CO_2. After purification, the sample would be divided for proportional counting and conversion to H_2CO by bubbling the CO_2 diluted with N_2 dried over Drierite through $LiAlH_4$ in diethyl carbitol. (Nynstrom, 1947). This procedure is approximately 81% efficient in converting CO_2 to H_3COH. The H_3COH is then quantitatively converted to H_2CO by the standard industrial process of oxidation of methanol over silver gauze heated to about 600°C. The H_2O is collected and liquified below its boiling point, -21°C., and placed in the reservoir of the system in Fig. 1.

The enriched CO_2 is then removed from the final trap and the $^{14}C/^{12}C$ determined in the usual manner by proportional gas counting. The enrichment factor would be determined by measuring the final $^{14}C/^{12}C$ of the standard in the second cell with the aid of the mass spectrometer.

Alternative approaches will also be investigated as possible methods for enrichment. For example, multiple photon pumping to auto-ionizing states in CO_2 or other gases, if done between two charged plates provides a means of separation by charge migration or detection through current measurement. Resonance scattering and Raman spectroscopy do not look as encouraging due to the initially low starting ratios. Hence there exists a great deal of fundamental research to be done in the area of detection and separation of naturally occurring rare isotopes which would provide opportunities for continued further research and additional educational opportunities.

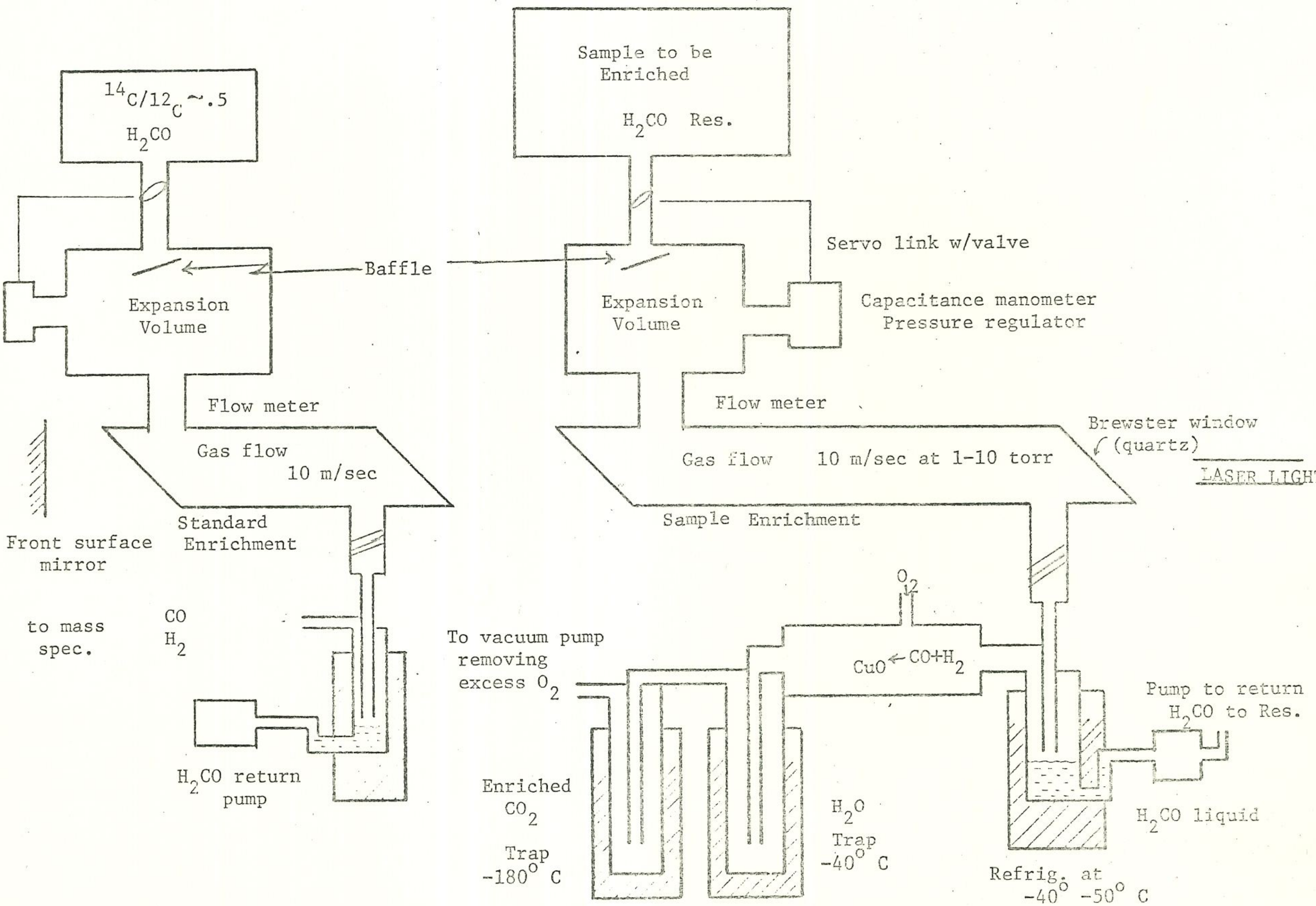


Fig. 1, Schematic of Model Enrichment Process

Project Management, Evaluation Plan, and Maintenance/Impact Potential

An advisory council of interested and highly qualified persons will be invited to be involved continually in evaluating and advising on the progress and development of the research and educational activities. Periodic (semi-annual) meetings will be convened to focus such evaluation into reports to the people involved both in leading and in carrying out their activities. Proposed members of such a council would include

Director of the University Museum,	Prof. Froelich Rainey
Assoc. Director of Research MASCA,	Prof. William Stephens
Dept. of Anthropology	Prof. Bernard Wailes
Dept. of Geology	Prof. Henry Faul
Dept. of Chemistry	Prof. John G. Miller
Dept. of Metallurgy	Prof. Robert Maddin

Such an Advisory Council would also advise the Principal Investigator as to improvements in the cost-benefit relation and ways to improve the quality of the research and educational activities.

Graduate students directly related to the proposed research project will be evaluated by faculty in their respective departments. The progress of those graduate students from the departments of Physics, Chemistry, Geology, Anthropology, etc. will be evaluated by individual thesis committees of three faculty members as is the usual method of evaluation in these departments.

The outcome of the research in enrichment of C-14 and in the use of such methods for archaeology and geology will be published in the appropriate research journals and in the MASCA Newsletter. Summary articles of wider interest will be made available to such journals as <u>Science</u>, <u>American Scientist</u>, <u>Scientific American</u>, allowing wide scientific evaluation and use of the developments to be expected.

It is planned that these activities and the use of the equipment will continue after the three-year period of the grant.

Facilities and Grants

A. Radiocarbon Laboratory, Department of Physics, David Rittenhouse Laboratory

1. One 8-liter CO_2 counter is supported by the University of Pennsylvania for the purpose of determining the ages of archaeological samples which have been collected by or are pertinent to the research of the curators, students, and staff of the University Museum.

2. A second 8-liter CO_2 counter and associated equipment, financed originally by NSF Grants (Division of Earth Sciences) G-3281 and G-5608, then supported by GA-993 and GA-12572, and now by DES-74-22233 (12/1/74 to 8/31/77, $78,600) is available for the continuation of the known-age dating program.

3. A small 1-liter CO_2 counter has been constructed, tested, and calibrated for use with undersized samples. At the moment (January 1976), this has been put in place of one of the 8-liter counters. However, shielding for this third counter has been acquired, and construction of new solid state electronic components is almost complete.

4. An additional low-level laboratory room (BW8) measuring 20 by 50 feet and adjacent to our present low-level rooms BW6 and BW4 (each 20 by 20 feet) was acquired in 1973. The conversion from what was formerly a storeroom into a low-level air-conditioned counting laboratory was financed mostly by NSF grant GS 36308X (Division of Social Sciences) and in small part by the University. This addition has provided space for the third CO_2 counter, and will provide adequate space for all of the equipment needed to do the laser experiments, including the mass spectrograph.

B. Laboratories of the Applied Science Center for Archaeology, University Museum.

Space and equipment for the preparation and storage of tree-ring samples and sections, for TL dating, geophysical prospecting instruments, aerial photography, information center, and new projects related to archaeology and anthropology. Current Grant: National Science Foundation No. SOC-75-04203. Continuing Research Support, Museum Applied Science Center for Archaeology (MASCA).

First Year:	3/1/75 - 2/29/76	Budget:	$100,000.
Second Year:	3/1/76 - 2/28/77	Budget:	$ 75,000.
		Total, two years:	$175,000.

Grant Pending:

In January 1976, a proposal entitled "Modernization of Mass Spectrograph for the Measurement of C^{13}/C^{12} and other Isotopic Ratios" was submitted to the Earth Sciences Division of the NSF. (Proposal No. EAR 7614258).

In this request for funds, it was proposed to upgrade an older existing mass spec. (the CEC 21-130). The budget for this was $22,500. However, for use in conjunction with the new laser experiment, the resolution of this revised mass spec. would be inadequate. Therefore, we have included a request for funds for a much better instrument in this proposal. If these funds are granted, we shall withdraw our previous request.

Current Personnel of the Radiocarbon Laboratory (February 1976)

A. Elizabeth K. Ralph, Ph.D., Principal Investigator (full-time salary supported by the University of Pennsylvania).

B. Barbara Lawn, Research Specialist I (full-time salary supported by the University of Pennsylvania).

C. Raymond Costa, Jr., Graduate Student in Anthropology (supported by the University of Pennsylvania).

D. Henry N. Michael, Ph.D., Research Associate (salary for 5 months supported by NSF-DES-74-22233).

E. Jeffrey Klein, Graduate Student in Physics (supported by NSF-DES-74-22233).

Condensed curricular vitae for Ralph, Stephens, Lawn, Costa, and Klein are attached as an Appendix.

Significant scientific achievements of key personnel in both ^{14}C and MASCA laboratories are as follows:

1) Dr. Elizabeth K. Ralph:

Dr. Ralph set up, operated, and has supervised the radiocarbon laboratory since 1951. A few outstanding achievements of the lab have been the correlation of the Mayan and Christian calendars, the determination of long series of ^{14}C dates for tree-ring-dated sequoias and bristlecone pines and their partial interpretation, and more than 2300 ^{14}C dates of archaeological significance from sites such as Hasanlu, Franchthi Cave, and Tikal.

Since 1962, she has been Associate Director of MASCA and has conducted numerous field trips with geophysical prospecting instruments as well as the immediate supervision and some of the experimentation in the MASCA laboratories.

2) Prof. Froelich Rainey:

Dr. Rainey has been director of the University Museum since 1947. He was a member of the original radiocarbon committee that assisted Dr. Willard Libby in proving that natural ^{14}C could provide a method of dating.

In 1951 he was instrumental in establishing the University of Pennsylvania Radiocarbon Laboratory.

For the past 15 years, he has been Director of MASCA and has helped to initiate the new techniques of thermoluminescent dating of pottery, the establishment of an information center, the development and use of archeological prospecting instruments, remote sensing by aerial photography at all heights, and other new techniques.

3) Prof. William E. Stephens:

Dr. Stephens has been Professor of Physics at the University of Pennsylvania since 1948. One of his main achievements in research was the establishment of a tandem accelerator with which he trained and supervised the theses of numerous graduate students.

During this time, he advised us in the ^{14}C lab in all scientific matters and many practical ones as well. Recently, he has become Associate Director for Research in MASCA and is now active in all of our research projects.

4) Ms. Barbara Lawn:

Ms. Lawn has conducted the daily operations of the radiocarbon laboratory since 1967, after previous experience in the laboratory from 1954 to 1956. This has included the development of new chemical techniques as well as the construction of new equipment and repair of existing components.

Ms. Lawn is presently a part-time Ph.D. student in the Geology Department.

APPENDIX

References Cited

Ambartsuman, R.V.; Y.A. Gorokhov, V.S. Letokhov, and G.N. Makarov.
1975 Sulphur isotope separation with an enrichment factor of 10^3 accompanying the actia of a CO_2 laser on SF_6 molecule. Zh. Eskp. and Theor. Fiz. Pis'Ma 21(6):375-8

Clark, J.H.; Y. Haas, P.L. Houston, and C.B. Moore.
1975 Carbon isotope separation by tunable - laser predissociation of H_2CO. Chem. Phys. Lett. 35(1):82-5

Greenstein, H.; and C.W. Bates, Jr.
1975 Line-width and tuning effects in resonant excitation. J. Opt. Soc. Am. 65(1):33-40

Haring, A.; A.E. De Vries, and H. De Vries.
1958 Radiocarbon dating up to 70,000 years by isotopic enrichment. Science 128:472

Kretner, R.; and G. Dickel.
1975 Enrichment of $^{14}CH_4$ by thermal diffusion for use in radiocarbon dating. Z. Naturforsch. 30A(4):554-60

Letokhov, V.S.
1972 On Selective laser photochemical reaction by means of photo-predissociation of molecules. Chem. Phys. Lett. 15:221-2

Libby, M.
1972 Multiple thermometry in paleoclimate and historic climate. J. Geophys. Res. 77(23):4310

Nynstrom, R.F.; W.H. Yenko, and W.G. Brown.
1947 Reduction of carbon dioxide to methanol by lithium aluminum hydride. J. Am. Chem. Soc. 70:441

Pandolfi, L.J.; P.H. Payton, L.M. Libby, and B. Becker.
1975 Correlation of climatic changes with variations in O^{18}/O^{16} ratio in Bavarian fir tree rings 1675-1950 A.D. Unpublished.

Schafer, F.P. (ed).
1973 Dye lasers. Springer-Verlag. New York.

Walther, H.
1975 Isotope separation by means of lasers. Korntechnik. 17(6):253-9