Established 1826

Alan Wood Steel Company

Conshohocken, Pennsylvania

January 21, 1963

Miss Elizabeth K. Ralph
University of Pennsylvania
33rd & Spruce Streets
Philadelphia 4, Pennsylvania

Dear Miss Ralph:

Mr. Reed Knox was employed by this Company as a Research Metallurgist from July 6, 1948 up to and including December 31, 1957.

Our file if very limited, but there are no indications that this man's performance was unsatisfactory.

I am sorry we are not able to be of more assistance.

Very truly yours,

Daniel G. Daywalt

Daniel G. Daywalt
Staff Manager Personnel Services

DGD/rd

77 Mass. Ave.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE 39, MASSACHUSETTS
Room 14N-321

25 June 1963
Dictated: 21 June 1963

Mr. Reed Knox, Jr.
The School of Metallurgical Engineering
University of Pennsylvania
Philadelphia 4, Pennsylvania

Dear Mr. Knox:

I enjoyed immensely my time with you in the metallographic laboratory yesterday afternoon, and the examination of the samples that you had prepared. The demonstration that you have made that it is possible to see in the corrosion products of steel objects relicts of the original carbide structures and hence deduce the approximate amount of carbon and the heat treatment, is a really important one! I would like to urge you to prepare a few perfect photographs and write a short note on it for prompt publication somewhere or other.

On the plane I studied the copy of your letter of June 14 to Miss Ralph and would like to make a few comments. On p. 2 you suggest that the black material left behind by the carbide is graphite that has resulted from decomposition of iron carbide during the long period at room temperatures. I rather doubt this. In the first place, if the rate of decomposition of carbide was sufficient to produce visible graphitization in 3,000 years at atmospheric temperatures there would be graphite in <u>all</u> old steel, including in the little patch of uncorroded steel in your sample. It is quite obvious in your Fig. 9 that there is never any black material in the uncorroded pearlite, although there are bits of uncorroded carbide embedded shiningly in the oxide. It seems to me almost certain that the black material is the result of corrosion and, since this occurs at room temperature, it is unlikely that it can be material of the structure that could be called graphite. It would, I think, be much safer to call it "carbon, probably amorphous." Incidentally, such residual colloidal carbon resulting from the solution of iron carbide was responsible for the color of solutions of steel samples in acid, which was used as an important rapid method of analysis of steel. It was invented by Eggertz in Sweden in 1862.

It would probably be worthwhile making several additional sections through the dagger in the hope of finding a few other spots of uncorroded metal. If there is this fragment on one section, there will be none on some, and--who knows?--a square millimeter or so on others.

Yours is a really exciting discovery, whatever the theory! In the note that you publish you should, I think, attempt to show diagrammatically the structure as distorted by the successive stages of corrosion, first the conversion to oxide (Fe_3O_4?) <u>in situ</u> with simple expansion of volume, second, the cracking of this and the filling in with a different material (ferric hydroxide?) supposedly via diffusion in an aqueous phase. I know absolutely nothing about corrosion, but it is more than ever important to get some idea as to whether the cracks form and then fill or whether the cracks form continuously because of a transition to a corrosion product of different volume.

On p. 3, paragraph 2, in discussing the Hasanlu dagger (Fig. 8)--why do you say so definitely that it is iron oxide that has formed along the [111] planes in the bronze? This may be, but one gets precisely similar structures in the corrosion of bronze alone, and it's more likely to be oxidation products of copper and tin. Incidentally, Fink and Polushkin (Trans. AIME [1936], 122, 90-118) show structures like this only in bronzes that have been slightly worked. I am inclined to think that it is simply enhanced corrosion along slip lines, and F. and P. are probably right, though it is not quite certain, that some prior deformation is needed to give this geometric form.

The fact that the markings in the sample are more intense near to the iron tang must be related to strain arising in the casting-on process. The difference of contraction between iron and bronze from 1000°C. to room temperatures is about 8×10^{-3}, i.e., nearly 1 per cent, far beyond the elastic limit. In looking at the sample yesterday I noticed that some bronze had run into a seam in the iron tang, and this positively confirms the suspicion that the bronze had been cast on, not shrunk or otherwise attached. The general appearance of the blade and the handle leaves little doubt about this. I have several daggers, reputedly from Luristan graves (1000 B.C.?), in which a decorative bronze handle is cast on to the tang of a steel blade. It was obviously a common procedure and, of course, not a difficult one. Perhaps you have seen the German book devoted entirely to its importance in archaeology, published about six years ago.

It was interesting to note (although this is not visible in your Fig. 8) that the interdendritic pools of what had been residual eutectoid material had all been converted to corrosion product, regardless of how far from the apparent surface they were. This supplies proof, if it were needed, that the isolated spots seen in a two-dimensional section are in three dimensional fact connected throughout the structure. (Both of the eutectoid phases are not corroded, only one--is it alpha or delta phase which is preserved?)

Last line, p. 3, there does not need to have been working, only heating after carburization, it seems to me.

Although it is unquestionable that the dagger had been made of steel, I do not think that there is any evidence that it was made by what might be called a carburization process, as you state. Terminology is difficult here. I mean that there is not any evidence that a forged dagger or a semi-fabricated piece of iron was packed in carbonaceous material and heated for a long time to produce deep surface carburization by diffusion at temperatures of 1000°C. or so. This is not the common opinion. The literature first describing real cementation is 1030 A.D. (Theophilus), and even then produces only very superficial hardening. In all structures of old steel that I have seen the carbon gradients can most logically be explained by variations in carbon content in an original rough spongy lump of metal as it came from the refining hearth or, in later pieces, by the welding and forging together of material of different carbon contents. Before the 16th century A.D. the carbon was, I think, introduced mostly by short time high temperature treatments in the hearth, perhaps even occasionally involving the momentary presence of small amounts of molten high-carbon cast iron running superficially over the surface and into the interstices of the loose and porous sponge. Though your dagger contains about 0.8 per cent carbon (or perhaps even a little more), in some places, it has much less in others, and the general distribution of these areas is attributable, I think, entirely to variability in the sponge. There may have been a number of separate irregular chunks welded together, but I have the impression that the variation is no more than would result naturally from an irregular lump in the reduction hearth, without conscious separate welding. There would be slag, of course, in both processes and only the overall geometry of their products would distinguish them clearly. A longitudinal section would help.

The difference in rate of corrosion between lamellar cementite and the small spheroidized blobs is remarkable; perhaps it is only a question of size, though there's something about the appearance of the carbide particles far removed from the uncorroded iron which makes me doubt this.

I believe that you could get some good structures by a modification of the electron microscopist's extraction replica technique. This was actually used by Osmond in the 1880's and it showed carbide distribution quite well. You could prepare a flat surface--preferably by petrographic lapping rather than a metallographic polish--and then cement this surface to a glass slide using the best acid-proof cement you can lay your hands on. Then dissolve away the sample (preferably not too thick) from the back leaving the amorphous carbon and the slag particles in the surface layer stuck in the cement, while all of the oxide and rust would quietly dissolve and disappear.

Once again, congratulations on your beautiful observation of carbide artifacts in the mass of corrosion products. It is most important.

With best regards,

Yours sincerely,

Cyril Stanley Smith
Institute Professor

CSS:mk
cc: Maddin, Ralph, Dyson

UNIVERSITY of PENNSYLVANIA
PHILADELPHIA 4

The School of Metallurgical Engineering

July 16, 1963

Dr. Cyril Stanley Smith
Institute Professor
Room 14N - 321
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

C
O
P
Y

Dear Professor Smith:

Many thanks for your very interesting, long and flattering letter of June 21. I, too, greatly enjoyed your visit and was much inspired by your contagious enthusiasm. However, I am not the first to notice relict structures in iron oxide. Nininger (Out of the Sky, chap. on weathering of Mtes.) called attention to a relict Widmanstatten pattern in the Coldwater siderite. I probably had this in mind while examining the oxidized Hasanlu samples. Even so, it would probably be desirable, as you suggest, to publish a short note ab out the archeological possibilities of this demonstration. Perhaps I should write a short "Letter to the Editor" of METAL PROGRESS and include a few photomicrographs. However, I would like to suggest a jointly written note, to be drafted by yourself, for publication in a journal more likely to be read by archeologists and metals historians than MP. Perhaps EXPEDITION, the magazine of the University Museum, would be suitable. In this case, I think, Mr. Dyson should also be asked to co-author the article.

I agree with your paragraph 2. I should not have jumped to the conclusion that the black particles are graphite. It seems fairly probable that they are an intimate mixture of iron oxide and amorphous carbon. I am enclosing a pmg. showing black and white particles in a region of the oxide (Hasanlu dagger) rich in these.

Mr. Dyson feels that we should examine additional dagger blades to check manufacturing consistency and possibly find larger metal particles.

I looked up your reference to Fink and Polushkin and agree there is doubt that iron oxide has formed along crystallographic planes of the bronze, unless the original 'bronze' oxides have been replaced by those of iron. I could see no difference in color between the oxidized tang (magnetic) and the oxide within and on the surface of the bronze. Perhaps there is an unfortunate identity in the reflectivity of the iron oxide and that of the oxides of tin and copper. It might be possible to distinguish among these by some method involving finely ground magnetized iron oxide.

I am still a little puzzled by the presence of fairly massive cementite particles in what appears to be a hypoeutectoid matrix in the small particle of the Hasanlu dagger. I suppose the temperature was never high enough to get these particles in solution, although the undistorted pearlite indicates final cooling from above Ac1. One wonders how these particles originated, possibly during hot working within the critical range.

After examining the Luristan pmgs. you left with me (I hope you have received them by this time), I entirely agree with your views as expressed in the last paragraph of your page 2. I have been too much "other directed" by orthodox opinion given in several books.

Your excellent suggestion that the extraction replica technique be applied to studies of ancient oxides should certainly be tried in future investigations of these "fossil structures," which might thereby be revealed in greater contrast than on a polished surface. I shall try to contact someone in the Earth Sciences Department about this.

The enclosed photographs are of the copper specimens from Iran. I regret that they are of such poor quality. Because of a photographic backlog at the Museum and the temporary absence of our camera, I attempted to expedite matters by using our enlarger as a camera. Although I have used this method successfully before, somehow some fogging resulted which I did not notice until prints were made after the specimens were cut up--a blunder I deeply regret. The pictures do show the sizes and shapes of the specimens and perhaps more detail could be brought out by persevering with the printing.

Unfortunately I have not yet been able to take any pmgs. of the Iran samples or to get any better ones of the Hasanlu dagger.

Thanks again for your kind words and please excuse the long delay in my reply; I expect to be on vacation between July 17 and August 8.

Sincerely yours,

Reed Knox, Jr.

Enc.

cc: Dr. Maddin
Miss Ralph
Mr. Dyson

Copy

October 31, 1963

Professor Cyril Stanley Smith
Room 14N-321
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Professor Smith:

Dr. Maddin has suggested that I send you our revised grant proposal. This is a preliminary copy, but if you do approve of it, we should appreciate it if you will sign and return the front page so that we can send it to the NSF as soon as possible. We shall be glad to make any changes that you suggest on the subsequent pages.

I think that Mr. Knox' small project conducted with your guidance is an excellent example of what may be accomplished by these combined studies.

Sincerely yours,

Elizabeth K. Ralph

EKR:pc
CC-Dr. R. Maddin
Dept. of Metallurgy

MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE 39, MASSACHUSETTS
Room 14N-321

8 November 1963

Professor Robert Maddin, Director
School of Metallurgical Engineering
University of Pennsylvania
Philadelphia 4, Pennsylvania

Dear Bob:

I had an enjoyable talk with Miss Clapp the other day to see if she would be interested in a program of graduate research at the University of Pennsylvania aimed at an interdisciplinary Ph.D. in archaeology and metallurgy. She expressed interest in this, for she sees the possibility, after such a training period, of an absorbing, almost unique, professional activity. I outlined the proposal that you are thinking of making to the National Science Foundation, and she expressed willingness to consider work under such conditions for perhaps three years, but I could not, of course, discuss the question of course prerequisites or other academic requirements. Her training in art history and the metallographic experience gained in her current employment give her a good background, but I assume that the University would need evidence of certain minimum levels of preparation in both archaeology and metallurgy before she could formally be admitted as a degree candidate. In fairness to her I think you should formalize these in the near future so that she knows what she will be up against in the way of course work before getting down to the research itself. Though the NSF program clearly envisages the provision of some support during the thesis period, will there be any kind of support available during the study stage?

I have talked to Miss Clapp on two rather brief occasions and have formed a very favorable impression of her intelligence and seriousness, though I have made no attempt to gauge her professional achievements.

Miss Clapp's address is: 1 Gray Street, Cambridge, Mass. I suggest that you get in touch with her directly and ask her for whatever information you think you need: she will certainly counter with requests for information from you.

I hope something happens with all this. It is an important and exciting field of activity.

A copy of my letter to Miss Ralph commenting on her research proposal is enclosed for your information.

With best regards,

Yours sincerely,

Cyril Stanley Smith
Institute Professor

CSS:mk
cc: Miss Clapp, Miss Ralph ✓
Encl. (2)

MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE 39, MASSACHUSETTS
Room 14N-321

8 November 1963

Miss Elizabeth K. Ralph, Associate Director
Applied Science Center for Archaeology
The University Museum
33rd and Spruce Streets
Philadelphia 4, Pennsylvania

Dear Miss Ralph:

Thanks for your letter of October 31 and the outline proposal. I think that Dr. Maddin should be the first "principal investigator," and that I should be classed as a consultant or something of the kind rather than a principal investigator. In any case, my name should not be first on the list since, after all, it is a University of Pennsylvania proposal. Also, I hope that it will be possible to get Robert Dyson officially involved and committed by calling him one of the principal investigators, for the chance of further discussion with him is one of the main reasons why I want to be associated with a project at the Universith of Pennsylvania.

I am enclosing a second letter to you which I have written with the idea that you might include it as an appendix, for the specific purpose of showing why somebody at MIT would want to work with the University of Pennsylvania.

On p. 1 at the end of the abstract paragraph, you might advantageously add, "And will develop laboratory methods for the study of metal artifacts which will enable better analysis of cultural contacts and the spread of technology."

P. 1, paragraph 3--I would prefer that you begin this by assigning leadership of the project to Professor Maddin and work me in at the end of the paragraph with a statement that I have promised full collaboration with the project.

Suggest inserting a new paragraph between paragraphs 2 and 3 reading something as follows:

> "Though there are good programs in several European countries--notably England, France, Germany and Poland--professional studies of archaeological metallurgy in the U.S. have somewhat lagged. Archaeologists have inveigled engineering colleagues to study isolated objects for them,

and there has been fine work carried out at both the Freer Gallery and at New York University aimed primarily at the authentication and restoration of works of art in metal, but this work, together with the astute observations of archaeologists themselves on their fields, has served to show what an important area of study exists and has not answered all the questions that it has raised."

On p. 2 after "intentional heat treatment" at the end of paragraph 1, suggest adding, "A project that needs the closest cooperation with archaeologists who have dug and studied in the Middle East."

P. 2, end of third paragraph, should there not be a specific statement regarding the formal mechanism that the University will set up for such an interdisciplinary degree? Supposedly a precedent has been established with a degree-granting committee or something of the kind.

In the budget after the entry of my name you might put something like "(partial summer employment: time during academic year will be donated by MIT)."

You are unfair to Reed Knox in suggesting that my "guidance" had anything whatever to do with his making of the initial all-important observation! All I did was to discuss with him a little of the significance of it, after he had done it, and he deserves full and undivided credit for the important observation.

Yours sincerely,

Cyril Stanley Smith
Institute Professor

Encl.
CSS:mk
cc: Maddin

MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE 39, MASSACHUSETTS
Room 14N-321

8 November 1963

Miss Elizabeth K. Ralph, Associate Director
Applied Science Center for Archaeology
The University Museum
33rd & Spruce Streets
Philadelphia 4, Pennsylvania

Dear Miss Ralph:

I have looked over the rough draft of your research proposal to the National Science Foundation. Though I have marked a few suggested changes on it, it meets with my enthusiastic approval. What you are proposing is, I believe, a fine program, and one which should enable a few individuals to devote their life work to a particularly fascinating combination of disciplines. The findings are bound to make an important contribution to our understanding of the nature of technology and its development in relation to broader cultural influences.

You should know that I have been considering the submission of a somewhat similar proposal via MIT, which is, after all, the center of my major professional activities. However, though in no way conceding that metallurgy at MIT is inferior to that at the University of Pennsylvania, I do believe that for the present purposes it is preferable that the program be carried out in a place where archaeology is flourishing, and in combining this with metallurgy the University of Pennsylvania is unique in the United States.

From the archaeological metallurgy that I have myself done more or less as a sideline, I am convinced that archaeologists have an immense contribution to make to a project of this kind, just as they have much to gain from it. Not only can proper samples of early metal for study only be selected by the critical eye of the archaeologist who understands the conditions of their excavation, but the very posing of specific questions for study requires an integral knowledge of entire cultural patterns. Familiarity with other techniques and materials provides an essential background for the study of metallurgy. Metallurgists, moreover, have much to learn from the archaeologist's methods of assaying evidence.

Some effort will be needed to maintain concentrated attention on one part of the inevitably broad field. It seems to me that the center should be (if the archaeologists concur) on the origin and early diffusion of the most important metallurgical techniques. My own interest is principally in the beginning of controlled steel making and hardening. T. E. Wertime's new thinking suggests that there is much still to be done on the origin of smelting, despite the stacks of analyses in the literature. Everything seems to center in the Near East, which is a particular reason for locating this project at the University of Pennsylvania. Though metallurgy is most important in Europe, European contributions to metallurgy were relatively late and in any case are being actively studied by locally-oriented archaeologists and metallurgists the other side of the Atlantic.

The spectacular deviations from the early steel techniques as they moved to India and China would be interesting to follow and, in the non-ferrous field, the introduction of intentionally-made brass, the origin and development of the marvelous Chinese bronze casting techniques, the supposedly independent origin of copper metallurgy in South America, the failure of North Americans to develop metallurgy beyond the use of native copper--these all are questions of broadest significance that could be followed for the light that they throw on man's attitude to matter. An alternate approach would be to follow the use of certain chemical or physical principles or, for example, to note the distribution of various methods of joining and surface treatment. Are there cultural factors which influence a preference for one material and shaping technique over another? What is the relationship between the highly special techniques used in making works of art and the common ones for tools and utensils? What can be deduced from the two-way relationship between joining techniques and design, and what social factors are involved in repair versus replacement?

The metallurgical techniques must always be considered in relation to other technical capacities, particularly the heat-using techniques, such as ceramics. Do sophisticated glazes and sophisticated alloys always go along together? And what can one say about the quantitative aspects of the use of materials? A few finds of treasured objects in graves can hardly reflect a widespread use of the techniques, though perhaps the first uses are always in producing treasures.

The student in this area can hardly be expected to know all of archaeology and all of metallurgy, but it is essential that the committee in charge of his program ensures an adequate breadth of knowledge in both fields combined with at least one really hard specific piece of research that impinges upon both. Only so will he have adequate training for an independent professional career.

I very much hope this proposal will go through and I am pleased at the possibility of being personally connected with the University of Pennsylvania in this important intellectual venture.

Yours sincerely,

Cyril Stanley Smith
Institute Professor

CSS:mk
cc: Maddin

November 15, 1963

Dr. Haydn Morgan
Project Research & Grants
3400 Walnut Street

Dear Dr. Morgan:

Twenty-two copies of a research proposal entitled "Training Program in Metallurgy and Archaeology" are included.

If this program meets with your approval, we should like to submit it to Dr. I. Warshaw, Division of Engineering, National Science Foundation.

Sincerely yours,

Elizabeth K. Ralph

EKR:pc
CC: Dr. Maddin

November 15, 1963

Professor Cyril S. Smith
Room 14N-321
MIT
Cambridge 39, Massachusetts

Dear Professor Smith:

Thank you very much for your two letters of Nov. 8th. I appreciate your helpful advice and have revised the proposal in accordance with your suggestions. Also, I have attached your thoughtful second letter to the proposal.

A copy of the revised proposal is included.

Sincerely yours,

Elizabeth K. Ralph

EKR:pc
Enc.

November 18, 1963

Prof. Cyril Stanley Smith
Room 14N-321
Mass. Institute of Technology
Cambridge 39, Massachusetts

Dear Prof. Smith:

After I mailed a copy of the revised grant proposal to you, Dr. Maddin suggested one change - namely, that Miss Clapp be listed as a possible graduate student on pages 5, 6 and 7. This change has been made on our copies.

If you should like any changes made, I will appreciate it if you will telephone me so that they can be made before the proposal leaves the office of Projects and Grants.

Sincerely yours,

Elizabeth K. Ralph

EKR:ek

UNIVERSITY of PENNSYLVANIA
PHILADELPHIA 19104

OFFICE OF PROJECT RESEARCH AND GRANTS

December 2, 1963

National Science Foundation
Washington 25, D. C.

Attention: Dr. I. Warshaw
Division of Engineering

Gentlemen:

Submitted herewith are twenty (20) copies of a proposal for a Training Program in Metallurgy and Archaeology to be conducted under the direction of

Dr. Robert Maddin
Dr. Robert H. Dyson
Dr. Froelich Rainey
Dr. Elizabeth Ralph

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:htl
Encl.
cc: Dr. Maddin
Dr. Dyson
Dr. Rainey
Dr. Ralph

University of Pennsylvania
Philadelphia 4, Pennsylvania

Submitted to: National Science Foundation

Title of Proposal: Training Program in Metallurgy and Archaeology

Principal Investigators: Robert Maddin, Director, Dept. of Metallurgy

Robert H. Dyson, Jr., Associate Curator, Near Eastern Section, University Museum

Froelich Rainey, Director, University Museum

Elizabeth Ralph, Associate Director, Applied Science Center for Archaeology

Starting Date: February 1964

Duration: 2 years

Total Funds Requested: $56,592

Date Submitted: 15 November 1963

Corporate Name of the University:
The Trustees of the University of Pennsylvania, (a Pennsylvania non-profit corporation)

Contracting Office: The Office of Project Research and Grants, 3400 Walnut Street, Philadelphia 4, Pa.

Approvals:

____
Robert Maddin, Principal Investigator,
Director, Department of Metallurgy

____
Robert H. Dyson, Jr., Associate Curator
Near Eastern Section, University Museum

____
Froelich Rainey, Principal Investigator,
Director, University Museum

____
Elizabeth Ralph, Principal Investigator,
Associate Director, Applied Science Center
for Archaeology, University Museum

____
David R. Goddard, Provost

Training Program in Metallurgy and Archaeology

I. ABSTRACT

A training program for graduate students in the combined fields of metallurgy and archaeology is proposed. The studies undertaken will contribute to the knowledge of metal fabrication from the archaeological point of view as well as to the history of metallurgy, and will develop laboratory methods for the study of metal artifacts which will enable better analysis of cultural contacts and the spread of technology.

II. DESCRIPTION OF RESEARCH

A unique combination of two disciplines - metallurgy and archaeology, is proposed. For many years metals have been studied by metallurgists from their point of view and by archaeologists, from theirs. There is much to be learned, however, from a combination of the two disciplines.

Though there are good programs in several European countries - notably England, France, Germany, and Poland, professional studies of archaeological metallurgy in the U. S. A. have somewhat lagged. Archaeologists have inveigled engineering colleagues to study isolated objects for them, and there has been fine work carried out at both the Freer Gallery and at New York University aimed primarily at the authentication and restoration of works of art in metal, but this work, together with the astute observations of archaeologists themselves in their fields, has served to show what an important area of study exists and has not answered all the questions that it has raised.

Under the guidance of Professor Maddin, Chairman of the Department of Metallurgy, with the participation of Professor Dyson, Associate Curator of the Near East Section, University Museum, and with the general support of Professor Rainey, Director of the University Museum, we propose to initiate a training program for graduate students in this combined field. The program will be ably assisted by Professor Cyril Stanley Smith, Institute Professor of Metallurgy and Professor of the History of Science at Massachusetts Institute of Technology, who has promised his full collaboration. (A letter from Prof. Smith to E. K. Ralph is included with this proposal).

In addition to the broadening of the interests and background of the students, the study of ancient iron (Prof. Smith's field of specialization) and non-ferrous (Prof. Maddin's field of specialization) objects will not only contribute to our present knowledge of iron and other metal fabrication from the archaeological point of view but will contribute also to the history of metallurgy. In regard to steel, particular attention will be paid to evidence for the origin of the intentional manufacture of steel and its intentional heat treatment, a project that needs the closest cooperation with archaeologists who have dug and studied in the Middle East.

The contribution to this program of the staff of the University Museum, in addition to invaluable consultations with the Curators and their assistants and the study of the objects which they and their predecessors have collected, will be enhanced because of the existence of the new Applied Science Center for Archaeology (abbreviated ASCA) (currently financed by NSF grant GS-294) with Prof. Rainey, Director, and Elizabeth K. Ralph, Associate Director. As part of the ASCA program, analytical studies of metals are being conducted and an information center, with card files and references to physical techniques applicable to archaeological research, has been established. In effect, therefore, insofar as the additional disciplines of chemistry, physics, and a specialized small library are pertinent to the metallurgical and archaeological studies, the program will be broadened by the existence of ASCA and its staff.

Although the specific curriculum for the combined studies will vary according to the background and interests of each student, it is safe to say that a program which includes one-half of the courses normally required in metallurgy and one-half of those in archaeology (or anthropology) would satisfy the requirements for the Ph.D. degree. A sub-group committee will be set up for this purpose.

The benefits to be derived from a combined project of this type, both for the training of personnel and for the information obtained, are illustrated by the pilot study of severely corroded ancient metallic specimens made by Mr. Reed Knox, metallurgical technician, in the spring, 1963. Mr. Knox' report entitled "Relict Iron Carbide Structures in the Oxide Remains of Ancient Steels" is included.

III. FACILITIES

A. Facilities Available

Facilities now available at the University of Pennsylvania and sponsored by the University Museum are the radiocarbon, chemical and the new laboratories of the Applied Science Center for Archaeology. Space for the latter two and for the expansion of the last has been provided in the University Museum. In addition, equipment is available in the Departments of Metallurgy, Chemistry, and Physics. The facilities contributed by the University will be greatly expanded by the addition of the new Materials Center (now under construction) in which a large well-equipped Analytical Laboratory, including all of the latest equipment for metallurgical, physical, and chemical analyses, will be located.

Major capital expenditures are not required because of the availability of instruments (X-ray apparatus, electron microscope, mass spectrograph, etc.) in these departments.

B. Facilities Needed

It is planned that this new project be located in the University Museum near the present laboratories of the Applied Science Center for Archaeology. Since the rooms in the Museum are not equipped as laboratories, it will be necessary to furnish them with electrical outlets, improved lighting, gas, benches, and shelves.

The basic tools for metallurgical research, those which will be used regularly, will also have to be purchased. These include a metallograph, polishing equipment, mounting press, and minor machine shop tools.

IV. PERSONNEL

A. Biographical sketches and bibliographies of the principal investigators are included with this proposal. The persons presently employed, who will be actively engaged in this program are as follows:

Dr. Robert Maddin: Non-ferrous Metallurgy, Principal Investigator
Mr. Robert Dyson: Principal Investigator, Associate Curator of Near Eastern Archaeology, University Museum
Dr. Froelich Rainey: Principal Investigator, Director of the University Museum and of ASCA
Miss Elizabeth K. Ralph: Associate Director of ASCA, Principal Investigator

Mr. Mark C. Han: Research Chemist
Mr. Robert Stuckenrath, Jr.: Radiocarbon Laboratory

Mr. A. E. Parkinson: Chemist
Miss Jeanette Flamm: Information Center

Collaborating archaeologists from the University of Pennsylvania are:

Dr. Alfred Kidder II: South America and Mesoamerica
Dr. Linton Satterthwaite: Mesoamerica
Dr. William R. Coe: Mesoamerica
Dr. Rodney S. Young: Anatolia
Dr. G. Roger Edwards: Anatolia
Dr. Ellen Kohler: Anatolia
Mr. George F. Bass: Underwater Archaeology
Dr. James B. Pritchard: Biblical Archaeology
Mr. Bernard Wailes: European Archaeology
Dr. George F. Dales: South Asian Archaeology

B. Persons to be employed with grant funds

Dr. Cyril S. Smith: Ferrous Metallurgy,
Consultant
(payment for part-time summer participation)

Possible ^ Graduate Students
Miss Katherine Clapp (biographical sketch included)
Graduate Student - to be determined

V. BUDGET

First Year:

Salaries -

Part-time summer participation of C.S. Smith (10 to 20 days during summer months) (Time during academic year will be donated by MIT)		$ 2,000.
Katherine Clapp, Possible Graduate Student, 50% - 9 mos. - $3450.; 100% 3 summer mos.-$1200.		4,650.
Graduate Student, 50% - 9 mos. - $3450.; 100% 3 summer mos. - $1200.		4,650.
Total Salaries and Consultation		$11,300.
Employee Benefits (9% of salaries)		837.
Equipment		
Metallograph	$ 4,500.	
Polishing equipment, mounting press and minor machine shop tools	3,000.	
Total Equipment		7,500.
Other Direct Cost Items		
Improved laboratory facilities (lighting, gas, etc.)	1,000.	
Books, references, periodicals	500.	
Expendable supplies, materials, and small apparatus	3,000.	
Travel -		
Expenses of Prof. Smith in commuting from Boston (10 trips)	500.	
Misc. travel, local trips and supervisory trips by one or more of principal investigators	500.	
Total Other Direct Cost Items		5,500.
Sub-Total		$25,137.
Overhead - 25%		6,284.
TOTAL FIRST YEAR		$31,421.

V. BUDGET (Continued)

Second Year:

Salaries -

Part-time summer participation of C.S. Smith (10 to 20 days during summer months) (Time during academic year will be donated by MIT)		$ 2,000.
Katherine Clapp, Possible Graduate Student, 50% - 9 mos. - $3450.; 100% 3 summer mos. - $1200.		4,650.
Graduate Student, 50% - 9 mos. - $3450.; 100% 3 summer mos. - $1200.		4,650.
Total Salaries and Consultation		$11,300.
Employee Benefits (9% of salaries)		837.
Equipment		
New instruments - metallurgical, physical or chemical		3,000.
Other Direct Cost Items		
Books, references, periodicals	500.	
Expendable supplies, materials, and small apparatus	3,000.	
Travel		
Delivery of papers at conferences (2 - 3 trips), local trips	1,000.	
Expenses of Prof. Smith in commuting from Boston	500.	
Total Other Direct Costs		5,000.
Sub-total		20,137.
Overhead - 25%		5,034.
TOTAL SECOND YEAR		$25,171.
TOTAL TWO YEARS		$56,592.

Relict Iron Carbide Structures in the Oxide Remains of Ancient Steels

The poor oxidation resistance of iron and steel hinders efforts of archaeologists to date the beginnings of iron smelting and the discovery of the "steeling" process that marked the opening of the iron age. Many ancient iron objects that have been brought to light appear to consist entirely of oxide. In such cases metallographic methods of study would seem to be incapable of determining the structure and composition of the original metal. That this is not necessarily true was shown when the oxide remains of two iron weapons from Hasanlu, Iran were recently examined metallographically.

These weapons, a spearhead and a steel bladed dagger with a bronze handle, were excavated in recent years by the University of Pennsylvania under the direction of Professor Robert Dyson and are estimated to date from about 800 B.C. The metallographic work was included in the program of the University's Applied Science Center for Archaeology.

Specimen sections were cut transversely through the handle of the spearhead and the blade of the dagger by means of a diamond impregnated cutting wheel. These were mounted in plastic, ground flat, and polished on successively finer metallographic papers. Final polishing was done with fine alumina powder on a wheel covered with Selvyt cloth.

Microscopic examination of the dagger section in reflected light revealed several particles of metal a few hundred microns in diameter, many scattered bright particles (Fig. 1) about 5 microns in diameter, about an equal number of dark particles of similar size and shape, some particles which were partly bright and partly dark, a dark finely lamellar constituent, and a number of slag stringers. All these were present within a hard, dark grey matrix of iron oxide and the whole was strongly attracted to a magnet.

Etching in a 2% solution of nitric acid in alcohol (Nital) disclosed the presence within the metal of lamellar pearlite and nodular carbide (Fig. 2). It is evident that the bright and dark particles in the oxide matrix are carbide nodules in various stages of corrosion and that the lamellar constituent is a pseudomorph of the lamellar pearlite in the metal.

Pearlite is always found in carbon steels which have been cooled at moderate to slow rates from above 725° C. It consists of alternate lamellae of iron and iron carbide (cementite). The inter lamelar spacing decreases with increasing cooling rate and the amount of pearlite present increases with carbon content until, at about .80% carbon, an entire section is composed of pearlite. When the carbon exceeds this <u>eutectoid</u> composition excess carbide forms a network around the pearlite grains. When the metal is forged by the smith at elevated temperatures, this network will break up and agglomerate as dispersed particles. The cementite nodules in the Hasanlu dagger may have been produced in this way.

Microscopic examination of the Hasanlu spearhead did not reveal the presence of nodular carbide in either the altered or unaltered form and little evidence of pseudomorphic pearlite was found. However, some smaller rounded altered carbides were present in relict grain boundaries of the original metal and scattered here and there in the oxide. Of the metal itself only a few scattered traces remained. The spearhead was evidently made of wrought iron or very low carbon steel.

These findings show that it is sometimes possible to distinguish ancient wrought iron from steel by metallographic means, although all metal has been converted to oxide and all the carbide has turned to a black carbonaceous residue. The approximate carbon content of different local regions in the original steel can be estimated from the ratios of the areas of pseudo-morphic pearlite to blank areas in the microstructure of the oxide, and from the frequency of the carbonaceous nodules.

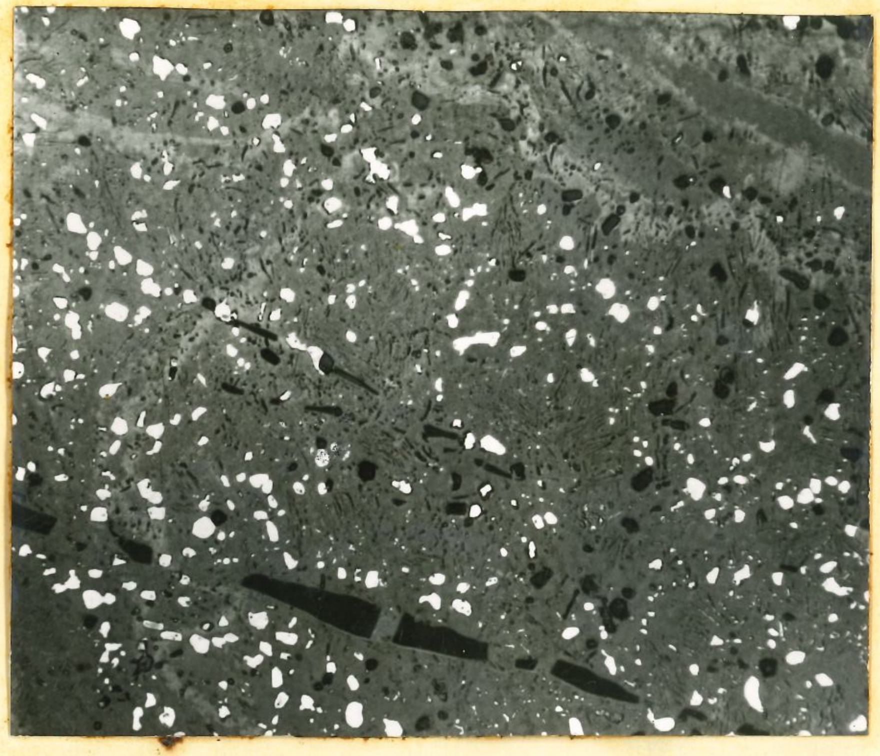
Professor Cyril Stanley Smith, who examined the Hasanlu specimens under the microscope, has suggested that the form and distribution of relict carbides might be more clearly revealed by means of extraction replicas. In this technique a flat oxide section is cemented to a glass slide with acid proof cement and the oxide is then dissolved in acid, leaving the altered carbides imbedded in the cement. Although the writer has not tried this technique, it would probably prove to be very useful.

The large change in volume involved in the transformation from metal to oxide inevitably causes cracks to form in the latter, and this, of course, leads to some confusion in interpreting areas of the oxide in which later forming rust has filled the cracks. However, in the case of the Hasanlu dagger the pseudomorphic structure between the cracks appears to give a reasonably faithful reproduction of the microstructure of the original metal over rather large areas.

The writer is not prepared to say whether or not the corrosion processes that have converted ancient steel objects to masses of oxide under widely varying climatic conditions have always been such as to permit the preservation of relict carbide structures; however, it would seem to be worthwhile to make metallographic studies of whatever iron oxide artifacts are available which date from before about 1500 B.C. This might permit recognition of steel objects dating from an earlier period than has heretofore been reported and thereby extend our knowledge of the opening of the iron age backward in time.

Reed Knox, Jr.
Laboratory for Research
on the Structure of Matter
University of Pennsylvania

Figure 1



Hansanlu Dagger Magnification: 500X
The white particles are unaltered iron carbide; the black material consists of the carbonaceous residue of corroded carbide and some stringers of slag.

Figure 2

Hasanlu Dagger Magnification: 500X
Pearlite in iron surrounded by pseudomorphic pearlite.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE 39, MASSACHUSETTS
Room 14N-321

8 November 1963

Miss Elizabeth K. Ralph, Associate Director
Applied Science Center for Archaeology
The University Museum
33rd & Spruce Streets
Philadelphia 4, Pennsylvania

Dear Miss Ralph:

I have looked over the rough draft of your research proposal to the National Science Foundation. Though I have marked a few suggested changes on it, it meets with my enthusiastic approval. What you are proposing is, I believe, a fine program, and one which should enable a few individuals to devote their life work to a particularly fascinating combination of disciplines. The findings are bound to make an important contribution to our understanding of the nature of technology and its development in relation to broader cultural influences.

You should know that I have been considering the submission of a somewhat similar proposal via MIT, which is, after all, the center of my major professional activities. However, though in no way conceding that metallurgy at MIT is inferior to that at the University of Pennsylvania, I do believe that for the present purposes it is preferable that the program be carried out in a place where archaeology is flourishing, and in combining this with metallurgy the University of Pennsylvania is unique in the United States.

From the archaeological metallurgy that I have myself done more or less as a sideline, I am convinced that archaeologists have an immense contribution to make to a project of this kind, just as they have much to gain from it. Not only can proper samples of early metal for study only be selected by the critical eye of the archaeologist who understands the conditions of their excavation, but the very posing of specific questions for study requires an integral knowledge of entire cultural patterns. Familiarity with other techniques and materials provides an essential background for the study of metallurgy. Metallurgists, moreover, have much to learn from the archaeologist's methods of assaying evidence.

Some effort will be needed to maintain concentrated attention on one part of the inevitably broad field. It seems to me that the center should be (if the archaeologists concur) on the origin and early diffusion of the most important metallurgical techniques. My own interest is principally in the beginning of controlled steel making and hardening. T. E. Wertime's new thinking suggests that there is much still to be done on the origin of smelting, despite the stacks of analyses in the literature. Everything seems to center in the Near East, which is a particular reason for locating this project at the University of Pennsylvania. Though metallurgy is most important in Europe, European contributions to metallurgy were relatively late and in any case are being actively studied by locally-oriented archaeologists and metallurgists the other side of the Atlantic.

The spectacular deviations from the early steel techniques as they moved to India and China would be interesting to follow and, in the non-ferrous field, the introduction of intentionally-made brass, the origin and development of the marvelous Chinese bronze casting techniques, the supposedly independent origin of copper metallurgy in South America, the failure of North Americans to develop metallurgy beyond the use of native copper--these all are questions of broadest significance that could be followed for the light that they throw on man's attitude to matter. An alternate approach would be to follow the use of certain chemical or physical principles or, for example, to note the distribution of various methods of joining and surface treatment. Are there cultural factors which influence a preference for one material and shaping technique over another? What is the relationship between the highly special techniques used in making works of art and the common ones for tools and utensils? What can be deduced from the two-way relationship between joining techniques and design, and what social factors are involved in repair versus replacement?

The metallurgical techniques must always be considered in relation to other technical capacities, particularly the heat-using techniques, such as ceramics. Do sophisticated glazes and sophisticated alloys always go along together? And what can one say about the quantitative aspects of the use of materials? A few finds of treasured objects in graves can hardly reflect a widespread use of the techniques, though perhaps the first uses are always in producing treasures.

The student in this area can hardly be expected to know all of archaeology and all of metallurgy, but it is essential that the committee in charge of his program ensures an adequate breadth of knowledge in both fields combined with at least one really hard specific piece of research that impinges upon both. Only so will he have adequate training for an independent professional career.

I very much hope this proposal will go through and I am pleased at the possibility of being personally connected with the University of Pennsylvania in this important intellectual venture.

Yours sincerely,

Cyril Stanley Smith
Institute Professor

CSS:mk
cc: Maddin

May 15, 1963

Name: Katherine P. Clapp

Address: 13 Shepard Street
Cambridge, Mass.
UNiversity 4-8464

Personal Data:

Age: 26		Date of Birth:	May 8, 1937
Height: 5' 7"		Marital Status:	Single
Weight: 125		Social Security Number:	334-30-4671

Education:

1959-60 University of Florence, Italy.
1955-59 Vassar College. A.B. degree.
1952-55 Shipley School, Bryn Mawr, Pa.

Major Field of Study: History of Art, minors in English and Chemistry.

Work Experience:

1960 - Present Metallographer, Wakefield Bearing Co. Wakefield, Mass.
Summer, 1954-56 Volunteer, Peabody Museum, Salem, Mass.
Summer, 1957-58 Laboratory Technician, Wakefield Bearing Co.

Foreign Languages: French, Italian, some German.

Travel: Summer, 1962 Travel in Mexico
Winter, 1959-60 Living in Florence, Italy, with travel to Austria, Belgium, France, England, Turkey and Greece.
Summer, 1955 Tour of Italy, France, and England.

References:

Mr. Donald G. Barnett, Vice President, Wakefield Bearing Corp. Wakefield, Mass.
Dr. J. H. Brophy, Massachusetts Institute of Technology, Cambridge, Mass.
Mr. Ernest Dodge, Director, Peabody Museum, Salem, Mass.
Vassar College Vocational Bureau, Poughkeepsie, N. Y.