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NUCLEAR APPLICATIONS IN ART AND ARCHAEOLOGY[*]

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INTRODUCTION

The archaeologist is concerned with the history of mankind, but his vocation has intrigued the curious in all walks of life in a manner not usually extended to other branches of history. Through the years, the scientist has not been immune to the peculiar excitement surrounding this pursuit. As the artifacts and concoctions of ancient man came to light, scientists lent their analytical skill to determine what the eye could not discern. There was a rich array of materials awaiting examination. Not only were minerals, building materials, metals, ceramics, and glass found in abundance but diverse organic materials also survived for millenia in the dry and sterile environment existing in such places as the Egyptian tombs. By 1926, the British scientist Alfred Lucas was able to come out with a book Ancient Egyptian Materials which has since been followed by three successively enlarged editions.

The desire to know more of man's heritage was a powerful magnet which drew scientists long before archaeology took form. As an example, the pervasive affinity of Western Man to the Land of the Bible needs no better testimonial than the publications at the very birth of modern chemistry on the analysis of waters from the Dead Sea and Jordan River (1). These analytical reports, among the first on any natural waters, bore names such as Lavoisier, Gay-Lussac, Klaproth, and Gmelin.

Much of the early work on archaeological materials had as the objective the identification of materials. A major turning point occurred with the finding of Willard Libby that the production of carbon-14 by cosmic radiation in the atmosphere provided a "clock" whose time scale embraced the period of interest to archaeologists. This discovery was not only intrinsically important but was probably a catalyst in directing attention to the wider array of modern techniques which could be addressed to problems in archaeology.

The medium for publication of the present review dictates that the subject matter be based on techniques indigenous to the nuclear sciences. Conceptually, this is an artificial distinction but it is found that a surprisingly large proportion of applications of science to archaeology do indeed depend upon just such techniques. It is difficult to conceive of a "clock" based on chemical alterations which has the inherent reliability of one based on radioactive decay. In similar vein, there are broad problems involving chemical analysis for which nuclear techniques appear pre-eminently, if not uniquely, suitable.

The subject of archaeometry is plainly receiving increased attention and, with this, some perspective is developing on what is required to make progress. In this field, it may be taken as a fact that one rarely knows *a priori* the variables with which one is faced. They can only be delineated after painstaking testing of large numbers of specimens. Stated succinctly, one can only know that five analyses would have been sufficient after one-hundred have been done. A misconception, slowly being dispelled, is that there is little incentive for achieving high accuracy in measuring archaeological materials because they cannot be very uniform. What is now known is that some problems cannot be solved at all unless materials are sufficiently uniform to merit and demand accurate measurements. Despite each such *caveat*, many studies have been reported which are imaginative and illuminating, and all have contributed in the inevitable groping necessary to know the nature of the unfamiliar materials with which we are concerned.

PROVENIENCE STUDIES

(General Comments)

A large part of archaeological inference is based upon a well-established affinity between a particular culture and the kinds of structures and artifacts which it produced. Objects have survived in large measure when made of durable materials such as stone, fired clay, metals, and glass; some were utilitarian, others objects of art. Even the most utilitarian artifacts were, in some degree, media for artistic expression and it is this aspect which has permitted archaeologists to make finer and finer distinctions between peoples separated by time or space.

Employing elaborate systems of classification based upon form, decoration, and subtleties of workmanship, an expert will know where an object was made (its provenience). The evolution of style also provides a relative chronology. It is unlikely that any archaeologist is completely untroubled in using these methods because the circumstantial evidence upon which they rest must, perforce, be incomplete in some measure. The importance of establishing provenience stems from the role assigned to movable objects in learning of contacts between peoples. The nature of contacts and what motivated them are at the essence of human history, yet it often proves difficult to define their exact nature even when the provenience of the objects is "known". The evidence may be too meager, but also <u>provenience</u> itself lacks sharp definition when indistinguishable artifacts, along with other material features of a common culture, are found over a wide area.

In some instances, deductions of provenience can be compromised by what we might term "prejudicial accident". An archaeologist may uncover a new pottery repertory and label it according to the excavation site. Later, vessels of this type are found elsewhere and, in the absence of substantial evidence to the contrary, these are described as imports from the site where first found. The logical fallacy of such a deduction is apparent but it is not very productive to be critical of the practice when there is little other evidence upon which to base an alternative.

It has been recognized for some time that an independent method of establishing provenience would be an important adjunct to the traditional methods of the archaeologist. Among the laboratory methods which come to mind are those based on the premise that the materials of which artifacts are made will have distinctive chemical compositions reflecting their places of origin. Such chemical "fingerprinting" applied to pottery, for example, assumes that the mineral progenitors and geochemical conditions involved in clay formation have resulted in different chemical compositions of clay in different places. More precisely stated, the heterogeneity encountered in one source of clay will be small compared with distinctions between sources. In principle, one could find the clay beds used by ancient potters and determine provenience in an absolute sense. If clay sources cannot be found, one can still hope to accumulate overpowering evidence for provenience from the pottery itself by analyzing a sufficient number of specimens.

It might be well to put in perspective the realizable goals of such work as they now appear. The capability of determining absolute (or near-absolute) provenience would hardly eliminate imagination and intuitive insight from the practice of archaeology even in a limited sense. It will correct specific errors of judgment which could be crucial in certain instances, and provide a more detailed view of what provenience means. The potential importance of this latter feature in providing greater scope and precision to archaeological inference should not be underestimated.

PROVENIENCE OF POTTERY

The choice of an analytical method for "fingerprinting" pottery is not arbitrary when one reflects upon the nature of the problem.

(1) In consideration of the huge number of potential clay sources which could pertain to a particular archaeological problem, one should determine a considerable number of elements encompassing chemical diversity.

(2) Many of these elements will be present only in trace amounts, so the method must be sensitive.

(3) The accuracy required need be no better than the homogeneity of each clay source, but the whole approach does not look promising unless clays from one source are indeed homogeneous.

(4) A large number of specimens may have to be analyzed for a single problem but these must be considered part of a much larger framework encompassing all possible problems relating to these materials. One must envision the continuous growth of a corpus of analytical information much as appears in technical handbooks. To permit this corpus to grow rapidly, the method must not be unduly tedious; and to allow for general use, the absolute accuracies of

must be known.

Neutron activation analysis involving gamma-ray spectrometry has congenial attributes for just this problem. Its outstanding property in this regard is the sensitivity of activation for the trace elements of the earth. In addition, modern equipment for obtaining gamma-ray spectra provides sufficient resolution to obviate the necessity for tedious chemical separations. Under carefully controlled conditions, results using this method not only can be reproduced with high precision but it is possible to know their absolute errors.

The earliest attempts on pottery analysis by neutron activation were severely handicapped in that they occurred before equipment adequate to the task was available. This work was reviewed in 1963 by E. V. Sayre (2) and only the references are listed here (3-6). Another publication during the same era aimed at seeing what could be learned about certain Mexican ceramics from a single element, manganese (7).

Others turned to different analytical methods for fingerprinting pottery; notable was the work at Oxford which employed optical spectroscopy (8).

This approach produced improvement in the array of elements which could be detected and continues to be employed, but the technique lies beyond the purview of this particular article.

The advent of germanium counters brought about a dramatic change in the power of neutron activation analysis. The first thorough study of what could now be accomplished was published in abbreviated form in 1967 (9) and in greater detail somewhat later (10). The central theme of this work was the elucidation of the errors inherent in analyzing many elements simultaneously, and the controls required to minimize these errors. An important experimental feature was the formulation and calibration of a composite standard to permit peak-for-peak monitoring of the gamma-ray spectra of the irradiated pottery. When the standards and specimens were packaged, irradiated, and measured in a prescribed manner, it was found possible to reproduce results to about 0.6% where gamma-ray counting statistics did not otherwise limit the precision. Beyond this small error, the precision of measurement for the respective elements depended upon counting statistics, and the absolute accuracies depended in most cases upon how well the standard had been calibrated. Employing a particular recipe for irradiation and cooling times, it was found possible to determine more than thirty elements, many with accuracies better than a few percent. A consequence of a system of analysis which is so elaborate is the necessity of computer data processing.

This same publication (10) also included a few case studies on the uniformity of actual archaeological materials. Table 1 shows some data from this paper illustrating contrasts between two pottery groups which both happen to be from the same site in Upper Egypt. Each value has its precision of measurement shown, whereas the dispersion limits indicated for the group mean values are the standard deviations for the group. It is clear from examination of the data of Table 1 that these two groups are clearly distinguishable and that the precision of measurement is not responsible for the spread found in each group.

The uses of such groups for matters of provenience depend upon further selection and analysis of materials with a particular problem in mind. If a vessel is found elsewhere which is of interest in this context, one can tell with some confidence whether or not it belongs to one of these groups. For a more discrete view of provenience, one must examine a considerable amount of potteries of these styles from other sites to show whether or not they are chemically distinguishable. If they cannot be distinguished between two sites, provenience is indeterminate to this extent.

It was stated earlier that the measurement of many elements might provide the necessary sensitive discrimination among the myriads of clay sources. Implicit in this assertion is the assumption that the various elements will function as independent variables. The data shown in Table 2 were extracted from another publication (11) in order to present some evidence on this point. The study concerned an archaeological problem which will be returned to presently but, for now, attention is called to the first four columns only.

The numbers shown for a few elements are group averages of typologically similar wares from three sites in Cyprus and one in Israel. A careful examination of these data will reveal an absence of coherence in variation of the elements between different sites. For example, even the two rare earth elements (lanthanum and lutetium) do not follow each other. The lutetium contents from Palaepaphos and Kition are indistinguishable, but lanthanum values differ by some 5 standard deviations. Between Ashdod and Palaepaphos the lanthanum values are the same, but lutetium differs by more than 5 standard deviations. The nickel contents do not follow iron among any inter-site comparisons. For the particular elements selected for display here, Palaepaphos and Ashdod show some general similarities but the hafnium values are grossly different. The examination of large amounts of data has led to the selection of some 18 elements for diagnostic purposes on the basis that they seem to exhibit this sort of random behavior.

The particular archaeological problem mentioned (11) pertained to the origin of the Philistine people. Mycenaean IIIC1 wares, having close stylistic similarities with such wares from Cyprus, were found at the earliest Philistine stratum at Tel Ashdod and these were compared with similar wares from three sites on Cyprus and with typical Philistine wares from Ashdod (Table 2, column 5). The complete chemical profile showed that these Mycenaean IIIC1 wares from Ashdod were made locally. The study thus far did not reveal the origin of the Philistines but did point up the perils of relying exclusively on stylistic criteria in matters of provenience. Some more subtle but useful archaeological inferences did come from these "negative" results but will not be reviewed here.

Another archaeological study (12) centered upon the provenience of a single sherd excavated in Cyprus and thought to be an import. Considerable importance was attached to this piece because it is one of few examples of its type found in Cyprus. In comparing the analysis of this piece with reference pottery from a number of sites possibly related to this problem, it was found that the vessel had been made where it was excavated. That is to say, it matched well a group of other wares from this site (of which there can be little doubt about local manufacture); it did not fit within groups from other sites, including those from which it was thought to come. This finding raises some provocative alternatives for archaeologists: either people who made this style of pottery existed at this site almost 200 years earlier than the bulk of other evidence would indicate, or the chronology adhering to this type of ware can be off by almost 200 years. Bringing such issues into sharp focus is probably where laboratory provenience determinations will prove of great utility. Other published work from this laboratory will be found through the indicated references (13-15).

The work mentioned so far was done at one laboratory following a particular analytical prescription on which considerable effort was expended in understanding and controlling sources of error. Much of this effort was concerned with standards and standardization of operating conditions. Other papers handled these problems in somewhat different ways and one (16) was clearly exploratory as it only aimed to show that the radioactivity from a few elements differed between two pieces of pottery, each from a different site.

Al Kital, Chan and Sayre (17) analyzed 41 stylistically related sherds from several sites in Yemen and one in Ethiopia. The method involved calibrated glass standards and yielded absolute values for eleven elements which they believed to have 10% accuracy or better. As seems characteristic of such studies, they found a few well-defined chemical pottery groups showing correlations and differences between sites, and sherds which did not agree with these groups or with each other. The objectives of this work were to establish provenience for pottery made according to visibly different potters' practices and to see if any of these had been exported. They were able to show that the grass-tempered* pieces from one site in Yemen all fell into one group providing strong evidence that these were locally made, particularly since the vessels represented a considerable span of time. Six sand-tempered sherds differed considerably from the grass-tempered sherds of this site and two of them agreed well with a group of four sherds (all that were analyzed) from a site in Ethiopia. Along with archaeological evidence that sand-tempering was common in Ethiopia for wares of this type, one has some basis for saying these had been exported to Yemen.

Another publication from Brookhaven National Laboratory (18,19) centered about Fine Orange Ware, a luxury product found sparsely but over a wide area in the Mesoamerica of the Mayans. It was hoped that provenience studies would shed some light on centers of the Mayan culture and the collapse of the Mayan civilization.

Pottery of this style covering several periods and a wide range of sites were found to fall in a single chemical group with relatively few exceptions, all from the eastern or northwestern extremities of the domain.

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*"Temper" is a non-plastic material added to clay (or already present in the raw clay) to prevent cracking during drying to firing.

These exceptions are surely of importance but larger numbers will have to be found before a definite picture emerges. The relative homogeneity of the large proportion of the wares is evidence for a single center of production for these. Attempts to locate this place, by analyzing common utilitarian wares from a number of sites, proved unavailing so far. Apparently the clay source used for this fine ware was not commonly used for others. (It might be mentioned editorially that, to establish provenience rather convincingly, one does not need to find many instances in which the potters lapsed from their normal practices in this regard).

Sometimes archaeological problems come up which hinge upon the identification of a single sherd or two with much of the world as the arena. It can be appreciated that a good deal of luck would be required to find the provenience at first try. Sir Francis Drake is supposed to have landed at a spot in Northern California, dutifully called Drake's Bay, as one stop in a trip which took him around the globe. Excavations at Drake's Bay produced two earthenware sherds which showed some resemblance to a coarse-ware made in North Devon during the sixteenth century.

The authors of a paper concerning this problem (20) determined the composition of these pieces and a collection of 10 Devon sherds from a kiln site. These wares included both coarse-ware and a fine decorated type characteristic of the period. It was shown that the Devon coarse and fine wares were made from the same clays and that the Drake's Bay pieces did not originate here nor were they like each other. The study also included analyses of related pottery from Jamestown, Va. and other settlements of Colonial America. Among these were found specimens that likely did come from Devon and others which did not. The study illustrates well the complexities which can arise in work of this kind and how a single objective can fan out into many.

A broad problem which continues to hold the attention of a considerable number of scholars has to do with the Greek Late Bronze Age. This period saw the rise and dispersion of the Mycenaean civilization and the pottery was marked by an unusual degree of stylistic homogeneity over a large territorial expanse. Plainly, the spread of this civilization during a time of great turbulence had important causes and results, yet many fundamental questions remain unanswered. Catling has outlined the necessity for a more detailed view of pottery proveniences and undertook to examine this problem by employing emission spectroscopy (8). The technique produced interesting results but left wide ranges of pottery indistinguishable. It is still not clear whether this is a shortcoming of the method of analysis or is inherent in the pottery.

Harbottle (21) measured ten elements in 20 sherds of stylistically homogeneous material from Mycenae (Greece) and from Knossos (Crete) employing neutron activation analysis. These same sherds had previously been analyzed spectroscopically at Oxford (8). Although only one third of the elements were common to both studies there was agreement where such overlaps existed and nothing was found among the other elements that produced contradictions. Both studies led to the conclusion that materials from each site were rather homogeneous and the potteries from two sites could be distinguished.

The Berkeley laboratory has analyzed some 800 pieces of Mycenaean wares from many sites but the results have not been published nor completely assessed. This study is mentioned here because it can add some perspective to the problem at hand. It is not possible nor proper to review this unpublished work here other than to say that some perplexing features turned up and to suggest caution in assigning provenience before a great amount of data have been taken and assessed. We do not question the differences between Mycenae and Knossos reported in the published work but wish to point out that similar differences appear among Mycenaean wares all excavated in Greece.

Before leaving the subject of pottery provenience it should be recalled that most of the analytical work cited has employed neutron activation. Whether or not other methods are suitable has only been alluded to in expressing doubt that the accuracy and sensitivity of emission spectroscopy are equal to the task. X-ray fluorescence analysis has also suffered some debilities in analyzing ceramics but there have been some recent changes in technique which alter this picture dramatically. The ability to obtain high accuracy depends upon meticulous technique in sample preparation in order to minimize absorption and enhancement effects and a number of recipes have been offered which cannot be reviewed here.

A major advance appeared with the introduction of <u>non-dispersive</u> x-ray analysis employing silicon and germanium counters developed for the analysis of nuclear radiations (22). Attention is called to a detailed review by Rhodes (22a) of non-dispersive x-ray analysis, and radioactive sources for excitation, which appeared before semiconductor counters of very high resolution were available. In the conventional apparatus Bragg scattering is employed to disperse the excited x-rays before detection and there results a great loss in detection efficiency. The high resolution semi-conductor detectors can resolve x-ray energies in a mixed beam and the only loss is a modest attenuation from the solid angle between the specimen and the detector. The initial publication (22) also employed a radioactive source (such as ^{241}Am mixed γ-rays and x-rays) to excite x-rays in the specimens instead of an x-ray tube source. Although a system such as this can be used to good effect (23) the weakness of a radioactive source, negates some of the sensitivity inherent in the analyzing system. It might be mentioned that the system employing a radioactive source is compact and can be powered by an automobile battery, therefore has applications in field work (24).

Further advances in detectors (25) and the development of a lower-power x-ray tube (26) (to replace the radioactive source) have now resulted in an instrument of great enough sensitivity to permit analysis in the parts-per-million range. The accuracy readily attainable in applications to pottery can be seen in Table 3 in comparison with data on the same specimen from neutron activation (27). The agreement is seen to be quite satisfactory and for a number of elements (Ni, Cu, Zn, Ga, Rb, Sr), the x-ray fluorescence results are more accurate. For perspective, it should be mentioned that these particular elements are those rather poorly determined by neutron activation whereas such elements as Al, Na, Sm, La, U, Co, Sc, Ta, Hf, Th, Cs, and others, are accurately determined. The point to be made is that x-ray fluorescence analysis has attained both accuracy and sensitivity for minor and trace elements, and some further improvements may be expected.

It should also be mentioned that conventional x-ray fluorescence methods can give accurate values on ceramics if sample preparation is rigorously controlled and attention is confined to relatively few elements. Picon et al (28) have published results on important problems relating to Terra Sigillata from sites in France and came up with some convincing archaeological information. The point to be made here, however, is that some of the same specimens were analyzed by neutron activation analysis in the Berkeley Laboratory and results agreed within experimental error for those elements which could be inter compared.

PROVENIENCE OF OBSIDIAN

Obsidian, a volcanic glass, lends itself to flaking technique as does flint and was much used for fashioning arrow points and other artifacts. Points of obsidian and other artifacts are often found far from any known sources, so one may infer that there was sizeable commerce in the raw materials or finished products. In order to trace these contacts, the determination of obsidian provenience becomes the primary goal. A number of methods have been tried for characterizing obsidian but the first thorough studies employed spectrographic analysis (29,30). Although these publications merit careful study, they fall beyond the purview of this review and will be mentioned but briefly.

Obsidian artifacts and source materials were selected from sites covering the Mediterranean Basin, a band from Anatolia to Lake Van, and a number of others as far removed as Ethiopia and Slovakia (29,30). Substantial progress was made in assigning provenience but there was considerable dispersion in composition of materials from each place with the attendant ambiguities which sometimes resulted. Data on only a few elements were found suitable for making correlations. As already stated under the discussion of pottery provenience, it is not easy to tell whether such inhomogeneities are intrinsic to the materials or are due to the inaccuracy of spectrographic analysis.

A later study (31) undertook to remove certain ambiguities by doing fission track counting. This device adds an independent criterion for distinguishing obsidians since it determines the age of a flow, and often the uranium content is measured accurately although this is not needed for dating. Materials were chosen from Melos and Giali in the Aegean Sea, from the Tokaj region of Hungary, and from Acigöl in central Anatolia--none of which could be clearly distinguished from the spectrographic analysis. Only 11 samples were analyzed in all and it was found that ages of ∿ 2 million years and ∿ 8 million years appeared both in the Aegean and in central Anatolia. The two samples from Hungary agreed with each other and gave a different age. When the uranium contents were included as a chemical variable, all of these regions were distinguishable. Finally, a test for provenience was made on three samples from a mesolithic site in southern Greece and these agreed very well with the dominant obsidian analyzed from Melos. They clearly did not agree with the obsidians from Hungary and Anatolia. If this evidence for importation into Greece from the Aegean does not have to be modified, the important fact is established that over-seas traffic existed at least by the beginning of the seventh millenium B.C.

It is reasonable to expect that chemical fingerprinting of obsidian would be less laborious than the comparable objective applied to pottery. Obsidian flows are relatively few in number, and absolute provenience is more easily achievable because these sources are not nearly so obscure as clay sources. Furthermore, the chemical composition of the obsidian remains unaltered in the hands of the artisan, whereas raw clays are refined and sometimes foreign materials are added. Finally, geochemists have provided some analytical evidence that an obsidian flow can be quite uniform in composition.

The question of how uniform is an obsidian flow is fundamental in chemical fingerprinting because this relates to the ease of distinguishing different sources and also defines the accuracy required to take advantage of intrinsic differences. It seems obvious that one cannot know what to expect and that careful sampling and analysis must be undertaken to learn the parameters pertaining to each source of interest. Table 4 gives some of the results obtained by Bowman et al (32) on 19 samples taken from four regions along a flow in Napa County, California. The analyses were done by neutron activation under carefully controlled conditions. Each entry in Table 4 is the mean value for the 19 samples and the standard deviation from the mean. The standard deviations vary considerably from element to element but in each case the spread can be accounted for by the precision of measurement for that element. For those elements in which the precision of measurement (counting error) is as low as 1%, the dispersion of composition is similarly low. Manifestly, this obsidian flow is extremely uniform. Griffin et al (33) published analyses on a number of obsidian sources and among these were three pieces from Napa County. They determined relatively few elements (Table 4) and with the exception of lanthanum the agreement with the results of Bowman is not bad. However, their results show considerably greater spread which is an inconsistency if the samples came from the same source. In this paper (33) the authors do not state clearly what accuracy of measurement they assign to the different elements.

Another group of obsidians from Borax Lake (Lake County, California) were analyzed by Bowman et al (32,34) and showed quite a different picture. There was considerable variation in composition among the 33 obsidian specimens and these were placed into 10 groups, graded according to iron content which varied from 0.67 ± 0.01% to 1.88 ± 0.03%. However, there was a remarkable coherence between all of the elements. If any element is plotted against iron (for example), the curve is linear over the entire range and the dispersion of the data points from the least-squares line can be shown as a band covering ± the RMS deviation. These bands are shown for six elements (among many) in Figure 1 taken from Reference 34. The five data points also shown in Figure 1 refer to five arrow heads of great antiquity excavated at Borax Lake. It is not a surprise to find that they were made locally but it is interesting to note that all fall in the region of lowest iron content. It should also be noted that if artifacts were made from any other obsidians from the flow, it would be just as easy to assign provenience.

There is some earlier experimental evidence by Stephenson et al (35) on Borax Lake artifacts bearing on this point. These authors employed x-ray fluorescence analysis and reported variability in composition of artifacts but did not convert their data to actual elemental abundances. They did give values for other obsidians analyzed by Bowman et al (34) and it is possible to normalize the measurements. One group of 7 artifacts proved to have an iron content of 0.65 ± 0.05% which corresponds well with the five artifacts shown in Figure 1. Another group of 9 artifacts had iron = 1.04 ± 0.07%, a value which is considerably higher than found in Borax Lake artifacts by Bowman et al (34). The same publication (35) also gave data for manganese and these were converted to manganese = 118 ± 15 ppm and 186 ± 24 for the two groups. These will be found to lie on the iron vs manganese sequence of Figure 1 and show that the ancient artisans at Borax Lake did indeed use obsidian with a range of compositions.

The data cited above show that, at least in principle, it can be dangerous to base provenience upon a single sample or two obtained from a source. It is an open question as to whether any source will be as uniform as the Napa County flow, show coherent variation as found at Borax Lake, or display still other patterns. Particular care is necessary where one region may have multiple flows of different geological history.

Gordus and co-workers have analyzed large numbers of obsidian samples by neutron activation. They have adopted a simpler scheme of analysis than that just reviewed, measuring relatively few elements and relying for interpretation on ratios of certain elements. One of the interesting problems concerned the origin of obsidian found in the Ohio Hopewell mounds and related sites principally in the Mississippi River basin (33,36). For reference materials they sampled heavily from sources in Yellowstone Park and lesser numbers from flows in California and Oregon among others. Provenience deductions were based on sodium to manganese ratios supplemented by some other elemental ratios where there was ambiguity. They concluded that the Hopewell obsidians came from Yellowstone Park and not from any of the others tested. In another publication (37) mean values and ranges are given for seven elements in obsidians from the Yellowstone region, a site in Mexico and three sites in California. All of these data help support the above conclusion.

Another important study concerned the trade of obsidian in the Near East during the ancient period which spanned the appearance of agriculture (36,38). Two well known areas of volcanism lie in Central Anatolia and in eastern Turkey around Lake Van, and several sources from each had been classified by Renfrew and co-workers (29,30). Gordus et al found members of these groups at various sites in the Levant and observed a complex picture of changes in trade patterns as a function of time. One region in which were found artifacts of imported obsidian is the Jordan Valley, believed by some scholars to be the seat of domestication of wild grains. The tracing of obsidian trade routes as early as 7000 B.C. suggests that the spread of agricultural arts may have followed the routes of obsidian trade.

In addition to the x-ray fluorescence data cited in Reference 35, another group of publications have appeared which used this technique (39-42). All of these are concerned in large part with obsidian sources and trade in Mesoamerica and two (41,42) involved considerable numbers of samples. The study by Jack and Heizer (42) included 151 artifacts collected from the single site, La Venta in Tabasco, Mexico. Only three elements (Sr, Rb, and Zr) were used for diagnostics and it was possible to separate the obsidians into five groups, three of which contained a very large proportion of the specimens. As for provenience, only a very few source samples were analyzed: one from Pachuca in Hidalgo, Mexico; two from Ixtepeque and one from El Chayal in Guatemala. Twenty-nine artifacts from La Venta matched the Pachuca source, a finding which supports earlier evidence based on a very few samples (39). A few of the others could possibly have come from the Guatemala sources, leaving the large majority of the La Venta artifacts still unplaced.

The paper by Stross et al (41) reported on 63 samples from 34 sites in Mesoamerica. The analytical data were segregated into only three groups based upon Sr-Rb-Zr ratios on a terniary diagram. For such a wide-range problem it is difficult to know what such groupings mean even though they are well separated from each other. The authors are well aware of the difficulties of interpretation, nevertheless the paper should be read by those interested in the archaeology of this area. One curious finding in this work concerned an artifact found in Lovelock Cave, Nevada which could be placed in one of these Mesoamerican groups.

Particular attention is called to another study on Mesoamerican obsidian trade because of the care with which a particular archaeological objective was coordinated with choices of artifacts and source materials (43). About 200 artifacts were chosen from a single area (San Lorenzo Tenochtitlan, Veracruz) which happens to be removed from any local source of obsidian. The samples were selected to emphasize the rise of the Olmec Civilization (∿ 1150 B.C.) but also included materials of the Pre-Olmec and Post-Olmec periods as late as 1200 A.D. Source obsidians were drawn from 25 places covering the east-west volcanic band of central Mexico and the highlands of Guatemala.

Provenience was determined with relatively few elements measured principally by x-ray fluorescence. The authors (43) were able to discern 8 sources for San Lorenzo materials but some 45 artifacts could not be placed within any of the 25 sources tested. The level of intensity of obsidian trade as a function of time was determined as was the appearance and disappearance of particular sources of supply. It is of interest to note that, although the closest possible source to San Lorenzo was well represented, large numbers belonged to sources 800 air kilometers to the northwest and to the southeast. Another intriguing finding was evidence that in an early Pre-Olmec period, obsidian was obtained from places which apparently had no local settlements at the time.

PROVENIENCE OF GLASS

The conscious production of glass was practiced in Egypt some 3500 years ago and there is some evidence that the technology is considerably older. Artistically and technically, objects of glass embody distinctions which make them eminently suitable for archaeological inference. Although glass-making is a sophisticated form of technology, there is a surprising paucity of the physical remains of glassmakers' tools and factories from ancient times (44). This factor has contributed to the large gaps in knowledge concerning glass provenience.

Analysis of ancient glasses by conventional chemistry, optical spectroscopy, and different forms of microscopy have yielded much information on different general formulations as well as the methods for producing various colors and other optical effects. In a broad sense, these measurements have revealed much about glass-making practices in different eras and areas, but if glass objects contain more detailed clues, they are largely untapped.

The quest for compositional characteristics which could earmark specific points of origin is not a light undertaking. A glass is formulated from at least three raw components which could very well come from diverse sources: the quartz or other material for SiO_2, the alkali and lime components, and the mineral colorant. The trace elements of each of these can provide clues but, when mixed, the problem of sorting out clues becomes multi-dimensional. If neutron activation is applied to this problem, some technical difficulties are encountered. Many glasses have high sodium content, and antimony in the "percent range" is not uncommon. The existence of high levels of sodium reduces the sensitivity for determining short lived radioactivities, and antimony places in the spectrum many intense γ-rays with half lives of 2.8 and 60 days.

Exploratory work has appeared (45) aiming to cope with these technical problems. In this study, which was addressed to medieval stained glasses, samples were irradiated and before gamma-ray analysis, the sodium and antimony were removed by chemical separation. If these separations can be made clearly and without undue labor, the ability to extract detailed information from glasses should be enhanced.

Another study (46) concerned glass beads found in Sub-Saharan Africa which were analyzed by non-dispersive x-ray fluorescence. (The same paper refers also to unpublished data obtained by neutron activation on the same materials.) The particular beads in this report were of a type termed "dichroic", exhibiting a blue color by reflected light and yellow by transmitted light.

Thirteen elements were determined on 27 specimens and it was found that the beads could be placed into two compositional groups. Group B consisted of lead glasses ($\sim$ 30% Pb) whereas Group A had Pb = 0.05%. Such glasses can be distinguished simply by specific gravity measurement but there were other distinctions of importance. All of Group B were very high in arsenic and relatively high in barium, whereas Group A beads were higher in manganese and cobalt.

Information was obtained on the distribution of these beads among different sites in West Africa and there appeared also a correlation with age. Group B beads were found in contexts belonging roughly to 1000 A.D., whereas Group B beads are apparently much newer. The earlier period coincides with that of Arab trade in this region yet the authors mention that the compositions of these beads have some relation to European medieval glasses analyzed by others. This study seems to be a good start in learning how these beads were introduced into West Africa but at this stage information is lacking on known source materials.

Glass provenience studies based upon stable iostope ratios are discussed in a later section of this review.

PROVENIENCES OF COINS AND OTHER METALS

When we leave the "earthy" materials such as ceramics and obsidians and turn to those which were altered by man, the problems of determining provenience by technical means can become more severe. Metals can be native materials, as with the precious elements, but can also be refined from ores in which case there is an obvious drastic alteration. The use of trace elements in provenience studies involves deductions based upon those elements which inadvertently accompany the metal during refinement. Further, there is the problem of alloys in which case one is dealing with particular recipes used by different artisans, and the components of the alloys may have come from different ores or even from the remelting of previously used metals. Other complications will be mentioned below.

The technical aspects of analyzing metals must contend with massive concentrations of the principal element or elements. This presents a serious handicap for a technique such as neutron activation in which the Compton background introduced by major constituents can strongly diminish the accuracy of measuring the photoelectric-peaks of minor constituents. Furthermore, the intensity of the neutron irradiation may have to be kept low in order to stay within the capacity of the pulse-analysis equipment. This particular set of problems is not so severe in analyzing materials such as pottery because the major constituents activate weakly or not at all if slow neutrons are used.

Coins have an important role in archaeology because they likely represented a government monopoly and can be identified with discrete regnal periods and the history surrounding these. It should be recognized that artifacts found with coins also become dated rather sharply. It is important to trace the coinage metal itself to its origin because patterns in commerce and discontinuities in these patterns can tell much about relations between various cities and those who controlled the metal sources.

A large number of publications have appeared concerning origins of coinage metals and the reading of these will emphasize the difficulties alluded to. Since we shall not be reviewing these individually, we provide a list of publication titles, their references, and brief descriptive statements:

LITERATURE CITED

Ref. 47. "Non-destructive analysis of ancient metal objects".

Qualitative test for gold, silver and copper in Gaulish coins; probably the first use of neutron activation on archaeological materials.

Ref. 48. "Neutron activation as applied to trace element determination in pottery and coins".

Outlines method for determining gold and copper in silver coins; applications in Ref. 49.

Ref. 49. "Gold and copper traces in early Greek silver".

Results on 133 coins, expanded upon in Ref. 50-52.

Ref. 50. "Gold on copper traces in early Greek silver - II".

Results on 315 coins from several sites in Greece, Sicily and Southern Italy. Expansion of work in Ref. 49.

Ref. 51. "Neutron activation analysis of ancient silver coins".

Expansion of study in Ref. 49 and 50; more detailed description of methodology.

Ref. 52. "The Composition of Greek Silver Coins: Analysis by Neutron Activation".

A monograph discussing in detail results of Ref. 49-51 and presenting a historical interpretation.

Ref. 53. "Activation analysis of silver by using a radium-beryllium neutron source".

A rapid method of silver determination applied to Japanese coins.

Ref. 54. "Gold and copper traces in late Athenian silver".

Neutron activation applied to coins of the late Hellenistic period (2nd and 1st centuries B.C.).

Ref. 55. "The silver content of Diocletian's early post-reform coins".

Analysis of 39 coins from two mints employing neutron activation and x-ray fluorescence.

Ref. 56. "Determination of silver content of Greek coins by neutron activation".

Ref. 57. "Non-destructive radio-activation analysis of Norman and Suebic coins of Italy".

Gold coins analyzed for gold, silver, copper.

Ref. 58. "Neutron activation analysis of silver in some late Roman copper coins".

Analyzed 147 coins minted in many places.

Ref. 59. "Analysis of electrum coins".

Copper content of gold-silver alloy called electrum measured by neutron activation.

Ref. 60. "The Coinage of Cyzicéne".

Neutron activation analysis for gold, silver, and copper in electrum coins.

Ref. 61. "Neutron activation analysis of Roman coins from 250-500 A.D. Part I".

Roman copper coins analyzed for silver, gold, and antimony.

"Part II" Analysis for silver, gold, antimony, cobalt, tin, and indium.

Ref. 62. "Non-destructive analysis of ancient silver coins".

Neutron activation determination of silver, copper, and gold in silver coins; x-ray fluorescence determination of lead.

Ref. 63. "Coins: Neutron activation analysis of Norwegian medieval coins".

Neutron activation determination of silver, copper, and gold.

Ref. 64. "A quantitative non-destructive analysis of silver coins by neutron activation".

Silver coins minted in Berne in 15th and 16th centuries. Measured gold, copper, silver in 373 specimens.

Ref. 65. "Quantitative non-destructive neutron activation analysis of silver in coins".

Silver content of 49 Islamic coins as a function of date.

Ref. 66. "Non-destructive activation analysis of ancient coins using charged particles and fast neutrons".

Analysis of 142 gold, silver and copper coins of various types. In addition to gold, silver, copper, and lead values, zinc, tin, nickel, arsenic, antimony, and iron also determined on copper coins.

Ref. 67. "Method of analysis by activation of ancient coins with fast neutrons".

Determination of gold, silver, and copper with stated accuracy.

Ref. 68. "Investigation of the silver content of Roman coinage by neutron activation analysis".

Silver content of 700 coins as function of minting date.

Ref. 69. "The metal contents of early Serbian coinage".

Silver coins of 13th and 14th centuries analyzed for gold and silver by neutron activation.

Ref. 70. "Non-destructive analysis of silver coins: A study of Sasanian and Umayyad coinage".

Some 1400 coins analyzed for gold, silver, copper using neutron activation.

The simple listing of titles does not imply homogeneity of archaeological consequence but rather that, technically, the analytical information and how it was obtained did not differ greatly in most of the studies. Since this review is aimed mainly at acquainting physical scientists with the development and evolution of techniques, there is little to be gained by elaborating upon small differences. Most of the studies employed slow-neutron activation analysis and only the major constituents - gold, silver, and copper - could be discerned. For these, information was obtained on sources of coinage metal from minor elements variations, evidence for alloying practices, and inferences on debasement of precious metals which could be correlated with historical events. Scholars who are concerned with the relations of coinage to ancient history are probably already aware of these studies. Only one of the studies (66) employed charged particles and fast neutrons in order to attain greater flexibility in determining the major constituents, and to bring out minor elements and those not activated by slow neutrons.

The technical difficulty of obtaining detailed trace element information on metals non-destructively using neutron activation has led Meyers and Sayre (71) to undertake chemical separation of the major constituents. Working on Sasanian silver objects, they removed 0.5 mg samples, and after irradiation and dissolution, the copper, gold, and silver were removed by ionic exchange with cuprous iodide or silver iodide. They then found that they could determine semi-quantitatively 14 trace elements. This analytical scheme should help greatly in giving greater latitude in provenience studies. The obvious advantage in removing the major constituents is accompanied, of course, by the added labor of the procedure. If applied to coins and other tiny objects, one also has to contend with the resistance against defacement in removing a sample.

Since the trace elements which occur in copper or other metallic objects must first exist in the ores, it is reasonable to turn to ores for some understanding of which elements exist therein and what happens to them during smelting. A different approach on provenience determination of copper objects is based on such considerations (72,73). Native copper metal was analyzed as were ores of "oxidized" types (oxides and carbonates) and "reduced" types (sulfides). Representative ore samples were reduced to the metal with carbon under simulated primitive conditions and the incorporation of impurities into the copper metal was measured. From this, it was found by spectrographic analysis that such elements as silver, arsenic, beryllium, iron, antimony, and lead were found in large part in the metal. Principal reliance was placed upon neutron activation analysis in subsequent measurements. Tests were made for 15 elements including silver, mercury, iron, scandium, cobalt, antimony, selenium, and chromium. For each ore type, a frequency table was presented showing how many samples were represented in successively decreasing levels of concentration for each element. Each table combined world-wide sources of the particular ore type. Similar tables were presented for artifacts which were grouped according to geographical region: Near East, Europe, South America, North America.

Although 350 ore samples and 100 artifacts were analyzed, the authors (72,73) believe that this was inadequate to show what this approach can accomplish because the materials were drawn from too wide a geographical range. They were able to show that trace element levels in native copper are different than those which appear in metals extracted from ores and some differences in artifacts between different geographical areas. Because of the vastness of a program which would simultaneously establish local compositional profiles over the world, the authors conclude that it might be more profitable to study intensively discrete problems of a local character.

Reports on the analysis of other metals employing neutron activation have been sparse but attention is called to a study of ancient bronzes (74), a steel sword (75), a gold ornament (76), silver and gilded-silver art objects (77,78).

The utility of accurate non-dispersive x-ray fluorescence analysis is shown in data obtained by Giauque (79) on metal art objects of the Yoruba culture of West Africa. The predominant metal used was brass (Cu-Zn alloy), of which 27 objects were analyzed. These could be divided into 9 compositional groups, two with eleven members and several with only one. One of the groups of eleven contained all of the objects with detectable cadmium for which the mean value was about 80 ppm. This is not an artificial grouping because the level of detection for cadmium was some 10-times lower. Another group of four objects had the only detectable nickel, in addition to other distinguishing characteristics. In addition to the brass objects, one was found to be a tin bronze, one was 97% zinc, and two were lead-tin alloys. All of these results were appended to a publication on Yoruba art forms and, unfortunately, no evaluation appeared as to what the analytical data had to say about Yoruban history or technology.

Further discussion on the provenience of metals will be found in a later section having to do with stable element isotopic ratios.

PROVENIENCE FROM ISOTOPIC RATIOS

Lead Isotope Ratios. The classical method of dating rocks from lead isotopic ratios depends upon the radiogenic components from thorium and uranium decay. To the extent that different sources of lead ores reflect different geological history, it is possible to relate lead-containing artifacts to places of origin. Brill and Wampler (80) have examined ore samples from a number of sites and lead artifacts from a much wider array, and have made groupings according to isotopic ratios.

The authors show that galena ore specimens and lead ingots found at widely separated places sometimes fall into the same compositional group. There can be little doubt that ore as well as lead ingot was an article of commerce, therefore such occurences are not unexpected. Where this occurs it is natural to assign provenience according to those members obtained in proximity to a well-known mining site. However, it is always possible, and even probable, that there are different geographical sources whose lead isotope patterns will not be distinguishable. The authors also present evidence that diverse sources of lead were used in one locality for making artifacts and that there could have been blending through remelting of artifacts.

This initial study was followed by more extensive measurements in which the precision and accuracy of the mass spectrometry was improved (81). It was pointed out that isotopic ratios which are good to about 0.1% are needed if the maximum amount of information is to be obtained. This report (81) includes a discussion of measurements made in the initial study, hence is the better source of information on this subject.

Four main lead types were discerned, and lead from a number of artifacts did not fit into these groups. Provisionally, provenience was assigned to the four types: Laurion (Greece) - Group L; Derbyshire (England) - Group E; Rio Tinto (Spain) - Group S; possibly Italy - Group X. These deductions were based upon source ores as well as from evidence on archaeological materials. Large numbers of the artifacts could be assigned among these groups, and these consisted of lead-containing coins, other bronzes, and glasses covering a wide geographical area and a long time span. However, the accuracy of the measurements brought into focus questions as to what a compositional group really means. This problem seems always to arise when accuracy is high.

One may define an assemblage of materials as a "group" when the compositions are reasonably compact and are distinctive from others. When the dispersion within a group cannot be attributed to experimental error, the question arises as to what causes the dispersion. It was noted, for example, that in Group L lead from bronze objects there was a general variation in composition which correlated with stylistic chronology. This might mean that all came from Laurion ores, but at different contact layers, and it might also be evidence for different mining sites with similar geological history.

This illustration is taken from a number of puzzling features which arose in this study. Such findings should not be considered discouraging; rather, they permit one to devise experiments systematically to elucidate the complexities of ancient trade patterns previously hidden from view. The authors discuss the possible historical meanings for a number of the individual glass and bronze specimens which they analyzed. Another publication employing the same technique determined origins of Roman lead pipes uncovered at a number of sites in Western Europe (82). Significant differences were found, and for some specimens, provenience was assigned.

Carbon and Oxygen in Marble. The interest in the provenience of marble goes back almost a century but the identification of sources has proved to be elusive. Particularly in the Greek world, marble was quarried extensively for buildings, statuary, and various forms of inscriptions. The solution of many problems in Greek archaeology retain some annoying gaps through the inability to know, with great confidence, where marble came from.

Petrography and morphology have yielded useful results in particular instances but do not seem to be applicable broadly. Studies of the chemical composition of marble have not been exhaustive but do show that the calcium carbonate lattice offers a hostile environment for the incorporation of other elements. The calcium carbonate seems to be extremely pure and levels of foreign elements therein are dwarfed by those in intrusive materials. This, in itself, does not negate the possibility of fingerprinting but experiment seems to show that these intrusions may be chaotic in a single quarry (83).

Craig and Craig (84) have determined the ^{13}C - ^{12}C and ^{18}O - ^{16}O ratios from a number of quarrying sites in Greece and the Aegean and have shown that these two parameters permit identification of these several sources. Only in marbles from Naxos, where two distinctive types were characterized, was it found that there is some overlap between one of these groups and that from Mt. Penteli in Attica.

The authors also analyzed ten archaeological specimens of structural marble. Five of these could be placed among three sources, and the other five have no counterparts among the source materials so far analyzed. It is interesting to note that some results of historical consequence have already come from this small sampling. One intriguing finding was the appearance of two distinctive marbles (neither yet placed with respect to provenience) in the immediate vicinity of one structure, the Tholos of Epidaurus.

The data are expressed in parts-per-thousand for the deviation of the isotopic ratio relative to a standard (per-mil difference). For example, the values for a typical Pentelic marble are ^{13}C, 2.63 ± 0.05 and ^{18}O, -7.90 ± 0.05; those for a Parian marble are ^{13}C, 3.89 ± 0.05 and ^{18}O, -3.10 ± 0.05. The error limits represent the precision of measurement but the spreads in values for the respective sources are only shown graphically in the report (84). The authors discuss the geological antecedents of isotopic variations and call attention to the possibility of compositional "coincidences" when only two variational parameters are employed.

Oxygen Isotopes in Glass. Brill (81) has reported on studies aimed at using ^{18}O to ^{16}O ratios to distinguish glasses. Experiments showed the isotope ratios in glasses could be calculated from those of the ingredients when the glasses were made under a variety of conditions and with different ingredients. It was also shown that for compositions encountered in ancient glasses the isotopic ratio would largely reflect that of the silica-bearing component even though the alkalis had considerable variability.

As for analyses on ancient glasses, the per-mil differences showed considerable variations among 75 specimens analyzed, although it was neither expected nor found that manifestly unrelated glasses were all different. One interesting experiment concerned waste glass (cullet) excavated in an ancient factory site at Jelemie in western Galilee. A typical cullet piece had a per-mil difference of $^{18}O/^{16}O$ from a mean-sea-water standard of 14.64. The authors obtained good glass-making sand from the nearest likely source some 24 km away. This sand contained lime (in the form of shell bits) and silica in about the proportion found in Jelemie cullet, and in this sand, the SiO_2 and CaO per-mil differences were respectively 10.93 and 29.02. They assumed that Wadi Natroun in Egypt was the likely source of soda, for which a mean value of 39.77 is reported. Choosing amounts of SiO_2, CaO and Na_2O so as to simulate Jelemie glass they calculated the per-mil difference as 14.55 for the mixture. This number is in excellent agreement with that found in Jelemie cullet, 14.64.

The authors point out the limitations of one-parameter measurements to settle questions of provenience broadly but believe that this particular technique can often be used effectively where specific archaeological questions arise.

DATING

Historical records, stratigraphy, pottery sequences and other tools used by the archaeologist, historian or art historian have provided a chronological framework for many of the studies in their fields. Most of these "records of time" are based upon inferential patterns, and even writings are often beset with ambiguities. The pervasive need for telling time has led to the development of several methods which, in large measure, are independent of the personal judgment which goes into the classical methods of archaeology and art history. Some of these techniques have achieved considerable refinement and have been extensively documented (85-89).

Radiocarbon Dating. Certainly the most widely used of these methods involves the measurement of radiocarbon (^{14}C) in organic residues. One recent issue of Radiocarbon (90) lists 83 laboratories currently making such measurements.

This technique, which was brilliantly conceived and developed initially by Libby (91-94) and his associates, provides ideally a reliable nuclear clock for events taking place up to 60,000 or 70,000 years ago. In actual age determinations, however, there are many complexities the archaeologist or art historian should consider before deciding whether, or to what extent, ^{14}C dating would be useful for a particular problem. That ^{14}C dating has had tremendous impact on archaeology was vividly presented by Renfrew (95) in his popular historical description of its effect on European prehistory. First, however, we will discuss briefly the general concept of radiocarbon dating. The history has already been presented in detail by Libby (96) and Berger (97), the methodology by Ralph (98), the accuracy has been analyzed by Neustupný (99), and the costs and other problems by Barker (100).

Carbon dioxide in the atmosphere contains a nearly steady state concentration of radioactive ^{14}C which is continuously produced by secondary cosmic rays interacting with atmospheric nitrogen. The concentration of ^{14}C is very minute, $\sim 10^{-12}$ of total atmospheric carbon, but it can be measured sensitively by counting the beta particles from ^{14}C radioactive decay. The particular interval in which a living organism assimilated atmospheric CO_2 and then died or became inactive represents the start of the "clock", and the decay of the ^{14}C records the time elapsed. The calculated age should depend only upon the measured proportion of ^{14}C in the carbon of the specimen, and the initial level of ^{14}C as inferred from reference materials (notably tree rings) having reliable dates determined independently. Age calculations made in this way would have the virtue of presenting absolute dates but they are not generally employed because of disagreement over which reference curve is most reliable.

Most published radiocarbon dates are based upon a set of conventions which are known to be arbitrary but, when used, put all dates on a common basis (101). To obtain a real age, these radiocarbon dates must be modified according to the calibration curve considered most acceptable by the individual. The conventions most often employed are the following: Radiocarbon dates are given in years before the present (B.P.) where the "present" is defined as 1950 A.D. The half-life of ^{14}C is taken to be 5568 years although the best value is currently 5730 ± 30 years. The ^{14}C atmospheric concentration in the past is arbitrarily assumed to have been constant and to be equal to 95% of the ^{14}C concentration in an oxalic acid primary standard supplied by the National Bureau of Standards. Wood of a known age is often used a secondary standard as the supply of the oxalic acid standard is about exhausted (102). There are other conventions concerned with fractionation of the carbon isotopes which will be mentioned briefly later.

Uncertainties in an absolute time scale revolve basically about the question of the atmospheric ^{14}C levels in the past. The variations with time have been measured most accurately by radiocarbon dating of tree rings (103,104, 109-111) whose ages have been determined by dendrochronological studies. A living tree such as the bristlecone pine can be measured throughout its ring sequence, and by methods of dendrochronology the range can be extended to still older trees which have long since fallen. Ferguson for example has developed a 7484-year chronology for bristlecone pine (114) and recently (115) extended it to nearly 8200 years.

Calibration curves for different parts of the Northern Hemisphere are thought to be the same (106) although some discrepancies have been reported for Japan (112). There appears to be a small latitude (106,113) effect and a slightly different calibration curve (106) should be used for the Southern Hemisphere. It is anticipated that the present calibration measurements, which go back 7000 radiocarbon years, can be extended to 10,000 (115) or perhaps even 15,000 (116) radiocarbon years.

Figure 2 shows the calibration curve of Suess (103) for the period between 1850 A.D. to 5200 B.C. in the Northern Hemisphere. The accuracy of the curve is given as better than 100 years for the period from the present to 2000 B.C. and better than 200 years from 2000 B.C. to 5200 B.C. Because of the windings or kinks in the curve and the uncertainty in its exact shape there can be considerable uncertainty in the measurement of some single radiocarbon dates. As an example, a radiocarbon date of 4400 ± 100 B.P. covers a range of about 3400-2950 B.C. (A different range of 2950-2500 B.C. given by Suess (103) for the same example may have been a typographical error.) The type of uncertainty can be reduced by more precise measurements, additional measurements on material of different ages but related dendrochronologically or stratigraphically, and by considering the calibration points themselves rather than the curve.

An example of very precise dating was given by Ferguson et al (117) on three timbers from the Thayngen and Burgäschisee-Süd Settlements of Swiss Lake Dwellers. These timbers were part of a well developed "floating" tree-ring chronology; i.e., the ages of the different parts of the timbers were known relative to each other. The radiocarbon ages of samples covering about a 200 year span were measured with an accuracy of about 35 years. By graphically matching the pattern of these radiocarbon ages with that of a comparable number of bristlecone pine samples of known absolute age, the "floating" tree-ring sequence could be dated within a standard deviation of 25 years. Consideration of possible local variations in ^{14}C content of 4 or 5 per mil, added an error of ±30 years for an overall error of ±40 years. Ferguson et al were able to conclude that the middle Thayngen Settlement was constructed in 3700 ± 40 B.C. and the lower one in 3760 ± 40 B.C. Without the calibration data, these dates would have been 800 years too low! Statistical treatment of the same data by Clark and Renfrew (118) gave a value of 3690 ± 40 B.C. for the zero point of the tree ring calibration compared to 3635 ± 40 B.C. for the graphical analysis. (The value of 3670 B.C. for this zero point in the caption of the figure in reference 117 is probably a typographical error (118a).)

A similar type of analysis has been made of two "floating" tree-ring sequences from the Neolithic site of Auvernier (103), where construction ages of 2710 and 2450 B.C. were found for the two settlements (103,119). Statistical analysis (118) of this data gave values up to 170 years older than found by Ferguson et al.

Sometimes stratigraphic information can remove ambiguities of radiocarbon dating occasioned by wiggles in the calibration curve. Vogel (120) discussed three carbon samples from a stratigraphic sequence at Olifantspoort in the Transvaal. Each of the samples would give two dates, in one case separated by almost 200 years. One of the choices for each sample was removed with the aid of the stratigraphy, leaving dates 1850 ± 20, 1750 ± 50 and 1695 ± 20 A.D. for the three levels. Thus, given proper materials, radiocarbon dating in concert with calibration curves can give dates of high accuracy.

Calibration Before 5000 B.C.

Other methods of calibration deriving from varve* counting (121-123) or pollen diagrams (124) go back further in time but are not as precise as tree-ring calibrations. Figure 3 was taken from an article by Tauber (122) and shows the change of the ^{14}C level in the atmosphere as a function of time for the period 4000 to 10,000 years B.C. By studying the relative ^{14}C content of ancient tree-rings of uncertain absolute age, Vogel (124) concluded somewhat differently that the ^{14}C level was nearly constant between 5000 and 6000 B.C., and Stuiver (123) has deduced from varve counting that the ^{14}C level underwent only a small decline at 6000 B.C. followed by another maximum at 8000 B.C. As an example of the difference implied by the Tauber and Stuiver chronologies, a conventional radiocarbon date of 9000 B.P. would correspond to a true date of ∿ 7000 B.C. with the Tauber calibration and ∿ 8000 B.C. with that of Stuiver. Measurements now in progress on wood going back to ∿ 6200 B.C. (115) should help remove this uncertainty.

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*"Varves" are seasonal sedimentary strata deposited during the period when glaciation of the last Ice Age retreated.

Calibration in Modern Times

The rise of industrialization in the 20th century and the consequent dilution of the atmosphere with fossil carbon caused a decrease in the ^{14}C level (125-126) (Suess effect). This trend was reversed by the nuclear bomb explosions. Figure 4 shows the atmospheric ^{14}C level in very modern times as given by Olsson and Klasson (127). A conventional radiocarbon calculation corresponding to the maximum in the curve ($\sim$ 1963 A.D.) would give an error of $\sim$ 5600 years.

The need for calibration measurements in the post-bomb period has also been confirmed by measurement of organic materials. Walton et al (128) measured the ^{14}C level in malt-whisky made from barley in the post-bomb period. With very little ambiguity the exact year of the growth of the barley could be determined. They calculated the mean ^{14}C level during the barley growth periods from data similar to that in Figure 4. Their resulting averages are shown in Figure 5 along with measurements of five malt whiskies. Measurements on carefully preserved seeds of known growth dates also demonstrate the bomb related enhancements (129).

Dating Materials

Certainly one of the most crucial needs for accurate radiocarbon dating is suitable materials (129a). Nesputný (99) considers the uncertainties in the age of wood at the time of use the greatest obstacle for better radiocarbon dating. For so-called class A (99) materials such as grains, grasses, cloth, twigs and other short-lived substances which are used within a few years after growth, there is no need for such a "growth" correction or allowance. Michael and Ralph (130) compiled data on 18 measurements of short-lived Egyptian material from 1200-3200 B.C. From their graph the average deviation from the historical values of the radiocarbon dates after correction from a table of calibration factors was 100 years. This is excellent agreement as the average experimental error was ∿ 80 years and the average historical error was ∿ 75 years. The use of a table, however, may cause some complications as, of necessity, it averages the kinks in the calibration curve in the various time ranges and makes the evaluation of errors difficult (131).

Berger (132) and also Edwards (133) have reported on very precise measurements made on Egyptian samples of well-known historical ages going back to ∿ 3100 B.C. In many cases both laboratories made measurements on the same samples. For 16 short-lived materials (class A), the average deviation between the results of these two independent laboratories is 130 years, i.e. 65 years from the average values. The deviation of these average values from the points on the Suess calibration curve shown in Figure 2 is ∿ 50 years and about evenly distributed on both sides of the curve. This is excellent agreement and well within the experimental errors. Berger et al (134) made measurements on six medieval parchments of known historical dates. The calibrated ^{14}C dates along with errors overlapped the historical dates satisfactorily, but because of the windings of the calibration curve there were two or sometimes three calibrated dates corresponding to a single radiocarbon measurement.

For class B materials (99) such as charcoal from hearth or ovens, the ages of the materials when burned could cover several decades. Vogel (135) found that his radiocarbon Egyptian dates (136) when corrected by the Suess curve were <u>on the average</u> about 50 years older than true dates and implied the difference might be due to this effect.

Among the radiocarbon dates reported by Berger (132) and by Edwards (133) for the Egyptian samples of known age were eight from wood or charcoal which both laboratories had run. The average deviation of their dates from each other is 100 years, i.e. 50 years from the average values. The deviation of the average values from the Suess calibration points is 125 years, and in seven out of the eight cases the corrected radiocarbon half-lives are too old. This behavior contrasts with the measurements on the short-lived material discussed earlier by the same laboratories and may indicate the wood or charcoal was on the average ∿ 100 years old when used.

It is also possible in areas where wood is scarce that old wood may have been re-used many times and hence cause errors of several centuries (99).

With long-lived materials (group C (99)) such as wooden beams from large buildings, errors of hundred of years can be introduced if it is not known from which part of the tree a particular sample came. On the other hand if the position of the wood sample can be established in the chronology of the tree from which it came, then the dating of different parts of the beam can result in unambiguous true dates of the wood. These dates of course reflect when the tree was felled which was not necessarily when it was used in a given construction.

Berger (97) has obtained excellent agreement (within 30 years) on a number of comparisons with known historical ages of construction timbers. Horn (137) presented a treatise on radiocarbon dating from an art historian's view, which explained in detail the radiocarbon dating of a number of buildings for which the traditional methods of the art historian were not adequate.

Fletcher (138), in his discussion of timber-framed medieval Cruck cottages, reported that an ambiguous radiocarbon date on a Harwell Church tie beam was resolved by another measurement on a part of the beam some 60 annual rings from the first.

Bones offer considerable problems in dating because of the exchange of their mineral carbonate with the environment. Bones which are extremely well-charred shortly after death are considered to give reliable dates (98) but Tamers and Pearson (139) have disputed this. Measurements on the bone protein, collagen (139-141), give more reliable dates than the carbonate fractions but these often are also too recent (142).

Many other materials containing carbon have been dated such as shells (141) and soil layers (142). Tamers (142), for example, dated a paleo-indian animal kill site as 13000 ± 2000 year old from radiocarbon analysis of soil layers. This may have in addition a calibration error of the order of 1000 years for reasons discussed under varve counting.

Some Problems in ^{14}C Dating

There is a need for interlaboratory comparisons of ^{14}C data to justify precise dates (99).. Säve-Söderbergh and Olsson (143) compared the ^{14}C obtained by different laboratories for the same sample and for the same types of sample. If solid-carbon counting is excluded (because of difficulties in counting technique) the different laboratories obtained the same date for measurements on the same sample. There was some scatter, but this was consistent with the listed standard deviations. On the other hand, dates of samples of similar material sometimes scattered much more than expected from the listed measuring errors. This would tend to indicate that the discrepancy might be in the processing or choice of wood rather than in the actual measurements of the different laboratories. As mentioned earlier, the results of Berger (132) and of Edwards (133) agree very well, almost within their counting errors.

Carbon isotopes can be fractionated by growth processes and by laboratory treatment, i.e., the ratio of ^{14}C to ^{13}C to ^{12}C in plants may be different from the atmosphere. The effect on ^{14}C is estimated to be twice the effect on ^{13}C, which can be measured by mass spectrometry. Berger (97) and Willis (144) among others have discussed the measurements and calculation of the fractionation effect. Errors of 100 or possible 200 years can be made on wood samples if this effect is not measured. With short-lived materials the errors can be even larger, up to 250 years.

The physical and chemical pretreatment of the various types of samples prior to measurement and the necessary quantities of starting material has been discussed by Ralph (98). Acid and base treatments of wood are common (106) to remove soluble carbonates and humic acids. More stringent chemical and physical treatments are needed for other types of material such as bone (140).

Thermoluminescence. Besides radiocarbon measurements the most prominent of the nuclear-related dating techniques involves measurement of accumulated thermoluminescent energy. The primary advantage of this technique is that the measurements can be made on pottery, a material associated with the vast majority of archaeological problems and upon which so many of the conclusions of archaeologists rest.

These measurements likewise utilize a nuclear clock which in this case comes from the natural radioactive decay of the uranium and thorium families and ^{40}K. The radiation from these decays is expended in part in the pottery fabric, and a small part of the energy is stored as trapped charge-carriers in the crystal lattices of the mineral inclusions. Heating causes the energy to be released as photons. This annealing process started the clock when the clay was originally fired and is the means for releasing the accumulated energy at the time of measurement.

The intensity of these photons or thermoluminescence (TL) is measured as a function of temperature, and peaks of TL are observed at different temperatures corresponding to different depths of the charge-carrier traps. Although some of the low energy traps de-excite at room temperature and hence are not suitable for storing energy over long periods of time, others do not de-excite until temperatures of more than 300°C are reached. These higher energy traps have lifetimes in excess of 10^5 years at ordinary temperatures and hence will not decay significantly over a period of a few thousand years.

There are two different methods (145) for making accurate absolute measurements on pottery or other clay materials which were developed at the Research Laboratory for Archaeology at Oxford University. These techniques involve either the use of only the fine grains (146-148) from pottery or only the larger quartz inclusions (149,150). Zimmerman (146) measured the TL dates of fourteen sherds from five archaeological contexts of known dates. Only fine grains of pottery were used, $\sim$ 1-8 microns in size, which emphasized the TL due to the internal alpha radioactivity over radiations from the surrounding soil and cosmic rays. Many corrections and calibrations were made to determine the radiation dose rate contributed by the samples and the environment. Examples of these are corrections for the loss of radon from the sherds, absorption of radiation by water in the sherd, calibration of the

TL response as a function of the alpha particle energy, and calibration of the response to beta particles. In addition it was found necessary to make substantial and variable corrections for the non-linearity of the TL response with respect to the radiation dose. These corrections varied from -15 to +45% of the TL age. The average deviation of the fourteen TL dates from the known archaeological dates was 9.5%. If the TL dates within a given context were averaged, the average deviation was only 6%.

If this accuracy can be improved, it should be of use in the calibration of ^{14}C dating. In this respect it is interesting to consider the TL dating of three upper paleolithic lumps of fired clay (151) found in Dolní-Věstonice, Czechoslovakia. With the techniques just described, Zimmerman and Huxtable found dates of 32,500 , 35,300, and 30,500 B.P. with an average value of 33,000 B.P. and a probable error of 3000 years. ^{14}C conventional dates from the same context were 28,300 ± 300 and 29,050 ± 200 B.P. If TL work can be done with a standard deviation of about 5%, in this region, it will begin to give useful calibrations for the more precise ^{14}C measurements.

While the use of fine grains in TL dating does render the environmental dose rate less important, the large surface to volume ratio emphasizes spurious

TL surface effects. In the inclusion technique (149) grains of ∿ 100 microns in size are treated with hydrofluoric acid which leaves intact only the quartz grains. This acid treatment also removes the outer layer of the quartz which is the region that contains clay impurities and radiation damage due to alpha particles. The remainder of the grains have only been damaged by beta and gamma-ray activity and are insensitive to the alpha dose. Since the material is pure quartz the TL peaks are well defined, one at 375°C which is suitable for accurate dating and one at 325°C which is not. The environmental dose rate was determined from a natural fluorite phosphor which was left in the same soil environment as the sherds for a year. This phosphor has a sensitivity 10^4 times greater than quartz. The beta dose from the pottery was measured with crystals of the flourite approximately the same size as the quartz inclusions.

In addition careful measurements were made of the non-linearity of the TL response to artificial radiation. As with the fine-grain technique these corrections were large and variable, and ranged from 0 to 55%. For 22 sherds the average deviation of the TL from the known archaeological ages was only 5.4%.

Aitken et al (145) have recommended that whenever possible both fine-grain and inclusion techniques should be used to serve as independent checks on the TL method. These authors also pointed out that the use of both types of measurements on material from a sherd can eliminate the environmental radiation as a parameter.

This procedure was used by Fleming et al (152) in an investigation of Etruscan wall-paintings on terracotta in which the environment of the burial chambers was uncertain. For two samples of known excavation context, the TL dates were 485 ± 260 B.C. and 570 ± 260 B.C. in good agreement with the expected age. Five other terracotta samples from different paintings, however, had maximum ages of 24 to 530 years from the fine-grain technique. Use of the inclusion technique reduced the range of these maxima to 12 to 188 years, and the authors concluded these paintings were of modern origin.

The greatest use of TL dating has indeed been in the testing of the authenticity of artifacts. For this type of measurement high precision is not essential and less experimental effort is necessary. Ralph and Han (153-156) measure only the amount of alpha radioactivity in a sample, the natural TL and the TL induced by a known artificial dose of radiation. The proportionality constant relating these quantities and the sample age is determined by similar measurements on artifacts of known age. This technique has worked satisfactorily for authenticating a number of objects (153). A cup from Hacilar, Turkey gave a TL date of 5100 B.C. in good agreement with the known age of the ancient site, while on the other hand several supposedly Etruscan statuettes turned out to be ∿ 100 years old.

Aitken, Moorey and Ucko (157) made authenticity tests on 66 sherds exhibiting the style of pottery from an ancient site near Hacilar. Although the authors found only 18 of these objects which could be classed definitely as old from the TL measurements, there was some question as to whether an ancient piece might have been refired recently and hence lost its TL. Aitken et al made use of a recently observed effect (158,159) pertaining to the quartz-inclusion technique to help resolve this question.

There is a peak in the TL of quartz at 110°C which de-excites in a few hours at room temperature. Nevertheless, even though the TL has decayed the quartz retains a memory of the total amount of radiation that has been trapped at this energy. This memory is evidenced by an increase in the TL output of the 110°C peak for a given artificial dose rate when the sample has been heated to 500°C before the dose was applied. The physics of this effect has been discussed by Aitken, Thompson and Fleming (160). With this technique Aitken et al (157) were able to show that 27 of the 48 artifacts with low TL response could not be objects seven millenia old which had lost their TL through refiring. Seventeen of the objects could not be measured in this way presumably because there was little or no quartz present and four of the objects had additional complications. However these were shown by other measurements to be of doubtful antiquity. The authors concluded from all of their measurements that only 18 of the 66 objects were genuinely old.

Other authenticity studies whose contents are indicated by their titles are: The thermoluminescent authenticity test of some "Six Dynasties'" figures (161), Thermoluminescent authenticity tesing of a Pontic amphora (162), and Thermoluminescent dating of a terracotta of the Nok Culture, Nigeria (163).

Some of the other recent TL dating measurements have been made on Japanese (164) and Danish (165,166) ceramics. It is interesting to note that although Mejdahl (165) used a rather low energy TL peak at ∿ 270°C for his measurements, he was able to conclude by comparison with known archaeological ages that fading of this TL response over the life of pottery was not serious.

Winter (167) in a descriptive review on TL has tabulated and classified all of the work relative to TL dating of pottery up to 1970. Each work is succinctly summarized with respect to number of specimens, archaeological attribution, and notations relevant to techniques and results.

Fission Track Dating. The technique for dating minerals and some other materials by exposing to view the tracks left by fragments of spontaneous uranium fission has been reviewed in this series in 1965 (168). At that time, a single publication had appeared pertaining to the dating of man-made glass (169).

The method is not inherently difficult but its accuracy does depend upon the reliability of the half life for spontaneous fission of ^{238}U, uniform control of the etching process for bringing out the tracks, and the uranium content of the glass (168,170). Man-made glasses are not generally susceptible to dating because the uranium content is too low in proportion to age. At a typical level of 1 ppm, the glass would have to be 10^5 years old in order to provide 100 tracks in a scanning surface of reasonable size.

It was only at about the year 1830 that uranium was deliberately added to glass to give it a greenish yellow color. The first publication (169) on on five such glass objects showed very good agreement between fission track dating and the ages know from other evidence. A candlestick containing 0.61% uranium provided the date 1840 ± 20, whereas the date specified by stylistic criteria was 1850-1860. A glass known to have been poured in December 1943, gave a date 1945 ± 4.

Another study (170) dated four Early Victorian glasses containing 0.16 - 0.25% uranium and also gives a careful evaluation of etching techniques. The authors calculated their results on the basis of two "best values" for the spontaneous fission half life, 1.00 (±0.03) × 10^{17} years and 8.5 (±0.8) × 10^{16} years, and found dates 1789 ± 19 and 1816 ± 22 for the oldest object. Giving credence to the evidence that uranium glasses were not made before 1830, they suggested that the shorter half life is more reliable. It should be noted that if an object were subjected to neutrons at any time, the apparent age would be older than its true age. The cosmic-ray induced fission appears to be negligibly small.

Attention is also called to archaeologically important applications on uranium-poor materials which are very old. Fossil hominoid man remains in Olduvai Gorge were found embedded in volcanic tuff containing datable pumice (171). The result was an age 2.03 ± 0.28 million years, which conforms well with the age given by another method. Dating can also be accomplished on more recent materials with low uranium content if one successively bares and etches sufficient surface (172,173). Some glaze containing 3 ppm uranium from a Japanese bowl gave an age of 520 ± 110 years based on 25 tracks found in scanning 71 cm^2 of surface. More aged materials were dated with equal or better accuracy and demonstrate the diversity of available archaeological materials (172,173). Included were slags, zircons segregated from baked earth, pottery, and tiles; obsidians which showed clear evidence of having been subjected to high temperatures from destruction of a building by fire.

Attempts are being made to overcome the lack of sensitivity of fission-track dating by observing imprints left by the α-decay process (174,175). The trajectory of the alpha particle itself has not yet been made visible but the heavy-ion recoil does provide a high enough density of ionization. The "tracks" appear as shallow pits after etching and are therefore not as easy to identify as fission tracks, and there are other complications because one is not dealing with a single emitter. It has also been found that visible pits can be developed only when several alpha decays have taken place at one site, that is, where the immediate parent of a short-lived decay sequence has undergone decay. Finally, only certain host materials have so far yielded visible pits and glass is not among these. Despite the difficulties and limitations so far encountered, the method is worthy of further effort because it is intrinsically more sensitive than fission-track dating by a factor of several thousand.

Other Dating Techniques. Although there are a number of other scientific methods of dating archaeological artifacts, our descriptions have perforce been limited by the scope of this review to nuclear-related techniques, and by space limitations to only those methods which have received the widest use in archaeological studies. Nevertheless, it should be worthwhile to mention, albeit only in the briefest way for a better perspective, some of the other methods.

Archaeomagnetic dating (176), which is not nuclear-related, is concerned with the magnitude and direction of the earth's magnetic field at the time a clay object was fired. The technique can be used on an object such as a kiln whose directional orientation has not been disturbed. It should obtain more prominence as better calibrations are made with samples of known age.

A number of dating techniques of primary interest to the geologist have application to archaeology in the time periods of 10^5 and more years. Some of these involve argon growth from potassium (177), helium growth from uranium (178), thermally-stimulated-current measurements (179), and electron-spin-resonance measurements (180).

AUTHENTICITY OF OIL PAINTINGS

Neutron activation analysis has been applied to the study of paint pigments with some success in establishing age, provenience and authenticity of an oil painting.

White-lead (2 $PbCO_3 \cdot Pb(OH)_2$) has been used extensively since the Middle Ages as a ground pigment mixed with an organic binder, usually oil, to prime a canvas before painting.

The techniques of lead purification have changed during the past centuries and analysis of the impurities has been used to determine the approximate date of manufacture at a particular factory. Caution must be taken to obtain a sample of the white lead uncontaminated by traces of other pigments which may be present in the painting. Houtman and Turkstra (181) have examined white lead from known Dutch and Flemish paintings dating from 1510 to 1909, pigment factories from about 1820 to 1963 and paint factories in 1960. One mgm samples were irradiated for 4 hours with 10^{11} neuts/$cm^2 \cdot$sec along with Cu, Ba and Mn standards (half lives less than 13 hr.), and similar samples were irradiated for 11 days at a higher flux with Sb, Ag, Hg, Zn, Co and Cr standards (half lives greater than 2 days). The inherently poor energy resolution of 3" × 3" NaI detectors necessitated chemical separation of the activated samples before counting. The lead concentration was determined spectrophotometrically. Their results are summarized in Table 5. They observed a significant drop in the amount of Ag, Cu, Hg and Mn in white lead manufactured after 1850 whereas the Cr content decreased after 1650 and the Zn and insoluble Sb increased sharply about 1940.

Lux and Braunstein (182) and Lux et al (183), in collaboration with Kuhn (184) using a similar procedure analyzed the white lead from 16th and 17th Century Dutch and 16th Century Venetian paintings and found that the trace element compositions were different in the two regions.

Bearing in mind the variation seen in trace element compositions according to region and time, proper authentication would require compiling a library of analyses of carefully documented paintings with which to compare statistically the painting in question. Hopefully the use of large germanium detectors can eliminate the laborious chemical separation steps. Then, in addition, if a white-lead standard with impurities of known chemical composition is irradiated at the same time and counted in the same way as the samples in question, most systematic errors in the measurement can be eliminated. Also eliminating the chemical separation would allow the same samples to be used in both the short and long bombardments.

Another technique useful for studying the age (18th and 20th Century) of white lead or other lead-containing substances has been developed by Keisch et al. (185) and Keisch (186). This method takes advantage of the radioactive secular equilibrium of ^{210}Pb and ^{226}Ra present in lead bearing ores. During refinement the ^{226}Ra is at least partially removed leaving the ^{210}Pb present to decay with its 22 yr. half life. If the original separation was not complete the ^{210}Pb will again reach equilibrium but with the lesser amount of ^{226}Ra left in the lead. By careful chemical separation and counting of the ^{210}Po, (the 138 day daughter of ^{210}Pb), and the ^{226}Ra, "old lead" can be distinguished from recently refined lead.

Figure 6 is Keisch's dating curve. The solid line is calculated assuming a separation factor of 100. The separation factor is the ratio of the initial ^{210}Po to ^{226}Ra. The dashed and dotted lines represent the limits on the ordinate for probabilities corresponding to one and two standard deviations respectively. One finds that for samples somewhat older than 80 years the actual data points are lower than the calculated values because of incomplete separation of the Ra. The errors of measurement increase rapidly as $\left(1 - \frac{Ra}{Po}\right)$ approaches zero, thus giving only a lower limit to the age for the older samples.

Conventional X-radiography is a non-destructive technique used for studying some of the internal structure of paintings. The X-radiograph will show the density and distribution of the white lead ground pigment and other pigments containing high atomic number elements present in the painting although in some cases they may obscure each other. In general, such pigments are made from metal oxides, sulfates, chromates or sulfides. The pigment burnt umber, for example, contains iron oxide, manganese dioxide, and clay; emerald green contains both copper and arsenic; and vermillion is mercuric sulfide. In contrast, the lake pigments which are obtained by precipitating aluminum hydroxide in the presence of an organic dye, do not absorb x-rays sufficiently to be visible.

In an effort to study in more detail the internal structure of paintings and the composition of pigments, Sayre and Lechtman (187,188) and Lechtman (189) have developed the technique of neutron activation autoradiography. This non-destructive technique can reveal the development of the painting, elements of the artist's style, the overpainting of areas on the canvas and the pigments common to the artist's palette and allow observation of some low atomic number elements obscured in X-radiography.

In this method the entire painting is irradiated for approximately 20 minutes in a thermal neutron flux of 3×10^9 neutrons/$\text{cm}^2\cdot$sec. Organic materials such as canvas, support, paint binder, varnish, and white lead are not strongly activated. The activated atoms of the elements in the pigments have characteristic half lives, beta-energy distributions, and gamma rays. Following irradiation the painting is placed in contact with x-ray film which is sensitive to the beta particles emitted by the activated atoms. Subsequent autoradiographs reveal an ever changing picture relating to the dominant radioactive species remaining.

This sequence of films allows a partial identification of the elements by their half life. Separation of two elements with similar half lives but different beta particle energies can be obtained by using an appropriate absorber between the film and the painting. Exposure times approximately equal to the time after irradiation are necessary for a satisfactory autoradiograph and longer exposures are needed if an absorber is used. If further discrimination between elements is necessary, individual portions of the painting can be spot-checked by gamma-ray analysis with germanium detectors.

When paintings are irradiated under conditions which exclude most fast neutrons and gamma-rays, they are subjected to about 200 rads with an additional 75 rads or so produced subsequently by the radioactive decay. This is a considerably higher dosage than the 1-20 rads routinely used for x-raying paintings. However, a careful study of the effects of radiation on paintings with respect to color stability, brittleness, and solubility of paints in various solvents showed no significant changes even at 6000 rads (189).

Cotter and Sayre (190) have used this technique in authenticating paintings attributed to Ralph Blakelock. They were able to establish criteria for the characterization and identification of Blakelock's work. The autoradiographs revealed that two of the six paintings studied had partial signatures which had been overpainted with Blakelock's signature. These two paintings also did not show the characteristic style of the other four and one contained pigments not seen in the others. A restored painting could contain pigments other than those present in the original but it is unlikely the restorer would alter the signature.

Although none of these techniques alone is necessarily conclusive in authenticating a painting, when several of them appropriate to a particular problem agree, it inspires confidence.

ADDENDUM

A number of reports have come to our attention too late to be incorporated into the review. One of these is an interesting study of the trace elements in faience beads by Aspinall and co-workers (191). Another, by Aspinall and Feather (192), was concerned with the mining and distribution of pre-historic flint in England and the Continent. Another paper on flint using neutron activation was that of deBruin and co-workers (193) which dealt with mines in the Netherlands, Denmark, and France. Cesareo and co-workers (194) showed the utility of a mobile x-ray fluorescence apparatus (radioactive source and proportional-counter detector) in analyzing paintings and enamel work which had to be examined *in situ*. A study by Poole and Finch (195) employed x-ray fluorescence analysis to determine the provenience of post-medieval pottery. Two papers (Schweizer and Friedman (196); Oddy (197)) compared analytical results on coins obtained by different techniques. Sampson and co-workers (198) used thermoluminescence dating of Colombian pottery to choose between conflicting dates which had been obtained by the radiocarbon method. Another paper on thermoluminescence (Göksu and Fremlin (199)) dealt with methodology.

Some topics which could well fall within the framework of this review have been omitted for one reason or another. As an example, Mössbauer spectroscopy studies pertaining to the iron in pottery will likely provide useful archaeological information but the results published so far may best be described as "exploratory" (200,201).

ACKNOWLEDGMENT

We regret to acknowledge that we have, no doubt, missed some pertinent publications. Part of this deficiency can be attributed to our bewilderment over the practices and modes of publishing in the realm of archaeology. For items we should have found, we have no such plausible explanation. We are greatly indebted to Dr. E. V. Sayre for placing at our disposal parts of the bibliography he keeps on subjects under review. Without his graciously tendered assistance, we would have missed more.

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Table 1. Two groups of pottery from Ballas in Upper Egypt*

	Mn	Lu	La	Fe(%)	Th
BAL 1	1151±18	.502±.016	32.86±.37	6.51±.06	6.80±.06
BAL 2	1269±19	.513±.016	31.33±.34	6.12±.06	6.65±.06
BAL 3	1209±18	.555±.016	33.28±.36	6.96±.06	8.20±.06
BAL 6	1178±18	.525±.017	30.90±.36	6.60±.06	6.49±.07
BAL 7	1250±18	.534±.017	32.96±.36	6.81±.06	6.91±.06
BAL 8	1228±17	.521±.016	33.52±.36	6.95±.06	7.60±.07
BAL 9	1059±15	.489±.016	31.54±.34	6.73±.06	6.79±.07
BAL 10	1154±16	.511±.016	35.66±.36	6.34±.06	7.72±.07
Mean	(1187±77)	(.519±.022)	(32.76±1.67)	(6.63±.35)	(7.15±.77)
BAL 12	350±7	.362±.014	37.69±.37	4.59±.04	9.90±.05
BAL 17	365±5	.334±.013	35.33±.33	4.41±.04	8.86±.06
BAL 18	387±5	.334±.013	38.32±.36	4.18±.04	10.08±.06
BAL 20	410±5	.325±.013	38.95±.37	4.55±.04	9.70±.06
BAL 21	372±5	.389±.014	40.27±.39	4.62±.04	10.18±.05
BAL 22	335±4	.378±.013	40.61±.39	4.58±.04	10.04±.06
BAL 24	454±7	.379±.014	37.48±.36	4.71±.04	9.32±.07
Mean	(382±45)	(.357±.033)	(38.38±1.99)	(4.52±.19)	(9.73±.55)

*Data abstracted from ref. 10.

Table 2. Provenience of Tel Ashdod Mycenaean IIIC1 Wares

	(4) ASH(Myc)	(5) ASH(Phil)	(1) ENK(Myc)	(2) PPAP(Myc)	(3) KIT(Myc)
Fe(%)	3.73±0.26	3.99±0.06	4.92±0.15	3.90±0.22	4.14±0.33
La	29.8±0.6	29.3±1.2	24.5±0.9	28.1±1.8	18.3±0.7
Lu	0.473±0.023	0.427±0.032	0.337±0.018	0.303±0.023	0.282±0.030
Ni	45±15	59±8	272±39	88±15	156±29
Hf	14.48±1.23	13.44±1.94	3.11±0.18	3.17±0.19	2.67±0.26

Unless indicated by "%", values are in units of ppm.

Dispersion limits are standard deviations for the group mean values.

The pottery groups indicated by ENK, PPAP, and KIT were excavated of Enkomi, Palaepophos and Kition in Cyprus; ASH refers to Tel Ashdod in Israel. The symbol "Myc" refers to Mycenaean IIIC1 wares, and "Phil" to Philistine ware.

Table 3. Comparison of X-ray Fluorescence and Neutron Activation Analysis*

	X-ray Fluorescence	Neutron Activation
Ti	.76% ± .02	.78% ± .03
Cr	114 ppm ± 6	115 ppm ± 4
Mn	47 ppm ± 5	40.9 ppm ± 0.5
Fe	1.05% ± .01	1.017% ± .012
Ni	301 ppm ± 6	279 ppm ± 20
Cu	55 ppm ± 2	60 ppm ± 8
Zn	60 ppm ± 2	59 ppm ± 8
Ga	40 ppm ± 2	44 ppm ± 5
As	29 ppm ± 2	30.8 ppm ± 2.2
Rb	58 ppm ± 2	70.0 ppm ± 6.3
Sr	123 ppm ± 3	145 ppm ± 22
Pb	31 ppm ± 2	——

*Data taken from ref. 27.

Table 4. Neutron activation analysis of Napa County obsidian*

	Bowman et al(32) (19 samples)	Griffin et al(33) (3 samples)
Th	17.93 ± 0.23	
U	6.85 ± 0.06	
Na(%)	3.37 ± 0.05	3.7 ± 0.4
Sc	2.86 ± 0.04	3.4 ± 0.4
Mn	149 ± 3	173 ± 22
Cs	15.5 ± 0.3	
La	31.3 ± 0.6	57 ± 3
Fe(%)	0.92 ± 0.02	1.0 ± 0.2
Al(%)	6.4 ± 0.2	
Hf	7.57 ± 0.25	
Ba	432 ± 14	
Rb	202 ± 6	143 ± 23
Lu	0.622 ± 0.015	
Ta	0.93 ± 0.06	
Cr	6.7 ± 1.0	

*Numbers shown are in ppm unless designated "%". Each entry is the mean value for the specimens and the standard deviation of the group.

Table 5. Impurities in Dutch White Lead

Period	Ag (ppm)	Cu (ppm)	Hg (ppm)	Mn (ppm)	Cr (ppm)	Zn (ppm)	Sb insol. (ppm)
1500-1650	18-27	150-220	3-7	70-110	225-500	0-60	<0.01
1650-1850	18-27	150-220	3-7	70-110	0-35	0-60	<0.01
1850-1940	0-5	0-60	0-1	0-12	0-35	0-60	<0.01
1940	0-5	0-60	0-1	0-12	0-35	600-6000	30-110

FIGURE CAPTIONS

Fig. 1. Variation diagram of obsidian from Borax Lake, California and data on several early artifacts.

Fig. 2. Caption: Conventional radiocarbon ages ($T_{1/2}$ ^{14}C = 5568 years, 0 = 1950) of tree-ring dated wood plotted against its tree-ring date for the period 5200 B.C. to the present. This figure was taken from ref. 103 "Bristlecone-pine Calibration of the Radiocarbon Time-Scale 5200 B.C. to the Present" by H. E. Suess.

Fig. 3. Deviations between corrected varve years and conventional and corrected ^{14}C years; and calculated atmospheric ^{14}C activity in per mil deviations from the atmospheric ^{14}C level in the 19th century after the birth of Christ (Δ ^{14}C values). The corrected "^{14}C years" curve is the same data with a ^{14}C half life of 5730 years. This figure was taken from ref. 122 "The Scandinavian varve chronology and ^{14}C dating" by H. Tauber.

Fig. 4. Per mil ^{14}C excess over natural concentration (Δ) at Abisko and on Kapp Linné. Points given with statistical errors are determined at the Uppsala ^{14}C laboratory. Points given without statistical errors are determined

at Heidelberg ^{14}C laboratory but collected through Uppsala Laboratory. Values from 1965 corresponding to contamination at Abisko are not included. This figure was taken from ref. 127, "Uppsala Radiocarbon Measurements X" by I. Olsson and M. Klasson.

Fig. 5. Correlation between ^{14}C concentrations in whisky and atmosphere. This figure was taken from ref. 128, "Carbon-14 Concentrations in Environmental Materials and their Temporal Fluctuations" by Walton, et al.

Fig. 6. A "dating curve" for white lead. Circles indicate values of [1 - Ra/Po] for samples of known age. Such values may be used to discern old and modern white lead and might be used to discern white lead of the 20th century, 19th century, and 18th century or earlier. SF, "Separation Factor". This figure is reproduced from Keisch's article: Science 160, 413-15 (1968). Copyright 1968, American Association for the Advancement of Science.

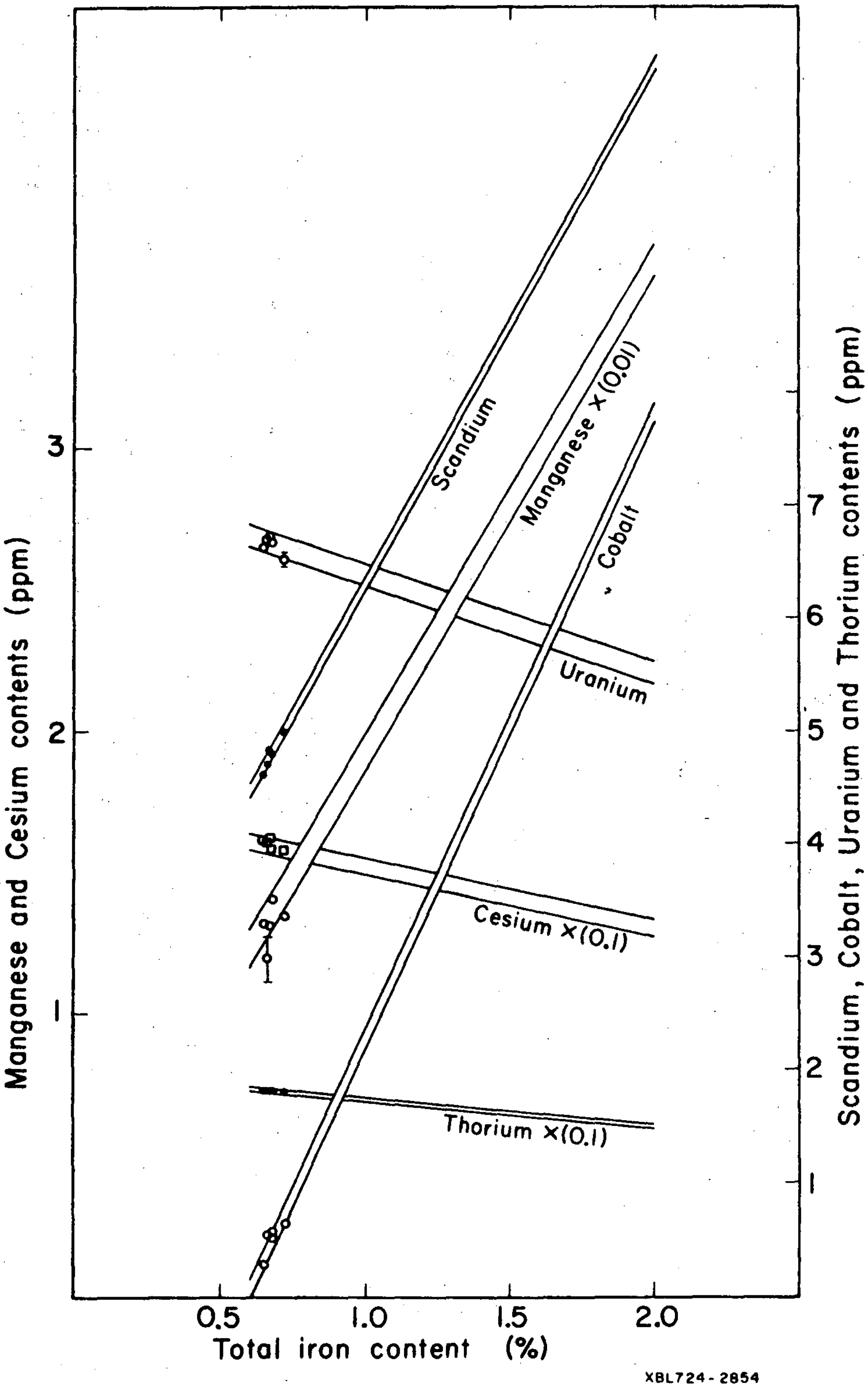
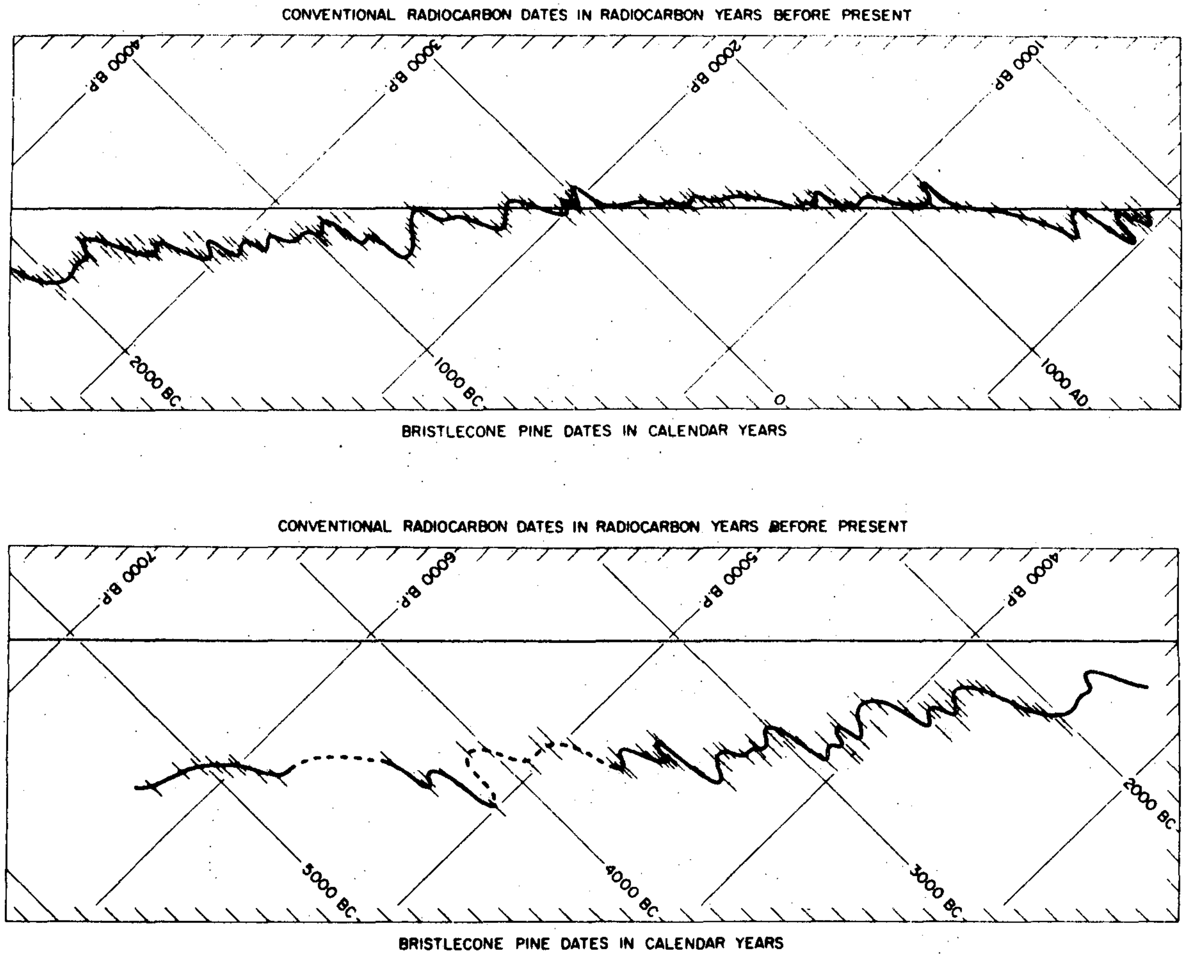

Manganese and Cesium contents (ppm)
Scandium, Cobalt, Uranium and Thorium contents (ppm)
Total iron content (%)
0.5
1.0
1.5
2.0
1
2
3
1
2
3
4
5
6
7
Scandium
Manganese ×(0.01)
Cobalt
Uranium
Cesium ×(0.1)
Thorium ×(0.1)
XBL724-2854

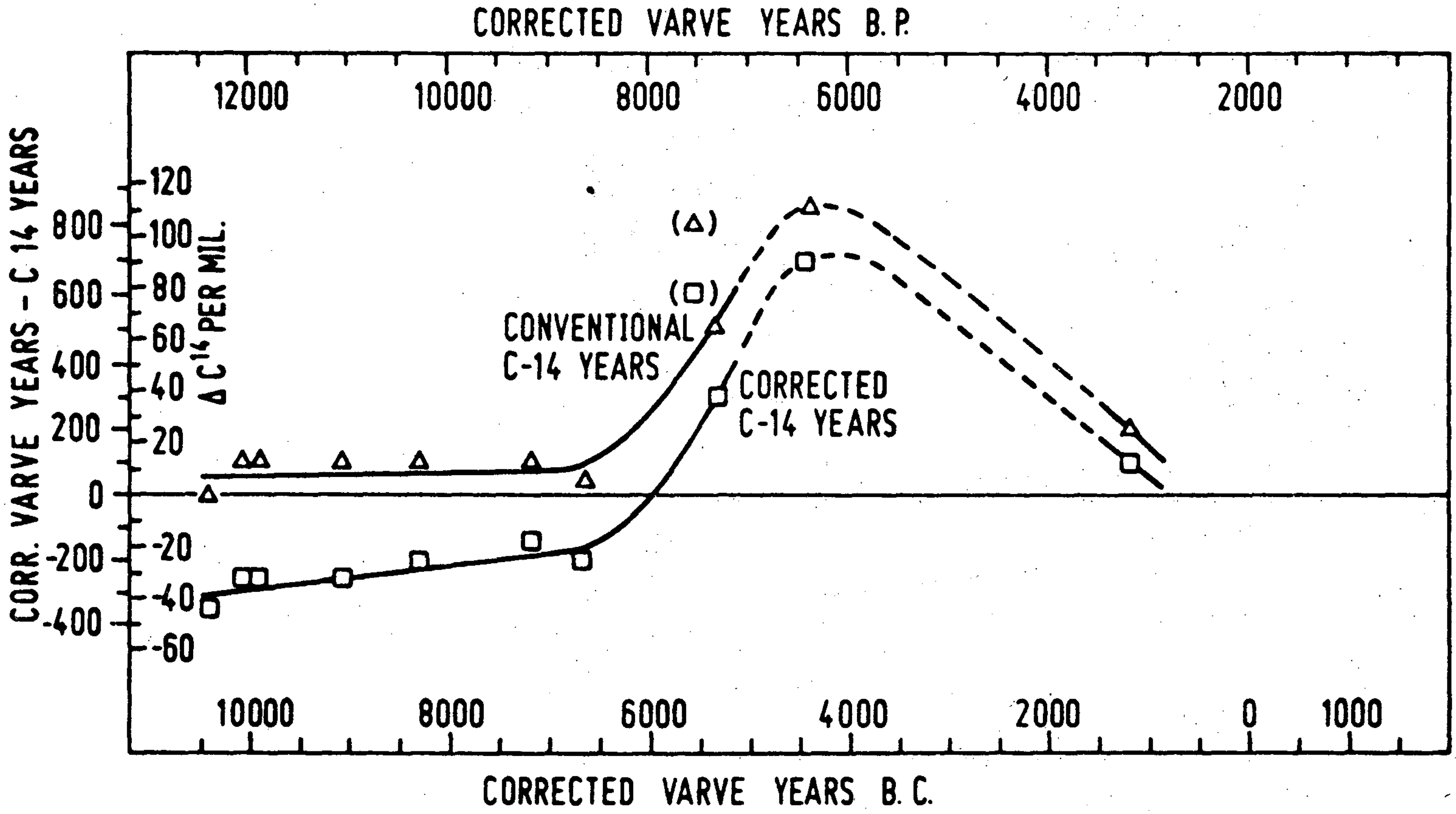
Fig. 1



XBL 725-858

Fig. 2

Fig. 3



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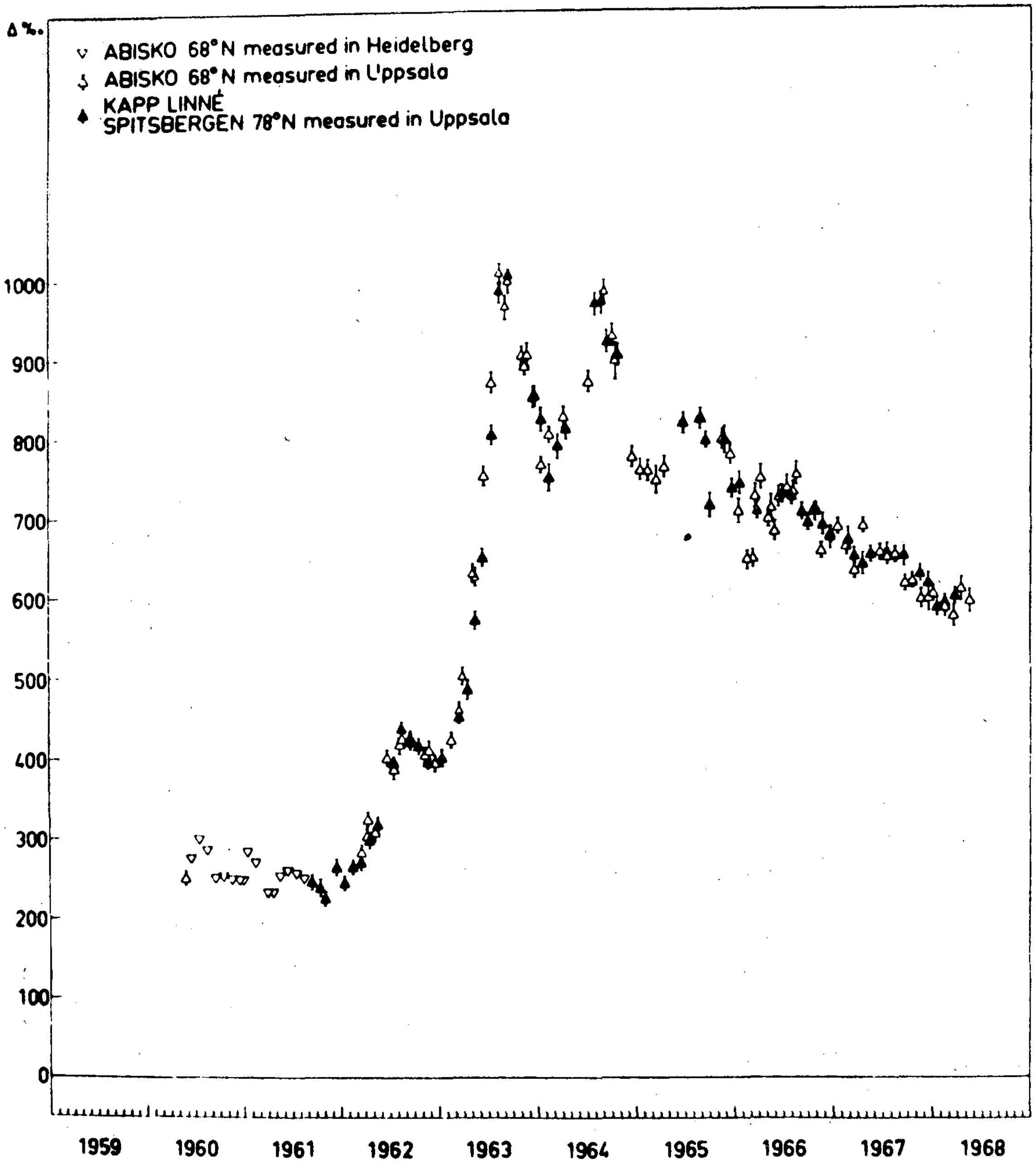
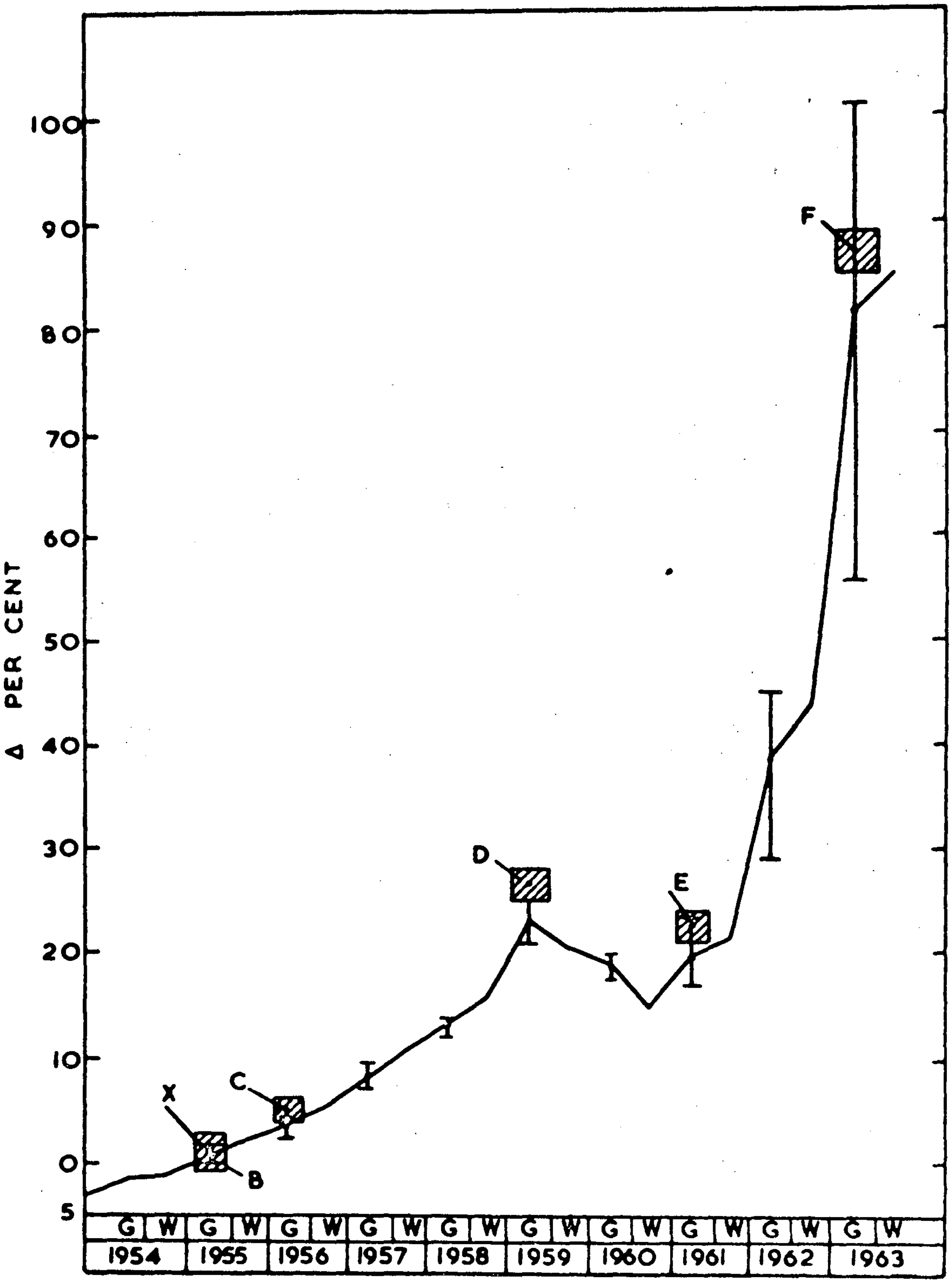


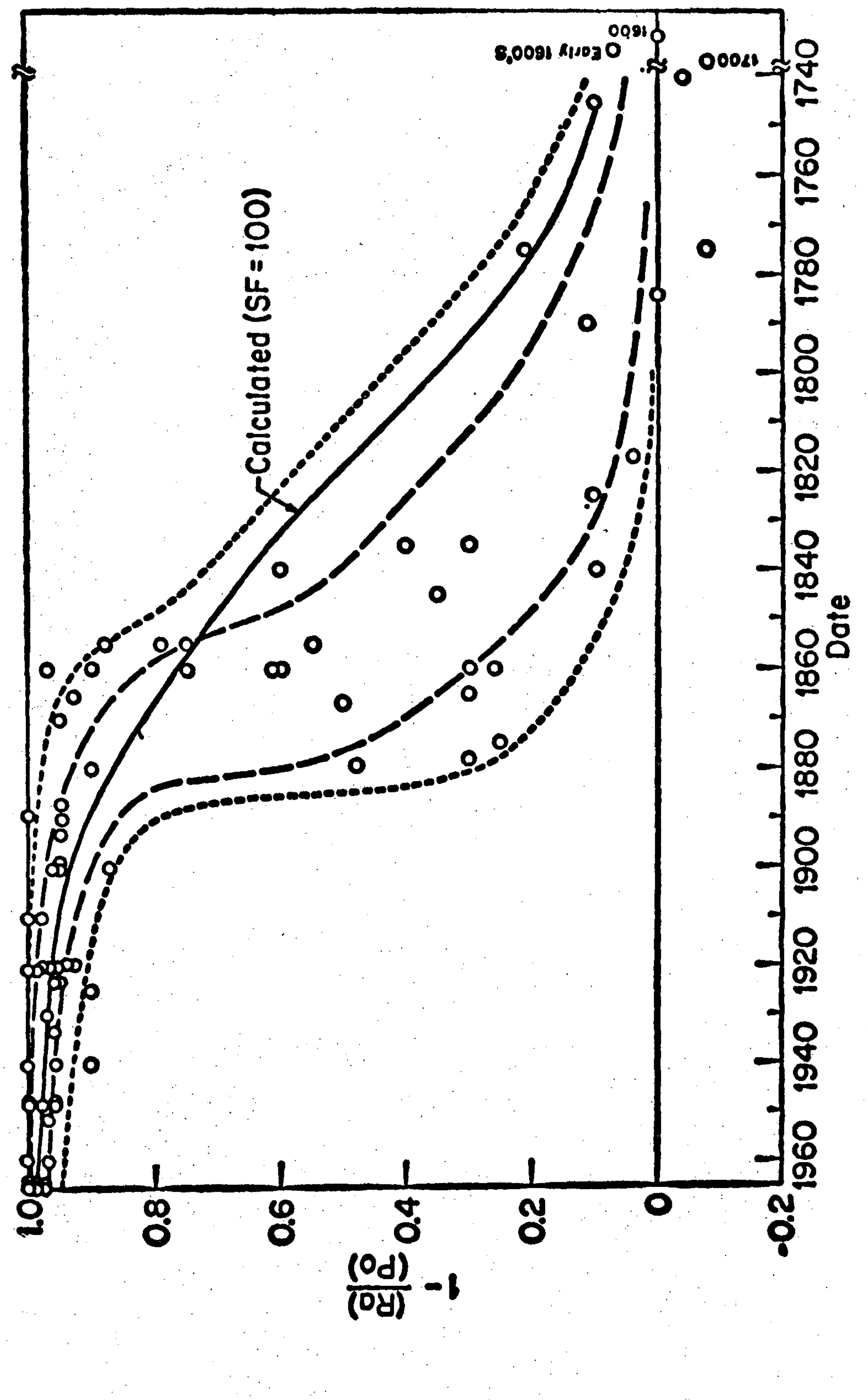
XBL 725-859

Fig. 4



XBL 725-860

Fig. 5



XBL 725-862

Fig. 6

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