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Introduction

During the past few years most archaeologists and museum curators have become familiar with the term *isotope*. Isotopes are atoms of the same chemical element which differ slightly from one another in mass. For instance, there are four stable isotopes of lead, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, having, respectively, approximate masses of 204, 206, 207 and 208 atomic mass units; and there are three isotopes of oxygen, ^{16}O, ^{17}O and ^{18}O, having masses of 16, 17 and 18. The isotopic composition of most elements is uniform throughout nature. That is to say, occurrences of a particular element in different places or in different chemical forms usually contain the same relative proportions of that element's isotopes. There are, however, a few notable exceptions, and wherever they occur they are invariably of interest to the scientist. The example most familiar to the archaeologist is the variation in the proportion of ^{14}C in the carbon present in archaeological objects. This variation constitutes the basis of radiocarbon dating, the discovery and remarkable advances of which are being commemorated at this Symposium.

In this paper we shall deal with two other elements, lead and oxygen, whose isotopic compositions vary in natural occurrences due to rather well defined mechanisms. Unlike the ^{12}C–^{14}C relationship, which involves the decay of a radioactive species and leads directly to a dating method, the research reported here with lead and oxygen does not involve radioactive decay in the same way, and neither investigation at this stage is aimed towards developing a direct dating method for archaeological finds. With lead, the isotopic variations observed are associated with differences in the geological ages and geochemical origins of lead deposits. (The differences arise because three of the four lead isotopes are continually produced within the earth by radioactive decay of uranium and thorium.) In the case of oxygen, physical and chemical fractionation processes are responsible for the isotopic variations.

Isotope determinations on archaeological specimens of lead can be used to learn something about the possible geographical origins of the ores from which the leads were originally smelted. This technique has been applied to a wide variety of archaeological and historic objects containing lead in several different forms. The usefulness of determinations of the isotopic compositions of oxygen in different types of early materials is still being explored, but already several applications show promise. The application reported here is for the classification of early glasses and for characterizing (to some extent) the ingredients from which they were made.

The findings of our research in both of these areas are now being prepared for comprehensive publications,† and therefore, we have restricted our aims here to a general discussion of the kinds of data that are emerging from these two investigations and the ways in which they can be translated into useful information for the archaeologist and curator. Consequently, we will

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† The single authorship of this paper is due to its nature as a review lecture. The forthcoming comprehensive publications will be co-authored with J. M. Wampler and W. R. Shields (on the lead research) and R. N. Clayton and Toshiko Mayeda (on the oxygen research).

not include here a catalogue of all of the objects studied, and list all the donors, nor will we present a detailed description of the experimental methods. The reader is cautioned, in the case of the lead experiments particularly, that a complete listing of the applictions and discussion of all the possible pitfalls in the interpretation of these data would have to be too lengthy to be included here. We therefore refer the reader to the previous publications on this subject, and invite interested persons to contact the author concerning future applications of either of these methods.

TABLE 1. LEAD ISOTOPE RATIOS FOR GALENA ORES FROM
THREE ANCIENT MINING REGIONS

	Laurion (Pb-77)	Great Rutland Cavern, Derbyshire (Pb-28)	Rio Tinto (Pb-89)
$^{207}Pb/^{206}Pb$	0.8307	0.8465	0.8598
$^{208}Pb/^{206}Pb$	2.0599	2.0814	2.102
$^{204}Pb/^{206}Pb$	0.05297	0.05413	0.05479

LEAD ISOTOPES IN ARCHAEOLOGICAL OBJECTS

In previous publications Brill & Wampler (1965, 1967; Brill 1967) have described the usefulness of lead isotope determinations for deducing the possible origins of the lead contained in several types of archaeological objects and materials. The logic behind the method is quite straightforward, although not without its complications. Galena ores (lead sulphide) occurring in different mining regions throughout the ancient world often have distinctly different isotope ratios, because they were deposited during different geological periods of the Earth's history, or were derived from different source rocks, or both. As can be seen from table 1, lead ores from Greece, England and Spain, three important mining regions in ancient times, can be readily distinguished from one another on the basis of their isotope ratios. By comparing isotope ratios determined for samples of lead from archaeological objects to the ratios for galena ores from these and other mining regions, one is enabled to decide whether or not the lead could possibly have been smelted from ores mined in those regions. Our initial results indicated that most of the archaeological objects tested (about 50 at that time) fell into one of four categories. These were labelled groups L, E, S and X. The first three letters stand for Laurion, England and Spain, although it was realized from the outset that these groups also include leads from regions other than those used to choose the letter designations. Group X contained several specimens from Italy and from various sites in the Near East. Figure 1 illustrates the range of isotope values we have seen so far and sets off a few reference points and stray values which do not fit on the figures which follow. In all about 200 specimens of various sorts were used to construct the groups shown on the graph.

As with all archaeometric methods, there are certain limitations imposed upon the interpretation of the results. The most important of these in this instance is that although the ratios of a galena ore may be characteristic of some mining region, they are but rarely uniquely so. It is often found that mines located in geologically similar environments may yield identical isotope ratios even though the regions themselves are widely separated.

Future studies may add new groups to those which have already been set off and can be expected also to add other mining locations to the original groups. As one works with these data, it becomes apparent that there is a great need for analyses of galenas from other mining

regions; and until such data are forthcoming, it will remain uncertain as to just how serious will be the problem of the overlapping of ratios from different regions. The extent of the problem depends not only upon how much overlapping occurs, but also upon which regions happen to be involved. With luck it may turn out that some of the ores which overlap will not lead to confusion because of archaeological arguments which will rule out certain of the overlapping ores in particular applications. Moreover, in many cases it may be useful to an archaeologist simply to know whether certain groups of ancient leads are alike or if they are different, regardless of whether or not specific origins can be assigned to the ores.
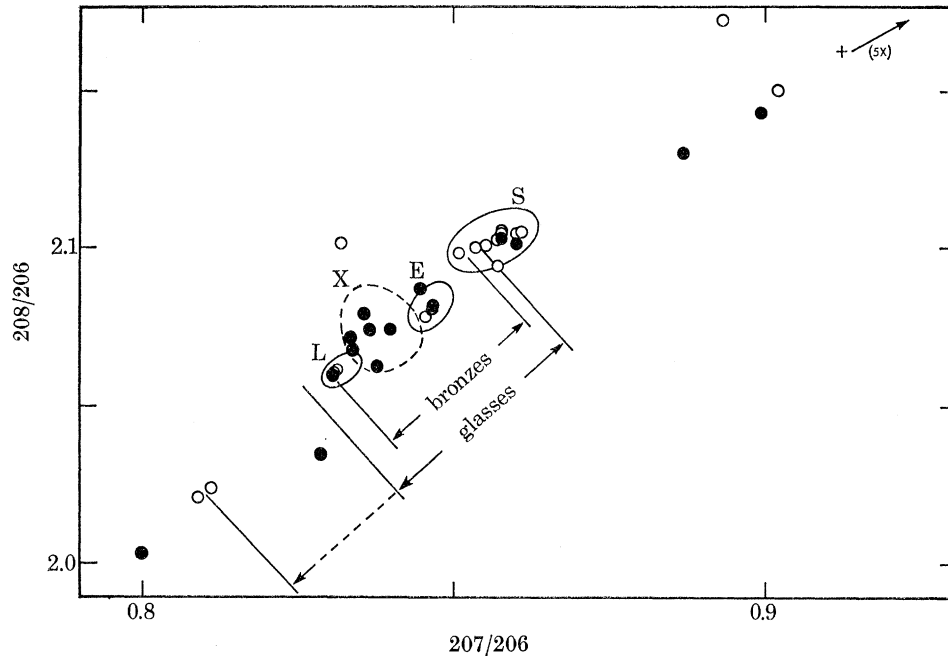

FIGURE 1. Ranges of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ lead isotope ratios determined for about 200 samples of ores and of lead from various types of archaeological objects. When all of the points are plotted they show a general trend running from the lower left to the upper right (which is roughly related to the geological age of the ore deposits), but most of the archaeological specimens fall within (or in between) the four empirical groups labelled L, X, E and S. (The extreme cases of deviation above and below the general trend are included.) The ranges of values determined for the leads extracted from the ancient glasses and bronzes discussed in the text are labelled accordingly. Most of the points plotted here are for future reference purposes. (O, this study; ●, previous data; ×, white lead pigment.) The ratios are determined to four significant figures.

Another complication arises from the mixing of leads in ancient times. There is no question that then, as now, metals were often salvaged and melted down together for reuse. If leads from different sources became mixed, the isotope ratios we determine today for such specimens will be somewhere intermediate between the values for the original leads. Unhappily, it will probably not always be possible to tell when this has happened, except possibly in cases involving unusual $^{208}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$ values.

But despite these two important qualifications, the advantages of this method are several. First, the chemical properties of the isotopes of lead are very nearly identical, and, therefore, the isotope ratios of a lead are almost entirely insensitive to any effects of its chemical history. Short of mixing together leads from different sources, there is little that can happen to lead which will alter its isotopic composition drastically. Thus, the ratio of the final sample analysed in the laboratory should be virtually identical to that of the original ore. This is in sharp and

very favourable contrast to the use of chemical analyses for characterizing early metals. When dealing with chemical analyses of metals, one must always be much concerned with the chemical history of the object, for every chemical step in the history of a metal from the time it was first removed from the earth as an ore until it is finally removed again from the earth upon excavation can—and usually does—affect the chemical composition.

The samples required for isotope studies are small. Samples with a mass as little as 50 to 100 μg have been successfully dealt with, although it is much more convenient, and the results are more accurate, if a sample of as much as about 20 mg is available.

Lead isotope determinations have been shown to be of value in the investigation of many different kinds of archaeological objects. These include metallic leads, corrosion products, lead-containing alloys, cosmetics, glazes, glasses and pigments. In theory, the method should be applicable to any historical material (and forensic specimens, too) from which a sufficient amount of lead can be extracted. We expect that one of the most valuable applications will prove to be the study of white lead pigments in paintings. The prospects for studying the works of individual artists or schools of painters, and the potential for authentication are very promising indeed. Our preliminary studies with a few specimens of white lead removed from paintings have borne this out. These experiments were carried out in conjunction with R. Feller and W. Shields.†

In the sections that follow, two significant recent developments are reported. The first involves the experimental procedure, and the second two new sets of data.

High accuracy mass spectrometry of lead isotopes

Although the earlier data (from the Brookhaven National Laboratory) served well for establishing the validity of this technique, we know now that in order to get the maximum benefit from studies of this sort, data of the highest accuracy are required. To some extent the interpretation of the original results was hampered by the fact that the experimental uncertainty was great enough to prohibit us from confirming several differences and similarities that we felt existed among the samples. In addition, two different experimental procedures had been employed and it was not possible to correlate the results of those two methods with much confidence. Thus we were hindered by having both a lower precision and lower accuracy than we would have liked. In the more recent studies to be described below the precision is probably smaller in magnitude than any differences among the specimens which we would presently regard as being significant, and furthermore, the results are accurate as well as being precise. As a result, two of the difficulties arising in the earlier studies have been overcome.

Through the help of W. Shields, Chief of the Analytical Mass Spectrometry Section of the National Bureau of Standards, Wampler undertook the study of a group of ancient bronzes and ancient glasses which were known to contain lead. The determinations were made by the surface ionization method, employing a triple filament, on a 12 in (30.5 cm), 68° sector, single-focusing mass spectrometer at the National Bureau of Standards (Cataranzo 1967). Most of

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† This technique for classification was suggested by the author in discussion at the Boston Museum of Fine Arts Conference on Application of Science in Examination of Works of Art (1965). It is not the same as that published by B. Keisch, R. L. Feller, A. S. Levine & R. R. Edwards (1967), which deals with a method of detecting lead recently smelted from ores by looking for ^{210}Pb. Dr Keisch has now also undertaken a study of lead isotopes for the classification purposes as mentioned above.

the runs were made by Wampler, but other persons working under Shield's direction also ran some samples.

The accuracy attainable with the instruments and procedures now used at the Bureau is perhaps as much as five to ten times improved over that which was possible in our earlier work. In Shields's laboratory accuracies of the order of 0.1 % are routinely attained for lead isotope ratios. As will be demonstrated below, this improvement allows one to make more closely refined classifications of the types of lead found in ancient objects and makes it possible unmistakably to distinguish differences between specimens which until now would have appeared indistinguishable. Moreover, Shields and his group are able to make determinations which they regard as yielding absolute values, so that the results they have obtained will be of long-standing validity and should be directly comparable to values obtained in the future, even at other laboratories, providing that equally accurate values are obtained. Until now it has not in general been safe to compare results from different laboratories because of systematic errors and biases which are often greater than the differences found among the archaeological specimens. This is unfortunate because it has frustrated many attempts to correlate our archaeological data with those on ores appearing in the earlier geological literature. In fact, we are even hesitant to attempt to compare our own Brookhaven determinations with those from the Bureau of Standards, except where rather large differences in the isotope ratios are found.

One other consequence of this instrumental improvement is that it necessitates a re-examination of the assumption that no fractionation has occurred in any of the archaeological specimens studied. But this should not pose serious problems. While it is doubtful that many findings would be affected it is possible that slow chemical changes (such as the corrosion of metallic lead), or chemical processes involving precipitation or partial solution of lead compounds (such as in the preparation of pigments or corrosion of glasses), or volatilization of molten lead-containing phases (such as in glass-making), could produce fractionation at a level commensurate with this precision.

As was mentioned above, one of the attractive advantages of this type of study is that only very small samples of material are required. The actual quantity of lead consumed in the mass spectrometer is of the order of 10 μg, and therefore, one of the limiting factors affecting the feasibility of running very small samples is the background contamination of lead introduced by the environment and by chemical processing. At the National Bureau of Standards procedures have now been developed which have reduced this background to a level of less than 1 μg of lead, which means that reasonably reliable results can be obtained for samples of lead with a mass as little as about 10 to 20 μg. Consequently, other new research possibilities are being opened up. For example, it now seems practicable to determine the isotopic composition of traces of lead in valuable museum objects made of gold or silver. For gold or silver objects which contain about 0.1 % of lead (and many ancient silvers, in particular, contain quite a bit more than this), lead isotope determinations would be possible with the sacrifice of only about 10 mg of metal from some inconspicuous or already damaged parts of the objects. A 10 mg sample of these metals corresponds to a volume of only about 1 mm³. There are a great many instances, such as in the study of the large Sasanian silvers which have recently been brought under such close scrutiny, where the value of the information gained from such a determination would by far outweight the aesthetic or historical value of the minute amounts of metal which would have to be sacrificed. Isotope determinations on traces of lead might also be a useful aid in settling some questions of authenticity which so frequently arise in connexion with

ancient gold objects. But it would have to be realized that the reworking of gold in the ancient world and the understandable reluctance to sample gold objects might stand in the way of developing a proper cataloguing of the types of lead found in ancient objects of known provenance. Perhaps a workable approach might be through a study of the lead in ancient gold coins.
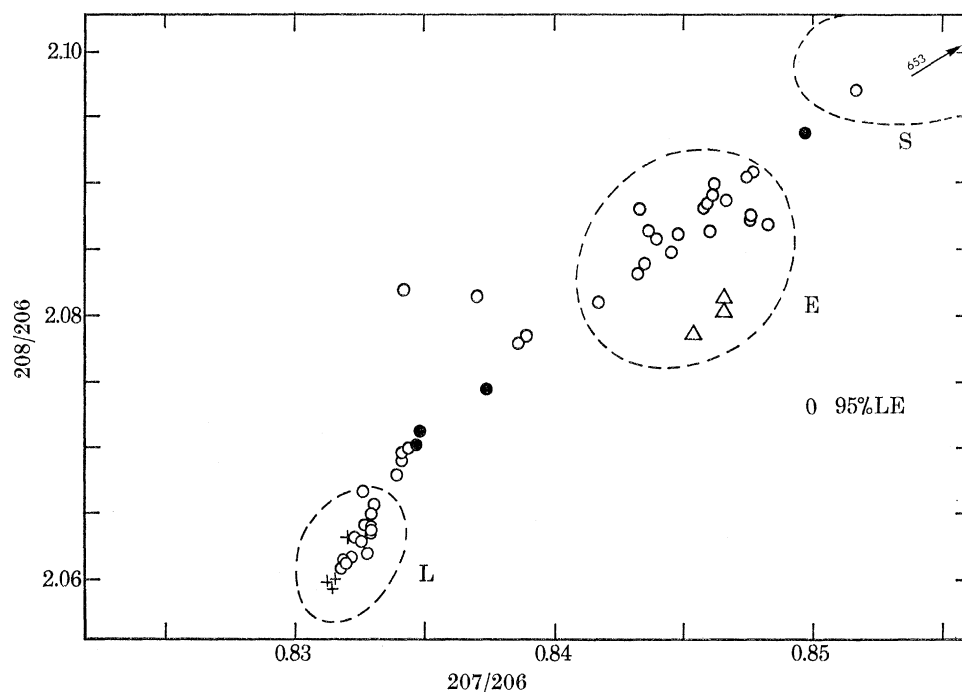

FIGURE 2. Lead isotope ratios determined for samples of lead extracted from some ancient bronzes. (○, bronze coins; ●, statuary bronzes; +, metallic lead associated with bronzes; △, high-accuracy determinations repeated for three known English leads among those reported in earlier studies.) The ratios are measured to four significant figures.

LEAD ISOTOPES IN SOME EARLY BRONZES

Among the leads studied recently are 42 samples extracted chemically from early bronze coins and eight samples extracted from (or associated with) ancient bronze statues and vessels. Most of the coins were provided by E. R. Caley and L. Cope, who had previously analysed them chemically. The coins ranged in date from *ca.* 330 B.C. to A.D. 310 and for the most part were struck in known mints. The lead contents were between 3 and 35 %. The samples of the statuary bronzes were supplied by Miss H. Lechtman, who had sampled and analysed them. Four specimens of lead fill material from bronze vessels of Greek or southern Italian provenance were provided by B. Shefton. A partial list of specimens and donors appears in the appendix, but in the final publication, a detailed catalogue will be included.

In figure 2 are plotted the results for all of the bronzes. Superimposed on this graph are modified limits of the original L, E and S groups. There are many useful and interesting conclusions to be drawn from these results, but a sample by sample interpretation will be deferred until our complete publication. It should suffice here simply to list a few observations and summarize the classifications which can be read directly from the graph.

(1) Eighteen leads of type L were found. Eight of these came from early Greek coins. Six samples, which did not come from early Greek coins, but appear to contain a type of lead very

similar to the Laurion lead, were struck in Egypt (or Cyprus), Syria, Asia Minor and Rome. All date from the second century B.C. and it is quite reasonable to assume that Laurion lead could have been in use in these places during the second century.

The lead fills in the handles of four bronze vessels all fell in group L. (These samples are plotted as crosses in figure 2.) Three of the specimens are identical within experimental error. Of these, two date from the mid-sixth century B.C. and are believed to be Spartan (Pb-654 and 656), and the third, which is Greek but of uncertain exact provenance, dates from the fifth century B.C. (Pb-659). The fourth object (Pb-655) is Greek but of unknown place of manufacture and dates from the 4th century B.C. or later. This fourth specimen, although still falling within group L, seems to differ slightly from the other three. Examples of similar specimens from Taranto and others from Sparta still remain to be studied.

With the increased accuracy of the present determinations, it is possible to see with certainty now significant differences among some of the leads falling within group L, the Laurion type. There seems to be a rough trend upward and to the right of the diagram associated with increasing date (with some exceptions), and it may possibly be that the differences reflect variations among leads from different contact layers of galena which were opened at different times in the history of the Laurion mines. It is also possible, of course, that other mines in Greece or the islands might have been in use and that their ores might differ slightly from the Laurion leads.

(2) High accuracy determinations also will allow some refinements in interpreting the data in group E. Consider, for example, the group of 11 bronze coins plotted as a cluster of points in the upper right portion of that group in figure 2. Eight of these date from about A.D. 300 and the other three are a little earlier. The coins were minted in London, Rome, Lyons, Trier, Milan, Siscia and Alexandria. The close similarity among these coins, and their relationships to three English leads rerun from our earlier work raise two interesting lines of thought.

First, it is possible that some or all of these leads actually did originate in England for by this time a good deal of English lead might be presumed to have been in circulation around the Roman world. But unfortunately, our earlier data on English leads are not sufficiently accurate to allow us to say whether they are the same or different from the leads in these coins. The question of whether these coin leads could be English can be answered only by repeat determinations of the known English leads by the high-accuracy procedures. Alternatively, keeping in mind that leads of this type certainly could have originated elsewhere, the possibility arises that they might have originated, for example, in some European location (or locations).

At present, high-accuracy determinations have been repeated for only three of our English leads. These are two lead pigs and one galena ore, all from Derbyshire, so we have no high-accuracy information on the actual range of isotope ratios expected for English leads. The repeat values differ slightly from the original less reliable values and also differ significantly from the eleven coin samples mentioned above. (They fall near the rim of the group at the 5 o'clock position.) This observation suggests that none of the leads in these particular coins came from Derbyshire, and possibly not from England at all.†

Thus we can hope to benefit from additional high-accuracy determinations of other English leads for they will probably enable us to distinguish either between Derbyshire leads and other

† Although the Derbyshire leads fall below the general trend shown by the bronzes, earlier work suggests that Derbyshire leads may be atypical in this respect. See, for example, the work of S. Moorbeth (1962), cited on p. 69 of Brill & Wampler (1967).

English leads or between English leads in general and some European leads in common use in Roman times. We hope to be able to clarify this and to confirm one view or the other by the time our comprehensive publication appears.

L. H. Cope has pointed out to the author (personal communication) that certain relationships found between the leads in the coins from London and Lyons are of special interest to the numismatist. The arguments are a little too complicated to go into here, but they may serve to substantiate—or to disprove—the suggestions put forth previously on the basis of numismatic evidence that mint workers coming from Lyons to London might have brought along some metal with their dies and tools. This case illustrates again the need for high-accuracy determinations.

The other coin specimens in group E (plotted more or less in the top-centre of the loop) all come from coins minted in Syria (mostly Antioch) or Alexandria. They fall within group E but seem to differ from the 'western' coins discussed above, and probably are better thought of as being related to other Syrian coins and Syrian leads falling to the left of group E.

Although this may all seem to make the picture very indefinite, it should be useful in itself to know that certain coins are obviously similar and others obviously different. While it is difficult to make positive assertions about the sources of the leads, it is nevertheless possible to be quite conclusive in making negative assertions. For example, none of the leads used for making the coins falling in group E could possibly have originated in Laurion or in any other suggested places having isotope ratios unlike the group E leads.

(3) Only two bronzes were found to contain lead of group S. One was a coin struck in Rome in A.D. 307, and the other, a statue of a bronze horse found in Ancona and dated to the first century A.D. Here again ambiguity arises as far as the origin of leads within the empirical groups. While some leads from Spain and Portugal are known to be of this type, we have already found, as originally reported, galena ores from Wales and Sardinia which are very similar to them.

(4) Five bronze coins were found to contain lead which falls in group X. These were coins struck in Sardis, Apameia, Antioch, and (one) in Athens. In addition, the lead from a second century A.D. bronze statue excavated at Casanuovo, near Reggio, is very similar. A good case could be constructed for believing that the lead in the first three coin specimens originated in Asia Minor, for there are lead deposits close to the two sites where the coins were minted. On the other hand, one might expect the lead in the statue to have been of local origin, so that it might well be an Italian lead. The coin from Athens, it will be noted, was of rather late date (27 B.C. to A.D. 14), and although it is surprising not to find a Laurion-like lead in this bronze, the date of the coin postdates the closing of the Laurion mines and the bronze might have come from Italy or Asia Minor or even elsewhere. Cope (1969) has pointed out that this might be taken as evidence of travelling mints accompanying military units in their movements.

(5) Seven other bronze coins (four from Syria, two from Alexandria, and one from Beth She'arim) contain lead showing an isotope ratio intermediate between group X and group E. Two of these (29 and 30) fall considerably above the general trend followed by the rest of the bronzes. Among other samples (not coins) from Syria and elsewhere in the Middle East we have found this same behaviour; that is, that the leads often scatter rather widely throughout the range of values of leads from other sources, and a similar displacement above the general trend has been seen among them.

(6) Two identical coins from Apameia (133–48 B.C.) serve as an important warning for

future interpretations of this kind of data. These two coins actually contain different kinds of lead even though they apparently were minted in a fairly remote region not far distant from sources of lead ore. One of these coins contains lead of the Laurion type, while the other is significantly different and falls in the group X category.

(7) While we have suggested geographic regions for some of these leads, it must be repeated again that mixing of leads from different sources is always a possibility to be considered, particularly where values fall in between recognizable groups.

(8) Sample Pb-652, the lead extracted from an Etruscan bronze thymiaterion of the third century B.C. falls within the limits of group X. It is reasonable to assume that the lead used in making this bronze would have been of local origin and this might, therefore, represent an example of an Italian lead. We have found other Italian leads, as mentioned before, which resemble this one. Samples Pb-650 and 651 referred to in an earlier note, were of lead removed from a bronze statue excavated in Casanuovo. This statue, now in the Boston Museum of Fine Arts, dates from the second century A.D. and its bronze also probably contains a native Italian lead.

(9) Sample Pb-653 is a sample of solder removed from an Etruscan candelabrum of the fourth century B.C. The object is in the collection of the City Art Museum of St Louis. The solder had been used to attach one of the three feet of the candelabrum to a small rectangular plinth, but Miss H. Lechtman, who provided the sample, was uncertain from her examination as to whether this was the original means of attachment, or if it is a modern repair. The lead was found to be of a type unlike any that we have encountered in the other bronzes, but it is almost identical to two samples of metallic lead excavated in Sardinia. (The sample is plotted as the open circle to the right in the S group in figure 1.) The leads from Sardinia, numbers 41 and 42 in our previous study, date from the second to the first century B.C. and the third century A.D., and are believed to have been smelted from a local Sardinian ore. We, therefore, believe that the lead is probably part of the original object. (An isotope determination of the lead in the bronze itself would be very helpful for confirming this conclusion.)

Lead isotopes in ancient glasses

Two types of ancient glasses, red and yellow opaques, often contain intentionally additive quantities of lead (Brill 1962, 1963, 1968). The red opaques owe their colour to the presence of minute crystals of cuprite which are precipitated in the glass by heating under reducing conditions. The cuprite forms more readily if lead oxide is present in the glass, and glassmakers seem to have learned this early in the history of glassmaking, for many red opaques dating back to at least the ninth century B.C. contain between 5 and 30 % PbO. Yellow opaque glasses owe their colour to the presence of a lead-antimony or lead-tin colorant-opacifier ($Pb_2Sb_2O_7$ or $PbSnO_3$) (Rooksby 1962). These glasses usually contain about 5 to 10 % PbO. The earliest examples are contemporary with the earliest types of glass vessels, that is, the cored vessels of Egypt and Mesopotamia which date from the fifteenth to fourteenth century B.C.

In our earlier studies, isotope ratios had been determined for seven examples of ancient lead-containing glasses. This work has been continued and determinations have been completed for about fifty additional glasses. The lead was extracted chemically from the samples and then analysed by the same procedure used for the other lead samples. The results for some of these glasses are presented in figure 3. (Thirteen specimens of mosaic glass tesserae were

excluded because they are of later dates and tend to confuse the graphical representation of the data.) It will be seen that the leads from these glasses cover about the same range of isotopic compositions as the ancient bronzes. This variation is not surprising in view of the wide span of dates (fourteenth century B.C. to fourth century A.D.) and their widely scattered places of excavation. A few general observations follow:

(1) Perhaps the most interesting kind of glasses included here are the early Egyptian and Mesopotamian cored vessels. The early Egyptian glasses (eighteenth dynasty) that we have studied number only three. Two of these (Pb-404 and 405) differ sufficiently from the rest of the data that they do not even fall on the graph as plotted. The two points which are well
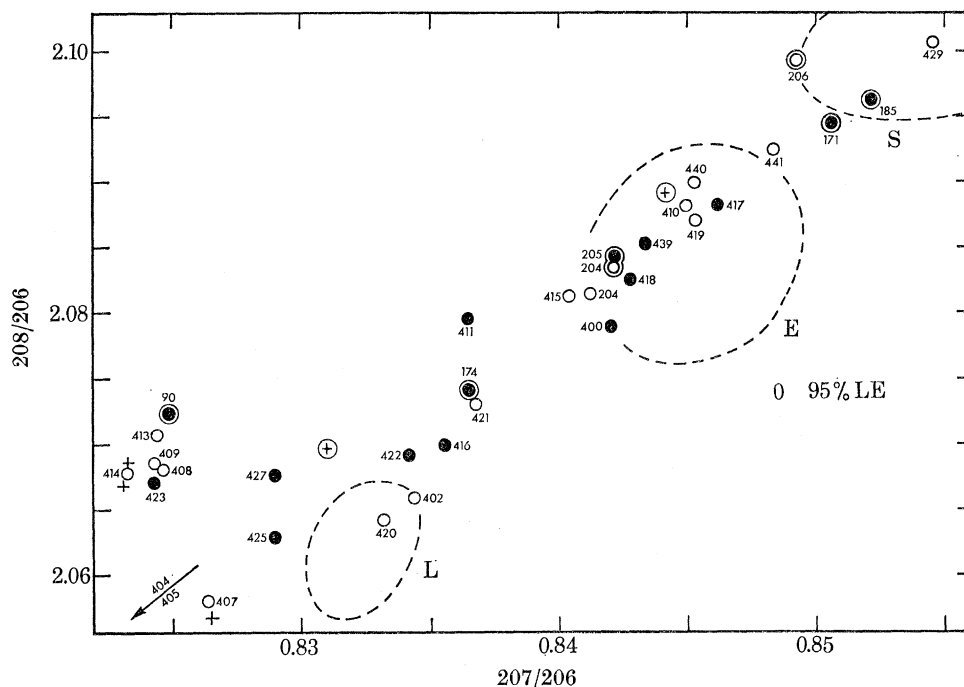

FIGURE 3. Lead isotope ratios determined for samples of lead extracted from some ancient glasses. (O, yellow opaques; ●, red opaques; +, metallic leads; ⊚, ⊙ and ⊕, data from earlier studies.) The ratios are determined to four significant figures.

outside the boundaries of figure 3 can be seen plotted as two open circles in the lower left corner of the larger scale plot of figure 1. We have also found, as have others (Delevaux, Doe & Brown 1967) some Egyptian lead ores which resemble these leads and although further substantiation is required, it seems plausible that these Egyptian cored vessels were indeed made with lead from deposits in the Red Sea area, probably in the Eastern Desert.

(2) A very interesting group of objects are those represented by the cluster of points above the general trend of most of the other leads (to the left of the figure). These six samples include two early red opaque glasses and four yellow opaques. All come from Mesopotamian or Iranian sources. They range in date from the fifteenth century B.C. up through the ninth century B.C. and into Hellenistic times. The glasses came from Nuzi, Rimah, Hasanlu, and Nimrud. There are also two pieces of metallic lead from Nimrud whose ratios fall among these leads from the glasses. (These are plotted as crosses in figure 3.) There can be little doubt but that the lead for making the yellow pigment in these glasses and for colouring the red glasses came from a common source, not necessarily the same mines, but a localized mining region. The most

striking fact is the long span of time throughout which this source was used for, among other things, glass-related activities. However, we already know that the picture is not a simple one, for there is a piece of metallic lead from Rimah which falls opposite this group on the general trend and is immediately adjacent to a piece of 18th dynasty yellow glass from Egypt. Also, two other glasses from Rimah and Hasanlu are entirely different from those forming this little cluster defining the unusual type of lead.

(3) The glasses from Nimrud are of special interest. Two examples of red cullet (Pb-90 and 423) contain the kind of lead referred to in the item above. These are known from excavation data to be of Hellenistic date. But two specimens of lead from red opaque inlays from the eighth to seventh century B.C. ivory inlay plaques fall to the right of that cluster, and nearer the general trend of the samples (Pb-425 and 427). These two leads may have come from ores of a similar genesis, because both deviate slightly from the general trend, and may also be from deposits nearby to one another. Nevertheless, unless some mixing of an alien lead is involved, they are significantly different from one another. Sir Max Mallowan (pers. comm.) has suggested the site of Berwari in Northern Iraq as a possible source. The most remarkable result among the Nimrud glasses is that the one yellow glass so far analysed contains a type of lead completely unlike that in the four red glasses.* The lead in the yellow pigment of this glass is plotted in the very upper righthand corner of the graph. It is very tempting to speculate on what might have been the origin of this lead, in spite of our previous expressions of caution about doing this. A little speculation, however, does no harm if we keep in mind that it is speculation. If the groups L, X, E and S were taken literally, it could be said that sample Pb-429 looks like a lead from Spain or possibly Wales or Sardinia. Because of the early date of this glass (eighth to seventh century B.C.), one may be inclined initially to dismiss this possibility summarily, but some recent evidence shows that this possibility should perhaps be given consideration. Blanco & Luzón (1969) in recent excavations at Rio Tinto in southern Spain have described remains of eighth to seventh century B.C. Phoenician mining installations in southern Spain. The fact that Phoenician miners might have been taking lead ore from Spain this early raises the possibility that some of this lead might have found its way back to Syria or Egypt or elsewhere in the eastern Mediterranean and have become incorporated into the lead-antimony pigments that were used for preparing these glasses. The possibility becomes even more enticing when one notes the occurrence of antimony with the lead-bearing jarosite which was being worked at the Phoenician site.

(4) It is a little puzzling and also disturbing to have found that the lead in red and yellow opaque glasses from the same site, or apparently even from the same factory sometimes do not have the same isotopic composition and thus, presumably, came from different sources. Examples of this were found among the glasses found in debris from a Hellenistic glass factory on Rhodes (Perrot & Weinberg 1968) in which two specimens of yellow opaque glass cullet did not agree closely with one another, nor with a red glass from the same site. It was also found that the leads in three specimens of mosaic glass from Pompeii vary significantly from one another, although this is less surprising because of the enormous number of glass tesserae from different mosaics at Pompeii. This could also be an indication of the re-use of lead and possible mixing of lead

* [*Note added in proof*, 29 *June* 1970.] Since this text was prepared we have analysed one additional yellow opaque glass from Nimrud. This is a flat rectangular tablet from the same source as the feather-shaped inlay mentioned in the text (Pb-429); but, unlike that specimen, this one contains a lead which is isotopically identical to the lead extracted from one of the red opaque glass inlays (Pb-427).

from different sources. Information of this sort in itself might even be turned to good use since it implies that the glasses were made in a place where there was not an overwhelming abundance of lead of one type, but instead, a place where many types of leads were available. Such a place would be expected to be remote from any lead-producing regions.

(5) With early glasses one must be careful not to identify unconsciously, places of excavation with places of manufacture. Glass vessels undoubtedly were traded over long distances, particularly those decorative highly coloured types with which we are dealing here. What we are really looking for in these glasses are similarities or differences between the leads found in different objects, for these may be traced back to a common origin of the yellow pigment or the lead in the red glasses. This origin obviously need not necessarily coincide with any of the places where the objects were found.

(6) Sample Pb-410, a yellow glass from an extremely interesting fused mosaic glass vessel from Rimah contains a type of lead that is quite unlike that of the other early vessels. In our earlier experiments we analysed the metallic lead from a small net sinker from El-Amarna dating from the eighteenth dynasty. Although the results may not be strictly comparable because the samples were run at different laboratories, the two leads appear to have almost identical isotopic compositions. Some inlay glasses from the Denderah shrine (second century A.D.) are also very similar. But before assigning an Egyptian source to the lead in the fused mosaic glass, one must consider the fact that its isotopic make-up also corresponds very closely to a piece of metallic lead excavated at Tepe Hissar in Iran, dating from about 2300 B.C. Once again then, the overlapping problem returns to cause difficulty.

(7) Sample Pb-411, lead extracted from the red glass in a fused mosaic beaker excavated at Hasanlu, has an unusual isotopic composition. It resembles some leads found in the bronze coins discussed earlier, notably those of Syrian origin. It is distinctly different from the lead in two yellow glass and faience beads from Hasanlu and from the Rimah fused mosaic vessel.

(8) The isotope data for the leads from ancient glasses should be first examined among themselves to look for possible associations between objects, but it is also clear that these data should not be considered in isolation only, but that they must be compared with the results from the bronze coins and also, even more importantly, with the metallic leads and ores which have been studied previously.

OXYGEN ISOTOPES IN ANCIENT GLASSES

The two isotopes of oxygen of interest to us here are ^{16}O and ^{18}O. The heavier isotope, ^{18}O, accounts for only one out of about every 500 atoms of oxygen occurring in nature. Because the difference in mass of two atomic mass units is a rather large percentage of the masses 16 and 18, and because oxygen occurs in forms which readily interchange with one another (such as water, ice, water vapour and atmospheric oxygen) it is especially susceptible to fractionation effects. Consequently, the ^{18}O contents of various occurrences of oxygen are often quite different. The range of variation of ^{18}O contents in representative natural occurrences is illustrated in figure 4. By convention the ^{18}O content is usually expressed in terms of δ which is the deviation in parts per thousand of the ^{18}O content of the sample of interest from that of an accepted standard designated as standard mean ocean water (s.m.o.w.). Thus, the ^{18}O content of standard mean ocean water has by definition a value of zero on the scale of δ values. Substances having a positive δ value have an excess of ^{18}O over the standard while those with negative values are deficient in ^{18}O.

^{18}O contents of many natural minerals have been measured for geochemical purposes. In particular, R. N. Clayton and his co-worker, Mrs T. Mayeda at the Fermi Institute, University of Chicago, have perfected a scheme for determining ^{18}O contents in silicate and carbonate rocks and minerals. (For general background information on oxygen isotope compositions in some natural substances see Engel, Clayton & Epstein 1958; Clayton & Epstein 1958; Keith & Weber 1963; Taylor & Epstein 1962; Brill 1968). Realizing that many of the raw materials of which glasses are made differ from one another in their ^{18}O contents and further that oxygen is actually the most abundant element in glasses, accounting for some 45 to 50 % by mass of the glass, it was postulated that ^{18}O contents of the glasses themselves might reflect the ^{18}O contents of the ingredients from which they were made. The ^{18}O contents of a series of 75 man-made glasses spanning some 34 centuries and coming from widely separated origins, have been determined in order to see what range of values of δ they show. All of these determinations were
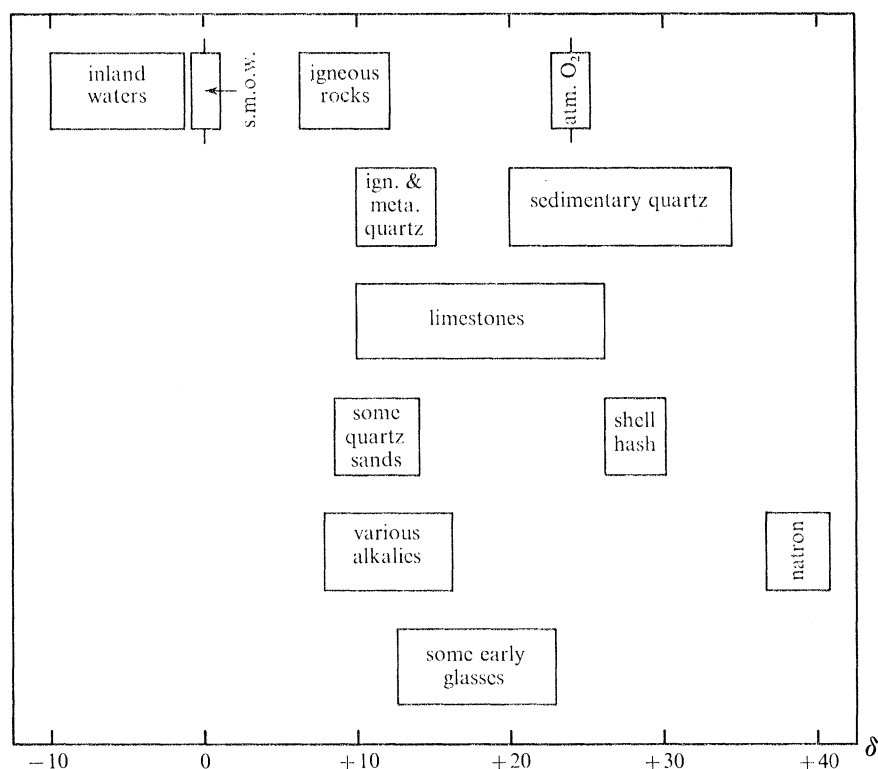

Figure 4. ^{18}O contents of some naturally occurring materials and glassmaking ingredients. δ, deviation in parts per thousand of $^{18}O/^{16}O$ from s.m.o.w. (standard mean ocean water).

made by Clayton and Mayeda using the same techniques they have used for their studies of rocks and minerals. As can be seen in figure 5, the range of δ values for these glasses is considerable. Thus the prospects look promising for developing a scheme for classifying early glasses on the basis of their ^{18}O contents in a manner similar to that based on chemical analyses. The oxygen isotope studies provide an essentially independent means of classification.

Before attempting to apply this reasoning, however, the validity of at least one important assumption had to be investigated. Since melting conditions, even within an individual early glass factory, probably changed from day to day, it is crucial to know to just what extent melting temperatures and melting times affect the ^{18}O contents of glasses prepared from the same raw

materials. In order to evaluate these effects, ^{18}O contents were determined for six selected glassmaking ingredients. These ingredients were then used in different combinations to prepare four glass batches. The glass batches represent two chemical compositions, but four different combinations of isotopic compositions. Portions of each of these batches were then melted at different temperatures and held at elevated temperatures for different times. The temperatures used were 1200 or 1300 °C and 1600 °C. The holding times (after initial melting) were 2, 16, or 24 h. The results of the ^{18}O determinations on the resulting sixteen glasses were most encouraging. With the exception of one glass, which yielded a slightly spurious result, it was found that only the isotopic composition of the original ingredients affected the δ values of the final glasses. Variations in the melting times and temperatures within the limits chosen had no measurable effect. Equally encouraging was the observation that the experimentally determined isotopic compositions of the oxygen in the glasses agree well with predicted values calculated by treating δ as a simple additive property. Moreover, the small deviations from the calculated values were diminished when fractionation effects were considered. The agreement of the corrected values is within the limits of experimental error, as shown in table 2.
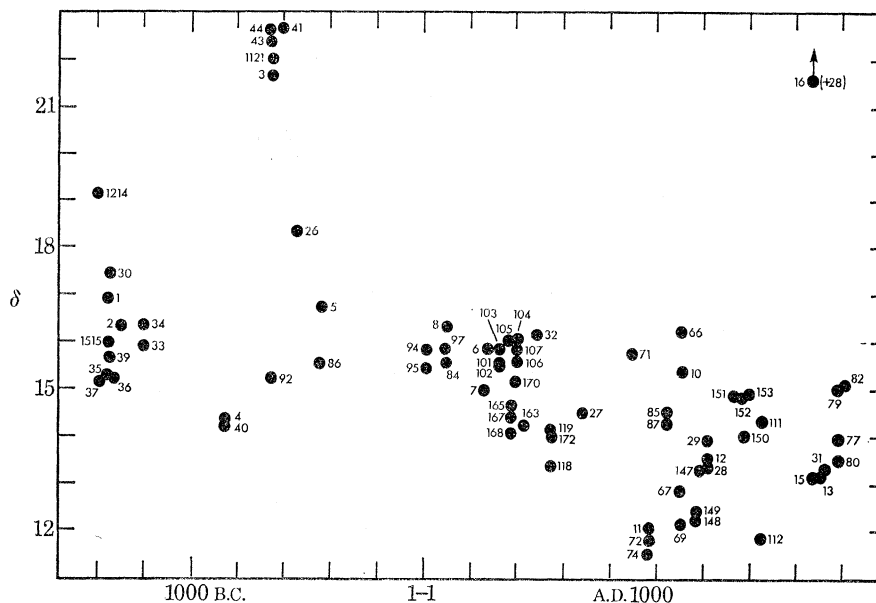

FIGURE 5. ^{18}O contents determined for some ancient glasses. Data are arranged in chronological order. (Note change of scale from figure 4.)

While it is true that these experiments included only two chemical compositions and a few sets of melting conditions, these results nevertheless can be taken as evidence that the ^{18}O contents of the glasses made in early times must depend primarily on the ^{18}O make-up of the raw materials used and that differences in melting conditions between different factories would not have had an important effect on the values we determine for samples of these glasses today. Consequently, ^{18}O determinations should prove to be a valuable index for classifying early glasses and the resulting classifications should reflect differences and similarities not only between the nature of the raw materials used in different factories but perhaps also between the origins of those raw materials. However, a few qualifications become evident immediately.

Different combinations of entirely different raw materials can produce glasses with identical ^{18}O contents. For example, the samples O-37, 151 and 79 are of widely disparate origins but

have, within experimental errors, the same δ values. Also, it is unlikely that there will be many cases where it will be possible to pin down the exact sources of raw materials used for making particular early specimens, despite the fact that one such instance to be cited below may belie this. But classification schemes are nevertheless still of value because when particular archaeological or historical questions arise, they can often be answered on the basis of whether groups of objects are similar or different. In other words, the relationships between the δ values for different glasses are useful even though we may not know exactly what differences in the ingredients have produced these relationships. The usefulness of oxygen isotope determinations may be enhanced by this aspect of diagnosis because values of δ apparently can be used to distinguish between glasses which are indistinguishable in their chemical analyses. This is well illustrated by glasses O-11, 71, 72 and 74. These are indistinguishable on the basis of chemical analyses, but the δ value for O-71 is so different from the other three that it obviously

TABLE 2. CALCULATED AND DETERMINED ^{18}O CONTENTS OF SOME GLASSES†

experimental melts			glasses from Jelemie				chemical compositions		
glass	δ_{calc}‡	δ_{exptl}§	sample	δ_{calc}‖	δ_{calc}‡	δ_{exptl}		I,Y	H,Z
I	11.47	11.54	0–163	14.7$_9$	14.3$_4$	14.17	SiO_2	70.0%	70.0%
Y	9.01	9.05	0–165	14.5$_5$	14.1$_3$	14.64	Na_2O	—	18.0
H	11.55	11.57	0–168	14.6$_7$	14.2$_4$	14.07	K_2O	17.0	—
Z	14.15	14.00					CaO	13.0	7.08
							MgO	—	4.92

Glasses H and Y were melted from the same sand
Glasses I and Z were melted from the same sand.

† δ_{calc} values were calculated by treating δ as an additive property.
‡ The following fractionation effects were assumed:

$$\text{in melts: } \delta_{CO_2} - \delta_{melt} = 3.0,$$
$$\text{for dolomite: } \delta_{CO_2} - \delta_{dol} = 4.0.$$

§ Values for glasses I, H and Z are means of four glasses melted under different conditions. Value for glass Y is the mean of three glasses. Variation in melting times and temperatures between 2 and 24 h and between 1200 and 1600 °C did not show any effect upon δ for the resulting glasses.
‖ The following values were assumed:

$$\delta_{SiO_2} = 10.93 \text{ (Belus River beach sand, quartz fraction)};$$
$$\delta_{CaO} = 29.02 \text{ (Belus River beach sand, shell-hash fraction)};$$
$$\delta_{Na_2O} = 39.77 \text{ (modern natron from Wadi Natroun)};$$
$$\delta_{K_2O} = \delta_{Na_2O}; \delta_{MgO} = \delta_{CaO}; \delta_{R_2O_3} = 15.0.$$

was melted from completely different raw materials. In this case, we happen to expect this result because the odd glass was excavated in Syria and two of the other three in Iran. But this example also serves to illustrate the potential usefulness of this technique in another way as well. The two glasses O-11 and 74 are both known to have been found in Iran, but glass O-72, an Islamic weight of roughly similar date, is of unknown provenance. The isotope data strongly suggest that the glass weight was made of very similar raw materials and could have been made in Iran.

It is clear that weathering can have a drastic effect on the ^{18}O content of a glass. For example, sample O-15 is from a wine bottle recovered from beneath the sea at Port Royal, Jamaica. It is known to have been submerged in sea water from at least as early as 1692 until 1959. The effects of this weathering are obvious for the glass bears a thick weathering crust (as much as 3 mm thick in some places) consisting of leached glass. The leaching of the glass involves an opening up of the glass network structure and makes the body of the glass susceptible to extensive exchange reactions. Thus one expects to find the ^{18}O content of the weathered remains of the glass to

differ from that of the glass itself. This proved to be true. The δ value for a sample of the un-weathered glass removed from the body of the object itself is 13.15, while the sample of the weathering crust has a δ value of 28.11. In the case of this glass, the alteration was obvious and the isotope effect was anticipated beforehand. In sampling all of the other glasses studied, special efforts were made to avoid including any of the weathered portions of the glasses and to use only intact, unweathered glass in the samples. (A few more examples of weathered and unweathered glass from the same objects are now being studied.

We cannot as yet, however, say for sure that our data are entirely free of variability due to weathering effects. There are types of early glasses which, although they remain glassy and intact, show certain properties which suggest that they may have taken up moisture and might, therefore, have undergone some oxygen exchange. Experiments are underway now to learn whether or not such invisible weathering effects could complicate the oxygen isotope studies.

The findings reported in figure 5 have been plotted in a rather arbitrary way. What we intend to illustrate is the variation in ^{18}O contents among these glasses of disparate age, provenance, and chemical composition. (If differences in δ had not emerged from a survey of such a wide sampling, it would have discouraged further studies on glasses.) Strictly speaking, only one coordinate was really needed to present this variation. A simple scale, like that of a thermometer, of δ values would have sufficed. But in order to organize the results and make them more readable, a second coordinate, time, was used to spread the graph out and facilitate comparisons between those glasses which most logically should be compared to one another. This means of plotting also served as a trial plot to uncover any time effects. Inspection of the chronological plot suggests a trend sloping downward towards the right which in turn suggests very loosely that the older glasses may have been altered by some ageing processes, the net effect of which was to increase the ^{18}O content. At present we are inclined to believe that this is coincidental because of the experimentally demonstrated dependence upon the ^{18}O contents of the ingredients. Even so, in view of evidence from other areas of research dealing with the weathering of ancient glasses, it is felt that the existence of some hidden ageing effect which does not manifest itself in a readily visible form cannot be ruled out until our other experiments, mentioned above, have been completed.

A consideration of the chemical composition of most early glasses leads to the conclusion that most of the oxygen in the glasses was probably contributed by the principal silica-bearing ingredient. After writing out equations which treat δ as a simple additive property, it seems that δ for the glass could almost be treated as δ for the silica-introducing ingredient (sand for example) modified by the δ values of other ingredients. Rather large variations in δ for the alkali, lime, and for the minor ingredients are required to account for differences as great as those observed among the glasses we have studied. A rough calculation shows that for two glasses of identical soda–lime–silica composition, both prepared with a silica ingredient having a δ of 14 but different sodium carbonates with δ values of 30 and 10 would yield, respectively, glasses with δ values of 15.5 and 13.5. We expect, therefore, that most of the variations seen in the glasses studied reside in variations among the primary silica ingredients.

Among the glasses studied were five fragments of cullet excavated at the site of the ancient glass factory of Jelemie in western Galilee (Weinberg 1965; Perrot 1965). The factory appears to have operated in the third quarter of the fourth century A.D. Four of the δ values of the glasses (numbers 163, 165, 167 and 168) agree very well with one another and the fifth, 170, seems to be just a little greater. Full quantitative chemical analyses have been made of three of these

samples, and thus it is possible to attempt a rationalization of these data by making some assumptions about the possible raw materials.

Because of the location of the Jelemie glass factory it seems very likely that the silica source used for making this glass was sand from the dunes near the mouth of the Belus River, which is only about 24 km away. (Actually there is some reason to believe that the glass itself was not made as a material at Jelemie but might have been made elsewhere and was brought to Jelemie to be resoftened and made into vessels. Even so, Belus River beach sand is still the most likely source of silica for glass factories located in this region.) We have calculated earlier that the Belus River beach sand contains just about the proper amount of lime in the form of shell hash to account for the lime content of early glasses from this region. That is to say, this sand could have been used along with soda to make a two-ingredient, soda–lime–silica glass without requiring a separate addition of a lime-bearing ingredient.

We assumed, therefore, that Belus River beach sand was used for the melting of the Jelemie glasses. This fixes δ for the silica at 10.93 and δ for the lime at 29.02. These values are the experimentally determined mean values for the quartz and $CaCO_3$-bearing fractions of three samples of sand collected from the dunes at the mouth of the Belus River. The δ values for other ingredients were estimated as shown in table 2. The remaining choice—an important one— was that of the δ value for the soda portion. Since we have no other values for possible ancient alkali sources, we selected a value of 39.77, the mean of experimentally determined values for two samples of modern natron from Wadi Natroun in Egypt. Actually this is not an unreasonable choice because natron from Egypt is the most likely source of alkali to have been used for the Jelemie glasses. (This follows from the analysed chemical compositions and gains some support from documentary evidence.)

In any case, by assuming an additive relationship and the experimentally determined values for δ of the assumed ingredients, δ values were calculated for glasses having the analysed chemical compositions of the Jelemie specimens. The results are in surprisingly close agreement considering the looseness of the assumptions made. (Corrections for fractionation processes occurring during melting were also applied in a second calculation.)

Even if one regards the very close agreement as being fortuitous, which is entirely possible, the fact that any agreement at all was obtained strongly supports the hypothesis that the Jelemie glasses were manufactured from ingredients closely resembling the Belus River beach sand, with its attendant shell ash, and an alkali source having an [18]O content closely resembling that of the two modern specimens of natron. It will be interesting to compare the results of similar calculations using δ values for various other alkali sources that we are now analysing.

It will already have been noted from the graphs that there is one group of glasses, those from Nimrud (figure 5), which are very different from any of the others we have studied. These are five specimens of glass which date from the eighth to seventh century B.C. The δ values for these glasses are virtually identical and must represent a glassmaking tradition characterized by the use of some special raw materials. This is not to say, of course, that this isotope composition is necessarily unique to Nimrud glasses. It is more likely that this just happens to be the only example that we have encountered so far. The agreement between the glasses is all the more remarkable because they represent two (or possibly three) very different types of glass objects. Two of the specimens are fragments of the hemispherical bowls found at Nimrud and the others are an inlay from one of the famous ivory inlay plaques and a piece of light blue opaque cullet which might or might not have been associated with the manufacture of the inlay glasses. If we

disregard any hidden ageing effects, considerations similar to those made for the Jelemie glass suggest that the silica source for these Nimrud glasses might have been an unusual one, as possibly was also the alkali source. To obtain δ values of 22.5 for the glasses, the silica source would have to have a δ value of about 20 (assuming the alkali to be about 40, like the natron). This value of 20 for the silica is somewhat greater than the value for most of the sands that we have studied so far. This may well be the result of the glasses having been prepared from some low-temperature form of quartz, such as chert or flint. Findings from other areas of research in ancient glass indicate that quartzite pebbles may have been the source of silica used by Meso-potamian glassmakers.
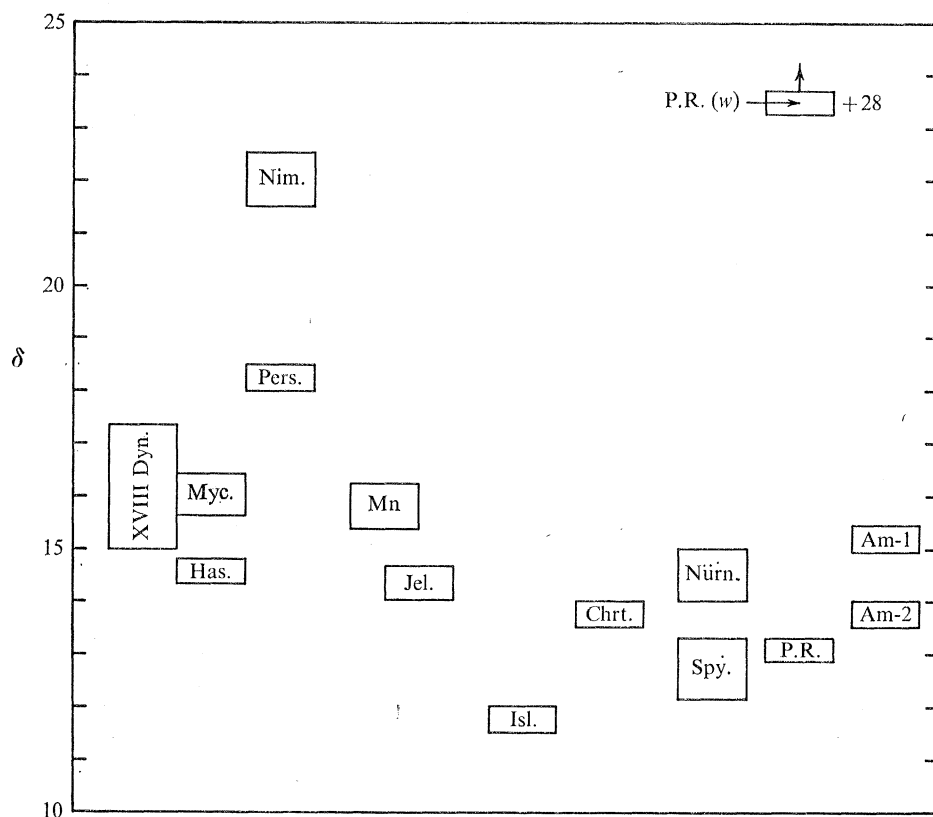

Figure 6. Selected data from figure 5 replotted to illustrate the classification of early glasses by [18]O contents (glasses are arranged in chronological sequence, but are not plotted here on an exact time scale): XVIII Dyn. —7 18th dynasty glasses from Egypt (*ca.* 1350 B.C.). Myc.—2 glasses from Mycenae (*ca.* 1200 B.C.). Has.— 2 glasses from Hasanlu (*ca.* 850 B.C.). Nim.—5 glasses from Nimrud (7th cent. B.C.). Pers.—1 glass from Perse-polis (6th cent. B.C.). Mn—10 Mn-rich glasses, Roman Period. Jel.—5 glasses from Jelemie (4th cent. A.D.). Isl.—2 glasses from Iran (10th cent. A.D.). Chrt.—3 stained glasses from Chartres (1225). Nürn.—4 stained glasses from Nürnberg (1379–86). Spy.—3 stained glasses from Speyer (*ca.* 1170). P.R. and P.R.(w)— 1 glass from Port Royal, with weathering crust (pre-1692). Am-1 and Am-2—4 glasses from the Amelung factory (1785–95).

Oxygen isotopes in ancient pottery

We have also carried out a few trial determinations of δ values for samples of ancient pottery. Only four sherds have been analysed so far but they show distinctly different values of δ ranging from 16 to 23. The sherds came from Jericho, Athens, Amarna, and Caerleon. Since pottery does not consist of a one phase system as glasses do, the study of pottery might possibly be complicated by the presence of oxygen bound in different chemical states within the sherd.

Nevertheless, it seems very worthwhile to investigate more pottery sherds to see if useful dating or classification schemes might not be developed for pottery. We have planned further experiments along these lines, as well as with some other archaeological and historical materials.

Possible archaeological applications of other isotope systems

There are indications that the small isotopic variations detected in occurrences of some copper minerals (Schields, Goldich, Garner & Murphy 1965) may lead to a means of determining the types of ores from which early specimens of copper were smelted. But the extent of isotopic variablity among copper ores is very small compared to that found in lead ores. W. R. Shields and his colleagues (unpublished results) have undertaken some determinations on copper extracted from archaeological objects and found a few examples of significant variation. Since the natural variations may be a result of very slow chemical alteration of the minerals, this raises the possibility that isotope determinations on samples of patination found on ancient copper-containing objects may provide a means of authentication. While this is highly speculative at the moment, the consequences of such a method would be of such extraordinary value that exploratory work should be undertaken.

Among other chemical elements, sulphur, which is known to be subject to fractionation in nature, may offer some possibilities. In fact, in view of the increasing refinement in instrumentation and growing compilations of data on other elements from geological and geochemical research, the prospects should be continually reviewed. Also, fractionation produced by biological systems, which might preferentially take up some isotopes over others, should not be overlooked.

Catalogue

This is not a complete list of all the samples plotted in the accompanying figures. Included here are only those which are discussed in the text. A full catalogue will appear in the final publications, which are now in preparation.

Lead extracted from ancient glasses and related materials

Pb-90. Lead extracted from a fragment of bright red opaque glass from the north end of the Burnt Palace at Nimrud. This glass was once thought to date from the early sixth century B.C. More recent considerations of its stratigraphy, however, have led to the conclusion that it probably does not date from before about 220 B.C. We have confirmed Plenderleith's and Bimson's chemical analysis (published by Turner) which showed that the glass contains about 22.8 % PbO. C.M.G. analysis no. 200.

Pb-404. Cane of yellow opaque glass, El Amarna, XVIIIth Dynasty. Contains $Pb_2Sb_2O_7$ colorant-opacifier (H. Smith, Department of Egyptology, University College, London).

Pb-405. Another specimen similar to Pb-404.

Pb-408. Cored vessel, Nuzi, *ca.* 1450 to 1375 B.C. Sample is of yellow opaque threading containing $Pb_2Sb_2O_7$ colorant-opacifier. Semitic Museum, Harvard University, Nuzi M 100/1. (See D. Barag in Oppenheim, von Saldern, Barag & Brill (1970.)

Pb-409. Cored vessel, Tell al-Rimah, *ca.* 1500 B.C. Sample is of weathered remains of yellow opaque threading, containing $Pb_2Sb_2O_7$ colorant-opacifier (D. & J. Oates, Institute of Archaeology, London. TR 3623.)

Pb-410. Fused mosaic glass beaker. Tell al-Rimah, *ca.* 1500 B.C. Sample is of weathered buff-coloured remains of glass which contains $Pb_2Sb_2O_7$, and was probably originally a light green

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