THE FISSION-TRACK DATING OF MAN-MADE GLASSES: PRELIMINARY RESULTS

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Most of the techniques that the geochemist uses for dating geological materials offer little promise of being usefully applied to dating man-made objects. Methods such as potassium-argon dating not only require elaborate and painstaking experimental procedures but also make use of time scales best suited to the measurement of ages of the order of millions of years. However, one of the newest techniques, fission-track dating,[1] will be shown here to have a definite though limited utility for dating man-made glass objects. This technique has been used successfully for the dating of minerals and of naturally occurring glasses such as obsidians, tektites, and impact glasses,[2] all of which are millions of years old. The most important requirement for applying the method to the much younger man-made glasses is that the samples contain appreciable concentrations of uranium.

The principle of the technique is quite simple. The natural glasses mentioned above contain very minute quantities of uranium, as do most naturally occurring materials. During the long history of the objects the uranium has undergone a very slow, spontaneous process of decay, which consists in part of the nuclear fission of individual atoms of uranium. This decay does not have any visible effect on the glass. However, if a freshly fractured surface, or a polished surface, is given a mild etching treatment with hydrofluoric acid, microscopic etch pits appear wherever a uranium atom has disintegrated near the surface. The fission of an atom releases a great deal of energy, which disrupts the surrounding glass network and makes it more susceptible to the chemical attack of the acid.

If one counts the etch pits microscopically, and also knows the uranium content of the

1. P. B. Price and R. M. Walker, "Fossil Tracks of Charged Particles in Mica and the Age of Minerals," *Journal of Geophysical Research*, Vol. 68, 1963, pp. 4847-4862.

2. R. L. Fleischer and P. B. Price, "Glass Dating by Fission Fragment Tracks," *Journal of Geophysical Research*, Vol. 69, 1964, pp. 331-339; "Fission Track Evidence for the Simultaneous Origin of Tektites and Other Natural Glasses," *Geochimica et Cosmochimica Acta*, 1964, to be published.

glass, it is then possible to use the known rate of decay of uranium to calculate the "age" of the glass. Actually, the age calculated is the time that has elapsed since the glass was last heated, because heating of the glass will anneal or repair the undeveloped fission-damage centers.

Instead of doing an actual chemical analysis for the uranium content of the sample, which is time-consuming and has other attendant difficulties, there is a simpler way to proceed. After making a count of the etch pits, the same sample, or one from an adjacent area, can be placed in a nuclear reactor and bombarded by a known dose of thermal neutrons. The neutron bombardment induces a further, much more extensive decay of the uranium in the glass. (This is induced fission as contrasted to the spontaneous fission discussed above.) By repeating the etching step and making another count of the pits, it is possible to calculate the age of the glass. Once this induced fission treatment has been made, the irradiated sample can never again be used for fission-track dating. Fig. 1 shows an example of the etch pits.[3] In this sample they are about four microns in diameter. It should also be noted that only a slight, transient radioactivity is introduced into the sample when dealing with glasses such as are being discussed here.

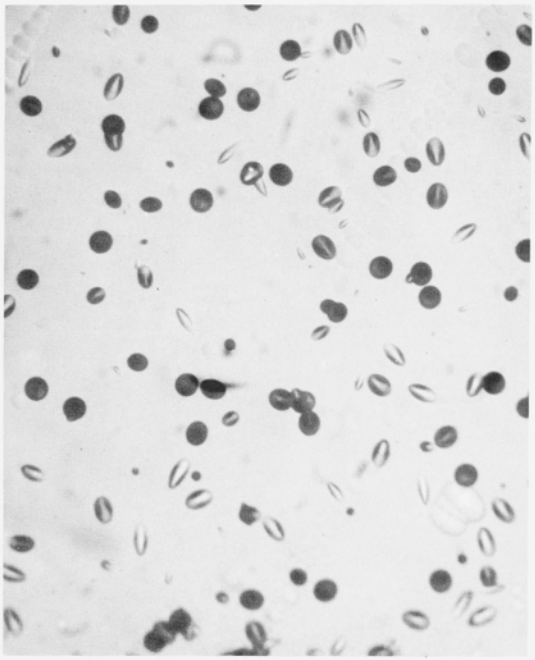

FIG. 1. *Etch pits developed from fission tracks formed by neutron-induced fission in glass from a candlestick (Sample 1). From the ratio of the number of tracks originally present to the number of new ones found here, an age of 124 years was determined. Sample was etched 5 seconds in 48 per cent HF. Approx. magnification 1300×.*

The rate of the spontaneous decay of uranium is very slow, and natural glasses contain but little uranium, of the order of 0.0002 per cent by weight. On an average, in each cubic centimeter of these glasses only one atom of uranium can be expected to disintegrate every two years. It is only because the ages of the glasses are so great that measurable numbers of pits can be developed and observed. In order to date man-made glasses, which are less than a thousandth of the age of most natural glasses, it is necessary that they contain considerably more uranium. To use fission-track dating on a sample 100 years old there must be a minimum of about 0.2 per cent uranium present; for a sample 2000 years old, 0.01 per cent uranium is necessary.

Among the hundreds of analyses of ancient glasses published, only one has made mention of a measurable uranium content. This was an analysis by J. J. Manley and E. G. Laws in 1912.[4] They reported that a yellow-green trans-

3. Fig. 1 also illustrates another point of interest. In the upper left hand corner, and elsewhere, can be seen microtrenches or "worm-tracks" consisting of a series of rounded pits occurring along a straight line. The same phenomenon is often seen in objects of ancient glass which have been weathered by natural means. In the case of the samples shown here, the trenches result from the acid etching of microscratches left by the polishing. In the ancient glasses the much slower decomposition caused by water develops similar microscratches into trenches that are often large enough to be seen by the unaided eye.

4. J. J. Manley and E. G. Laws, "Analyses of Green and Blue Glass from the Posilipan Mosaic," *Archaeologia*, Vol. 63, 1912, pp. 106-108.

lucent tessera removed from a first century mosaic at the Imperial Villa at Cape Posilipo near Naples contained 1.25 per cent U_3O_8. This analysis has always appeared a bit dubious, largely because the glass was also said to contain about 20 per cent potash instead of the soda which is usually found in Roman glasses. Unfortunately, the analysts seem to have left no record of their chemical procedures. Professor Caley[5] discussed this analysis at length and recalculated the uranium content to a probable value of 1.5 per cent UO_2. In a recent publication Professor Franz Kirchheimer[6] confirmed that a sample of this glass he had obtained from the Ashmolean Museum at Oxford, did indeed contain 1.6 per cent UO_3.

Since uranium is radioactive, one quick way of determining whether or not a glass contains uranium is to scan it with a Geiger counter. A survey of the collection of The Corning Museum of Glass with this type of counter revealed many examples of uranium-containing glasses of nineteenth and twentieth century origins, but not a single piece of ancient glass was found which had enough radioactivity to register on the counter. A similar survey was made of part of the collection of ancient glass of The Metropolitan Museum of Art,[7] and Professor Kirchheimer had previously surveyed the Roman glass in the Römische-Germanisches Museum in Cologne.[6] Both of these examinations also yielded negative results. It must be added, however, that these conventional gamma-ray counters would have only detected the radioactivity resulting from a concentration of 0.2 per cent uranium or greater. Therefore, it is entirely possible that objects of ancient glass having enough uranium to be datable could have been missed because they did not have enough to register on these counters.

It appears at this point that the usefulness of fission-track dating for studying ancient glass will be limited to some of the yellow-green glasses made in the neighborhood of Naples or to a few other unusual glasses that might contain uranium as an accidental inclusion. Nevertheless, if interested persons should know of any suspiciously bright yellow-green or honey-colored glasses from other places and periods, it would be worthwhile to test the objects for uranium. The yellowish uranium glasses can be quickly detected for they should produce a brilliant green fluorescence under ultraviolet light. The brownish or honey-colored glasses may show a weaker fluorescence. In fact, if the uranium is present only in a chemically reduced state or if a good deal of lead is present, the fluorescence may be very slight, even though the glass would still be datable by this technique. Either color of uranium glass should show a significantly greater radioactivity than other ancient glasses. If the uranium content is greater than 0.2 per cent, the radioactivity should show up on an ordinary portable Geiger counter; but if it is only of the order of 0.01 per cent (still datable) it could only be detected by a more sensitive instrument such as an alpha-particle counter.

Although fission-track dating may not be widely applicable to ancient glasses, it definitely can be used to date more recent glasses.

The intentional addition of uranium to glass as a colorant is attributed to the German chemist Martin Heinrich Klaproth. In 1789 Klaproth became the first to recognize uranium as a chemical element. At about the same time he prepared some uranium-containing glasses, but the whereabouts of these glasses seem to be no longer known, if indeed they still exist at all.[8]

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5. Earle R. Caley, *Analyses of Ancient Glasses 1790-1957*, The Corning Museum of Glass, Corning, 1962.

6. Franz Kirchheimer, "Urangläser in alter Zeit," *Glastechnische Berichte*, 36, No. 12, December 1963, pp. 488-490.

7. The authors thank Mr. Murray Pease of The Metropolitan Museum of Art for his assistance in making the survey.

8. Klaproth was also the first chemist to publish (in 1798) and apparently the first to accomplish, the chemical analysis of any kind of glass. It is in keeping with his reputation as an archaeometrist that he analyzed

The exploitation of uranium as a colorant for glasses gathered momentum about 1840, and uranium has frequently been used since then. The concentrations often range upwards from one per cent, making it possible to date even relatively new uranium-containing glasses by the fission-track method.

During the past year five objects (Figs. 2, 3 and 4) of known dates of manufacture were studied at the General Electric Research Laboratory in Schenectady, New York. The fission-track dates determined are in agreement with the known dates of manufacture, as can be seen in Table I. The estimated errors reported result from statistical fluctuations in counting and decay and from errors in specifying the exact dose of neutron bombardment. It is possible that further refinements in the technique, which was originally designed for much older samples, will reduce the magnitude of these errors.

These objects were obtained specifically for these experiments and therefore no special efforts were made to do non-destructive testing. In general, however, it is not necessary to sacrifice as much glass as was consumed in these experiments. A chip of glass a few millimeters on each edge could ordinarily be studied successfully. Alternatively, it would be possible to polish and etch a small patch on some inconspicuous surface of an object.

It may appear somewhat premature to publish findings based on the study of only five samples. It seems worthwhile to announce these findings now, however, in the hope that some readers may have access to examples of uranium-containing glasses of well-established dates which they would be willing to submit as samples for the continuation of this study. In the months to come the authors hope to further substantiate the basis of this technique, to extend it to older glasses if samples become available, and possibly to extend it to other archaeological materials.

FIG. 2. *Candlestick, Sample 1.*

FIG. 3. *Footed beaker, Sample 2.*

glass tesserae from a Roman mosaic. He undertook the analyses to determine what agents were used by the Romans to produce colored glasses. One of the tesserae he analyzed was described as a "light verdigris." Klaproth did not report finding any uranium in these glasses, although he was familiar with the analysis for uranium and conceivably might even have had it in mind to see if the Romans had used uranium. It is ironic—or at least a tantalizing coincidence—that the glasses he chose to analyze came from the Imperial Villa of Tiberius on the Isle of Capri, only thirteen miles across the water from Cape Posilipo, the source of the only piece of ancient glass presently known to contain uranium.

For a general history of uranium and its early uses the reader is referred to Franz Kirchheimer, *Das Uran und seine Geschichte,* Stuttgart, 1963.

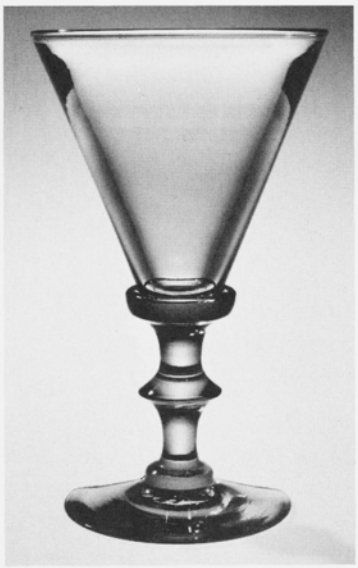

FIG. 4. *Wineglass, Sample 3.*

TABLE I: Ages of Samples

Sample	*Uranium Content as UO_3*	*Known date and evidence*	*Date obtained by fission-track counting**
1.	0.61%	1850-1860 on stylistic basis	1840 ± 20
2.	0.44	Last quarter of 19th century on stylistic basis	1860 ± 18
3.	2.5	Made 1925-28	1924 ± 7
4.	1.21	Made prior to Jan. 1939	1938 ± 6
5.	5.3	Glass melted and poured Dec. 1943	1945 ± 4

*Ranges quoted include the likely errors from statistical counts plus an additional 10 per cent possible error in the neutron dose measurement.

DESCRIPTION OF SAMPLES

1. Candlestick, American, New England area, probably made at the Boston and Sandwich Glass Co. ca. 1850-1860 (Fig. 2). Pressed in two pieces and joined; bright yellow glass showing brilliant green fluorescence under ultraviolet. H. 20.7 cm., maximum D. of hexagonal base 10.4 cm. Scientific Department, The Corning Museum of Glass.

2. Footed beaker, probably French or Bohemian, last quarter of the 19th century (Fig. 3). Pressed in a four-section mold; bright greenish-yellow glass showing brilliant green fluorescence under ultraviolet. H. 11.0 cm., D. of rim 8.3 cm., maximum D. of eight-petalled base 6.3 cm. Scientific Department, The Corning Museum of Glass.

3. Steuben "Topaz" wineglass made in 1925-28 (Fig. 4). Yellow-amber glass showing green fluorescence under ultraviolet. H. 12.3 cm., D. of rim 7.2 cm. Scientific Department, The Corning Museum of Glass.

4. Commercial glass tubing containing 1.19 per cent U_3O_8; light yellow glass. Made by Osram, Berlin, before January 1939. Through courtesy of Dr. Louis Navias of General Electric Research Laboratories.

5. Sample of experimental uranium-containing glass prepared by Alan Werner of Corning Glass Works in December 1943.

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NOTE ADDED IN PROOF

Professor Kirchheimer has kindly sent the authors a specimen of glass which he obtained from the Ashmolean Museum. This specimen is believed to have come from Manley's laboratory. Our own chemical analyses confirmed that this glass contains 20-22% K_2O and 1.56% UO_3. The fission-track age, however, was found to be only about 50 years instead of the anticipated 1900 years. We can therefore conclude that this sample is a bit of the glass which Manley and Laws made in about 1912 in an attempt to duplicate the Cape Posilipo tessera, or else it is a piece of the tessera which they melted down for some experimental purpose. Unfortunately, until other samples from Manley's laboratory can be studied, or even better, a direct survey can be made of the mosaics in the Naples area, we must remain uncertain concerning the presence of uranium in ancient glass.