ANALYSIS BY X-RAY FLUORESCENCE OF SOME AMERICAN OBSIDIANS

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Analysis of minor or trace components of minerals has shown that the relative concentrations of these components often are uniquely characteristic of the source of the mineral, while those of the major components, e.g. silica or alumina, are not. In the case that there exist relatively few sources of the mineral but relatively many sites on which artifacts made from this mineral are found, such analysis can provide significant information on the mode of distribution and related attributes of the object. Obsidian is an example of such a mineral; a recent analytical study of European, Asian, and African obsidians (Cann and Renfrew 1964) has evolved information of the type mentioned. Recently developed instrumental methods of analysis are highly sensitive and rapid, and can often be carried out without damage to the specimen. It is the object of this and the following paper to describe the application of a technique of this kind aimed at relating obsidian objects found in Middle America to putative sources of the mineral, and to distinguish the sources from each other. This, we hope, will provide insight into the mutual contact of the various cultures with each other in prehistoric times.

Obsidian has also lent itself to other types of examination. A fresh surface of obsidian absorbs water from the ambient to form hydration layers (Friedman and Smith 1963) that can be measured under the microscope. The hydration begins when the piece is chipped or flaked, and continues at a knowable rate. Measurement of the thickness of the hydration layer thus provides an estimate of the time elapsed since the surface was worked. The rate of hydration is affected by the average temperature of the site (corrections are easily applied), but the average relative humidity seems to have no significant effect because there is always enough water in a natural ambient to saturate the outer surface with a molecular film of water. This technique, then, may be useful in direct dating of an artifact, but the analytical method to be described here is to be applied to correlations of a quite different kind.

To attain our objective, we must find the distinguishing components that are similar in concentration within a source, but differ between

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sources. To ascertain the presence of such components a limited number of carefully chosen obsidian materials from the same, and from different, sources and a few artifacts found on different sites were subjected to analysis. In view of the promising and consistent results, a more detailed study has been planned.

The successful correlation obtained by Cann and Renfrew (1964) was based on the analysis of obsidian by means of optical emission spectroscopy. The use of that method represented a real advance over conventional chemical analysis since it permits the detection and determination of about seventy elements in a mere fraction of the time required by the latter methods. This suggested to us that an additional saving in time might be effected by the use of the x-ray fluorescence technique. It has attained much favor in recent years because of the great rapidity with which many kinds of samples may be analyzed; all elements having atomic numbers greater than 11 (Na) can be detected with conventional apparatus.

METHOD

The x-ray fluorescent method is simple both in principle and practice. When atoms are irradiated with sufficiently energetic x-rays, each different kind of atom emits a characteristic spectrum of x-rays; these x-rays are sorted according to wavelength, by means of a crystal, analogous to the sorting of visible light by means of a diffraction grating, and they are detected by electronic devices. In practice, the sample, either as a solid or in solution, is placed in a cell and its spectrum recorded on a strip chart. This gives a sort of "finger print" analysis, and is the technique applied in this study. In the more elaborate quantitative mode of operation, careful intensity measurements are made at discrete wavelengths without recording the complete spectrum.

The instrument used was a General Electric XRD-6 with a chromium-target tube operated at 50 kv and 60 ma. In order to record the entire region of interest, two scans were made on each sample. A lithium fluoride crystal ($2d = 4.0267$ A) and a dual flow proportional counter - scintillation counter were used to cover the range 5^{o} to 145^{o} ($2\ \theta$); EDT (ethylenediamine tartrate) crystal ($2d = 8.8030$) was used with the flow proportional counter and a helium path to record the range 60^{o} to 145^{o} ($2\ \theta$). Both scans were made at the rate of 2^{o} ($2\ \theta$) per minute.

Fragments of the obsidian were ground to a fine powder in an alumina-lined vial. The vial, containing the chips and an alumina ball, was shaken by means of a Spex Industries Mixer/Mill (Model 8000) for ten minutes. A shallow container was filled level full with powdered sample (about 2.5 g), inserted into the instrument, and the fluorescent peaks were recorded on the strip chart. Every recorded peak was identified and its approximate intensity in terms of counts per seconds was read from the chart.

Results

Nine specimens of obsidian were analyzed; the results are shown in Table 2. It is most important to understand that the units are observed counts per second for specific lines ($K\alpha$ in every case except Ba, where $L\alpha_1$ was used), and that a given concentration of one element will not necessarily produce the same count rate as the same concentration of a different element. In other words, it is possible, from these data, to deduce differences between samples, but not differences between elements.

DISCUSSION

Study of Table 2 reveals some interesting differences in composition of obsidians from different sources, and some rather striking similarities between the artifacts believed to be from the Pachuca source (Numbers 6 and 7) and the Pachuca mineral specimen (Number 3). It is also encouraging to note the chemical similarities between the Papalhuapa specimens (Numbers 4 and 8) despite the gross difference in physical appearance (black and red).

The data are suggestive but by no means conclusive. The usefulness of the technique could only be demonstrated by analyzing numerous samples from each of the various sources of obsidian. One hopes that a distinctive and consistent composition will be found within each source, but even if this is not so (and it is unlikely), a single element may serve as the distinguishing characteristic. Since the x-ray fluorescent procedure is so rapid and is capable of detecting many elements even at low concentrations, it seems an ideal method for examining many samples in the essential process of finding which elements provide valid correlations. Although the instrument time was approximately two hours per sample, the time required of the operator during the recording process is trivial; with a little practice the analyst can probably identify and measure the significant peaks in about fifteen minutes per sample.

Table 2. X-RAY FLUORESCENCE ANALYSES OF OBSIDIAN

Units: Counts/second above background

1 = "Glass Mt., Napa Co., Calif." (Mineral)
2 = "Site Sol-2, Solano Co., Calif." (Mineral)
3 = "Pachuca, Hidalgo, Mexico" (Mineral)
4 = "Papalhuopa, Jutiapa, Guatemala" (Mineral)
5 = "Copan" (Artifact)
6 = "Teotihuacan, green obsidian presumed to be from Pachuca source" (Artifact)
7 = "La Venta green obsidian (from Pachuca source?) (Artifact)
8 = "Red obsidian from Papalhuapa" (Mineral)
9 = "El Chayal obsidian - Guatemalan (second Guatemalan source)" (Mineral)

	1	2	3	4	5	6	7	8	9
Zr	210	205	720	160	120	600	800	150	110
Nb	30		85			60	70		
Rb	140	165	140	80	65	160	150	80	120
Sr				110	90	20		140	110
Cu	135	145	135	150	135	135	160	135	145
Zn	25	32	78	15		85	75	20	25
Ni	18	23	25	15		25	25	20	25
Fe	1130	1140	1880	1080	1060	1900	1940	1180	780
Co	Trace					Trace	Trace	15	15
Cr a)	840	820	820	750	760	810	840	740	740
Mn	90	80	180	.170	110	180	200	120	35
Ba	32	25	Trace	65	60			65	50
Ti	75	60	140	170	150	145	150	160	120
Ca	85	70	30	230	208	35	35	245	130
K	340	370	305	345	325	360	345	370	330
Cl	100	150	200	90	90	180	150	40	60
Si	1480	1410	1360	1440	1260	1380	1290	1460	1520
Al	510	490	510	510	500	480	450	430	400

a) Most, but probably not all of the Cr intensity is from the Cr target x-ray tube. The difference between samples may still be significant.

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