TECHNICAL CONSIDERATIONS IN X-RAY FLUORESCENCE ANALYSIS OF OBSIDIAN

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This paper discusses the application of x-ray fluorescence (XRF) to archeological research, specifically to the study of the chemistry of obsidians. Recent technological advances in XRF analysis have emphasized the effectiveness of the technique as well as the need to adhere to specific basic procedures. The XRF laboratory at the Department of Geology and Geophysics at the University of California at Berkeley has participated in the chemical analysis of archeological obsidians from throughout the Americas since 1965.

XRF utilizes a primary X-ray beam to displace electrons, generally from the K, L, and M shells. These electrons are replaced by electrons from outer shells producing secondary or fluorescent X-rays. Each element displays a characteristic X-ray spectrum that can be detected and measured, enabling the various elements in a given sample to be identified and quantified.

There are two basic types of XRF detection systems: energy dispersive and wavelength dispersive. Energy dispersive XRF systems generally utilize low power X-ray tubes (40 to 60 watts) to produce the primary x-ray beam, and a lithium drifted, silicon, semi-conductor to detect the fluorescent x-rays (Woldseth 1973). This detection system discriminates between x-rays with different energies. Wavelength dispersive systems utilize higher power X-ray tubes (2000+ watts) to produce the primary beam, and fluorescent X-rays are discriminated by diffraction off of crystals in the detection system that are set to be wavelength-specific according to Bragg's Law (Jenkins 1974; Jenkins and DeVries 1975). In both systems the detected X-rays may be displayed graphically, or the data may be reduced by computer into numerical form.

Hughes (1983: Figure 2-2) illustrates the basic features of the energy dispersive system; the wavelength dispersive system appears in Nelson (this volume). The greater distance between the sample and the detector in the wavelength system, in combination with the decrease in beam intensity that accompanies diffraction, requires that the wavelength system has a higher power X-ray tube. The following discussion pertains to energy dispersive systems similar to the United Scientific Spectrace 440 system in use in the Geology Department at Berkeley.

There are two basic methods of preparing samples for XRF analysis: destructive and non-destructive. The destructive method consists of grinding the sample to minus 400 mesh, and pressing the resulting powder into a pill at approximately 20,000 psi. This technique allows the investigator to accurately analyze for elements with characteristically low energy X-rays, i.e., those elements in the sodium to iron section of the Periodic Table. Although this technique provides a more complete characterization of a given sample, it is often not suitable for archeological specimens. Non-destructive analysis consists of putting the intact specimen into the XRF unit for analysis. This method eliminates time consuming sample preparation, allows the sample to be preserved, and although the scope of the analysis is somewhat limited, it often is sufficient for the archeologist.

It is often desirable to define an "average" composition of source material for artifacts. Either method can be used to define an average composition. The average can be determined by either grinding a number of samples from an obsidian source, mechanically blending the resulting powders, and then analyzing a number of intact specimens and taking the numerical average of the analyses.

Figure 1 is a graphic respresentation of an XRF scan of the U.S.G.S. BCR-1. Notice that the K-beta peaks of rubidium, strontium, and yttrium interfere respectively with the k-alpha peaks of yttrium, zirconium, and niobium. This interference effectively increases the area of the K-alpha peaks, and since the area of each peak is considered to be a function of the concentration of the element in the sample, these interferences must be subtracted before the concentration can be calculated (see Schamber 1977). The problem of over-lapping peaks is resolved by stripping, a process that involved subtracting that part of the peak area contributed by interfering elements by comparing the spectrum of interest with pure element reference spectra (see Figure 2).

Figure 2 is an XRF scan of an intact obsidian flake from the Fish Springs source located in Owens Valley, Inyo County, California. Figure 3 is an XRF scan of a Fish Springs obsidian sample that has been pulverized and pressed into a pill. Note that the peak heights of the elemental and Compton scatter peaks differ from those in the previous figure, due in part to differences in the smoothness and the size of the illuminated surfaces. However, since the Compton peak serves as a scale factor, the calculated concentrations are approximately equal regardless of the absolute number of x-rays detected. Table 1 shows the results of analyzing an intact flake and a powder of the same specimen.

The Compton peak technique works satisfactorily for elements with atomic numbers in the range of 27-41 (Franzini, Leoni and Saitta 1976), and is particularly applicable to elements in the range 37-41 when analyzing archeological samples. It is also possible to analyze for elements in the 55-60 range if a high energy source (such as the Americium 241 source at Berkeley) is available.

This technique is not applicable to elements with atomic numbers less than 27, since the Compton peak does not fall within the energy range of the x-rays produced by these elements. When analyzing for these elements standards must be used for comparison. The standards should resemble the unknowns as much as possible in terms of composition so that the effects of matrix absorption and fluorescence will be minimal in data reduction. Elements within this range may be analyzed only in samples that have been pressed into pills.

The archeologist is generally concerned with keeping his artifacts intact, and is therefore limited to the analysis of trace and light rare earth elements, and it is these values that are generally reported in the literature. It is extremely important that both the method of analysis and the results of an analysis of an international rock standard be included in each report. The inclusion of this information helps analysts in other laboratories evaluate the accuracy of the data included in the report (see Stross et al. 1983). Without such comparative data no such evaluation is possible, and therefore the validity of conclusions based on these data cannot be determined.

Trace element	Unmodified Obsidian flake (ppm)	Pressed Powder (ppm)
Rb	208.3	206.6
Sr	11.5	11.2
Y	34.9	31.9
Zr	95.7	87.6
Nb	38.1	35.2

Table 1. Comparison of trace element concentration values (in ppm) between an unmodified flake and a pressed powder sample from the Fish Springs obsidian source (cf. Jack 1976: Table 11.5).
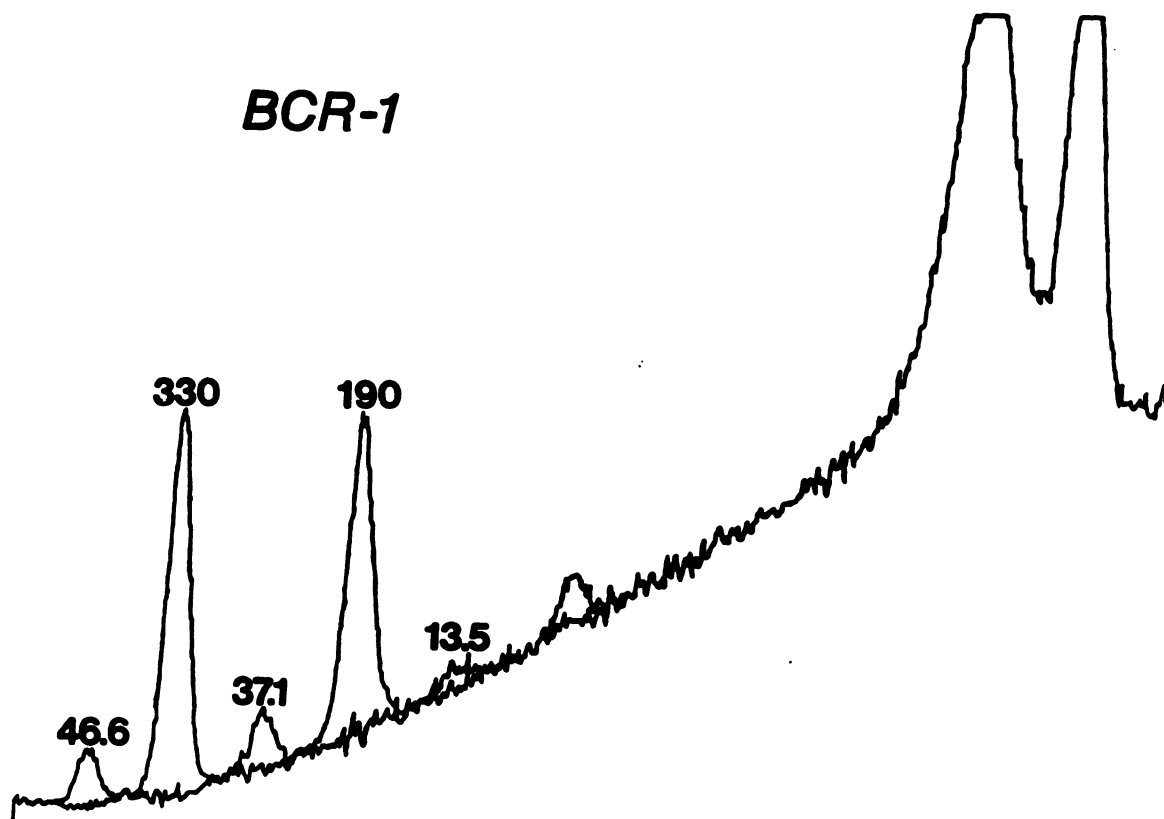

Figure 1. Energy dispersive x-ray fluorescence scan of the 12-20 keV region of the energy spectrum in the U.S. Geological Survey BCR-1 rock standard. Numbers above energy peaks are concentrations in parts per million for Rb (46.6), Sr (330), Y (37.1), Zr (190) and Nb (13.5).
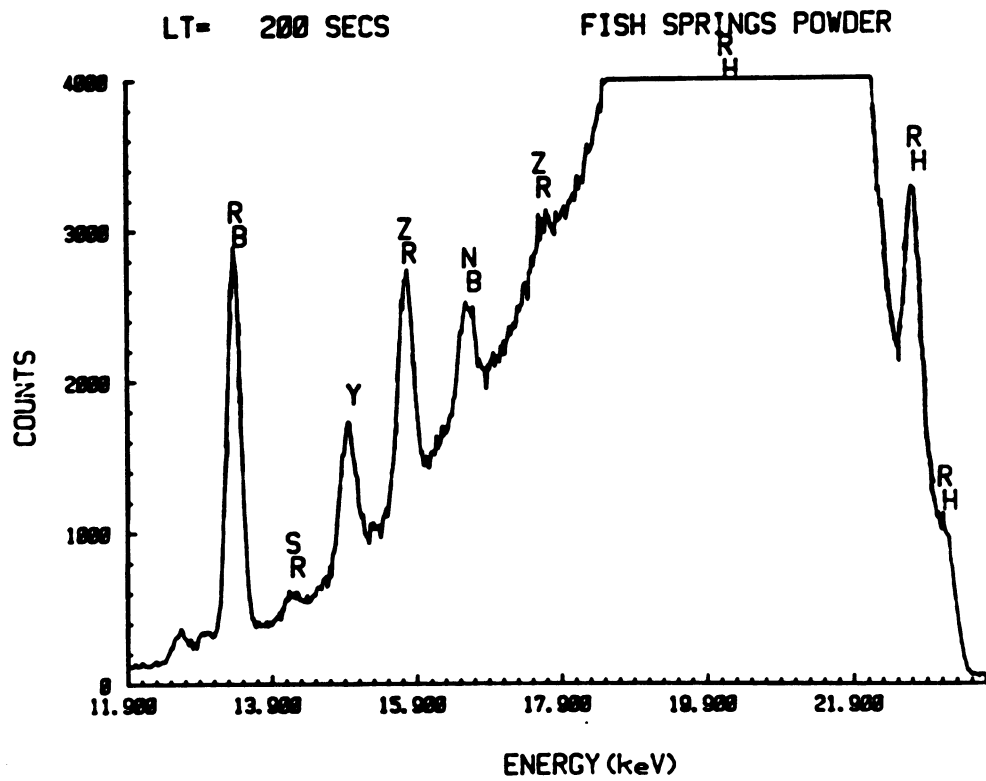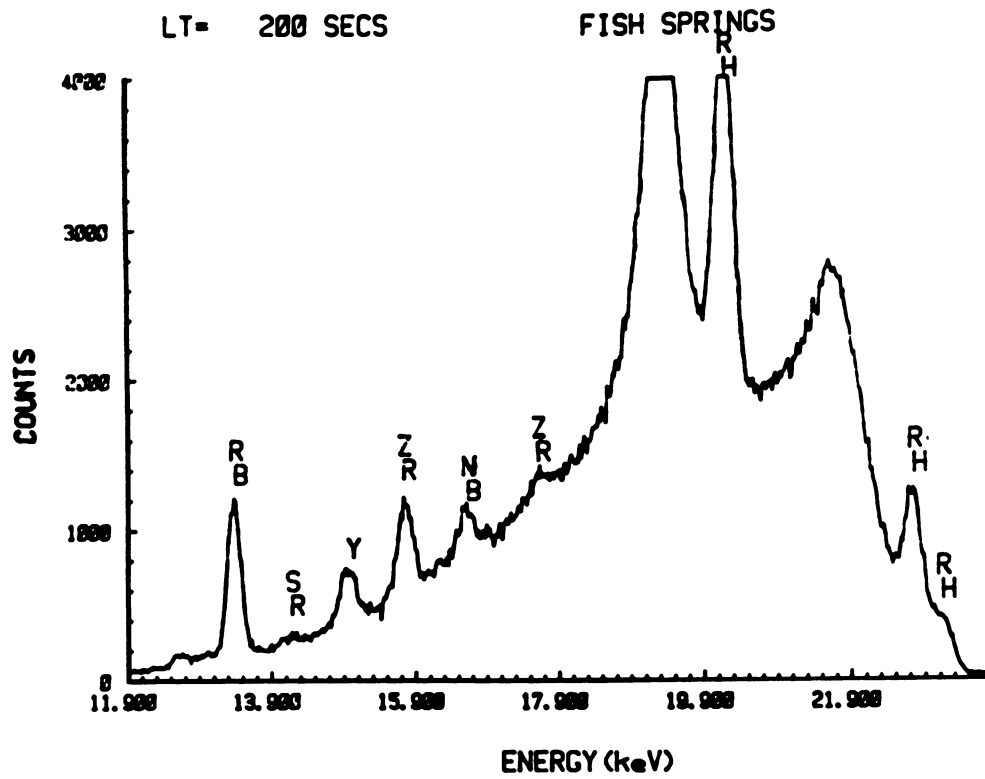
Figure 2 (top). Energy dispersive x-ray fluorescence scan of an
unmodified obsidian flake from Fish Springs.
Figure 3 (bottom). Scan of a pressed powder obsidian sample from Fish Springs.

References

Franzini, M., L. Leoni and M. Saitta
    1976   Determination of the x-ray mass absorption coefficient by measure-
            ment of the intensity of Ag Kα Compton scattered radiation. *X-ray*
            Spectrometry 5: 84–87.

Hughes, R.E.
    1983   Exploring diachronic variability in obsidian procurement patterns
            in northeast California and southcentral Oregon: geochemical
            characterization of obsidian sources and projectile points by energy
            dispersive x-ray fluorescence. Ph.D. dissertation, Department of
            Anthropology, University of California, Davis.

Jack, R.N.
    1976   Prehistoric obsidian in California I: geochemical aspects. In:
            Advances in Obsidian Glass Studies: Archaeological and Geochemical
            Perspectives, edited by R.E. Taylor. Pp. 183–217. Noyes Press,
            Park Ridge, New Jersey.

Jenkins, R.
    1974   *An Introduction to X-ray Spectrometry.* Heyden and Son, Ltd., London.

Jenkins, R. and J.L. DeVries
    1975   *Practical X-ray Spectrometry.* Philips Technical Library, Springer-
            Verlag, New York.

Schamber, F.H.
    1977   A modification of the linear least-squares fitting method which
            provides continuum supression. In: *X-ray Fluorescence Analysis of*
            Environmental Samples, edited by T.G. Dzubay. Pp. 241–257. Ann
            Arbor Science Publishers.

Stross, F.H., P. Sheets, F. Asaro and H.V. Michel
    1983   Precise characterization of Guatemalan obsidian sources, and source
            determination of artifacts from Quirigua. *American Antiquity* 48(2):
            323–346.

Woldseth, R.
    1973   *X-ray Energy Spectrometry.* Kevex Corporation, Burlingame, California.