CHEMICAL CORRELATION OF VOLCANIC ASHES FOR USE AS STRATIGRAPHIC MARKERS IN ARCHAEOLOGY

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Chemical Correlation of Volcanic Ashes for

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Abstract

Volcanic ashes from three Holocene eruptions in the Pacific Northwest (Mazama, 6,600 y.b.p., Bridge River 2,440 y.b.p. and Mt. St. Helens Yn 3,400 y.b.p.) are distributed throughout south central British Columbia. These tephras are often found in local (B.C.) archaeological deposits and once identified could provide archaeologists working in this region with excellent time-stratigraphic markers. In this work, we investigated the use of energy dispersive X-ray fluorescence (XES) analysis and alpha counting analysis of glass concentrates for identifying tephras on the basis of their major and trace element chemistry. Neutron activation analysis (NAA) was also used in order to verify results obtained by the other techniques.

As sample purification proves to be the greatest barrier to the rapid use of these instrumental techniques for routine analysis, a great deal of effort was directed towards simplifying sample preparation procedures. By extensively studying the effects of sample preparation on composition, we discovered that the <62μm size fraction of sieved ashes is mostly glass and can be used to identify the B.C. tephras with only simple pre-treatments. With such pre-treatments both XES and alpha-counting proved to be simple instrumental techniques that allowed the identification of the B.C. tephras with high degrees of reliability and a minimum of effort. With XES, Zr and K were useful elements for distinguishing among the three B.C. tephras; alpha counting permitted the ready identification of Mt. St. Helens Yn on the basis of U and Th concentrations. XES offered the advantage of rapid laboratory analysis while alpha-counting offered simple analysis with the potential of identifying tephras in the field.

In addition to developing these routine methods for identifying the B.C. tephras we used the three instrumental techniques to analyze glass separates from the B.C. tephras plus three additional sources. The results showed that by using the three instrumental techniques either singly or in combination one can readily distinguish most or all of these tephras. These methods could therefore be useful for characterizing tephras in an unknown region.

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Chapter 1

INTRODUCTION

Certain volcanoes tend to produce catastrophic (Plinian style) eruptions spreading tephra over thousands of square miles. Volcanic ashes from three such Holocene eruptions in the Pacific Northwest (Mazama, 6,600 y.b.p.; Bridge River, 2,440 y.b.p., and Mt. St. Helens Yn, 3,400 y.b.p.) are distributed throughout south central British Columbia, Canada and are often discovered in local (B.C.) archaeological deposits. Many of the major eruptions in the Northwest have been dated by independent means. Once identified, therefore, these tephras could provide archaeologists working in this region with excellent time-stratigraphic markers.

The idea of fingerprinting tephras for correlative purposes is not new, and a variety of methods has been used to identify tephras with varying degrees of success. Most methods, however, require tedious amounts of sample preparation. Because in our work there are relatively few tephras to identify, our main objective was to develop a simple, rapid, yet reliable method for routinely identifying tephras discovered in local archaeological sites. To this end, the use of energy dispersive X-ray fluorescence, or X-ray energy spectroscopy, (XES) was developed for the routine identification of the three B.C. tephras. With an extensive study of the effects that sample preparation and analyzing conditions have on results, we were able to simplify identification procedures. Neutron activation analysis (NAA) and alpha counting were also examined as alternative means of fingerprinting tephras.

1.1 Widespread Holocene Tephras in the Northwest

The widespread tephra layers in the Northwest are mainly dacitic. Rhyolitic obsidian glass, however, comprises the main bulk with less abundant phenocryst inclusions. Silica content of the magma (determining its viscosity) and gas content ultimately control the eruptive style of a volcano; some excellent texts cover this topic, (e.g. Bullard 1976, 1979; Francis 1976). The Mt. St. Helens 1980, May 18, eruption is a good example of a Vulcanian to Plinian style eruption. Both Vulcanian and Plinian eruptions are extremely violent producing large amounts of air fall deposit. While the tephra produced during a Plinian eruption is composed mainly of new magma, the tephra produced during a Vulcanian eruption includes lithic materials which derive from older volcanic or detrital material. These eruptive styles undoubtedly characterize many of the tephra-producing eruptions throughout the Holocene.

Although we were primarily interested in the Mt. St. Helens (Yn), Bridge River (BR) and the Mazama (M) tephras, samples of Glacier Peak (GP) and White River (WR) were available and were analyzed for comparison. We were also occasionally required to identify some "non-B.C." tephras when samples of tephras commonly found in B.C. were collected within the fallout regions of other tephras. The distributions of the well known Northwest tephras are mapped in Figures 1.1 to 1.5 and a number of the tephras in the Northwest will be surveyed below. There are numerous references covering the identification, dating, and distribution of the tephras discussed in this thesis (e.g. Crandell and Mullineaux 1975; David 1970; Powders and Wilcox 1964)

The 6,600 y.b.p. Mazama eruption (M) from southern Oregon was larger than that of Mt. St. Helens 1980 (cf. Williams 1968). It produced up to 30 cubic km. of tephra which covered over a million square kilometers (Kittleman 1979). This eruption eventually caused the collapse of the summit of Mt. Mazama to produce Crater Lake. Deposits of Mazama ash extend well into southern B.C., Alberta, and Saskatchewan (e.g. Nasmith et al. 1967; Royse, 1967). Samples have been collected as far north as Edmonton, Alberta (e.g. Westgate et al. 1969; Westgate and Dreimanis 1967), and as far east as Empress, Saskatchewan (David 1970). The Mazama tephra may actually be composed of tephra produced from at least 2 eruptions which occurred between 6,600 and 7,000 y.b.p. (Mack and Okazaki 1979). Chemical analyses of

FIGURES 1.1 TO 1.4

Distribution of Widespread Holocene Tephras

1.1 Mazama (6,600 y.b.p.) (cf. 2,9)

1.2 Mt. St. Helens:
Yn (3,400 y.b.p.) (cf. 1,9)
Wn (450 y.b.p.) (cf. 4,8)
T (150 y.b.p.) (cf. 4,7)

1.3 Bridge River (2,440 y.b.p.) (cf.5,9)

Glacier Peak:
G (~14,000 y.b.p.) (cf. 6)
B (~12,000 y.b.p.) (cf. 6)

1.4 White River:
North Lobe (1,900 y.b.p.) (cf. 3)
East Lobe (1,250 y.b.p.) (cf. 3)

1) Crandell, 1962
2) Fryxel 1965
3) Lerbekmo et. al. 1975
4) Mullineaux et. al. 1975
5) Nasmith et. al. 1967
6) Porter, 1978
7) Smith and Okazaki 1975
8) Smith and Okazaki 1977
9) Westgate et. al. 1970

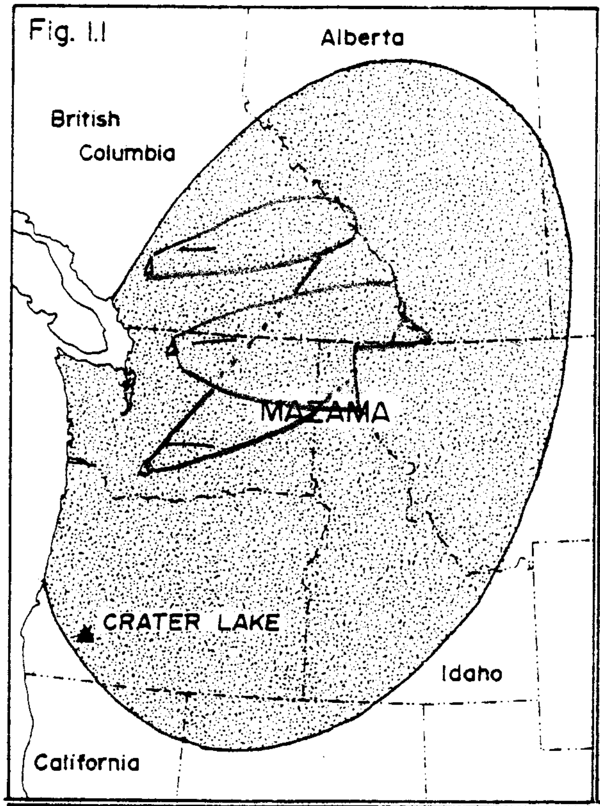


Fig. 1.1

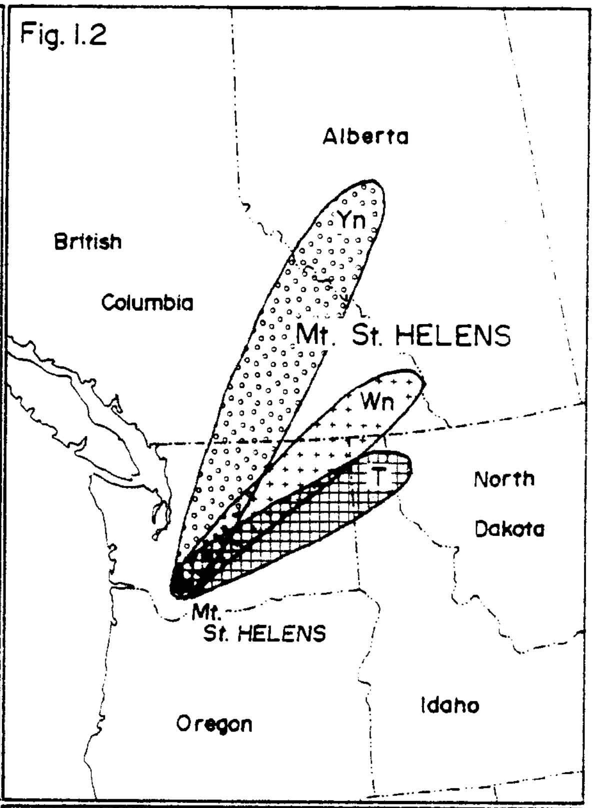


Fig. 1.2

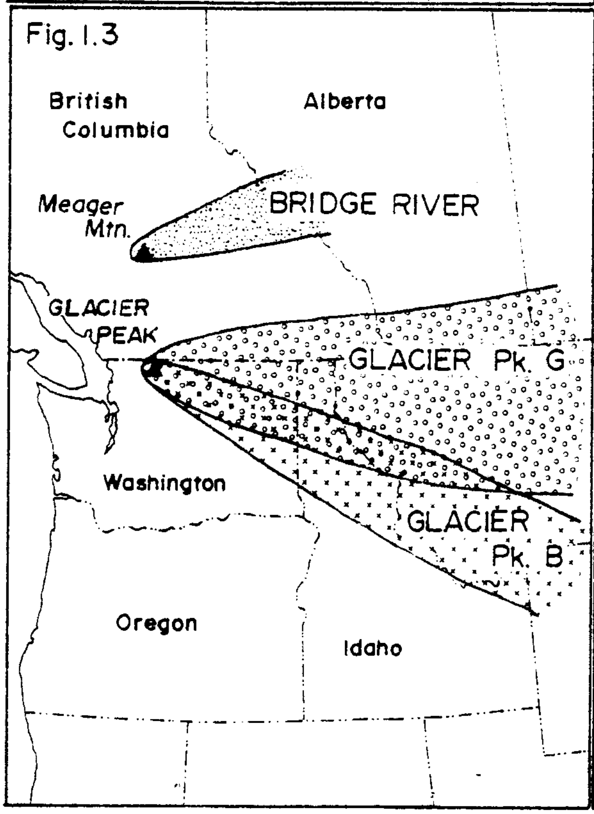


Fig. 1.3

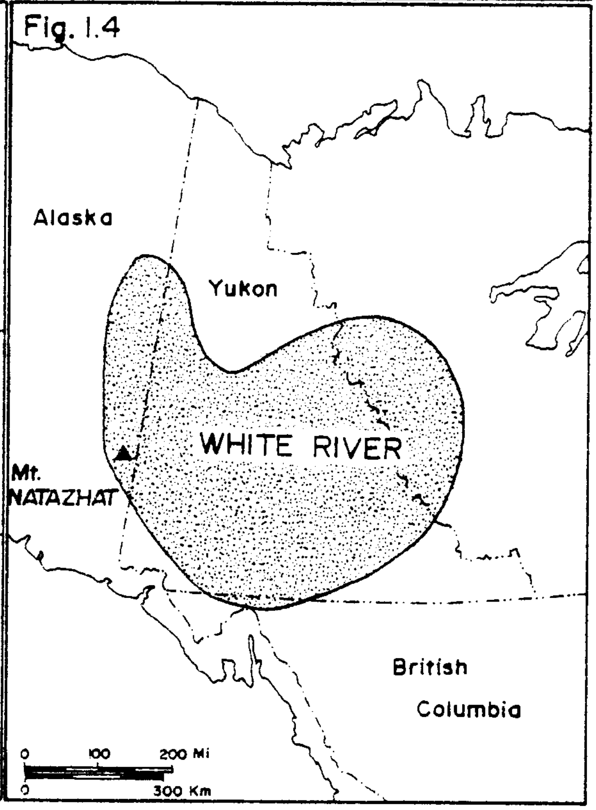


Fig. 1.4

glass, however, show no discernible chemical differences between the layers (cf. Borchardt et al. 1971a; Borchardt and Howard 1971).

The 3,400 y.b.p. Mt. St. Helens (Yn) tephra from Washington forms a narrow northeast trending lobe cutting across South Central B.C. into Alberta and samples have been collected near Entwistle, Alberta (Westgate et.al. 1970). Tephra resembling a second but younger (450 y.b.p.) layer from Mt. St. Helens (W) has been collected near Osoyoos and Kaslo (Smith and Okazaki 1977), but has not yet been discovered further west in B.C.. The 150 y.b.p. Mt. St. Helens (T) tephra (Okazaki et al. 1972) has not yet been found in Canada. Mt. St. Helens has undergone a complicated series of eruptions throughout the Holocene, and up to 8 eruptive sequences have been identified near the source (e.g. Crandell and Mullineaux 1973; Mullineaux et al. 1975). Two additional Mt. St. Helens-like tephras have been identified in Canada. One dated at 2,070 y.b.p. is possibly from the Mt. St. Helens P eruption. The other dated at 4,400 y.b.p. was discovered near Hinton, Alberta and is possibly from the Mt. St. Helens Yb eruption (cf. Westgate 1977; Brewster and Barnett 1979). In the Okanagan region, no more than one layer attributable to Mt. St. Helens has ever been discovered in a land-based deposit.

The 2,440 y.b.p. Bridge River (BR) eruption from Meager Mt. in the Lillooet Valley, B.C. spread tephra across central B.C. into Banff and Jasper national parks (e.g. Nasmith et al. 1967; Reed 1977; Westgate and Dreimanis 1967; Westgate et al. 1970). Recent samples collected from Phair Lake, B.C., extend the southern boundary of the deposit beyond that previously recorded (R. Mathews 1980:pers.comm.). A thin layer in the Otter Creek bog, possibly from Bridge River, suggests that a younger (~2,000 y.b.p.) lobe of BR tephra travelled south (Westgate 1977). In early microprobe work three chemical sub-groups of the Bridge River tephra were identified (Westgate et al. 1970)

Though ash from the ~14,000 y.b.p. Glacier Peak (G) eruption (GPG) has been collected in the Southern portion of Alberta (Westgate et al. 1970), it is believed that glaciation in B.C. precludes its deposition in B.C. (Fulton 1971; Westgate et al. 1970). The Glacier Peak sequence is only recently being fully studied near the source; up to 9 tephra layers may exist near the source vent (Porter 1978). Two of these are from major eruptions, ~14,000 y.b.p. G-layer and ~12,000 y.b.p. B-layer. Westgate and Evans (1978) have discovered a possible third layer (the Irvine bed) near Walsh, Alberta.

The source of the White River (WR) tephra is believed to be under the Klutlan Glacier of Mt. Natazhat in the Yukon and is represented by two lobes. One (1,900 y.b.p.) is a north trending lobe. The other (1,250 y.b.p.) is a more widespread east trending lobe (Lerbekmo et al. 1975). Samples of an earlier tephra (approximately 30,000 to 80,000 y.b.p.) were discovered by J.V Matthews at the Old Crow Site in Northern Yukon (N.W. Rutter 1980:pers. comm.).

1.2 Chemical Methods of Correlation

In order to fingerprint tephras for correlation purposes, one must find some property of the tephra which is consistently the same for ashes produced by a single eruption yet is consistently different for ashes produced by separate eruptions. The study of the ash particle size, grading, color and stratigraphic relationships near the source vent has produced sufficient information for the identification of separate deposits in the vicinity of the eruption (e.g. Porter 1978; Mullineaux et al. 1975). Identification of tephra deposits from distal fallout regions, however, is not easy. The fortuitious association of organic materials with some of these distal deposits has produced C-14 dates which (along with petrological studies) helped identify some distal layers (e.g. Westgate and Dreimanis 1967). However, organics are only rarely associated with tephra deposits, and these layers are discontinuous in distal fallout regions. Alternate means for correlating tephras must therefore be used. Mineral suite identification and determination of refractive indices of mineral or glass shards have allowed the successful identification of tephras in a limited number of cases (e.g. Steen-McIntyre 1977; Wilcox 1965; Westgate and Dreimanis 1967). Recently, instrumental techniques have made rapid chemical analysis possible so that correlating tephras on the basis of their chemical properties has become a worthwhile endeavor. For identification by chemical means, samples must be chemically homogeneous for a single eruption yet chemically distinguishable from tephras produced by different eruptions. As the abundance of minerals decreases with distance from the source, bulk analysis of whole ash samples is an unreliable means for identifying tephras. Only glass or mineral separates have proven to be sufficiently homogeneous for correlation by chemical means (e.g. Dudas et al. 1972; Smith and Westgate 1969; Theisen et al. 1968).

Glass comprises the largest bulk of tephra samples (particulary in distal regions) and is fairly easy to separate in quantity. Glass also is durable through time, second only to quartz and the tectosilicates in its slow rate of weathering (cf. Ambrose 1976; Ericson 1975). Finally, although the minerals in a deposit could be from a variety of origins, any natural glass in a deposit is almost always volcanic. Glass is, therefore, the most commonly analyzed fraction for correlation purposes. In order to separate out the glass, however, a series of treatments is required. Soluble contaminants (carbonates, metal oxides, salts) are generally removed with chemical treatments.

Inherited, detrital and phenocryst minerals are removed with heavy liquid separations or with separations using a Franz magnetic separator. Most techniques of sample preparation prove long and tedious.

Microprobe analysis has been the most widely applied instrumental technique for correlating tephras in the Pacific Northwest (cf. Smith and Westgate 1969). By focusing the electron beam associated with the scanning electron microscope, one can visually select separate glass or mineral shards and analyze them for their major element composition by way of electron beam induced X-ray fluorescence. Theoretically, analysis by such means should eliminate the need to separate out bulk samples of glass or minerals. In practice, however, sample preparation has proven to be as tedious as that required for bulk sample analysis with the other instrumental techniques. For microprobe analysis, glass is first concentrated using heavy liquid separation. Sample purity is then verified under a binocular microscope. The sample is then mounted in epoxy resin, thin sectioned to about 50 µm and coated with carbon in preparation for analysis (Smith and Westgate, 1969). This procedure can be modified by first removing organics and iron oxide coating with peroxide, sodium citrate and sodium dithonite treatments. Forceps are used to select glass shards which are then mounted on a glass slide with epoxy resin. Prior to analysis the interior of a shard is exposed by grinding and polishing (Smith and Okazaka 1977).

One advantage of the microprobe method is that the analysis of the unweathered interior of glass shards and the use of the electron microscope to avoid analyzing microcrystals should produce a more accurate measure of glass composition. The greatest disadvantage of the microprobe technique, however, is that only analysis of major elements is possible. Potassium, calcium, and iron are the most common elements for correlation purposes. Analysis of a larger range of elements, including high Z trace elements, have several advantages over major element analysis. These are: 1) tephra glasses are quite similar in their major element composition, but trace elements can be expected to exhibit greater variability between tephra sources (cf. Bird et al. 1978); 2) for any chemical group, higher Z trace elements have larger ionic sizes and are less likely to leach during hydration or weathering (cf. Jambon et Carron 1973); 3) the larger the number of elements one is able to analyze with a single technique, the greater the possibility of finding at least one element which is useful for discriminating between different tephras. Recently, microprobe users are advocating the use of more than one technique to improve ones potential for identifying tephras (Westgate 1980). Identification of comagmatic tephras may be particularly problematic when using major element chemistry.

The next most widely applied instrumental chemical method for fingerprinting tephras is neutron activation analysis (NAA) (e.g. Borchardt et al. 1971a, 1972). Though NAA has been applied fairly extensively elsewhere, we know of only one study in which NAA was used to identify a number of the tephras from the Pacific Northwest (Borchardt et al. 1971a). With NAA a large range of trace elements can be analyzed. Some disadvantages are that long turn-around times may be required for analysis, it is costly, analysis of bulk samples of glass or mineral separates is necessary, and access to a nuclear reactor or other similar facility is required.

X-ray fluorescence trace element analysis has been used on occasion in tephrochronology (e.g. Sarna-Wojcicki 1976; Smith and Nash 1976), but has not been used to characterize the Pacific Northwest tephras. XRF is cheaper than NAA with considerably shorter turn-around times. In XRF it is necessary to analyze bulk samples of glass or mineral separates.

1.3 Methods of Tephra Correlation Used in This Study

There are two forms of X-ray fluorescence analysis: 1) wavelength dispersive (XRF); and 2) energy dispersive (XES). The X-ray fluorescence work in tephrochronology has been almost exclusively done with wavelength dispersive systems. Use of XES analysis, on the other hand, has several advantages over XRF for trace element analysis of bulk samples. Smaller amounts of sample are required, typically 1 gram for pellets as opposed to about 4 grams for pellets analyzed with wavelength dispersive systems. Though XRF provides better analysis of the major elements, XES provides more efficient analysis of higher Z trace elements. Multi-channel analyzers are easily incorporated into the energy dispersive systems, making the simultaneous measurement of a wide range of elements possible. Analysis times are short in XES, typically 5 to 10 minutes per sample. For these reasons and because it was available, XES was the main instrumental technique used in this study.

With XES one is able to measure not only the major elements, K to Fe, but also the trace elements, Rb to Nb. Although bulk analysis of glass is necessary, It seemed that if at least one element proved to be very different in concentration between a specific pair of tephra sources, steps could be taken to simplify preparation procedures without affecting ones ability to distinguish between the tephra pairs. A great deal of effort was therefore directed towards understanding the effects that sample preparation and analytical conditions have on the results produced by XES.

NAA was also available for the analysis of a limited number of samples. We decided to use NAA to cross check results obtained with XES analysis on pure glass separates. With NAA one could use a different range of elements to verify that bulk glass samples were homogeneous for each tephra source yet chemically distinct from tephras from different sources. The NAA results could also be cross-checked with those appearing within the literature. Two tephra groups in this study, BR and WR, have not previously been characterized using NAA.

Alpha counting is a simple method for determining the uranium and thorium content of a sample. The potential of alpha counting for identifying tephras on the basis of their U and Th concentrations has not yet been examined by other researchers.

Because the alpha counter is a simple piece of equipment it seemed feasible that, if tephras could be distinguished on the basis of their alpha count rates, alpha counting could be adapted into a field method for identifying tephras.

Chapter 2

MEASUREMENT THEORY AND PRACTICE

2.1 General Requirements For a Correlation Technique

The main goal of our work is to identify individual samples as belonging to one or another of the tephra sources. In order to chemically characterize each tephra source one must determine the average concentration and the standard deviation for a number of samples analyzed from each tephra source. The standard deviation is a measure of the variation among the samples used to characterize each source. In order to chemically identify individual samples it must be shown that there is at least one element for which there is no overlap at the two standard deviation range in concentration between the different tephra sources.

In this work we have decided to separate the glass to produce specimens of adequate homogeneity for correlation purposes. In chapter 4 we show that the concentrations of a number of such samples analyzed from each tephra source are Normally (or Gaussian) distributed. We can, therefore, devise a simple test (eq. 2.1) which allows us to determine whether or not a particular element is useful for distinguishing between and identifying individual samples from two different sources with a reasonable degree of certainty.

eq. 2.1

$$A_{y,1,2} = \frac{\left|\bar{x}_{1,y} - \bar{x}_{2,y}\right|}{\left(2S_{1,y} + 2S_{2,y}\right)}$$

$\bar{x}$ = average concentration of element (y) for sources 1 and 2
S = standard deviation

Equation 2.1 uses the 95% confidence interval of the Normal distribution (2 sigma range) as the decision point. If A is greater than 1, there is no overlap at the two sigma range in concentration and the element y is, therefore, useful for distinguishing between and identifying individual samples from tephra sources 1 and 2. It is important to note that the A-coefficient allows us to compare populations of individual samples rather than populations of averages, as would have been the case if we had used the t-test. Comparing populations of individuals is necessary as we are interested in identifying the source of individual samples. The selection of the two sigma range as our decision point is somewhat arbitrary and the significance of the two sigma range for making a probabilistic statement is more fully discussed in Section 6.4.

Given that an element proves useful for identifying samples, the A-coefficient can be modified so that individual samples can easily be compared to each of the characterized sources on the basis of the element (y).

eq. 2.2

$$I_{y,1,2} = \frac{|x_{i,y} - \bar{x}_{1,y}|}{2S_{1,y}}$$

xi = concentration of element (y) for sample (i)

x, S } see eq. 2.1

A value for I of greater than 1 means that the sample (i) does not belong to the tephra source characterized by $\bar{x}1$, and S1. If more than one element is necessary for distinguishing sources, each sample must be compared to all tephra sources using all diagnostic elements. In our work we found that making comparisons element by element was a useful exercise. Some elements are sensitive to low levels of contamination and scanning concentrations of these elements immediately signals problems of this type.

It is evident from the above that we must know three things about our tephras: 1) the average elemental concentrations ($\bar{x}$) for a source; 2) the spread of data (S) about the mean; and 3) whether the concentrations of particular elements are significantly different (A>1) between pairs of tephras.

Our techniques of sample preparation and our analytical procedures are designed to provide an accurate measurement of the composition x of the magmatic glass for each tephra. We must, therefore, attempt to reduce the uncertainty S of our measurement of $\bar{x}$. However, if a particular element y proves to be very different in concentration between two tephra sources, and if a particular sample treatment does not seem to affect greatly the concentration of that element we may eliminate the treatment procedure. A certain increase in the scatter about the mean concentration may be observed but, if the concentration of an element is very different between different tephra sources, such increases in the uncertainty can often be tolerated without affecting our ability to distinguish between tephras. In our work we seek a balance between the requirements for preparation and our ability to identify individual samples from each tephra source. If at least one element allows us to distinguish between tephra sources at an intermediate stage in sample preparation we believe that any additional effort to prepare samples is a waste of time. The factors which will affect $\bar{x}$, S and ultimately A are listed below and must be studied in detail before such simplifications in identification procedures can be made:

Average concentration ($\bar{x}$): The average concentration of samples of glass separates from a particular source will be affected if contaminants are present in the samples. The contamination could be primary phenocrysts present in the magma or xenoliths and detrital material acquired during transport and deposition. These materials are commonly removed during sample preparation. In Ch.3 we study the effects that each step in preparation has on our measurement of $\bar{x}$. If an element proves useful for distinguishing between tephras we can, therefore, know the effect that each step in sample preparation has on that element and whether that treatment is of any value. During these studies we will be examining the partitioning of elements between the glass and mineral phases of the tephra samples.

Our calculations of $\bar{x}$ will also depend on ionic diffusion in the glass during hydration and other forms of weathering. Weathering effects will be discussed in Ch.3 but there is little that can be done in the way of sample preparation to reduce the effect that these phenomena will have on our measures of concentration. We can, however, determine the effect that weathering has on the uncertainty of our measurements of $\bar{x}$ and whether or not such effects significantly reduce our ability to distinguish between tephras.

Standard Deviation (S): The spread in data about the mean will be affected by: variable levels of contamination among samples; different weathering and leaching of samples; uncertainty in our measurement of concentration due to instrumental and operational errors; mode of sample presentation; and counting statistics. In Ch 4 we examine all these factors that can affect the spread in data about the mean concentrations.

Distinguishability (A): Information on factors affecting S and $\overline{x}$ is of no value unless we know whether there are any elements detectable by XES which allow us to distinguish between the different tephra sources (A>1). In our work we studied A by carefully separating the glass from the whole ash for the Northwest tephra groups of interest. Both pure and nearly-pure samples were analyzed. A-coefficients were calculated comparing all tephras element by element (chapter 5). Results obtained using NAA and alpha counting analysis of the samples were compared to those in the literature and were used to cross check results obtained with XES analysis.

Simplification: Once we had information on $\overline{x}$, S and A we attempted to identify a number of individual samples which had undergone a minimum of preparation (Ch. 6). When we were certain of our identification procedures we characterized each of the three B.C. tephras using all samples identified at intermediate stages of sample preparation. By characterizing each source in this manner we could thereby identify future samples with reduced preparation.

2.2 Analytical Techniques and Practice

A) Principles of X-ray Energy Spectroscopy (XES)

Excitation and Fluorescence: A high energy photon or particle beam can be used to create vacancies in the inner electron orbits which, under the appropriate conditions, can cause the sample to emit X-rays that characterize the elements comprising it. There are a number of texts dealing with the principles and practice of X-ray fluorescence analysis (e.g. Bertin 1970; Woldseth 1973). Only information necessary to understand some of our methods will be discussed here.

In XES, we use a monochromatic beam of primary X-rays to induce fluorescence. The desired form of beam absorption for XES is that which produces the photoelectric effect, leaving vacancies in, mainly, the K shell. This is followed by a series of electron transitions with emission of characteristic X-rays. During fluorescence the energies of the X-rays emitted by the sample are exactly equal to the difference in binding energy between the innermost (K) and outer electrons of the elements excited in the sample. As the spread in energy between inner and outer electrons increases with increase in Z higher energy X-rays are emitted by higher Z elements. When K vacancies are created the probability is highest that the ensuing electron transition will produce K-alpha secondary X-rays. Other transitions are also possible in which K-beta, L-alpha, beta or gamma X-rays are produced. Each element, therefore, can be identified by examining X-rays emitted at more than one energy.

The probability of producing the photoelectric effect is greatest when the energy of the incident beam (E) is slightly higher than the K-absorption edges (EB) of the target (K) electrons. When E < EB no absorption by the photoelectric effect is possible. When the energy of the incident beam is less than or greatly exceeds the K-absorption edges of the elements comprising the sample, absorption by the photoelectric effect decreases and other forms of X-ray scatter (Compton and Rayleigh) begin to dominate. In our system we control the energy of the excitation beam and reduce scatter by producing a monochromatic excitation beam. This is done by using Bremstrahlung X-rays, produced by an X-ray tube, to excite a secondary target of pure material. The spectral lines of the secondary target are passed through a filter, composed of the same material as the secondary target, and are then used to fluoresce the sample. We use a silver secondary target to preferentially excite the elements Rb to Nb and a Zn secondary target to analyze better the elements K to Fe.

Monitoring the levels of Compton (Cp) and Rayleigh (R) background scatter can provide valuable information about the composition of a sample matrix. Rayleigh (elastic) scatter occurs when the energy of the incident beam greatly exceeds the binding energy of the electrons in the sample. Rayleigh scatter increases in proportion to Z^2. Compton (inelastic) scattering occurs when the energy of the incident beam is less than that of the binding energy of the electrons in the sample and increases in proportion to Z. The Cp/R ratio varies in proportion to Z^{-1} and serves as an indirect measure of the average Z and the mass absorption coefficient (u/p) of the sample matrix (cf. Kunzendorf 1971; Neilson 1977).

Detection: When a beam of secondary X-rays emerges from a sample it is necessary to identify the energy of each X-ray comprising the beam and count the number of photons arriving at each energy. In an energy dispersive (XES) system, such as that used in this study, the photon energies and intensities of the X-rays are measured with a semi-conducting solid state crystal detector and associated electronics. In wavelength dispersive systems (XRF) the beam of secondary X-rays is first dispersed into separate beams of different wavelengths using a diffraction crystal. These photons are then detected and counted at each wavelength using a variety of detectors or photographic plates. The advantages of XES for our type of work were discussed in section 1.3.

Analysis: In energy dispersive systems one generally uses a multi-channel pulse height analyzer in order to count simultaneously the photons arriving to the detector at a wide range of energies. In figure 2.1 we give an example of a typical energy spectrum produced by analyzing a tephra sample with a Ag secondary target. In fig. 2.2 a sample is analyzed with a Zn secondary target. Using our analyzer the entire spectrum is spread over 400 channels. The position along the X-axis indicates the energy of photons emitted by the sample; each peak identifies an element in the sample. The height (or area) of each peak is proportional to the amount of analyte in the sample. The Compton and Rayleigh scatter peaks are included in our spectra. For high Z materials the Rayleigh scatter peak will be highest; for low Z materials, such as that in our example, the Compton peak will dominate. Additional back-scattering of secondary X-rays in the sample produces most of the background continuum under the peaks. This must eventually be subtracted in order to calculate net peak areas.

Instrumentation: At SFU the Bremstrahlung X-rays are produced with a Siemens X-ray tube. The sample chamber houses a stainless steel multi-sample changer equipped to hold up to 16 samples. The sample chamber is evacuated for analysis and, with remote control, samples can be rotated consecutively to the analyzing position. For the analysis of solid specimens and pellets we use aluminum sample cups with changeable mylar

FIGURE 2.1

Typical Tephra Spectrum Analyzed with
a Silver Secondary Target

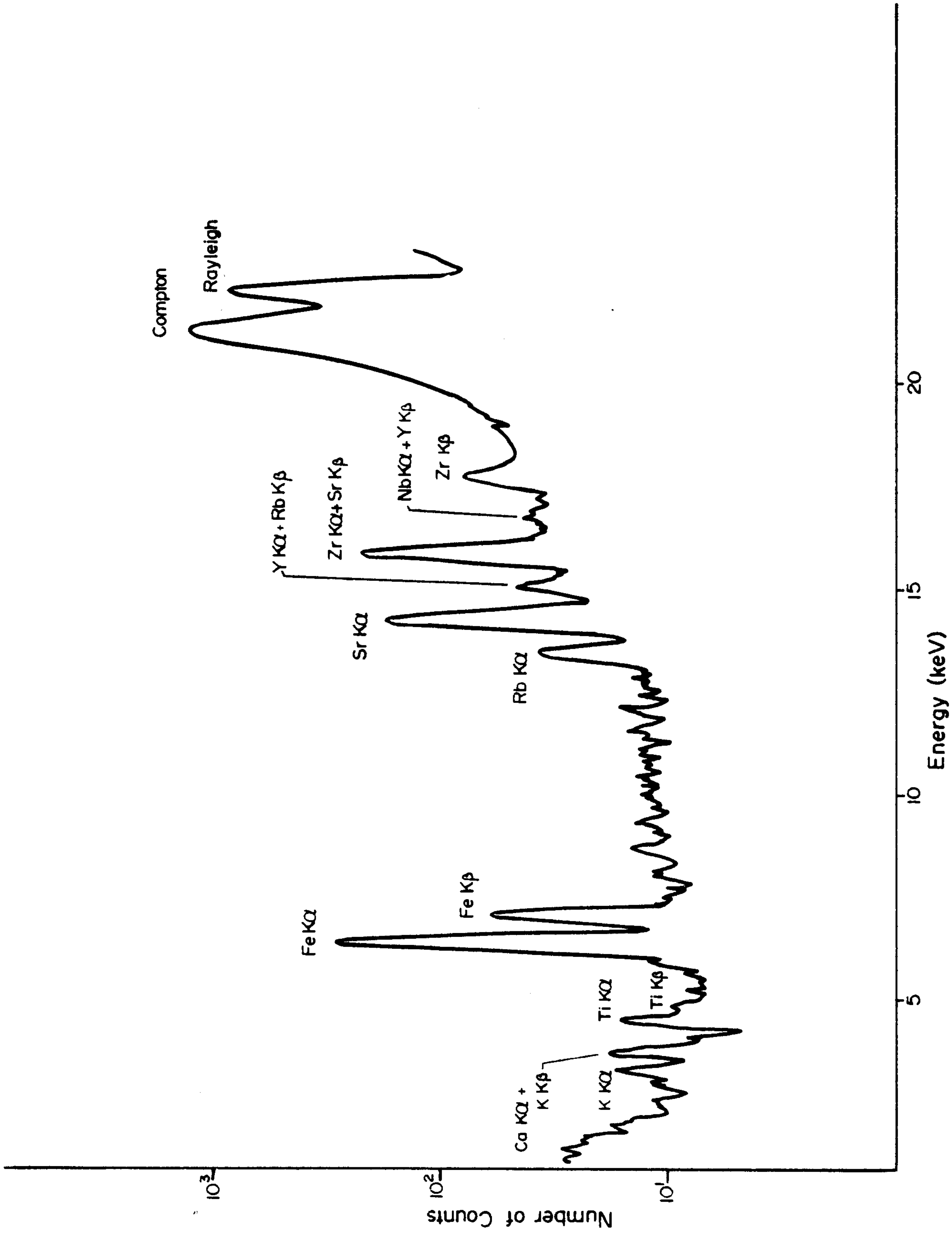
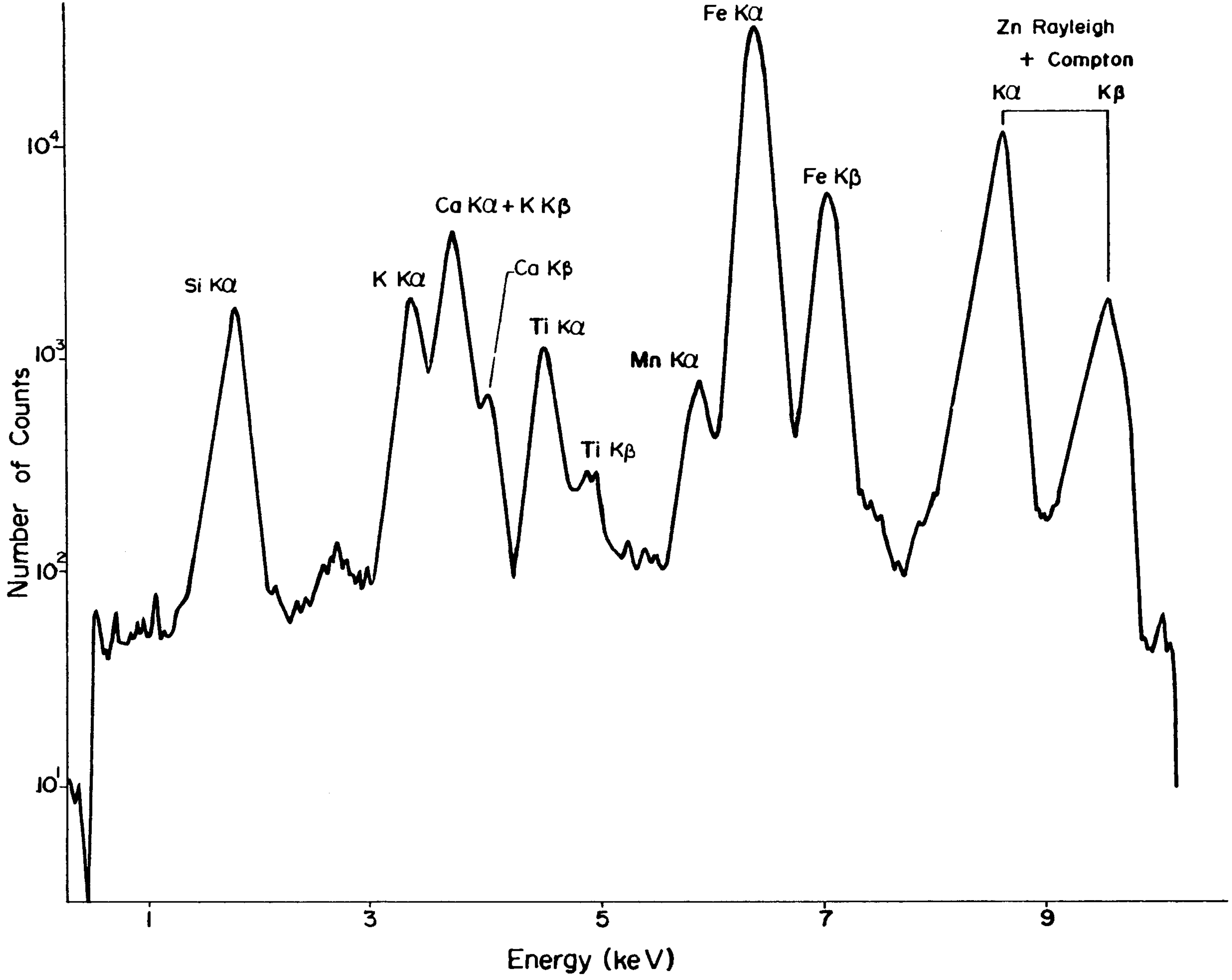

Number of Counts
10^3
10^2
10^1
Energy (keV)
5
10
15
20
Ca Kα + K Kβ
K Kα
Ti Kα
Ti Kβ
Fe Kα
Fe Kβ
Rb Kα
Sr Kα
Y Kα + Rb Kβ
Zr Kα + Sr Kβ
Nb Kα + Y Kβ
Zr Kβ
Compton
Rayleigh

FIGURE 2.2

Typical Tephra Spectrum Analyzed with
a Zinc Secondary Target


Number of Counts
10^4
10^3
10^2
10^1
1
3
5
7
9
Energy (keV)
Si Kα
K Kα
Ca Kα + K Kβ
Ca Kβ
Ti Kα
Ti Kβ
Mn Kα
Fe Kα
Fe Kβ
Zn Rayleigh
+ Compton
Kα
Kβ

windows. For the analysis of loose powder specimens we place the sample in 13 mm dia. Somar #340 plastic Spectro cups with mylar windows.

Detection is by way of a Kevex lithium drifted silicon Si(Li) semi-conducting detector crystal connected to the appropriate electronics. Because of limited detector resolution (FWHM of roughly .2 KeV for Fe) we are unable to distinquish between the K-beta lines of K, Rb, Sr, and Y and the respective K-alpha lines of Ca, Y, Zr, and Nb.

Two separate multichannel analyzers, the Nuclear Data (ND) 812 and the Victoreen Scipp model 104TP multichannel anayzer (SCIPP), were used for this project. Malfunctioning of the ND812 required that we complete most of our work using the SCIPP. The settings on the SCIPP could be adjusted so that each spectrum could be accumulated in anywhere from 100 to 9600 channels. In our work a series of 24 spectra, each occupying 400 channels, is typically counted into the 9600 channels. The data (number of counts per channel) are recorded in digital form onto magnetic tape and then transferred to an IBM 370 computer. With a packaged program (SAMPO) (cf. Routti 1969) we recognized the presence of peaks, fitted idealized peak forms to the peaks, subtracted background, calculated peak areas by integrating the number of counts under each peak, and identified the energy at which each peak occurred. Two sub programs, SHAPEDO and FITDO, were run after each XES session in order to calculate the shape and fit parameters necessary to run properly the SAMPO program. A supplementary program calculated the ratio of each peak to the Compton height for each spectrum. A program performing similar calculations to those of SAMPO was built into the ND812 analyzer so that results of peak area calculations were immediately available on teletype. In the ND812 background is calculated by linearly interpolating a line under the peak from two points measured on either side of the peak. With this less sophisticated method for calculating background it is likely that larger variabilities exist in the peak area calculations made by the ND812.

Relationship Between Peak Intensity and Concentration: Each element has a different probability of being excited by the incident beam. A number of additional instrumental conditions can affect the count rate recorded for each peak. It is therefore difficult to calculate absolute concentrations directly from peak areas. Calibration to some standard, containing elements in known quantities, is almost always necessary. Determining absolute concentrations from line intensities is further complicated by a number of phenomena which can render the intensity a non-linear function of concentration. These factors which cause variations in intensity are discussed in Bertin (1970) and are summarized as follows: specimen errors resulting from particle size effects, micro-inhomogeneities, and changes in sample thickness; interfering peaks from other analytes (i.e. K-beta peaks); background peaks from contaminants in sample holders, binders etc, as well as peaks resulting from flucrescing materials in the analyzing chamber; background scattering from sample holders and geometry effects due to differences in the placement of samples in the sample chamber; interelement effects or specific absorption enhancement effects; matrix effects due to change in average Z between samples; variable counting times resulting from machine dead time; and changes in flux of the incident beam.

Specimen Errors and Specimen Preparation for XES: The best method for producing homogeneous, fine-grained (<45 µm), well mixed, and smooth-surfaced specimens for XES is to produce pressed pellets in a manner outlined in Appendix B.

Given a set of analyzing conditions and a specific mass absorption coefficient for the sample for a specified analyte line there can be variations in intensity with variations in sample thickness. This is illustrated both in equation B.3 (Appendix B) and in figure 2.3.

Absorption of a monochromatic, collimated X-ray beam follows an exponential function. Although a great deal of material would be required to absorb completely all the X-rays, most of the X-rays are absorbed in the first few millimeters of sample (fig.

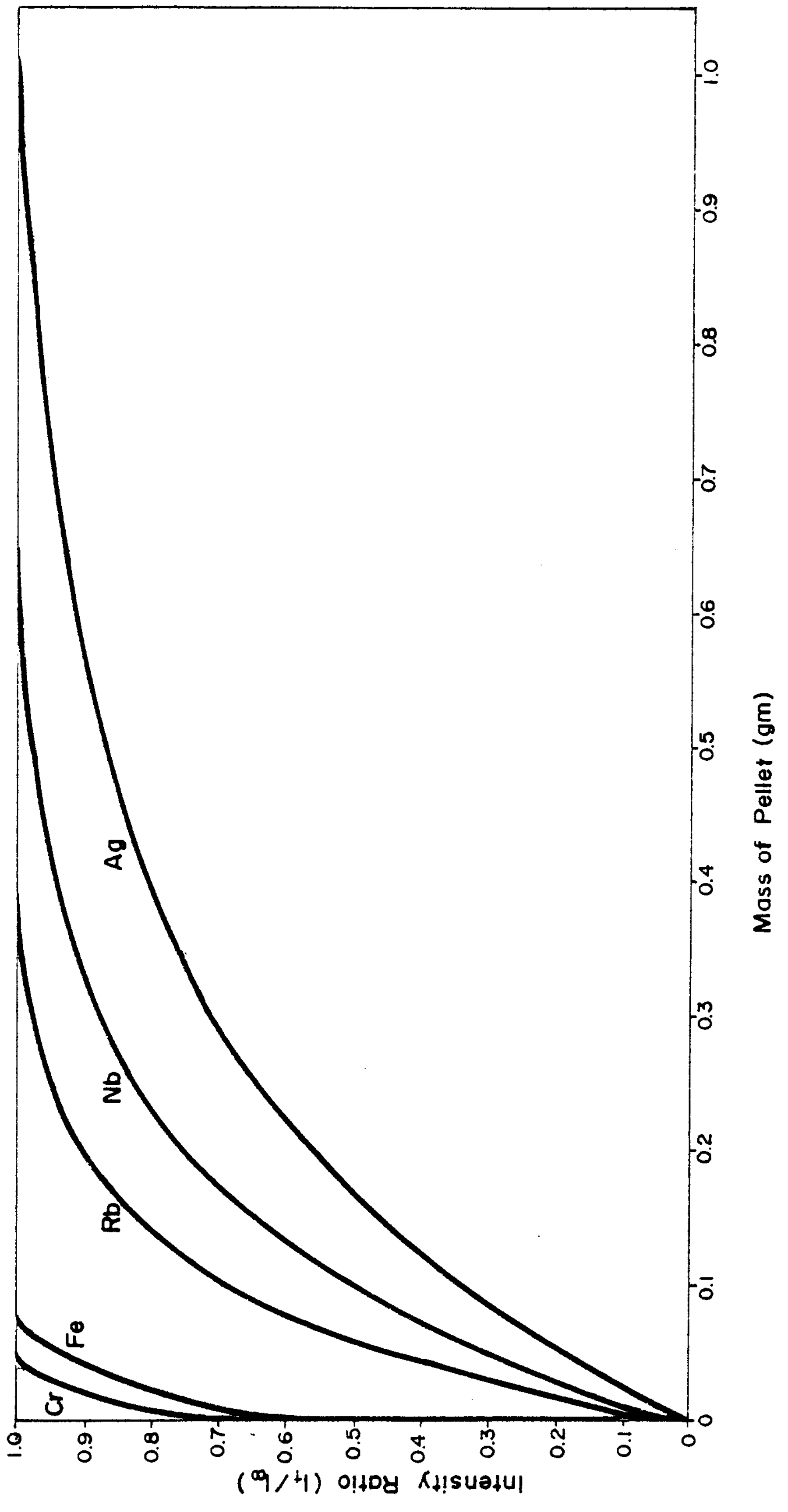
FIGURE 2.3

Relationship Between Intensity Ratio and Sample Mass

I_t = intensity of analyte line at thickness t

I_∞ = intensity of analyte line at infinite thickness

note: As illustrated in eq. B.3, mass serves as an indirect measure of pellet thickness. Mass was calculated for pellets having diameters of 13 mm.


Intensity Ratio (I_t/I_∞)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Mass of Pellet (gm)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Cr
Fe
Rb
Nb
Ag

2.3). An operational definition of infinite thickness is usually that amount of material required to absorb most of the X-rays, say 97 to 99%. Infinite thickness will be different for X-rays of different energies. If a sample is greater than about 97% of infinite thickness for a particular analyte line, then the change in intensity is relatively unaffected by slight changes in thickness. As samples become thin, however, large changes in intensity are observed with each change in thickness. The intensity of the background (from multiply scattered Compton and Rayleigh photons) begins to undergo the greatest decrease in intensity with decrease in thickness, therefore, the signal to noise ratio is improved in samples of intermediate thickness. In very thin samples the absorption curve is linear. Matrix and interelement effects are minimized, and sample thickness is the only variable affecting intensity.

Our separated glass specimens are typically powder in the 62-210 micron size range. Perhaps the optimum in specimen preparation would occur if thin pelletized specimens are prepared. However, a great deal of effort is involved in preparing pellets. Moreover, if thin pellets were prepared all samples would have to be accurately weighed because large variations in intensity result from small changes in sample thickness. If loose powders could be analyzed instead of pellets a great deal of effort could be avoided. If the powders could be poured into a sample cup to greater than 97% of infinite thickness careful weighing of samples would be unnecessary. In chapter 4 we empirically study the effects that such simplifications in specimen preparation have on the uncertainty of our results. Because the Cp/R ratio increases as samples become thin, monitoring the Cp/R ratio will signal problems related to sample thickness.

Interfering peaks and subtraction of K-beta peaks: In order to study the changes in the concentrations of Y, Zr, or Nb or to calculate absolute concentrations from peak areas, it is essential that the K-beta peaks of Rb, Sr, and Y be subtracted from the K-alpha peaks of Y, Zr, and Nb. Once the K-beta/K-alpha ratios are determined for Rb, Sr, and Y in a matrix similar to glass, we can estimate the K-beta areas from the K-alpha areas and then subtract the respective K-beta peaks from Zr to Nb. It is necessary to determine the K-beta peak areas in samples for which the elements Y, Zr, and Nb are absent. We found that laboratory centrifuge glass and watch glass were suitably void of these elements. Three pulverized glass samples were heavily laced with nitrates of Rb, Sr, and Zr. These were then analyzed for 15 minutes each and the K-beta/K-alpha ratios were calculated. As the K-beta peaks are relatively small they were only subtracted when absolute concentrations were determined.

Background Peaks, Background Scattering and Geometry Effects: We analyzed the sample holders and binders to verify that no contaminant peaks were present. We also analyzed a piece of lucite to observe whether there were background peaks arising from the materials in the analyzing chamber. No background peaks were observed. Nevertheless, erratic variations in our iron concentrations (Ch.5) led us to believe that back-scattering X-rays were fluorescing an iron oxide coating that is present in the analyzing chamber.

During loose powder analysis standardized lucite rings were placed around all our sample cups. This was so they could be placed within the multi sample changer in a standardized fashion and additional movement of the samples during analysis could be avoided. The contribution that the effects of geometry and scattering might have on the uncertainty in our results (which were not corrected by the above measures) were studied empirically (Ch. 4).

Other Effects - Use of Compton as Variable Internal Standard: In our work interelement effects can be ignored because the elements in which we are interested are present in quantities less than 5% (cf. Jenkins 1967). Most of the matrix effects are negligible because we are analyzing high Z trace elements in a predominantly low Z matrix and monitoring the Cp/R ratio has revealed that the average Z's of our matrices do not change significantly between samples (cf. Jenkins 1967:131).

Many of the above effects, however, are minimized if one normalizes the analyte peak areas to another peak within each spectrum. We found that the Compton peak height was the most suitable variable internal standard: 1) It is of an energy only slightly higher than the trace elements of interest. 2) Unlike other elements which can vary due to changes in concentration the Compton varies with change in average Z and, therefore, in our case, it changes only slightly from sample to sample. 3) Because the Compton is affected by geometry, scattering, specimen errors, and matrix effects, some changes in these conditions are corrected by normalizing to the Compton. 4) Conditions that are likely to produce large changes in the Compton height (i.e. large changes in sample thickness, or average Z) can be monitored by examining the Cp/R ratios (e.g. Giauque et al. 1977; Feather and Willis 1976).

We tried normalizing to the Zr peak but found it unsatisfactory. In Chapter 4 we discuss the advantages and disadvantages of normalizing to either of these variable internal standards.

Absolute versus relative concentrations: In our work we are interested in identifying tephras on the basis of differences in chemical composition between different tephra sources. Relative concentrations (Peak(Pk)/Cp ratios) are as useful for this purpose as are absolute concentrations. We were able to eliminate a great deal of effort and reduce errors by not calibrating to standards and by using relative concentrations (Pk/Cp ratios) for correlation purposes. Communicating results to other workers, however, is easiest with absolute concentrations. In Appendix C we have, therefore, characterized each of our tephra sources using absolute values. Our particular calibration technique is detailed in the Appendix while alternative methods are discussed in Bertin (1970).

B) Principles of Alpha Counting

Trace quantities of U and Th are easily determined by counting the alpha emissions associated with their radioactive decay. The principles of alpha-scintillation spectrometry are outlined in Cherry (1963) and Aitken (1974), while the alpha counter and methods used are discussed by Huntley and Wintle (1981). For alpha counting the sample is placed on a ZnS phosphor screen. The ZnS fluoresces with each alpha emission and the scintillation pulses are then detected with a photomultiplier tube. The number of alpha particles counted per time period is proportional to the amount of uranium and thorium in the sample.

We spread powder to a thickness greater than .05 mm on a commercial 13.85 cm dia. ZnS disk held in a plastic container. As infinite thickness is about .05 mm for alpha particles, weighing of samples was unnecessary. The sample holder is placed on a 5 cm. diameter photomultiplier tube fitted with the appropriate counting devices.

The alpha counts are an indirect measure of uranium and thorium concentrations and, as with XES, we simplify the method of tephra identification by simply looking for differences in the count rates between different tephra groups. The methods outlined in Huntley and Wintle (1981) were used by Dr. Huntley to calculate absolute concentrations of U and Th. From these data we characterized each tephra group on the basis of its absolute (ppm) U and Th concentrations (Table C.5, Appendix C).

C) Principles of Neutron Activation Analysis

For neutron activation analysis (cf. Tite 1972) the samples are bombarded with slow neutrons, usually in a nuclear reactor. The neutrons interact with the nuclei of the atoms in the sample to produce unstable isotopes. These then decay to stable daughter products and gamma-rays of discrete energies are emitted in the process. The gamma-rays characterize the isotopes and, ultimately, the elements excited by the slow neutrons. The gamma rays are generally detected in a semi-conducting Ge(Li) solid state crystal with associated multi-channel pulse height analyzer in a system similar to that required for XES analysis. Analysis times for each element will vary according to the half-lives of the isotopes. Some are best analyzed after several weeks when interfering peaks from short-lived isotopes are eliminated. Due to the longer ranges of the gamma-rays all samples are infinitely thin, matrix effects are eliminated, and the calculation of absolute concentrations is easier than with XES analysis. Calculation of absolute concentration is usually accomplished by calibrating to samples of a standard material which are activated along with each sample and which contain elements present in known concentrations.

Our samples were analyzed by Novatrack Inc. at TRIUMF, Vancouver B.C. Novatrack's neutron beam is produced by unconventional methods using a proton beam from a cyclotron accelerator.

Chapter 3

THE EFFECTS OF CONTAMINATION, WEATHERING, LEACHING, AND SAMPLE PREPARATION ON COMPOSITION OF SPECIMENS

In section 2.1 we discussed the factors which can affect $\overline{X}$, the average concentration of elements for a number of bulk glass samples analyzed from each tephra source. In this chapter we look at the potential effects that weathering, contamination, and sample preparation can have on our measure of $\overline{X}$. We also present the results of empirical tests carried out to determine the effects that sample preparation have on composition.

3.1 The Samples

To show that our method of fingerprinting tephras will allow us to identify tephra samples independent of their depositional environment, we studied samples collected from a variety of locations and depositional environments including land, lake or bog deposits. For most tephras, samples were collected both near the source and in distal fallout regions. We collected reference samples from spots where the tephras had already been identified. The samples are catalogued and mapped in Appendix A and sub-samples of limited size may be obtained from the author. All reference samples were labelled according to the identifications that were given by these geologists. We guessed the sources of the unknown samples on the basis of their geographical location, grain size, etc. and these samples were similarily labelled according to their a priori identifications. The benefits of such a priori analysis will be discussed in Ch. 6. The samples used in this study are catalogued and mapped in Appendix A.

3.2 Sample Preparation

A) The Contamination Problem

There are an infinite variety of soil types. Because any one of these could contaminate an ash layer the contamination problem is complex. While it is obvious that we cannot deal with all possible sources of contamination, an understanding of the average soil composition allows us to treat the sample to eliminate ubiquitous contaminants. Any remaining contamination not removed by the treatments will contribute to the uncertainty of our characterizations of tephra sources.

B) Sources of Contamination

An average soil contains, in addition to air and water, about 45% minerals and about 5% organics (Brady 1974). The mineral fraction consists of primary minerals as well as the secondary minerals or weathering by-products such as: amorphous and recrystallized silica (clay minerals), and compounds that have percolated into the soil such as colloids of metal oxides (mainly Fe_2O_3, Al_2O_3), salts and carbonates, (i.e. $CaCO_3$, $MgCO_3$, K_2CO_3, K_2SO_4). The organic portion may contain partially decayed plant and animal remains as well as the humus colloids (fluvic and humic acid and humin). The mineral fraction tends to concentrate the alkali elements while high concentrations of alkaline earths are found in the organic portion. Both clay and organic colloids contain excess anions and adsorb free cations. (cf. Brady 1974). In addition to these external sources of contamination, as we are interested in analyzing separated glass, we consider that phenocrysts present in the magmas are an internal source of contamination.

C) Anticipated Changes in Average Composition with Removal of Contaminants

The phenocryst suites of the tephras are listed in Appendix E. In table D.1 we compare the major element composition of whole ash samples with that of separated glasses, using the literature as our source. The chemical composition of most minerals and other soil compounds can be found in a number of texts (e.g. Brady 1974; Deer et al. 1972; Dixon and Weed eds. 1977). Using information from Appendix D, Appendix E, and the above references we can make the following general comments about the chemical changes one might expect with removal of the various types of contaminants. 1) Primary minerals: removal of the primary mineral fraction should cause a relative increase in alkali metals, a decrease in alkaline earth metals, and a decrease in most transition elements (particularly Fe). 2) Solubles: with removal of metal oxides we would expect a reduction in the transition elements. The removal of carbonates and salts should cause a reduction in the alkaline earths with some reduction in alkali metals. 3) Organics: there should be a reduction in the alkaline earths with some reduction in alkali metals. 4) Clay minerals: with removal of clays we might expect a reduction in alkali metals, a reduction in the transition elements (particularly Fe and Ti) and some reduction in alkaline earths. Rare-earth trace element chemistry also reveals that transition elements tend to concentrate in the clay fraction (cf. Borchardt et al. 1971b).

D) General Methods for Removing Contaminants

A number of texts deal with methods for removing soluble contaminants as well as primary and secondary minerals (cf. Allman and Lawrence 1972; Black et al. eds. 1965; Steen-McIntyre 1977). We chose rather standard procedures of sample preparation; the details are outlined in Appendix B (Methods 1 to 6).

Primary Minerals: Three methods exist for removing the crystal fraction from the tephras. 1) Minerals are more dense than glass and can therefore be removed through separations with heavy liquids (Method 4). 2) Most minerals are more magnetic than glass, except for the tectosilicates which are less magnetic. A Franz magnetic separator separates minerals on the basis of their magnetic properties (Method 5). Highly magnetic minerals such as magnetite and titano-magnetite can be removed with a hand magnet (Method 1). 3) Minerals tend to be concentrated in larger size fractions (i.e. greater than 62 microns) (cf. Brady 1974). Sieving to concentrate the glass in the fine grained fractions (i.e. less than 62 microns) may be an effective method for separating the glass. We do not know of examples in tephrochronology where sieving has been routinely used for concentrating the glass; an empirical study comparing results produced by heavy liquid separations to those produced by sieving will be presented in our study.

Soluble Secondary Minerals: Strong HCl is a good all-purpose cleaner capable of removing metal oxides, carbonates and salts.

Organics: Several reagents exist for removing organics. Although NaOH is the most efficient method for removing organics (Mortensen 1965), it forms an insoluble compound (FeOH) with the iron oxides we are seeking to remove. It would, therefore, be necessary to follow the NaOH treatments with acid treatments to dissolve the iron precipitates. Also, strong alkali solutions can dissolve silica glass (Ambrose 1976). For removal of a less than 5% source of contamination we therefore decided to use a less potent reagent. Thirty percent H_2O_2 is of neutral pH and is an effective method for removing most organics except cellulose. As H_2O_2 is unstable in alkali environments it is best used after the acid treatments. Steen-McIntyre (1977) suggested that H_2O_2 might attack tephra glass by leaching out Fe. She proposed that 5% NaOCl (adjusted to 9.5 pH with HCl) should be used instead of H_2O_2 for removing organic stains. Initially we followed her suggestion but, during the studies described below we found that 5% NaOCl was not a very efficient method for removing organics, and it did not appear to do any less damage to the glass than did the treatments with peroxide.

Clay Minerals: Clays are partially dissolved by peroxide, strong alkali solutions, and strong acid solutions, but dissolution is slow (Dixon and Weed (Eds.) 1977; Grim 1968). Most clay minerals are less than 2 microns and can be removed through centrifugation (Method 2). We found that centrifugation was a simple method for washing out reagents following other chemical treatments, and could be easily adapted for removal of colloids. When we extract the larger particles (i.e. 62 to 210 microns), most clays have automatically been removed during sieving. Nevertheless, use of the ultrasonic bath following chemical treatments guarantees removal of fine grained material from the larger size fractions (Method 2).

E) Effects of Leaching and Weathering on Obsidian Glass

Following are several factors which can affect the composition of obsidian tephra glass: 1) leaching of elements in the lab during chemical treatments, 2) leaching of the elements during chemical weathering, and 3) hydration. There have been few controlled studies on chemical changes in obsidian glass produced by each of these phenomena. We therefore supplemented the studies in the literature with a few tests of our own.

Obsidian Leach Studies: In our work we specifically wished to determine what effect the 20% HCl, 30% peroxide and 5% NaCCl reagents would have on concentrations of elements in obsidian glass. These laboratory leaching studies might also mimic leaching that could occur during accelerated weathering such as that which occurs in extremely acid or alkaline environments.

Anahim Peak obsidian was ground to a fine powder (less than 62 µm) and subdivided into 4 sub-samples. One sub-sample of this standard remained untreated and one sub-sample was treated with the 20% HCl and 30% peroxide treatments in a manner identical to that used for treating tephra samples (Method 2). Two more sub-samples of this standard were leached for 10 days each, one in 30% H_2O_2 solution, the other in 5% NaOCl solution. Small amounts of NaOH and HCl were added to the NaOCl solution to adjust it to pH 9.5. The peroxide was of neutral pH (about 6 to 7) and the HCl solution was extremely acid (about 0 to .5 pH). The pH of both the NaOCl and peroxide solutions was again tested after the 10 day leaching period. The treated obsidian samples were washed, dried and analyzed for 5 minutes each, using both silver and zinc secondary targets. The percentage differences in composition between treated and untreated samples were calculated and the results appear in table 3.1. Changes in values which were not greater than the two sigma range in analytical uncertainty (Ch. 4) for each (Pk/Cp) ratio were not considered significant.

Results show that calcium, iron, and possibly rubidium are leached from obsidian glass by the acid treatments. Iron concentrations decreased most rapidly. It is possible that the smaller ionic size of Fe contributed to a diffusion rate which was faster than that of Ca. Results on peroxide treated tephras showed that none of these elements undergoes significant changes with peroxide treatments. Most of these effects are, therefore, caused by acid leaching. Potassium concentration did not significantly change as a result of acid leaching.

TABLE 3.1

Percentage Change in Concentration of Obsidian with Leaching

Samples have been analyzed with a silver (Ag) and a zinc (Zn) Secondary Target

	Analytical Uncert. (2CV)[a]		$HCl + H_2O_2$ (%)		H_2O_2 (%)		NaOCl (%)	
	Ag	Zn	Ag	Zn	Ag	Zn	Ag	Zn
K	14	12	-12	4	-10	-4	-8	-8
Ca	28	26	-12	-30	3	-8	1	-9
Ti	30	13	-4	-13	-58	-41	-47	-24
Fe	4	4	-17	-9	-3		-4	
Zn	145		-13		13		-6	
Rb	4		-5		-5		-2	
Sr	74		nd		-72		-26	
Y	4		3		1		-1	
Zr	6		0		8		1	
Nb	4		-1		3		1	
C/R	3		0		-5		-5	

[a] $2[(\text{instrumental uncertainty})^2 + (\text{Poisson counting uncertainty})^2]^{1/2}$

nd not determined

Both H_2O_2 and NaOCl leached Ti; H_2O_2 caused a slight reduction in Rb; while the NaOCl treatments may prefentially leach K and Rb (these effects of NaOCl are mainly seen in later experiments sumarized in Fig. 3.1). After 10 days of leaching the pH of the NaOCl solution had changed to pH 8. This indicates that either anions are leached from the obsidian glass, or OH- is adsorbed on the glass surface (cf. Bornemisza 1971; Loughnan 1969). Because alkali solutions dissolve silica (Loughnan 1969; Smith 1980) it can be assumed that K and Rb are preferentially leached along with Si.

Conclusions: If we combine our results with those in the literature we can make the following tentative statements about the possible effects of leaching and hydration on the composition of obsidian tephra glass:

1) Strong acid environments cause the preferential leaching of alkali earth elements (Ca, Mg, Ba) and the transition elements (Fe, Pb, Cd, Mn, Zn) which function primarily as network modifiers (cf. this study; Belousova and Tonkonogov 1968; Smith 1980). The leaching effects may be accelerated for elements having smaller ionic sizes. Potassium concentration is relatively unaffected by acid leaching (Belousova and Tokonogov 1968).

2) Strong alkaline environments will cause preferential leaching of network formers such as Si and other anions (Cl, B, F), with a concomitant reduction in K, Ca, Li, U, and V (cf. this study; Smith 1980)

3) In most weathering environments the pH is not as extreme as that of the leaching experiments carried out in this study. Under moderate weathering environments slow hydration is probably the dominant form of weathering for silicic glasses. During hydration there is an inward diffusion of protons (H+) or hydronium ions (H_3O+), with concomitant outward diffusion of alkali and alkaline earth metals (Doremus 1975). Oxidation of Fe can also occur (W. Ambrose 1980; pers. comm.). The alkali metals are removed from the hydration rind, while the alkaline earths tend to be leached from the hydrated portion but are concentrated at the surface of hydrated specimens (Tsong et al. 1978). During hydration higher Z trace elements have lower diffusion rates than major elements from the same chemical groups (e.g. K versus Rb) (Jambon et Carron 1973).

4) There are some discrepancies in the literature as to the relative solubilities of K and Ca during chemical weathering. Some writers claim that K is quite soluble during weathering (e.g. Rankama and Sharma 1950; Teria and Hayami 1975). Others suggest that Ca is easily removed while K tends to remain in the weathered products (Loughnan 1969:49).

Applications: In our study (Chs. 4 and 5) we analyze separated glass from the 62-210 micron size range as well as glass samples from the silt-sized (<62 µm) size rance. Samples have been collected from different locations, and an effort was made to standardize methods of chemical treatments in order to reduce variability introduced through leaching during sample preparation. Due to the relatively larger surface area of the particles in the fine grained specimens (<62 µm), we can expect that a larger volume in the fine grained samples will be affected by both leaching and hydration. Samples collected from distal fallout regions (being mainly fine grained) should likewise contain larger volumes of hydrated and leached glass. Nevertheless, if we can distinguish between tephra sources and identify distal samples while analyzing samples from either size range, and if there are no real chemical differences between separated glass fractions from the different size ranges, we consider that both weathering and leaching have had negligible effects on the glass composition of young (Holocene) tephras.

3.3 Empirical Results of Effects of Sample Preparation on $\overline{x}$

In the following sections we study the effects that five steps in sample preparation have on concentrations of elements in bulk samples of tephra analyzed from various tephra sources. These are as follows: 1) glass separation, 2) sieving as an alternate method for glass separation, 3) HCl treatments, 4) H_2O_2 treatments, and 5) NaOCl as an alternative to H_2O_2.

General Methods: The effects of sample preparation were studied during a number of different experiments using the following general approach to the problem. 1) A few samples were selected from various tephra sources. The samples were then subdivided into sub-fractions. 2) One sub-sample remained untreated, while other sub-samples were treated by one or more of the above 5 steps in sample preparation. 3) Treated and untreated samples were then analyzed, and the averages and standard deviations were calculated for all samples analyzed from each tephra source at various stages in sample preparation. The effects of sample preparation on the standard deviations (S) are examined in Ch 4, while the effects of sample preparation on the average composition for each tephra source $\overline{x}$ will be studied here. We first subtracted the average (K-beta/Cp) ratios of Rb, Sr, Y from the average (Pk/Cp) ratios of Y, Zr, and Nb. We then calculated the percentage differences in the average concentrations between treated and untreated samples. The changes in average concentrations with sample preparation are plotted in figure 3.1 (cols. A to D). A negative deviation in the values means that the concentration of an element has decreased. A positive deviation means that the average concentration of an element has increased with preparation. Any deviation less than twice the analytical variability for each ratio (Ch. 4) was not considered significant.

FIGURE 3.1

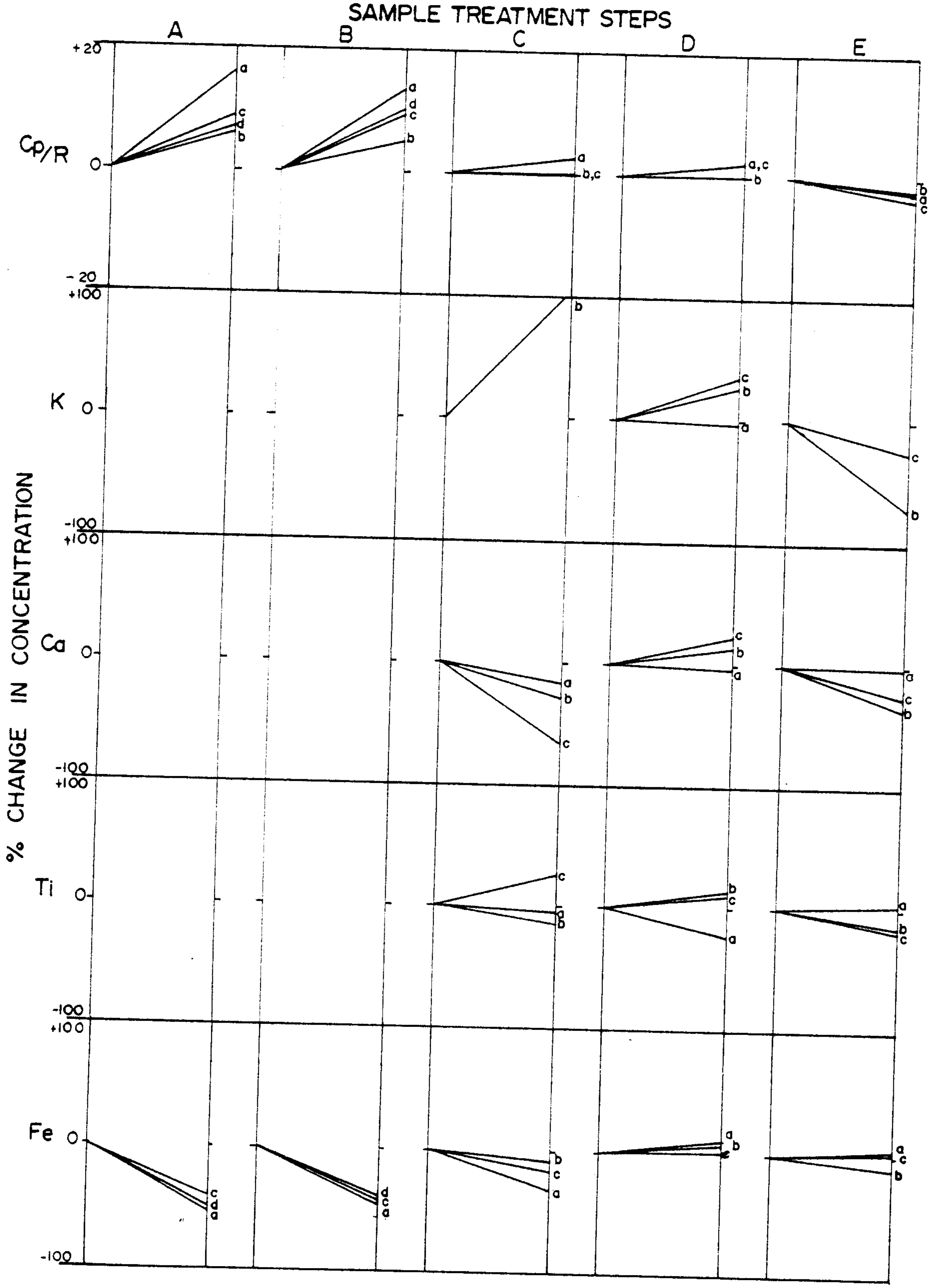
Percentage Difference in Concentration With Sample Preparation

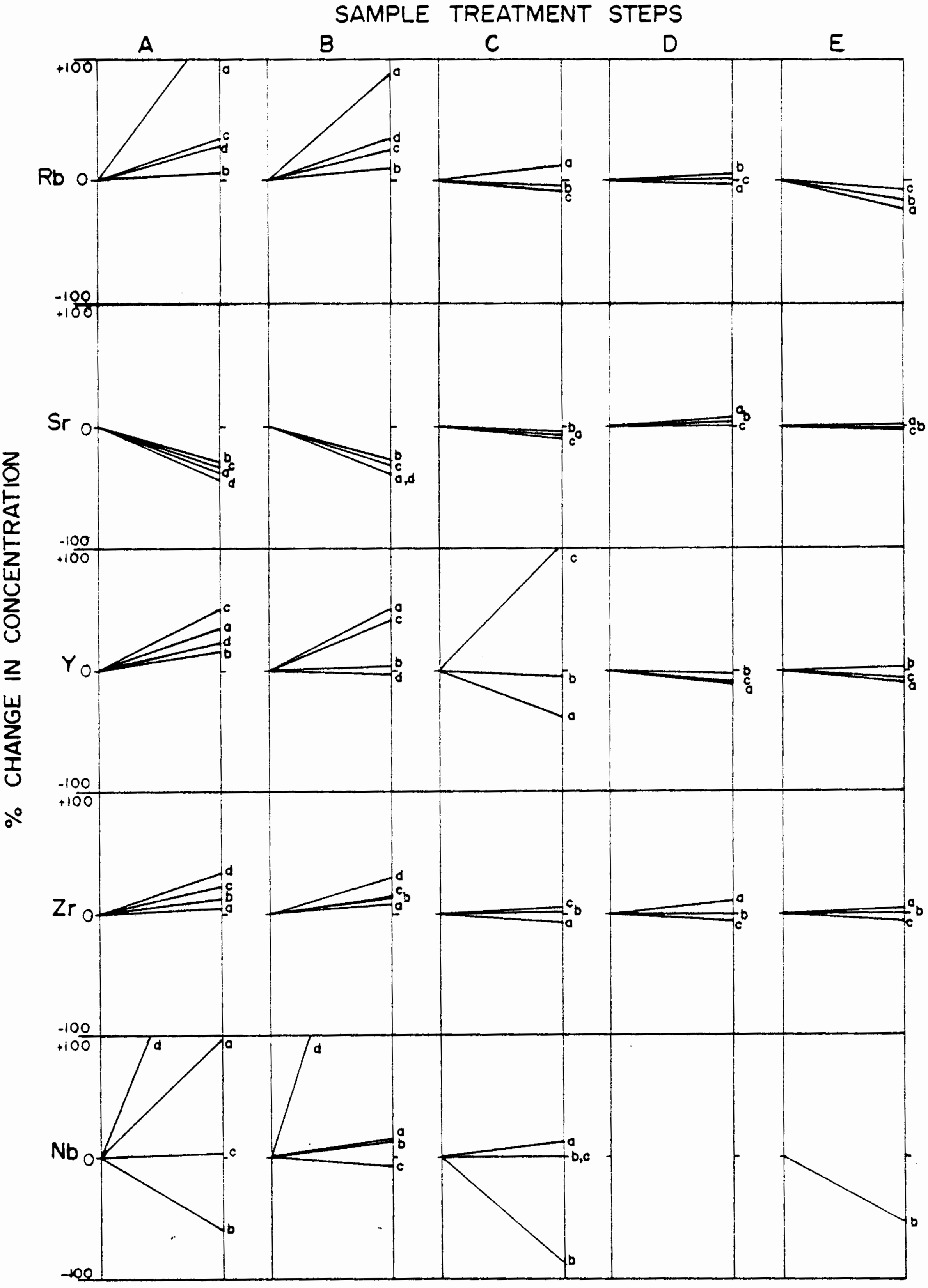
Column:

- A) glass (62-210µm) vs. whole (62-210µm)
- B) <62µm (whole) vs. 62-210µm (whole)
- C) HCl (<62µm) vs. untreated (<62µm)
- D) H_2O_2, HCl (<62µm) vs. HCl (<62µm)
- E) NaOCl, HCl (<62µm) vs. H_2O_2, HCl (<62µm)

Key:

- a) Mt. St. Helens Yn
- b) Mazama
- c) Bridge River
- d) Mt. St. Helens W or T-like Samples


SAMPLE TREATMENT STEPS
A
B
C
D
E
% CHANGE IN CONCENTRATION
Cp/R
+20
0
-20
K
+100
0
-100
Ca
+100
0
-100
Ti
+100
0
-100
Fe
+100
0
-100
a
b
c
d
a,c
b,c


SAMPLE TREATMENT STEPS
A
B
C
D
E
% CHANGE IN CONCENTRATION
Rb
Sr
Y
Zr
Nb
+100
0
-100
a
b
c
d
b,c
a,d

Glass Separation: Three groups of samples having undergone three different types of treatment were analyzed from four tephra sources (3 Yn, 3 BR, 4 M., and 2 unknown (U or L)). Samples had been treated as follows: samples from the 62 to 210 micron size range were submitted directly for analysis; samples from the less than 62 micron size range were submitted for analysis; glass separates from the 62-210 micron size range were analyzed. All samples had been pre-treated with HCl and NaOCl (or H_2O_2) prior to separation. Results on the separated glass samples and on the fine grained samples were compared to results obtained on the unseparated specimens from the 62-210 micron size range.

The percentage changes in concentration with glass separation by sieving or by heavy liquid separations are plotted in columns A and B (fig. 3.1). Results show that concentrating the glass, using either method, produces a consistent increase in the concentrations of alkali metals, a consistent decrease in the concentration of alkali earth metals, a consistent decrease in the average Z of the matrix, and a sharp decrease in the concentration of iron. Most transition elements are probably removed with the high Z ferro-magnesium minerals, while Ca and Sr are probably removed with the plagioclase feldspars. Some of these elements could also decrease with removal of clay minerals. The transition elements Y, Zr, Nb, and the alkali metals (K, Rb) are concentrated in the glass phase of the separated specimens.

The only exception to this rule is Mazama for which Nb is concentrated in the mineral phase. Mazama had the lowest proportion of minerals, while Yn had the greatest.

The results produced by sieving to concentrate the glass (col. B) are almost identical to those produced by the heavy liquid separations (col. A). This indicates that the fine fraction (<62 µm) of sieved ashes is mainly composed of glass. Judging by the magnitude of change produced through glass separation with heavy liquids as opposed to that produced by sieving, sieving is only a slightly less effective method for separating the glass.

HCl Treatments: During 2 different experiments a few samples were treated with HCl and the results were compared to untreated samples of the same. In one experiment 10% HCl was used on 2 samples of Mazama glass (62 to 210 microns). In a second experiment 20% HCl was used to treat less than 62 micron sized samples of Mazama (3), BR (1), and Yn (1).

The percentage changes in concentration with the acid treatments are plotted in column C. The HCl treatments produced consistent reductions in Ca, Fe and Sr; these elements were probably removed with iron oxides, calcium carbonates and salts. A significant amount of iron may be removed from the glass itself (see section 3.2). No other elements showed significant changes except for the Yn samples. In the Yn samples the decreases in the transition elements Y, Zr, Fe, Ti, with concomitant increase in Rb and decrease in average z, suggests that some clays as well as oxides are being dissolved by the acid. The sharp reduction in Ca and Sr in the BR sample indicates that this sample was heavily contaminated with carbonates or salts.

H_2O_2 and NaOCl: Two groups of samples (3 M, 1 BR and 1 Yn) were treated with HCl and H_2O_2 and HCl and NaOCl. In a second experiment 2 samples of Mazama glass (62-210 microns) were treated with 10% HCl and 10% H_2O_2. The results of the HCl and H_2O_2 and the HCl and NaOCl treated samples were compared to samples which had undergone only the HCl treatments.

Results are plotted in columns D and E and show that neither the peroxide nor the NaOCl treatments produced significant changes in relative concentrations in the samples. This is probably because none of the samples of this study was heavily contaminated with organics. Nevertheless HCl and H_2O_2 (or NaOCl) treatments sometimes caused slight increases in Ca, Ti, Fe, Sr when compared to HCl treatments used alone. Residual peroxide or NaOCl left on the samples might be interfering with the subsequent HCl treatments. In later experiments this problem was circumvented by using the HCl treatments before the NaOCl or peroxide treatments.

When compared to H_2O_2, NaOCl seems to cause additional decreases in K, Ca, Rb, and Sr in some samples. As K is concentrated in the glass phase of separated tephras, it seems possible that the NaOCL solution is leaching this element along with network formers from the glass.

3.4 Relative Effectiveness of Each Treatment Step and Conclusions

When examining the results in figures 3.1, it is clear that by far the most significant change for all the elements is obtained through separation of the glass by sieving or by heavy liquid separations. The next largest effect is produced by the HCl treatments.

The alkaline earth and major transition elements are most affected by glass separation followed by the acid treatments. The transition elements (Y, Zr, Nb), on the other hand, are most affected by glass separations but remain relatively unaffected by the chemical treatments. The erratic changes in the small peaks, Y and Nb produced by sample preparation are partly due to statistical fluctuations in the data as well as a systematic error in the SAMPO calculations of peak areas on the small peaks (see Ch.4).

As most of the treatment steps produced changes for most elements that were quite predictable (see section 3.2), we can deduce that our treatments are effective for removing most forms of contamination. It is also evident that sieving is a relatively simple method for separating out the glass and could replace heavy liquid separations as the preferred method of separation, provided that the uncertainty is not greatly increased and provided that we can still identify samples which have undergone such simplified treatments. Depending on the elements which are found useful for identifying tephras, the above information will help us further decide which steps can be safely eliminated without drastically affecting the concentrations of the elements of interest.

Chapter 4

FACTORS AFFECTING UNCERTAINTY (S)

4.1 Introduction

In section 2.1 we discussed why we must understand the uncertainty associated with the analysis of a number of samples from each tephra source. In addition to isolating the uncertainties from various sources we will also study the Normality of the distributions of the relative concentrations. For convenience in this chapter we will study the relative percentage error or coefficient of variation (CV) as defined by equations 4.1 and 4.2 (cf. Thomas 1976;83).

eq. 4.1

$$CV = \frac{100S}{\bar{x}}$$

$\bar{x}$ = average concentration of element
S = standard deviation

eq. 4.2

$$LV\,(\text{relvariance}) = (CV)^2$$

The total uncertainty for a number of samples analyzed from each tephra source, LV(t), contains the uncertainty due to each of the factors listed in section 2.1 added in quadrature.

eq. 4.3 LV(t) = LV(counting statistics) + LV(short term instability and operational errors) + LV (long term instrumental and operational errors) + LV(specimen presentation) + LV(replicate sample preparation) + LV(weathering effects) + LV (contamination).

To study the uncertainty from each of the above 6 factors we set some of the uncertainties to zero through controlled experimentation, and then we used equation 4.3 to subtract other uncertainties of known magnitude. When we study any of the 6 factors in equation 4.3, however, we are simultaneously studying a number of sub-factors which are included in the uncertainty for that factor. These can be summarized as follows:

1) Counting statistics are simply the Poisson counting statistics of the Pk/Cp ratios given by equation 4.4:

eq. 4.4

$$CV(\text{counting}) = 100\left[\frac{N+2B}{N^2} + \frac{C_p}{C_p^2}\right]^{\frac{1}{2}}$$

N = net peak area
B = background
C_p = Compton height

2) Short-term instrumental instability and operational errors (within-run variability) are those which occur during a single XES session. These include instability in: X-ray tube potential and current; detector bias and efficiency; pulse

amplification; electronic noise; shifts in pulse height distribution; dead time correction; and variations inherent in the method by which the peak areas are calculated by computer.

3) Long-term instrumental and operational errors (between-run variability) are those which occur between different XES sessions. These are long-term changes in excitation, detection, and analyzing conditions including computer peak calculation routines.

4) The factors included in specimen errors were listed in section 2.2. In addition to particle size, thickness, and micro-inhomogeneity effects, there will be variations due to geometry, background scatter and interfering peaks.

5) With sample preparation we expect that the uncertainty of the measured concentrations in a number of samples from a tephra source will decrease as contaminants are removed. However, other factors besides contamination can affect the uncertainty associated with sample preparation and could cause an increase in the uncertainty with removal of contaminants: a) Some uncertainty may result from replicating sample preparation. b) Large changes in concentration of a particular element will affect the relative uncertainty due to counting statistics. c) If the level and type of contamination is fortuitously the same for a group of samples, treatment could cause an increase in the

uncertainty. An increase in uncertainty with replicate sample preparation can also occur when preparation leads to large changes in concentrations of elements. d) Large shifts in background from sample to sample could increase the uncertainty in the net peak calculations. e) Large uncertainties in the elements Rb, Sr, Y, increase the uncertainty of Y, Zr, Nb due to variations in the underlying K-beta peaks. f) If the uncertainty is estimated using a standard deviation calculated on but a few specimens from a single tephra source, the uncertainty in this estimate is large. Some of the changes in the standard deviation following preparation will therefore be random.

4.2 General Methods

The relative percentage errors (CV's) were defined during experiments described below. The CV's were isolated via eq. 4.3 for samples analyzed with a Ag secondary target and are listed in Table 4.1. Some uncertainties were isolated for samples analyzed with a Zn secondary target and are listed in Table 4.2.

In some circumstances we used the results of more than one experiment in to order define the uncertainty of a specific factor. Under these circumstances we used equation 4.5 to calculate the weighted average of the standard deviations (S_p) (cf. Johnson 1976:372).

TABLE 4.1

Isolated Uncertainties (CV) for Samples Analyzed with a Ag Secondary Target

	Instrumental & Operational			Specimen Presentation			Contamination, Weathering Sample Prep.			Total Observed Uncert. for HCl, H_2O_2 treated 62um loose powder
	5 min. Counting	Within-[b] Run Var.	Between-[b] Run Var.	Pellets (Glass <45μm)	Loose Powder (Glass 62-210μm)	Loose Powder (Sieved <62μm)	Replicate Prep.	Pure Glass (as loose powder)	Whole Ash (as loose powder)	
n[a]	9	27	9	10	10	10	15	13	26	41
K	8	*	47	-	0	4	-	9	17	16
Ca	6	5	16	-	2	6	-	6	50	16
Ti	15	28	*	-	0	26	-	22	32	38
Fe	1	0	3	2	6	8	0	10	34	17
Rb	6	*	5	0	4	10	0	10	12	13
Sr	1	0	0	0	4	5	3	5	18	14
Y	9	*	4	0	0	8	10	28	10	17
Zr	2	2	0	0	0	3	0	2	8	7
Nb	22	*	19	108	0	0	21	12	24	19
C/R	1	0	3	0	7	6	0	0	4	3

[a] number of analyses

[b] calculated using obsidian standard

* total uncertainty was less than counting statistics

\- uncertainty not measured

TABLE 4.2

Isolated Uncertainties (CV) for Samples Analyzed with a Zn Secondary Target

	Instrumental, Operational			Specimen Presentation	
	5 Min. Counting	Within run Var.	Between run Var.	Loose Powder (Glass 62-210μm)	Loose Powder (Sieved <62μm)
n[a]	9	12	5	10	10
K	1	6	4	2	3
Ca	1	13	15	4	15
Ti	1	3	8	2	5
Fe	1	0	4	1	3

eq. 4.5

$$S_p^2 = \frac{\Sigma(n_i-1)S_i^2}{\Sigma(n_i-1)}$$

Si = standard deviation of experiment (i)
ni = number of analyses used to calculate Si

In the text we will occasionally refer to uncertainties which are significantly different from each other. In such cases a one-tailed F test at .05 level of significance was used to decide whether or not there were any significant differences between variances (see Johnson 1976:361 for details of the test used).

4.3 Study of Uncertainty

A) Statistical Uncertainty Due to Counting Errors

The Poisson counting statistics were determined for each peak of a typical tephra sample using eq. 4.1.

The results in Table 4.1 (col. 1) show that for a 5 minute counting period, the CV's of the major peaks are about 1 to 2 %, and for minor peaks are about 6 to 22%. Increasing the counting time will mainly reduce the CV's of the smaller peaks. Further, as indicated in Table 4.2, use of a Zn target greatly reduces the counting uncertainty associated with major element analysis.

B) Uncertainty Due to Operational and Instrumental Errors

Within-run and Between-run Variabilities: A "mahogany" obsidian standard was cut to infinite thickness and its surface was polished. This was routinely analyzed during each XES session. We calculated the average and standard deviation on results over 9 separate XES sessions to produce one estimate of uncertainty due to between-run variability. The standard was also analyzed 10, 6, 6, and 5 consecutive times in four separate XES sessions and we pooled the four estimates of within-run variability via eq. 4.5. Because some concentrations in the standard were quite different from those in a typical tephra sample some uncertainties calculated on the standard (particularly between-run variability for K and Ca) over-estimate those that would occur in a tephra sample. Ignoring the magnitude of uncertainty calculated on the standard, however, similar types of instrumental and operational errors exist for both standard and tephras.

The uncertainty due to within-run variability for the small peaks (K, Rb, Y, Nb) was smaller than that due to the counting errors for these peaks (Table 4.1 col. 2). There is evidently a systematic error in the SAMPO fitting routine on the small peaks, producing artificial uniformity. Conversely, the small peaks have the largest between-run variabilities (col. 3). This indicates that we cannot reproduce the fits on the small peaks between different XES runs. The large peaks (Zr and Sr) have no such additional uncertainty due to the between-run variability. Therefore, with the exception of fitting problems on the small peaks, there are no additional long-term instrumental or operational errors. By routinely analyzing a calibration standard during each XES session, we could, if necessary, calibrate to reduce some of the between-run variability on the small peaks.

Results in Table 4.2 show that both within-run and between-run variability are improved for the major elements when analyzing with a Zn secondary target. However, because in our system we cannot completely resolve the Ca and K peaks, fitting problems are still evident.

SAMPO fit errors: We ran the SAMPO program on a group of spectra, first using fit parameters from the previous XES session, and then calculating new peak fit parameters. We found that re-calculation of new fit parameters after each XES session significantly improved the within-run precision by 7 to 10% for most peaks. The systematic error in the small peaks was also reduced by such measures.

C) Uncertainty Due to Specimen Presentation

Analysis of Pellets Versus Loose Powders: Ten pellets of separated glass from a single large sample of Mazama treated with HCl and H_2O_2 were prepared in identical fashions (Method 6). Prior to pelletization the samples were ground (to less than 45 µm) and mixed in a porcelain ball mill. Ten loose powder samples of separated glass from a single sample of Mazama (62-210 µm) were analyzed for comparison. We also analyzed 10 loose powder samples from the <62 µm size range of sieved but otherwise untreated specimens from the same large Mazama sample. (Glass in the <62 µm size range is typically slightly less pure than glass separated by heavy liquid separations from the 62-210 µm size range.) The pellets were greater than 99% infinitely thick (sect. 2.2), and we estimated that the loose powders (about 4 grams) were poured to greater than 98% of infinite thickness in the sample cups.

The uncertainty due to replicate preparation and analysis of pellets was insignificant (0 to 2% for most peaks). Evidently, the pellets are very homogeneous. When analyzing loose powders in the 62-210 µm size range instead of pellets, the uncertainty was larger by up to 7% for some elements. The uncertainty in the fine grained size range (<62 µm) was the largest (0 to 10% for most elements). Evidently, micro-inhomogeneities are more of a problem than particle size effects when analyzing loose powder specimens. Otherwise the uncertainty of the larger size range would be larger than that of the smaller size ranges (cf. Bertin 1970). This is also evident from the results obtained with a Zn target where the uncertainty of the less homogeneous samples is larger than the uncertainty associated with analysis of samples having larger particle sizes.

Uncertainty Due to Variable Thickness: Although our pellets were infinitely thick, we wished to see if there were any correlations between the Pk/Cp ratios and pellet mass (thickness) which might increase the uncertainty associated with the analysis of pellets. As pellets become thin, the Pk/Cp and Cp/R ratios should increase, and the correlation between Pk/Cp ratios and mass should be negative (Fig. 2.1). We calculated Spearman's rank order coefficient comparing the Pk/Cp intensities to pellet mass (cf. Johnson 1976:533). At the 5% level of significance we found that none of the coefficients of correlation was significantly large and none was negative. Therefore, when analyzing samples of greater than 99% infinite thickness, slight changes in thickness have no significant effect on peak area.

D) Sample Preparation

In order to estimate the uncertainty due to contamination we compared the uncertainties associated with the analyses of a number of purified glass specimens and of a number of whole ash specimens from 3 tephra sources. The pooled uncertainty calculated on the whole ash samples (14 M, 7 Yn, 5 BR) was compared to the pooled uncertainty calculated on a number of glass samples separated from the 62-210 µm size range and treated with HCl and NaOCl (4 M, 7 Yn, 2 BR). In order to improve sample purity in the treated samples, we followed the heavy liquid glass separations with additional separations using a Franz magnetic separator. The isolated uncertainties due to whole ash analysis and analysis of glass separates are listed in Table 4.1 (cols 9, 8).

When comparing all the isolated uncertainties in the table, it is clear that the largest source of uncertainty (4 to 50%) is caused by contamination in the whole ash samples. The greatest improvement in precision is, therefore, accomplished through sample preparation. In comparison, a relatively small improvement in the uncertainty is achieved by analyzing pellets instead of loose powders. A fairly large uncertainty was associated with the analysis of purified glass specimens (0 to 28%), indicating that some weathering or contamination affects the homogeneity of the glass specimens even after most of the contaminants are removed. However, this uncertainty is still quite small in comparison to the uncertainty associated with analyzing untreated specimens.

Because sample treatment can have such a large effect on the uncertainty in our measurements, we further studied the change in uncertainties due to sample preparation.

Effects of Replicate Sample Preparation on Uncertainty: In order to define the uncertainty introduced in the lab during replicate sample preparation, we subdivided large tephra samples and the sub-fractions were prepared in identical fashions (Methods 1, 3, 4, and 6). We found that the uncertainty due to such replicate sample preparation was minimal, about 0 to 10% for most peaks.

Effects of Removal of Contaminants on Uncertainty: In order to study the effects that each step in sample preparation has on the uncertainty, we compared the coefficient of variation (CV) associated with different steps in preparation;

eq. 4.6

$$\Delta CV = CV_2 - CV_1$$

1 = treatment step 1
2 = treatment step 2

The CVs studied in this portion of our work were calculated from the experiments described in Chapter 3. Glass separation by heavy liquids or sieving produced the largest differences in the uncertainty (+5 to -33%) with preparation. This was followed by the HCl treatments (+3 to -30%) then the peroxide or NaOCl treatments (+4 to -2%). Glass separation by sieving produced results almost identical to glass separation using heavy liquids, but the magnitude of difference was slightly less (+1 to -15%) for the sieved samples. All peaks, particularly the transition elements Y, Zr, and Nb, derived some benefit from glass separation (CV2-CV1 = -2% (Fe), -4% (Y), -3% (Zr), -33% (Nb)). The HCl treatments caused some decreases in the uncertainty of all peaks except Ti and Y. The uncertainties of K, Ca, Fe, Rb, Sr, Zr, Nb in the treated samples were smaller by 86, 20, 1, 2, 5, 1, and 30%. Hydrogen peroxide caused decreases in the CV's of Rb (-2%) and Y (-3%) while use of NaOCl caused decreases in the uncertainty of Y (-6%) and Nb (-4%). Of the tephras, Yn was originally the least homogeneous and registered the largest changes in uncertainty with preparation.

Chemical Treatments on the <62 µm Size Range: In the experiments described above we calculated the standard deviations on but a few samples from each tephra source. We therefore carried out a second experiment on 4 BR, 8 M, and 3 Yn samples in order to define better the changes in uncertainty associated with HCl and H_2O_2 treatments on samples from the <62 µm size range (Methods 1 and 2). The uncertainties for the following ratios decreased significantly: K, (-5%), Ca (-30%), Ti (-7%), Fe (-7%), Rb (-4%), Sr (-7%) and Cp/R (-5%). The uncertainty of the transition elements Y to Nb, however, did not significantly improve.

E) Test for Normality of the Distribution of Relative Concentrations

We indicated in section 2.2 that we can correct many instrumental, operational and specimen errors by normalizing to the Compton height or to the zirconium peak area. We also discussed why it was important that our measures of relative concentration be Normally distributed.

We carried out two tests on a group of 41 analyzed samples of Mazama ash from the less than 62 micron size range. In one test we determined whether the uncertainty when normalizing to the Compton height was larger or smaller than when normalizing to the Zr peak. In the second test we determined whether for a select group of elements both sets of ratios were Normally distributed. For the second experiment we used the Kolmogorov-Smirnov (K-S) one-sample test (as described in Thomas 1976:336) to compare our data to a Normal distribution having the same parameters.

When normalizing to the Cp height as opposed to the Zr peak, the CV's were smaller for the elements Ti, Fe, Sr (CV(C)-CV(Zr) = -1% to -4%). For the remaining elements the CV's were larger (0 to 17%). At the .05 level of significance (two-tailed test), we found that the elements Rb, Y, K were Normally distributed whether normalized to the Zr peak or Cp height. However, while the distributions of Fe/Cp and Sr/Cp were Normally distributed, the distributions of Fe/Zr and Sr/Zr were non-Normal and were positively skewed. In Chapter 2 we show that, with contamination, there is a negative correlation between concentrations of Fe, and Zr, and between Sr and Zr. The positive skew can therefore be attributed to contamination and correlation between the elements Sr, Fe, and Zr. This would also explain why, when normalizing to Zr, the uncertainty is larger for the elements which are negatively correlated with Zr (Ti, Fe, Sr).

4.4 Summary and Conclusions

Most of the uncertainties due to instrumental, operational, and specimen presentation errors remain small in comparison to those due to sample contamination, but the following simple methods can be used to improve analytical precision: 1) Increasing counting times improves precision in our measure of the small peaks. 2) Analysis with a Zn target improves analytical precision in our measure of major elements. 3) Calibrating results helps reduce between run variability for the smaller peaks. and 4) Re-calculation of fit parameters after each XES session reduces within and between run variability.

Although there is an increase in the uncertainty associated with loose powder analysis (as opposed to analysis of pellets) this uncertainty is small in comparison to that associated with the analysis of contaminated samples. The improvements in uncertainty that can be made by preparing pellets are probably not sufficiently large to merit such an increase in effort.

The greatest improvment in precision can be accomplished through sample preparation, particularly through glass separation. Sieving to extract the <62 micron size fraction produces samples of a purity comparable to that resulting from glass separation by heavy liquids and could provide us with a greatly simplified technique for separating the glass. As HCl and H_2O_2 (or NaCCl) treatments have little effect on both the uncertainty and the concentrations of some elements, these treatments could be eliminated if concentrations of the appropriate elements prove to be distinctively different between tephras from different sources.

Chapter 5

CHARACTERIZATION OF TEPHRA GROUPS

In this chapter we examine whether XES, NAA, or alpha-counting analysis can be used to distinguish between samples from 6 tephra sources (White River (WR), Glacier Peak G (GPG), Glacier Peak B (GPB), Mt. St. Helens Yn (Yn), Mazama (M) and Bridge River (BR)) (see Appendix A). Use of the A-coefficients will allow us to determine if the separate sources are distinguishable and if concentrations are sufficiently different between sources so that individual samples can be identified. The results using the three instrumental techniques will be compared to each other and to data appearing within the literature. If one of the techniques proves useful for distinguishing tephras, we need to determine which steps in preparation can be sacrificed without hampering our ability to identify samples.

5.1 Analytical Methods

A) The Samples and Sample Preparation

Our methods for collecting samples were described in Ch.3. In this test five of the Mt. St. Helens Yn samples had been collected near the source and two (U1-4a, UL-10) were collected in the Okanagan region of B.C. All samples had been prepared as outlined in Appendix B. The samples were ground (if necessary) and treated with HCl, NaOCl solutions to remove salts, metal oxides and organic stains. (Three samples, UL-10, UL-4a, U-43, seemed to be more heavily contaminated than the others and underwent the HCl treatments for longer times than usual, 30 to 45 minutes.) We then sieved the samples to isolate the 62-210 µm and <62 µm size ranges. Glass was separated from the 62-210 µm size range by means of heavy liquid separations followed by separations with a Franz magnetic separator for additional purity. As NaOCl, HCl treated samples from the less than 62 micron size range were available from the same samples for which we separated the glass, we submitted such samples directly for analysis in order to compare results of the <62 µm specimens to those of the separated glass specimens.

B) XES Analysis

In all, 31 samples of purified glass separates and 31 samples of fine grained samples (<62 µm) pretreated with NaOCl and HCl were analyzed by XES using a silver secondary target. The Pk/Cp ratios for the elements K, Ca, Ti, Fe, Rb, Sr, Y, Zr, and Nb were thus determined. Analysis times were 15 minutes per separated glass sample and 10 minutes per <62 µm sample.

C) NAA

The 31 separated glass samples were also analyzed by NAA at TRIUMF. In preparation for analysis we weighed approximately 0.7 grams of powdered sample into 12 mm diameter, 24 mm long polyethylene vials. We pulverized Anahim obsidian and weighed similar portions of this standard into separate polyethylene containers. One standard was prepared for each sample. All vials were then heat sealed and pairs of vials (one containing a tephra sample, one containing a standard sample) were placed into larger unsealed polyethylene containers. Six additional obsidian standards were prepared. During NAA these would eventually be cross-calibrated against an international granite standard (NIM-G).

D) Alpha Counting

Twenty-two of the purified glass and 14 fine-grained samples were further analyzed by alpha counting to determine their U and Th concentrations. Three of these samples (M-54, M-56, U-48) had been treated with peroxide instead of NaOCl to remove organics.

5.2 Results

Tables 5.1 to 5.3 show the average concentrations and standard deviations on the averages as determined for each tephra

TABLE 5.1

XES Results

Tephras Characterized Using HCl, NaOCl Treated Glass Samples (62-210μm) Analyzed with a Ag Secondary Target

All values in relative concentrations (PK/Cp ratios)

	M(±1σ)	BR(±1σ)	Yn(±1σ)	GP30(±1σ)	GP40(±1σ)	WR(±1σ)	L[b](±1σ)	U[b]-43
n[a]	4	2	7	5	5	5	2	1
K	3.87(.31)	4.73(.32)	2.87(.29)	4.93(.31)	4.97(.55)	4.05(.32)	3.51(.18)	2.62
Ca	3.90(.12)	4.38(.13)	5.66(.62)	4.94(.17)	3.60(.45)	4.59(.22)	5.57(.31)	4.16
Ti	2.45(.22)	1.91(.17)	0.98(.29)	1.44(.17)	1.38(.13)	< 1	1.21(.11)	1.06
Fe	93(1)	83(1)	77(12)	69(2)	58(8)	71(1)	97(2)	70
Rb	9.58(0.5)	8.5(0.4)	8.5(1.1)	11.2(0.4)	11.2(1.0)	9.5(0.4)	11.2(0.3)	9.1
Sr	60.9(1.2)	69.0(5.1)	81.6(6.5)	88.6(6.7)	48.5(8.5)	122.1(5.2)	67.4(2.6)	59.6
Y	8.5(0.4)	6.3(0.4)	4.4(1.7)	5.0(0.5)	6.7(0.4)	4.2(0.5)	7.0(0.4)	5.9
Zr	94.9(1.0)	66.1(1.0)	53.0(2.2)	64.5(3.5)	50.7(8.5)	73.4(2.9)	75.0(1.0)	66.5
Nb	2.31(.40)	3.31(.99)	1.58(.20)	< 1	1.71(.38)	< 1	2.58(.78)	1.86
C/R	1.43(.12)	1.46(.09)	1.49(.03)	1.47(.03)	1.46(.02)	1.40(.01)	1.46(.01)	1.44

[a] number of samples analyzed

[b] Mt. St. Helens W-or T-like samples

TABLE 5.2

XES Results

Tephras Characterized Using HCl, NaOCl Treated Samples ($\leq$62μm) Analyzed With a Ag Secondary Target

All values are in relative concentrations (Pk/Cp ratios)

	M(±1σ)	BR(±1σ)	Yn(±1σ)	GP30(±1σ)	GP40(±1σ)	WR(±1σ)	L[b](±1σ)	U[b]-43
n[a]	4	2	7	5	5	5	2	1
K	3.79(.23)	4.09(.61)	2.66(.26)	4.10(.39)	4.57(.27)	4.59(.72)	3.33(.20)	2.82
Ca	3.89(.18)	4.27(.38)	6.77(.75)	5.94(.66)	4.65(.68)	5.30(.75)	5.51(.25)	5.01
Ti	2.48(.27)	2.15(.24)	1.52(.28)	1.40(.19)	1.51(.35)	1.35(.23)	1.66(.18)	1.28
Fe	97(6)	79(9)	103(13)	81(61)	73(10)	85(10)	99(3)	85
Rb	8.55(.50)	7.19(.89)	7.26(.75)	8.91(.79)	9.72(.39)	9.27(.97)	10.47(.83)	8.71
Sr	62(2)	71(7)	85(5)	105(11)	60(13)	121(8)	63(3)	55
Y	8.00(.82)	5.47(.33)	4.75(.45)	5.42(.43)	5.26(.32)	4.17(.43)	7.14(.43)	5.70
Zr	93.4(3.0)	64.7(1.7)	60.9(5.0)	67.5(2.6)	57.7(9.7)	77.3(3.9)	74.2(0.7)	69.9
Nb	2.12(.40)	3.78(.60)	1.98(.40)	< 1	1.75(.52)	< 1	2.22(.90)	1.96
C/R	1.41(.12)	1.42(.03)	1.44(.04)	1.44(.04)	1.45(.03)	1.43(.02)	1.44(.02)	1.39

[a] number of samples analyzed

[b] Mt. St. Helens W-or T-like samples

TABLE 5.3

NAA Results

Tephras Characterized Using HCl, NaOCl Treated Glass Samples (62-210μm)

All values (except iron) are in ppm concentrations by weight

	M(±1σ)	BR(±1σ)	Yn(±1σ)	GPB(±1σ)	GPG(±1σ)	WR(±1σ)	LK[c] (±1σ)	U[c]-43
n[a]	4	2	7	5	5	5	2	1
Fe[b]	1.45(.06)	1.19(.19)	0.99(.08)	0.82(.07)	0.90(.07)	1.15(.05)	1.24(.01)	1.26
Th	5.4(0.7)	6.1(0.3)	3.6(1.0)	7.7(1.0)	8.0(0.4)	5.8(0.5)	4.2(0.4)	3.8
Sc	11.19(.83)	8.55(.92)	3.96(.40)	4.90(.62)	5.39(.56)	3.30(.10)	6.76(.13)	7.00
Ce	42.7(3.3)	45.8(2.6)	29.1(2.9)	31.1(3.6)	34.2(4.9)	39.0(7.8)	27.5(0.4)	33.0
Hf	5.49(.30)	3.90(.14)	2.42(.34)	3.10(.24)	3.36(.43)	3.39(.19)	4.00(.35)	4.30
Cs	3.03(.30)	1.15(.42)	1.89(.12)	2.18(.75)	2.39(.32)	1.19(.29)	2.60(.35)	2.30
Co	3.3(0.6)	3.5(0.0)	3.0(0.8)	2.7(0.4)	4.7(1.8)	3.2(0.4)	3.2(0.3)	3.5
Cr	8.7(1.4)	10.5(2.1)	7.2(1.4)	7.3(2.4)	6.4(1.5)	7.8(1.5)	10.00(0.0)	7.00
Eu	2.05(.06)	1.40(.42)	1.48(.20)	1.27(.38)	1.40(.36)	1.32(.25)	1.60(.14)	1.30

[a] number of samples analyzed

[b] % concentrations by weight

[c] Mt. St. Helens W-like samples

source for all elements analyzed by XES and NAA. Individual analyses obtained by alpha counting appear in Fig. 5.1 while the averages and two sigma ranges of the alpha count rates for each tephra source are plotted in Fig. 5.2. All averages were calculated after scanning the data to verify that the groupings of samples for each tephra source seemed reasonable. Three samples (L-23, L-24, U-43) did not appear to belong to any of the 6 tephra groups. As we were also unsure of our field identifications of these samples, we did not include these in the averages but list them for comparison in Tables 5.1 to 5.3. The averages and standard deviations calculated for the NAA and alpha counting results were weighted by 1/Vi (eq. 5.1 and 5.2). When calculating NAA statistics, Vi is the variance due to analytical variability and, when calculating alpha-counting statistics, Vi is the variability due to counting uncertainty.

eq. 5.1

$$\bar{x} = \frac{\sum \frac{x_i}{V_i}}{\sum \frac{1}{V_i}}$$

Xi = concentration
1/Vi = weighting factor
N = number of samples

eq. 5.2

$$S^2 = \frac{N}{(N-1)\left(\sum \frac{1}{V_i}\right)^2} \left[\sum \frac{1}{V_i} \left(\sum \frac{x_i^2}{V_i}\right) - \left(\sum \frac{x_i}{V_i}\right)^2 \right]$$

A-coefficients were calculated in order to compare the 6 tephra sources by XES, NAA, and alpha counting and appear in

FIGURE 5.1

Alpha Particle Count Rates for Individual Samples ± 1σ (counting uncertainty)

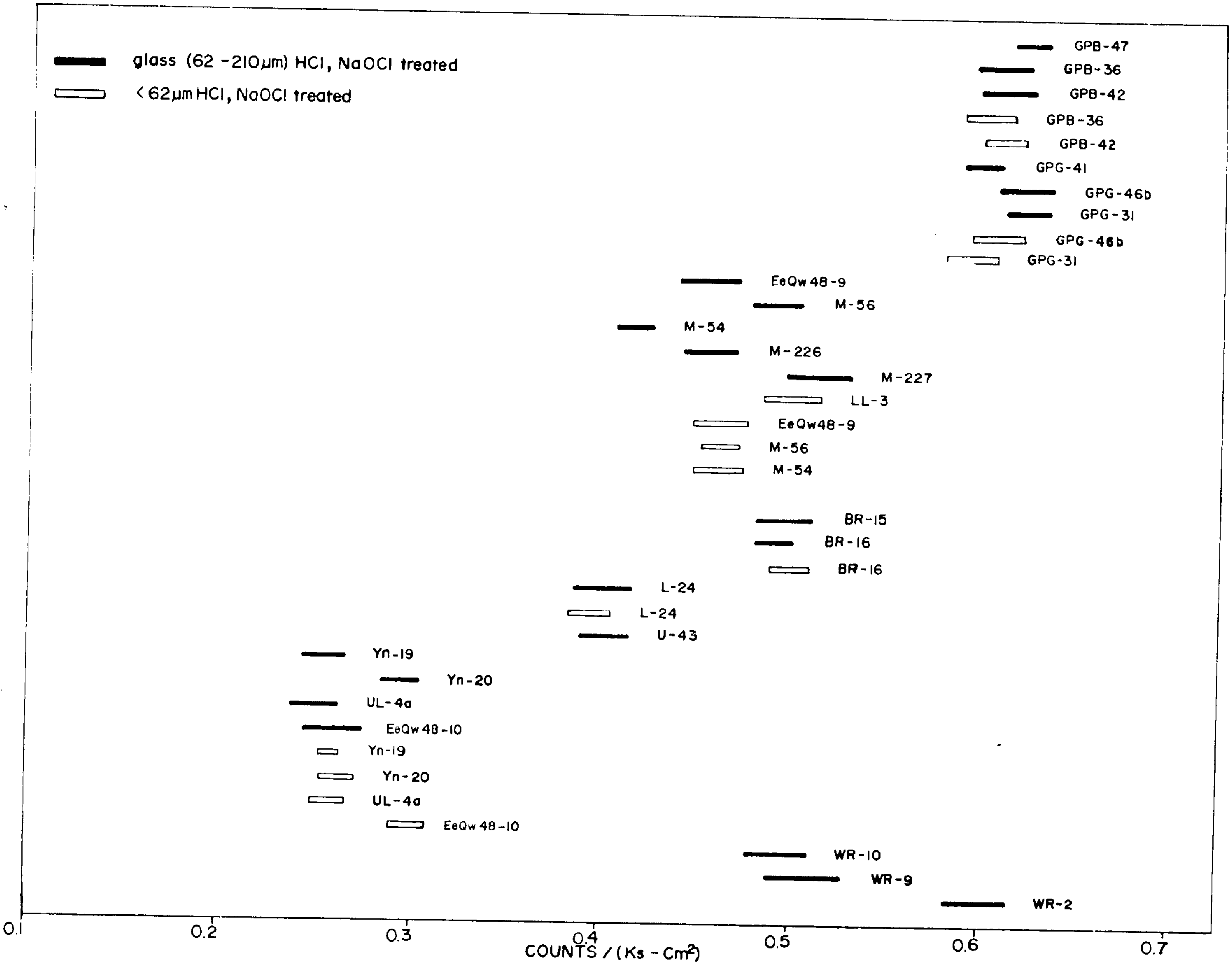
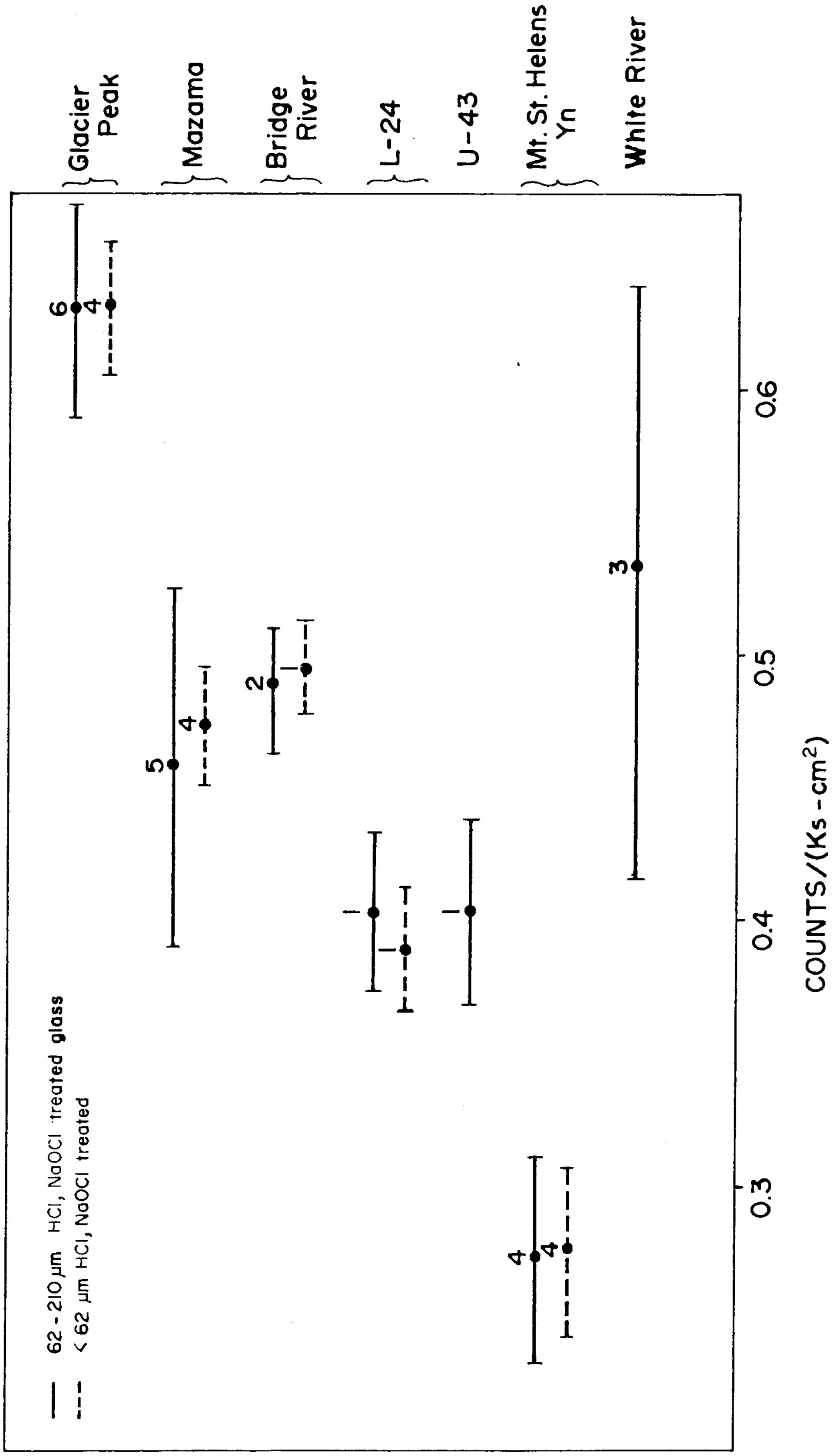

glass (62 -210μm) HCl, NaOCl treated
< 62μm HCl, NaOCl treated
GPB-47
GPB-36
GPB-42
GPB-36
GPB-42
GPG-41
GPG-46b
GPG-31
GPG-46b
GPG-31
EeQw 48-9
M-56
M-54
M-226
M-227
LL-3
EeQw48-9
M-56
M-54
BR-15
BR-16
BR-16
L-24
L-24
U-43
Yn-19
Yn-20
UL-4a
EeQw 48-10
Yn-19
Yn-20
UL-4a
EeQw 48-10
WR-10
WR-9
WR-2
0.1
0.2
0.3
0.4
0.5
0.6
0.7
COUNTS / (Ks - Cm²)

FIGURE 5.2

Alpha Particle Count Rates for Tephra Sources. The number of samples is shown above each point and the error bars are ± 2σ.


Glacier Peak
Mazama
Bridge River
L-24
U-43
Mt. St. Helens Yn
White River
6
4
5
4
2
1
1
1
1
3
4
4
62 - 210 μm HCl, NaOCl treated glass
< 62 μm HCl, NaOCl treated
0.3
0.4
0.5
0.6
COUNTS/(Ks -cm²)

Tables 5.4 to 5.7. In Appendix C we have converted the alpha counting results into absolute concentrations of U and Th. Similarly, the relative concentrations determined by XES appear as absolute concentrations in the Appendices. In Table 5.7 in addition to A-coefficients comparing tephras by their alpha count rates, we include A-coefficients comparing them on the basis of their U and Th concentrations.

5.3 Discussion of Results

A) XES

The A-coefficients in Table 5.4 show that, when analyzing purified glass separates by XES, at least 1 element will allow us to distinguish between all but one of the tephra pairs (WR/GP) at the two sigma range in relative concentration. This indicates that for the elements analyzed by XES, the glass separates are sufficiently homogeneous for correlation purposes. The distal samples of Yn collected in the Okanagan region of B.C. (UI) are indistinguishable from the Yn samples collected near the source. This indicates that XES analysis of the glass separates is a valid method for identifying samples from distal fallout regions.

TABLE 5.4

A-Coefficients Comparing Tephras on the Basis of XES Results on HCl, NaOCl Treated Glass Samples (62-210μm)

Analyzed with an Ag Secondary Target

	M/BR	M/Yn	M/GP	M/WR	BR/Yn	BR/GP	BR/WR	Yn/GP	Yn/WR	GP/WR	GP GP 30/40	GP 30/WR	GP 40/WR	U1[b]/Yn
n[a]	4/2	4/7	4/10	4/5	2/7	2/10	2/5	7/10	7/5	10/5	5/5	5/5	5/5	2/5
K	.691	.829	.746	.151	1.51*	.147	.533	1.45*	.969	.609	.030	.699	.532	.721
Ca	.960	1.19	.225	1.01*	.853	.062	.300	.500	.639	.160	1.09*	.453	.740	.546
Ti	.692	1.44*	1.40*		1.01*	.773					.105			.645
Fe	3.00*	.586	1.74*	5.42*	.215	1.12*	2.62*	.340	.237	.393	.603	.257	.728	.928
Rb	.493	.290	.742	.008	.005	1.25*	.552	.769	.308	.834	.016	1.07*	.679	.857
Sr	.641	1.39*	.162	4.76*	.559	.008	2.58*	.339	1.76*	.971	1.32*	1.40*	2.68*	.134
Y	1.38*	.976	1.66*	2.39*	.458	.531	1.24*	.204	.056	.571	.917	.454	1.41*	.343
Zr	9.34*	6.95*	1.81*	2.86*	2.28*	.421	.987	.197	1.99*	.636	.578	.696	.947	.167
Nb	.357	.608	.386		.726	.585		.135						.241
C/R	.592	.495	.419	.641	.188	.072	2.01*	.083	2.90*	1.03*	.122	2.90*	.598	.745

[a] number of samples analyzed from each source

[b] Mt. St. Helens Yn collected in Okanagan region of B.C.

* element is useful for distinguishing between tephra pair

TABLE 5.5

A-Coefficients Comparing Tephras on the Basis of XES Results on HCl, NaOCl Treated Samples (<62μm)

Analyzed with a Ag Secondary Target

	M/BR	M/Yn	M/GP	M/WR	BR/Yn	BR/GP	BR/WR	Yn/GP	Yn/WR	GP/WR
n[a]	4/2	4/7	4/10	4/5	2/7	2/10	2/5	7/10	7/5	10/5
K	.179	1.15*	.421	.474	.819	.120	.188	1.28*	.990	.115
Ca	.338	1.54*	.632	.754	1.11*	.395	.459	.432	.489	.002
Ti	.324	.873	.064	1.13*	.606	.129	.851	.059	.163	.101
Fe	.577	.187	.661	.352	.572	.060	.159	.631	.410	.219
Rb	.488	.517	.321	.248	.019	.668	.560	.710	.589	.012
Sr	.475	1.49*	.352	3.00*	.583	.180	1.78*	.034	1.39*	.573
Y	1.10*	1.28*	1.19*	1.53*	.462	.170	.855	.398	.325	.799
Zr	3.04*	2.04*	1.35*	1.17*	.288	.103	1.13*	.065	.927	.595
Nb	.670	.084			.900	.371				
C/R	.112	.336	.364	.296	.190	.195	.112	.014	.123	.121

[a] number of samples analyzed from each source

* element is useful for distinguishing between tephra pair

TABLE 5.6

A Coefficients Comparing Tephras on the Basis of NAA Results on HCl, NaOCl Treated Glass Samples (62-210μm)

	M/BR	M/Yn	M/GP	M/WR	BR/Yn	BR/GP	BR/WR	Yn/GP	Yn/WR	GP/WR
n[a]	4/2	4/7	4/10	4/5	2/7	2/10	2/5	7/10	7/5	10/5
Fe	.519	1.64*	2.15*	1.29*	.362	.630	.075	.465	.596	1.27*
Th	.349	.512	.828	.161	.930	.777	.225	1.19*	.731	.848
Sc	.754	2.94*	2.10*	4.24*	1.74*	1.11*	2.53*	.584	.660	1.25*
Ce	.258	1.11*	.618	.167	1.52*	.862	.323	.190	.464	.262
Hf	1.81*	2.40*	1.83*	2.14*	1.54*	.755	.915	.575	.915	.192
Cs	1.31*	1.36*	.427	1.56*	.685	.555	.028	.268	.854	.614
Co	.156	.096	.017	.059	.309	.046	.432	.078	.066	.053
Cr	.251	.278	.262	.163	.468	.479	.372	.032	.105	.119
Eu	.677	1.06*	.869	1.18*	.065	.051	.060	.143	.178	0

[a] number of samples analyzed from each source

* element is useful for distinguishing between tephra pair

TABLE 5.7

A Coefficients comparing Tephras on Basis of Alpha-Counting Results on:

A) HCl, NaOCl treated glass (62-210μm) and B) HCl, NaOCl treated samples (<62μm)

		M/BR	M/Yn	M/GP	M/WR	BR/Yn	BR/GP	BR/WR	Yn/GP	Yn/WR	GP/WR
A)	n[a]	5/2	5/4	5/6	5/3	2/4	2/6	2/3	4/6	4/3	6/3
	total[b]	.347	1.76*	1.57*	.404	3.77*	2.34*	.326	4.50*	1.59*	.617
	U (ppm)	.200	.833	.643	.417	1.20*	.583	.300	1.36*	1.25*	.286
	Th (ppm)	.000	.553	.429	.068	.656	.500	.079	1.08*	.474	.500
B)	n	4/1	4/4	4/4		1/4	1/4		4/4		
	total[b]	.554	3.65*	2.73*		4.30*	2.40*		5.63*		
	U (ppm)	.100	1.10*	.419		1.20*	.344		1.29*		
	Th (ppm)	.094	.821	.217		.706	.272		.763		

[a] number of samples analyzed from each source

* element is useful for distinguishing between tephra pair

[b] total count rate

Sieved Samples: The uncertainties associated with the sieved samples (Table 5.2) are slightly larger than those calculated on the separated glass samples (Table 5.1). Nevertheless, the A-coefficients calculated for the sieved samples in Table 5.5 show that we are able to use such samples of intermediate purity to distinguish between all tephras except GP/BR and GP/WR. Our inability to distinguish between GP, WR and BR is, of course, of only academic importance as none of these tephras is found within the same geographical regions. (We shall illustrate later that, if one has any doubts whether GP occurs in B.C., alpha-counting could be used to distinguish between the GP and BR layers.)

Even though the distal Yn's were indistinguishable from the source Yn's when analyzing glass samples, if we compare fine grained (<62 μm) samples of UL-4a and UL-10 on an individual basis to the 5 source samples, concentrations of the elements Ca, Fe, Rb, Y, and Zr are too low. Such anomalies were not reproduced in later tests. We therefore suspect that the extended HCl bathing times caused additional leaching of these elements in the distal Yn samples. Efforts were made to standardize all subsequent chemical treatments.

B.C. Tephras: Using both separated glasses and sieved samples, Mazama ash is easily distinguished from all tephras on the basis of its high Zr content. As was shown in sections 3.3, 3.4, and 4.3, Zr is unaffected by the HCl and peroxide treatments. It is therefore feasible that Mazama could be distinguished from both BR and Yn by directly submitting the fine grained untreated portions of sieved samples for analysis. BR and Yn can be distinguished from each other on the basis of their major elements. Potassium is characteristically low in Yn (Table 5.1 and 5.4), and calcium may be characteristically high in Yn (Table 5.2 and 5.5). As the uncertainty is large when analyzing major elements with a silver secondary target, future analysis with a zinc secondary target will, undoubtedly, allow us to distinguish better between tephras on the basis of their major elements.

White River: All glass samples except WR are of the same average composition as evidenced by the Cp/R ratios. White River is of higher average Z than the rest and can be distinguished from GP on the basis of its Cp/R ratio.

Glacier Peak: We found the Glacier Peak tephras to be extremely variable in Ca, Sr, and Zr indicating the existence of more than one chemical group. We observed at least 2 chemical groups among the GP samples. These groups, however, did not coincide with the upper (B) and lower (G) layers, but, rather, with samples collected near the source (GP30's) and samples collected farther away (GP40's). The GP30 samples have unusually high Sr and Ca concentrations. Concentrations of Ca and Sr are significantly different between GP 30's and 40's when analyzing separated glass from the 62 to 210 micron size range. Separating the two GP subgroups reduced the variability to the point that each individual GP subgroup was distinguishable from the other and GP30 was distinguishable from WR. Although discrepancies in Ca in the GP30 samples could be explained by contamination or weathering effects, we doubt that this is the case. Firstly, it is unlikely that the strong acid baths would leave behind any carbonates or salts. Secondly, hydration and most other forms of weathering should cause a decrease rather than increase in Ca content. Large variabilities among samples of Glacier Peak tephra have been noted by some researchers (cf. Westgate and Evans 1978) and may be due in part to the high crystal content in the GP tephras. However, other researchers suggest that up to 9 different GP tephra groups may exist near the source (c.f. Porter 1978)) and only recently is the stratigraphy being fully explored near the vent (cf. Bejet 1980). As we cannot solve the problem of GP variability until the tephra sequence is better understood near the source vent, we will be content with our ability to distinguish Glacier Peak as a whole from the other major tephra groups.

Unknowns: Neither the L nor U-43 samples belong to any of the groups analyzed. The low potassium concentrations in these tephras suggest, however, that both groups of samples belong to some Mt. St. Helens eruption, probably W or T, (see Appendix D).

B) NAA

The results in Table 5.6 indicate that, at the two sigma range in concentration, the analysis of three elements (Sc, Hf, and Th) allows us to discriminate between most of the major Pacific Northwest Tephras on the basis of their rare earth trace element chemistry. L23, L24, and U43 are chemically indistinguishable from each other and, as a group, are unlike any of the other tephras examined (Table 5.3). The Mt. St. Helens Yn samples collected in the Okanagan region of B.C. are chemically identical to those collected near the source. Rare earth trace element chemistry of bulk glass samples is, therefore, a reliable means for identifying tephra samples collected in distal fallout regions.

Using NAA we cannot distinguish between Mt. St. Helens Yn and WR but, once again, owing to the distributions of the tephras, this does not have any practical consequence for tephrochronology. With NAA we cannot distinguish between the GPB and GPG layers, nor can we distinguish between the GP30 and 40 groups.

C) Alpha counting

The results in Figures 5.1 and 5.2 indicate that there is a definite clustering of the count rates for some ash groups and a clear distinction between the alpha count rates attributable to Mt. St. Helens Yn, Glacier Peak and all other tephras except WR. The count rates of L24 and U48 are identical and confirm our suspicion that neither of these is the result of the Yn eruption. The Mt. St. Helens Yn samples collected in the Okanagan are identical to those collected near the source. This indicates that concentrations of U and Th can be reliably used for identifying distal samples. The count rates produced by the sieved samples are almost identical to those produced by the purified glasses which suggests that simplifying sample preparation will not affect our ability to distinguish between the tephras. Finally, when comparing the standard deviations due to individual counting statistics (Fig. 5.1) to the standard deviations calculated on a number of samples from a tephra source (Fig. 5.2), we see that most of the uncertainty is due to contamination or weathering rather than counting statistics. We calculated that by reducing our counting times to about 2 days we should still be able to distinguish between the tephras.

We cannot use the alpha count rates to distinguish between the following tephra pairs: BR and M, GPB and GPG (or 30 and 40), M and L or U; WR and all other tephras except Yn. The unusually large variance attributable to White River appears to be due to its Th content and remains a mystery. Separating the counts due to U and Th does not improve our ability to distinguish between the remaining tephra pairs.

5.4 Comparison with Work in the Literature

In Appendix D results of NAA and Microprobe analyses for the literature are listed for comparison to our data. In Table 5.8 we ordered the tephra sources (from highest to lowest) according to the relative concentrations of each element determined by the 3 instrumental techniques. With this method we are able to compare our data with that of the literature in order to verify whether our characterizations of tephra sources are reasonable in light of results obtained by other researchers. We place a "+" at the bottom of the columns in which the rank orders of 4 major tephra groups in our study (GP, M, Yn, BR) correspond to the rank orders of the same tephra groups in the literature.

XES: Table 5.8 shows that the rank order of K concentration in our tephra groups is consistent with that of the literature. The XES results for Fe do not compare with the literature, but the NAA analysis of the same samples do. Our XES analyses of iron are apparently unreliable, probably due to an internal source of iron contamination (see section 2.2). If we ignore the GP30 samples in our rank orders in Table 5.8, we find that our data on calcium also conforms to that of the literature.

NAA: By comparing our data to results in the literature (Appendix D), we show that our NAA results (particularly for Mazama ash) compare quite favorably with Borchardt's, except for

TABLE 5.8

Comparison to the Literature Tephras are ordered (from highest to lowest) according to concentrations of elements.

Literature

	Microprobe						Neutron Activation Analysis (NAA)									
	K	K	Ca	Ca	Fe	Fe	Fe	Rb	Cs	Ce	Eu	Th	Hf	Co	Sc	Cr
	GPLL	BR	Yn	T	M	T	T	W	M	M	M	GP	M	T	T	Y
	BB	GPLL	BR	Yn	BR	M	Y	M/T	W	T	Y/W	M	W	Y	M	GP
	GPUL	GPML	M	Wn	BB	BR	M	GP	GP	W	T	W	T	GP	W	W
	BR	GPUL	GPUL	BR	Yn	Wn	W	Y	Y	GP	GP	T	GP	W	GP	T
	M	M	BB	M	GPUL	Yn	GP		T	Y		Y	Y	M	Y	M
	Yn	Wn	GPLL	GPUL	GPLL	GPML										
		T		GPML		GPLL										
		Yn		GPLL												
Reference:	1	3,4,5,6	1	3,4,5,6	1	3,4,5,6	2	2	2	2	2	2	2	2	2	2

Ours

XES			NAA	XES	NAA				α Counting	NAA			
K	Ca	Fe	Fe	Rb	Cs	Ce	Eu	Th	Th	Hf	Co	Sc	Cr
GP40	Yn	L	M	L/GP	M	M	M	GP	GP	M	U-43	M	L
GP30	L	M	U-43	M	L	U-43	L	M	M	U-43	GP	U-43	M
BR	U-48	BR	L	U-43	U-43	GP	Y	L	L/U-43	L	M	L	Yn
M	GP30	Yn	BR	Yn	GP	Yn	GP	U-43	Yn	GP	L	GP	U-43
L	BR	U-43	Y		Yn	L	M-43	Yn		Yn	Yn	Yn	GP
Yn	M	GP30	GP30										
U-48	GP40	GP40	GP40										
+(1)			+(2)	+(2)	+(2)	+(2)	+(2)		+(2)				

[1] Westgate et. al. (1970a)

[2] Borchardt et. al. (1971a)

[3] Smith et. al. (1968)

[4] Smith and Okazaki (1975)

[5] Smith and Okazaki (1977)

[6] Smith et. al. (1977)

T = Mt. St. Helens T

W = Mt. St. Helens W

U-43)
L   ) Mt. St. Helens W or T-like samples

+(ref.) = our orders are the same as those in the literature for M, BR, Y, GP.

the elements Eu, Sc, and Cr. Our results are considerably higher for these elements. The discrepancies in the data are possibly due to differences in the laboratory methods of calibration. The rank order of our data also compares favorably to Borchardt's for all elements except Fe, Rb, Co, Cr. However, the concentrations of Co in our data and of Rb and Cr in both our own and Borchardt's data are sufficiently variable to render them undiagnostic. Inconsistencies in our rank orders of these elements are probably due to nothing more than random fluctuations in the data. Our NAA results for iron are apparently more accurate than Borchardt's, as ours compare favorably with the microprobe results while Borchardt's do not. The placement of the L and U samples in the rank orders suggests that, if these belong to a recent Mt. St. Helens eruption, they are chemically more like the W than the T layer.

The A-coefficients with which we distinguish between separate tephra groups are a conservative measure. Using this criterion, we cannot use Borchardt's data to distinguish between Yn and GP, Mt. St. Helens W and GP (Table D.6). We used chemical treatments to remove carbonates, organics, and some clays while Borchardt did not. This may be one reason why our data appears to be better for distinguishing between some tephra groups than do Borchardt's.

5.5 Conclusions

We can use XES, NAA or alpha counting analysis of bulk samples of glass to distinguish between most of the Pacific Northwest tephras. Reducing sample preparation and analyzing the less than 62 micron size fraction of sieved ashes, should still allow us to use XES and alpha counting to distinguish between most tephra pairs. Mazama can be distinguished from the other tephra groups on the basis of Zr. As chemical treatments do not greatly affect concentrations of Zr such treatments could probably be eliminated when identifying Mazama. The BR and Yn sources are best distinguished by using alpha counting, or by using XES to analyze for major element concentrations. With a Zn secondary target we can greatly improve the major element analyses of the BR and Yn samples. For major element analysis the HCl, H_2O_2 treatments will probably be necessary to remove possible post depositional sources of K contamination. Finally, because many tephras can be distinguished on the basis of their alpha count rates with reduced sample preparation, and, because the alpha counter is a relatively simple piece of equipment, alpha counting could potentially be developed into a field method for identifying tephras.

5.6 Applications

The results suggest that we should be able to identify the 3 B.C. tephras by using XES to analyze the <62 µm size fraction of sieved ashes. Since we have not yet analyzed a large number of samples from each of the three B.C. tephras, we consider the results presented in this chapter to be preliminary. It will now be important to increase the number of samples analyzed with such reduced sample preparation and to attempt to include the analysis of a number of samples from different locations and, presumably, different depositional environments. This will give a better idea of the variation that is possible among nearly-pure samples from each source. In chapter 6 we will use the information from this chapter to expand upon the XES method for identifying tephras: 1) We characterize the B.C. sources using nearly-pure samples from a variety of environments. 2) We identify some previously unknown samples. 3) We re-characterize each source using all identified samples. and 4) We use the A-coefficients to determine whether, in the future, samples from the 3 B.C. tephras can be identified while using samples of intermediate purity.

Chapter 6

FURTHER TESTING OF XES METHOD FOR THE ROUTINE IDENTIFICATION OF TEPHRA SAMPLES

The results of Chapter 3, 4, and 5 suggested that Mazama (M) could be distinguished from Mt. St. Helens (Yn) and Bridge River (BR) on the basis of its Zr concentration by submitting the <62 µm size fraction of sieved samples directly for analysis. Bridge River and Yn, on the other hand should be distinguishable on the basis of their K concentrations by analyzing HCl, H_2O_2-treated (<62 µm) samples with a Zn secondary target.

In this chapter we first examine whether samples can be identified using HCl, H_2O_2-treated <62 µm samples analyzed with a Ag and Zn secondary targets. We will then reduce preparation by submitting the <62 µm size range of sieved samples directly for analysis to see if samples can still be identified. Although our main goal was to identify nearly-pure samples of BR, Yn, and M during these experiments we discovered other samples which resembled the U-43, and L-23, L-24 type samples mentioned in Chapter 5. Such information on other tephras will be included in this chapter.

6.1 Identification of Tephras Using <62 µm HCl, H_2O_2-treated Samples

A) B.C. Tephras

A group of reference samples (section 3.1) (5 M, 8 Yn, 14 BR) were sieved to extract the <62 µm size fraction. This size fraction was treated with HCl and H_2O_2. Twenty-two unknown samples were included for analysis. We suspected that 5 of these were M, 5 were BR, 4 were Yn, and 8 were of unknown origin. These a priori guesses were based upon information about the geographical locations from which the samples were collected, as well as upon preliminary XES results obtained through previous analysis of whole ashes (<62 µm). All samples were analyzed for 5 minutes each with a Ag secondary target.

A number of HCl, H_2O_2-treated (<62 µm) reference samples (16 BR, 5 M, 9 Yn) were then analyzed for 5 minutes each using a Zn secondary target. Because we had not yet analyzed samples of other northwest tephras with a Zn secondary target, HCl, NaOCl-treated (<62 µm) samples of White River (WR) and Glacier Peak (GP) tephras were analyzed for comparison. We included the analysis of 21 unknowns. We guessed that 4 were M, 4 were BR, 4 were Yn and 8 were of unknown origin.

The Pk/Cp ratios were calculated for the samples analyzed with the Ag secondary target, and the Pk/Cp+R ratios were calculated for samples analyzed with the Zn secondary target. We characterized each source using the reference samples. The results of the unknowns were then compared to the reference samples on an individual basis. Comparisons were also made to results obtained earlier (in Ch. 5). We found that samples of M were easily identified on the basis of their high Zr concentrations, while Yn could be identified on the basis of its low K concentration. In the final analysis (Tables 6.1 and 6.2) all samples identified as M, Yn, BR etc. were used to characterize each source. A-coefficients comparing the tephra sources on the basis of results obtained using the Ag and Zn secondary targets appear in Tables 6.3 and 6.4.

Three examples of spectra of BR, Yn, and M analyzed with a silver secondary target are given in figure 6.1 and show that Zr is considerably higher for M than for the other two tephras. The K concentration is also lower for Yn in these spectra, but this difference is best seen through analysis with a Zn secondary target as presented in fig. 6.2. In Table 6.3 we show that at the 2 sigma range in concentration, M can be distinguished from BR and Yn on the basis of both its Zr and Y concentrations. In Table 6.4 and fig. 6.3 we show that at the 2 sigma range in concentration, Yn can be distinguished from both M and BR on the basis of its low K concentration.

TABLE 6.1

Tephras Characterized Using HCl, H_2O_2 Treated <62µm Samples Analyzed With a Ag Secondary Target

All values are in relative concentrations (Pk/Cp ratios)[a]

	B.C. Tephras			Mt. St. Helens W-like Samples
	M(±1σ)	BR(±1σ)	Yn(±1σ)	U(±1σ)
n[b]	10	19	12	8
K	4.23(.37)	4.42(.69)	2.73(.38)	3.03(.22)
Ca	4.5(1.0)	5.7(1.0)	6.3(1.0)	6.4(1.5)
Ti	3.0(0.4)	2.2(0.8)	1.8(1.0)	1.8(0.5)
Fe	115(12)	91(16)	100(18)	105(14)
Zn	1.44(.65)	.90(.18)	1.51(.64)	1.09(.13)
Rb	9.55(.64)	7.09(.91)	7.48(.94)	8.66(.82)
Sr	70(5)	89(17)	79(5)	73(12)
Y	9.02(.64)	5.43(.55)	4.24(.46)	6.14(.64)
Zr	98.1(4.0)	67.1(3.7)	58.8(5.5)	74.0(2.3)
Nb	2.99(.44)	3.16(.54)	2.95(.61)	2.32(.45)
Ca/K	1.05(.22)	1.34(.35)	2.40(.45)	2.10(.55)
Sr/Rb	7.4(0.6)	12.9(3.9)	10.7(1.6)	8.5(2.1)
C/R	1.47(.03)	1.48(.04)	1.48(.05)	1.47(.04)

[a] calibration was used to reduce between-run variability

[b] number of samples analyzed

TABLE 6.2

Tephras Characterized by XES Using HCl, H_2O_2 (or NaOCl) Treated Samples (<62μm) Analyzed With a Zn Secondary Target

All values are in relative concentrations (Pk/Cp+R ratios)[a]

	B.C. Tephras			Tephras from other sources of interest			
	M(±1σ)	BR(±1σ)	Yn(±1σ)	GP30(±1σ)	GP40(±1σ)	WR(±1σ)	U[b](±1σ)
n[c]	10	20	13	3	3	3	8
K	211(12)	197(16)	132(10)	192(25)	231(12)	237(7)	147(8)
Ca	203(23)	235(18)	271(30)	231(22)	192(21)	273(22)	240(30)
Ti	110(21)	91(28)	71(29)	44(3)	54(9)	57(8)	60(12)
Mn	-	-	35.9 (2.4)	40.9 (1.8)	-	-	-
Fe	266(20)	224(31)	254(45)	172(8)	174(21)	208(13)	240(47)
Ca/K	.96(.14)	1.16(.33)	2.06(.18)	1.21(.10)	.83(.14)	1.01(.09)	1.63(.26)

[a] calibration was used to reduce between-run variability

[b] Mt. St. Helens W-like samples

[c] number of samples analyzed

TABLE 6.3

A-Coefficients Comparing B.C. Tephras on Basis of HCl, H_2O_2 Treated <62μm Samples Analyzed with a Ag Secondary Target[a]

	M/Yn	M/BR	Yn/BR
n[b]	10/12	10/19	12/19
K	.996	.088	.791
Ca	.611	.390	.154
Ti	.412	.330	.104
Fe	.243	.425	.142
Zn	.028	.326	.377
Rb	.652	.794	.106
Sr	.439	.437	.226
Y	2.17*	1.51*	.588
Zr	2.08*	2.02*	.455
Nb	.017	.085	.091
Ca/K	1.02*	.256	.666
Sr/Rb	.783	.686	.221
C/R	.045	.040	.012

[a] calibration was used to reduce between run variability

[b] number of samples analyzed from each source

* element is useful for distinguishing between tephra pair

TABLE 6.4

A-Coefficients Comparing Tephras on Basis of HCl, H_2O_2 Treated <62μm Samples Analyzed with a Zn Secondary Target[a]

	n[b]	K	Ca	Ti	Fe	Ca/K
M/Yn	10/13	1.80*	.642	.390	.092	1.72*
M/BR	10/20	.250	.390	.194	.412	.213
M/GP	10/6	.227	.115	1.09*	1.19*	.184
M/WR	10/3	.684	.778	.914	.879	.109
Yn/BR	13/20	1.25*	.375	.175	.197	.882
Yn/GP	13/6	1.03*	.456	.324	.591	1.14*
Yn/WR	13/3	3.04*	.019	.189	.347	1.94*
BR/GP	20/6	.014	.200	.611	.446	.053
BR/WR	20/3	.870	.475	.472	.182	.179
GP/WR	6/3	.732	.543	.313	.446	.136
GP30/GP40	3/3	1.15*	.453	.417	.034	.792
GP30/WR	3/3	1.88*	.477	.591	.857	.526

[a] calibration was used to reduce between run variability

[b] number of samples analyzed from each source

* element is useful for distinguishing between tephra pair

FIGURE 6.1

Three Examples of spectra of Mazama, Bridge River, and Mt. St. Helens Yn Analyzed by XES with a Silver Secondary Target

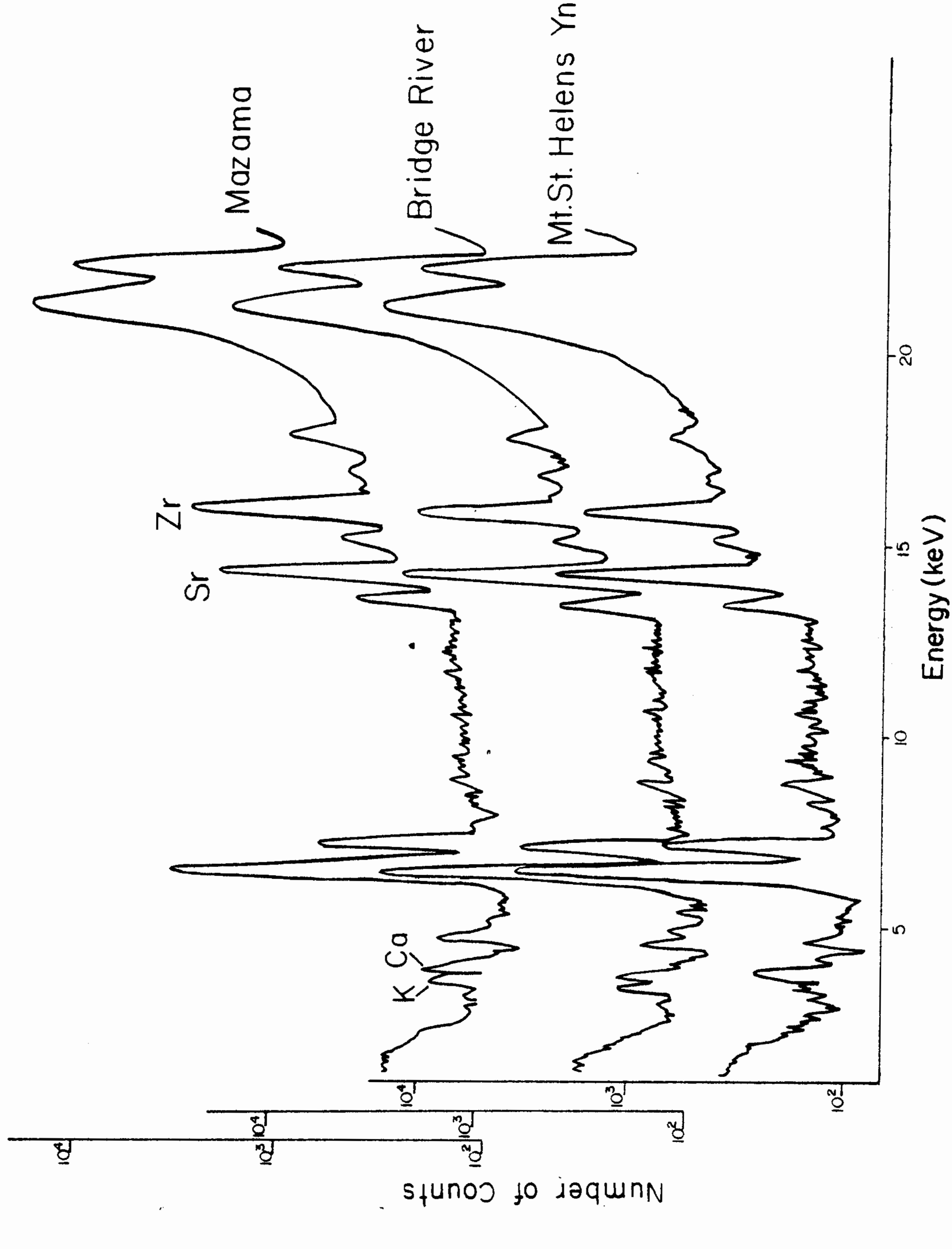

Mazama
Bridge River
Mt.St. Helens Yn
Sr
Zr
K
Ca
Energy (keV)
5
10
15
20
Number of Counts
10^4
10^3
10^2

FIGURE 6.2

Two Examples of Spectra of Bridge River and Mt. St. Helens Yn Analyzed by XES with a Zinc Secondary Target

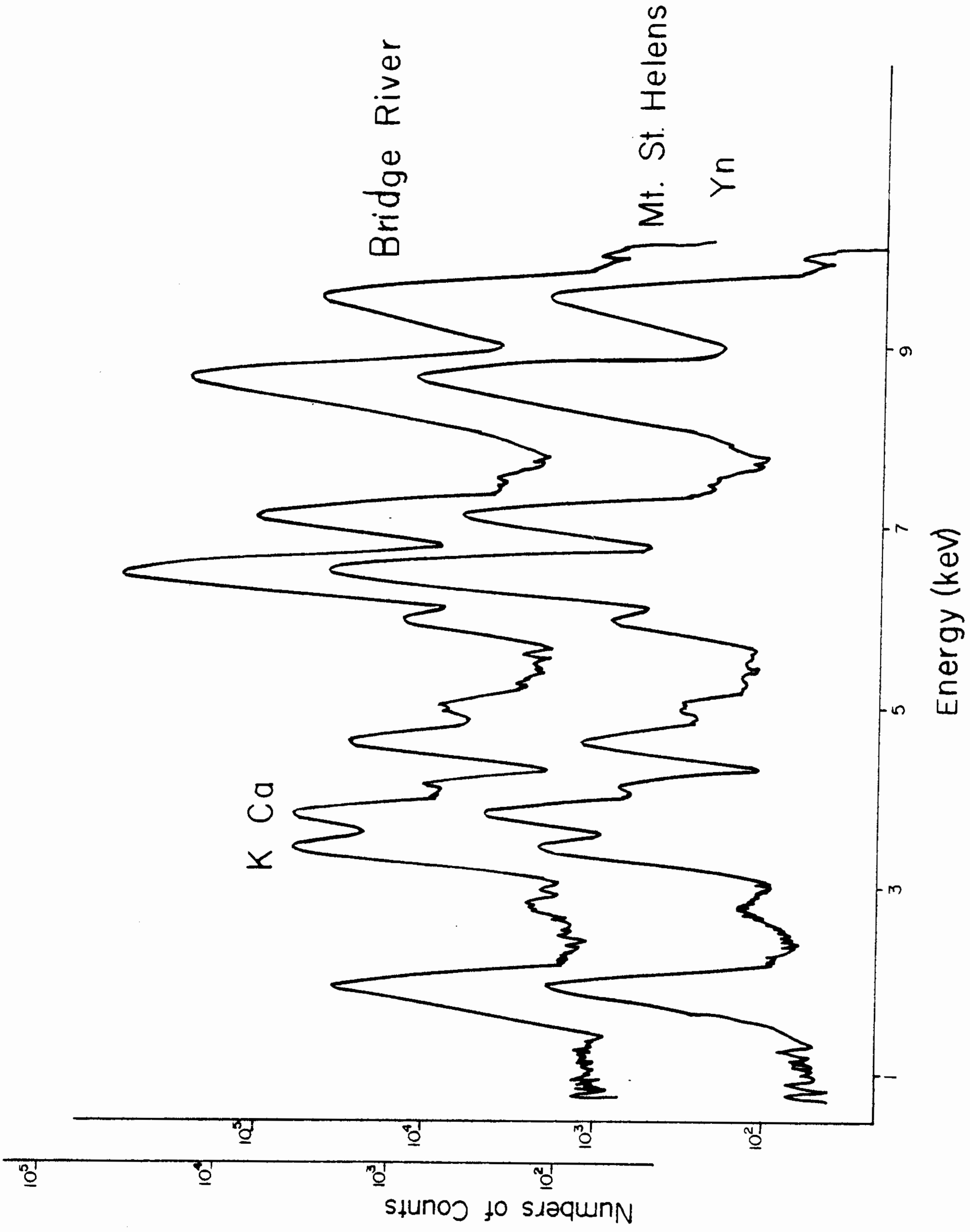

Bridge River
Mt. St. Helens
Yn
K Ca
1
3
5
7
9
Energy (keV)
10^5
10^4
10^3
10^2
10^5
10^4
10^3
10^2
Numbers of Counts

FIGURE 6.3: K area/Compton-Rayleigh peak height ratios for three tephras measured by XES. The number of samples analyzed is shown above each point and the error bars are ± 2σ in all three figures.

FIGURE 6.4: Zr area/Compton peak height ratios for three tephras measured by XES.

FIGURE 6.5: K area/Compton-Rayleigh peak height ratios for Bridge River and Mt. St. Helens Yn using untreated samples (<62µm).

Fig. 6.3

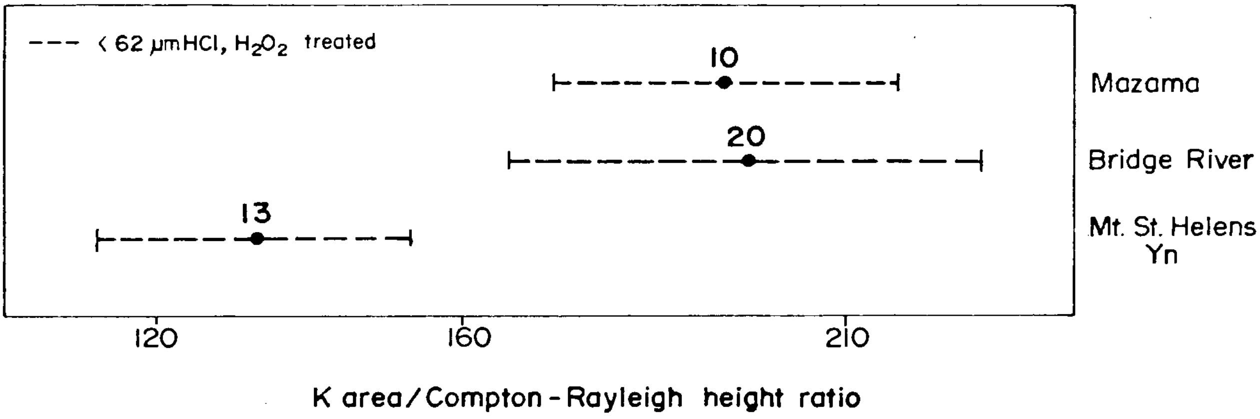


Fig. 6.4

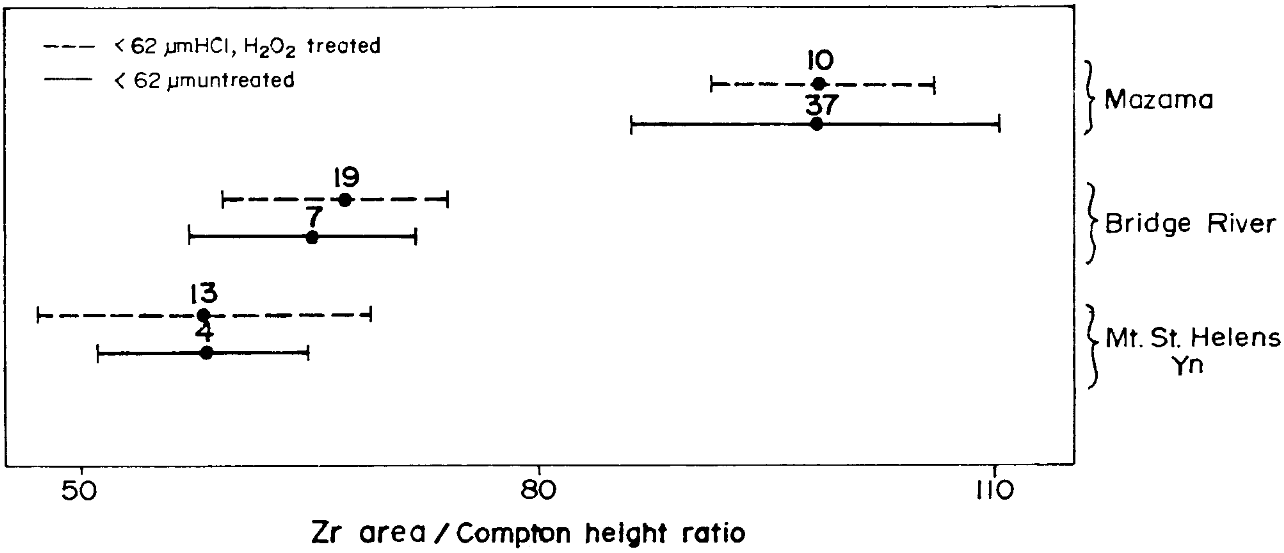
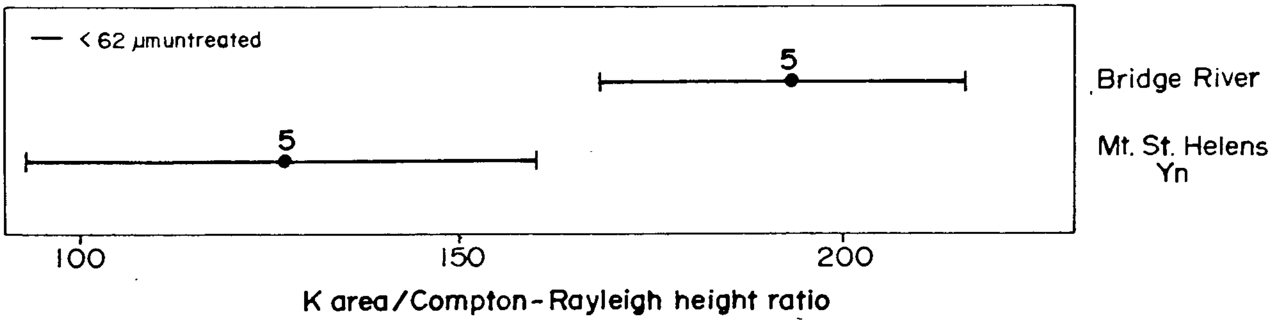


Fig. 6.5



B) Glacier Peak and White River Tephras

In Table 6.4 we show that Yn can be distinguished from both GP and WR either on the basis of its low K concentration, or on the basis of its high Ca/K ratio. Concentrations of Ti and, possibly, Fe also allow us to distinguish between M and GP. No other tephra pairs are distinguishable on the basis of the major element chemistry of HCl, H_2O_2 (or NaOCl)-treated samples from the less than 62 micron size range. We found that GPB and GPG were not distinguishable on the basis of their major element chemistry, but that GP 30 and 40's had different concentrations of potassium. This further supports the evidence in Chapter 5 that GP30 and GP40 belong in different chemical groups. Separation of the GP30 and 40 groups now allows us to distinguish between GP30 and WR.

C) U-Tephras

On the basis of their trace and major element chemistry, the samples U-25, U-27, U-29, and U-48 resembled the L-23, L-24, and U-43 samples mentioned in Chapter 5. Analyzing the separated glasses of these samples did not change the results and we therefore do not believe that contamination alone can explain the differences between these and the Yn samples. All such samples were collected in spots where Mt. St. Helens W, T, or both W and

T tephras are found; because of their low concentrations of K, all samples are certainly the result of one of the Mt. St. Helens eruptions. When compared to Mt. St. Helens Yn, these samples almost invariably had higher Zr concentrations and lower Ca/K ratios than the Yn samples. Other features which help characterize this group and distinguish it from Yn are: higher concentrations of alkali elements, lower concentrations of alkali earth elements, and higher concentrations of Y and Zr (Table 6.1). We had only one reference sample of Mt. St. Helens Wn; it also had higher Zr concentrations than the Yn samples. We also had one reference sample of Mt. St Helens Ys which resembled the Yn samples more closely than the unknowns.

6.2 Identification of Tephras Using Untreated Samples From the Less than 62 µm Size Range

A) Trace Element Analysis

Because the Zr concentration in M was extremely different from that of the other tephras, and because the HCl and H_2O_2 treatments have little effect on Zr, we believed that M could be identified by submitting the <62 µm size fraction of samples directly for analysis without the chemical pre-treatments. We have discovered that most samples of tephra discovered in B.C. are M and we realized that a great deal of time could be saved if these could be identified without the chemical pre-treatments.

In this experiment we first characterized M using 10 untreated reference samples (<62 µm). Similarly 4 untreated BR and 4 untreated Yn samples (<62 µm) were analyzed for comparison. We verified that none of the BR or Yn samples could be confused with the M samples. Next we analyzed 39 untreated (<62 µm), unknown samples which, on the basis of a priori information, we believed to be M. All but 4 of the 39 samples had Zr concentrations which were unmistakably those of M. The four samples had Zr concentrations which were slightly lower than the 2 sigma range of Zr concentration defined by the 10 reference samples. Previous tests (section 6.1) indicated, however, that if we had any doubt as to the correct identification of a sample, such samples could be treated with HCl and H_2O_2 and then identified with almost certainty. By treating the 4 samples we were able to verify that they were Mazama. In the final analysis all 49 untreated samples were used to characterize M.

Mazama, BR, and Yn tephras are characterized in Table 6.5 using untreated (<62 µm) samples. A-coefficients comparing these tephras appear in Table 6.6. Results indicate that at the 2 sigma range of Zr concentration, M can be distinguished from both BR and Yn using untreated samples from the <62 µm size range. Mazama can also be distinguished at the 3 sigma range. In figure 6.4 we plot the two sigma ranges for the 3 B.C. tephras to show that M can be identified using either treated or untreated

TABLE 6.5

Tephras Characterized Using Untreated <62μm Samples Analyzed With a Ag Secondary Target

All values are in relative concentrations (Pk/Cp ratios)

	M/(±1σ)	BR/(±1σ)	Yn/(±1σ)
n[a]	49	7	4
K	4.2(0.8)	3.3(1.1)	3.3 -
Ca	6.8(4.7)	6.0(1.3)	6.4(3.2)
Ti	2.8(0.7)	2.3(1.1)	1.7(0.8)
Fe	135(32)	119(52)	149(36)
Zn	1.61(.61)	1.77(.87)	1.69(.44)
Rb	9.6(1.0)	6.8(1.1)	8.3(2.5)
Sr	73(10)	93(18)	79(14)
Y	9.2(0.9)	6.1(0.9)	5.6(1.1)
Zr	97.7(5.7)	65.1(3.8)	57.9(3.6)
Nb	2.58(.75)	3.15(.88)	2.55(.12)
Ca/K	1.7(1.1)	1.8(0.3)	2.1
Sr/Rb	7.7(1.4)	13.7(3.5)	9.8(1.9)
C/R	1.4(.06)	1.44(.04)	1.51(.11)

[a] number of samples analyzed

TABLE 6.6

A-Coefficients Comparing B.C. Tephras on Basis of Untreated <62µm Samples

Analyzed with a Ag Secondary Target

	M/Yn	M/BR	Yn/BR
n[a]	49/4	49/7	4/7
K	.563	.411	0
Ca	.162	.181	.040
Ti	.365	.144	.139
Fe	.103	.094	.170
Zn	.040	.056	.032
Rb	.187	.672	.210
Sr	.115	.348	.220
Y	.918	.885	.114
Zr	2.16*	1.72*	.495
Nb	.015	.177	.303
Ca/K	.191	.038	.503
Sr/Rb	.332	.602	.368
C/R	.141	.127	.243

[a] number of samples analyzed

*element is useful for distinguishing between tephra pair samples. The HCl and H_2O_2 treatments do not significantly change the results and therefore do not improve our ability to identify Mazama on the basis of Zr.

B) Major Element Anlysis

We assumed in section 5.5 that the HCl, H_2O_2 treatments would be necessary if K were used as a diagnostic element for distinguishing between Yn and BR. Nevertheless, we analyzed 5 untreated samples from each of BR and Yn. The results in figure 6.5, though preliminary, show that even without the HCl and H_2O_2 treatments, we may still be able to distinguish between BR and Yn using concentrations of K.

6.3 Comparison to Other Work in the Literature, and Conclusions

When we compare the major element chemistry of the 6 test samples (Table C.1) to the microprobe data of Westgate (Table D.1), we find that the average composition of our samples conforms reasonably well with results in the literature. This means that our modified treatments have produced bulk samples of glass which are remarkably pure.

With untreated samples from the fine grained size range no elements but Zr and K will allow us to distinguish between the 3 B.C. tephras. Nevertheless, in Appendix D we have applied our A-coefficients to some of the microprobe results appearing within the literature (Tables D.4, D.5). We show that, at the two sigma range in concentration, other researchers cannot distinguish between BR and M. With our methods, on the other hand, we can distinguish between Yn, BR and M with a high degree of reliability and a minimum of effort.

6.4 Discussion

Since one of the main goals of our work was to provide local archaeologists with a routine, rapid, reliable, and inexpensive method for identifying tephras discovered in local deposits, it is worthwhile indicating to archaeologists just how reliable our results are likely to be. The following discussion should establish that the real value of our technique lies in its flexibility.

In our work we find that the chemical composition of the glass does not depend greatly on depositional environment. We also believe that the problems inherent in identifying individual samples are likely to be similar to those already encountered. In order to identify the B.C. tephra samples we must know two things about the samples: 1) they must be from S. central B.C.;

and 2) they must be from Holocene eruptions. With I-coefficients we can then use concentrations of K and Zr to identify samples from any of the 3 B.C. tephra sources with greater than 95% certainty. If less than 20 samples are used to characterize a source (as was the case for Yn) this probability drops to that defined by the Student's t distribution: 80-90% (n = 2 to 5), 90 to 93% (n = 5 to 10), 93 to 95% (n = 10 to 20) samples.

A) Improving Reliability of Results with Additional Treatments - Value of Comparing Samples Element by Element

The probability of correctly identifying a sample increases if more than one element proves useful for distinguishing between tephra deposits. Perhaps one of the best methods for combining such probabilities would be offered through Bayesian statistics (cf. LaValle 1970; Phillips 1974; Winkler 1972). The total probability of correct identification is increased by each individual probability of identification offered by each element. One thereby increases the possibility of correct identification by, for example, treating M with HCl and H_2O_2 so that Y becomes diagnostic, or by supplementing XES with alpha counting so that U and Th can be used to distinguish between BR and Yn.

In our work, by analyzing less than pure samples, we have accepted the fact that some elements will be virtually useless for identifying tephras. For example, Zr is the sole useful element for identifying M with less than pure samples. Other elements, though unreliable for identification purposes, are still extremely useful for other purposes. High concentration of elements such as Ca, Sr, Fe, and Ti immediately signal that high levels of contamination are present in the sample. For example, among the 39 untreated samples of M ash, 17/39 samples had Ca concentrations that were too high and outside the acceptable range defined by the 10 reference samples for this source; 9/39 samples had Ti concentrations which were also too high; and 7/39 had Cp/R ratios which were too low. Approximately 1/20 or, in our case, 1 or 2 samples would be expected to fall outside the two sigma range due to statistical fluctuations in the data. Therefore, we know that most of the anomalies are probably the result of the presence of large amounts of carbonates and clays in the samples. In spite of the high levels of contamination in this many samples, relatively few of the Zr concentrations were abnormal (4/39 as discussed earlier). This is 2 or 3 more than that expected by statistical fluctuation alone, but in all 4 cases, the concentrations of other elements indicated that large amounts of contamination were present. The Zr concentrations of these samples fell within the 3 sigma range of Zr concentration for M and did not fall within the 3 sigma ranges of Zr concentration for the other B.C. tephras. There was little doubt that these samples were M. As discussed, our general procedure was to treat such samples with the HCl and peroxide reagents to verify that the concentrations of all elements in the treated samples fell within the two sigma ranges defined for M on the basis of the reference samples, but by then including the results of the untreated contaminated samples in the final calculations used to characterize each source, we hoped that, in the future, most contaminated samples could still be identified without the chemical treatments.

Although approximately 18/20 samples can be identified using only those treatments outlined above, there is no reason why samples which have undergone additional treatments cannot still be identified along with untreated samples (concentrations in treated samples fall within the ranges of concentration of all elements defined for each source). Extremely contaminated samples are generally easy to spot prior to analysis, or following analysis if concentrations of all elements are scanned. We have shown that, in most cases, additional treatments will not be required, but we have not eliminated the option of using additional treatments to aid identification in difficult cases.

B) Using Additional Information to Improve Reliability of Identifications

We believe that we are actually able to identify tephras with much better than 95% certainty, even without additional sample treatments. This is because we have recorded prior information about each of our samples. It is not our aim to provide exact probabilities or to delve heavily into a branch of statistics (Bayesian statistics) which allows one to use information from a variety of sources in order to improve the calculated credibility of one's results. There are a number of excellent texts covering this topic (see above references). One use of the Bayesian methods is quite simple. Prior to analysis, we knew with a relatively high degree of certainty to which source each of our samples belonged. For example, we can guess that a sample sent from B.C. is likely to be either M, BR or Yn, and not GP or WR. If it is collected in the Okanagan region of B.C. and is from the upper layer in a deposit containing two ash layers, it is likely to be Yn. If it is collected near Lillooet, it is likely to be BR but could be M, and is probably not Yn. If it is coarse grained it is almost certainly BR. In the lab we can improve our guesses depending on such criteria as grain size, color, relative abundances of minerals, etc. With experience we became extremely good at the a priori identification of samples. The results of chemical analyses often came as no surprise and merely strengthened our belief that a sample belonged to a particular source. Not only do we feel that the use of a priori identifications improves the reliability of the final results, but we also found that this skill, developed with experience, enabled us to simplify identification procedures. Because M can be identified without chemical treatments, it is worthwhile analyzing untreated (<62 µm) samples to isolate first Mazama. Non-Mazama samples could then be chemically treated and re-analyzed with a Zn secondary target to identify BR and Yn. In our work we simply used our a priori information to pretreat all samples according to whether or not we initially believed them to be M. The "M" samples were submitted directly for analysis and the "non-M" samples were pretreated with HCl and H_2O_2 prior to analysis. All samples, whether M, BR, or Yn, could therefore be analyzed within the same XES session and additional time spent setting up the XES equipment and refitting SAMPO parameters could be eliminated. In our case, all our initial guesses proved correct and a great deal of time was saved. Of course, if a particular researcher is not good at the a priori identification of samples, time can be lost, by unnecessarily treating M samples, or by having to pretreat and re-analyze samples from other sources. Each researcher must evaluate the utility of his method for his particular circumstances. If a more exact indication of the reliability of our identifications is required, we can use Bayesian statistics to calculate such figures. In any case, we can safely assume that all of our identifications are better than 95% certain.

Chapter 7

SUMMARY AND ARCHAEOLOGICAL APPLICATIONS

Most past methods for identifying tephras with a high degree of reliability have required tedious amounts of sample preparation or long analysis times. The results presented in this work have shown that, if the problem is to identify routinely samples from a limited number of well known tephra sources, the techniques of tephra identification can be greatly simplified. Both XES and alpha-counting are simple instrumental techniques that can be used to identify samples of B.C. tephras with high degrees of reliability and a minimum of effort. One (XES) offers rapid laboratory anlaysis; the other (alpha-counting) offers simple analysis and the possibility of identifying tephras in the field.

By extensively studying the effects of sample preparation on composition, we discovered that the <62 µm size fraction of sieved ashes is mostly glass and can be used to identify the B.C. tephras with only simple pre-treatments. A great deal of tedious sample preparation is thereby eliminated. We have further simplified the XES method for identifying tephras by analyzing loose powders instead of pressed pellets, and by using relative concentrations instead of absolute concentrations to characterize tephras. Use of the I-coefficients provides us with a simple statistical method for identifying individual samples. Although we have concentrated on developing routine methods for identifying samples of well known tephras in B.C., results on separated glass samples have indicated that alpha-counting, XES or NAA analysis of the glass separates make the analysis of a wide range of elements possible and can be very useful for characterizing tephras in unknown regions.

7.1 Applications to Archaeology

Only 7 of our samples were directly archaeological. The results of individual analyses of the archaeological samples are listed in tables 7.1 and 7.2. The locations from which the archaeological samples were collected are revealed in Appendix A, while descriptions of the archaeological sites near (or in) which these samples were found appear in various reports. Only a brief summary will be given here.

Perhaps the most interesting of the samples analyzed were the EeQw48-10 and EeQw48-9 samples collected from a spot adjacent to the Gore Creek Site (EeQw48) near Kamloops, B.C. Human skeletal remains were discovered .5 to 1 meter below the bottom ash layer in a deposit containing two ash layers (cf. Elmore et. al. 1979). We identified the bottom layer as Mazama ash and the top layer as Mt. St. Helens Yn. Approximately 2 meters of

TABLE 7.1

Results (Pk/Cp ratios) of Archeological Samples Analyzed with a Ag Secondary Target

Sample	EeQw48-9[a]	EeRb5[b]	EeRK4-2[a]	EeQw48-10[b]	EeRa4[b]	EeRa6-3[b]	EeRa6-1[c]	EdQx5[c]
Source	M	M	M	Yn	Yn	Yn	Yn	Yn
K	nd	2.77	5.26	2.66	2.81	3.30	3.65	4.46
Ca	3.5	3.2	7.3	5.2	5.5	5.4	4.6	5.7
Ti	2.9	2.7	3.8	1.5	2.3	1.2	1.4	2.1
Fe	141	108	145	92	93	84	90	96
Zn	1.53	1.25	2.00	1.30	<1	1.49	<1	<1
Rb	9.37	10.78	11.46	8.03	6.79	7.86	8.04	8.38
Sr	72	71	74	73	76	71	76	83
Y	10.19	11.16	10.79	4.63	3.69	4.34	4.31	4.70
Zr	99.3	98.0	102.4	53.9	58.2	54.7	52.4	54.0
Nb	2.08	<1	<1	<1	2.08	3.54	1.26	<1
Ca/K	-	1.15	1.39	1.96	1.95	1.64	1.26	1.27
Sr/Rb	7.7	6.6	6.4	9.1	11.1	9.1	9.5	9.9
C/R	1.54	1.46	1.61	1.48	1.52	1.52	1.50	1.53

[a] untreated (<62μm)

[b] HCl, H_2O_2 treated (<62μm)

[c] HCl, H_2O_2 treated glass (62-210μm)

TABLE 7.2

Results, (Pk/Cp+R ratios), of Archeaological Samples Analyzed With a Zn Secondary Target

Sample	EeRb5[a]	EeRK4-1[a]	EeQw48-10[a]	EeRa4[a]	EeRa6-3[a]	EdQX5[b]	EeRb5[a]
Source	M	M	Yn	Yn	Yn	Yn	Yn
K	207	197	132	133	138	140	140
Ca	124	226	246	271	238	235	232
Ti	90	148	57	69	47	58	54
Fe	254	303	238	230	200	217	221
Ca/K	.91	1.14	1.86	2.03	1.72	1.68	1.66

[a] HCl, H_2O_2 treated (62μm)

[b] HCl, H_2O_2 treated glass (62-210μm)

sediment had accumulated between the top and bottom ash layers. By calculating the average rate of deposition for the site, we estimated that the skeletal remains are about 8,400 radiocarbon years old. This site is, therefore, one of the earliest evidences for man in B.C. A radiocarbon age of 8,250 ± 115 y.b.p. (S1737) obtained on the bone indicates that our tephrochronological age estimate is reasonably accurate.

At the Moulton Cr. Site (EdQx5) near Chase, B.C., a volcanic ash layer separated two cultural components (Eldridge 1974). Eldridge guessed that the ash was Mt. St. Helens Yn (3,400 y.b.p.), and our analysis confirmed his hypothesis. The "above-ash" component was identified as an early Kamloops phase, while the "below-ash" component has some resemblance to the Old Cordilleran Tradition.

Geological samples were collected from a road cut a few hundred meters from the Bell Site (EeRk4) on Kettle Brook Cr. near Lillocet, B.C. (Stryd 1971; 1980:pers. comm.). This sample was identified as Mazama ash. Another site (EeRk5) was discovered in the immediate vicinity of the EeRk4 sampling location. One meter above the ash at EeRk5 was a paleosol containing basalt flakes and butchered bone. The oldest component at the Bell Site is of the Nesikep tradition and appears above the paleosol horizon described at EeRk5. The cultural material at EeRk4 must, therefore, be considerably younger than 6,600 y.b.p.

The remaining archaeological samples were found in, or near, sites which were examined during a 1979 survey (Heritage Conservation Branch of B.C.) conducted in the vicinity of Kamloops, B.C. (B. Chisolm 1980:pers. comm.). Two samples collected near EeRa6-3 were identified as Mt. St. Helens Yn. Two flakes and a core were discovered 1/2 m above the ash in a stratified site. The sample from a cut bank near EeRa4 was also identified as Mt. St. Helens Yn. The site at EeRa4 was heavily disturbed with a small surface scatter of flakes. The exact relationship between ash and flaking debris was unclear. At EeRb5, flakes were scattered at a below ash level in a wind-blown depression. Ash identified as Mazama was collected from a cut adjacent to the site but the exact relationship between the ash and flaking debris is not understood. None of these sites from the 1979 survey have been studied in detail. We are hoping, however, that the prior identification of tephra samples will not only facilitate future interpretation of site stratigraphy, but will also provide regional archaeologists with a means of making inter-site comparisons of cultural materials.

APPENDIX A

TABLE A.1

Sample Information

Sample	Location	Number on Map	Collectors	References	Source a priori	Source a posteriori	Reference Samples(*)
Yn-18	Inside W. boundary Mt. Ranier Park, Wash.; 3 Km. N.E. of Longmire	1	Project[a]	1	Yn	Yn	(*)
Yn-19	~ 10 Km. S. of Ashford, Wash. on Skate Cr. Road	2	"	1	Yn	Yn	(*)
Yn-20	~ 6 Km. S. of Hat Cr. & Skate Cr. Road Junction near Ashford, Wash.	3	"	1	Yn	Yn	(*)
Yn-21	~ 3 Km. S. of Randle, Wash. on Woodscreek Rd.	4	"	1	Yn	Yn	(*)
Yn-22	~ 5 Km. S. of Randle, Wash. on Woodscreek Rd.	5	"	1	Yn	Yn	(*)
L-23	~ 1 Km. S. of Randle, Wash. on Woodscreek Rd. - Lacustrine Deposit	6	"		Yn?	U	
L-24	~ 2 Km. E. of Randle, Wash. on Hwy. 12 - Lacustrine Deposit	7	"		Yn?	U	
U-25	~ 3 Km. Inside E. Boundary of Mt. Ranier Park, Wash.	8	"	1	Yn?	U	
U-26	~ 4 Km. Inside E. Boundary of Mt. Ranier Park, Wash. on Hwy. 706 - top layer?	9	"	1	W?	U	
U-27	Same location as U-26 - bottom layer?	10	"	1	Yn?	U	
U-29	~ 6 Km. N.W. of Junction of Hwy. 706 & Hwy. 410, Wash.	11	"	1	Yn?	U	
GPB-30	~ 11 Km. W. of Hwy. 209 on Road to Trinity, Wash. along Chiwawa R. - upper layer	13	"	2	GPB	GP30	(*)
GPG-30	Same location as GPB-30 - lower layer	14	"	2	GPG	GP30	(*)
GPG-35	Trinity, Wash., 34 Km. N. of Hwy. 209 - lower layer	15	"	2	GPG	GP30	(*)
GPB-35	Same location as GPG-35 - upper layer	16	"	2	GPB	GP30	(*)
GPB-36	~ 100 m. from GPG-35 - upper layer	17	"	2	GPB	GP30	(*)
GPG-41	~ 3 Km. N.E. of Lake Chelan, Wash. along Mitchell Creek - lower layer of 3 layers	18	"	2	GPG	GP40	(*)
GPB-42	Same location as GPG-41 - middle layer of 3 layers	19	"	2	GPB	GP40	(*)

TABLE A.1 (continued)

- 2 -

U-43	Same location as GP-41 - top layer of 3 layers	20	"	2	M?	U	
GPG-44a	~ 3 Km. N.E. of Wapato L., E. of Lake Chelan, Wash. - lower layer	21	"	2	GPG	GP40	(*)
GPG-46b	~ 7 Km. N.W. of Columbia R. along Antoine Cr., Wash. - lower layer of 3 layers	22	"	2	GPG	GP40	(*)
GPB-47a	Same location as GPG-46a - middle layer of 3 layers	23	"	2	GPB	GP40	(*)
U-48	Same location as GPG-46b - top layer of 3 layers	24	"	2	M?	U	
M-54	~ 8 Km. N.W. of Hwy. 97 Junction, Near Mowich, Oreg., Hwy. 58 - upper (Cl) layer	30	"	3	M	M	(*)
M-56	~ 21 Km. N.W. of Hwy. 97, New Crescent L. Oregon., Hwy. 58 - upper (Cl) layer	31	"	3	M	M	(*)
BR-65	~ 6 Km. N.E. of Plinth Peak,at mouth of Salal Cr., in Lillooet Valley, B.C.	40	"	4,5	BR	BR	(*)
BR-66	At same spot as BR-65 - upper layer?	41	"	4,5	BR	BR	(*)
BR-67	~ 4 Km. S.W. of Salal Cr. along Lillooet R., B.C.	42	"	4,5	BR	BR	(*)
BR-68	~ 3 Km. N. of Bralorne, B.C.	43	"	4	BR	BR	(*)
BR-69	~ 2 Km. S. of Gold Bridge, B.C.	44	"	4	BR	BR	(*)
BR-10	~ 4 Km. E. of Minto Mines, B.C., along Bridge R. Rd.	45	"	4	BR	BR	(*)
BR-70	~ 6 Km. E. of Minto Mines, B.C., along Bridge R. Rd.	46	"	4	BR	BR	(*)
BR-9	~ 8 Km. of Minto Mines, B.C., along Bridge R. Rd.	47	"	4	BR	BR	(*)
BR-8	~ 11 Km. of Minto Mines, B.C., along Bridge R. Rd.	48	"	4	BR	BR	(*)
BR-7	~ 13 Km. E. of Minto Mines, B.C. along Bridge R. Rd.	49	"	4	BR	BR	(*)
BR-71	~ 10 Km. W. of Rexmount, B.C., along Bridge R. Rd.	50	"	4	BR	BR	(*)
BR-6	~ 8 Km. W. of Rexmount, B.C., along Bridge R. Rd.	51	"	4	BR	BR	(*)
BR-5	~ 4 Km. W. of Rexmount, B.C., along Bridge R. Rd.	52	"	4	BR	BR	(*)
BR-4	~ 2 Km. E. of Rexmount, B.C., along Bridge R. Rd.	53	"	4	BR	BR	(*)
BR-16	~ 4 Km. E. of Rexmount, B.C., along Bridge R. Rd.	54	"	4	BR	BR	(*)

TABLE A.1 (continued)

- 3 -

BR-15	~ 6 Km. E. of Rexmount, B.C., along Bridge R. Rd.	55	"	4	BR	BR	(*)
M-3	~ 3 Km. S.E. of Antoine Cr., B.C., along Yalakom R.	56	"		M	M	
M-5	~ 5 Km. S.E. of Antoine Cr., B.C., along Yalakom R.	57	"		M	M	
M-1	~ 7 Km. S.E. of Antoine Cr., B.C., along Yalakom R.	58	"		M	M	
BB-11	~ 3 Km. N. of Jesmond, B.C.	59	"		BR	BR	
BB-14	~ 4 Km. N.E. of Big Bar Creek, B.C.	60	"		BR	BR	
BB-2	Big Bar Creek, B.C.	61	A. Stryd		BR	BR	
BR-100	~ 12 Km. S. of Lillooet, B.C., W. Side of Fraser - lake core	62	R. Mathews	6	BR	BR	(*)
BR-101	Same location as BR-100, Second lake core	63	"	6	BR	BR	(*)
M-202	~ 1 Mi. E. of Pavilion, B.C., alluvial for deposit along Fraser R.	64	H. Nasmith	4,7,8 (Sample 61W4)	M	M	(*)
EeRk4-1	~ 6 Km. N.E. of Fountain, B.C., near the Bell site (EeRk4); alluvial fan and earth flow deposit	65	Project	9	M	M	
EeRk4-2	Same location as EeRk4-1	65	"	9	M	M	
M-203	~ 2 Km. W. of Cache Creek, B.C.	67	"		M	M	
M-204	~ 1 Km. W. of Cache Creek, B.C.	68	D.J. Huntley		M	M	
M-205	~ 1 Km. S. of Cache Creek, B.C.	69	Project		M	M	
M-206	~ 4 Km. W. of Cache Creek, B.C.	66	"		M	M	
M-207	Bethleham Coper Proj, Highland Valley, E. of Ashcroft, B.C. - peat deposit	70	H. Nasmith	4,7,8 (Sample 62W5)	M	M	(*)
M-208	~ 10 Km. S. of Spences Bridge, near Drynoch, B.C., Hwy. 1	71	Project		M	M	
M-209	~ 7 Km. S. of Spences Bridge, B.C., Hwy. 1	72	"		M	M	
M-210	Near Drynoch, B.C., same location as M-208	73	K. Fladmark		M	M	
M-211	~ 18 Km. S.E. of Spences Bridge, B.C., Hwy. 8	74	Project		M	M	

TABLE A.1 (continued)

- 4 -

M-212	~ 25 Km. S.E. of Spences Bridge, B.C., Hwy. 8 (2 samples)	75	"		M	M	
M-213	~ 12 Km. W. of Lower Nicola, B.C., along Nicola R. - lower layer? (3 samples)	76	"		M	M	
M-214	Same location as M-213 - upper layer? (2 samples)	77	"		M	M	
M-215	~ 8 Km. E. of Nicola, B.C., along Nicola L.	78	"		M	M	
M-216	Same location as M-215 (2 samples)	79	"		M	M	
EeRb5	~ 5 Km. S.E. of Kamloops Junction, near Kamloops, B.C.	80	B. Chisolm		M	M	
EeRa6-1	~ 3 Km. N. of S. Thompson R., B.C., along Shiedam Cr.	81	B. Chisolm		Yn	Yn	
EeRa6-3	375 M. S. of EeRa6-1	82	B. Chisolm		Yn	Yn	
EeRa4	150 M. N. of Site (EeRa4), Confluence of Shiedam Cr. and S. Thompson R., B.C.	83	B. Chisolm		Yn	Yn	
LL-217	~ 6 Km. W. of Pritchard, B.C., on N. side of S. Thompson R. - lower layer	84	K. Fladmark		M	M	(*)
UL-218	Same location as LL-217, - upper layer	85	K. Fladmark		Yn	Yn	(*)
EdQx5	~ 1 Km. E. of Moulton Cr., B.C. along N. Side of Thompson R. - Alluvial fan deposit	86	M. Eldridge	11	Yn	Yn	
EdQw48-9	~ 2 Km. N. of Pritchard, B.C., near Gore Creek Site (EeQw48) - lower layer - lacustrine deposit	87	Project	4,7,8,12 (sample 62W4)	M	M	(*)
EeQw48-10	Same location as EeQw48-9 - upper layer	88	"	4,7,8,12 (sample 62W3)	Yn	Yn	(*)
M-219	~ 22 Km. S. of Chase, B.C., along Chase Creek	89	J. Brandon		M	M	
LL-3	~ 2 Km. S. of Monte Lake, B,C., Hwy. 97 - lower layer	90	Project	13	M	M	(*)
UL-4a	Same location as LL-3 - upper layer	91	"	13	Yn	Yn	(*)
UL-5	~ 80 M. from LL-4A - upper layer	91	"	13	Yn	Yn	(*)
M-220	~ 2 Km. W. of Westwold, B.C., Hwy. 97	92	"		M	M	

TABLE A.1 (continued)

- 5 -

M-221	~ Westwold, B.C., Hwy. 97 (2 samples)	93	"		M	M	
M-222	Kelowna, B.C. - lake core	94	G.E. Rouse	10	M	M	(*)
M-223	~ 3 Km. N. of Olalla, B.C.	95	Project	4,7,8 (Sample 61W40)	M	M	(*)
M-224	~ 8 Km. W. of Keremeos, B.C., Hwy. 3, at Old Tom Cr.	98	"		M	M	
M-225	Same Location as M-224 (2 samples)	99	"		M	M	
M-226	~ 11 Km. W. of Keremeos, B.C., Hwy. 3, N. Side of Similkameen R.	100	R. Percy		M	M	
M-227	Same spot as M-226	101	K. Fladmark		M	M	
M-228	Same spot as M-226	102	Project		M	M	
M-229	Marion L. ~ 22 Km. N.E. of Vancouver, B.C. - Lake core	103	R. Matthews	14	M	M	(*)
M-230	Skaha L, B.C.	104	B. Matthews	13	M	M	(*)
M-231	~ 10 Km. N. of Elkford, B.C., along Elk R. Alberta Border	(105)	J. Brandon		M	M	
WR-2	~ 80 Km. N. of Ross R., Yuk., along Pelly R.	120	D.J. Huntley	15	WRE	WR	(*)
WR-5	~ 30 Km. N.W. of WR-2, along Pelly R., Yuk.	121	D.J. Huntley	15	WRE	WR	(*)
WR-7	~ 10 Km. N.E. of Mt. Hodder, Yuk. Along Pelly R.: ~ Km. N.W. of WR-5	122	D.J. Huntley	15	WRE	WR	(*)
WR-9	~ 50 Km. N.W. of Mt. Hodder, Yuk., along Pelly R.	123	D.J. Huntley	15	WRE	WR	(*)
WR-10	A few Km. E. of Tetlin Junction, Alaska, along Alaskan Hwy.	124	D.J. Huntley	15	WRN	WR	
M-232	Mazama Standard from Kittleman (sample 61K54/55)		L. Kittleman	16	M	M	(*)
M-236	Mazama Standard from Lower Methow Valley, Wash.		S. Porter	2	M	M	(*)
Ys-238	Mt. St. Helens Ys standard from S. Porter		S. Porter	2	Ys	Ys	(*)
W-239	Mt. St. Helens W. Standard from S. Porter		S. Porter	2	W	W	(*)

a "project" = D.E. Nelson or A.B. Cormie

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FIGURE A.1

Sampling Locations in Washington State

FIGURE A.2

Sampling Locations in Oregon State

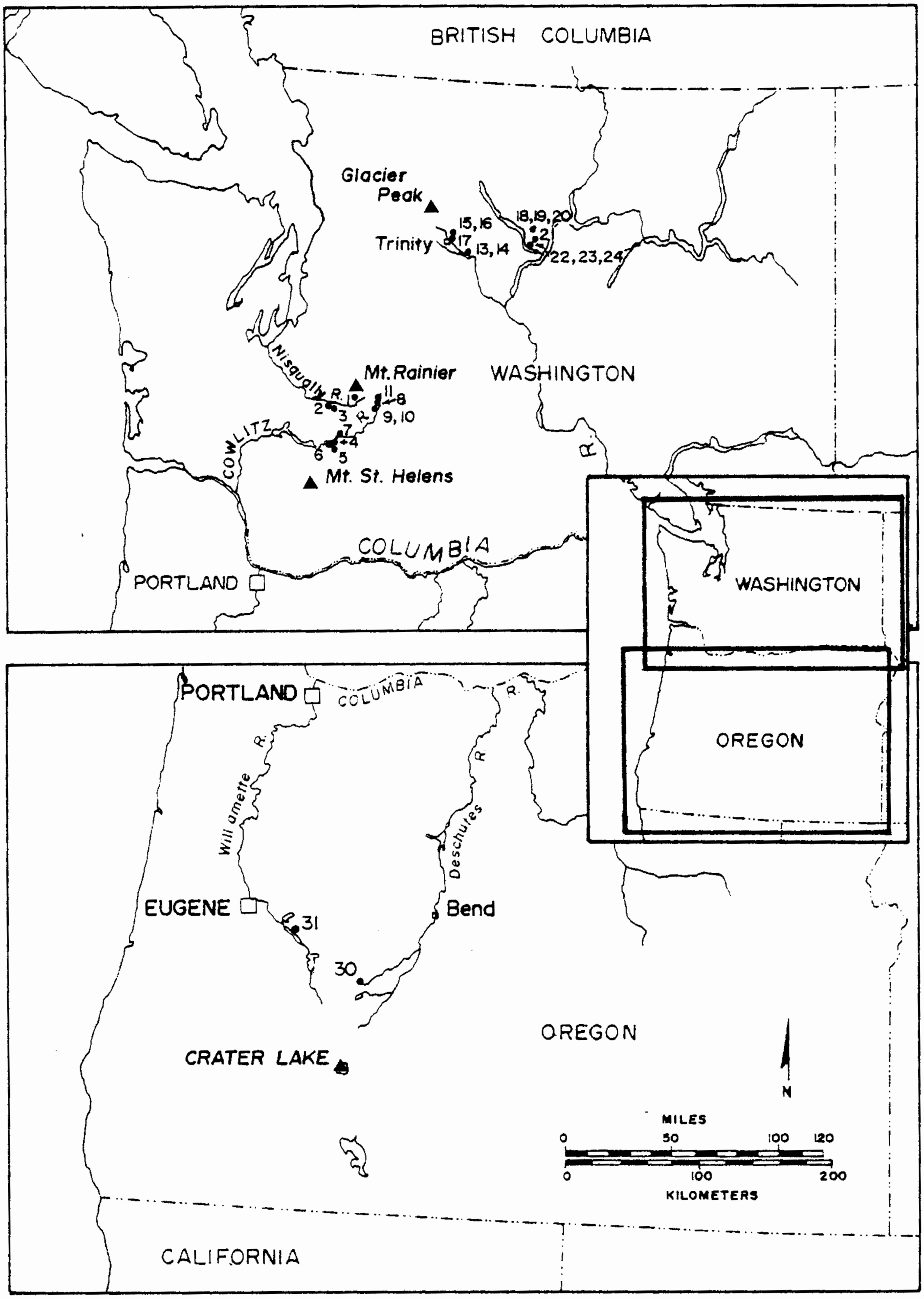

BRITISH COLUMBIA
Glacier Peak
Trinity
15,16
17
13,14
18,19,20
21
22,23,24
Mt. Rainier
WASHINGTON
Nisqually R.
1
2
3
R.
11
8
9,10
7
4
6
5
COWLITZ
Mt. St. Helens
R.
COLUMBIA
PORTLAND
WASHINGTON
OREGON
PORTLAND
COLUMBIA
R.
Willamette R.
Deschutes R.
EUGENE
31
Bend
30
CRATER LAKE
OREGON
N
MILES
0
50
100
120
0
100
200
KILOMETERS
CALIFORNIA

FIGURE A.3

Sampling Locations in the Okanagan Region, B.C.

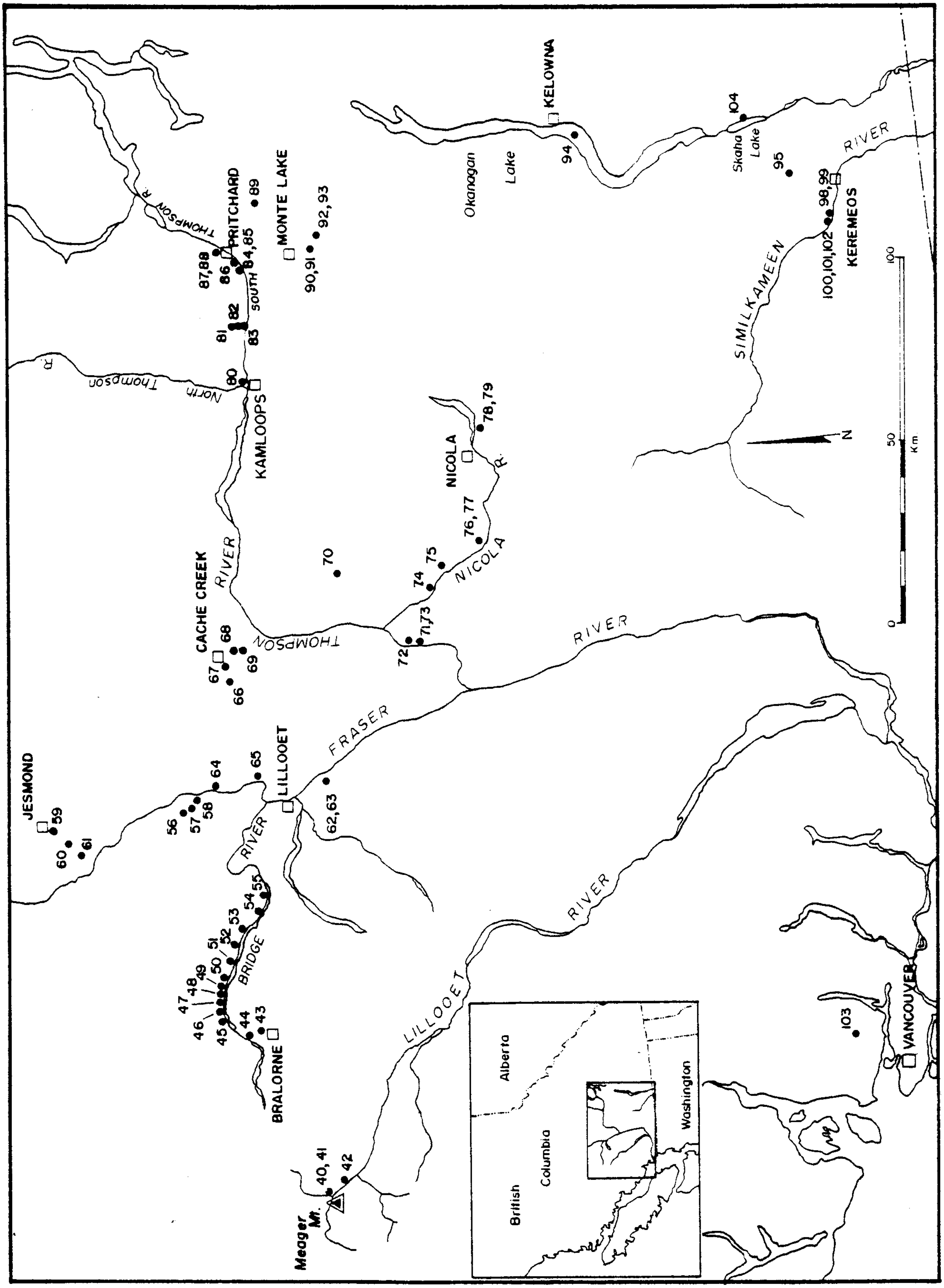
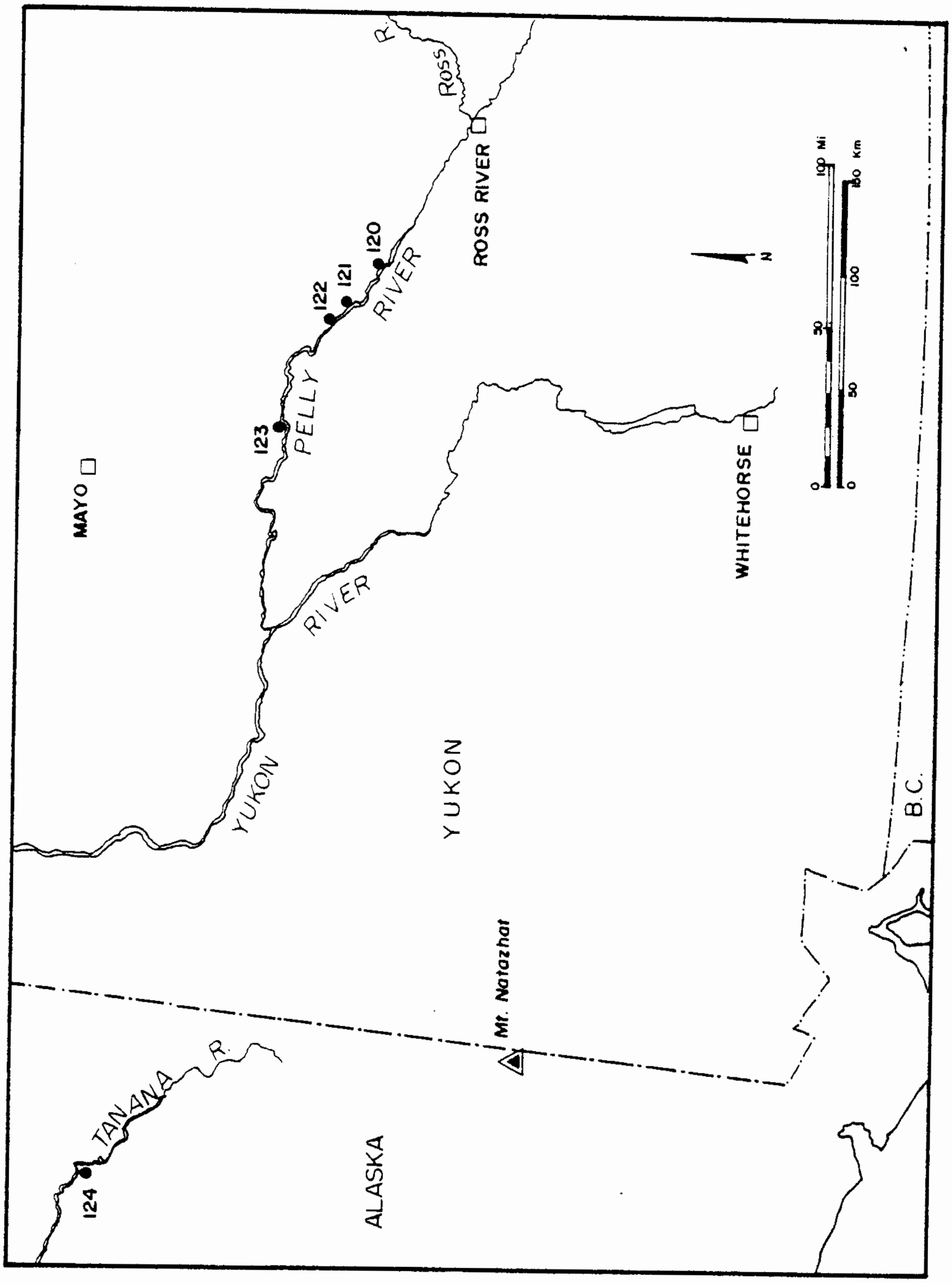

Meager Mt.
40,41
42
BRALORNE
43
44
45
46
47
48
49
50
51
52
53
54
55
BRIDGE
RIVER
JESMOND
59
60
61
56
57
58
64
65
LILLOOET
62,63
FRASER
RIVER
LILLOOET
RIVER
CACHE CREEK
66
67
68
69
THOMPSON
RIVER
70
72
71,73
74
75
NICOLA
76,77
NICOLA
R.
78,79
KAMLOOPS
80
North Thompson R.
81
82
83
SOUTH
86
87,88
84,85
PRITCHARD
THOMPSON R.
MONTE LAKE
89
90,91
92,93
Okanagan
Lake
KELOWNA
94
Skaha
Lake
104
95
SIMILKAMEEN
RIVER
98,99
100,101,102
KEREMEOS
103
VANCOUVER
N
0
50
100
Km
Alberta
British
Columbia
Washington

FIGURE A.4

Sampling Locations in the Yukon


MAYO
ROSS RIVER
ROSS R.
PELLY RIVER
120
121
122
123
YUKON RIVER
WHITEHORSE
N
0 50 100 Mi
0 50 100 150 Km
YUKON
B.C.
Mt. Natazhat
ALASKA
TANANA R.
124

Appendix B

METHODS OF SAMPLE PREPARATION

In trace element analysis it is essential that all glassware and apparatus be kept scrupulously clean between treatments. Most of the glassware of this study was washed in reagent grade Nitric acid before being used. Reagent grade chemicals were always used. We further reduced the possiblity of contaminating samples with high Z trace elements by using grinders and sieves which were composed of low Z materials. By analyzing ground samples as well as the grinder materials, we determined that no significant trace element contamination was picked up from the grinders.

Method 1: Grinding and Sieving

Where possible, we sieved large samples to reduce the relative proportion of cross-contamination (between samples) that could be picked up by any one sample during sieving. We used lucite sieves (5.5 cm. dia. 5 cm. high) with disposable nylon screens; the sieves could be washed between samples.

Fine Grained Samples: with tweezers we picked out the large contaminants (roots, stones, etc.). A hand magnet (wrapped in paper) was then passed over the sample to remove the magnetic minerals (ie. magnetites, ilmenites)). We then sieved the samples for roughly 1/2 hr. each to isolate the 62-210 µm and the <62 µm size ranges. Four samples were sieved at a time using a Cenco-Meinzer mechanical sieve shaker. Greater than 50% to 60% of a typical sample by weight was less than 62 µm while roughly 40% was in the 62-210 µm size range.

Pumice Samples: We first used a standard (21 cm dia.) brass sieve to remove the less than 1.4 mm size fraction containing soils and other non-pumice debris. The larger pumice fragments were then ground in a Fisher roller mill using a 1.1 litre Burundum Rcalox porcelain jar mill with porcelain disks. The jar was carefully washed out with alcohol between samples. We ground the pumice sized fragments for 10 minutes then sieved the sample using lucite sieves to separate out the <210 µm size fraction. As we wished to concentrate the glass in the <62 µm size range, we were able to avoid pulverizing crystalline minerals to less than 62 µm by keeping our grinding times to less than 10 minutes. Pumice in the >210 µm size range was re-submitted for additional 10 minute periods of grinding. The less than 210 micron size fraction on the other hand, was pre-treated and sieved in a manner similar to that described above for the fine grained samples.

Method 2: HCL and H_2O_2 Treatments

Up to eight sieved samples at a time were chemically treated for removal of soluble contaminants. Each sample was placed in a standard 40 ml centrifuge tube. HCl (20%) was poured into the tubes so that the solid to volume ratio was 1 to 1. The mixtures were then placed in an 80 degree C water bath and stirred intermittently for 10 minutes. We centrifuged the samples, decanted the acid solutions, and washed the samples three times each with distilled water.

Occasionaly, the H_2O_2 treatments preceded the acid treatments, Normally, however, we added the 30% reagent grade hydrogen peroxide to the samples direcly following the acid treatments. The mixtures were placed in a 60 degree C water bath and stirred intermittently for 10 minutes. The samples were then washed 6 times with distilled water, three times with acetone, and placed in a 70 degree C water bath to dry.

Centrifugation was used to remove all chemical and wash solutions. At the same time we removed the <10 µm (containing clay minerals) from all our samples. With an IEC International Chemical Centrifuge run at approximately 3,000 rpm we used eq. B.1 to estimate the centrifuge times for which the >10 µm particles would settle to the bottom and the <10 µm particles would remain in suspension.

eq. E.1

$$t = \frac{9.4503 n \times 10^{10}}{S^2 r^2 (d_1 - d_2)} \times K$$

$$K = \log_{10} \frac{x+a}{a}$$

t = time in seconds for particle to fall to bottom of centrifuge tube
n = viscosity in poises of liquid at 20° C
r = particle size (dia. in µm)
s = centrifuge speed in rpm
d1 = sp.g. of particle
d2 = sp.g. of separating liquid
x = distance for particle to fall to bottom of tube
a = distance from centre of rotation to the particle before fall

When dealing with the 62-210 µm size range, most of the fine grained particles were automatically removed during sieving. However, following the chemical treatments and during the acetone washes, we placed the 62-210 µm sample/acetone mixtures in an ultrasonic bath for a few seconds each to remove the remaining fines. Such removal of fines proved more important for samples which were to undergo magnetic separations (Method 5).

Method 3: HCl and NaOCl treatments

Method 3 is identical to Method 2 except that reagent grade 5% NaOCl solution was used to remove organic stains instead of H_2O_2. We generally used the NaOCl treatments before the HCl treatments. Prior to treatment we added 20% HCl to the NaOCl solution in order to reduce its pH to 9.5.

Method 4: Glass separation with Heavy Liquids

The average specific gravity of obsidian glass is 2.4 while that of minerals including most clays is greater than 2.6. We can therefore floatate glass in a heavy liquid set at sp.g. = 2.4. General methods for separating minerals using heavy liquids are outlined in Allman and Lawrence (1972).

In our work, glass was separated from the 62-210 µm size range and, prior to separation, samples were chemically treated using method 2 or 3 to remove soluble contaminants. About 30% to 50% glass (by weight) was typically recovered from a 4 to 6 gram sample added to the heavy liquids.

For our work we used a custom made plummet in order to adjust liquid bromoform/acetone mixtures to sp.g. 2.4. The plummet was a 2 ml glass bulb filled with lead and suspended into the beaker of bromoform on a nickel thread hung from an analytical balance. We stirred acetone into the bromoform until the plummet reached the desired weight in the bromoform/acetone mixtures (calculated by eq. B.2).

eq. E.2

$$Fl = Fa - sp.g.(Fa - Fw)$$

Fa = weight of plummet in air
Fw = weight of plummet in water
Fl = weight of plummet in heavy liquid
sp.g. = specific gravity of heavy liquid

Separation was by centrifugation with 4 samples treated at a time. For separation we used tapered tubes which were placed into standard 40 ml centrifuge tubes. The samples were stirred into the bromoform/acetone mixture in the inner tubes and during centrifugation the heavy minerals would settle to the bottom of the centrifuge tube by passing through an opening at the bottom of the inner tube. By stoppering the inner-tube, the glass could be easily removed with the inner tube. We generally centrifuged the samples for about 10 seconds so that the majority of heavy minerals would settle. We then stirred the sample remaining in the inner tube a second time and, finally, we centrifuged all samples for about 10 minutes. The glass and mineral separates were filtered on #1 Watman filter paper, washed several times with acetone, and allowed to dry. By scanning the bromine peak during XES anaysis we determined that no residual bromoform was left on the samples after the acetone wash.

Method 5: Glass separation with a Franz Magnetic Separator

General methods for separating minerals using a Franz Magnetic Separator are described in Allman and Lawrence (1972) and Hess (1966). In table B.1 we list the settings that we found most useful for separating glass from tephra samples in the 62 to 210 micron size range.

Table B.1

Settings for Magnetic Separations

	range	most common
foreward angle (degrees)	25-30	25
side angle (degrees)	4-9	9
amperage (mafics)	.40-.80	.65
amperage (non magnetics)	1.50	1.50

Approximately 1 to 2 hours were required to separate a 4 to 8 gram sample with the Franz Magnetic Separator. Magnetic separations were therefore used only in a few cases when we wished to purify samples which had already undergone heavy liquid separations. We estimated that after such purification, the samples were composed of less than 1% mafics (by weight).

Method 6: Pelletization

Somar-Mix binder was added to 1.3 gms of powdered sample in a 1:8 binder-to-sample ratio. We ground the sample-binder mix for 10 minutes in a porcelain ball mill after which particles in the 62-210 µm size were typically ground to less than 45 µm. The samples were then pelletized at 10 tons using a Beckman K-13 KBR die in a hydraulic press. The pellets produced were 13 mm diameter, approximately 1.25 grams, .45 cm thick, and greater than 99% infinite thickness. Equation B.3 was used to calculate the sample mass required to produce specimens of the desired thickness (cf. Bertin 1970).

eq. E.3

$$\text{mass (gm)} = \frac{A \ln\left(1 - \frac{I_t}{I_\infty}\right)}{\left(\frac{\mu}{\rho}\right)_{\lambda p} \csc\phi + \left(\frac{\mu}{\rho}\right)_{\lambda L} \csc\psi}$$

$(u/p)_{\lambda p}$ = mass absorption for incident beam

ϕ = angle of incidence = 52 deg.

$(u/p)_{\lambda L}$ = mass absorption for analyte line

ψ = angle of takeoff = 52 deg.

(I_t/I_∞) = proportion of infinite thickness

A = area (cm) of surface of specimen

Appendix C

ABSOLUTE CONCENTRATIONS

A) XES: Major Element Analysis

Six HCl, H_2O_2 treated samples of ash (<62 µm) were analyzed for their major element composition at Chemex Inc, Vancouver, B.C. We re-calculated these data to 100% oxide composition on a water free basis as presented in Table C.1. In this way the data could be compared to data in the literature such as those of Westgate, (1970a). As the calculation of absolute concentrations was not a major goal of this thesis, we did not attempt to convert further results of samples analyzed with a Zn secondary target into absolute concentrations. The six test samples therefore provide our best estimate of absolute concentrations of K, Ca, Ti, Fe for samples of M, BR, GP, WR, and Y.

B) XES: Major and Trace Element Analysis With A Ag Secondary Target

Trace Element Analysis: The method of standard additions (cf. Bertin 1970) was used to derive a set of calibration curves for the calculation of absolute concentrations of the trace elements Rb, Sr, Y, Zr, Nb. We selected a large sample of Mazama ash from the less than 45 micron size range. A stock solution

TABLE C.1

Major Element Analysis of 6 Test Samples HCl, H_2O_2 treated (<62µm)

(All values are in % oxide concentrations recalculated to 100% on a water free basis)

Sample	(±1σ)	M-223	BR-65	UL-218	GPG-35	WR-9	U-48
Source		M	BR	Yn	GPG	WR	U[a]
SiO_2	.50	72.01	71.23	72.06	73.07	72.53	73.00
Al_2O_3	.10	14.62	14.57	15.10	14.57	14.82	14.91
CaO	.05	1.83	2.74	2.75	2.82	2.33	2.67
MgO	.03	.55	.86	.85	1.00	.57	.81
Na_2O	.02	5.06	4.61	4.58	3.83	4.09	4.49
K_2O	.01	2.95	2.79	2.11	2.65	3.30	2.11
FeO	.01	2.13	2.27	1.98	1.56	1.79	2.29
MnO	.005	.05	.15	.05	.05	.06	.11
TiO_2	.01	.51	.45	.30	.26	.27	.39
P_2O5	.005	.06	.11	.06	.03	.06	.07

[a] Mt. St. Helens W-or T-like samples

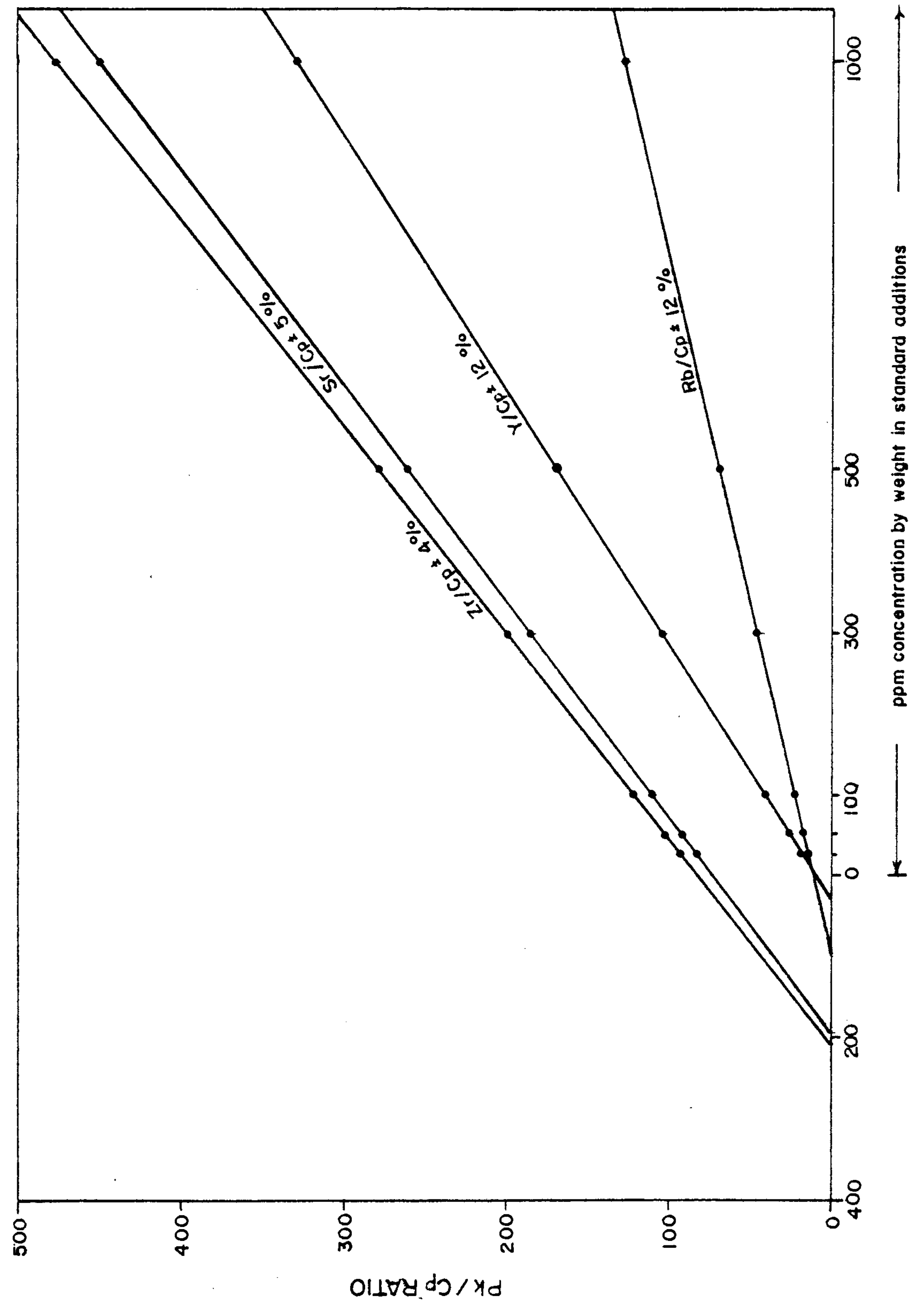
Source: (by) Chemex Inc.

was prepared in which we dissolved approximately 1000 ppm of each of Rb, Sr, Y, Zr (as nitrates) into distilled water. With a syringe (accurate to .05 ml) we diluted the stock solution to produce 10 ml aliquots having approximately 25, 50, 100, 300, 500, and 1000 ppm concentrations of each trace element. A seventh aliquot was distilled water only. We then evaporated each 10 ml aliquot onto 7 powdered sub-samples of ash of 4 grams each. The amount of solution was chosen so that all of it would soak into the sample and little would be lost on the sample container. The samples were dried, well mixed (in a shaker bottle), and analyzed for 15 minutes each as loose powders. The Pk/Cp ratios were calculated, the K-beta interfering peaks were subtracted from the Y to Nb peaks, and the ppm concentration versus Cp/R ratios were plotted (Fig. C.1). Using Figure C.1 we were able to verify that the Pk/Cp versus ppm concentration was a linear relationship.

Because the extremely delequescent nitrate standards could not be accurately weighed, we were uncertain whether we actually had 1000 ppm of each element in the original stock solution. We therefore had a number of the spiked samples analyzed by XRF at the Geology Department of the University of British Columbia (UBC) in order to cross-calibrate our results against the UBC standards. The unweighted P/Cp ratios determined in this study were plotted against the UBC measured concentrations (ppm). A least squares fit of these data produced the calibration

FIGURE C.1

Standard Additions for Trace Element Analysis


PK / Cp RATIO
500
400
300
200
100
0
400
200
0
100
300
500
1000
Zr/Cp ± 4 %
Sr/Cp ± 5 %
Y/Cp ± 12 %
Rb/Cp ± 12 %
ppm concentration by weight in standard additions

constants which appear in Table C.2. A description of the regression methods used appears in Bevington (1969). Equation C.1 was then used to convert the average Pk/Cp ratios of each tephra source into ppm concentrations for the elements Rb, Sr, Y, Zr. (Concentrations of Nb were estimated from the Y K-beta peak.)

eq. C.1

$$C(\pm S_c) = a(\pm S_a) \cdot \bar{x}(\pm S_x) + b(\pm S_b)$$

C = absolute concentration
$\bar{x}$ = average relative concentration of element for source
a = slope
b = intercept

In Table C.3 we list absolute concentrations of separated glass samples from Ch. 5. In Table C.4 we present absolute concentrations for some HCl, H_2O_2 (<62 µm) treated samples from Ch. 6.

Major Element Analysis: The K, Ca, Ti, Fe peaks also appear in a typical spectrum analyzed with a Ag secondary target (Figure 2.1). We converted the results of the 6 samples analyzed by Chemex (Table C.1) into % element concentration for the elements K, Ca, Ti. Linear regression analysis was then used (% concentration versus Pk/Cp ratio) in order to produce the calibration constants in Table C.2 for the major elements. We then converted the average Pk/Cp ratios of samples analyzed

TABLE C.2

Calibration Constants Used in eq. C.1 for Calculating Absolute Concentrations for Samples

Analyzed with a Ag Secondary Target

(Values are % concentration by weight for K to Fe; ppm concentration by weight for Rb to Nb)

	a	b	Sa	Sb	S	r
K %	.4075	.6050	.1023	.3716	.1661	.8915
Ca	.2819	.2880	.1138	.5604	.1845	.7780
Ti	.0713	.0708	.0087	.0167	.0154	.9723
Fe	.0114	.3470	.0014	.1318	.0556	.9702
Rb ppm	5.235	.3551	.1323	4.697	8.023	.9984
Sr	3.713	34.05	.1156	17.15	20.89	.9976
Y	3.998	-4.570	.0043	3.548	6.931	.9997
Zr	2.717	-5.363	.0099	15.55	19.384	.9967
Nb	3.424	4.342	.1627	2.517	4.201	.9966

a = slope
b = intercept
Sa = standard deviation of slope
Sb = standard deviation of intercept
S = standard deviation about regression line
r = Pearson's product moment

TABLE C.3

XES Results in Absolute Concentrations for Samples of HCl, NaOCl treated glass

Analyzed with a Ag Secondary Target

(Results are in % concentration by weight for K to Fe, ppm concentration by weight for Rb to Nb)

	M(±1σ)	BR(±1σ)	Yn(±1σ)	GP30(±1σ)	GP40(±1σ)	WR(±1σ)	L[a](±1σ)	U[a]-43(±1σ)
n[b]	4	2	7	5	5	5	2	1
K %	2.16(.56)	2.51(.62)	1.76(.49)	2.59(.64)	2.61(.67)	2.24(.57)	2.02(.52)	1.66(.47)
Ca	1.39(.71)	1.52(.75)	1.88(.87)	1.68(.80)	1.30(.71)	1.58(.77)	1.85(.85)	1.46(.74)
Ti	.25(.03)	.20(.03)	<.15	.17(.02)	.17(.02)	<.15	.16(.02)	.15(.02)
Fe	1.28(.24)	1.17(.23)	1.10(.27)	1.00(.21)	.87(.21)	1.02(.21)	1.22(.25)	1.01(.21)
Rb ppm	50(6)	45(5)	45(8)	59(5)	59(7)	49(5)	59(5)	48(6)
Sr	260(19)	290(27)	337(30)	363(32)	214(36)	487(31)	284(21)	255(19)
Y	21(4)	13(4)	6(8)	6(4)	21(4)	4(4)	14(4)	11(4)
Zr	219(18)	136(17)	94(17)	121(19)	106(28)	127(18)	162(17)	143(17)
Nb	12(3)	16(4)	10(3)	< 8	10(3)	< 8	13(4)	11(3)

[a] Mt. St. Helens W-or T-like samples

[b] number of samples

TABLE C.4

XES Results in Absolute Concentrations for HCl, H_2O_2 (<62μm)

Samples analyzed with a Ag Secondary Target

(Values are % concentration by weight for K to Fe; ppm concentration by weight for Rb to Nb)

		M(±1σ)	BR(±1σ)	Yn(±1σ)	U^a(±1σ)
n^a		10	19	12	8
K	%	2.31(.59)	2.38(.65)	1.70(.49)	1.82(.49)
Ca		1.56(.81)	1.89(.90)	2.06(.96)	2.09(1.01)
Ti		.29(.04)	.23(.06)	.20(.08)	.20(.04)
Fe		1.54(.31)	1.26(.31)	1.38(.33)	1.43(.31)
Rb	ppm	56(6)	40(7)	42(7)	46(6)
Sr		294(25)	365(67)	327(25)	305(48)
Y		22(4)	10(4)	5(4)	20(4)
Zr		230(21)	133(22)	115(22)	196(18)
Nb		15(3)	15(3)	14(3)	12(3)

[a] number of samples

(Chapters 5 and 6) into % concentrations (Tables C.3, and C.4). As both % concentrations (NAA) and Pk/Cp ratios (XES) were available for Fe in 31 separated glass samples (see Ch. 5), we used linear least square fitting of these data to calculate the calibration constants for Fe.

TABLE C.5

α-Counting Results in Absolute Concentrations

(Values are in ppm concentration by weight)

A) HCl, NaOCl treated glass (62-210μm)

	M(±1σ)	BR(±1σ)	Yn(±1σ)	GPB(±1σ)	GPG(±1σ)	WR(±1σ)	L-24(±1σ)	U-43(±1σ)
n[a]	5	2	4	3	3	3	1	1
U	2.4(0.3)	2.6(0.2)	1.4(0.3)	3.4(0.4)	3.0(0.3)	2.9(0.3)	2.3(0.3)	2.7(0.3)
Th	5.1(1.1)	5.1(0.8)	3.0(0.8)	6.6(0.9)	7.3(1.0)	4.8(1.1)	3.5(0.8)	2.3(0.8)

B) HCl, NaOCl treated samples (<62μm)

	M(±1σ)	BR(±1σ)	Yn(±1σ)	GPB(±1σ)	GPG(±1σ)	L-24(±1σ)
n	4	1	4	2	2	1
U	2.6(0.3)	2.7(0.3)	1.5(0.2)	2.9(0.3)	3.6(0.4)	2.3(0.2)
Th	5.2(0.8)	4.9(0.8)	2.9(0.6)	7.0(1.5)	5.0(1.0)	3.5(0.7)

[a] number of samples

APPENDIX D

TABLE D.1

Major Element Analysis in the Literature

(% oxide concentration recalculated to 100% on a water free basis)

	Whole ash analysis			Microprobe analysis of glass shards					proximal [p] and distal [d] samples of whole ash	
	M(±1σ)	BR(±1σ)	GP(±1σ)	M(±1σ)	BR(±1σ)	GPG(±1σ)	GPB(±1σ)	Yn(±1σ)	WR[p]	WR[d]
n[a]	9	2	3	58	7	4	12	9	1	1
SiO_2	68.1(5.0)	67.4(1.5)	68.0(4.9)	72.59(.27)	73.13(.37)	77.04(.19)	76.73(.20)	75.02(.15)	62.2	70.2
Al_2O_3	17.5(2.9)	16.49(.63)	17.1(2.7)	14.42(.16)	14.20(.18)	12.73(.16)	12.98(.16)	12.98(.16)	17.8	13.9
CaO	2.5(.5)	3.36(.08)	3.7(.4)	1.71(.09)	1.73(.04)	1.21(.06)	1.40(.06)	1.58(.07)	6.3	3.3
MgO		1.48(0)		.54(.08)	.58(.08)	.29(.02)	.30(.03)	.48(.09)	2.5	1.6
Na_2O	4.2(1.0)	4.46	3.8(.4)	5.15(.16)	4.75(.14)	3.87(.09)	3.94(.04)	4.40(.23)	5.2	3.9
K_2O	2.4(.3)	2.29	2.3(.5)	2.70(.06)	2.89(.07)	3.36(.09)	2.99(.07)	1.98(.05)	1.9	2.8
FeO	3.9(8)	3.50(.29)	4.1(1.1)	2.08(.06)	1.92(.08)	1.05(.03)	1.21(.12)	1.40(.06)	3.45	3.55
MnO		.07		.04(.02)	.04(.01)	.03(.01)	.02(.01)	.03(.01)		
TiO_2	.65(.09)	.50(.04)	.51(.11)	.48(.02)	.43(.02)	.22(.02)	.23(.02)	.16(.01)	.5	.5
P_2O_5		.24		.06(.02)	.03(.01)	.04(.01)	.03(.01)	.04(.02)		
Reference	1	2	1	3	3	3	3	3	4	4

[a] number of samples

[1] Czamanske and Porter, 1965

[2] Nasmith et. al., 1967

[3] Westgate et. al., 1970

[4] Lebebmo and Campbell, 1969

TABLE D.2

Major Element Analysis in the Literature

(microprobe analysis of glass in % concentration by weight)

	M(±1σ)	BR(±1σ)	Yn(±1σ)	Wn(±1σ)	T(±1σ)	GPUL(±1σ)	GPML(±1σ)	GPLL(±1σ)
n[a]	14	2	3	17	8	7	5	10
K	2.17(03)	2.34(08)	1.61(.02)	1.96(.09)	1.65(.15)	2.25(.10)	2.32(.04)	2.51(.10)
Ca	1.13(.03)	1.16(0)	1.25(.03)	1.19(.06)	1.90(.15)	.91(.05)	.86(.06)	.83(.04)
Fe	1.54(.04)	1.42(.06)	1.04(.03)	1.40(.13)	2.26(.30)	.81(.03)	.83(.05)	.74(.04)
reference	5	5	5	6	7	8	8	8

[a] number of samples

[5] Smith and Westgate, 1969

[6] Smith and Okazaki, 1977

[7] Smith and Okazaki, 1975

[8] Smith et. al., 1977a

TABLE D.3

NAA Results on Separated Glass in the Literature (Borchardt et. al. 1971a)
(all values except Fe are in ppm concentration by weight)

	M(C1)(±1σ)	M(C2)(±1σ)	Y(±1σ)	W(±1σ)	T(±1σ)	GP(+1σ)
n[a]	4	4	2	3	2	3
Fe[b]	1.51(.11)	1.46(.09)	1.49(.47)	1.37(.40)	1.92(.62)	1.17(.30)
Th	6.6(.3)	6.3(.4)	4.6(.4)	5.4(1.3)	4.8(.1)	7.7(2.8)
Sc	6.6(.5)	6.2(.3)	3.2(.4)	4.2(.5)	6.5(4.2)	3.7(1.1)
Ce	45(3)	42(2)	30(7)	32(2)	33(0)	31(4)
Hf	6.6(.5)	6.2(.3)	2.7(.2)	4.9(.4)	4.3(1.2)	3.0(1.0)
Cs	3.7(.6)	4.0(1.0)	2.4(.2)	3.4(.7)	2.1(.2)	3.0(.4)
Co	2.8(.3)	2.5(.4)	3.8(.6)	3.0(.4)	5.2(.1)	3.2(.6)
Cr	1.6(.6)	1.5(.7)	2.9(.4)	2.1(.9)	1.9(.4)	2.2(1.9)
Eu	.94(.05)	.84(.09)	.51(.35)	.66(.42)	.64(.01)	.58(.09)
Rb	52(12)	48(5)	41(15)	70(8)	50(14)	48(4)

[a] number of samples

[b] % concentration by weight

TABLE D.4

A-Coefficients Comparing Tephras Characterized by Westgate (1970)

Using Microprobe Analysis of Glass Shards

Source	n[a]	K_2O	CaO	FeO	TiO
M/BR	58/7	.731	.071	.571	.625
M/Yn	58/9	3.27*	.438	2.83*	5.33
M/GPUL	58/12	1.12*	1.03*	2.41*	3.13*
M/GPLL	58/4	2.20*	1.67*	5.72*	3.25*
BR/Yn	7/9	3.79*	.546	1.86*	4.50*
BR/GPUL	7/12	.357	1.65*	1.78*	2.50*
BP/GPLL	7/4	1.47*	2.60*	3.96*	1.00*
Yn/GPUL	9/12	4.21*	1.73*	.528	1.17*
Yn/GPLL	9/4	4.93*	2.46*	1.94*	1.00*
GPUL/GPLL	12/4	1.16*	.792	.533	.125
BB/BR	6/7	1.42*	3.43*	1.56*	.800

[a] number of samples

*tephra pair can be distinguished on basis of this element

TABLE D.5

A-Coefficient Comparing Tephras Characterized
by Smith et.al. (See refs. Table D.2)
Using Microprobe Analysis of Glass Shards

Source	n[a]	K	Ca	Fe
M/BR	14/2	.773	.500	.600
M/Yn	14/3	5.60*	1.00*	3.57*
M/Wn	14/17	.875	.233	.411
M/T	14/8	1.44*	2.14*	1.06*
M/GPUL	14/7	.308	1.38*	5.21*
M/GPML	14/5	1.07*	1.51*	3.94*
M/GPLL	14/10	1.31*	2.14*	5.00*
BR/Yn	2/3	3.65*	1.51*	2.11*
BR/Wn	2/17	1.12*	.250	.053
BR/T	2/8	1.50*	2.47*	1.17*
BR/GPUL	2/7	.250	2.50*	3.39*
BR/GPML	2/5	.083	2.80*	2.68*
BR/GPLL	2/10	.472	4.13*	3.40*
Yn/Wn	3/17	1.59*	.333	1.13*
Yn/T	3/8	.118	1.81*	1.85*
Yn/GPUL	3/7	2.67*	2.13*	1.92*
Yn/GPML	3/5	5.92*	2.16*	1.31*
Yn/GPLL	3/10	3.75*	3.00*	2.14*
Wn/T	17/8	.646	1.69*	1.00*
Wn/GPUL	17/7	.763	1.27*	1.84*
Wn/GPML	17/5	1.39*	1.38*	1.58*
Wn/GPLL	17/10	1.45*	1.80*	1.94*
T/GPUL	8/7	1.20*	2.48*	2.19*
T/GPML	3/5	1.76*	2.48*	2.04*
T/GPLL	8/10	1.72*	2.82*	2.24*
GPUL/GPML	7/5	.100	.217	.125
GPUL/GPLL	7/10	.250	.444	.800
GPML/GPLL	5/10	.650	.150	.500

[a] number of samples used to characterize source.

* tephra pair can be distinguished on basis of this element.

TABLE D.6

A-Coefficients Comparing Tephras Characterized by Borchardt et. al. using NAA Analysis of Glass Separates (1971a)

	M/Y	M/GP	M/W	M/T	Y/GP	Y/W	Y/T	GP/W	TP/T	W/T	MC1/MC2
n[a]	8/2	8/3	8/3	8/2	2/3	2/3	2/2	3/3	3/2	3/2	4/4
Fe	.009	.397	.112	.310	.208	.069	.197	.143	.408	.270	.125
Th	1.19*	.188	.324	1.70*	.484	.235	.200	.281	.500	.214	.214
Sc	2.00*	.900	1.21*	.011	.167	.556	.359	.156	.264	.245	.250
Ce	.700	.479	1.20*	1.83*	.046	.111	.214	.083	.250	.250	.300
Hf	3.08*	1.21*	.938	.656	.125	1.83*	.571	.679	.296	.188	.250
Cs	.750	.375	.167	.900	.500	.556	.375	.182	.750	.722	.044
Co	.600	.300	.250	2.60*	.250	.400	1.00*	.100	1.43*	2.20*	.167
Cr	.650	.120	.167	.150	.152	.308	.625	.018	.065	.076	.036
Eu	.431	.861	.726	1.75*	.080	.097	.181	.078	.300	.023	.357
Rb	.188	.077	.588	0	.184	.650	.155	.197	.056	.455	.118
Na	.833	1.50*	.230	.088	.672	.263	.375	.565	.649	.088	.385
Ba	1.58*	.611	.647	1.54*	.667	.727	1.45*	0	.385	.432	.029
La	.167	.250	.250	.500	.400	.800	.750	.083	.143	.300	.125
Nd	.389	.167	.611	.667	.020	.200	.250	.060	.080	.050	.091
Sm	1.33*	1.00*	1.17*	.722	.333	.500	.300	.500	.389	.100	.056
Tb	.011	.829	.648	.068	.332	.204	.007	.483	1.25*	1.23*	.113
Yb	1.39*	1.00*	.750	.786	.063	1.00*	.167	.611	.154	.380	.030
Lu	1.15*	.882	.666	.432	0	.278	.220	.227	.190	.019	.188
Ta	.719	.441	.818	.571	.235	.296	.280	.457	.033	.500	.722

[a] number of samples used to characterize source

*tephra pair can be distinguished on basis of this element

Appendix E

Mineral Suits of Some Well Known Tephras

	M	BR	Yn	W	T	GP	WR
Albite							3
Amphibole							3
Anorthite							
Apatite	2,5,8,9	8					
Augite	10				4		
Biotite	8	5,8,9	8(Yb)				7
Clinopyroxene	2,5,8,9,10	5,8		4	10		
Cummingtonite			4,5,8,9,10	4,5			
Hornblende	2,5,8,9,10	5,8,9	4,5,8,9,10	4	4	1,9	3,7
Hypersthene	2				4	9	3
Ilmenite	9	9	9			9	3
Magnetite	2,5,9	5,9	5,9	5		9	3,7
Orthoclase							3(glass)
Orthopyroxene	1,5,8,9,10	5,8	8	5,10	10	1	
Oxyhornblende	8	8	8				
Plagioclase	1,2,5,9,10	5,9	5,9,10	5,10	10	1,9	3,7

[1] Dudas et. al., 1972

[2] Kittleman, 1973

[3] Lerbekmo and Campbell, 1969

[4] Mullineaux et. al., 1975

[5] Nasmith et. al., 1967

[6] Porter, 1978

[7] Stuiver, 1964

[8] Westgate and Dreimanis, 1967

[9] Westgate et. al., 1970

[10] Wilcox, 1965

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