



A tephrochronologic method based on apatite trace-element chemistry

Bryan Keith Sell ^{*,1}, Scott Douglas Samson ¹

204 Heroy Geology Laboratory, Department of Earth Sciences, Syracuse University, Syracuse, NY 13244, USA

ARTICLE INFO

Article history:

Received 23 June 2010

Available online 7 May 2011

Keywords:

Apatite

Trace elements

Tephrochronology

Electron microprobe

Bentonite

ABSTRACT

Geochemical correlation of ash-fall beds with conventional tephrochronologic methods is not feasible when original glass composition is altered. Thus, alternative correlation methods may be required. Initial studies of heavily altered Paleozoic tephra (K-bentonites) have suggested the potential for employing trace-element concentrations in apatite as ash-fall bed discriminators. To further test the utility of apatite trace-element tephrochronology, we analyzed apatite phenocrysts from unaltered volcanic rocks with an electron microprobe: nine samples from rocks erupted during the Quaternary and one sample from a rock erupted during the Paleogene. The resulting apatite trace-element data provide unique bed discriminators despite within-crystal variability. Each of the volcanic rocks studied possesses unique trends in Mg, Cl, Mn, Fe, Ce and Y concentrations in apatite. The results from this study establish an important tephrochronologic method that can be applied to nearly all portions of the Phanerozoic stratigraphic record and greatly assist development of an advanced timescale. In addition to establishing a fingerprint for a particular eruption, apatite chemistry provides useful information about the source magma.

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Introduction

Large volcanic eruptions are invaluable for stratigraphic correlation of widely separated geologic sections. Tephra from such eruptions are often deposited over long distances in a variety of geologic settings and therefore have potential to provide an unparalleled tool for correlation in the sedimentary record. Before tephra from different locations can be used for correlation, the beds must be demonstrated to be of similar age on the basis of available stratigraphic and lithologic criteria (Pearce et al., 2008). When stratigraphic age constraints are established, a conventional practice in tephrochronology is to determine the major elemental composition of volcanogenic glass so as to establish a geochemically unique 'fingerprint'. The chemical identity of the glass in a particular ash layer can then be used as a powerful correlation tool (e.g., Alloway et al., 2007 and references therein). However, a given tephra bed was typically erupted over various depositional settings and may have been subsequently exposed to different diagenetic conditions and thus original glass compositions might not be preserved for all samples (e.g., Shane et al., 2003; McHenry, 2005; Suzuki, 2008). In pre-Cenozoic sedimentary rocks the tephra are often heavily altered (e.g., bentonites and tonsteins) such that all glass is completely

devitrified. With these cases there is an obvious need to employ different tephrochronologic methods so that the tephrostratigraphic record can be fully exploited.

In our studies of Ordovician tephra (K-bentonites) we have found that apatite trace-element chemistry is a useful bed discriminator for stratigraphic correlation. However, we have been uncertain about whether the original apatite trace-element composition has been altered during the intervening 450 Ma of geologic history. Also, it was uncertain whether apatite trace-element trends from Ordovician K-bentonites represented a unique geochemical setting, i.e. apatite from other tephra may not yield consistent trace-element concentration values that are unique among different tephra. Furthermore, it was unknown whether such apatite trace-element concentration trends could be expected to be unique, perhaps reflecting specific conditions in the parent magma. Despite our concerns, apatite appears to have robust tephrochronologic potential because 1) it is considered relatively stable (Morton and Hallsworth, 2007; i.e., it resists compositional modification during diagenesis), 2) it has the ability to incorporate nearly half of the elements in the periodic table in its crystal structure (Hughes and Rakovan, 2002), 3) trace elements in apatite display a large range of concentrations (Piccoli and Candela, 2002), and 4) its partition coefficients for many trace elements are very sensitive to changes in magmatic conditions (Watson and Green, 1981; Sawka, 1988).

As a result of these attributes there have been many recent petrogenetic studies based on the minor element (Piccoli and Candela, 2002 and references therein) and trace element (e.g., Roeder et al., 1987; Jolliff et al., 1989; Rakovan and Reeder, 1994; Peng et al., 1997; Sha and Chappell, 1999; Tepper and Kuehner, 1999; Belosuova et al.,

* Corresponding author at: University of Geneva, Rue de Maraîchers 13, 1205 Geneva, Switzerland. Fax: +41 22 379 32 10.

E-mail addresses: Bryan.Sell@unige.ch (B.K. Sell), sdsamson@syr.edu (S.D. Samson).

¹ Fax: +1 315 443 3363.

2001; Dempster et al., 2003) composition of igneous apatite. The potential to discern magmatic processes via apatite composition lends itself as a provenance indicator (Morton and Yaxley, 2007). Use of apatite as a correlation tool has been shown for heavily altered Paleozoic tephra (Samson et al., 1995; Emerson et al., 2004; Mitchell et al., 2004; Carey et al., 2009), but this has not been demonstrated for Cenozoic tephra.

One way to test whether it is a valid approach to use apatite trace elements for correlating heavily altered tephra is to compare our results with those from unaltered rocks. In this study we determined the trace-element composition of volcanogenic apatite from some deposits of historical volcanic eruptions (Table 1). We analyzed Mg, Cl, Mn, Fe, Ce, and Y in apatite from 10 previously sampled volcanic rocks that erupted in a variety of settings (the apatite samples were originally sampled and prepared by Peng et al., 1997). In addition, the composition of apatite phenocrysts from several extremely altered Paleozoic tephra deposits was determined to compare with that of the Cenozoic apatite phenocrysts (see data appendix). The selected elements were chosen because they are in sufficient abundance in apatite to be measured by electron microprobe analytical techniques, because several of these elements are common replacements for Ca in the apatite structure due to similar charge and ionic radii (Hughes and Rakovan, 2002), and because some elements in apatite, like Ce and Y, have proven useful for distinguishing certain kinds of igneous rocks (Roeder et al., 1987). The volcanogenic apatite samples in our study were chosen because they were previously sampled by Peng et al. (1997), prepared for apatite analysis via EPMA, and encompass a wide variety of volcanic rocks (Table 1). Samples from the Fish Canyon Tuff were selected because this is an extensively studied, major Cenozoic eruptive rock and because apatite from this tuff is available as a fission-track age standard.

Previous applications of phenocryst tephrochronology

Volcanic glass composition is excellent for discriminating tephra; however, it is thermodynamically unstable and is more susceptible to

Table 1

Sample registry (modified from Peng et al., 1997). NMNH = Smithsonian Institution National Museum of Natural History.

Bogoslof, U.S.A.
Bog I and Bog II: pumice from 1796 eruption.
Etna, Italy
NMNH no. 115482-4: mugearite from Poggio Laca.
NMNH no. 100021: andesite from Grotta Delle
Lassen, U.S.A.
NMNH no. 116619-53: banded pumice from May 22, 1915 eruption.
NMNH no. 116619-54: dacite of Lassen Peak.
Santa Maria, Guatemala
NMNH no. 113100-9 and NMNH no. 113100-10: pumices from the 1902 eruption.
Santorini, Greece
NMNH no. 98696: lava from Mikra Kameni dome.
NMNH no. 98697: lava from Nea Kameni dome.
NMNH no. 115999: dacitic pumice from ashflow unit B03 (about 1450) from Phira Quarry.
Tambora, Indonesia
NMNH no. 116570: pumice from 1815 eruption.
Pinatubo, Philippines
NMNH no. 116534-1 and NMNH no. 116534-2: pumices from a June 15, 1991 pyroclastic-flow deposit.
St. Helens, U.S.A.
NMNH no. 115379-7: pumice from May 18, 1980 eruption.
NMNH no. 115379-15: pumice from pyroclastic-flow deposit erupted on July 22, 1980.
Krakatau, Indonesia
NMNH no. 35516: andesitic pumice collected floating in water soon after 1883 eruption.
Fish Canyon Tuff
Apatite donated by Paul Fitzgerald, Syracuse University.

modification than virtually all accompanying mineral phases (Fisher and Schminke, 1984). Weathering, devitrification, and diagenesis of volcanic glass can cause sufficient alteration to preclude its use in conventional tephrochronologic studies of altered tephra (Cerling, et al., 1985; Pollard et al., 2003). Several studies have attempted to circumvent the problem of alteration of volcanic glass in Cenozoic tephra by determining the composition of different phenocrysts. McHenry (2005) had greater success in correlating altered Pliocene tephra using the major and minor element compositions of feldspar, titanomagnetite, and augite than glass composition. Suzuki (2008) used the chemical composition of titanomagnetite to correlate strongly weathered Pleistocene tephra. Likewise, elemental compositions of plagioclase/biotite (Cronin et al., 1996), sanidine/hornblende (Lipman and Weston, 2001), titanomagnetite (Kohn, 1979; Westgate and Gorton, 1980; Harangi et al., 2005), and biotite (Yen and Goodwin, 1976; Shane et al., 2003) were used to correlate Cenozoic tephra. In Paleozoic tephra, where glass is completely devitrified, some phenocryst phases such as quartz, zircon, apatite, and biotite can survive complete post-depositional diagenetic alteration. Some of these, such as apatite and quartz, have proven useful for stratigraphic correlation (Delano et al., 1994; Samson et al., 1995; Emerson et al., 2004; Mitchell et al., 2004; Carey et al., 2009). Other minerals, such as biotite, are susceptible enough to alteration that their chemical compositions have produced less unambiguous results (Haynes et al., 1995; Shane et al., 2003; Bergström et al., 2004).

To date, we are unaware of any published studies of the composition of apatite in Quaternary tephra that suggest it as a robust tephrochronologic method. However, Belosuova et al. (2001) used trace elements in apatite to characterize the provenance of igneous rocks. Hildreth (1979) demonstrated a distinct trend in apatite trace-element content that may have been temperature and oxygen fugacity controlled. Similarly, distinct trends in apatite from granites were suggested as being useful for distinguishing magma bodies (Tepper and Kuehner, 1999 and Dempster et al., 2003) and igneous rock types (Roeder et al., 1987). Also, intra-crystal “stratigraphy” derived from compositional zoning of apatite has been used to distinguish hydrothermal veins in ore deposits (Knutson et al., 1985) and magma devolatilization history (Boyce and Hervig, 2008). These studies all indicate promise in using trace elements in apatite as discriminators for a given volcanic rock as an elemental or chemical fingerprint. This provenance potential combined with robust preservation potential compared to other accessory minerals common in ash-fall beds could make apatite the best among the candidates for geochemical correlation of problematic tephra.

Materials and methods

We used thin sections of volcanic rocks and grain mounts of apatite crystals that were previously prepared by Peng et al. (1997). Samples from Peng et al. (1997) were obtained from the Smithsonian National Museum of Natural History, Department of Mineral Sciences. The grain mounts and thin sections were coated with a 25-nm-thick layer of carbon, where thickness was monitored using the method of Kerrick et al. (1973). All samples were then analyzed with a JEOL JXA 8600 Superprobe in the Department of Earth Sciences at Syracuse University. Using Geller Analytical's dSpec software, Mg, Mn, Fe, Y, and Ce were analyzed at 60 nA for 60 s on peak, with 30 s on background, and Cl was measured at the same current for 30 s on peak and 15 s on background. Ca, P, and F were analyzed at 10 nA for 10, 40, and 60 s, respectively. Probe diameter was maintained at 1 μm for trace elements so as to detect micron-scale variability. Where permitted by crystal size, three spots were analyzed per apatite crystal. Where there was no obvious chemical zoning of Mg, Cl, Mn, and Fe in apatite crystals, the three analyses per crystal were averaged to increase analytical precision. Olivine, scapolite, fayalite, YPO₄, and CePO₄ standards (Jarosewich et al., 1980) were used for wavelength

dispersive spectrometer calibrations of Mg, Cl, Mn + Fe, Y, and Ce, respectively. For all analyses we used the Conventional Philibert/Duncomb-Reed ZAF correction within the Geller Analytical dQuant32 software.

We attempted to analyze at least three 1- μm spots on each grain to test for within-crystal variation and inclusions that affect the final analysis. Our findings indicate that fewer analyses per crystal may be adequate to characterize tephra with EPMA, with only a slight increase in sample variability. Spot size could be increased to further minimize intracrystal chemical variation and increase X-ray counts while using a decreased beam current.

Analytical precision for the electron microprobe was assessed using a secondary standard (NMNH 104021 apatite) from the Smithsonian National Museum of Natural History (Table 2). However, elemental concentrations of Mg, Mn, and Fe in this standard were either at or near minimum detection limits. As a consequence, precision was also monitored with repeat analyses of the Fish Canyon Tuff apatite. Also, precision of the NMNH 104021 apatite analyses for Cl is poor, as these analyses were found to be heterogeneous, with four concentration groups (Fig. 1). However, the precision of Cl analyses within each group is better, with standard deviations of <10%. The standard is distributed as shards from crushed crystals, thus making it difficult to assess crystallographic orientation, which is known to have an effect on Cl analyses (Stormer et al., 1993). Examination of several shards by cathodoluminescence imaging showed no obvious compositional zonation. The Cl concentration group with the highest values comprised most of the analyses and had an analytical precision comparable to that of Mg, Mn, and Fe. Tests revealed that Cl migration, observed by Stormer et al. (1993), occurs at higher beam currents regardless of crystallographic orientation, and that shorter counting times (<30 s) at high current (60 nA) provides reproducible results.

The apatite trace-element data from closely spaced Ordovician K-bentonites were analyzed for principle components using the non-linear iterative partial least squares (NIPALS) algorithm in the software package The Unscrambler®. The PCA results were compared with other statistical software that showed similar results. The analysis was repeated after removing outliers that were greater than 3-sigma of the sample population.

Results

Apatite samples from one Paleogene and nine Quaternary (Table 1) volcanic rocks were analyzed for Mg, Cl, Mn, Fe, Ce, and Y via EPMA (Table 2). All elements analyzed display a large range of concentrations among samples and restricted concentrations (Fig. 2) for individual samples (Appendix A). Samples from nine closely spaced tephra (K-bentonites) in a single outcrop of the Late Ordovician Salona Formation from State College, Pennsylvania, U.S. A. demonstrate that Mg, Cl, Mn, Fe, Ce, and Y are useful for distinguishing chemically similar groups of apatite crystals. Additionally, apatite crystal geometry appears to be a useful for distinguishing beds in a given section.

Discussion

Tephrochronology is the study of ash-fall deposits for the purpose of correlating and dating stratigraphic events (see review by Lowe, 2011). While geochemical characterization (chemical fingerprinting) of ash-fall beds does not necessarily involve direct dating, it is critical for linking stratigraphic phenomena that have been dated by other methods. A fingerprint means that the tephra sample or bed is identified by a pre-determined set of criteria, although this does not include all possible laboratory and field-based observations. Here we define the criteria on the basis of Mg, Cl, Mn, Fe, Ce, and Y for the purpose of testing apatite as a bed discriminator. Additional criteria are important because tephra definitions typically require continual re-evaluation, as relevant analytical techniques become more refined and certain tephra become geologically important. A relatively large number of geological and analytical problems can lead to miscorrelation of tephra (Lowe, 2011); however, in this paper we only focus on ambiguous chemical characteristics, because tephra from a given region can have defining criteria such that two or more beds cannot be easily distinguished. This means that proposed correlations must be rigorously interrogated with advanced statistical methods and additional kinds of data. A single dissimilarity can invalidate a tephra correlation, whereas the subsequent discovery of additional similarities does not change a negative correlation.

Table 2
Average apatite trace-element concentrations (wt.%).

Sample of name	Number of analyses	Number of crystals	Mg ^a (8.7)	Cl (3.5)	Mn (8.4)	Fe (8.1)	Ce (9.2)	Y (5.8)
Bogoslof	22	9	0.018 ^b (0.020)	0.314 (0.191)	0.125 (0.056)	0.082 (0.200)	0.172 (0.333)	0.026 (0.025)
Etna	30	8	0.142 (0.111)	0.786 (0.327)	0.058 (0.047)	0.354 (0.812)	0.195 (0.229)	0.034 (0.051)
Lassen	30	10	0.083 (0.190)	1.23 (0.640)	0.141 (0.071)	0.369 (0.600)	0.249 (0.212)	0.055 (0.039)
Santa Maria	46	16	0.090 (0.020)	1.144 (0.392)	0.202 (0.029)	0.372 (0.359)	0.085 (0.057)	0.040 (0.015)
Santorini	20	9	0.105 (0.016)	1.028 (0.466)	0.104 (0.029)	0.452 (0.97)	0.162 (0.401)	0.074 (0.028)
Tambora	35	9	0.107 (0.069)	0.478 (0.134)	0.065 (0.026)	0.164 (0.088)	0.105 (0.175)	0.037 (0.062)
Pinatubo	47	20	0.058 (0.015)	1.115 (0.474)	0.125 (0.035)	0.203 (0.228)	0.133 (0.079)	0.028 (0.039)
St. Helens	20	20	0.088 (0.015)	0.731 (0.208)	0.057 (0.019)	0.466 (0.357)	0.094 (0.280)	0.035 (0.024)
Krakatau	14	9	0.090 (0.058)	0.889 (0.317)	0.108 (0.057)	0.276 (0.232)	0.142 (0.195)	0.102 (0.073)
Fish Canyon	128	18	0.022 (0.004)	0.944 (0.259)	0.128 (0.028)	0.071 (0.026)	0.273 (0.172)	0.041 (0.034)
Apatite NMNH 104021 (Durango)	201	–	0.009 (0.005)	0.421 (0.145)	0.023 (0.03)	0.011 (0.021)	0.361 (0.105)	0.063 (0.026)

^a Typical analytical error (%).

^b Sample error at two standard deviations in parentheses.

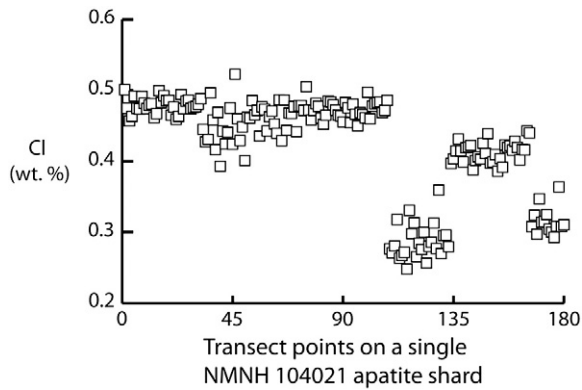


Figure 1. Cl variation in a single shard of NMNH 104021 apatite standard.

It is nearly impossible to unequivocally demonstrate that two or more rock samples are exactly the same (i.e., derived from the same source at the same time). This is because it is unlikely that all possible aspects of the rock samples can be measured, such as isotopes, elemental concentrations, crystal habit, such that future observations could show that two samples are likely different. However, it is much easier to show that two or more rocks have a certain level of probability in being similar or different on the basis of some stated criteria. In this way statistics can be applied for hypothesis-testing. In statistical terms, the null hypothesis is that two or more rock samples are likely similar. Various methods of comparing statistical parameters will give a probability statistic that can be used to accept or reject the null hypothesis on quantitative grounds.

Proposed correlations made on the basis of geochemical characterization of phenocrysts and volcanic glass shards are often plagued by complexity. This is because data are multidimensional (three or more different element concentrations) and display complex trends when plotted on multivariate plots. The geochemical character (fingerprint) of one tephra bed may show some similarities, or overlap with the character of another bed in the same stratigraphic sequence. Additionally, the data for a given sample or element can be non-normally distributed. In cases such as these, basic statistical hypothesis testing of proposed correlations cannot always be used for overlapping multidimensional fingerprints of beds in a given sequence. Another approach is needed, namely with respect to multivariate statistical methods, which is a continually evolving pursuit among tephrochronologists (see

Lowe, 2011). In the following we discuss a set of multidimensional criteria for defining a chemical fingerprint (Mg, Cl, Mn, Fe, Ce, and Y concentrations in apatite) and illustrate one multivariate statistical method for distinguishing beds from a single stratigraphic sequence that show overlapping fingerprints.

Trace-element variation

Single crystals from the Fish Canyon Tuff were tested for variations in trace-element concentrations by analytical transects across polished sections of crystals (Fig. 3). Zones of varying REE content can typically be viewed in cathodoluminescence images (e.g., Dempster et al., 2003). Even where cathodoluminescence did not show any visible zones, analytical transects and three-point analyses across polished crystal sections do show systematic variation in Ce and Y. Cl showed variation within single crystals and among crystals of the same sample. Although we did not systematically examine Cl zoning in apatite, the variation may be due to the kind of halogen zoning reported by Boyce and Hervig (2008). For all crystals analyzed, Mg, Mn, and Fe are relatively homogeneous over an entire crystal regardless of variation in Ce and Y contents and zonation visible by cathodoluminescence.

Although there are significant variations among crystals with respect to Ce and Y concentrations in all apatite samples, ratios of Ce and Y are relatively consistent (Fig. 4). For example, some individual crystals from the Fish Canyon Tuff display the entire range of trace element concentrations as found in all crystals analyzed, whereas other single crystals have a narrow range of values (Fig. 5). Variation of Mg, Cl, Mn and Fe among crystals is relatively low for most samples. A few samples (e.g., Mount Lassen and Mount Etna) did show significant variation with respect to Mg, Cl, Mn, and Fe (Table 2).

Bed discrimination

All apatite samples can be distinguished on the basis of elemental compositions or distinct trends when plotted using various combinations of Mg, Cl, Fe, Mn, Ce, and Y. The selected volcanic rocks can be discriminated with only minimal overlap (Fig. 2). Cl shows the greatest variation between and within samples (Table 2), whereas Mg and Mn display the second and third greatest variation, respectively, between samples. The limited number of crystals per sample did not allow full examination of the elemental variation. Nevertheless, our data do show that distinct apatite trace-element differences occur

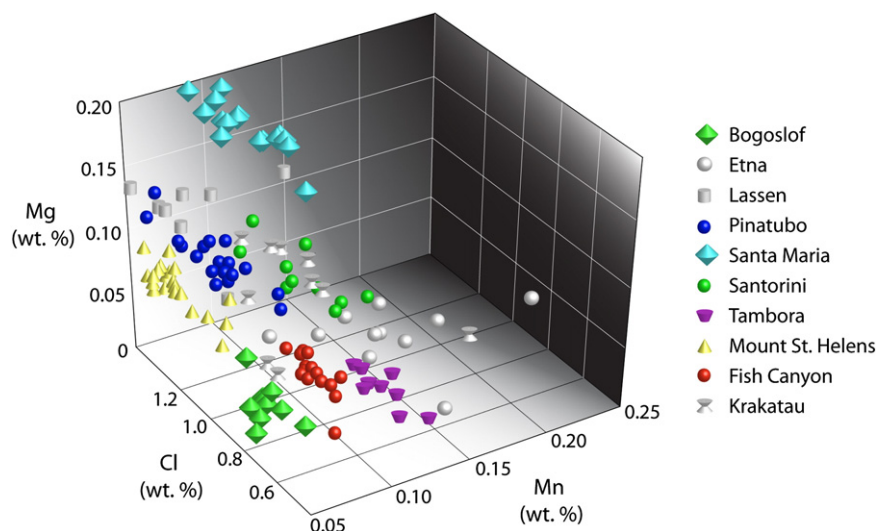


Figure 2. Three-dimensional plot of Mg, Cl, and Mn concentrations in apatite from various unaltered tephra. These analyses confirm our ability to characterize a given tephra. The plot is oriented and scaled to show the differences between each sample. Some trace-element values overlap but it is the overall data trend that distinguishes each sample.

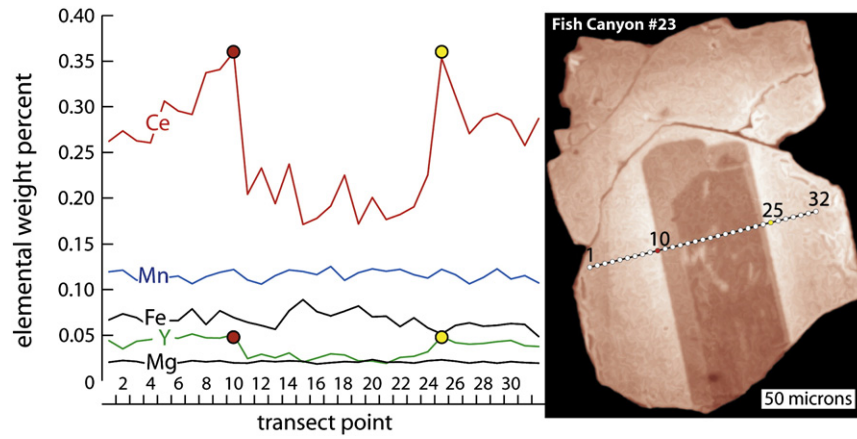


Figure 3. Trace-element profile of an apatite crystal from the Fish Canyon Tuff. Mg, Mn, and Fe are homogeneous despite considerable heterogeneity of Ce and Y. Nearly all of the examined apatite crystals from unaltered tephra display at least subtle zonation with respect to Ce and Y concentrations. Cathodoluminescence image was digitally enhanced to highlight visually subtle zonation. Digital enhancement does not add or subtract any apparent zones.

between all of the rocks examined. Mean Cl values for each sample are adequate for discrimination of most ash beds (Table 2). When combined with data for Mg and Mn, all of the volcanic rocks plot in unique clusters. Fe content and Ce/Y ratios provide additional discriminating power.

Element concentrations of volcanogenic apatite from Paleozoic tephra samples reported in the literature (Samson et al., 1995; Emerson et al., 2004; Mitchell et al., 2004; Carey et al., 2009) are very similar in range and variation with the apatite from the Quaternary tephra. This is important because it strongly suggests that the apatite composition from tephra that are millions of years old is a primary feature and not one that was acquired post-deposition. Thus there is now an empirical basis to show that analysis of volcanogenic apatite should provide the ability to distinguish Quaternary tephra, when the original glass composition is significantly altered. It must be noted, however, that the Cenozoic tephra samples are from completely different volcanic systems from around the world. Trying to distinguish multiple eruptions from the same volcanic system would undoubtedly be more challenging because of the chemical similarity of magma sources. However, combining the discriminating power of several elements should be sufficient for individual bed identification.

For trace-element concentrations, variation about the mean is only partially due to analytical error. For example, in apatite from the Fish canyon Tuff the variation at two standard deviations from the mean for Ce and Y is 63% and 82%, respectively. However, Ce and Y define a trend along a straight line with a correlation coefficient of 0.89. The variation along this straight line could be explained by changing

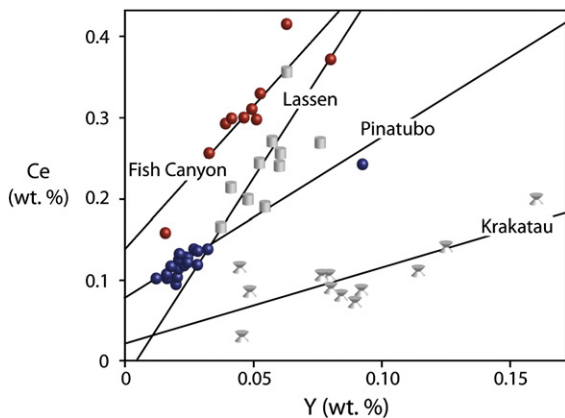


Figure 4. Ce and Y plot of selected apatite analyses from each sample. Analytical precision was poor for several samples; however, trends in the Ce and Y concentrations are evident.

conditions in the magma while the apatite was crystallizing (e.g., Tepper and Kuehner, 1999 and Dempster et al., 2003). Mg, Cl, Mn, and Fe in apatite do not show any simple covariance with one another. However, these elements show different ranges of trace-element concentration values in apatite for each sample. Bivariate plots of these elements display complex patterns with respect to these concentration ranges. Because there are no accepted natural apatite trace-element standards, it is not possible at this time to completely assess how much of this variation is due to analytical error. However, variation from mean values is low for Mg, Mn, and Fe.

Cl concentrations show the greatest differences between samples. Narrowly defined ranges of trace-element concentrations, except for Cl, in some samples suggest that most of the Cl variation is not analytical. The cause of variation of Cl in our analyses cannot be conclusively determined because 1) crystallographic orientation in thin section cannot be controlled (Stormer et al. 1993), 2) there appears to be beam damage from previous analyses, and 3) there is the possibility of Cl compositional zonation (Boyce and Hervig, 2008). Despite these problems in obtaining Cl data, the differences between samples is much greater than the within sample variation. Thus, Cl concentrations still allow for meaningful discrimination.

The ranges of trace-element concentration values for each sample do form trends when plotted. Samples with relatively low ranges of concentration values require fewer than 20 analyses to define a trend, because the mean and variation cease to change with increasing number of analyses. The exceptions are for samples from Krakatau and Mount Lassen. For these samples the variation for Mg, Cl, Mn, and Fe concentrations are too large to define a trend because of the limited number of analyses (Fig. 2 and Table 2). However, Ce and Y concentrations show covariation in both samples.

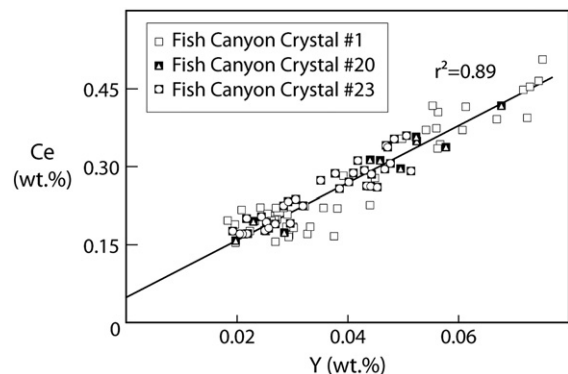


Figure 5. Ce and Y values from different Fish Canyon apatite crystals.

Petrologic significance

Ce and Y trends for all samples suggest similar crystallographic and magmatic controls for the distribution of these elements in apatite. Different slopes for the covariation may be due to differences in the source magma composition (Sha and Chappell, 1999). The differences in the mean elemental concentrations among all samples suggest different compositions and tectonic settings of the volcanic sources. For example, Sha and Chappell (1999) found the Mn and Fe concentrations in apatite depended on the magma's oxygen fugacity and peraluminosity. S-type and felsic I-type granites contained apatite with higher Mn and Fe concentrations than mafic I-type granites. These relationships may hold true for magmatic apatite in general, but differences in magma source composition may play the largest role. Within a restricted range, trace element variation in apatite from a cogenetic suite of tephra would reflect other magmatic conditions such as magma mixing, contamination, kinetic effects, or fractional crystallization. Determining exactly what controls the composition of the volcanogenic apatite presented here is beyond the scope of this study.

Concentric compositional zoning with respect to Na, Si, and S was previously reported to be present in nearly half of the samples analyzed here (Peng et al., 1997). Similar compositional zoning is reported within apatite crystals from granite (Tepper and Kuehner, 1999; Dempster et al., 2003) and an ignimbrite (Boyce and Hervig, 2008). Compositional zoning in apatite can be due to a variety of processes that include magma mixing, changes in crystal/melt partitioning, inheritance, and kinetic effects (Tepper and Kuehner, 1999). Several other investigators have examined compositional zoning in apatite (Knutson et al., 1985; Roeder et al., 1987; Jolliff et al., 1989; Rakovan and Reeder, 1994; Piccoli and Brown, 2005; Lux and Yates, 2009) and have discussed its possible causes. Whatever the cause of compositional zoning within the apatite crystals, most apatite trace-element concentrations are in a restricted range for each sample. Variations within single crystals did not contribute significantly to apatite Mg, Cl, Mn, and Fe variation of any sample, although the averaging of three EPMA analyses per crystal may decrease the apparent variability of the total apatite sample (Appendix A). Ce and Y ratios for a volcanic rock sample define unique trends, consistent with the findings of Roeder et al. (1987) and Sha and Chappell (1999), that REE concentration variation among crystals from a granite is considerable yet does not alter the REE pattern for that sample.

One or more clusters and a restricted range of concentration values represent trends in the trace-element data. These trends likely reflect different crystal populations, namely phenocrysts, antecrysts, xenocrysts, and microlites, that were derived from a varied history of melting and crystallization (Jerram and Martin, 2008). Within each apatite crystal is a compositional record similar to that described as "crystal isotope stratigraphy" (Davidson et al. 1998), which is useful for discerning what contributed to the magma while providing a relative timescale for magmatic processes. Also, crystal-size distributions (e.g., Bindeman, 2003) are useful for understanding the evolution of silicic magma systems. Trace-element concentrations and compositional zonation in apatite have been shown to provide similar information on magma chamber dynamics (Tepper and Kuehner, 1999; Dempster et al., 2003). Perhaps a combination of trace-element concentrations and zonation, with crystal-size distribution and crystal-isotope stratigraphy, would help in understanding the history of a particular eruption such that a clearer fingerprint could be established beyond simple pattern identification.

Tephrochronologic significance

No single tephrochronologic method is infallible. Conventional glass shard tephrochronology can be complicated by diagenesis (e.g., McHenry, 2005; Suzuki, 2008), aeolian fractionation (e.g., Pollard et al., 2006; Pearce et al. 2008), mixing of ash from two or more

eruptions (e.g., Riehle, et al., 2008), a variety of post-depositional reworking processes (McCoy, 1980; Westgate and Gorton, 1980; Kennett, 1981), geochemical heterogeneity in the source magma (e.g., Shane et al., 2008), non-unique compositions amongst a suite of tephra (e.g., Turney et al., 2008), and analytical issues (e.g., Hunt and Hill, 2001). In some cases, more precise measurements of trace elements in glass shards can overcome ambiguous results derived from major element concentrations (Pearce et al., 2004). However, in other cases, precise determination of trace elements in glass shards can still produce ambiguous correlation results (Shane, 2000). As discussed above, mineral (i.e., augite, biotite, and titanomagnetite) composition can be useful for correlation, but these minerals can be absent from the crystal load of tephra. For example, Shane et al. (2003) reported that biotite is present in only 25% of the tephra from their study. Likewise, our experience with Paleozoic tephra has shown that less than 10% of over 300 individual samples contain biotite (unpublished data). And even where these minerals are present in altered tephra their compositions can be so affected that they begin to lose their discrimination power (e.g., McHenry, 2005).

Apatite provides the benefit of being a ubiquitous accessory mineral across a large variety of volcanic rocks (e.g., Izett, 1981). Consequently, minor and trace-element contents in apatite can provide independent constraints for particularly difficult tephrochronologic problems in which glass and other mineral phases are so altered that their compositions are no longer useful as a discrimination tool. For example, in classic tephrochronologic studies, where glass shard chemistry is successfully employed for large numbers of samples, there are typically several geochemically anomalous samples that may have been affected by diagenesis (e.g., Sarna-Wojcicki et al., 1984 and references therein). Perhaps trace elements in apatite could help solve some conventional tephra-correlation problems.

Apatite trace-element chemistry has been invaluable in correlating Late Ordovician rocks of eastern North America. We compare apatite trace-element analyses from several selected K-bentonites (Appendix A) with the unaltered Cenozoic volcanic rocks (Fig. 6). Many of these K-bentonites, such as the Deicke (Fig. 7), can be found in locations across almost half the area of the contiguous United States (Carey et al., 2009). Until now, we have been uncertain about the extent to which, if any, post depositional alteration has affected the trace-element signature in these ancient and heavily altered beds. The apatite trace-element concentrations from unaltered and altered volcanic rocks have similar patterns, thus suggesting that any alteration of the Late Ordovician K-bentonites has had a minimal effect on apatite chemistry.

Self-similar tephra suites

Apatite trace-element data from Cenozoic volcanics show encouraging potential for tephrostratigraphic correlation; however, the data are from globally distributed volcanic arcs (with the exception of the two arcs represented by Mount St. Helens, Lassen, Krakatua, and Tambora) while many tephrochronology studies are regionally based. Suites of tephra in a given region would be expected to be self-similar in that one of the tephra is at least approximately similar to all other stratigraphically close tephra. This is because the tephra are more likely to share a common magma source. This is apparent with apatite from suites of closely spaced K-bentonites from the Late Ordovician of North America, for which many beds from this intensively studied stratigraphic interval show apatite chemical composition that overlaps with other beds (Emerson et al., 2004; Mitchell et al., 2004). Two of the beds in this interval have been correlated across the eastern United States (Carey et al., 2009).

We illustrate new data from an outcrop in central Pennsylvania that is within this same stratigraphic interval (Fig. 7). Several of the beds appear to be indistinguishable and show complex patterns with three of the beds showing multiple apatite components that overlap

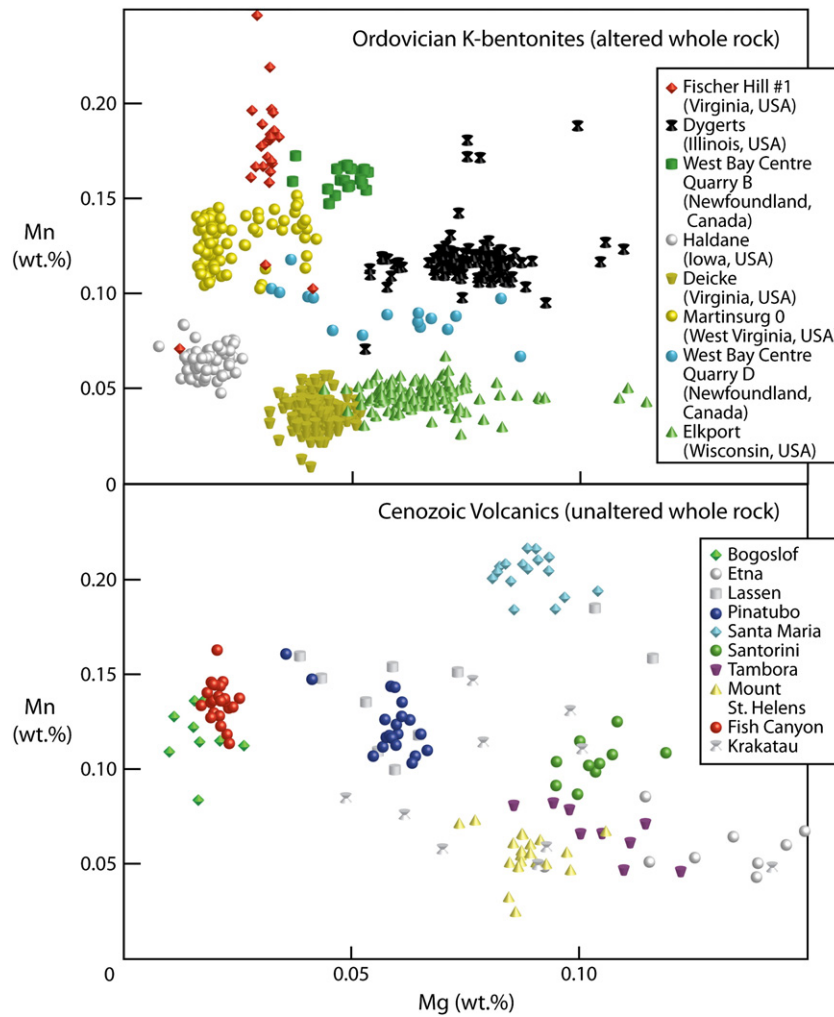


Figure 6. Comparison of volcanogenic apatite in heavily altered volcanic rocks (from our ongoing correlation study of Ordovician K-bentonites) and relatively unaltered Cenozoic volcanics.

with other samples. All samples appear to plot, at least in part, along a similar overall trend or PCA field (Fig. 7). It seems likely that a common process and/or source influenced the apatite composition of all of the beds and that a few have additional unique influences. Elemental data from three beds (4.5, 12, and 39 m) are non-normally distributed. A multivariate statistical method is needed to test if the beds can be distinguished on the basis of six elements (Mg, Cl, Mn, Fe, Ce, and Y) in apatite.

Principle component analysis (PCA) appears to be an adequate method for distinguishing beds on the basis of non-normally distributed and multivariate trace-element data (Fig. 7). An elementary explanation of PCA is that it takes into account all variables (Mg, Cl, Mn, Fe, Ce, and Y) and provides a means of visualizing the maximum differences between all samples. The first principal component (PC1) explains most of the variance as indicated by the percentage in parentheses of bivariate plots A and B in Figure 7. The second principal component (PC2) has the second greatest explanatory power for variance among samples. The PCA method also provides a way to identify data clusters and outliers within and among samples and determine which components (elements) explain the differences between samples. The majority of the outliers are from three beds that display multiple components or element concentration groups that overlap with groups from other beds (plots A and B, Fig. 7). Removing these outliers shows that most of the beds follow a general trend or have components that fall within one PCA field. Beds at –19 m and

–25 m appear difficult to distinguish; however, a Student's *t*-test of crystal size, Cl, and Fe concentrations show that similarities between the two beds can be rejected ($p < 0.00$).

The variance between groups that follow the main diagonal trend (from lower left to upper right) in the PCA plot is explained by elements Cl, Mn, and Fe as indicated by the correlation-loading ellipse. The correlation-loading ellipse illustrates which elements contribute to the greatest variance between samples (those elements with the highest loading score). Elements Mg, Y, and Ce explain very little of the variance between groups in the main PCA trend in plot A, Figure 7. Beds at 4.5, 12, and 39 m have components that are outside of this trend. When these multi-component beds are analyzed separately for principle components the element Mg is included with Cl and Fe to explain most of the variance between samples, while Mn loses its ability to be a powerful discriminator. The other elements, Y and Ce, do not explain as much variance for all samples when compared to the other elements (Mg, Cl, Fe, and Mn), however, bivariate plots of elemental concentration for Y and Ce (plot F, Fig. 7) indicate some discrimination potential that is excluded by examining the first two principle components. Perhaps greater analytical precision by another method (e.g., laser ablation inductively coupled plasma mass spectrometry) would increase the discrimination potential of Y and Ce as well as other rare earth elements.

Regardless of analytical considerations and which elements are most successful for discrimination, it appears that comparing all beds

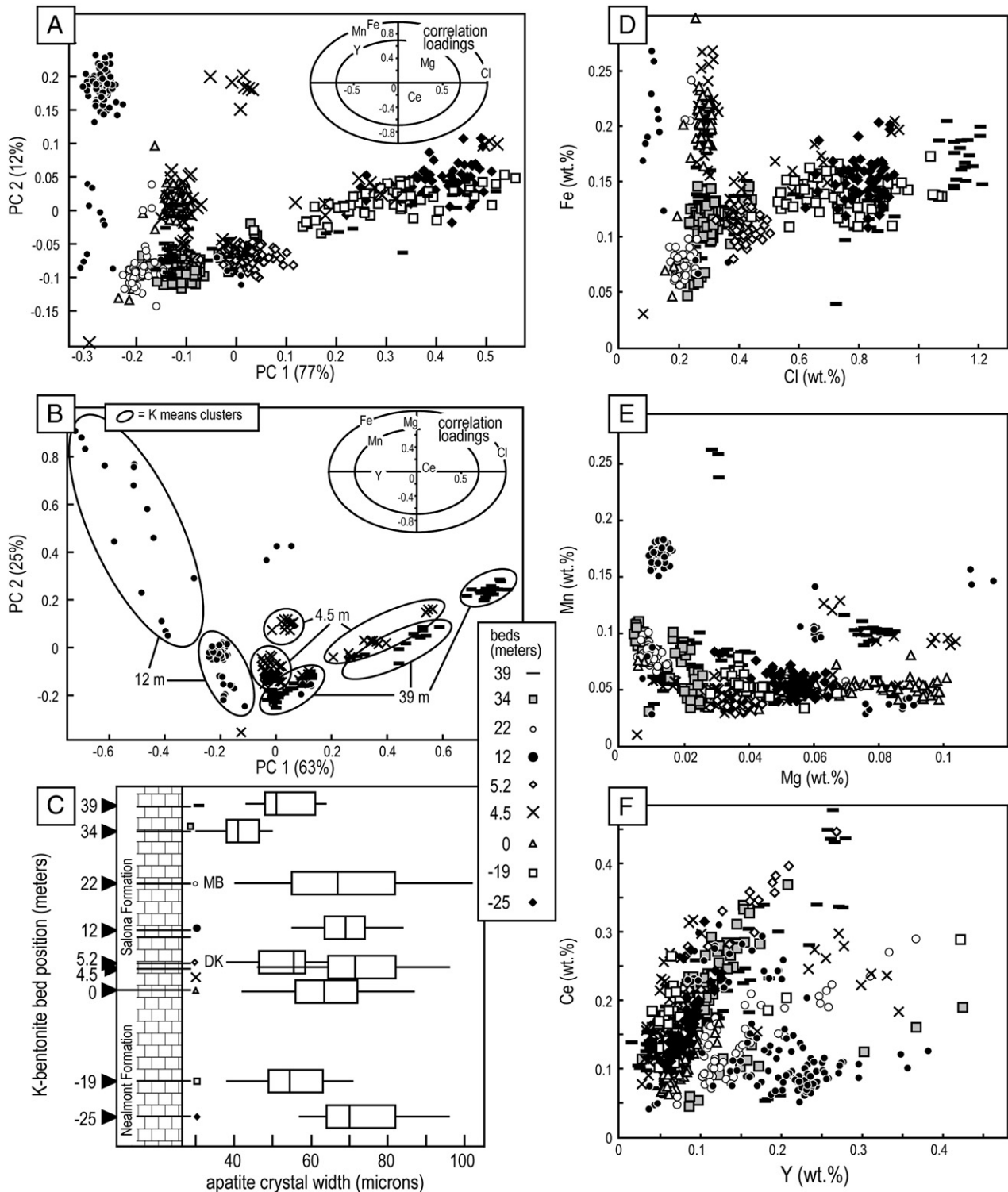


Figure 7. Principle component analyses (PCA) of apatite trace elements and crystal size analysis of apatite crystals from nine closely spaced tephra (K-bentonites) from the Late Ordovician Salona Formation in State College, Pennsylvania. The symbols represent the same samples in all plots. The bivariate plot in A shows the PCA plot of all samples minus outliers. The bivariate plot in B shows the PCA plot of the three samples that contain the outliers. Each principle component shows the percentage of explained variance in parentheses. Correlation loadings show which elements, which are those in the outer ellipse, explain most of the differences between samples in each plot. The box plots in C show mean, upper and lower quartile, and range of apatite crystal width measurements. Crystal width is measured perpendicular to the c-axis. Bivariate plots of original apatite trace element in D, E, and F, are shown for direct comparison with PCA following the suggestion of Pearce et al. (2008). Samples labeled MB and DK in plot C are the Millbrig and Deicke K-bentonites, respectively, which have been successfully correlated by apatite chemistry across much of the eastern United States.

with the exact same elements obscures differences between beds. Processes that controlled the partitioning of elements in apatite from beds 4.5, 12, and 39 are likely different from the other beds, thus suggesting distinctly different sources and/or magmatic conditions.

Apatite trace-element data for beds 4.5, 12, and 39 are non-normally distributed because the crystals likely represent different populations from mixing of two or more magmas, ash layers from separate eruptions, or both. Demonstrating a correlation between two

multi-component tephra samples is more difficult than distinguishing beds in a given section because of the statistical distribution of the data. Proposed correlations require additional testing through the examination of other criteria. The most robust multivariate statistical tests typically require the data to be normally distributed. To satisfy this normality requirement, the data need to be stratified on the basis of *a priori* geological information, by some statistical method such as K-means clustering (e.g. Lowe, 2011), or by outlier selection as in some PCA software packages. Stratifying means that the data are grouped into more homogenous or normal distributions. It is known that magmas are composed of different crystal populations of the same phase (Jerram and Martin, 2008), which can be shown with isotopic compositions, elemental concentrations, and geometry of crystals. It is likely correct to assume that the apatite trace-element variation in some samples represent distinct crystal groups. On the basis of this assumption, the trace-element data can be stratified by PCA or a clustering method. Applying a K-means clustering algorithm, for example, was successful at identifying data clusters that can then be visualized in PCA bivariate plots (plot B, Fig. 7). Subsets of data that do not pass normality tests may be an indication that more analyses are needed to fully characterize the sample. Data subsets that are normally distributed can be tested with a variety of multivariate statistical methods that have proven useful for correlating tephra, such as discriminate function analysis and Hotelling's T² (Lowe, 2011 and references therein).

Future research

Future phenocryst-based tephrochronologic studies might do well to employ more advanced methods that permit better analytical precision and a greater number of analyzed trace elements. Laser ablation-inductively coupled mass spectrometry (LA-ICP MS) has been very successful in discovering subtle elemental differences between glass shard samples (Lowe, 2011 and references therein) and is routinely used for high-precision trace-element analyses. However, future crystal-based tephrochronologic studies should address the issue of finding adequate matrix-matched standards (i.e. apatite) so that the results can be reproducible and comparable among laboratories. Also, the phenocryst size may be a limitation in some samples as analytical precision can show a general decrease with laser beam diameter. Many apatite crystals in this study are less than 15 μm in width while routine LA-ICP MS laser beam diameters are between 15 and 50 μm . Within-crystal chemical zonation, which may be useful for characterizing a sample, appears to be at a scale of less than a few microns. Additionally, halogen element concentrations can be diagnostic for many samples, but have poor ionization potential (Potts, 2003) with LA-ICP MS.

Zircon is another robust phase that commonly occurs as an accessory in volcanic rocks and may be useful in helping correlate highly altered tephra. Trace elements in zircons, such as the rare earth elements, have been useful in many petrologic studies, however their utility in provenance studies appeared questionable (see review by Hoskin and Schaltegger, 2003). Subsequently, zircon trace elements, crystal morphology, and Hf isotopes were found to be useful in modeling petrogenesis, i.e. specific batches of magma or processes can be identified (Belousova et al., 2006). Also, trace elements were used to "fingerprint" ocean crust zircon crystals (Grimes et al., 2007). More recently, a combined approach that involves age determination by chemical abrasion-thermal ionization mass spectrometry (CA-TIMS) and subsequent trace-element analysis (TEA) on the same crystals shows some promise for tephrochronology (Schoene et al., 2010). Likewise, oxygen isotopes in zircons could be employed to characterize a given tephra (see review by Valley, 2003). It appears that zircon tephrochronology, combined with other tephrochronologic criteria, may be a powerful approach in cases where tephra are highly altered given that a high-precision U–Pb age, trace-element finger-

print, and other isotopic information could be determined from the same crystal.

Summary

Apatite tephrochronology is an essential tool for correlating heavily altered tephra that can be employed in concert with a variety of other field and laboratory-based correlation methods. It appears that many of the major historical eruptions can be easily distinguished using the trace-element concentrations of apatite phenocrysts. Trace-element composition patterns in apatite from unaltered volcanic rocks show striking similarities with those in heavily altered tephra, which validates our current use of apatite trace-element concentrations for correlating K-bentonites. Apatite tephrochronology can be applied to nearly all portions of the stratigraphic record where apatite is present as an accessory phase in tephra that are either partially altered or completely devitrified. In other cases, where conventional tephrochronology (i.e., glass chemistry) produces ambiguous correlations, apatite tephrochronology may prove to be an invaluable independent constraint. This study also supports suggestions (Roeder et al., 1987; Tepper and Kuehner, 1999; Dempster, et al. 2003) that apatite chemistry and compositional zonation within crystals may be useful for discriminating sources of plutonic igneous rocks.

Acknowledgments

This research was partially supported by a grant from the National Science Foundation (EAR 0519106). Special thanks go to Michael Cheatham, John Fornelle, and Philip Piccolli for EPMA analytical advice. Paul Fitzgerald is thanked for donating samples of Fish Canyon apatite. Julie Griswold and John Pallister are thanked for their help in our search for samples. Warren Huff and John Westgate are thanked for thoughtful reviews that greatly improved this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at [doi:10.1016/j.yqres.2011.03.007](https://doi.org/10.1016/j.yqres.2011.03.007).

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