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Identifying the Origins of Volcanic Ash Deposits Using Their Chemical and Physical Compositions

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

IDENTIFYING THE ORIGINS OF VOLCANIC ASH DEPOSITS USING THEIR CHEMICAL AND PHYSICAL COMPOSITIONS

A thesis submitted in partial fulfillment of

the requirements for the degree of

MASTER OF SCIENCE

in

GEOSCIENCES

by

Emmanuel Soto

To: Dean Michael R. Heithaus College of Arts, Sciences and Education

This thesis, written by Emmanuel Soto Esguerra, and entitled Identifying the Origins of Volcanic Ash Deposits Using Their Chemical and Physical Compositions, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

Laurel Collins

Grenville Draper

Rosemary Hickey-Vargas, Major Professor

Date of Defense: March 29, 2018

The thesis of Emmanuel Soto Esguerra is approved.

 Dean Michael R. Heithaus College of Arts, Sciences and Education

Andrés G. Gil Vice President for Research and Economic Development and Dean of the University Graduate School

Florida International University, 2018

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DEDICATION

I dedicate this Thesis to my parents, for all their love and support.

ACKNOWLEDGMENTS

First, I would like to thank my academic advisor, Dr. Rosemary Hickey-Vargas for her kindness, wisdom, and guidance from the very beginning to the end. I will forever be grateful you chose me as your student. Secondly, to the members of my committee for accepting their role and for challenging my work whenever necessary. Lastly, I would like to thank my life partner Adhly Huertas, for her understanding, patience, and motivation throughout this journey. Without her contribution, this work might have never been finished. I also thank Tom Beasley, of FIU's Florida Center for Analytical Electron Microscopy, and Dr. Sarah Jantzi, of FIU's Trace Evidence Analysis Facility, for instruction and assistance with chemical analyses.

I have found my coursework throughout the Curriculum and Instruction program to be stimulating and thoughtful, providing me with the tools with which to explore both past and present ideas and issues.

ABSTRACT OF THE THESIS

IDENTIFYING THE ORIGINS OF VOLCANIC ASH DEPOSITS USING THEIR CHEMICAL AND PHYSICAL COMPOSITIONS

by

Emmanuel Soto

Florida International University, 2018

Miami, Florida

Professor Rosemary Hickey-Vargas, Major Professor

Pleistocene-Recent ocean sediments collected offshore Chile by Ocean Drilling Program Leg 202 contained layers of volcanic ash of unknown origin. These deposits may have originated from sources in the Southern Volcanic Zone (SVZ) within the Andean Volcanic Belt to the east, or from explosive volcanoes in the southwestern Pacific transported by westerly prevailing winds. In this study, mineral and glass textures and compositions of Leg 202 ashes were evaluated to try to determine the sources of the ash layers. Ash fragments were imaged and analyzed for major elements using an SEM with X-Ray detector and for trace elements using LA-ICPMS. Results show that the ash samples are rhyolitic and that they formed in a subduction zone setting or a continental margin. The ash samples have distinct physical and geochemical features that can be used in the future to identify their source(s) by comparison to databases of Pleistocene-Recent explosive volcanic eruptions.

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ABBREVIATIONS AND ACRONYMS

INTRODUCTION

Volcanic ash is the finer (under 2mm) particulate material ejected during a volcanic eruption. It is mainly composed of volcanic glass fragments, along with mineral grains and lithic grains. The eruption column, a cloud of volcanic ash, can rise over 40 km, reaching the stratosphere where it can create short term climatic changes (Prata et al., 2007). Clouds formed by volcanic ash can become a serious security risk to air transportation since they do not appear on radar and look similar to weather clouds (Roth and Guritz, 1995). The volcanic eruption from Mount Redoubt in 1989 caused a plane crash when a passenger jet flew through the ash cloud and experienced complete engine failure.

Volcanic ash can have a large impact on the climate and biogeochemical processes as it can absorb infrared light differently from water and ice. Volcanic ash can also alter the chemistry, cloudiness, and radiation budget of the atmosphere for a few weeks (Niemeier et al., 2009). Once in the atmosphere, wind patterns can carry the ash over great distances, making it difficult to identify their origin (Figure 1). Large explosive eruptions have the potential to cover continental scale areas with ash (Baines and Sparks, 2005). Well-preserved volcanic ash sediments in the geological record represent an invaluable reconstruction tool for past eruptions in any given location. Ash also provides key stratigraphic markers for paleoenvironmental studies, and aids with the investigation of volcanic eruption impacts on the environment (Carel et al., 2011). For analytical purposes, the ideal location in which volcanic ash can be found is within

oceanic sediments on the ocean floor, unlike terrestrial fallout deposits, it is rarely disrupted (Keller et al., 1978). As a key indicator of geologic history, volcanic-ash layers found in oceanic sediments are among the most well preserved stratigraphic markers known today (Carel et al., 2011). Not only are they important chronological tools when dated radiometrically, volcanic-ash layers can also provide us with information about past climatic events (Bard et al., 1994). Oceanic sediments can be dated using marine biostratigraphy, which is the use of fossils of marine organisms to identify time intervals. A specific organism can provide the information needed to place a sediment into age brackets. In some cases, minerals in the ash can be dated radiometrically (Turner et al., 1980).

The study of volcanic activity in the Southern Volcanic Zone is of great importance due to the limited amount of data available for the chemical composition of different eruption points. Although the Chilean's active margins have been studied extensively, large gaps of information are still missing. Many volcanic eruptions in the Andes from different time periods have not been geochemically recorded, which creates large gaps in the literature. This makes it harder to locate the origin of an unknow sample of volcanic ash. This project aims to contribute a significant amount of data which can be of use in future studies.

Figure 1. Eruption from the Puyehue-Cordon Caulle Volcano in Chile taken 06/06/11. Picture taken via satellite by NASA.

Expedition 202 of the Oceanic Drilling Program

In the present study, volcanic ash was found in oceanic sediments off the coast of Chile in areas with sedimentation rates of 80-2000 m/m.y. (Mix et al., 2003a), in close proximity to the Andean Southern Volcanic Zone (SVZ). The ash samples were uncovered in the year 2002 by the Ocean Drilling Program (ODP), now known as the International Ocean Discovery Program (IODP); (Figure 2). The IODP is an international research consortium that studies oceanographic and earth science problems by drilling and analyzing rock cores and sediments from the ocean floor (Anonymous, 2007). The expedition had a total of eleven drill sites in the Southeast and Equatorial Pacific, of which, four were near the SVZ. These four sites had a total of fifteen ash layers divided amongst them, one ash layer was chosen per site. This was based on factors such as thickness (the selected ash layers were at least half an inch thick) and depth (layers at similar depths). The four drill sites (1232, 1233, 1234, and 1235) located west of the Andes had a depth range of 120-360m, and basal ages from 0.26-1.69 Ma, which places them in the Pleistocene to Recent.

Figure 2. Drill sites from the ODP Expedition 202. Sites 1232, 1233, 1234, and 1235 all contained ash layers and are in close proximity to the Southern Volcanic Zone. Image taken from the ODP expedition 202 log.

Site 1232A is located in the Chilean basin, between the Mocha and the Valdivia fracture zones. The major grain composition of this site is siliciclastic silty clay in a record dominated by turbidite deposits. This late Pleistocene sequence is 390.6 meters composite depth thick, with a basal age of 0.78 Ma (Mix et al., 2003b). Site 1233C is located in a small forearc basin on the continental slope, shoreward of the Chile trench, at a water depth of 838m. According to ODP researchers, the volcanic ash layers on this site consist of 95% unaltered volcanic glass to acidic to intermediate composition. The mineral composition consists of plagioclase, quartz, biotite, and small amounts pyroxene. The ash layers with intermediate composition contain labradorite plagioclase, less quartz

and biotite, and has abundant pyroxenes. The layers were created during periods of high sedimentation rates ranging from 11 to 170 cm/Ka during the Holocene epoch. The presence of *E. huxleyi*, a unicellular, eukaryotic phytoplankton at the bottom of the hole indicates that the entire sequence is younger than 260 Ka (Mix et al., 2003b). Site 1234A is located on a flat bench of the continental slope, around 60 km shoreward of the Peru-Chile trench. At this site, thin silt-rich layers and volcanic ash layers are present as minor lithologies. The basal age of the sequence is less than 0.26 Ma, but no age model was created because of the very high sedimentation rates and low datum count (Mix et al., 2003b). Site 1235 is located on a sloping terrace on the upper continental slope, with a 5 cm-thick layer of pale ash recovered that represents the third minor lithology of the core. The mineral composition of the volcanic glass shards shows minor amounts of labradoritic plagioclase and trace amounts of quartz, mica, hornblende, and orthopyroxene (Mix et al., 2003b).

As a consequence of the proximity of the drill site to the SVZ and the Pleistocene-Recent volcanic activity of this area, it can be hypothesized that the volcanic ashes originated somewhere in the SVZ. However, numerous other explosive volcanic centers with Pleistocene-recent activity are located at similar latitudes in the southern hemisphere. On the basis of the great distance of transport inferred for some eruptions (Baines and Sparks, 2005, Fig. 1) and the overall westerly prevailing wind direction at this latitude (Moreno et al., 2007) it is also possible that the ashes originated at another location. The overall purpose of this research is to provide information bearing on the origin of the ash layers at ODP Sites 1232, 1233, 1234, and 1235.

Geologic Setting

The Andean Southern Volcanic Zone

Andean volcanic activity is created by the subduction of the Nazca and the Antarctic oceanic plates under the less dense continental lithosphere of western South America (Moreno et al., 2007). The tectonic activity has created more than 200 Pleistocene-Recent arc volcanoes which are divided into four zones: The Northern Volcanic Zone (NVZ), the Central Volcanic Zone (CVZ), the Southern Volcanic Zone (SVZ), and the Austral Volcanic Zone (AVZ), all together, they make up the Andean volcanic arc. The Southern Volcanic Zone (33°S and 46°S) is made up of rhyolitic to andesitic volcanic products dating back to before the Pliocene, which in turn are underneath Plio-Quaternary volcanoes. (Moreno et al., 2007). The volcanoes are composed of basaltic through rhyolitic rocks and tephra and reach elevations of over 6000m. The SVZ chain of volcanoes is located at the border between Chile and Argentina and has more than 70 Pleistocene-Recent stratovolcanoes in Chile alone. The SVZ continues to be a high-volcanic-activity area, with up to one eruption per year on average for the last 15,000 years (Moreno et al., 2007). Volcanoes in this area are mainly calc-alkaline, containing high alumina basalts and andesites (Carel et al., 2011).

Figure 3. Map of Southern Chile showing the divisions of the Andean SVZ. Blue circles indicate the location of each Site (Fontijn et al., 2014).

The Pleistocene and Holocene volcanoes of the SVZ are divided into four different segments on the basis of petrologic and geochemical considerations, as well as tectonic movements (Moreno et al., 2007, Figure 3). These are the Northern SVZ (33.3°S–34.4°S), the Transitional SVZ (34.4°S–37°S), the Central SVZ (CSVZ; 37°S– 42°S) and the Southern SVZ (SSVZ: 42°S–46°S). The NSVZ has eight composite stratovolcanoes and the giant Diamante caldera. During the Pleistocene and Holocene, the NSVZ had relative low rate of magmatic extrusion from stratovolcanoes, with the largest being Marmolejo (Moreno et al., 2007). The TSVZ shows the arc widening considerably eastward. The main features of this volcanic zone are compound stratovolcanoes and large volcanic complexes on top of old basaltic shield volcanoes. Giant calderas and volcanic fields are also present with some caldera systems producing large volumes of Pleistocene rhyolites, for example, the Descabezados-Quizapu-Cerro Azul, Laguna del Maule, and Calabozos volcanic fields which contain well over 200 vents (Moreno et al., 2007). The CSVZ is wide on its northern side until it reaches 39° S. It then narrows into a chain 80 km wide without intra-arc basins. The volcanic front of CSVZ has stratovolcanoes from the Pleistocene to Holocene which overlie eroded Pliocene and Pleistocene volcanic features. The CSVZ is an important volcanic zone, since it is the most volcanically active segment along the Andes with two of the most active volcanoes in South America, Llaima and Villarrica (Moreno et al., 2007). Because of its high volcanic activity, the sizes of the volcanoes (biggest in the SVZ), and their proximity to the eastern edge of the Central Valley, the CSVZ is considered an area of high volcanic risk. South of the CSVZ lies the SSVZ which consists of 13 Quaternary volcanoes of which, at least ten have had medium to large explosive eruptions during the

Holocene. The volcanic centers of the SSVZ are in general covered with snow a result caused by the cool climate and high precipitation. Melted snow during eruptions increases the chances of creating natural disasters around populated areas by forming lahars (Moreno et al., 2007).

Many eruptions in the SVZ have been explosive, with a high Volcanic Explosivity Index (VEI). Volcanoes Calabozos and Villarrica both had massive volcanic eruptions during the Pleistocene epoch with a Volcanic Explosivity Index (VEI) of 7 and 6, respectively (Smithsonian, 2011). The VEI is a measurement of the explosiveness of volcanic eruptions, a relative scale ranging from 1 to 8 that enables volcanic eruptions to be compared with one another by measuring the eruption cloud height, the volume of product ejected, and qualitative observations (Smithsonian, 2011). Eruptions that have a high VEI count (8 being the highest) produce massive amounts of volcanic-ash that can cover long distances extending all the way around the world. The high volcanic activity in the SVZ (Table 1, APPENDIX C), the high VEI count of eruptions, and the proximity to the location the ash samples were recovered favor the original source of the volcanic ashes to be somewhere in the SVZ. In contrast, wind patterns are not consistent with an origin for the ash in the SVZ. The trajectory of the prevailing winds in the Andes is from West to East in the Troposphere, as shown by the widespread deposition of Pleistocenerecent volcanic ashes from the SVZ to the East, in Argentina and the Atlantic Ocean (Fig. 1, Moreno et al., 2007). Therefore, it is also worth considering an origin at centers having explosive eruption elsewhere in the southern hemisphere such as the Okataina Volcanic Complex in the Taupo Volcanic Zone in New Zealand.

OBJECTIVE OF PROJECT

For the present research, I have chosen the uppermost (most recent) ash layer from each of ODP Sites 1232, 1233, 1234 and 1235. The objectives of this research are: 1) To determine whether the ash layers from the different sites originated from the same volcanic source or different ones.

2) To collect information that can be used to identify the source of the ashes, and, if possible, to identify that source or eruption.

The methods used to characterize the ash include detailed physical analysis of each sample, as chemical analyses of major and trace elements. Data were compared to those available in geologic databases such as Earthchem, LaMEVE, and the Smithsonian Institution Global Volcanism Program. Data on the physical and chemical properties of ash obtained in this study will also be contributed to these databases for use in volcanological studies.

METHODOLOGY

Sample collection and selection

For the purpose of this project, prepared samples were obtained from the International Oceanic Discovery Program. Core samples were collected during the 202 expedition by the Ocean Drilling Program (ODP) in 2002. Once an oil exploration vessel (Anonymous, 2007), in 1985, the JOIDES Resolution became a scientific research vessel

for the ODP. The vessel has a drilling capability of up to 8,385 m total depth. It is an outfitted drill ship that can be positioned over a specific seafloor location while drilling on the desired penetration level below the seafloor. The ship is equipped with laboratory rooms and equipment allowing core analysis and borehole data collection to be performed.

During expedition 202, oceanic sediments in the southwest and equatorial Pacific were collected (Mix et al., 2003a). The four sites nearest to the Andes, which are in the Chile Basin and the Chile Margin, have basal ages of 0.26-1.69 million years, which places them in the Pleistocene to Recent (Figure 4). For Site 1232A, a depth of 4,091.4m below the rig floor (mbrf) was established by the precision depth recorder measurement (Mix et al., 2003a). To drill the core, a 136m-long advance piston corer (APC) and an extended core barrel (XCB) bottom-hole assembly (BHA) were used. For Site 1233C the calculated seafloor recovery for the core was 848.7 mbsf (Mix et al., 2003a). Site 1234A had issues in many of its cores due to expanding gasses during recovery. This resulted in gas voids and expanding cores prior to processing. To relieve the gas pressure, holes were drilled into the cores before they were processed (Mix et al., 2003a). Site 1235B also underwent some complications. Core 19H received damage from deceleration forces created when the formation prevented a full stroke of the corer. Another issue with Site 1235B happened at Core 16H, where the liner was being cut into sections on the catwalk and it fragmented into pieces and the sediment exploded as a result of excessive of gas pressure (Mix et al., 2003a).

In total, fifteen volcanic ash layers were identified at the four sites, with varying thickness and depth. For my project, the uppermost layer from each site was analyzed, four in total. These are: Site 1232A (selected ash layer is in core 034X, section 03W, intervals 116-117), Site 1233C (core 002H, section 06W, intervals 76-77), Site 1234A (core 003H, section 03W, intervals 49-50), Site 1235B (core 014H, section 05W, intervals 120-121.5).

Figure 4. Depth and location of the four drill sites in expedition 202. Black lines indicate the location of the studied ash samples.

Laboratory Procedures

Sample Preparation

Before the chemical analysis, samples underwent a series of treatments. First, samples were wet sieved, to separate the fine and coarse grains using de-ionized water to break down agglomerates. For this project, two mesh sizes were utilized, 200 mesh (74 microns) and 120 mesh (125 microns). After wet sieving, the samples were oven-dried at 100 degrees C and labeled by size and origin. After the wet sieving process, the samples were placed in the ultrasonicator. This instrument is designed to remove unwanted material such as fossils from samples without compromising their physical properties. The samples were placed in a small glass bottle with de-ionized water and then closed. The ultrasonicator was filled with water and turned on for at least 20 minutes. If during this process, a substantial amount of residue was seen floating in the bottle, the process of ultrasonication could be repeated. After the samples were ultrasonicated, they are sieved one more time to ensure that only the clean particles, free of adhering materials are recovered.

Observation of Physical Properties

The morphology of glass shards (shape, vesicularity, color, and surface alteration) have proven to be useful identification tools (Turner et al., 2004). Glass shape measurements can aid in locating the origins of fragments and to predict particle behavior, such as scattering properties (Liu et al., 2015). Volcanic ash can be found in a diverse spectrum of shapes, each with different physical and chemical properties. The shapes of glass shards also reflect the fragmentation mechanisms that occur during an

eruption, which are controlled by magmatic properties (such as viscosity, temperature, chemical composition, and water content); (Liu et al., 2015).

Physical analysis was done through a transmitted light microscope for a primary assessment of the minerals and glass fragments present, their shape, and abundance. The morphology of the glass fragments was then described and photographed using both an optical digital camera and the Scanning Electron Microscope (SEM). The SEM is used to inspect samples at high magnifications using signals produced by the interaction between focused electrons and an area of the sample. The SEM uses an electron gun which shoots focused electrons on a fine beam. The interactions between the atoms of the sample and electron beam creates radiation products such as Backscattered Electrons and Secondary Electrons (SE) (Goldstein et al., 2003). The radiation product is collected by a detector which is then amplified, analyzed, and transformed into topographic images of the area's surface. Backscattered Electron are especially useful to distinguish one material from another because specimens with higher atomic numbers display higher brightness than specimens with smaller atomic numbers. Backscattered Electron images (APPENDIX B) will show compositional differences as well as glass orientation, both of which are important for physical analysis.

During the sample preparation process, glass samples (10 glass fragments per site) were collected and placed on a thin section with double-adhesive carbon tape for chemical analysis. An additional batch of samples was generated and carbon coated to

obtain images at high vacuum. Carbon coating is used to improve the imaging of samples. Creating a conductive layer of metal on the sample inhibits charging, reduces thermal damage while improving the secondary electron signal required for analysis in the SEM. Conductive fine carbon layers are needed for x-rays microanalysis.

Chemical Analysis of Glass Fragments

After the physical analysis, major and trace element analysis was performed on the selected individual glass shards from each interval. Major elements are those with concentrations greater than 2 wt%, while trace elements are present in concentrations below 0.1 wt% (Blatt et al., 2006). Petrologists have developed many chemical and mineral indices to categorize igneous rocks based on the fundamental patterns they show, for example, Harker diagrams showing two elements on x and y axes. Trace element concentrations for example can be very distinctive for igneous rocks and can provide a base line for comparison with a specific chemical reservoir (Blatt et al., 2006). The two most commonly used chemical reservoirs are the primordial earth modeled by chondritic meteorites (Sun, 1982), and the primordial mantle (McDonough and Sun, 1995; Sun and McDonough, 1989). The values in chondritic meteorites are chosen to normalize the standard because they provide relatively unfractionated samples of materials from the solar system and are commonly used as geochemical references in many studies. The primordial mantle approach is based on an estimate of the chemical composition of primitive mantle with bulk silicate earth (BSE). It uses compositional trends in upper mantle peridotites which are interpreted as melting trends. The primordial mantle is the preferred reference model because it is based on terrestrial samples that does not require

assumptions of the chemical composition of Earth but it incorporates cosmo-chemical data such as chondritic values for relative abundances (Lyubetskaya and Korenaga, 2007). In spider diagrams, the selected trace elements are plotted horizontally (in order of increasing atomic number) and the normalized element abundance is plotted vertically typically using a log scale for a smoother pattern (Blatt et al., 2006).

After performing chemical analysis on glass samples, data were plotted on Harker and spider diagrams, also known as a multi-element plots. These plots are useful in determining whether two or more ash layers from different sites originated from the same volcanic source.

Major element analysis was performed on glass shards using the EDS (Energy Dispersive X-ray) system of the Scanning Electron Microscope (SEM) JEOL JSM 5900LV in the Department of Earth and Environment at Florida International University (FIU). Backscattered images were also collected for the physical evaluation of the glass shards, providing important information regarding their homogeneity. Trace elements were analyzed using the Element 2 LA ICP-MS in the Department of Chemistry and Biochemistry at FIU. The compositional data for volcanic ashes contains major elements $(>10,000 \text{ ppm})$ and trace elements $(<10,000 \text{ ppm})$, with typical analyses for interpretation including 10 major elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, and Mn), and 30 or more trace elements (Hickey-Vargas et al., 2016b). For the present project, 16 trace elements were analyzed (Ti, Ce, Nd, Gd, Dy, Hf, La, Ba, Zr, Nb, Rb, Sr, Yb, Th, Y, and Eu .

Figure 5 was created using the data collected from the SEM for all samples and standards, illustrating the percentage of the major elements as oxides. On figure 5, the recommended values for BHVO-2 and Rhy-2 are shown to determine the type of rock from which the samples originated (mafic, intermediate, or felsic).

Figure 5. Major element concentrations for all samples and standards.

To identify trace elements present in glass fragments, the samples were analyzed using Laser Ablation Inductive Coupled Plasma-Mass Spectroscopy (LA ICP-MS). The laser is focused on a flat surface of the sample and ablates with a pulsed laser in a gas tight chamber. The ablation produces a stream of particles called aerosols that are transported in a carrier gas to the ICP. Here, the particles are converted to ions, which are then separated by their mass-to-charge ratios using the mass spectrometer. Using a standard for external calibration, the ion signals are converted to the element

concentration. The software utilized to process and convert the data is Glitter 4.4.4, which provides real-time interactive data reduction for LAM-ICPMS analysis. After the data were collected, the standard deviation and/or the mean deviation was calculated for the standards and samples. The standard runs provide proof of the stability of the instrument and determine if there is any instrument drift. By looking at the averages at the beginning of the run, the middle, and the end, any systematic changes in the concentrations could be determined. If the instrument drift is substantial, corrections need to be made. Once the values meet acceptable criteria, the standards are compared to recommended concentrations published by the United States Geological Survey (USGS). Afterwards, a multi-element plot is created illustrating all trace elements from the samples with increasing atomic number on the x axis and their concentration divided by primitive mantle showing on the y axis using a log scale to create a smoother pattern. The pattern created by the plots show characteristics of the primary mantle and determines the samples geologic setting. The trace element data collected is also used to create a variety of x-y plots which facilitate the comparison of glass compositions by illustrating any variations between ashes from each site. Trace elements can be plotted against one another or plotted versus a major element oxide depending on the purpose of the study (Blatt et al., 2006).

Ash Identification

Following the collection of chemical data, the chemical results were compared with each other and with published analyses of volcanic rocks from different data sources. One such source is EarthChem (earthchem.org), which develops and maintains

the database, software, and services that support the preservation, discovery, and analysis of geochemical data, EarthChem also facilitates their integration with the broad array of other available earth science parameters used to compare the ash results to those from explosive volcanic centers in the SVZ and other large eruptive volcanoes worldwide. EarthChem is operated by a team of geoscientists, data scientists, data managers and information technology developers who are part of the NSF-funded data facility Integrated Earth Data Applications (IEDA). Analyses drawn directly from the geological/geochemical literature were also used for comparison. The samples were also compared to volcanic eruptions of the same time period shown on the Global Volcanic Program (GVP) of the Smithsonian Institution National Museum of Natural History and The Large Magnitude Explosive Volcanic Eruptions (LaMEVE) databases. The GVP (volcano.si.edu) documents and disseminates information about volcanic activities through reporting, archiving, researching, and outreach. Collecting data since 1968, the GVP has documentation of current and past volcanic activities for the last 10,000 years. The LaMEVE is a searchable database of the location, age, and magnitude of Quaternary Large Magnitude Explosive Volcanic Eruptions with information on nearly 3,000 volcanoes and over 1,800 Quaternary eruption records.

DATA AND RESULTS

Physical characteristics of samples:

Physical analysis of the samples reveals several differences in their overall appearances. As seen in figure 13a (Appendix A), the ash layer at Site 1232 is made
almost entirely out of glass shards. Minerals present in the sample consist mostly of biotite, quartz, and feldspars, with some fossils (foraminifera) appearing in small quantities. The glass shards possess thin vesicular walls with angular shapes. The ash layer from Site 1233 consists of dark materials with few glass particles. Magnetic minerals are found in large quantities at Site 1233 (figure 13b). The glass shards present in the site 1233 sample are thick and seem to be devitrified. Before wet sieving, samples from sites 1233 and 1234 (figure 13c) looked alike to the eye. Both possessed a brownish to grayish color and were fine grained. After wet sieving the differences became evident. While Site 1234 also has magnetic materials and dark particles, they are found in smaller quantities, compared with Site 1233. There is also a large proportion of glass shards present in sample 1234, with thick walls and better-preserved vesicles than at Site 1232. The edges are also angular. Biotite is present in the sample, as is feldspar. Ash from Site 1235 (figure 13d) shows a large amount of glass with angular shapes and thin walls. Unlike any of the other samples, Site 1235 has a large number of white particles present (devitrifed glass perhaps). No further analysis was done on the minerals present in each site because that was outside the scope of the study.

Major element results:

The semi-quantitative data collected from the SEM provided important information regarding major element composition of the samples. Figure 5 shows all major elements presente in the samples and compares them to the standards BHVO-2 and Rhyolite. The three columns on the right are the recommended values provided by the USGS. Data from SiO² collected with the EDS is ploted against trace elements. These oxide vs trace elements tables are an important factor for ash identification.

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Figure 6a. Major element comparison, SiO2 vs Al2O3.

Figure 6b. Major element comparison, SiO2 vs CaO.

Figure 6c. Major element comparison, SiO2 vs FeO.

Figure 6d. Major element comparison, SiO2 vs K2O.

Figure 6e. Major element comparison, SiO2 vs Na2O.

Major elements from Site 1233 (Figure 4) show that the concentration of oxides from aluminum, sodium, and phosphorous are very high in comparison to those from the other sites while silica is very low. Trace element data for ash from Site 1233 showed samples with very low trace element concentrations and others with very high concentrations. Since these properties are not consistent with those of volcanic glass, but are most likely mineral grains, Site 1233 is not shown in the element plots or the multielement plots. Data for Site 1233 are presented in the Appendix.

Trace element results:

The Spider Diagram

The spider diagrams or multi-element plots show very consistent readings for all sites. The Y axis is shown in log scale for a smoother pattern. All sites show somewhat smilar high and low peaks. Titanium is depleted at all three sites, as well as Strontium and Niobium. Sites 1232 and 1234 have a high Thorium peak, but Site 1232 also has a high Rubidium peak. A small Barium peak is seen in Site 1235.

Figure 7a. Multi-element plot for Site 1232. Each line represents the data collected for a glass shard.

Figure 7b. Multi-element plot for Site 1234. Each line represents the data collected for a glass shard.

Figure 7c. Multi-element plot for Site 1235. Each line represents the data collected for a glass shard.

Trace Element Bivariate Plots

Figure 8. X vs Y plots for trace elements.

Lastly, chemical analysis of selected trace elements plotted against SiO2.

Figure 9. SiO2 vs Trace Elements.

Interpretations derived from the physical characteristics of samples

Physical observations of samples from all sites reveal differences among them. Samples from sites 1233 and 1234 possessed darker tones even before wet sieving, in contrast with the lighter tones of sites 1232 and 1235. Because of the darker tones, and the fact that samples from sites 1233 and 1234 were collected at similar shallow depths, the possibility of the selected glasses having the same volcanic origin seemed possible. However, after closer observation under the light microscope (Figures 10b and 10c), their differences became evident. While glass shards in Site 1234 were easily located, Site 1233 was mainly composed of devitrified glass and feldspars. Because devitrified volcanic glass is harder to identify using chemistry, no further analysis was performed on samples from Site 1233. To be thorough, another sample from Site 1233, in the same core and section, but at different intervals (69.5-70 instead of the original 76-77) was collected and prepared using the same techniques yielding similar results. Devitrified glass shards with highly magnetic mineral were consistently present in the 1233 sample.

Physical traits to consider for glass morphology analysis are shape and vesicularity (Scasso and Carey, 2005). The shape of the glass shards shows the conditions in which they were deposited (Scasso and Carey, 2005). The geometry shown in shards is a result of transportation after deposition, which in turn explains any changes in the chemical composition associated with weathering. Post-depositional weathering can result in crystallization in the glass shards, a process called devitrification. Backscattered images produced using the SEM show that all samples except from Site 1233 are highly

angular with little to no rounded edges, which is a trait observed in undisturbed sediments. The angular shapes lead to the conclusion that the samples traveled by wind from their place of origin towards the Pacific coast of Chile and descended to the ocean floor, without being transported from land by water. Latter methods of transportation would produce abrasion which could be detected by simple physical observations. The glass shards were for the most part colorless and transparent, only samples from Site 1233 possessed traces of coloration (yellowish). Transparent glass shards are obtained by little to no alteration by seawater. These characteristics are consistent with the particles being ash, transported in the atmosphere and deposited from the air and settling through the ocean water column. The vesicular properties of the ash samples provide the other half of the story. Vesicles are the empty cavities on glass shards produced by gas bubbles. As the bubbles grow, magmatic viscosity increases exponentially due to the loss of water in the form of gas and other volatile components, a process caused by diffusion during magma ascent (Scasso and Carey, 2005). Magmas with higher $SiO₂$ content tend to be more viscous and have a higher dissolved gas content. This means that the number of vesicles, and their size shows the magmatic origins, and by doing so, the eruption type. The glass shards from all sites contained vesicles at some point, illustrated by the patterns of fragmentation. A great example of this can be seen in glass shards from Site 1235 (Figure 11d). In figures 11d E and F, the path of fragmentation is shown to be caused by the ruptures of the walls of the gas filled vesicles. On the basis of these physical observations, it can be inferred that the ash samples possess high concentrations of SiO2, and that they originated from viscous, gas-rich magmas which produce explosive eruptions.

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Interpretations derived from the major element composition of the samples

These observations are backed up by the major element analyses of individual glass shards. The chemical composition on all shards from sites 1232, 1234, and 1235 show a consistent rhyolitic composition (SiO₂ for Site $1232 = 75.88 \pm 0.44$ wt%, Site 1234= 71.42 \pm 0.62 wt%, and Site 1235= 76.68 \pm 2.93 wt%). Plotting the samples on a Harker diagram reveals some clear distinctions between samples from all sites. Figure 10 shows samples from Site 1232 being between alkaline and high calc-alkaline. While samples from sites 1234 and 1235 range from high-K calc-alkaline and calc-alkaline, with samples from Site 1235 being less K rich than samples from Site 1234. For Site 1232, the oxides vs SiO² diagrams show a general decrease in CaO and FeO total, with increasing SiO2. Site 1234 has the highest weight percentage of FeO total which correlates with a lower content of SiO2. This shows that, as silica content increases, mafic minerals, especially Fe-Ti oxides, are differentiated out of the magma. Al2O3 is fairly constant in all samples, as is CaO and Na2O.

Figure 10. The SiO2 vs K2O Diagram for sites 1232, 1234, and 1234.

Interpretations based on trace element patterns in the samples

The major element analysis shows that all samples belong to regions with arc magmatism with late-stage fractionation. However, major elements cannot distinguish between continental magmatic arcs and island arcs (Blatt et al., 2006), or between different explosive eruptions. Trace elements on the other hand, can reveal much more about the diverse origins and evolution of magmatic arc rocks. Trace elements will either substitute for a major element inside the crystal structure of the mineral or remain in the liquid phase (Blatt et al., 2006). During magmatic differentiation, some elements are excluded from the minerals that form (incompatible elements), while others are incorporated into the mineral structure (compatible elements). Incompatible elements can be divided into several groups: the large-ion lithophile elements (LILE, K, Rb, Ba), highfield strength elements (HFSE, Nb, Zr, Hf, Th), and rare earth elements (La, Sm, Eu, Gd, Yb and Y). These elements can be plotted on a graph to show enrichment or depletion of trace elements compared with each other. Elemental abundances are normalized to a standard set of values, such as "primitive mantle" (McDonough and Sun 1989) for comparison and plotted from left to right in order of increasing compatibility during mantle melting. Trace element analysis of the ash samples shows features predominant in magmas from active continental margins and subduction zones generally, such as depletion of Nb in all 30 samples, enrichment of LILE compared with light rare earth elements (LREE) (Kilian and Behrmann, 2003). Sr plots below other elements, indicating the differentiation of feldspar in the magmas. Titanium is also depleted in all samples which is a common trait in silic rich magmas resulting from crystallization of Fe-Ti oxides. Overall, the primitive mantle-normalized patterns display enriched LREE

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relative to the heavy rare earth elements (HREE), which can be an original feature of primitive magmas or a sign of interaction between the magma with the crust. An important point is that the average normalized trace element patterns of the different sites have some characteristics that are distinct. For example, for all sites highly incompatible elements Rb, Ba and Th have different relative abundances, and enrichment of LREE relative to HREE is greater at Site 1232 compared with sites 1234 and 1235.

Plots of incompatible elements versus each other show linear trends with concentrations of elements within glass shards from the three sites varying by factors of $1.5 - 2$. These trends converge on zero, which indicates constant ratios of the elements compared with each other. Some of the variation of incompatible element concentrations in the glass shards is probably related to magmatic differentiation, although SiO² does not vary much at the high rhyolitic values. The variation may reflect the dilution of the elemental signal during laser analysis by minute feldspar and quartz crystals and open space in vesicles. None of the three sites have exactly the same incompatible element ratios as another. For example, Sr is higher relative to Y in Site 1235 ash. La is high relative to REE Gd and Yb at Site 1232, confirming LREE-enrichment. Ba/Th, and Th/La are also higher at Site 1232, while Zr/Nb is lower. These differences can be used to distinguish ash from the different sites and potentially to identify their volcanic source.

DISCUSSION

Based on comparisons of major and incompatible element patterns in Figure 9, it is clear that none of the three ash layers were deposited from exactly the same volcanic source. Therefore, the studied ash layers in the selected Leg 202 sediments cannot be correlated or used as a time horizon.

In order to attempt to identify potential volcanic sources, I compared the ash patterns to those of some known SVZ volcanic sources. The lists of Pleistocene and recent explosive eruptions collected from the LaMEVE and the Smithsonian databases provides a useful starting point from which to determine the origin of the samples. A more specific eruption database for the SVZ compiled by Fontjin et al. (2014) was filtered to provide SVZ eruptive centers having: 1) VEI $>$ 5, 2) Pleistocene to Recent age, and 3) rhyodacite and rhyolitic products. This yielded 3 centers: Quizapu (escabezados Grande/Cerro Azul); Puyehue Cordon-Caulle and Chaiten Volcano. Chemical data were extracted for rhyolites from these locations using the EarthChem database, as well as literature sources. These comparisons are shown in figure 11a, b, and c.

Figure 11a. Multi-element plot of Puyehue Cordon-Caulle.

Figure 11b. Multi-element plot of Quizapu.

Figure 11c. Multi-element plot of Chaiten.

Comparing the selected data to the samples yields some interesting results (Figure 15, Appendix C). Site 1232 resembles the multiplot for the Chaiten volcano except for the negative Sr and Ti values in 1232, which are much more depleted (>1) than those in Chaiten. Depletion of Ti is a common trait in all sites, with some degrees of variation in Site 1235, a trait seen in Puyehue Cordon-Caulle as well. Although overall values for Site 1235 are a bit lower than those in Puyehue Cordon-Caulle, their patterns

are very similar. From the late Pleistocene, Cordon Caulle emitted only rhyodacites and rhyolites (Lara et al., 2006) which makes it a viable location for Site 1232's origins. Site 1234 and Chaiten share some similarities as well, with the LILE (except for Rb), and Th, Nb, La, Ce, and Sr plotting similar results. However, the rest of the elements are not compatible.

In addition, data were compared with the Okataina volcanic complex in the Taupo Volcanic Zone, NZ, at latitiude 38°S, which has produced numerous eruptions with VEI >5 during the Pleistocene/Recent. This comparison is shown in Figure 12, where depletion of Nb, Sr, and Ti resembles that of Site 1234. And unlike Chaiten, the results are consistent.

Figure 12. Multi-element plot of Taupo-Okataina.

Conclusions

Analysis for all samples were based upon physical and chemical interpretations. Information gathered in this project indicate that the ashes have distinct geochemical signatures which could be matched to specific eruptions. However, it is impossible to accurately determine the source(s) at this time without a more thorough compilation of a database for comparison. The compilation of tephra records for Chile shows a vast majority of insufficiently characterized layers to allow for the sources to be properly identified (K. Fontijn et al., 2014). Even the most widely used method of tephra identification, major element analysis of individual glass shards, has some particular complications in southern Chile. Take for example the two most recent explosive eruptions in the area, the 2008 rhyolitic eruption in Chaiten, and the 2011 rhyodacite in Puyehue Cordon-Caulle. The chemical composition of major elements was almost indistinguishable from the previous eruptions at the same volcanoes (K. Fontijn et al., 2014). Taking this into consideration, the one definitive conclusion is that the same explosive eruption did not produce the three ash layers.

Future directions

Additional research such as analysis of radiogenic isotopes could prove useful as an additional parameter for narrowing the gap between the known and the unknown. The study of selected minerals such as biotite present in Site 1232 and 1234, and Site 1235 in smaller quantities, could be used as geochronological indicators. Microfossils such as foraminifera, found at Site 1232, might also be used to determine the age of the samples, making it easier to locate its origin.

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APPENDICES

APPENDIX A

Sample images taken using a digital camera from an Optical Microscope.

Figure 13a. Digital image from Site 1232. Figure 13b. Digital image from Site 1233.

Figure 13c. Digital image from Site 1234. Figure 13d. Digital image from Site 1235.

APPENDIX B

Images from all sites taken with the SEM with 25 kV.

Figure 14a. Glass images taken with the Scanning Electron Microscope for Site 1232.

Figure 14b. Glass images taken with the Scanning Electron Microscope for Site 1233.

Figure 14c. Glass images taken with the Scanning Electron Microscope for Site 1234.

Figure 14d. Glass images taken with the Scanning Electron Microscope for Site 1235.

APPENDIX C

Figure 15. Spider diagram for sites 1232, 1234, and 1235 together with the plots of different volcanoes.

APPENDIX D

Table.1. Data of volcanic eruptions in Chile from the Pleistocene epoch to recent.

Volcano Name	Volcano Type	Year BP	Dating technique	Bulk deposit volume	Bulk DRE volume	Magma Type	Magnitude	VEI
Krakatau	Caldera(s)	1534	Historical records	0.1	0.04	Rhyolite	7.1	6
Merapi	Stratovolcano(es)	1930	Radiocarbon (corrected)	0.1	0.04	Not Available	4	
Tengger Caldera	Stratovolcano(es)	2814	Radiocarbon (corrected)	0.1	0.04	Andesite	4	
Merapi	Stratovolcano(es)	3274	Radiocarbon (corrected)	0.1	0.04	Not Available	4	
Parker	Stratovolcano(es)	4323	Radiocarbon (corrected)	0.1	0.04	Not Available	4	4
Galunggung	Stratovolcano(es)	4645	Radiocarbon (corrected)		0.4	Not Available	5	5
Dieng Volcanic Complex	Complex volcano(es)	19233	Radiocarbon (corrected)	78	30	Andesite	6.9	6
Batur	Caldera(s)	24380	Radiocarbon (corrected)	10	5.5	Andesite-Dacite	6.1	6
Batur	Caldera(s)	24380	Radiocarbon (corrected)	10	5.5	Andesite-Dacite	6.1	6
Batur	Caldera(s)	34565	Radiocarbon (corrected)	27	18	Dacite	7.4	7
Tengger Caldera	Stratovolcano(es)	38249	Radiocarbon (corrected)	0.1	0.04	Not Available	4	4
Tambora	Stratovolcano(es)	43000	Other technique	0.1	0.04	Not Available	4	4
Maninjau	Caldera(s)	52000	Other technique	235	175	Andesite	7.2	
Toba	Caldera(s)	74000	Other technique	2800	2750	Dacite-Rhyolite	8.8	8
Toba	Caldera(s)	74000	Other technique	2800	2750	Dacite-Rhyolite	8.8	8
Tangkubanparahu	Stratovolcano(es)	108358	Radiocarbon and stratigraphy	0.1	0.04	Not Available	4	4
Tengger Caldera	Stratovolcano(es)	152000	K Ar	3.79	1.52	Not Available	5.6	5
Tangkubanparahu	Stratovolcano(es)	190000	Not Available	10	4		6	6
Maninjau	Caldera(s)	280000	K Ar	175	70	Andesite-Rhyolite		
Maninjau	Caldera(s)	280000	K Ar	175	70	Andesite-Rhyolite		
Toba	Caldera(s)	501000	Ar-Ar	60	26.09	Rhyolite	7.1	
Ranau	Caldera(s)	550000	K Ar	100	40	Rhyolite		
Toba	Caldera(s)	840000	Not Available	820	800	Dacite-Rhyolite	8.4	8
Toba	Caldera(s)	840000	Not Available	820	800	Dacite-Rhyolite	8.4	8
Toba	Caldera(s)	1200000	ITPFT isothermal plateau fission track age	80.5	35	Dacite	8	6

Table 2. Data of volcanic eruptions in Indonesia from the Pleistocene epoch to recent.

Volcano Name	Volcano Type	Year BP	Dating technique	Bulk deposit volume	Bulk DRE volume	Magma Type	Magnitude	VEI
Healy	Submarine volcano(es)	590	Radiocarbon (corrected)	12.5	3	Dacite	5.9	$\sqrt{2}$
Okataina	Lava dome(s)	640	Radiocarbon (corrected)	15.85	7.9	Rhyolite	6.3	5
Okataina	Lava dome(s)	640	Radiocarbon (corrected)	15.85	7.9	Rhyolite	6.3	5
Taupo	Caldera(s)	1720	Radiocarbon (corrected)	30 1	10	Rhyolite	6.9	6
Tongariro Taupo	Stratovolcano(es)	2500 3410	Radiocarbon (corrected)	20	0.48	Not Available Rhyolite	5.1 6.2	5 6
Taranaki [Egmont]	Caldera(s) Stratovolcano(es)	3904	Radiocarbon (corrected) Radiocarbon (corrected)	$\,2$	7.1 0.8		5	5
Okataina	Lava dome(s)	5530	Radiocarbon (corrected)	2.8	0.87	Rhyolite	6	5
Mayor Island	Shield volcano(es)	7010	Radiocarbon (corrected)	5.5	2.39	Rhyolite	5.7	5
Okataina	Lava dome(s)	8010	Radiocarbon (corrected)	6	2.609	Rhyolite	5.8	5
Okataina	Lava dome(s)	9510	Radiocarbon (corrected)	5.6	2.43	Rhyolite	5.7	5
Taupo	Caldera(s)	10080	Radiocarbon (corrected)	4.6	1.4		5.5	5
Taupo	Caldera(s)	11190		3	0.23	Rhyolite	5.4	5
	Stratovolcano(es)		Radiocarbon (corrected)	0.8	0.32		4	5
Tongariro		11300	Tephrochronology					
Tongariro	Stratovolcano(es)	11400	Radiocarbon (corrected)	0.4 0.4	0.16	Andesite-Dacite Andesite-Dacite	4.9 4.9	5
Tongariro	Stratovolcano(es)	11400	Radiocarbon (corrected)	1.3	0.16 0.42		5	5 5
Taupo Tongariro	Caldera(s) Stratovolcano(es)	11410 11600	Radiocarbon (corrected) Radiocarbon (corrected)	0.2	0.07	Rhyolite Andesite-Rhyolite	4.6	5
Tongariro	Stratovolcano(es)	11600	Radiocarbon (corrected)	0.2	0.07	Andesite-Rhyolite	4.6	5
Okataina	Lava dome(s)	13598	Radiocarbon (corrected)	18	11	Rhyolite	6.4	6
Okataina	Lava dome(s)	15425	Radiocarbon (corrected)	$\boldsymbol{7}$	1	Rhyolite	5.4	5
				τ	5			6
Okataina	Lava dome(s)	17625	Radiocarbon (corrected)	$\mathbf{1}$	0.4	Rhyolite	6.1	5
Yasur	Stratovolcano(es)	20000	Not Available			Not Available	5	
Okataina	Lava dome(s)	21800	Radiocarbon (corrected)	6	3.6	Rhyolite	5.9	6
Taranaki [Egmont]	Stratovolcano(es)	23649	Radiocarbon (corrected)	1.88 5	0.75	Andesite	5.3	5
Okataina	Lava dome(s)	25271	Radiocarbon (corrected) Radiocarbon (corrected)		13	Rhyolite	6.5	6 $\,$ 8 $\,$
Taupo	Caldera(s) Caldera(s)	27100		1170	530	Rhyolite	8.1	5
Taupo		28181	Radiocarbon (corrected)	1	0.5	Rhyolite	5	
Taupo	Caldera(s)	30092	Radiocarbon (corrected)	6	3	Rhyolite	5.8	5
Okataina	Lava dome(s)	31400	Radiocarbon (corrected)	4.3	1.3		5.5	5
Okataina	Lava dome(s)	32301	Radiocarbon (corrected)	16.2	4.1		6	6
Okataina	Lava dome(s)	32800	Radiocarbon (corrected)	0.77	0.23		4.7	5
Okataina	Lava dome(s)	33000	Radiocarbon (corrected)	19.9	6		6.2	6
Okataina	Lava dome(s)	35000	Radiocarbon (corrected)	2.5	0.63		5.2	5
Okataina	Lava dome(s)	36100	Radiocarbon (corrected)	15.2	3.9		6	6
Okataina	Lava dome(s)	36700	Radiocarbon (corrected)	0.9	0.34		4.9	5
Okataina	Lava dome(s)	36800	Radiocarbon (corrected)	11	2.8		5.8	6
Okataina	Lava dome(s)	39000	Radiocarbon (corrected)	4.6	1.2		5.4	5
Taupo	Caldera(s)	41000	Radiocarbon (corrected)	1	0.5	Rhyolite	5.1	5
Taupo	Caldera(s)	42000	Stratigraphy, sediment accumulation	$\overline{4}$	2.2	Rhyolite	5.7	5
Taupo	Caldera(s)	42000	Radiocarbon (corrected)	\overline{c}	1	Rhyolite	5.4	5
Taupo	Caldera(s)	46000	Stratigraphy	5	3		5.8	5
Taupo	Caldera(s)	55000	Stratigraphy	3.5	1.4		5	5
Kapenga	Caldera(s)	61000	Ar-Ar	15.5	7		6.4	6
Okataina	Lava dome(s)	61000	Ar-Ar	350	100	Rhyolite	7.4	7
Maroa	Caldera(s)	212500	Not Available	1	0.434	Rhyolite	5	5
Okataina	Lava dome(s)	225000	Not Available	100	40		7.5	7
Maroa	Caldera(s)	229000	Not Available	1	0.434	Rhyolite	5	5
Reporoa	Caldera(s)	230000	Ar-Ar	230	200	Rhyolite	7.4	7
Rotorua	Caldera(s)	230000	ITPFT isothermal plateau fission track age	339	145	Rhyolite	7.7	$\boldsymbol{7}$
Maroa	Caldera(s)	256000	Not Available	$\overline{2}$	0.868	Rhyolite	5.3	5
Kapenga	Caldera(s)	270000	ITPFT isothermal plateau fission track age	43.5	100		7.4	7
Maroa	Caldera(s)	272000	Not Available	2	0.868	Rhyolite	5.3	5
Kapenga	Caldera(s)	275000	Ar-Ar	230	100	Rhyolite	7.4	7
Okataina	Lava dome(s)	280000	Ar-Ar	345	150	Rhyolite	7.5	7
Maroa	Caldera(s)	283000	Not Available	1	0.434	Rhyolite	5	5
Maroa	Caldera(s)	325000	Ar-Ar	1150	500	Rhyolite	8	$\,$ 8 $\,$
Kapenga	Caldera(s)	330000	ITPFT isothermal plateau fission track age	115	50	Rhyolite	7	7
Maroa	Caldera(s)	335000	Ar-Ar	1000	650	Rhyolite	8.2	8
Okataina	Lava dome(s)	340000	ITPFT isothermal plateau fission track age	25	10.9	Rhyolite	6.4	6
Okataina	Lava dome(s)	550000	Not Available	225	90		7	7
Kapenga	Caldera(s)	680000	Ar-Ar	150	65	Rhyolite	7.2	7
Kapenga	Caldera(s)	710000	Ar-Ar	460	200	Rhyolite	7.7	$\boldsymbol{7}$
Kapenga	Caldera(s)	720000	Ar-Ar	69	30	Rhyolite	6.8	6
Kapenga	Caldera(s)	805000	Stratigraphy	149.5	65	Rhyolite	7.1	7
Kapenga	Caldera(s)	890000	Ar-Ar	69	30	Rhyolite	6.8	6
Mangakino	Caldera(s)	950000	Ar-Ar	115	50	Rhyolite	6.7	7
Mangakino	Caldera(s)	970000	Ar-Ar	300	200	Rhyolite	7.5	$\boldsymbol{7}$
Mangakino	Caldera(s)	1000000	Ar-Ar	1495	650	Rhyolite	7.5	$\boldsymbol{7}$
Mangakino	Caldera(s)	1000000	Not Available	1000	400		8	8
Mangakino	Caldera(s)	1010000	Ar-Ar	2760	1200	Rhyolite	8	8
Mangakino	Caldera(s)	1180000	Ar-Ar	230	100	Rhyolite	6.7	$\boldsymbol{7}$
Mangakino	Caldera(s)	1200000	Ar-Ar	230	100	Rhyolite	6	$\boldsymbol{7}$
Mangakino	Caldera(s)	1210000	Ar-Ar	920	400	Rhyolite	7.5	$\,$ 8 $\,$
Mangakino	Caldera(s)	1240000	Ar-Ar	1000	400		8	$\,$ 8 $\,$
Mangakino	Caldera(s)	1400000	Ar-Ar	115	50	Rhyolite	6	τ
Mangakino	Caldera(s)	1530000	Ar-Ar	230	100	Rhyolite	7.4	$\boldsymbol{7}$
Mangakino	Caldera(s)	1550000	Ar-Ar	460	200	Rhyolite	6.7	$\boldsymbol{7}$
Taupo	Caldera(s)	1600000	K Ar	69	30	Rhyolite	6.8	6
Mangakino	Caldera(s)	1630000	Not Available	1000	400		8	8

Table 3. Data of volcanic eruptions in New Zealand from the Pleistocene epoch to recent.

APPENDIX E

Table 4. Concentrations in Parts Per Million (PPM) of trace elements. Raw values collected from the LA ICP-MS. A. Site 1232 B. Site 1234 C. Site 1235.

Eu153 0.705 0.589 0.635 0.65 0.81 0.74 0.532 0.655 0.78 0.72 Gd157 3.73 3.84 3.125 3.47 3.57 4.61 2.28 3.125 3.93 4.1 Dy163 3.585 3.415 3.26 3.34 4.1 4.18 2.75 3.52 4.2 3.58 Yb174 2.575 1.95 2.075 2.03 2.2 2.99 1.68 2.065 2.19 2.01 Hf178 3.535 3.18 2.85 3.06 3.47 4.03 2.4 3.28 4.01 3.47 Th232 3.36 2.9 3.15 2.99 4.05 3.93 2.3 3.235 3.66 2.86

APPENDIX F

Tables of the concentrations (in parts per million) of trace elements plotted in x-y graphs.

Table 5a. Concentrations of Ti and Y for sites 1232, 1234, and 1235.

Table 5b. Concentrations of Ti and Zr for sites 1232, 1234, and 1235.

> 19.395 21.53 17.78 23.34

13.53

23.73 18.97

Table 5c. Concentrations of Sr and Y for sites 1232, 1234, and 1235.

Table 5d. Cocentrations of La and Y for sites 1232, 1234, and 1235.

26.41 8.25 13.565 5.05
33.98 10.86 12.94 4.78

Table 5e. Concentrations of La and Yb for sites 1232, 1234, and 1235.

Table 5f. Concentrations of La and Nb for sites 1232, 1234, and 1235.

Table 5g. Concentrations of Zr and Nb for sites 1232, 1234, and 1235.

Table 5h. Concentrations of Zr and Y for sites 1232, 1234, and 1235.

1232		1234		1235	
Ba137	Th ₂₃₂	Ba137	Th ₂₃₂	Ba137	Th ₂₃₂
563.045	18.585	595.415	9.88	392.21	3.36
1210.49	39.555	513.38	8.76	356.5	2.9
535.79	19.09	467.355	7.63	376.715	3.15
817.33	30.535	607.95	10.48	353.55	2.99
425.71	16.73	592.14	10.45	482.72	4.05
836.94	32.715	603.08	10.04	479.69	3.93
514.94	19.84	488.73	7.91	296.84	2.3
682.61	27.29	433.17	7.57	398.375	3.235
623.115	22.9	634.84	10.79	483.02	3.66
734.17	26.16	629.39	10.31	409.19	2.86

Table 5i. Concentrations of Ba and La for sites 1232, 1234, and 1235.

Table 5j. Concentrations of Ba and Th for sites 1232, 1234, and 1235.

1232		1234		1235	
Th ₂₃₂	La139	Th ₂₃₂	La139	Th ₂₃₂	La139
18.585	29.45	9.88	34.525	3.36	14.98
39.555	64.345	8.76	28.75	2.9	13.335
19.09	30.03	7.63	26.41	3.15	13.565
30.535	48.59	10.48	33.98	2.99	12.94
16.73	24.955	10.45	34.8	4.05	16.55
32.715	50.065	10.04	34.34	3.93	17.62
19.84	30.13	7.91	28.13	2.3	10.74
27.29	42.62	7.57	27.04	3.235	14.045
22.9	35.37	10.79	37.46	3.66	17.76
26.16	40.19	10.31	36.04	2.86	13.6

Table 5k. Concentrations of Th and La for sites 1232, 1234, and 1235.

 $\begin{array}{|c|c|c|c|c|}\n \hline\n 1232 & \text{Hf178} & \text{259} & \text{Hf178} & \text{269} \\
\hline\n 20.525 & 4.285 & 244.055 & 0.56 & 104.1 \\
\hline\n\end{array}$ $\frac{\text{Zr90}}{0.635}$ $\frac{\text{Hf178}}{4.385}$ $\frac{\text{Zr90}}{244.055}$ $\frac{\text{Hf178}}{0.56}$ $\frac{\text{Zr90}}{104.1}$ $\frac{\text{Hf178}}{3.535}$ 120.535 4.385 244.055 9.56 104.1 3.535

Table 5l. Concentrations of Zr and Hf for sites 1232, 1234, and 1235.

Table 5m. Concentrations of Zr and La for sites 1232, 1234, and 1235.

Table 5n. Concentrations of Zr and Nd for sites 1232, 1234, and 1235.

Table 5o. Concentrations of La and Gd for sites 1232, 1234, and 1235.

Table 5p. Concentrations of Gd and Yb for sites 1232, 1234, and 1235.

Table 5q. Concentrations of Dy and Yb for sites 1232, 1234, and 1235.

APPENDIX G

1232					
SiO2	Zr90	La139	Nb93	Ba137	Nd146
75.6074	120.535	29.45	13.73	563.045	23.69
76.3202	257.66	64.345	28.22	1210.49	50.55
75.6596	123.11	30.03	12.85	535.79	24.84
76.1133	198.165	48.59	18.005	817.33	39.315
76.092	108.1	24.955	9.94	425.71	20.58
75.9181	210.05	50.065	18.815	836.94	40.255
76.1915	123.14	30.13	12.08	514.94	23.93
75.692	169.08	42.62	15.88	682.61	33.41
75.447	139.005	35.37	14.025	623.115	28.97
76.094	168.06	40.19	16.76	734.17	31.36

Data utilized to create the oxide vs trace elements plots.

Table 6a. Concentrations of SiO2 and Zr, La, Nb, Ba, and Nd for site 1232.

1234					
SiO2	Zr90	La139	Nb93	Ba137	Nd146
71.5878	244.055	34.525	10.615	595.415	40.14
71.0745	207.76	28.75	8.4	513.38	34.59
71.6362	188.99	26.41	8.25	467.355	31.16
70.8048	253.71	33.98	10.86	607.95	40.83
71.2851	263.69	34.8	10.32	592.14	39.21
71.7489	256.81	34.34	11.225	603.08	40.84
71.2101	208.93	28.13	8.35	488.73	33.99
72.0447	201.27	27.04	6.99	433.17	32.72
71.7904	287.35	37.46	10.79	634.84	41.59
71.7516	262.975	36.04	12.425	629.39	42.18

Table 6b. Concentrations of SiO2 and Zr, La, Nb, Ba, and Nd for site 1234.

Table 6c. Concentrations of SIO2 and Zr, La, Nb, Ba, and Nd for site 1235.

APPENDIX H

Concentrations of trace elements from samples along with the recommended values as established by McDonough and Sun (1995). The Multi-element plots are created by dividing the sample concentrations by the recommended values.

Table 7a. Concentrations of trace elements from samples of site 1232 and the primitive mantle.

Table 7b. Concentrations of trace elements from samples of site 1234 and the primitive mantle.

Table 7c. Concentrations of trace elements from site 1235 and the primitive mantle.

APPENDIX I

 Major element concentrations are collected from the EDS and are measured in weight percent. The standards used are Basalt, Hawaiian Volcanic Observatory (BHVO-2) and Rhyolite, Glass Mountain (RGM-2).

Site Averages				Standards	
M. E.	1232	1234	1235	Gl Rhyolite BHVO-2	
Na2O	3.59761	5.2184	3.85834	3.3946809	2.2045
MgO	θ	0	0.0796	0	6.5935
Al2O3	12.9602	13.8119	13.3248	12.094158	12.6035
SiO2	75.9135	71.4934	78.1255	77.46383	45.3415
P ₂ O ₅	0	0	0.01265	0	0
K2O	4.91191	2.93951	2.18082	4.8595628	0.8705
CaO	0.57741	1.51162	1.58134	0.4853659	14.8575
TiO ₂	0.1835	0.29002	0.15638	0.0822581	2.9705
MnO	0.04563	0.04723	0.05199	0.0177628	0.3205
FeO Total	1.01468	3.52637	1.51133	1.3597122	14.2385

Table 8. Average of readings of all major element concentrations and standards.