

Volcanic Ash Collection and Analysis

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1.0 INTRODUCTION

The specific effects that environmental particulates (EP) such as volcanic ash (VA) have on working gas turbine engines (GTE) and airframes will be the subject of numerous studies over the next decade. The military and economic impacts of VA and its associated gas clouds have forced the military of allied NATO nations to consider VA a real threat to their peace and security. A catalog of VA and its characteristics will be a very useful aid to developing an understanding of what happens or can happen in a GTE or to an airframe when exposed to this material. The Materials Durability and Sustainment Branch of the US Air Force Research Lab (AFRL/RXSS) has been collecting samples of environmental particulates such as volcanic ash and reactive dusts and reported information about EP from around the globe since the 1990's. Unfortunately, the existing information about most classes of EP is rarely collected in a form that is useful to understanding what the EP will do to military hardware or personnel. In this paper we will demonstrate methods of EP sample collection and the related analyses that can be performed by a well-equipped physical or geological laboratory. The intent of this work is to bundle data collected by willing NATO participants into a common NATO catalogue of natural EP materials that will enable non-specialists and specialists alike to quickly understand the nature of the problem, if there may be potential military issues, and what useful recommendations could be made for remediation or recovery of an exposed military asset.

The physical collection of volcanic ash as well as other natural EP materials have several characteristics in common. The date, time, and location description of where the sample was collected are very valuable and should be collected with each specimen. General guidance for location descriptions is to have enough detail that someone without familiarity with the collection area but a good quality map could locate the collection spot. Photographs of the collection spot and the surrounding area with a visible landmark are ideal when possible and practical. The physical distribution of natural specimens means that ground distances of less than a kilometer may be important.

The material of interest for VA effects on air vehicles is nearly always collected from 'ground-fall' material. General guidance for ground fall collection is to try to get only material that has clearly fallen from the sky and has not been transported and redeposited by water. Collection from drifting piles of ash is certainly

Volcanic Ash Collection and Analysis

appropriate because wind transported material has the potential to become airborne again. Likewise, it is best to collect ash before rain has fallen and become water washed if possible. Collection containers should be clean and dry and free of holes. Plastic bags, glass jars, and cloth bags are the preferred collection containers.

The general rule is to not collect specimens in something that will contaminate the specimens or allow them to contaminate each other. Likewise, collected materials from different locations should be segregated so they do not contaminate one another. Each container needs to have its own unique identifier that will allow the material to be paired with its collection location. A minimum useful amount is about 50 cubic centimeters (4 centimeters deep in a typical water glass) but any amount of material larger than 500 cubic centimeters is probably not necessary for the activities to be described in the analytical methods section.

2.0 EXAMPLE ANALYTICAL METHODS

Analysis of the collected materials should follow good geologic sampling and handling practice. This includes making polished sections of the collected ash as illustrated in the following figure. The image in Figure 1-1 was collected through a standard reflectance light microscope. The image should be taken at a resolution large enough that image analysis may be used to determine characteristics of the ash such as grain size distribution, degree of angularity, and the relative porosity of a particular VA. A freeware image analysis program such as Image Java or Gimp may be used to determine the ratio of gas vesicle area to solid particle area to gain an estimate of particle density versus observed particle size. Simple water displacement pycnometry may be used to determine the density of an ash specimen that has been crushed to eliminate trapped porosity. The degree of porosity can also give an indirect measure of the gas content of the erupting mass.

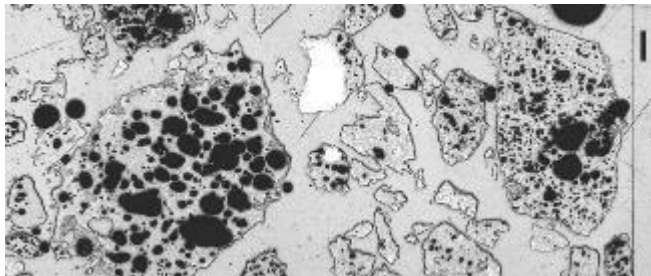


Figure 1-1: Volcanic ash from Mt. Okmok in the Aleutian Islands east of Anchorage Alaska. Specimen was a sieved size-separate of particles larger than 250 microns. Specimen supplied by the US Geological Survey. Size bar is 200 microns.

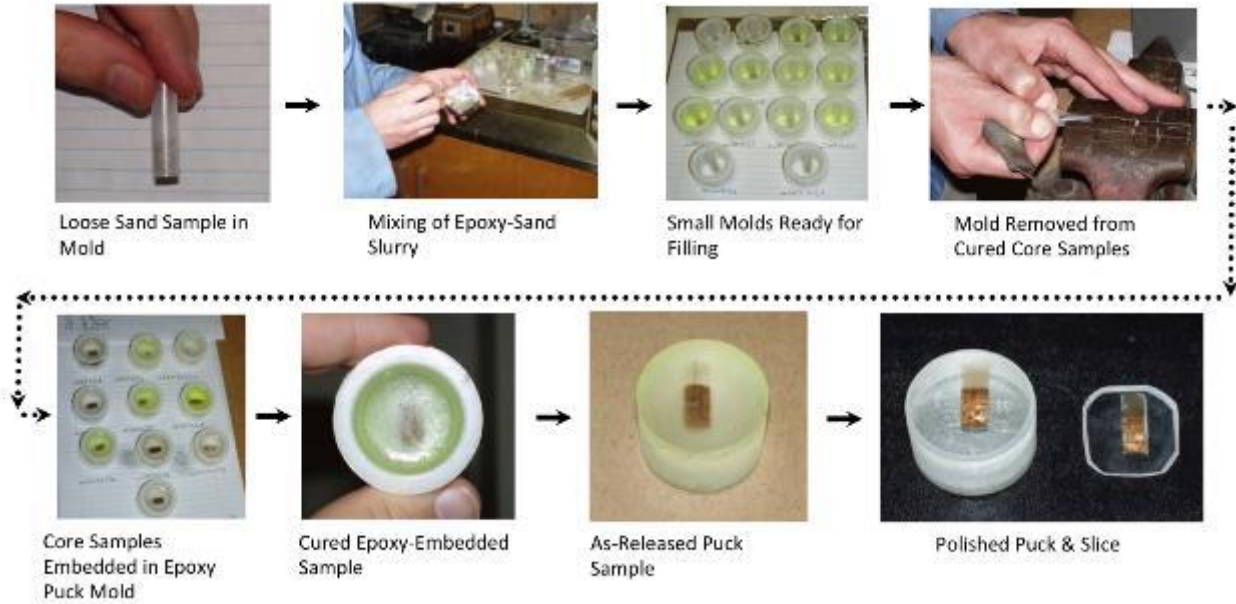


Figure 2-1: Making an analysis puck from a powder specimen so powder settling doesn't affect counting particle sizes.

Figure 2-1 demonstrates the making of a specimen puck like that used for the photomicrograph in Figure 1-1. An additional suggested step is shown where a polished slice is collected at the time the sample puck is being polished so a thin section may be made for examination in a petrographic microscope. Petrographic analysis may allow an estimate of the glass to mineral ratio to be made as well as identifying the most prevalent minerals.

There are many characterization tools that could give additional insight into how a particular VA might behave before, during, and after ingestion into a GTE. The tools applied most frequently after optical examination, density, and DSC analysis are, in no particular order, X-Ray diffraction, X-Ray Fluorescence, scanning electron microscopy (SEM), thermogravimetric mass spectroscopy, sieve size analysis, melt viscosity, energy dispersive X-Ray analysis (EDS), infrared (IR) and Raman spectroscopies, and high performance liquid chromatography (HPLC) among others.

Differential scanning calorimetry (DSC) is a very useful test to be performed on volcanic ash as well as reactive dusts of most kinds. DSC has shown itself to be a very powerful tool in evaluating the risk that VA poses to the hot section of gas turbine engines (GTEs).

Volcanic Ash Collection and Analysis

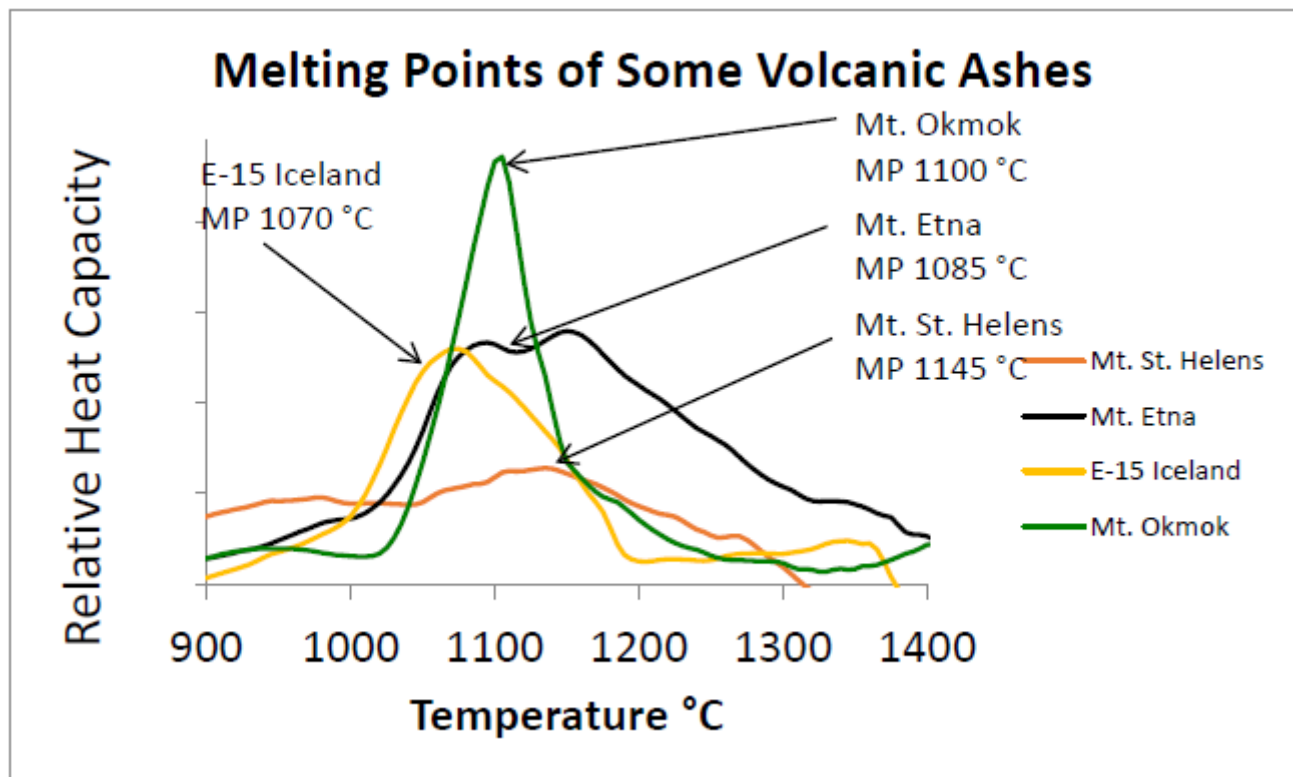


Figure 3-1: DSC curves for several volcanic ashes of interest to NATO Allies. Lower softening and melting points of some ashes would limit the use of some NATO assets for not emergency activities.

Figure 3-1 shows the collected DSC curves for several collected volcanic ashes of interest to aviation. All of these volcanoes have produced ash plumes that have halted air traffic, both civilian and military, at some time in the past 35 years. The softening and melting points of these ashes could aid planners in deciding which vehicles might be better suited for use during a particular extended volcanic eruption based on normal engine hot section temperatures.

3.0 EXAMPLE RESULTS

Each ash sample was physically examined by optical microscopy, each had its melting point determined by scanning differential calorimetry (DSC), and some had their water soluble content analyzed by liquid chromatography (LC). The DLC and LC tests were performed on loose powder. Optical microscopy was performed on a polished epoxy mount prepared to yield an accurate cross section through each powder.

Various volcanic ashes demonstrate their unique character best in photomicrographs. The following figures show each specimen in detail. The first ash examined was the one that was responsible for this latest round of activity. The ash was collected from the April 2010 eruption of Eyjafjallajökull (E-15 or Eja-15) in Iceland. Figures 4-1 and 5-1 are from two separate samples of Icelandic materials. Examination of the images shows that the two different ashes are similar in grain size and overall character. The ashes are black and generally very porous. Some individual crystals are seen that represent material carried up to the earth's surface with the molten rock that formed the ash as it was ejected into the air. This type of ash is unusual for a volcano on a mid-oceanic spreading ridge because of the higher volatile content as can be seen in most of the grains. The bubbles indicate

that there was a fair amount of volatiles dissolved into the liquid melt that then boiled out of solution as the containing pressure was released as the liquid neared the earth's surface.

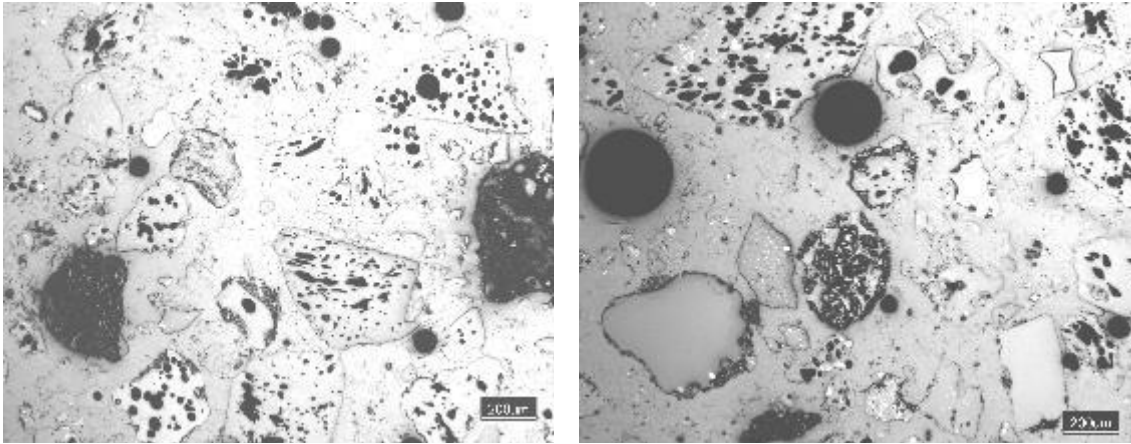


Figure 4-1: Volcanic ash collected in Reykjavik Iceland from fallout of the Eja-15 volcanic eruption of 2010. Size bar is 200 microns.

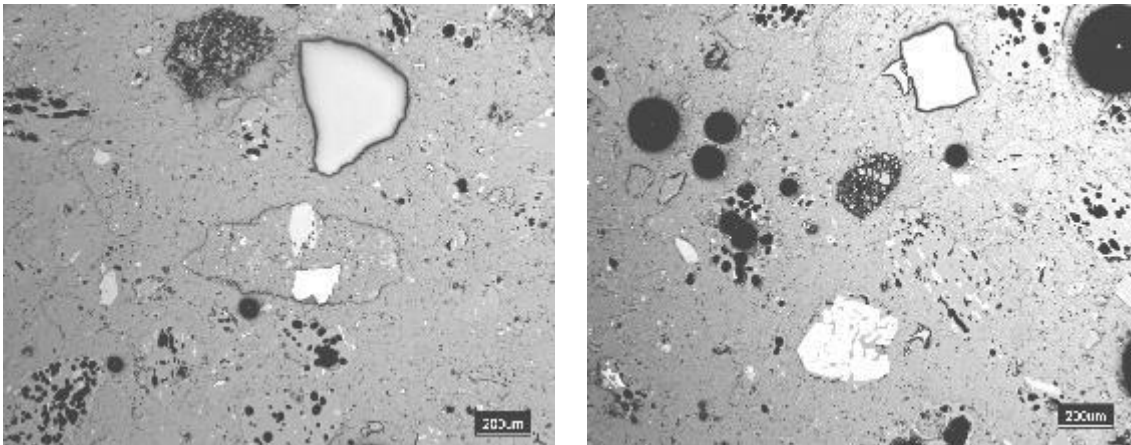


Figure 5-1: Volcanic ash collected from a different Reykjavik Iceland location from fallout of the Eja-15 volcanic eruption of 2010. Size bar is 200 microns.

The lack of an exact collection location for either of these specimens limits their ultimate usefulness.

Figure 6-1 is of ash collected from the side of Mt. Etna on the island of Sicily in the Mediterranean Sea. This ash is very porous and dark. The right image shows that the 'glass' surrounding the large mineral crystal is actually a mass of smaller crystals and not truly 'glassy'.

Volcanic Ash Collection and Analysis

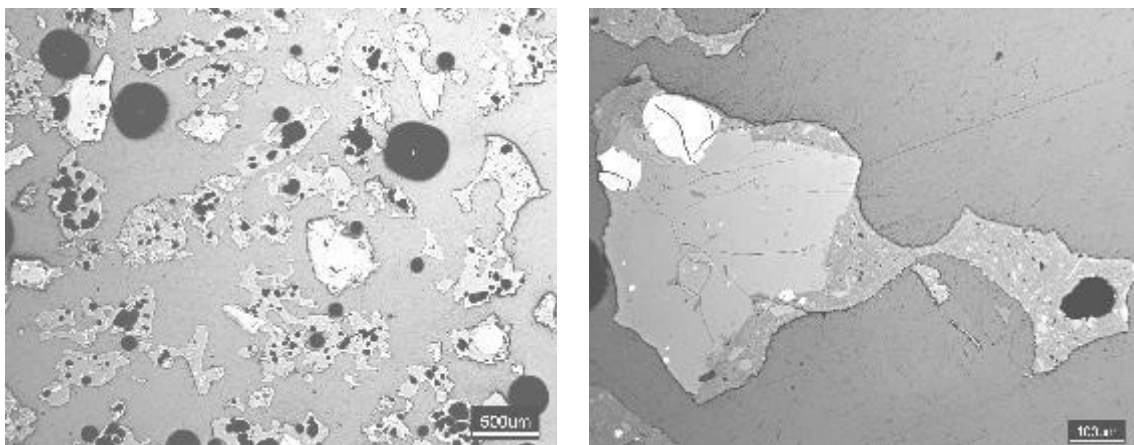


Figure 6-1: Volcanic ash collected from Mt. Etna. Size bars are 500 and 100 microns respectively.

Figure 7-1 shows the location of Homer Alaska on the Kenai Peninsula with respect to Mt. Redoubt across the channel. Mt. Redoubt has been responsible for shutting down military and civilian airspace several times around Anchorage Alaska. This material was collected the day it fell on the outside porch of a house in Homer. Figure 7-1 shows that the ash has very little porosity compared to the material from Mt. Etna or Iceland and its individual particles are very angular and blocky. The particles do not look glass-rich like the highly vesiculated (filled with gas vesicles) like the material from Iceland.

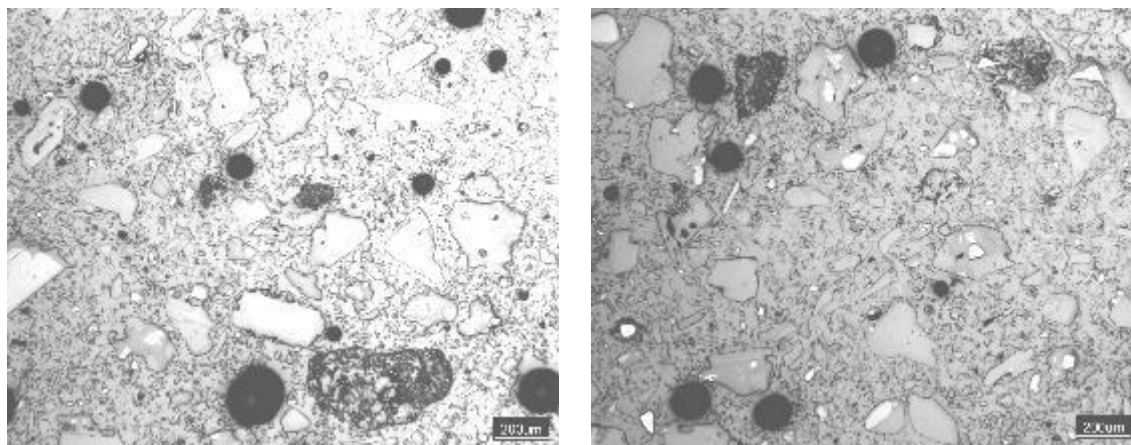


Figure 7-1: Volcanic ash collected in Homer Alaska from an eruption of the Mt. Redoubt volcano. Size bars are 200 microns.

The ash from Okmok in Figure 1-1 is very vesicular but also has a large crystalline content. It is these two characteristics that make it bear a resemblance to the Mt. Etna material. The last volcanic ash that will be examined is from Mt. St. Helens, Washington State. This ash was collected at the time of the eruption in 1980 and was placed in tightly sealed glass jars and looks much like the day it fell. Figure 8-1 and Figure 9-1 are photomicrographs of ash that was collected near the eruption and in Pullman, Washington State, respectively. The large particle size difference is a result of the heavier and larger grains of ash falling out of the ash plume well before it reached Pullman. This also gives an indication of the size of particle that can be suspended in the

air column at 300 miles away from a volcanic eruption epicenter.

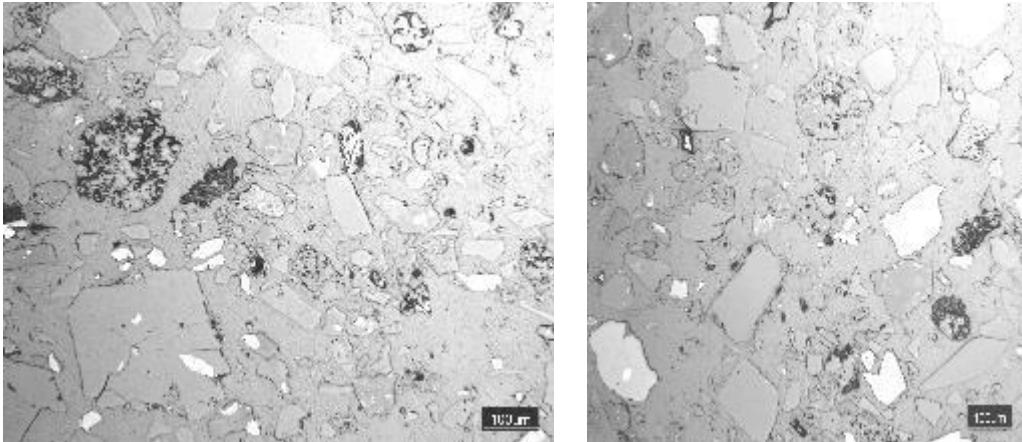


Figure 8-1: Volcanic ash collected near Mt. St. Helens from the 1980 eruption. Size bars are 100 microns.

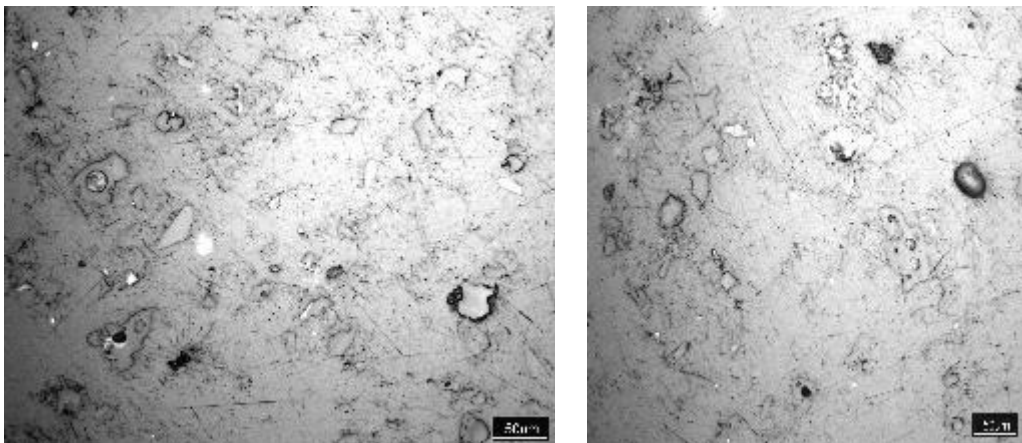


Figure 9-1: Volcanic ash collected from the Mt. St. Helens eruption collected in Pullman Washington. Size bars are 50 microns.

The ash deposited near the volcano contains mostly angular grains like Mt. Redoubt with a few vesicular grains mixed in while the material in Figure 9-1 indicates that very little of the vesicular material survived the cross country trip. There maybe remnants of the vesicular material in the ash collected from Pullman but it would be in the form of extremely small ‘spicules’ or shards of the larger foamy grains.

Liquid chromatography was performed on several of the ashes from above. Table 1-1 lists the amount of water-soluble anions that were released from the ashes by using ASTM Method D4327-2003, Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography. No Bromide or Nitrite was found for any of the specimens. The E-15 material analyzed here was the same as that shown in Figure 2-1 from Iceland. The Mt. St. Helens ash was the fine material collected in Pullman Washington as shown in Figure 10-1. The reason for using the finer Mt. St. Helens material for this analysis was to identify the anion content of material that could easily be encountered in the air column at a significant distance away from the center of the eruption. The

Volcanic Ash Collection and Analysis

concentrations listed may be thought as typical for volcanic ashes. Here, typical means very non-uniform.

Sample/Anion	Fluoride ppm	Chloride ppm	Nitrate ppm	Phosphate ppm	Sulfate ppm
Okmok Ash	0.569	1.068	0.665	0.567	NDet
Mt. Redoubt	1.300	231	NDet	NDet	3473
E-15 Iceland	5.497	19.801	2.450	NDet	183.855
Mt. St. Helens	1.549	24.289	2.189	NDet	139.533

Table1-1: Liquid chromatographic analysis of assorted volcanic ashes.

The one unusual feature of the data from Table 1-1 is the content of the ash from Okmok. This particular specimen from Okmok was a sieve-size separate that was prepared using Taylor Calibrated Test Sieves to screen out all of the particles larger than 250 microns in sieve diameter. This mechanical pre-processing was performed to produce an appropriate dust for applying to electronic circuit boards to determine the influence that volcanic ash might have on the degradation of their performance in a humid environment. The concentrations of all of the water-soluble anions from the Okmok are substantially less than expected. The amounts of anions for Okmok are present as traces only. The method and timing of collection of the Okmok material is unknown. The best explanation for the low concentrations of anions is that the ash was not a fresh fall but a fall that had been exposed to the wet North Pacific weather for some amount of time before being collected. This material looked chemically as if it had been washed.

4.0 DIFFERENTIAL SCANNING CALORIMETRY

DSC of volcanic ashes and reactive dusts is being performed to produce information regarding the high temperature behavior of these materials. These tests were performed by keeping the heating rate constant and the system calibrated for temperature runs up to 1400 °C. The data was extracted for every 5 °C step and the spectra were displayed together in Figure 3-1. The ashes used for this analysis were from the same batch as those that had LC performed on them in Table 1 with the addition of Mt. Etna. Mt. St. Helens was material collected in Pullman Washington State.

A typical DSC experiment simply involves the progressive change in a powdered material as the temperature is raised in a controlled manner. The first Okmok DSC scan went into negative heat capacities. In the present study, negative heat capacities have no real meaning. What had happened to the first DSC became clear after the polished section of Okmok was completed. The relatively large amount of trapped gasses in the vesicles of the larger than 250 micron Okmok drove the baseline of that specific DSC run out of range on their release. This gas release would change both the weight of the test powder but also its bulk heat capacity. A second DSC run was performed using the smaller than 250 micron Okmok material and that curve was very well behaved. The apex of the highest heat capacity is usually identified as the melting point for crystalline minerals. Some of the peaks are sharper than others and represent a well-defined narrow melting point. This may be thought of in terms of the heat capacity being greatest at the point of physical transformation where the material needs to acquire excess energy to change its physical state. The melting points of the different ashes determined by inspection of the curves in Figure 3 are presented here in Table 2-1.

Volcano	Melting Temp. °C	Melting Temp. °F
Mt. Redoubt	1225	2237
Mt. St. Helens	1135	2075
Okmok	1100	2012
Mt. Etna	1085	1985
E-15 Iceland	1070	1958

Table2-1: Melting points of some volcanic ashes derived from DSC curves.

Three main features of the volcanic ashes examined in this study can be applied directly to aircraft interactions with airborne volcanic ash. The first fact is that ash with a large amount of porosity will have the same bulk density (buoyancy in the air column) as ash with a lower amount of included gas. This could lead to under or over estimating the distance and speed that a foamy ash plume might travel based solely on detection methods that count particles or determine sizes. The degree of foaminess of the different ashes is different with each ash. Accurate transport models would either have to have an actual sample of the material from a particular eruption or they will need to make a band of estimates for the ash transport based on a range of particle sizes and densities.

5.0 RESULTS ANALYSIS

A second aspect is that volcanic ash can carry substantial amounts of water-soluble anions with them as they are carried through the air column. The ash can be considered an ion-exchange zeolite that releases its chemical “package” in the presence of water. The only way to be confident that there will be no negative effects from the dust sitting on a metal surface is to remove it with excess volumes of water (if the ash has not melted onto the surface). The ash will be a corrosion accelerant if it becomes wet. Likewise, those same water-soluble anions can cause problems if the ash were to melt in the hot zone of an engine and release hot-corrosive sulfate and chloride vapors.

Data from the recommended analyses in this paper are not typically collected for wind blown ashes or dusts. If data like this is collected then it may not be in a useful format but it is this kind of data that can help create hazard estimates for exposure to and damage from volcanic ashes. The particle size results can be combined with the collection location distance from eruption/epicenter to determine actual particle density estimates. These estimates may be checked against the degree of vesicularity of the ash versus its crushed density to determine if densities used to determine ash cloud drift rates and lifetimes are correct. HPLC can help determine if an ash will produce aggressive mineral acids on mixing with combustion condensation or rain water that may collect in a GTE after flight.

6.0 EXAMPLE METHOD OF FIELD COLLECTION

Physical distribution of natural specimens means that ground distances of less than a kilometer can be important. The material of interest for VA effects on air vehicles is nearly always collected from 'ground-fall' material. General guidance for ground fall collection is to try to get only material that has clearly fallen from

Volcanic Ash Collection and Analysis

the sky and has not been transported and redeposited by water. Collection from drifting piles of ash is certainly appropriate because wind transported material has the potential to become airborne again. It is best to collect ash before rain has fallen and become water washed if possible.

Collection containers should be clean and dry and free of holes. Plastic bags, glass jars, and cloth bags are the preferred collection containers. Collected materials from different locations should be segregated so they do not contaminate one another. Each container needs to have its own unique identifier that will allow the material to be paired with its collection location. A minimum useful amount is about 50 cubic centimeters (4 centimeters deep in a typical water glass) but any amount of material larger than 500 cubic centimeters is probably not necessary for the activities to be described in the experimental section.

6.1 FIELD COLLECTION SPECIFICS

The physical collection of Environmental Particulates places them in a special shipping classification for transport to the United States. All of the material of interest in this work are wind-blown geologic mineral specimens. The specimens to be collected are NOT “soil,” “dirt,” or “sod” that had a vegetable or insect component in their place of origin. The samples should be free of all but the mineral matter that is of interest to this study. These specimens should be collected from spots that have no plant or animal life. **EXTREMELY IMPORTANT** do NOT intentionally collect any insects or plant matter with your geologic mineral test specimens. Any material found to contain plant or animal matter will be destroyed and not be of use to anyone. Material of interest for engine ingestion and environmental effects on mechanical and electrical hardware is always ‘ground-fall’ material and comes from no deeper than about 1 cm on the ground surface.

Important points to consider when collecting samples:

- try to collect material that has clearly fallen from the sky or been wind transported
- material that been transported and redeposited by water is of interest only if it has the capability of becoming airborne
- collection from drifting piles of volcanic ash is appropriate because wind transported material has the potential to become airborne again
- it is best to collect ash before rain has fallen and become water washed
- A paint brush or soft whisk broom are useful tools to sweep loose mineral dust into a collection container.
- Collection containers should be clean and dry and free of holes. Plastic bags, glass jars, and cloth bags are the preferred collection containers.
- Collected materials from different locations should be segregated so they do not contaminate one another.
- Each container needs its own unique identifier that will allow it to be paired with its collection location and data sheet.
- A minimum useful amount is about 50 cubic centimeters (4 centimeters deep in a typical water glass).
- Material greater than 500 cubic centimeters is not necessary for the activities described in the experimental section.
- **EXTREMELY IMPORTANT** do NOT intentionally collect any insects or plant matter with your geologic mineral test specimens

6.2 DATA COLLECTION SPECIFICS

The date, time, and location description of where the sample was collected are very valuable and should be collected with each specimen. Location descriptions need enough detail that someone without familiarity with the collection area or who is from another country could locate the collection spot. Photographs of the collection spot and the surrounding area with a visible landmark are ideal when possible and practical. Ground sampling at distances of less than a kilometer can be important.

Mineral Specimen Collection

1. Collected by: Name, Organization, Country
2. Collection Location: Name, Latitude, Longitude
3. Collection Date:
4. General weather conditions at collection location: (for example: raining, overcast, -5C, 36C, sunny)
5. Location description: (for example: runway apron, open field, roadside, base of boulder, window sill, engine casing, vehicle floorboard)
6. Approximate volume or mass:

Database Organization – The ‘product’ of this effort

1. Specimen Name and Origin: (Same as above)
2. Unique Laboratory Specimen Identifier
3. Volcanic Ash or Mineral Dust
4. Microscopy:
 - Optical reflectance of polished sections
 - Petrographic mineral analysis
 - Scanning electron microscopy (SEM) of polished sections and grain mounts
5. Size Shape Texture Analysis:
 - Sieve size distribution
 - Automated particle size analysis
 - Angularity and elongation
 - Vesicularity
6. Elemental Analysis:
 - Energy dispersive X-ray spectroscopy (EDS) bulk and individual grain compositions
 - X-ray florescence (XRF) of as-received and milled specimens
7. Fourier Transform Infrared Spectroscopy (FTIR) 100cm⁻¹ to 2000cm⁻¹
8. X-ray diffraction (XRD) of as-received smaller than 100 mesh and bulk milled to smaller than 100 mesh
9. Differential Scanning Calorimetry (DSC) (300 C to 1500 C)
 - melting point
 - softening point
 - glass transition (T_g)
10. Water soluble components
 - Sulfate content or concentration
 - Total chloride content

Volcanic Ash Collection and Analysis

7.0 ACKNOWLEDGEMENTS

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