Volcanic Ash: Properties, Atmospheric Effects and Impacts on Aero-Engines

Andreas Vogel

Section of Meteorology and Oceanography
Department of Geosciences
University of Oslo

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Preface

This thesis is submitted for the degree of Philosophiae Doctor (PhD) at the Department of Geosciences, Section of Meteorology and Oceanography, University of Oslo. The first part of this document describes the motivation and background for this PhD research project as well as presents the achieved results and places them into a broader perspective. The second part is comprised of three scientific publications published in or submitted to peer review journals as part of the PhD thesis.


The PhD research has been carried out at the Norwegian Institute for Air Research (NILU), Department of Atmospheric and Climate Research (ATMOS) and has been undertaken during the VERTIGO Marie Curie Initial Training Network project, funded through the European Seventh Framework Programme (FP7 2007-2013) under Grant Agreement number 607905. The PhD work has been performed between May 2014 and June 2017 under the supervision of Professor Kirstin Krüger (University of Oslo), Andreas Stohl (Norwegian Institute for Air Research), Spyros Diplas (SINTEF Industry) and Adam J. Durant (Satavia Ltd.).
Other relevant contributions

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Conference publications
Abstract

Airborne volcanic ash particles from explosive volcanic eruptions are a known hazard to society, climate, and the environment as well as to aviation. To assess their potential threats, atmospheric measurements and models are used. Sensor and model algorithms depend on accurate and quantitative information about volcanic ash properties to calculate different parameters such as the temporal and spatial distribution and concentration as well as the particle size distribution and mass concentration of volcanic ash clouds. However, often only a single set of parameters for all types of eruptions and ash types is assumed. This oversimplification can introduce significant uncertainties in both measurements and model simulations of volcanic ash. This is especially problematic for aviation, as exact information about the location and concentration of ash clouds is vital for an immediate safety assessment. Additional uncertainties exist for the understanding of volcanic ash ingestion mechanisms into aero-engines and resulting critical safety concentrations inside the engine core section, which is the most vulnerable engine part.

This PhD thesis has the aim to reduce volcanic ash uncertainties and limitations in both atmospheric observations and models. Ultimately, it is expected that this will lead to improved products needed for a better hazard assessment. The PhD thesis consists of three scientific papers. One paper investigated volcanic ash particle ingestion into an aero-engine using computational fluid dynamics simulations including a Lagrangian particle model. The paper quantified the influence of the engine fan stage on volcanic ash ingestion into an aero-engine and shows that particles, which interact with the fan stage are centrifuged out of the engine core flow, thus reducing the ash concentration inside the engine core. Another paper studied the physicochemical and optical properties of a representative selection of volcanic ash samples using a range of analytical measurement techniques and theoretical methods. The findings of this paper are compiled in a new and comprehensive volcanic ash reference dataset that can be used for various applications such as transport models or satellite observations of drifting ash clouds. Moreover, improved volcanic ash properties were applied in a study of in-situ measurements of an artificially created volcanic ash plume using an optical particle counter, described in an additional thesis paper.

The findings of this PhD thesis will help to reduce uncertainties of detecting and modelling volcanic ash clouds as well as to assess their threats during future volcanic eruptions.
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Part I.

Thesis
1 : Introduction

1.1. Motivation

Volcanic eruptions are fascinating natural phenomena on Earth, with glowing lava flows, fountains of ejected molten material, pyroclastic density currents, volcanic lightning and kilometre-high plumes of thick ash. Worldwide around 1500 volcanoes are classified as being active. How they erupt, depends on the individual type of the volcano as well as the magma type or if the released material interacts with the surrounding environment (i.e., ice, water and mud) (Self and Walker, 1994).

During eruptions, volcanoes emit vast amounts of gases and tephra (all solid ejecta) into the atmosphere. While the large fraction of tephra (i.e., blocks and bombs) quickly falls to the surface, the smallest tephra fraction, namely volcanic ash, and gases can be emitted up into the mid and upper troposphere and even into the stratosphere. From there the emissions can be transported by the atmospheric circulation hundreds to thousands of kilometres downstream away from the source of the eruption (Carey and Bursik, 2015). Volcanic ash particles have a great variety of physicochemical, optical and thermal properties and span over several orders of magnitude in size (a few hundred nm to 2 mm). The global annual fraction of emitted and transported fine ash (< 63 $\mu$m) is estimated to be approximately 33 Tg/year (Warneck, 1988; Andreae, 1995).

In present days, with high populations living on or around volcanoes as well as advanced vulnerable technologies such as jet engines, volcanic ash can pose severe impacts on society and the environment. When released to the atmosphere, volcanic ash particles have the potential to influence the Earth’s radiation balance as they reflect and absorb solar and terrestrial radiation, and therefore they impact weather and climate (Robock, 2000; Rolf et al., 2012; Flanner et al., 2014; Vernier et al., 2016). After sedimentation to the surface, they also cause respiratory health effects (Horwell and Baxter, 2006; Baxter et al., 2014), affect air quality (Thorsteinsson et al., 2012), pose hazards for infrastructures such as ground transport and water supplies (Wilson et al., 2012) as well as natural environments (Durant et al., 2010; Gislason et al., 2011) and they can affect soil and ocean fertilization (Duggen et al., 2009; Ayris and Delmelle, 2012; Achterberg et al., 2013; Arnalds, 2015).

Another risk of volcanic ash particles is their threat on aviation as they decrease visibility (Weinzierl et al., 2012; Blake et al., 2018) and cause dangerous damage to airframes and especially to aero-engines (Casadevall, 1994; Miller and Casadevall, 2000). Given that
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Figure 1.1.: Eruption plume of the Eyjafjallajökull on 11 May 2010 as seen from (a) research aircraft from 10 km distance from the plume in north-western position (Weber et al., 2012) and (b) MODIS Satellite (NASA-MODIS, 2010)

major aviation flight routes intersect the world’s most active volcanic regions (Guffanti et al., 2010), volcanic ash clouds can affect commercial air traffic routes significantly (Prata et al., 2014; Prata and Rose, 2015).

The 2010 Eyjafjallajökull eruption on Iceland demonstrated, impressively, how susceptible air traffic is to drifting volcanic ash clouds in the dense airspace over Europe. Figure 1.1 shows the plume as seen from a research aircraft (10 km distance) and from space on 11 May 2010. As visible on the two images, the eruption plume was first transported by strong, stable north-westerly winds away from the source in a narrow and almost straight cloud before the particles were spread out over large areas of Europe. While large particles (> 2 mm) fall quickly back to the surface as seen by the region underneath the plume (Eliasson et al., 2014), the fine fraction of volcanic ash (< 63 \( \mu m \)) stayed aloft for several days (Rose and Durant, 2009; Stohl et al., 2011).

Although the eruption was relatively small (6-11 Tg of fine ash particles were injected into the mid-troposphere (Stohl et al., 2011; Prata and Rose, 2015)), the European authorities were forced to impose flight restrictions and re-routing in more than 30 countries including a total airspace closure of 6 days. The airspace closure led to a widespread cancellation of 100,000 flights and several billion US$ economic losses (Oxford, 2010).

In a situation such as the Eyjafjallajökull crisis, a combination of transport and dispersion models as well as measurements, both from the ground, inside the atmosphere and space are used to assess the potential threat for aircraft operations. They give both real-time and forecast information about the spatial and temporal position of ash in the airspace that is needed to inform decision-makers such as the national and international flight authorities. In retrospect, the large-scale airspace closure during the Eyjafjallajökull eruption was a product of a conservative forecast approach that overestimated the real atmospheric ash concentrations (Prata et al., 2018). The reason for the conservative approach was primarily...
1.1 Motivation

based on safety concerns, but also due to considerable uncertainties, both from an atmospheric and an aero-engine point of view that were either not well known or characterised.

To improve volcanic ash modelling and detection techniques as well as the understanding of the susceptibility of aero-engines (Watson, 2015; Clarkson et al., 2016) for future eruptions, there is a drive to minimise these uncertainties. For example transport and dispersion models, as well as measurement algorithms, often assume only a single set of parameters for all types of eruptions and ash types (Grainger et al., 2013), which leads to significant uncertainties in calculations of the atmospheric location (vertical and horizontal distribution) and concentration (particle size distribution and mass concentration) of volcanic ash clouds. Mackie et al. (2016) concluded that by analysing ash characteristics of real ash samples (size, shape, and mass density, as well as chemical and optical properties), uncertainties can be minimised for future eruptions.

Other uncertainties are based on the understanding of the relationship between aero-engine damage mechanisms and volcanic ash dose. Clarkson et al. (2016) indicated that various aspects need to be considered from both an atmospheric and an aero-engine point of view. While damage to engine components is a subject of ongoing research, only little is known about the transition of the particles from the atmosphere into the engine core section, the most safety critical part of the engine. An often neglected source of uncertainties is the influence of the turbofan on the particle separation (Tabakoff et al., 1991; Weaver et al., 1996). Coarse volcanic ash particles might deviate from the original fluid streamline during the ingestion process due to their momentum. This deviation provokes that large particles (in contrast to small particles) touch or hit the turbofan surface, from where they are centrifuged out into the engine bypass due to the high circumferential velocity of the fan. This effect is essential to relate an atmospheric mass concentration to mass concentrations inside the engine core and to relate these concentrations to potential engine damage. To avoid a situation such as the 2010 crisis, uncertainties, both from an atmospheric and an aero-engine point of view, need to be analysed and minimised.
1.2. **Aim and objectives**

This PhD thesis aims to minimise these uncertainties and limitations in observations and models leading to enhanced products (or outputs) that are needed for a better assessment of volcanic ash hazards on climate, the environment, health, and especially on aero-engines. The primary objectives of this thesis are to:

(a) **investigate** the effect of the engine fan on ingested volcanic ash particles into an aero-engine and to relate ash concentrations in the ambient atmosphere to concentrations inside the engine core section;

(b) **analyse** volcanic ash particle characteristics using a range of analytical methods and techniques to determine their physicochemical and optical properties to reduce uncertainties in model and observation inputs;

(c) **apply** physicochemical and optical properties to in-situ volcanic ash measurements to improve measurement accuracy and to calculate atmospheric concentrations of a volcanic ash cloud;

![Figure 1.2: Overview of the three scientific publications as part of this PhD thesis.](image)
1.3 Thesis outline

Objective (a) is addressed in Paper I, where volcanic ash particle interaction with the engine fan is studied to calculate the engine core concentrations from given atmospheric concentrations (Figure 1.2). The engine core concentrations are needed to assess the impact of volcanic ash particles on the operability of modern aero-engines. Paper II focuses on objective (b) by analysing particle properties in an extensive set of volcanic ash samples, which are needed as input parameters for measurements and models. The results from Paper II are used in the following two presented papers. Objective (c) is addressed in Paper III, where physical and optical properties are applied to an optical particle counter instrument used to measure in-situ volcanic ash concentrations inside an artificial volcanic ash cloud. These results were crucial to validate another deployed infrared spectral imaging remote sensing sensor (also Paper III).

1.3. Thesis outline

Part I of the PhD thesis is structured as follows; Section 2 provides the background for the scientific aim and objectives in this thesis. Section 3 gives a short description of volcanic ash samples, measurement techniques and models used to address the objectives. A short presentation of the primary findings of each of the three scientific publications is given in Section 4, while conclusions and an outlook of the thesis are provided in Section 5. Part II of this PhD thesis consists of the three scientific publications (see Preface).
2: Scientific background

This chapter provides background information for the understanding of this PhD thesis, more detailed than presented in the individual scientific publications. The chapter starts with a description of volcanic eruptions and their emissions, with a particular emphasis on volcanic ash particles. This information is vital for the understanding on how volcanic ash affects aviation (i.e., aero-engines) and how to use volcanic ash particle characteristics in measurement and modelling algorithms, which are also briefly described.

2.1. Volcanic eruptions and emissions

Every volcanic eruption is different from another in eruption style, strength and duration. How volcanoes erupt often depends on their specific geological location. Statistically, every year between 50 and 60 volcanoes erupt (U.S. Geological Survey, 2011), and each of them is triggered by magma movements that result from movements of the Earth’s lithosphere (i.e., tectonic plates). Therefore, it is essential to know how volcanoes form and where they are located.

Volcanic eruptions are based on one of three tectonic processes (Figure 2.1). The first process is the subduction of thin and dense oceanic plates beneath thicker and less dense continental plates. As the ocean plate descends, the plate material is exposed to higher temperatures, which leads to partial melting of tectonic materials and a creation of a magma chamber above the oceanic subduction plate. From there the molten material can ascend to

![Figure 2.1: Plate Tectonic settings of volcanoes (modified from Railsback (2007))](image-url)
the surface, due to the lower density of the material compared to the surrounding material, which can trigger volcanic eruptions. This process is the dominant process and represents the majority of volcanism on this planet (Siebert et al., 2015). The second process is based on the divergence of two tectonic plates. The divergence occurs beneath a thick continental plate, which is arched as the two plates move apart. This process forces the end of the plates upwards, which creates a rift shaped structure, and the middle part downwards, which allows hot mantle material (i.e., magma) to flow into that area from below and to form an elongated rift. The uprising magma can also contribute to the divergence of the plates, but it is more likely that it is a combination of both processes. The third process is caused by convection of stationary and boiling upper-mantle material (hotspot) below a moving plate to the surface. The magma material can rise in thin streaks through the mantle and crust to the surface as it is lighter than the surrounding solid rock material. Figure 2.2 shows the location of approximately 1500 terrestrial volcanoes declared as being active. The vast majority of these volcanoes (~90\%) are located near plate boundaries (light red lines), but some appear at random locations above hot spots (worldwide around 40 hotspots). Recent examples of

![Figure 2.2: Map of active volcanoes worldwide including volcanoes responsible for damaging encounters of aircraft with ash clouds grouped into their severity indices (circles) (modified from www.volcano.oregonstate.edu and Guffanti et al. (2010)). Red triangles represent the 1500 volcanoes declared as active and the light red lines show the tectonic plate boundaries.](image)
eruptions for the three formation types are the 2014 eruption of Mt. Kelud (subduction of the Indo-Australian tectonic plate and the Eurasian plate), the 2011 Grímsvötn eruption (divergence of the Eurasian and the North American plate) and the continuous Hawaiian lava flows (hotspots). Volcanic ash samples from the former two are part of the thesis and analysed in one of the research papers (Paper II).

The different formation processes lead to different eruption styles, which can be described using a semi-quantitative measure of the explosiveness of volcanic eruptions, the total ejected volcanic material, eruption column height as well as eruption duration. It is known as the ‘Volcanic Explosivity Index’ (VEI) (Newhall and Self, 1982), where a VEI = 0 eruption is a non-explosive eruption and a VEI = 8 a very large (or most disruptive) eruption. The index also separates eruptions into two main eruption styles: Effusive and explosive eruptions.

Effusive eruptions, i.e., fissure and Hawaiian eruptions, are mainly dominated by constant low viscous magma flows (mainly fluid basaltic lava) and strong gas emissions. During the transport of very hot magma (1000 - 1250°C) to the surface, large amounts of volatile constituents (H₂O, CO₂) that are initially dissolved in the magma are released silently into the atmosphere, with a low-pressure difference between the gas and the surrounding air. Main gas components are H₂O, CO₂, SO₂ and H₂S as well as halogens (bromine, chlorine and fluorine) (Oppenheimer et al., 1998; Krüger et al., 2015). In cases of a sudden release of a large volumes of gas trapped inside the rising magma, the magma rapidly expands as well as fragments, which produces lava fountains (Sparks, 1978). These lava fountains often produce volcanic ash, but compared to the vast total gas emissions (Steensen et al., 2016), the ash fraction is small. As an example, the 2014 Holuhraun fissure eruption emitted 35 kt SO₂ per day, but almost no ash (Schmidt et al., 2015). The VEI of effusive and Hawaiian eruptions range between 0 and 2 (gentle effusive, non-explosive eruptions).

In contrast, explosive eruptions produce vast amounts of volcanic ash, pumice and ballistic material (i.e., tephra) as well as gases. Gas pressure builds up inside the conduit, as the gas does not escape easily in high viscous magmas, until the gas is released violently and explosively out of the volcano (conversion of potential energy into kinetic energy). Depending on the magnitude of the pressure difference between the gas and the surrounding air, and the conduit geometry, the eruption column can reach altitudes up to several kilometres. Explosive eruptions are divided into three eruption types: Strombolian, Vulcanian, Plinian and phreatomagmatic eruptions. Strombolian eruptions are small, with small eruption energies and explosions in a short time interval (VEI 1-2). During an explosion, small, sharp bursts of fluid magma (basalt and basaltic-andesite) from a magma-filled summit conduit are released, which produces mainly tephra material (e.g. lava bombs) and short lava flows. The eruption column usually only reaches a few hundred meters and eruptions last only a few minutes. A good example of strombolian eruptions can be seen at Stromboli volcano in Italy, from where they have their name. Vulcanian eruptions are also small, but explode more violently (VEI 2-4). Explosions of viscous lava (usually andesite, dacite, or rhyolite)
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create tephra, gases and occasional pyroclastic density currents (e.g. Mt. Sakurajima, Japan). They are already powerful enough to propel emission products several kilometres into the atmosphere, and the eruptions can go on for days and months (Woods, 1995). The most vicious explosive eruptions are Plinian eruptions (VEI 4-8). They are so powerful that they can transport large amounts of ash and gases into the upper troposphere or even the stratosphere within a short amount of time (Bonadonna and Phillips, 2003). Plinian eruptions are triggered by extraordinarily gas-rich, and very viscous magmas (dacite and rhyolite) that produce high pressures inside the magma chamber and the conduit. After reaching the surface, the magma material is fragmented into tephra and in large amounts of volcanic ash due to very high-pressure differences between the gas and the surrounding air. Given the high eruption column height (up to 45 km) (Wilson et al., 1978), the emissions can be transported hundreds to thousands kilometre away from the eruption location. These eruptions are so destructive, they can even destroy the top of the volcano and areas around the volcano through dome collapses and pyroclastic density currents, as shown by the 1980 Mt. St. Helens eruption (Fink et al., 1990) or the 1992 Mt. Spurr eruption (McGimsey et al., 2001). Because of their vast amount of erupted material and volatiles and high eruption column, they have a high potential to impact global aviation, and they can even influence the climate (McCormick et al., 1995; Vernier et al., 2016).

Another explosive eruption type is phreatomagmatic eruptions. They result from the interaction of rising magma with ground and surface water, as well as surface ice. They can be highly explosive (Zimanowski et al., 2015) and can produce, depending on the magma to water ratio, large amounts of very fine volcanic ash particles through rapid expansion of the water phase (Sigurdsson et al., 2000; Gudmundsson et al., 2012; Kristiansen et al., 2012). An excellent example of a phreatomagmatic eruption was the 2010 Eyjafjallajökull eruption. In this PhD thesis, volcanic ash samples from explosive and phreatomagmatic eruptions as well as from a Dome collapse are investigated (Paper II).

2.2. Eruption plume dynamics

Volcanic plumes can be distinguished between strong and weak plumes, where they are expressed by their ratio of horizontal wind speed to upward plume speed (Carey and Bursik, 2015). The eruption column consists of a mixture of volcanic tephra and hot gases produced by the expansion of the gas out of the conduit that is controlled by both the volatile magma content and shape of the conduit (Wilson et al., 1980). During the expansion to the surface, the high potential energy is converted into kinetic energy (high pressure), which leads to exit velocities of 100 m/s for Strombolian to > 600 m/s for Plinian eruptions (Carey and Sparks, 1986; Koyaguchi and Ohno, 2001). This, in combination with the mass eruption rate and magma temperatures (Bonadonna et al., 1998), creates an extremely high
2.2 Eruption plume dynamics

Figure 2.3.: Schematic illustration of the two different types of volcanic plumes. a) Umbrella cloud with the three characteristic plumes regions (i.e., the gas thrust region, the convective region, and the umbrella (neutral buoyancy) region. b): Weak plume that is bent over due to high horizontal wind velocity (modified from Engwell and Eychenne (2016)).

momentum that transports the gas-particle mixture vertically into the atmosphere (Woods, 1995), although the mixture is denser than the surrounding air (gas thrust plume region) (Sparks, 1986). The gas thrust region, which is the first momentum driven region of the column, extends typically up to several kilometres in height with narrow column width (Figure 2.3).

As the mixture rises, colder atmospheric air is entrained into the plume by turbulent mixing, which leads to a heat transfer from the hot gas-particle mixture to the entrained ambient air. During the heating, the ambient air expands, which leads to a reduction of the plume bulk density relative to the surrounding air and an even stronger advection of the plume. If the gas thrust region does not entrain enough surrounding air into the gas-particle mixture, the column will rise until reaching a zero velocity, before it eventually collapses and falls back to the surface (bulk density of column denser than surrounding air). Near the surface, the collapsed plume can produce pyroclastic density currents (e.g. 1980 Mt. St. Helens VEI 4 eruption or the 2018 Mt. Sinabung eruption) or co-ignimbrite plumes. However, if sufficient ambient air is entrained into the gas-particle mixture and if the eruption momentum is high enough (conversion of thermal energy into potential energy), the eruption column becomes buoyant during the ascent (convective region) (Woods, 1995; Valentine, 1998). The velocity of the convective ascent region is lower than in the gas thrust region but is still high enough to produce enough momentum (vertical velocity inside the plume is still higher than the horizontal wind). In the presence of water vapour, the plume rise can be even stronger, as latent heat released by condensation can heat up the plume, which creates a higher degree of buoyancy. Other factors that can influence the plume rise are meteorological conditions (i.e., wind speed, atmospheric stability or humidity) (Costa et al.,
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2016) and in-plume processes such as particle aggregation (Rose and Durant, 2009, 2011; Brown et al., 2012; Mueller et al., 2017a). Additionally, the smaller the particles, the more significant is the heat loss as they have a larger surface to volume ratio and can, therefore, transport more heat to the surrounding air (Rose et al., 2001). Last, the fallout of particles is also essential for the plume rise as it decreases the density of the gas-particle mixture.

As more and more cold air is entrained into the plume, the difference between the plume and the surrounding air decreases (density also decreases with height) until it reaches equilibrium (neutral buoyancy). At this point, buoyancy is no longer the driving force meaning that the plume will start spreading horizontally, which creates the typical umbrella form (Figure 2.3 a)). However, often the plume is so energetic that it overshoots the umbrella region (maximum column height), which leads to a collapse of the mixture back into the neutral buoyancy region in the form of gravity currents (Bursik et al., 1992). From the umbrella region, the mixture can spread over great distances due to the momentum of gravity currents and meteorological conditions (winds speeds) (Engwell et al., 2014; Marti et al., 2016). Carey and Bursik (2015) reported that if volcanic material reaches a height of 20 km, it is highly likely that the resulting plume will form an umbrella cloud. Umbrella clouds were observed during the 1989 Redoubt, the 2011 Grímsvötn and the 2014 Kelud eruptions (Paper II).

The second volcanic plume type is a weak plume. Weak plumes are less vigorous and have lower injection forces compared with buoyancy driven volcanic plumes. During the vertical ascent, they initially maintain a cloudlike structure due to their uprising motion until the horizontal crosswind speeds are equal or greater (maximum cloud height) than the uprising motion (Figure 2.3 b)), which leads to a bending of the plume. The bent-over plume can have a profoundly irregular shape due to prevailing wind conditions and their susceptibility to local atmospheric motions (Carey and Bursik, 2015). In the process of bending over, the plume mixes with the ambient atmosphere. Through the combination of initial vertical movement of the plume and the strong horizontal winds, the plume can be transported far away from the eruption location (wind dominated plume transport). The plume slowly thins out and spreads during the transport. An example of this plume type is the 2010 Eyjafjallajökull eruption, which can be seen in Figure 1.1.

Both volcanic plume types transport volcanic ash particles in the atmosphere away from their source. Their properties, atmospheric effects, identification of their source and impacts on aero-engines are investigated in this PhD thesis.
2.3. Volcanic ash and its atmospheric lifetime

Volcanic ash is one of the primary products of volcanic eruptions, along with larger rocks, gases and water vapour. Volcanic ash is the smallest fraction of all ejecta (tephra) and is defined as having the size of less than 2 mm in diameter. Volcanic ash is categorised into coarse ash \( (D_p \leq 2000 \mu m) \), where \( D_p \) denotes the particle diameter, and fine ash \( (D_p \leq 63 \mu m) \) (Rose and Durant, 2009) and is formed when magma and rocks fragment (Wohletz et al., 1989; Heiken, 1991; Schmith et al., 2018). Fragmentation always takes place when magma rises to the surface, but depending on eruption styles and associated driving forces of magma movements, fragmentation occurs through various processes. These include (a) rapid expansion of the gas-particle mixture (Cashman and Scheu, 2015; Mader et al., 1994), (b) rapid decompression (Alidibirov and Dingwell, 1996), (c) quenching of melt (Jones and Suryanarayana, 1973; Webb and Dingwell, 1990) (all primary fragmentation processes) or (d) through continuous breakage after solidification (Rose and Durant, 2009) (secondary fragmentation).

Rapid expansion is primarily driven by magma acceleration, resulting in high strain rates that cause either fragmentation due to magma instabilities (low viscosity basaltic melts) or if the tensile strength of the melt is exceeded in the magma (high viscosity melts) (Cashman and Rust, 2016). Rapid decompression, in contrast, is driven by dome collapses and flank failures (Ghenaiet, 2012) that create vast pressure differences that lead to fragmentation. Quenching of melt is the fragmentation process when magma intersects with external water or ice and thermally expands (Cashman and Scheu, 2015). The expansion of magma rapidly converts potential energy into kinetic energy that forms the gas thrust region of volcanic eruption columns (Figure 2.3) or lateral pyroclastic flows (Cashman et al., 1999). Secondary fragmentation processes happen after magma is solidified. That includes material breakup after a solid particle-particle collision or solid particle rounding (i.e., reduction of particle size and mass) during abrasion.

Direct observations of fragmentation are not possible due to the complex nature of the process. However, numerical models (Freundt and Rosi, 1998; Perugini et al., 2011), analog experiments (Kueppers et al., 2006; Dufek et al., 2012) and analysis of volcanic deposits (Liu et al., 2015) have contributed substantially to an enhanced understanding of how volcanic ash particles are formed by magma and rock fragmentation (Bonadonna and Houghton, 2005) as well as how they are transported into the atmosphere (Woods, 1995).

Once injected into the atmosphere, volcanic ash particles can be transported over long distances far away from the eruption source by prevailing winds, large-scale advection and smaller scale processes such as turbulent diffusion and convection (Durant et al., 2012). How long these particles stay aloft depends on eruption source, eruption column height and strength, meteorological conditions, i.e., wind velocities and directions and eventual uplift (e.g., in convective clouds or fronts), and how fast they are removed from the atmosphere.
Scientific background

(Mele et al., 2011). The latter processes involve wet and dry deposition, gravitational settling, as well as particle aggregation.

Wet deposition can be described by scavenging of particles by clouds and precipitation and by particle nucleation during their transport in the atmosphere. Scavenging can occur both inside (rain-out) and under the cloud (washout). Volcanic ash particles can also serve as ice-nuclei (Durant et al., 2008) and cloud condensation nuclei (Lathem et al., 2011; Rolf et al., 2012) for ice and cloud droplet formation, which contributes to the atmospheric removal.

The dry deposition of particles involves processes such as particle impaction, diffusion and sedimentation, all based on physical properties of volcanic ash particles (Mills and Rose, 2010; Folch, 2012; Bagheri et al., 2013). Dry deposition describes the collection of particles by the Earth’s surface and vegetation near the surface and particle deposition by gravitational settling, which is the dominant process for volcanic ash particles. The atmospheric lifetime of ash particles span minutes to hours (sedimentation velocities of $\sim 1 \text{ km/h}$ for coarse ash particles, $2 \text{ mm} < D_p > 63 \mu m$) to days and months ($\sim 0.01 \text{ km/h}$ for fine ash particles, $D_p < 63 \mu m$) (Bonadonna et al., 1998; Rose et al., 2001; Durant, 2015; Mastin et al., 2009), as illustrated by the 2010 Eyjafallajökull eruption. Coarser particles tend to deposit closer to the eruption source (proximal deposits), whereas fine particles can be transported further away (distal deposits). However, the rate at which volcanic ash particles settle through the atmosphere to the surface cannot only be described by the particle size, but also by their shape (morphology), their mass densities or if particle form aggregates that alters their mass, size and aerodynamic behaviour.

The size and morphology of volcanic ash particles are both influencing factors for determining their aerodynamic behaviour and they are controlled by the individual magma fragmentation process and external factors such as interaction with water, turbulence and particle collision inside the eruption column (Heiken, 1972; Sparks, 1978; Zimanowski et al., 2015). The non-spherical shape of the particles can alter the aerodynamic behaviour of particles, e.g. the atmospheric sedimentation velocities can decrease by up to 50 % (Mele et al., 2011). Thus, non-spherical particles can be transported over longer distances in the atmosphere than spherical particles (Stevenson et al., 2015; Bagheri and Bonadonna, 2016b). How volcanic ash particles look like is illustrated in Figure 2.4. Volcanic particles can be elongated, can have voids and sharp edges as illustrated. An intensive investigation of the shape and size of volcanic ash particles, all from volcanic eruptions with different magma compositions, eruption styles and external interactions is given in Paper II.

The particle mass density also controls the atmospheric lifetime of volcanic ash particles. The mass density is a function of the chemical composition of the ash types as well as of the fragmentation type that can produce either blocky particles or particles that have a high vesicularity (degree of presence of cavities within a particle formed during solidification by expansion of the gases present in the magma). The higher the vesicularity, the lower is the
2.4 Chemical composition of volcanic ash

Figure 2.4.: Scanning electron microscope images of volcanic ash particles from the 2010 Grímsvötn eruption, Iceland (Paper II).

density, which is vital for determining the terminal settling velocity and deposition of ash particles (Bonadonna and Phillips, 2003; Costa et al., 2006; Folch et al., 2009).

Another dry removal process involves particle aggregation, as observed during the 2010 Eyjafjallajökull eruption (Durant and Brown, 2016). Particles of different sizes, shapes and mass densities have different fall velocities, which leads to adhesion of particles and a formation of aggregates (Durant and Brown, 2016; Rose and Durant, 2011). The aggregation rate is dependent on the atmospheric water content (Durant et al., 2009), electrostatic forces (Brown et al., 2012) and/or the salt content (Mueller et al., 2016, 2017a,b) to hold them together. Aggregation can lead to a faster deposition of particles due to an increase of particle mass (Rose and Durant, 2011; Brown et al., 2012; Mueller et al., 2017a).

2.4. Chemical composition of volcanic ash

The mineralogical and chemical composition of volcanic ash varies substantially between different magmas that are usually a mixture of melt and mineral crystals. Ash compositions depend on the specific magma composition from corresponding tectonic settings, but also on the distance from the volcano. Volcanic ash is a heterogeneous mixture of a variety of minerals (phenocrysts), broken volcanic glass (quenched melt), and lithic fragments (Freundt and Rosi, 1998; White and Houghton, 2006; Dingwell et al., 2012); all liberated during material fragmentation. Typical crystals in various quantities are feldspars, silica minerals and olivine. A full overview of possible crystals in volcanic ash is published by Nakagawa and Ohba (2002).
Ash compositions range from basaltic (low SiO$_2$ and high in Mg and Fe) to rhyolitic (high SiO$_2$ and high Al), typically with variable proportions of glass and crystal fragments (Cashman and Rust, 2016). Every volcanic ash type can be classified following classification of igneous rocks introduced by Le Bas and Streckeisen (1991). The classification was established to define boundaries of rock species that are based on modal mineral or chemical compositions.

The chemical composition is relevant for considerations of effects on health, scavenging processes in clouds (e.g., ice nucleating capability), ecosystems, aero-engines, or remote sensing as well as in-situ measurement systems. For example, the individual chemical composition of volcanic ash particles can be used to calculate parameters such as the mass density (Paper II), needed for transport and mass concentration calculations, e.g. Stohl et al. (2011); Mastin (2014), or to calculate the glass transition and melting temperatures and viscosities under different environmental/ surrounding temperatures (Giordano, 2003), relevant for engine damage calculations. The composition is also relevant for parameter such as the harness material hardness or the melting point of each mineral composition. Furthermore, they can be used to analyse/study complex refractive indices needed for optical measurement systems (Paper III) or to identify the origin of ash samples. Therefore, it is essential to analyse the chemical composition in detail to be able to calculate other related values (Paper II).

2.5. Impact of volcanic ash on aviation and aero engines

Volcanic ash injections into the atmosphere are a threat to global aviation, and related hazards are known since the 1950s. Scientists from the U.S. Geological Survey (USGS) documented 129 aircraft encounters with drifting volcanic ash clouds between 1953 and 2009 (Guffanti et al., 2010). Most of the cases happened in situations where the crew had no information about the presence of ash in the airspace (or information about a starting eruption) or where ash was not visible (e.g., at night). All 129 encounters together resulted in hundreds of million US$ of damage to airframes and engines. However, considering that presumably not all encounters have been reported in the past decades, the real number of aircraft encounters and associated costs might be even higher.

Two notable aircraft encounters of drifting volcanic ash clouds are those of British Airways Flight 9 over Java (Mt. Galunggung eruption) in 1982 and KLM Flight 867 over Alaska (Redoubt eruption) in 1989. Both flights experienced multi-engine failures including an in-flight shutdown of all four engines (following engine surge) after flying through thick volcanic ash clouds 250-1000 km from the eruption source (Przedpelski and Casadevall,
2.5 Impact of volcanic ash on aviation and aero engines

1994; Witham et al., 2012; Clarkson et al., 2016). After a significant loss of performance on the engines, and descending several thousand feet out of the ash cloud, in both cases the pilots managed to restart the engines and gain sufficient power to safely land the aircraft (Przedpelski and Casadevall, 1994). However, the potential threat to safe fly operations was obvious. Figure 2.2 gives an overview of the 129 encounters, including their severity classes (circles). The classes reach from 0 (only minor signs of volcanic ash) to 5 (loss of aircraft). Fortunately, until today no class 5 encounter was reported (Guffanti et al., 2010). It can be seen that most of the reported encounters happened in countries with a high density of volcanoes (i.e., Indonesia, Japan, USA, including Alaska, Hawaii, and the Cascades, Philippines and Chile). Christmann et al. (2017) updated the list of encounters and documented a total of 260 reported events. An overview of the most severe encounters with damage of engines is given in Table 2.1.

Eruptions, such as the 1980 Mt. St. Helens eruption with overall nine reported encounters, the 1982 Gallunggung eruption (BA9) with four encounters and the 1989 Redoubt eruption (KLM867) with seven encounters, illustrated the hazard of volcanic ash for aviation and especially for aero-engines as well as the need for better forecast information of volcanic ash clouds for aviation. The aviation industry paid little attention to the hazards of ash clouds before the 1991 VEI6 Pinatubo eruption caused further 17 encounters. Only after that event, the International Civil Aviation Organization (ICAO), an agency of the United Nations and managed by International Airways Volcano Watch Operations Group (IAVWOPSG), decided to set up nine Volcanic Ash Advisory Centres (VAAC) for different areas of the global airspace. The VAACs provide observations and forecasts and issue Volcanic Ash Advisories (VAA) about the temporal and spatial distribution of atmospheric volcanic ash clouds to inform decision makers and aircraft operators.

In the first years, the VAACs decided to have a strict principle of “Volcanic ash encounters shall be avoided (do not operate in visible and discernible ash)” following the guidance of the European Space Agency. The IAVWOPSG defined visible ash as “volcanic ash observed by the human eye” (quantitative definition) and discernible ash as “volcanic ash detected by defined impacts on/in aircraft/engine or by agreed in-situ and/or remote-sensing techniques”. Interpretations for such cases are not always straightforward as volcanic ash is not visible during the night or if mixed in water clouds. Both parameters are also not linked to a specific concentration level.

However, after volcanic ash emissions from the 2010 Eyjafjallajökull eruption, the national aviation authorities, along with EASA and the VAACs, discussed possible safe to flight concentration levels. On 21st April 2010, the engine manufacturers agreed to a concentration level of up to 2 mg/m$^3$. Shortly after, on the 10th May 2010, the European regulators (EASA and national authorities) also agreed to a formal procedure for operating in volcanic ash based on the concentration limits of 2 and 4 mg/m$^3$. After controversial debates about the ash concentration, the engine manufacturers declared that operators could fly in any
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Table 2.1: Most notable aircraft encounters with volcanic ash clouds including distance between eruption and encounter and resulting engine failures (adapted from Giehl et al. (2016))

<table>
<thead>
<tr>
<th>Volcano</th>
<th>Ash Composition</th>
<th>Year</th>
<th>Distance (km)</th>
<th>Damage to engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt St. Helens</td>
<td>Dacitic</td>
<td>1980</td>
<td>100-480</td>
<td>Accumulation of ash and glass on high-pressure nozzle guide vanes (Kim et al., 1993)</td>
</tr>
<tr>
<td>Mt Galunggung</td>
<td>Basaltic</td>
<td>1982</td>
<td>150-200</td>
<td>Substantial accumulation of ash and glass on high-pressure nozzle guide vanes (Taylor and Lichte, 1980)</td>
</tr>
<tr>
<td>Soputan</td>
<td>Basalt</td>
<td>1985</td>
<td>80</td>
<td>Observations of St Elmo’s fire and dust in the cabin. 747 had all four engines damaged (Guffanti et al., 2010)</td>
</tr>
<tr>
<td>Redoubt</td>
<td>Andesite</td>
<td>1989</td>
<td>150-300</td>
<td>Accumulation of ash and glass on high-pressure nozzle guide vanes (Chambers, 1985)</td>
</tr>
<tr>
<td>Mt Pinatubo</td>
<td>Dacitic</td>
<td>1991</td>
<td>200-1000</td>
<td>Substantial accumulation of ash and glass on high-pressure nozzle guide vanes (Casadevall et al., 1995)</td>
</tr>
<tr>
<td>Hekla</td>
<td>Andesite</td>
<td>2000</td>
<td>1300</td>
<td>Abrasion of compressor blades, blocked cooling holes and coatings on blades (Casadevall et al., 1994)</td>
</tr>
<tr>
<td>Kelud</td>
<td>Basalt-Andesite</td>
<td>2014</td>
<td>240</td>
<td>Successful restart of engines after exposure to ash and glass (Casadevall et al., 2010)</td>
</tr>
<tr>
<td>Volcán de Tungurahua</td>
<td>Basalt</td>
<td>2015</td>
<td>200</td>
<td>Successful restart of engines after exposure to ash and glass (Casadevall et al., 2010)</td>
</tr>
</tbody>
</table>

* The distance range corresponds to multiple encounters during the same eruption.
forecast concentration (if the airspace is open), but need to avoid ‘visible’ ash. At the same time, the VAACs changed their forecast products from a simple outline of the cloud location (polygons) to define zones of ash concentrations (0.2 – 2 mg/m$^3$, 2-4 mg/m$^3$ and > 4 mg/m$^3$) calculated by atmospheric dispersion models. In 2015, five years after the Eyjafjallajökull eruption, EASA published new engine level regulations that stated that “the susceptibility of turbine engine features to the effects of volcanic cloud hazards must be established” (EASA, 2015). After years of research, the engine manufacturers concluded that engine system degradation, damage, and failure mechanisms are not caused by volcanic ash concentration alone, but depend to a great extent on their volcanic ash exposure dosage (i.e., total exposure concentration integrated over time of exposure) (Clarkson et al., 2016). Finally, in 2017 Rolls-Royce stated that they clear operation at a dosage of 14.4 g·s /m$^3$, but no more than a mass concentration of 4 mg/m$^3$.

To understand how volcanic ash particle impact aero-engines, it is essential to understand how the engines work. Civil aero-engines (Figure 2.5) are turboshaft driven engines that consist of multiple sections. The first section is the fan section, which produces approximately 70 to 80 % of the overall engine thrust with air mass flowrates up to 500 kg/s. Depending on the bypass flow to core flow ratio (between 5:1 to 10:1) 10 – 20 % of the air is sucked into the core section of the engine (Koff, 2004; Walsh, 2004). After passing the turbofan, the incoming air is first compressed in the compressor section to very high pressures before the compressed air is mixed and ignited with fuel in the combustion chamber. The expansion energy of this reaction is used to drive the turbine section that in turn powers the compressor and the fan section. As a result, air passing through the different engine sections is susceptible to significant temperature gradients as shown in Figure 2.6. For a cruise flight condition at 35000 ft (∼ 11 km), the air is warmed up from atmospheric conditions at around -50°C to ∼ 500°C at the end of the compressor section. Once arrived in the combustion chamber the air is heated up even more to temperatures between 1200°C and 1575°C (older and modern engine design, respectively), temperatures that are hotter than the melting temperature of turbine vanes and blades (nickel superalloy with melting points around 1270°C). The components are designed for a long component life with internal cooling passages and thermal barrier coatings. The cooling system feeds air from the high-pressure compressor section through small holes in turbine blades and vanes that distribute the air around the aerofoils and keeps them cool (compared to surrounding air). Thin ceramic thermal barrier coatings offer additional heat management to the metallic vane and blade surfaces as they insulate components from large and prolonged heat loads (Clarke and Phillpot, 2005). Both the cooling systems and the coatings allow for higher operating temperatures, reduce thermal exposure, oxidation and thermal fatigue of rotating and structural components, which all leads to an extended lifetime of the components. In fact, low concentrations of volcanic ash can already lead to significant damage that is very costly to repair (Grindle and Burcham, 2002). Once volcanic ash particles enter
Figure 2.5.: Example of temperature profile through engine cross section for a modern aero-engine including the turbofan, the engine section inside the engine core, i.e., compressor, combustor, and (high-pressure) turbine, and the bypass region. The grey shaded area represents the glass transition temperature of volcanic ash.

The engine core, they have the potential to rapidly cause damage to engine components, which might lead to a loss of operability, reduction of engine performance and to a reduced component lifetime (Wood et al., 2017). Primary impacts are fan and compressor blade erosion, accretion of molten material on combustor and turbine components (hot section) as well as contamination of air, oil, fuel systems and all supporting systems such as pneumatic, hydraulic, electric and electronic systems (Carter, 2005; Chen and Zhao, 2015).

Erosion is caused by particle interactions with fan and compressor blades. The non-spherical and angular shape of volcanic ash particles (see Paper II) make them highly abrasive (Brown et al., 1981; Wang and Yang, 2008; Ghenaiet, 2012) and during their transission through the engine, they erode forward facing surfaces as well as remove material at the tips of rotor blades (tip clearance growth). The removal of material (see Figure 2.6) leads to a loss of compression efficiency that results in a loss of the overall engine surge margin (Tabakoff et al., 1990, 1991; Carter, 2005; Corsini et al., 2012). The rate of erosion is highly dependent on factors such as material properties (hardness of blades and particles), exposure time, impact speed and the incident angle of the particles, as well as
2.5 Impact of volcanic ash on aviation and aero engines

Figure 2.6.: Compressor section with incoming volcanic ash particles and resulting erosion effects as illustrated by the yellow lines at leading edges of blades (left) and combustion and high-pressure turbine section with illustrated solidified volcanic ash particles on high-pressure nozzle guide vanes after British Airways encounter, 1982 (right) (courtesy of Rolls-Royce) (Przedpelski and Casadevall, 1994).

their size, where their chemical and mineralogical composition determines the hardness of the particles. All these mechanisms lead to a reduced lifetime of fan and compressor blades.

After passing the compressor section and entering the engine’s hot section, incoming volcanic ash particles undergo a phase transition (Kueppers et al., 2014; Song et al., 2014) from their solid into a more semi-solid viscous phase based on their lower pre-melting softening temperature (also known as the transition temperature, \(T_g\)) compared to the operating temperature of the engine (1200-1575°C). The transition and melting temperature can have hundreds of degrees differences for different volcanic ash samples due to their chemical composition and glass content (Dingwell and Webb, 1989). For the main igneous rock types (Basalt to Rhyolite) the transition temperature varies from 900°C to \(\sim\)1000°C. However, it is well known that the transition temperature is not only dependent on the chemical composition of the samples but also on the mineral and glass content, which has a more significant effect. The higher the glass content of the samples, the higher is the chance of sticking on surfaces (Dean et al., 2016; Giehl et al., 2016). As a consequence, ash particles deform while they become soft (Przedpelski and Casadevall, 1994; Song et al., 2016), or even melt and adhere onto fuel spray nozzles and high-pressure nozzle guide vanes (HP-NGVs) (Przedpelski and Casadevall, 1994; Dunn et al., 1996; Grindle and Burcham, 2002; Dunn, 2012; Davison and Rutke, 2013). The semi-soft or molten volcanic ash material then re-solidifies on these materials, due to their lower metal temperature compared to the particle and air temperature (cooled materials). While accretion of volcanic ash on fuel spray nozzles leads to fuel starvation, HP-NGV accretion leads to clogging of cooling holes (Kim et al., 1993; Wylie et al., 2016), to chemical reaction (corrosion) or infiltrations of the thermal-barrier coating layer around the vanes (Clarke and Phillpot, 2005; Drexler et al.,
2011; Mechnich et al., 2011; Shinozaki and Clyne, 2012; Vidal-Setif et al., 2012; Schulz and Braue, 2013) and to a material build-up on the vanes. Song et al. (2016) found that wetting and corrosion of the material already happens at a temperature between 900°C and 1100°C and adverse effects on thermal insulation, and thermal cycling behaviour was observed (Mechnich et al., 2011). Additionally, cooling air, which is taken from the high-pressure compressor (HPC) section, transports solid ash particles to the cold side of air-cooled turbine components (vanes and blades) and contributes to cooling hole blockages as they might melt when they are exposed to extremely turbine high temperatures. The build-up of material on the turbine components leads to overheating of components in the absence of cooling air, an aerodynamic reduction or blockage of the internal throat area between vane airfoils, causing loss of main annulus flow capacity and loss of critical surge margins (loss of controllable thrust). The latter effect has been the cause of KLM876 and the BA9 flights as can be seen in Figure 2.6 (right panel).

Engine system degradation, damage, and failure mechanisms (volcanic ash susceptibility) depend to a great extent on three key aspects: (1) engine specific properties, (2) volcanic ash particle properties and (3) exposure dose. Engine properties mainly depend on the design of the engine (i.e., bleed systems, pressure ratios, core temperatures, cooling and combustion technology), the condition of the engine (i.e., residual surge and turbine gas temperature margin) and the flight condition during the encounter (i.e., engine thrust at take-off, climb, cruise and descent, idle). In addition to the engine design, physical and chemical properties of volcanic ash particles including their abrasiveness, pre-melting softening temperature and viscosity (Song et al., 2016) are essential for the various damage mechanisms. Dunn et al. (2012) reported that volcanic ash characterisation and classification of historical eruptions are needed so that they can be applied to future encounters to relate ash types and its concentration to engine and component damage (Paper II). Numerical and laboratory-based experiments with the focus on an understanding of processes that cause damage inside the engine have shown that the ash melting, adhesion, and wetting processes are always a function of volcanic ash composition, crystal/glass ratio, operating temperature of the engine (i.e., particle and metal temperature) and velocity of the molten material (Shinozaki and Clyne, 2012; Dean et al., 2016; Giehl et al., 2016; Taltavull et al., 2016). For example, knowledge about the alkali metal content of a sample, i.e., Ca, K, Na, can inform about the stickiness of ash in the engines’ hot section. Generally, the severity of engine damage and performance deterioration is a function of ash type and concentration. Ash types with a low SiO₂ content, e.g. Basaltic and Basaltic-Andesite ash, and a high glass content have the highest adhesion efficiency and thus the highest potential accumulation rate of material on engine surfaces due to their lower glass transition and melting temperatures as well as their lower viscosities at high temperatures. In contrast, ash types with a high SiO₂ content, e.g. Dacitic and Rhyolitic ash types, have slight melting temperatures and higher viscosities at higher temperatures and will therefore not stick as easy to surfaces as the Basaltic ash types.
2.6 Measurements and modelling of volcanic ash

(Clarkson et al., 2016; Taltavull et al., 2016). Experiments by Dean et al. (2016) and Giehl et al. (2016) have shown that ash with a low SiO$_2$ content are almost fully molten at relevant engine temperatures and easily stick to blade surfaces. This would lead to a material build up over time (function of exposure concentration and time), including blockage of cooling holes and turbine throat areas, whereas high SiO$_2$ content samples still remain in shape (almost no phase change), which leads to a rebound of particles after hitting component surfaces.

The last aspect is the particle concentration and the overall exposure dose (Watson, 2015; Clarkson et al., 2016). The engine dose is defined as the time integral of atmospheric volcanic ash mass concentration over the duration inside the cloud (Prata et al., 2018). The dose is the most relevant parameter when it comes to engine damage meaning that the accumulation rate increases as a function of ash mass concentration. To calculate the dose, atmospheric data of the spatial and temporal location of the ash clouds, as well as their concentration, are combined with flight data (i.e., flight phase, condition). The data are usually obtained by satellite, ground-based and airborne measurements as well as dispersion models (often also a combination of them) and flight route data. However, the exposure dose that is relevant for the engine core section susceptibility is not the total mass of volcanic ash the engine is exposed to (i.e., atmospheric concentration). One of the main reasons for this is that the fan imposes centrifuging effect on the ash particles which significantly influences the ash concentration going into the engine core section. While engine damage mechanisms and atmospheric volcanic ash particles have been studied extensively, only a small amount of information exists on the influence of the turbofan on the ingestion of particles into the engine core section (Tabakoff et al., 1991; Weaver et al., 1996) (Paper I). Assuming an atmospheric ash concentration of 4 mg/m$^3$ (upper ‘safe to fly’ ash limit, EASA), the core airflow can potentially transport up to 1 kg of ash within 15 minutes into the core section of the engine.

2.6. Measurements and modelling of volcanic ash

Volcanic ash cloud measurements and modelling are both vital to track volcanic ash cloud movements and to calculate ash mass loadings for assessing their impacts, particularly for the mitigation of aviation hazards (Prata and Rose, 2015; Clarisse and Prata, 2016). Measurements are used to locate airborne volcanic ash in real time and to give information about the spatial and temporal distribution in the atmosphere. Measurements sensors operate at different spectral resolutions, such as in the ultraviolet (UV), visible (VIS), near-infrared (NIR) and infrared (IR) wavelength range and are either ground-based, airborne or spaceborne sensors. An extensive overview of the most used instruments for volcanic ash particle tracking was published by Prata et al. (2013); Prata and Prata (2015); Carn and
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Figure 2.7: Satellite image of the 2010 Eyjafjallajökull eruption cloud (13th May 2010) retrieved assuming andesitic ash (a/c), obsidian ash (rhyolitic glass) (b/f) (Pollack et al., 1973), mineral dust (c/g) (Balkanski et al., 2007) and volcanic dust (d and h) (Volz, 1973). Panels a-d show the ash height and e-h the ash column load (Modified from Francis et al. (2012)).

Krotkov (2016). Common measurement sensors are based on scattering, absorption and transmission of light by particles in the atmosphere. Each of the radiative transfer and light detection algorithms have their limitations, and they all rely on accurate and quantitative input parameter. Assumptions of these parameters can introduce large uncertainties in calculations of the atmospheric dispersion or mass concentrations as these properties can differ substantially from reality (Grainger et al., 2013). To minimise uncertainties more detailed and interrelated characterisation of volcanic ash properties is needed (Rocha-Lima et al., 2014) (Paper II). The most significant limitations are based on assumptions about optical properties, i.e., complex refractive index, particle shape, the presence of water or ice in the atmosphere and total ash cloud thickness. For instance, the assumption of a spherical particle can lead to an underestimation of the mass loadings by \(\sim 30\%\) (Kylling et al., 2014) and up to \(\sim 40\%\) (Corradini et al., 2008). Water or ice in ash clouds can lead to a misinterpretation of the ash cloud height and ash thickness (Rose et al., 1995; Kylling, 2015) and assumptions of the optical properties lead to an under- or overestimation of the particles size, and therefore to an under- or overestimation of the particle distribution and ultimately the mass concentration. All limitations combined lead to an insufficient detection of the ash clouds, which is especially problematic for aviation operations as they depend on reliable information to relate atmospheric concentrations to safe-to-fly operations and to damage assessment of components.
As an example, Figure 2.7 shows satellite images of the 2010 Eyjafjallajökull eruption cloud (13th May 2010) (Francis et al., 2012). The different subplots show the ash height (a-d) and column loading (e-h), all measured and calculated using optical properties that are based on andesite ash (a/e), rhyolite ash (b/f), mineral dust (c/g) and volcanic dust (d/h). It can be seen that the overall shape of the ash cloud is in all cases similar, but areas with smaller concentrations can appear smaller. Analysing the ash height and the ash column load, it is noticeable that the retrievals are extremely sensitive to their input parameters. Knowing that the ash type of the Eyjafjallajökull ash was reported to be andesite (Francis et al., 2012), both the column height and column loading can be calculated to be up to 2-3 times higher than the real values by using the wrong input values. Paper II investigates the optical properties as a function of chemical compositions in more detail.

Atmospheric transport and dispersion models are used to monitor and forecast the transport of volcanic ash particles in space and time. They are based on a full description of the advection-diffusion sedimentation equation (Costa et al., 2006) and use meteorological data from numerical weather prediction models (e.g. from the European Centre for Medium-Range Weather Forecasts) as the underlying input. These model are either Eulerian or Lagrangian tracking models. Eulerian models calculate ash at fixed locations by 3D fluxes through grid boxes, e.g. Fall3D (Folch et al., 2009), Ash3D (Schwaiger et al., 2012) or the eEMEP model (Steensen et al., 2017). On the other hand, Lagrangian models compute the trajectories of an ensemble of particles describing the transport and diffusion of particles in the atmosphere (Stohl et al., 1998). Examples for Lagrangian particle transport and dispersion models are the NAME model (Numerical Atmospheric Dispersion Modelling Environment) used by the UK met office and the VAAC London (Jones et al., 2007), the HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory) used by the Washington and Anchorage VAAC (Draxler and Hess, 1998) or FLEXPART (FLEXible PARTicle dispersion model) (Stohl et al., 2005). As already mentioned, atmospheric transport and dispersion models are used by the different VAACs to monitor and forecast volcanic ash clouds, but the volcanic ash cloud output strongly depends on modelling inputs, which all have their uncertainties. These inputs are parameters such as time series of 3-dimensional meteorological fields, which describes the state and evolution of the atmosphere, volcanic ash physical properties, e.g. the size distribution of ash particles and their mass densities, removal processes of particles and the emission source term.

The source term is expressed by the mass eruption rate that is traditionally based on the relationship to the plume height (Mastin et al., 2009). However, this does not account for wind conditions or the atmospheric humidity or changing eruption conditions, and often the height and the material density can be wrong. A recent comparison by Costa et al. (2016) was made using nine plume models, and they concluded that for weak plumes a simplified 1D model is adequate to resolve the behaviour of the plume, but that there is a need to improve volcanic plume models for strong plumes. The mass eruption rate can also be
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**Figure 2.8.** VAAC forecast of volcanic ash after the 2010 Eyjafjallajökull eruption following an old forecast output approach (left) and a new output approach (right).

calculated using satellite images, where the cloud height can be measured and compared with theoretical curves (Van Eaton et al., 2016).

Another source of uncertainties is removal processes. Gravitational settling of volcanic ash particles is either realised by setting a fixed size dependent sedimentation velocity (NAME) or is a function of air density and temperature which determine the viscosity and therefore settling (FLEXPART). Dry deposition, i.e. through particle impaction and diffusion with the earth surface, is treated using a resistance method to estimate a deposition velocity. Wet deposition processes depend on the precipitation intensity and are determined by species-specific scavenging coefficients (Kristiansen et al., 2012). A few studies have also investigated the effect of aggregation in dispersion and transport models (Folch, 2012), but such an aggregation scheme is not yet included in most of the models.

In addition to the traditional transport and dispersion models, inversion schemes have been developed, e.g. (Stohl et al., 2011), to improve the eruption source term. The method uses secondary information from measurement systems (satellite, ground-based or in-situ), to compare modelled plume concentrations to observational data (ash column loadings). This approach results in a new source term description that can be used to restart the model dispersion calculations. Operational VAAC model forecasts are routinely validated and verified against available observations and compared to model outputs from the other VAACs (Dacre et al., 2013).

Since the 2010 Eyjafjallajökull eruption, the volcanic ash advisory centres (VAACs) have changed their model outputs to quantitative products (Figure 2.8, right). Before 2010, they simply outlined the dimensions of the ash cloud with no information about the concentration (Figure 2.8, left). After the 2010 eruption, the London VAAC (here an example from 17th May 2010) changed their rules, and defined zones of defined ash concentrations (0.2 – 2 mg/m$^3$ in cyan, 2 – 4 mg/m$^3$ in grey and above 4 mg/m$^3$ in red).
3 : Methodology

This chapter gives a short overview of the models and measurements techniques used in this PhD thesis to study the transport of volcanic ash from the atmosphere into aero-engines, to characterise volcanic ash particle properties, and to measure airborne and sedimented volcanic ash samples. The chapter first describes the numerical model principle used in Paper I, particle characterisation instruments used in Paper II, and the measurement and calibration techniques used in Paper III.

3.1. Modelling

Aero-engine experiments are complex and expensive to run, especially when complete engines are to be used. Therefore, analytical tools such as computational fluid dynamics models are employed to investigate and understand specific problems such as the ingestion of volcanic ash particles into engines.

The used numerical fluid dynamics particle tracking model (Star-CCM+) was developed and designed for solving multidisciplinary problems in both fluid and solid continuum mechanics and was set up to model the interaction of volcanic ash particles with the fan surface and to model the ingestion of particles into the engine core section. For this, a high-bypass ratio gas-turbine engine design, representative of many related engine types, was first discretized into a numerical mesh before numerical fluid dynamics experiments were performed for two different altitudes (10000 and 35000 ft) and three different engine flight conditions (climb, cruise, descent). The altitudes were chosen as most of the encounters, described in Section 2.5, occurred in these altitudes. Furthermore, the investigated flight conditions are those that are most likely for a volcanic ash cloud encounter.

The calculations were solved by a two-step procedure. The first step involved the calculation of the 3D steady-state fluid flow. In these calculations, the governing equations for the conservation of mass, momentum, and energy were solved simultaneously using an implicit coupled flow and energy algorithm including a two-equation turbulence model. The thermodynamic relationships of the conservation equations were realised by the use of the ideal gas law, whereas the rotation of the fan was realised using a moving reference frame (MRF) approach. In this approach, the rotating parts (i.e., the fan and the spinner) were captured in a frame, which rotates relatively to the stationary frame used for the non-rotating parts and
transfers circumferentially averaged flow properties across the frame interface. This allows the transfer of mass, momentum, energy and other conserved quantities from one frame into the other.

In a second step, a stochastic Lagrangian particle-tracking model was used for the calculation of volcanic ash particle trajectories. This model is based on the translational force balance and rotational momentum balance of volcanic ash particles and also considers turbulent velocity fluctuations as the particles move through the engine. The translational force balance was calculated as the particle acceleration \( \frac{d}{dt} \frac{dx_p}{dt} \), where \( x_p \) is the particle position described as a function of particle velocity \( u_p \) and time \( t \), and the sum of the main external forces \( f_{p,i} = F/m_p \) acting on the particles

\[
\frac{d}{dt} u_p = \sum f_{p,i},
\]

where \( m_p = \rho_p D_p^3 \pi / 6 \) is the mass of a particle (\( \rho_p \) is the particle density and \( D_p \) the particle diameter). \( f_{p,i} \) represents all external forces acting on the particle. During the particle transport in the surrounding gas-phase the rotational (angular) momentum is transported by the particle-fluid interface that is defined as the angular velocity of the particle \( \Omega_p \) and the torque from the gas-phase acting on the particle \( t_{p,g} \)

\[
\frac{d}{dt} \Omega_p = t_{p,g},
\]

The exerted torque, \( t_{p,g} = \frac{\mu_g D_p^3 C_R \Omega_p Re_R}{64 \pi \rho_p} \), was calculated using the drag coefficient of rotation \( C_R \) that depends on the particle rotational Reynolds number \( (Re_R) \), the particle fluid rotation velocity \( \Omega_p \), and the moment of inertia of a spherical particle \( (I_p = m_p D_p^2 / 10) \) (Rubinow and Keller, 1961). The turbulent velocity fluctuations (turbulent local disturbances, i.e. eddies, to the Reynolds-averaged gas-phase flow field) were calculated using a discrete random walk (DRW) model (Gosman and Ioannides, 1983), where the influence of instantaneous turbulent velocity fluctuations changes the particle drag, as the particle movement increases with decreasing particle Stokes number (defined as the characteristic response time of the fluid divided by the characteristic response time of the particle.)

**Particle properties and wall treatment**

The particles in the particle tracking study were set to be spherical, rigid and internally homogeneous solid particles with a constant mass density of \( \rho_p = 2.7 \text{ g/cm}^3 \), representing the most frequent volcanic ash type (andesitic volcanic ash analysed in Paper II). The particle-fan interaction was realised using a particle rebound (or bounce-off) wall collision model that assumed an ideal and smooth fan blade surface. The momentum loss after a particle-wall interaction is described as the ratio of the particle velocity before and after impact, where the particles are assumed to have a perfect elastic response, meaning that
the particles bounce back (energy transfer without losses) into the domain and do not break up after impact. The assumptions are acceptable as currently no volcanic ash experimental data of restitutions coefficients and particle break-up distributions after impact are available. Inelastic collision might have an effect on the results, but the difference between perfect elastic and inelastic particle behaviour is unknown. Another assumption is the use of a constant drag coefficient \( C_D = 0.44 \), which is based on the fact that the Reynolds numbers are sufficiently large \( Re = 1000 \) for inertial effects (Newton’s regime) to dominate viscous effects, which leads to the drag coefficient to become independent of the Reynolds number.

**Calculation of mass concentration inside the engine core section**

Analysis of the interactions between the volcanic ash particles and the fan and the particle transport from the core flow into the bypass flow facilitated the investigation of the size-dependent volcanic ash particle number concentration reduction inside the core flow. To express the reduction of particles inside the engine core, a new core reduction factor was introduced

\[
\chi_c(D_p) = \frac{n(D_p)_i}{n(D_p)_c}
\]

(3.3)

that is defined as the particle size-dependent ratio of the initial particle number inside the core streamflow in front of the fan stage \( n(D_p)_i \) (i.e., in the ambient atmosphere) and after the fan stage, thus inside the engine core \( n(D_p)_c \). With this new factor the mass concentration inside the engine core section can be calculated following the following equation,

\[
M_{p,\text{core}} = \int_{D_{p,\text{min}}}^{D_{p,\text{max}}} \rho_p D_p^3 \pi \left( \frac{n(D_p)_i}{\chi_c(D_p)} \right) dD_p
\]

(3.4)

where the particle mass of a single particle \( m_p = \rho_p D_p^3 \pi / 6 \) is multiplied by the total number of ambient particles of a given particle size in the size range between \( D_{p,\text{min}} = 1 \mu m \) and \( D_{p,\text{max}} = 100 \mu m \) and divided by the reduction factor. A full description of the equations and the factors are given in Paper I.
3.2. Measurements

3.2.1. Physicochemical and optical characterisation

Laboratory-based measurements of volcanic ash samples were used to investigate their physicochemical and optical properties. The following sub-section gives a short overview of the used ash samples and the main analytical methods. For this study, a total of nine different measurement systems and analytical methods were used. A full description is given in Paper II.

Volcanic Ash Samples
For the investigation of the microphysical, chemical and optical properties, nine volcanic ash samples from different volcanoes and eruptions were selected (Table 3.1). The selection of the samples was based on (a) the wide range of silica contents, (b) their origin from explosive (Volcanic Explosivity Index \( \leq 5 \)) eruptions with a high content of fine ash particles and (c) the fact that the selected eruptions all had a large impact on the society (i.e., on infrastructures and aviation).

Chemical properties
To measure the chemical composition, including the glass content, three different measurement principles and techniques were used. The chemical characterisation of volcanic ash particles is vital for other parameters such as the mass density, optical properties and thermal properties. The bulk material compositions were analysed using field-emission gun scanning electron microscopy (FEG-SEM) with an integrated energy dispersive spectrometer (EDS). The elemental composition was recorded with an EDS micrometre-sized beam allowing determination of average compositions of the total cross-section area of particles. The resulting elemental data of each component were first converted into weight percent of the corresponding oxides (oxide wt. %) and then normalised (processing option: Oxygen by stoichiometry). The measurement of the bulk chemical composition was performed in Paper II. The surface material compositions were analysed using an X-ray photoelectron spectroscopy (XPS). With XPS measurements, the uppermost 2-10 nm of the sample surface was analysed using a monochromatic X-ray source. Additionally, using an optical microscope equipped with light polarisation and image capture software, the glass and crystalline component phases were measured following a technique introduced by McCrone et al. (1978). The three techniques combined give a representative overview of the overall composition of the nine ash samples.
Table 3.1.: Overview of investigated volcanic ash types, including information about their tectonic setting, the VEI of the eruption, the plume type as well as the igneous rock classification.

<table>
<thead>
<tr>
<th>Volcanic ash sample</th>
<th>Eruption date</th>
<th>Tectonic setting</th>
<th>VEI</th>
<th>Eruption Type</th>
<th>Plume type</th>
<th>Igneous rock type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grimsvotn, Iceland</td>
<td>May 2011</td>
<td>Divergence zone</td>
<td>4</td>
<td>Explosive, Phreatomagmatic</td>
<td>Umbrella cloud</td>
<td>Basalt</td>
</tr>
<tr>
<td>Mt. Kelud, Indonesia</td>
<td>February 2014</td>
<td>Subduction zone</td>
<td>4</td>
<td>Explosive, Sub-plinian</td>
<td>Umbrella cloud</td>
<td>Basalt-Andesite</td>
</tr>
<tr>
<td>Eyjafjallajökull, Iceland</td>
<td>April-June 2010</td>
<td>Divergence zone</td>
<td>4</td>
<td>Explosive, Phreatomagmatic</td>
<td>Bend plume</td>
<td>Andesite</td>
</tr>
<tr>
<td>Mt. Spurr, US</td>
<td>September 1992</td>
<td>Subduction zone</td>
<td>4</td>
<td>Explosive, Sub-plinian, Dome collapse</td>
<td>Umbrella cloud, Co-Ignimbrite plume</td>
<td>Andesite</td>
</tr>
<tr>
<td>Mt. Sakurajima, Japan</td>
<td>August 2013</td>
<td>Subduction zone</td>
<td>-</td>
<td>Explosive, Vulcanian, Explosive, Plinian, Dome collapse</td>
<td>Bend plume</td>
<td>Andesite</td>
</tr>
<tr>
<td>Mt. St. Helens, US</td>
<td>May 1980</td>
<td>Subduction zone</td>
<td>5</td>
<td>Explosive, Plinian, Dome collapse</td>
<td>Umbrella cloud, Co-Ignimbrite plume</td>
<td>Dacite</td>
</tr>
<tr>
<td>Soufriere Hills, UK</td>
<td>February 2010</td>
<td>Subduction zone</td>
<td>-</td>
<td>Explosive, Sub-plinian, Dome collapse</td>
<td>Umbrella cloud, Co-Ignimbrite plume</td>
<td>Dacite</td>
</tr>
<tr>
<td>Mt. Redoubt, US</td>
<td>December 1989</td>
<td>Subduction zone</td>
<td>3</td>
<td>Phreatomagmatic, Dome collapse</td>
<td>Bend plume</td>
<td>Dacite</td>
</tr>
<tr>
<td>Chaiten, Chile</td>
<td>May 2008</td>
<td>Subduction zone</td>
<td>4</td>
<td>Explosive, Sub-plinian</td>
<td>Bend plume</td>
<td>Rhyolite</td>
</tr>
</tbody>
</table>
Methodology

Physical properties
The particle size and the complex shape were measured with an automated static particle imaging (ASPI) instrument (Malvern Instrument Morphologi G3) following the procedure introduced by Leibrandt and Le Pennec (2015). The ASPI is an optical analyser that characterises the size and morphology of particles on a two-dimensional projection area and provides reliable and reproducible particle information for a statistically significant number of particles with a low relative standard deviation on average values (< 0.2 %). I used two different microscope objective lenses, a 20x magnification objective lens for particles in size range between 1.8 - 100 $\mu m$ and a 5x magnification objective lens for the size range of 6.5 - 420 $\mu m$. The total number of individual particles measured for each ash sample was between $10^6$ and $10^7$ based on an initial sample volume. The light source was set to be diascopic, which means that the light shone from below the carrier unit to produce a sharp contrast between the dark ash particles and the light illuminated background. Based on the setup, the particle perimeter, the particle area, and the longest, intermediate and shortest length of a single particle were derived. Based on the measured parameters, the circle-equivalent particle diameter, the aspect ratio, the Cox circularity, and the Wilson shape parameter were calculated. Information about the different shape parameters are needed, for instance, for radiative transfer models when non-sphericity of the ash particles is considered (Kylling et al., 2014) or as one of the shape descriptors for estimating drag coefficients of non-spherical particles (Bagheri and Bonadonna, 2016a). In addition to the size and the shape of volcanic ash particles, we also determined the dense-rock equivalent mass density. We conducted direct measurements of the particle skeleton using Archimedean densitometry and additionally calculated the theoretical density based on mass fractions for the major oxides as obtained from the compositional analysis (EDS measurements) and crystalline volume data from Lange and Carmichael (1987).

Optical properties
The complex refractive index (RI), $N_\lambda = n_\lambda + i k_\lambda$, is a quantitative measure of the reflectance ($n_\lambda$), transmittance and absorption properties ($k_\lambda$) of a substance and is a function of the light wavelength ($\lambda$) and the chemical composition of the sample. Information about the RI is essential to relate optical measurement signals to particle information such as size (effective radius), size distribution and ultimately the ash mass concentration (see Section 3.2.2). Furthermore, the RI is needed in radiative transfer models for a quantification of the impact of volcanic ash on the Earth’s radiative budget. To determine the complex refractive index, we used a measurement-model combination. For determining the absorption properties, a double-beam UV/Vis/NIR spectro-photometer was used. The scattering properties were then calculated following a combination of a Sellmeier dispersion model (Weber, 2003) and a theoretical calculation of the refractive index from chemical composition data as described by Church and Johnson (1980). The obtained optical properties are in the wavelength range
3.2 Measurements

between $\lambda = 300$ and 1500 nm. The optical properties of the Eyjafjallajökull sample were used in Paper III for the calibration of the instrument.

3.2.2. In-situ measurements with an optical particle counter

For the airborne in-situ measurements of an artificially created ash cloud, but using real volcanic ash from the 2010 Eyjafjallajökull eruption (Paper III), an optical particle counter (OPC) was used. OPCs are laser-based instruments that measure particulates in the size range of 0.2 up to 50 $\mu m$ in real-time. They combine the principles of light scattering of small particles (they operate in the visible to near-infrared wavelength range) with single particle counting. By the interaction of a particle with the laser band, a light pulse travels in a specific size depended direction. A pin diode detects the scattered radiation signal from each particle and inverts the pulse height into a spherical equivalent diameter assuming a complex refractive index of the particle material (Heim et al., 2008).

In order to use OPCs for volcanic ash measurements, they need to be calibrated for the specific ash particle type. The basis for the calibration is that the pulse height signal is linear proportional to the scattering cross section ($C_{\text{sca}}$) of the particle. The scattering cross-section is the area where radiation will be scattered by particles and depends on the wavelength of the incident light ($\lambda$, linear polarized, monochromatic wave), the particle size, usually expressed as the dimensionless size parameter ($\alpha$, ratio of the circumference of the particle to the wavelength of light), and the complex refractive index. The scattering cross section is defined as the integral of the phase function,

$$
\sigma = \frac{\pi}{\lambda^2} \int_0^{2\pi} \int_0^\pi (|S_1(\theta)\lambda D_p m|^2 + |S_2(\theta)\lambda D_p m|^2) \sin(\theta) \omega(\theta \phi) d\theta d\phi \quad (3.5)
$$

where $\theta$ and $\phi$ represent the angles between the incident light and the scattering direction as well as the direction of the scattered radiation around the incident beam, $D_p$ is the particle diameter, $S1$ and $S2$ are the complex scattering amplitudes for two different directions, parallel and perpendicular to the scattering plane and $\omega_{\text{optics}}$ is the device-specific optical weight function (Rosenberg et al., 2012). The two different directions are referred to the same scattering plane that represents the reference system.

$$
S_1(\mu) = \sum_{n=1}^{N} \frac{2n+1}{n(n+1)} [a_n \pi_n(\mu) + b_n \tau_n(\mu)] \quad (3.6)
$$

$$
S_2(\mu) = \sum_{n=1}^{N} \frac{2n+1}{n(n+1)} [a_n \tau_n(\mu) + b_n \pi_n(\mu)] \quad (3.7)
$$

In those equations, $\mu$ is the cosine of the instrument’s scattering angle, $\tau_n(\mu)$ is the Legendre polynomial, and $a_n$ and $b_n$ the Mie coefficients that depend on the complex refractive index.
$N_\lambda = n_\lambda + i k_\lambda$. Knowledge of the complex refractive index is essential as different volcanic ash types have different scattering and absorption properties as shown in Paper II. For example, basaltic ash particles have the highest scattering as well as absorption properties, whereas rhyolitic ash particles have the lowest scattering and absorption properties. For the analysis of the airborne experiment (Paper III), the complex refractive index and mass density of ash from the 2010 Eyjafjallajökull eruption was measured (Paper II) and applied in a Mie calibration code (Wiscombe, 1980) to calibrate the instrument. The ash type had an andesitic composition, with a density of 2.81 g/cm$^3$ and a complex refractive index of $1.552 \pm 0.0016i$ (Paper II). Thus, by knowing the scattering cross-section and the complex refractive index, the particle diameter can be calculated (Figure 3.1). I applied the calibration functions to the OPC instrument that I used during the in-situ measurements of the artificial ash cloud experiment (Paper III).

![Figure 3.1.](image)

**Figure 3.1.** Conversion of three exemplary particle scattering cross-sections, detected by the optical particle counter, into material dependent particle size using a material specific calibration function. The function was calculated using the complex refractive index values for Eyjafjallajökull measured in Paper II.
4 : Summaries of papers

4.1. Paper I

Simulation of volcanic ash ingestion by a large turbofan aero-engine: Particle-fan interactions


Objective
Investigate the effect of the engine fan on ingested volcanic ash particles into an aero-engine to relate ash concentrations in the ambient atmosphere to concentrations inside the engine core section.

Summary
In this paper, particle-fan interactions and resulting engine core reduction factors for volcanic ash particles entering the engine core were calculated using numerical computational fluid dynamics simulations including a Lagrangian particle-tracking algorithm. The simulations were carried out using a representative engine high-bypass gas-turbine engine design that powers current wide-body aircraft and for three different fan power conditions and two different flight altitudes. The parameters describing volcanic ash particles were based on published volcanic ash properties. The resulting size-dependent core reduction factors were first applied to generic particle probability density functions and then to volcanic ash concentration data of a real aircraft encounter, to calculate mass concentration reductions.

Main findings
- The particle-fan interaction experiments and thus the obtained engine core reduction factors (\(\chi_c\)), clearly showed that the fan acts like a particle separator and has a significant influence on the engine core exposure (core entry concentration and dosage). The interactions between volcanic ash particles and the fan resulted in a centrifuging of particles from the core stream flow into the bypass flow. The real engine core exposure is needed to relate concentrations within the engine core to damages of
components, where traditionally only atmospheric volcanic ash mass concentration data were considered.

- Particles < 2 µm did not often interact with the fan surfaces (probability < 5 %), but with increasing particle diameter the particle-fan interactions and the particle separation increased. Furthermore, the interaction is strongly dependent on the rotation speed of the fan, where the highest investigated fan power (i.e., 90 % of full power) resulted in a 100 % interaction probability for volcanic ash particles larger than 63 µm (upper size of the fine fraction of volcanic ash). Volcanic ash particles with the largest diameter (100 µm) and the highest fan power condition (high power) in this study resulted in a maximum core reduction factor of $\chi_c = 2.53$ at 35000 ft.

- Calculations of generic atmospheric volcanic ash mass concentration reductions after applying the core reduction factors showed a significant decrease of volcanic ash mass for particle size distributions with a mean diameter > 3 µm. Furthermore, the mass reduction showed the substantial impact of the fan on engine core exposure calculations (core entry exposure and dosage). The maximum potential particle mass concentration reduction was calculated to be up to $\sim 30 \%$ for a generic particle density function with a mean diameter of 16 µm. The calculations of the particle distribution also confirmed the mass reduction calculations of the real volcanic ash particle encounter (Mt. Kelud eruption 2014).

- Findings of this study are crucial for future volcanic ash encounters, to relate atmospheric volcanic ash mass concentrations and particle size distributions to potential damage inside the engine core section (i.e., erosion rates, tip clearance growth, melting behaviour of particles inside the combustion chamber and adhesion of volcanic ash material). Furthermore, the presented data can be used to calculate the engine core applicable dose rate, exposure and dosage needed to calculate their impact on the operability of aero engines and to assess their potential safety risk. Combined with calculations of atmospheric volcanic ash exposure and dosages along flight routes, this would allow judging the volcanic ash threat to engine cores much more reliably in the future.

**Author contribution**
I planned the CFD model setup, collected and implemented the engine geometries (inclusive the geometry manipulation and preparation) used in the numerical computational fluid dynamics calculations. I designed and conducted the numerical experiments, and processed the interaction, separation, generic particle distributions and the real aircraft encounter data. I generated all figures and wrote the publication with contributions from my co-authors.
4.2 Paper II - Physicochemical and optical properties of volcanic ash

4.2. Paper II

Reference dataset of volcanic ash physicochemical and optical properties


Objective

Analyse volcanic ash particle characteristics using a range of analytical methods and techniques to determine their physicochemical and optical properties to reduce uncertainties in model and observation inputs.

Summary

In this study, the physicochemical and optical properties of volcanic ash particles were measured using a range of analytical measurement techniques and theoretical methods. The measurements were carried out using a representative selection of volcanic ash samples of different volcanic eruption and different igneous rock types. The measured and calculated properties are also used in Paper III for measurement system calibration and thus for mass concentration calculations.

Main findings

- All investigated ash samples could be classified into igneous rock type groups according to their SiO$_2$ and total alkali contents that play a crucial role in governing the mass density and the complex refractive index. Thus, the nine volcanic ash samples cover a wide range of SiO$_2$ contents ranging from basalt (~50 wt % SiO$_2$) to rhyolite (~80 wt % SiO$_2$). Comparing the bulk composition with the composition of the particle surface (2 to 10 nm depth), we found - despite the overall similarities - also notable differences between the surface and bulk chemical composition. The ratios of the elements Ca, Na, Mg, and Fe showed slightly higher concentrations in the bulk material compared to the surface, whereas Si was enriched on the surface due to a potential dissolution of an external layer by corrosive mixed gaseous/aqueous fluids.

- The light microscopy measurement showed that the glass contents vary from the bulk SiO$_2$ content and we found that the glass content within each igneous rock group can vary significantly especially in the intermediate region (andesite to dacite).
Summaries of papers

- The particle morphology shows a systematic dependency on the particle size (in the size range $D_p < 100 \mu m$), and our findings were consistent over the entire sample set. The aspect ratio and the Wilson shape parameter showed no significant difference between fine and coarse ashes, whereas the Cox circularity (sphericity) showed significant differences. The overall shape parameters for the fine ash fraction are 0.71, 0.84, and 0.85 for the aspect ratio, the Cox circularity, and the Wilson shape parameter, respectively, and for the coarse ash fraction ($D_p > 63 \mu m$) corresponding values are 0.72, 0.74, and 0.84. This consistent pattern in the shape parameters can be used to parameterise the particle shape in ash transport and dispersion, climate, fluid dynamics or theoretical terminal velocity calculation models.

- The dense-rock equivalent (DRE) mass densities showed an explicit dependency on the individual chemical composition of each sample and decreased with increasing SiO2 content. Thus, the DRE mass density was found to be in the range from $\rho = 2.49 \pm 0.06$ g/cm$^3$ for rhyolitic ashes to $\rho = 2.98 \pm 0.04$ g/cm$^3$ for basaltic ashes.

- The complex refractive index over a broad wavelength range ($\lambda = 300$ to 1500 nm) was analysed for the first time for a comprehensive silica range and a high number of different ash samples. The complex refractive index showed an explicit dependency on the individual chemical composition of the samples, and especially on the SiO$_2$ content, shown, both in our data and comparable literature data. For the real part, $n_\lambda$, we found a decrease of values with increasing wavelength, where the ash with the highest SiO$_2$ content had the highest $n_\lambda$ value. For the imaginary part, $k_\lambda$, we found that the values increase with increasing wavelength, where basaltic, basaltic-andesitic, and andesitic showed stronger dependency on wavelength, due to a higher potential to absorb light.

- This data set will contribute to minimize uncertainties in the calculation and detection of ash clouds for future or historic volcanic eruptions even when only information about the magma composition is available.

Author contribution
I planned the measurements and assembled as well as prepared the volcanic ash particle samples. I conducted the physical, chemical and optical measurement with various instruments and processed all data. For the publication, I generated all figures and wrote the publication with contributions from the co-authors.
4.3. Paper III

Artificial cloud test confirms volcanic ash detection using infrared spectral imaging


**Objective**

Apply physicochemical and optical properties to in-situ volcanic ash measurements to improve measurement accuracy and to calculate atmospheric concentrations of a volcanic ash cloud.

**Summary**

In this airborne experiment, the ability to detect and quantify volcanic ash of an artificial volcanic ash cloud both remotely and in-situ were investigated using infrared spectral imaging and optical light scattering instruments. Three aircraft were used during the experiment; one carried the remote sensing instrument that measured the ash cloud remotely, one carrying the in-situ measurement instrument to measure inside the ash cloud and one for the release of volcanic ash particles. The used ash was very fine ash particles collected on Iceland after the Eyjafjallajökull eruption in 2010. For the first time, airborne remote detection of volcanic ash has been successfully demonstrated from a long-range flight test aircraft simultaneously with in-situ measurements of a second aircraft inside the ash cloud. In-situ measurements were vital to verify the remote sensing measurements and to indicate the extent and the concentration of the ash cloud during the experiments.

**Main findings (own contribution)**

- The optical particle counter instrument used to measure volcanic ash inside the artificial ash cloud was re-calibrated based on calculated and measured complex refractive index data of Eyjafjallajökull ash particles (Paper II, Figure 19 and Table 5).

- Based on the re-calibrated instrument, the uncertainties related to particle size distribution, as well as mass concentration calculations, were minimised.

- In-situ measurements were used to measure the vertical extent of the ash cloud by
Summaries of papers

ascending and descending out and in the ash cloud and the horizontal extent until negligible particle numbers were counted. They also showed that the ash cloud had a high heterogeneity.

- The optical particle counter calibration procedure can be used for future eruptions to have accurate atmospheric mass concentration data of volcanic ash.

Author contribution
I planned and coordinated the DA42 flights. I prepared the aircraft experiments, e.g. implementation of the optical particle counter measurement systems into aircraft and acquisition of in-situ data including satellite datalink into other aircraft. I participated in the experimental trials and conducted the in-situ particle measurements. I analysed, interpreted and plotted the measurement data and participated in the discussions and writing of the publication, i.e., measurement principle, experimental setup, data description and link to remote sensing sensor instrument.
5: Summary and Future Outlook

The PhD thesis had the aim to minimise volcanic ash uncertainties and limitations in observations and models that can lead to the development of improved products needed for a better hazard assessment on climate, health, the environment and especially on aero-engines. Two PhD thesis papers dealt with the physicochemical and optical characterisation of volcanic ash particles and how they are ingested into aero-engines. Use of particle property data was also shown in a study of in-situ detection of an artificial ash plume. This chapter summarises and discusses each of the primary objectives raised in the Introduction and gives an overall summary of the PhD work, before it finishes with an outlook about future research.

(a) Investigate the effect of the engine fan on ingested volcanic ash particles into an aero-engine and to relate ash concentrations in the ambient atmosphere to concentrations inside the engine core section.

The ingestion of volcanic ash particles into an aero-engine was investigated in Paper I, using a numerical computational fluid dynamics (CFD) and Lagrangian particle-tracking model. The model was set up to track volcanic ash particles during their transition from the atmosphere, into the engine, through the turbofan stage and into the engine core section. The most demanding task of this study was the setup of the particle-tracking model. While Lagrangian particle-tracking models are used in many applications, the presence of high-speed flows and shocks, in combination with fast rotating parts made it difficult to set up. I set up the model in a way, that can be easily adapted to other engines types and flight conditions, which could make it operational for future applications.

With my newly established particle-tracking model, it was possible to calculate the probability of particle-fan interactions and the reduction of particle number concentrations entering the engine core section. The calculations show the significant influence of the fan on ingested volcanic ash particles. Moreover, to demonstrate the effect of particle separation, the reduction factors were first applied to generic volcanic ash size distributions to quantify the particle reduction as a function of particle size, before they were applied to a real volcanic ash cloud encounter event (Mt. Kelud eruption 2014). For that the CFD particle tracking data were combined with dispersion and transport modelling data obtained using an atmospheric transport model. The results show how valuable numerical engine models are.
Summary and Future Outlook

in combination with atmospheric models to obtain engine core concentrations that are more accurate than the hitherto applied assumption that the engine core concentration is identical to the ambient atmospheric concentration. This improved knowledge will be crucial for future volcanic ash encounters, to relate atmospheric volcanic ash mass concentrations and particle size distributions to potential damage inside the engine core section. Furthermore, the presented data can be used to calculate the engine core applicable dose rate, exposure and/or dosage needed to calculate their impact on the operability of aero engines and to assess their potential safety risk. An essential aspect of this study is that the reduction factors are calculated for main flight altitudes and conditions and a representative volcanic ash type (Paper II). Thus, they can be applied for other eruptions and to atmospheric transport model calculations and measurement sensors.

(b) Analyse volcanic ash particle characteristics using a range of analytical methods and techniques to determine their physicochemical and optical properties to reduce uncertainties in model and observation inputs.

Of special interest to this PhD thesis was the characterisation of volcanic ash properties. Paper II investigated the different ash properties and summarised them in a comprehensive data set that can be used for various volcanic ash applications, such as transport and climate models, as well as measurement algorithms or in fluid dynamic models (Paper I). Moreover, Paper II is, to my knowledge the first and most comprehensive analysis of volcanic ash particle microphysical, chemical and optical characteristics for a wide range of silica contents. These properties are partly related and, thus, a significant contribution of Paper II is that all parameters were derived for the same ash samples, thus allowing consistency checks and allowing to investigate relationships between different particle parameters. For example, the paper shows that the particle shape is a function of particle size or that the mass density and the complex refractive indices are a function of the bulk chemistry of the ash particles. This also means that the dataset can be used for future eruptions even when only information about the magma type is available. Improved knowledge of the investigated properties is vital for more accurate detection and forecasting of volcanic ash clouds as well as the estimation of their potential impacts on climate, environment, aviation and human health. Thus, this dataset contributes to reducing the uncertainties in the measurements and simulation of ash clouds for future and past volcanic eruptions even when only information about the magma composition source is available.
(c) Apply physicochemical and optical properties to in-situ volcanic ash measurements to improve measurement accuracy and to calculate atmospheric concentrations of a volcanic ash cloud.

My PhD thesis contribution in Paper III was a rare opportunity to measure volcanic ash inside an artificially generated volcanic ash cloud with elevated concentrations (∼1 mg/m³) for a longer period (∼60 min). However, to achieve reliable information about the extent of the ash cloud as well as its concentrations, measurement systems needed to be calibrated to relate to a volcanic ash particle size, and ultimately to a mass concentration. For this, I calibrated the optical particle counter instrument employed during the airborne experiment by using the complex refractive index data obtained in Paper II. The deviation between the calibration for the real ash type and the standard (non-absorbing particles) resulted in a two times higher concentration for the ash type.

Overall summary of PhD thesis

Overall, my PhD thesis helped to minimise uncertainties and limitation in observations and models and to improve volcanic eruption hazard assessments. To assess a volcanic ash concentration that is causing damage inside an aircraft engine, it is crucial to consider reduction mechanisms, i.e., the fan separation factor (Paper I), as well as to get more accurate atmospheric volcanic ash cloud information. Accurate atmospheric data can only be achieved if model and detection algorithms are using reliable input parameters. These volcanic ash parameters were investigated and compiled with the new and comprehensive reference data set in Paper II. Moreover, the volcanic ash studies helped to quantify airborne measurement uncertainties (Paper III). Combining information from Paper I and Paper II in atmospheric transport models and measurement schemes will help to minimise uncertainties of detecting and modelling volcanic ash mass concentrations in the future.

Future Outlook

Numerical computational fluid dynamics modelling

The particle-tracking model is found to be valuable to model the ingestion of volcanic ash particles into an aero-engine, but further improvements in the numerical setup are desirable in future work. This should involve using different particle densities (taken from Paper II), a microphysical scheme that includes particle breakup after particle interactions with the fan surface, as well as the consideration of non-spherical particles (also taken from Paper II). However, I believe that the most significant influence on the particle separation is based on different fan designs. Therefore, it would be beneficial to investigate more and different engine geometries under various flight-relevant conditions (i.e., take off, idle, hold,
Volcanic ash particle characterisation
The reference dataset (Paper II) has proven its value in this PhD study for in-situ measurements sensors as well as to relate the volcanic ash properties to ground-based dust samples (Paper III and other studies). However, it would be good to include at least three samples in each igneous rock group to have a statistically more robust dataset and to add high total alkali content samples (e.g. Foidite, Phonolite) as well. Moreover, parameters such as the mineral compositions or thermal properties under static and dynamic considerations, i.e., the glass transition and the melting point of ash samples, would be valuable, especially for an aero-engine damage assessment. One of the most urgent parameters to investigate in the future would be the complex refractive index in the near-infrared to the infrared region as a large number of volcanic ash remote sensing instruments operate in this wavelength range.
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Part II.

Scientific publications
Paper I:

Simulation of volcanic ash ingestion by a large aero-engine: particle-fan interactions

Vogel, A., Durant, A. J., Cassiani, M., Clarkson, R. J., Slaby, M., Diplas, S., Krüger, K., and Stohl, A.

*Journal of Turbomachinery*, 2018, under review
Paper II: 

Reference data set of volcanic ash physicochemical and optical properties


Reference data set of volcanic ash physicochemical and optical properties

A. Vogel1,2, S. Diplas3,4, A. J. Durant2,5, A. S. Azar3, M. F. Sunding3, W. I. Rose5, A. Sytchkova6, C. Bonadonna7, K. Krüger2, and A. Stohl1

1Atmosphere and Climate Department, Norwegian Institute for Air Research, Kjeller, Norway, 2Department of Geoscience, Meteorology and Oceanography Section, University of Oslo, Oslo, Norway, 3SINTEF Materials and Chemistry, Oslo, Norway, 4Centre for Material Science and Nanotechnology, Department of Chemistry, University of Oslo, Oslo, Norway, 5Geological and Mining Engineering and Sciences, Michigan Technological University, Houghton, Michigan, USA, 6Energy Technologies Department, Optical Components Group, ENEA Casaccia C.R.E, Rome, Italy, 7Department of Earth Sciences, University of Geneva, Geneva, Switzerland

Abstract

Uncertainty in the physicochemical and optical properties of volcanic ash particles creates errors in the detection and modeling of volcanic ash clouds and in quantification of their potential impacts. In this study, we provide a data set that describes the physicochemical and optical properties of a representative selection of volcanic ash samples from nine different volcanic eruptions covering a wide range of silica contents (50–80 wt % SiO2). We measured and calculated parameters describing the physical (size distribution, complex shape, and dense-rock equivalent mass density), chemical (bulk and surface composition), and optical (complex refractive index from ultraviolet to near-infrared wavelengths) properties of the volcanic ash and classified the samples according to their SiO2 and total alkali contents into the common igneous rock types basalt to rhyolite. We found that the mass density ranges between \( \rho = 2.49 \) and \( 2.98 \text{ g/cm}^3 \) for rhyolitic to basaltic ash types and that the particle shape varies with changing particle size \( d < 100 \mu\text{m} \). The complex refractive indices in the wavelength range between \( \lambda = 300 \text{ nm} \) and \( 1500 \text{ nm} \) depend systematically on the composition of the samples. The real part values vary from \( n = 1.38 \) to \( 1.66 \) depending on ash type and wavelength and the imaginary part values from \( k = 0.00027 \) to \( 0.00268 \). We place our results into the context of existing data and thus provide a comprehensive data set that can be used for future and historic eruptions, when only basic information about the magma type producing the ash is known.

1. Introduction

During explosive volcanic eruptions, volcanic ash (VA) particles can be released into the atmosphere and transported hundreds to thousands of kilometers away from the eruptive vent. Depending on the eruption conditions (e.g., height of release), atmospheric conditions, and microphysical properties of VA, the particles have atmospheric lifetimes that can span hours (sedimentation velocities of \(~1 \text{ km/h}\) for coarse ash particles, \(d > 63 \mu\text{m}\)) to days and months (\(~0.01 \text{ km/h}\) for fine ash particles, \(d < 63 \mu\text{m}\)) [Bonadonna et al., 1998; Rose et al., 2001; Durant, 2015]. During their atmospheric long-range transport, VA particles have the potential to influence the Earth’s radiation balance as they reflect and absorb solar and terrestrial radiation, and therefore, they may impact weather and climate [Robock, 2000; Vernier et al., 2016]. They also present a major threat for aviation operations as they decrease visibility and cause dangerous airborne engine damages [Prata and Tupper, 2009; Guffanti et al., 2010]. Near the Earth surface VA particles pose hazards to human health [Baxter et al., 2014], affect air quality [Thorsteinsen et al., 2012], infrastructures such as ground transport and water supplies [Wilson et al., 2012], and to natural environments [Jones and Gislason, 2008; Durant et al., 2010].

Atmospheric models, such as particle transport and dispersion, radiative transfer, or climate models, and ash retrieval algorithms rely on accurate and quantitative information about the different properties of VA. These properties deviate greatly between different volcanic ash types as they depend on individual magma properties (e.g., composition, rheology, and gas content), the particle formation processes, and the distance from the eruptive vent (particle size). However, in most cases, models and measurement algorithms use only a single set of parameters for all types of eruptions. This oversimplification can introduce large uncertainties in calculations of the atmospheric dispersion or mass concentration calculations as these properties differ...
substantially from reality [Grainger et al., 2013]. To minimize these uncertainties, there is an urgent need for more detailed and interrelated characterization of the properties of VA [Rocha-Lima et al., 2014].

Figure 1 shows an overview about the main volcanic ash properties subdivided into chemical (mineralogical and chemical compositions of particle bulk and surface), physical (particle size, morphology, and mass density), and optical (complex refractive index) properties of VA. Accurate parameters describing these properties are needed in atmospheric dispersion and climate models as well as in remote sensing and in situ detection algorithms to provide reliable output products such as deposition rates, mass concentrations, and radiative forcing that are vital in the assessment of VA hazards.

1.1. Chemical Properties

The mineralogical and chemical compositions of VA are very complex and consist of glassy juvenile components, crystals from multiple mineral phases (quartz, feldspar, micas, pyroxenes, amphiboles, and olivine) formed in the magma, and lithic fragments of eroded vent and wall rock [White and Houghton, 2006; Dingwell et al., 2012]. Typical VA composition ranges from basaltic (high in Mg and Fe) to rhyolitic (high in Si and Al) [Stevenson et al., 2015] and is mostly described on the basis of the composition of the bulk material [Bayhurt et al., 1994; Weber et al., 2012; Lieke et al., 2013], but can also be classified by the composition of the particle surface. The particle composition provides important information about the magma mixture and the erosion of the conduit rock [Heiken, 1972] and has an influence on scavenging processes in clouds and effects on the natural environment such as ocean and soil fertilization [Duggen et al., 2009; Achterberg et al., 2013]. The composition is also fundamental for deriving other VA properties such as the mass density or the complex refractive index.

The surfaces of the erupted VA particles represent a mixture of preeruptive, syneruptive, and posteruptive surfaces [Ayris and Delmelle, 2012]. Preeruptive surfaces are those generated at the boundaries between the silicate melts and the bubbles created during exsolution of magmatic volatiles [Sparks, 1978] and those generated by a permeable network of fractures [Gonnermann and Manga, 2003]. These surfaces are equilibrated via processes such as atomic rearrangement or ionic recombination. Syneruptive surfaces originate from the magma fragmentation in its brittle (solid-like) regime. Crystallization of mineral phases in silicate
melts introduces bulk material defects along phenocryst boundaries that act as fracture planes during magma fragmentation. As crystallization may involve diffusion of specific elements from the amorphous phase to the crystalline phase, fracture at the amorphous phase may generate surfaces depleted in the elements that were diffused into the crystalline phases. Post-eruptive surfaces are generated by collision between ash particles or between particles and conduit wall rock after magma fragmentation. Ash particle surfaces are also influenced by high- and low-temperature heterogeneous chemical reactions in the eruption plume. Further, physical processes (e.g., adsorption and aggregation) and chemical reactions (e.g., leaching) occur during transport of the ash in the atmosphere. Both the bulk and surface compositions of VA particles have impacts on cloud microphysical processes [Durant et al., 2008; Rolf et al., 2012], radiative forcing [Flanner et al., 2014], respiratory effects [Horwell and Baxter, 2006], and soil and ocean fertilization effects [Duggen et al., 2009; Achterberg et al., 2013].

1.2. Physical Properties

Knowledge of the physical properties of VA particles is fundamental to constrain the size and style of volcanic eruptions [Bonadonna and Houghton, 2005] and to predict atmospheric lifetimes controlled by transport, deposition, and sedimentation processes [Riley et al., 2003; Durant and Rose, 2009; Mills and Rose, 2010; Folch, 2012; Bagheri et al., 2013]. Particle size and morphology are controlled by magma fragmentation processes [Sparks, 1978], magma ascent rate, and by external factors such as particle collisions or interaction with water [Rose and Durant, 2009; Dellino et al., 2012]. The deviation from spherical shape decreases atmospheric sedimentation velocities by up to 50% [Mele et al., 2011; Bagheri and Bonadonna, 2016a], due to the altered aerodynamic behavior of elongated particles. Thus, nonspherical particles can be transported over longer distances in the atmosphere than spherical particles [Stevenson et al., 2015; Bagheri and Bonadonna, 2016a].

To date, in measurement algorithms and atmospheric models, VA particles are often assumed to be spherical, although they are known to be nonspherical due to their formation processes [Wilson and Huang, 1979]. It has been shown that assuming mass-equivalent spheres instead of accounting for more realistically shaped porous nonspherical particles may lead to underestimates of the total retrieved mass of an ash cloud by approximately 30%. The assumption also leads to an overestimation of the ash cloud optical depth in radiative transfer algorithms that are used to interpret satellite measurement data [Wen and Rose, 1994; Krotkov et al., 1998; Kylling et al., 2014]. Bagheri and Bonadonna [2016a], however, reported that even the most commonly used corrections for the estimation of nonspherical drag-coefficients (relevant for calculations of settling velocities) can introduce large errors (mean error up to 13% to maximum errors up to 80%) depending on the calculation method.

In another study, Bagheri and Bonadonna [2016a] reviewed commonly used nonspherical drag models for estimating VA particle drag coefficients and benchmarked them against analytical and experimental results. They showed that nonspherical drag models are on average associated with errors between 8% and 55% depending on the particle size (in the particle size of fine ash to lapilli-sized particles). The individual reported errors are 2–10% for fine ash, 23–55% for coarse ash, and 10–33% for lapilli-sized particles. Interestingly, spherical models outperformed some nonspherical models in terms of accuracy, which indicates the importance of proper shape characterizations if one wants to avoid such pitfalls of nonspherical models. They also showed that by considering simple particle characteristics (i.e., flatness and elongation) it is possible to obtain relatively accurate estimation of VA drag coefficient (average error of 8%).

Earlier quantitative shape analyses were limited to measurements of only a small number of particles [Heiken, 1972; Bayhurst et al., 1994; Riley et al., 2003; Mills and Rose, 2010], whereas recent instrumental developments allowed measurements of a high number (100,000 s) of projected and three-dimensional particle shapes [Durant and Rose, 2009; Bagheri et al., 2015; Leibrandt and Le Pennec, 2015; Liu et al., 2015]. Analyzing a high number of particle shapes as a function of size is necessary for deriving statistically robust shape parameters that help minimizing the uncertainties in transport and mass concentration calculations [Bagheri et al., 2015; Liu et al., 2015]. The higher the number of measured and analyzed particles, the smaller is the uncertainty of derived relevant shape descriptions such as the particle form or roundness.

Another parameter that controls the atmospheric lifetime and calculations of mass concentrations of VA particles is the mass density. The mass density is also needed to convert the particle volume to particle mass both in atmospheric measurements and in models. The mass density depends on the chemical composition
and on the vesicularity. The vesicularity is defined as the volume percent of internal void space in volcanic ash particles. Higher vesicularity results in lower densities. Thus, if vesicularity depends on particle size, the particle density varies with particle size as well. This is of importance for determining the terminal settling velocity and deposition patterns of ash particles [Bonadonna and Phillips, 2003; Costa et al., 2006]. Incorrect mass density assumptions also lead to errors in gravitational settling and dry deposition schemes in atmospheric models and to an overestimation or underestimation of mass concentration calculations in both model and measurements products. Typical mass density values are in the range of $\rho = 2.35–2.45$ g/cm$^3$ for glass shards, $\rho = 2.70–3.30$ g/cm$^3$ for crystals, and $\rho = 2.60–3.20$ g/cm$^3$ for lithic particles [Wilson et al., 2012; Clarisse and Prata, 2016].

### 1.3. Optical Properties

The most severe lack of information concerns the optical properties of VA particles. The optical properties are described by the complex refractive index,

$$ N_i = n_i + i k_i, \quad (1) $$

where $n_i$ is the real part, related to the refraction, and $k_i$ is the imaginary part related to the attenuation of incident light. The complex refractive index is therefore a quantitative measure of the particles’ refraction properties, i.e., how they transmit, reflect, and absorb incident light, and is dependent on the chemical composition [Ball et al., 2015] of the material and on the particles’ shape and density and hence can vary significantly.

Reliable information about the complex refractive index is necessary for ash remote sensing retrievals [Krotkov et al., 1997], optical ash measurement methods [Bukowiecki et al., 2011; Tesche et al., 2012], and also for quantifying weather and climate impacts of the ash [Timmreck, 2012; Flanner et al., 2014; Vernier et al., 2016] (see Figure 1). For example, the refractive index is a needed input parameter in radiative transfer models that are employed to simulate the backscattered top-of-the-atmosphere radiance to derive the aerosol optical depth and the effective particle radius of an ash cloud for remote sensing retrievals [Krotkov et al., 1999a; Carn and Krotkov, 2016].

Although the complex refractive index is known to be highly important for the detection and modeling of volcanic ash clouds, existing studies are limited. Different studies used different particle types such as volcanic ash particles, terrestrial rocks, and pure glasses [Pollack et al., 1973; Volz, 1973] to investigate either the complex refractive index or only the absorption part ($k_i$) for either single wavelengths [Ball et al., 2015] or a broad wavelength range. Thereby, these studies used different theoretical and experimental approaches such as measurements of the diffused reflectance [Patterson, 1981; Patterson et al., 1983; Krotkov et al., 1999b; Rocha-Lima et al., 2014], direct transmittance [Grainger et al., 2013; Ball et al., 2015], a combination of both [Pollack et al., 1973], or calculations based on the chemical composition [Kandler et al., 2011]. In fact, many studies can be traced back to a single source of data [Pollack et al., 1973], which is based on the characterization of terrestrial rocks and glasses.

An overview about all available refractive index values for volcanic ash and glasses found in the literature is provided in Figure 2. The complex refractive index data are sorted by the igneous rock groups of the samples that are depending on the silica and total alkali contents ranging from basalt to rhyolite, and the wavelength. The overview also shows the main measurement systems operating in the relevant wavelength range.

The real part of the complex refractive index can be estimated by using different approaches such as the Becke line technique, where the particles are immersed in a matrix of resin or liquid with well-characterized optical properties, through reflectance measurements from bulk material or theoretical calculations. The total reflectance proportion is derived using the reflectance data directly or by using the information about the chemical composition of the samples. In the ultraviolet (UV) to near-infrared (NIR) wavelength range, typical values range between $n_i = 1.5$ and 1.6 for silicate glasses and between $n_i = 1.45$ and 1.65 for naturally occurring rocks and VA (depending on sample composition and wavelength) [Pollack et al., 1973; Ball et al., 2015].

The imaginary part of the complex refractive index can be retrieved either using both reflectance and transmittance data or based only on transmittance measurements. It can also be estimated from reflectance measurement only using the Kubelka-Munk theory, a phenomenological correlation between the total diffuse
reflectance of the sample and a concentration of bulk absorbing species using a scaling factor (absorption-to-scattering ratio of the material) as demonstrated by Patterson [1977, 1981]. This technique requires information about the size distribution and particle shape and relies on iterative procedures and complex forward modeling [Nobbs, 1985].

Direct transmittance measurements, however, allow determining the absorption properties of the ash samples directly, as soon as $k$ is related to the portion of light that is absorbed, described by the Lambert-Beer law [Zaccaconti and Bruscaglioni, 1988]. The samples can be either rock material with varying thicknesses [Pollack et al., 1973], particle powder embedded in a host matrix, or single particles immersed in liquid as demonstrated by Ball et al. [2015]. Furthermore, the absorption properties, other than the reflectance properties, can also be derived from satellite data [Ishimoto et al., 2016] directly, but these retrievals are subject to their own assumptions and limitations.

Earlier studies reported high variations in absorption values in the range of $k_\lambda = 0.1$ and 0.0001 [Patterson, 1981; Patterson et al., 1983], whereas later studies reported smaller variations with values in the range between $k_\lambda = 0.001$ and 0.00001 [Krotkov et al., 1999a; Grainger et al., 2013; Rocha-Lima et al., 2014; Ball et al., 2015]. Generally, basaltic ash samples with a low silica content (<48 wt % SiO₂) show the highest absorption, while rhyolitic ash samples with a high silica content (>70 wt % SiO₂) show the lowest absorption. For a more general characterization of the scattering and absorption characteristics of volcanic ash, it would be important to have an extensive set of measurements of $n_\lambda$ and $k_\lambda$ values for many different ash types as well as over the a wide wavelength range relevant for atmospheric measurements and modeling.
1.4. Scope of This Study
To date, few studies exist that present measurements of both the physicochemical and optical properties of volcanic ash particles, and we are not aware of any other study that has made such measurements in a systematic way for ash particles originating from different eruptions from different volcanoes. In this study, we provide a data set for physical (particle size, morphology, and density), chemical (bulk and surface chemistry as well as glass contents), and optical properties (complex refractive indices in the UV-Vis-NIR range) of a representative selection of volcanic ash samples from nine different volcanic eruptions covering the full variability in silica content (50–80 wt % SiO$_2$). A user of our data set, who is interested in another eruption for which the magma type that produced the ash is known, will be able to select the physical and optical properties of our most representative ash samples and use these values for, e.g., satellite retrievals or model calculations for the eruption of interest. Our data set may thus serve as a reference for future studies requiring parameters describing VA properties. We captured the natural variability of ash physicochemical and optical characteristics through a combination of empirical analytical methods (e.g., image analysis, Archimedean densitometry, energy dispersive spectroscopy, X-ray photoelectron spectroscopy, light microscopy, and UV/Vis spectrophotometry) and theoretical calculations. This paper is structured as follows: In section 2 we introduce the methods we used, in sections 3 and 4 we present the results and discuss their implications and their context to existing studies, and in section 5 we present conclusions.

2. Methods
2.1. Sample Selection, Origin, and Sampling
For the investigation of the microphysical, chemical, and optical properties, we selected nine VA samples from different volcanoes and eruptions (Figure 3). The selection of the samples was based on (a) the wide range of silica contents (from basaltic to rhyolitic ash), (b) their origin from explosive (volcanic explosivity index $\leq$ 5) eruptions with a high content of fine ash particles (particle diameter, $d < 63 \, \mu m$), and (c) the fact that the selected eruptions had a large impact on the society (impact on infrastructures and aviation). Furthermore, the samples represent proximal-medial to distal fallout samples as well as one sample from a pyroclastic density current (PDC). Material from most of the samples was used in various studies before (see references in Table 1), but no study has made a comprehensive analysis of particle microphysical, chemical, and optical characteristics for the complete silica content range. Table 1 presents an overview of the different ash types, their chemical classification, and details about sample location and distance from the volcano sorted according to geographic location from North America to the western Pacific region.
Table 1. Overview of Volcanic Ash Samples Included in This Study Including Sample ID, Classification Into the Main Igneous Rock Types, Volcanic Explosively Index (VEI), and Information About Eruption Date, Sample Location, and Distance From the Volcano

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Volcano</th>
<th>Eruption Date</th>
<th>VEI</th>
<th>Lat.</th>
<th>Lon.</th>
<th>Distance from Volcano (km)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRI</td>
<td>Grimsvötn, Iceland</td>
<td>May 2011</td>
<td>4</td>
<td>63.78°N</td>
<td>18.09°W</td>
<td>80</td>
<td>–</td>
</tr>
<tr>
<td>KEL</td>
<td>Mount Kelud, Indonesia</td>
<td>February 2014</td>
<td>4</td>
<td>63.63°N</td>
<td>19.62°W</td>
<td>250</td>
<td>McGimsey et al. [2001], Rose et al. [2009], Durant and Rose [2009]</td>
</tr>
<tr>
<td>EYJ</td>
<td>Eyjafjallajökull, Iceland</td>
<td>April–June 2010</td>
<td>4</td>
<td>63.63°N</td>
<td>19.62°W</td>
<td>35</td>
<td>Gislason et al. [2011], Gudmundsson et al. [2012]</td>
</tr>
<tr>
<td>SPU</td>
<td>Mount Spurr, United States</td>
<td>September 1992</td>
<td>4</td>
<td>61.74°N</td>
<td>47.60°W</td>
<td>215</td>
<td>McGimsey et al. [2001], Rose et al. [2009], Rose and Durant [2009]</td>
</tr>
<tr>
<td>SAK</td>
<td>Mount Sakurajima, Japan</td>
<td>August 2013</td>
<td>–</td>
<td>31.59°N</td>
<td>130.67°E</td>
<td>10</td>
<td>Bagheri et al. [2016]</td>
</tr>
<tr>
<td>MSH</td>
<td>Mount St. Helens, United States</td>
<td>May 1980</td>
<td>5</td>
<td>46.25°N</td>
<td>122.18°W</td>
<td>6</td>
<td>Adams et al. [1996], Rose and Durant [2009]</td>
</tr>
<tr>
<td>SOU</td>
<td>Soufriere Hills, United Kingdom</td>
<td>February 2010</td>
<td>–</td>
<td>16.72°N</td>
<td>62.18°W</td>
<td>5</td>
<td>Cole et al. [2005]</td>
</tr>
<tr>
<td>RED</td>
<td>Mount Redoubt, United States</td>
<td>December 1989</td>
<td>3</td>
<td>62.54°N</td>
<td>150.24°W</td>
<td>265</td>
<td>Bayhurst et al. [1994], Schneider and Rose [1994]</td>
</tr>
<tr>
<td>CHA</td>
<td>Chaitén, Chile</td>
<td>May 2008</td>
<td>4</td>
<td>43.33°S</td>
<td>72.47°W</td>
<td>60</td>
<td>Alfano et al. [2011]</td>
</tr>
</tbody>
</table>

The Mount Spurr (SPU) ash sample from the 1992 eruption was collected ~250 km east of the eruption location by the United States Geological Survey (USGS) Alaska Volcano Observatory. The eruption plume reached, at a peak altitude, the stratosphere and traveled eastward with the prevailing winds [Schneider et al., 1995], where the fine fraction of the deposits was collected under 23 cm of snow on Barry Glacier (23.2 g in 0.0625 m²) shortly after deposition [McGimsey et al., 2001; Rose et al., 2001; Durant and Rose, 2009]. The Mount Redoubt (RED) ashfall sample from the 15 December 1989 eruption was collected ~265 km NE of the volcano by the USGS in March 1990. The sample was taken from the lower tephra layer embedded in a 1.5 to 2 m thick snow cover at Dateli Lake [Bayhurst et al., 1994; Schneider and Rose, 1994]. It is possible that a commercial aircraft that had a failure on all four engines due to volcanic ash ingestion [Casadevall, 1994] passed through the same cloud on the date of the Mount Redoubt eruption. The Mount St. Helens (MSH) ashfall sample from the 18 May 1980 pyroclastic density current (PDC) was taken from the Pumice Plain ~6 km north of the 1980 crater. The sample was collected in August 1981 from a cliff exposure where the unit could be clearly identified. The fine ash fraction in this sample is mostly coigimbrite ash that was elutriated from the PDC, rose to tropopause heights by convection, and fell out distally [Adams et al., 1996; Munoz et al., 2004]. The Chaitén (CHA) ashfall sample from the May 2008 eruption was collected ~60 km SE from ashfall deposits with consistent thicknesses [Alfano et al., 2011] in January 2009. The Soufriere Hills volcano (SOU) ashfall sample from the February 2010 dome collapse pyroclastic density column was collected ~5 km NE of the eruption by the Montserrat Volcano Observatory. The eruption plume reached altitudes up to 15 km, where an umbrella cloud was formed and dispersed by SE winds [Coles et al., 2015]. The Eyjafjallajökull (EYJ) ashfall sample from the 2010 eruption was collected ~35 km SW of the volcano by the Institute for Earth Sciences of the University of Iceland. The sample was taken after the first phase of the eruption in April 2010 [Gislason et al., 2011; Gudmundsson et al., 2012]. The Grimsvötn (GRI) sample from the 2011 eruption was taken ~80 km SW of the volcano near Skógar by the Düsseldorf University of Applied Sciences. In this case, the sample was collected on a car surface in an open barn. The Kelud (KEL) sample from the 2014 eruption was sampled at ~215 km distance from the volcano by the Indonesia Centre for Volcanology and Geological Hazard Mitigation. The eruption plume rose up to the stratosphere and dispersed particles over long distances. The ashfall sample was collected from the ground in April 2014, approximately 6 weeks after the eruption in Yogyakarta. Finally, the Mount Sakurajima (SAK) ash sample is associated with a Vulcanian explosive eruption event on 3 August 2013. It was collected at ~10 km distance directly after the eruption event. The ash-rich eruption plume reached 2.3 km [Bagheri et al., 2016].

2.2. Sample Preparation

For the different analytical approaches in this study, we separated the samples into two different subgroups: (1) loose powder samples and (2) embedded particles in a host matrix. The sample groups are illustrated in Figure 4. For simplification, the two subgroups will be mentioned in the text as powder samples and pellet samples. Powder samples were used for the measurements of particle size and complex morphology (form
and shape parameters), mass density, and the chemical composition of the particle surfaces. The particles were used without any additional treatment apart from a moderate sample drying (at 60°C) prior to each measurement. Pellet samples were used for the characterization of the bulk chemical composition and for the measurements of the optical properties. The pellets were prepared by embedding defined volume fractions ($f$) of ash particles in a clear polymeric host matrix (Struers Clarofast, hot mounting resin). We selected a resin that is transparent in the relevant wavelength range ($\lambda = 300$–$1500$ nm) and sufficiently conductive, stable under an electron beam and suitable for mechanical grinding and polishing. The mixture composed of ash and resin was subsequently pressed into a pellet using a hot embedding press (Struers LaboPress-3) under constant pressure (15 kN) and heating conditions (180°C). This approach ensures a porosity-free and compact embedded material for further analysis. The resulting pellet was then cut, ground, and polished in several steps (final step was polishing with 2 $\mu$m diamond particle suspension) to produce a flat sample surface. After this process the samples were cleaned and dried in hot air. The final thickness $t$ of these samples was $t = 2$–3 mm with a volume fraction of embedded volcanic ash particles between $f = 0.01$ and 0.05. Important to note is that this preparation procedure produced cross sections of the embedded particles near the pellet surface; therefore, the same samples were used for measuring both the bulk chemical composition and optical properties discussed in sections 3 and 4.

### 2.3. Chemical Characterization

The chemical characterization of VA provides key data for most of the measured and derived parameters in this study. The different ash samples were grouped, following a classification based on the total alkali ($Na_2O$ and $K_2O$) and silica ($SiO_2$) content (so-called TAS classification) [Le Bas and Streckeisen, 1991], into the main igneous rock types basalt, basaltic-andesite, andesite, dacite, and rhyolite. In addition to the chemical composition of the bulk material, we also analyzed the chemical composition of the particle surface.

#### 2.3.1. Bulk Material

For the measurement of the chemical composition of the bulk material, the embedded particles in the pellet sample were analyzed using field-emission gun scanning electron microscopy (FEG-SEM) with an integrated energy dispersive spectrometer (EDS). The FEG-SEM measurements were performed on a Nova NanoSEM650 microscope and the EDS analysis on an X-Max50 spectrometer. The samples were analyzed in high-vacuum mode and with a 20 kV accelerating voltage. A backscatter detector was used at a working distance of 8.1 mm. The SEM field of view was set to 300 $\mu$m × 300 $\mu$m to capture the microstructure and shape of embedded particles of sizes 1–100 $\mu$m. The sample elemental composition was recorded with an EDS micron-sized beam allowing determination of an average composition of the total cross-section area of the embedded particles. This approach gives representative results of all elements over the entire sample area and minimize measurement uncertainties. For each volcanic ash sample, the elemental compositions of several hundreds of particle cross sections (produced by the embedding and polishing process) were measured and processed. Major elements present in the composition of volcanic ash particles are Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn, and O in varying concentrations. The elemental data of each component were first converted into weight percent of the corresponding oxides (oxide wt %) and subsequently averaged using a Gaussian

<table>
<thead>
<tr>
<th>GRI</th>
<th>KEL</th>
<th>EYJ</th>
<th>SPU</th>
<th>SAK</th>
<th>MSH</th>
<th>SOU</th>
<th>RED</th>
<th>CHA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pellet samples</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>1 vol.%</td>
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<td></td>
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<tr>
<td>5 vol.%</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td><strong>Powder samples</strong></td>
<td></td>
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</tr>
</tbody>
</table>

Figure 4. Overview about the two different sample subgroups. The top and middle rows show the 1 vol % and 5 vol % pellet samples, respectively, of the nine ash types.
filter function (2-sigma ranges). The reported data do not account for the presence of water and are normalized (processing option: oxygen by stoichiometry).

### 2.3.2. Particle Surface

X-ray photoelectron spectroscopy (XPS) was used to measure the elemental composition and chemical state of the particle surfaces down to an average depth of 2–10 nm. The XPS analysis was carried out using a Kratos Axis UltraDLD spectrometer with a monochromatic Al Kα X-ray source ($hν = 1486.7$ eV). The spectra were acquired at a zero angle of emission using the hybrid analyzer mode (i.e., using both the electrostatic and magnetic lenses) at pass energies of 160 eV and 20 eV for the survey and high-resolution scans, respectively. The samples were placed in Cu-based stubs, and charge compensation was achieved by using a flood gun producing coaxial low-energy electrons, which resided on the sample surface providing charge neutralization. During the XPS analysis, the vacuum of the standard analysis chamber was set to $8 \times 10^{-10}$ hPa. The measured spectra were energy corrected using the C1s peak for adventitious carbon (285 eV). For peak fitting we used linear and Shirley background types and for the quantification high-resolution peaks and Wagner sensitivity factors. The area of analysis was 700 μm × 300 μm and included several thousand particles. The averaged elemental composition were converted, like the EDs data, into weight percent of the corresponding oxides (oxide wt %).

### 2.3.3. Glass Contents

The measurements of glass and crystalline component phases within the selected ash samples were performed on a Leica Reichert Polyvar2 optical microscope equipped with light polarization and image capture software (Leica IM 500). The powder samples were mounted on a microscope glass sample holder using Crystalbond 509. We employed three modes of operation: (1) transmitted light (TL) bright-field (BF) illumination, (2) TL cross-polarized (PL) illumination at two different angles at 0° and 45° (two images) using polarized light, and (3) TL interference contrast (IC) illumination [McCrone et al., 1978].

Figure 5 shows an overview of images of the three modes for the example sample GRI. The TL-IC image (Figure 15b) was used to determine the total pixel area of the particles, after removing the background by an image processing procedure, whereas the TL-PL images were used to determine the total pixel area of component phases within the samples. It was then possible to calculate the total glass (amorphous)
fraction by analyzing these two areas. TL-BF images were used to correct for the presence of opaque particles, where no discrimination between the glass and crystal phases was possible.

2.4. Microphysical Characterization
2.4.1. Image Analysis of Particle Size and Morphology
For the measurement of particle size and morphometric characterization, we used an automated static particle imaging (ASPI) instrument (Malvern Instrument Morphologi G3). The ASPI is an optical analyzer for the characterization of the particle morphology on a two-dimensional projection area. A full description of the instrument and all relevant features can be found in Leibrandt and Le Pennec [2015] and Liu et al. [2015]. The ASPI instrument is a state-of-the-art instrument, which provides reliable and reproducible particle information for a statistically significant number of particles with a low relative standard deviation on average values (<0.2%) [Leibrandt and Le Pennec, 2015]. Therefore, the data acquired with this instrument can be used for a parameterization of different shape descriptions in particle transport and dispersion as well as climate models (Figure 1).

For the instrumental setup, we used the standard operation procedure described by Leibrandt and Le Pennec [2015] for two different microscope objective lenses. A 20X magnification objective lens was used for the particle sizes between 1.8 and 100 μm and a 5X magnification objective lens for the size range of 6.5–420 μm. The use of the 20X magnification objective was important as the 5X objective has a poorer resolution below 63 μm particles [Leibrandt and Le Pennec, 2015]. The particle sample area was set to 314.16 mm² for the 20X objective and 1256.64 mm² for the 5X objective to capture a high number of particles. The difference between the two sample areas guaranteed the characterization of a statistically adequate number of the less abundant larger particles. The total number of individual particles measured for each ash sample was between 10⁶ and 10⁷ based on an initial sample volume of 7 mm³, providing high statistical significance.

The light source was set to be diascopic, which means that the light shone from below the carrier unit to produce a sharp contrast between the dark ash particles and the light illuminated background. Due to the very narrow depth of field of the individual objective lenses, we used a two layer Z-stacking option. Z stacking is a function that takes several images, each at different heights, before these pictures are overlaid to form a single composite picture. This option ensures accurate focusing and a quasi-three-dimensional representation of the particle projection area.

The particle area is defined as the sum of individual pixels \( A = \sum a_j \) within the borders of the detected area that is set by the threshold settings of the different objective lenses. The border represents also the particle perimeter \( P \) that is calculated using the Cauchy-Crofton equation \( P = \frac{\pi}{4} \sum l_i d_i \), from the number of intercepts \( l \), formed by a series of parallel lines, with spacing \( d_i \), exploring \( N \) directions, from \( \alpha \) to \( \pi \). Within this detected area, the distances (longest, intermediate, and shortest) of each particle axis can be directly measured. The particle length is defined as the maximum distance between two points on the perimeter parallel to the major axis, which is the angle of the major axis from a horizontal line. The particle width is defined as the maximum distance parallel to the minor axis, which passes through the center of mass at right angles to the major axis. The intermediate particle length is defined as the minimum distance between points on the particle axis with 45° inclination to the major axes. Illustrations of the particle area, the different distances, and the particle perimeter that are essential for further particle size, form and shape descriptions, are illustrated in Figure 6.

For the description of the particle size, we used the circle equivalent particle diameter \( d_{2D} \), also known as the Heywood diameter, that relates the measured two-dimensional particle area to a particle size by the assumption that the measured particle has the same two-dimensional projected area as a circle

\[
d_{2D} = \sqrt{4A/\pi}.
\]  

To describe particle form and shape, we chose three different nonsphericity parameters: the aspect ratio (AR), the Cox circularity (\( \phi \)), and the Wilson shape parameter (WSP) introduced by Wilson and Huang [1979]. The AR is defined as the ratio between the longest distances of each major axis of the projected particle area

\[
AR = \frac{d_{\text{max1}}}{d_{\text{max2}}}.
\]
and is a classical description of the particle elongation. The AR, for example, is employed in radiative transfer models when nonsphericity of the ash particles is considered [Kylling et al., 2014] or as one of the shape descriptors for estimating drag coefficients of non-spherical particles [Bagheri and Bonadonna, 2016b]. The true particle sphericity is a three-dimensional characteristic of particle shape, which is defined as the ratio of surface area of a sphere with the same volume as the particle to the surface area of the particle [Wadell, 1932]. For irregular particles, however, the surface area is not an absolute value and depends on the scales at which the measurements are carried out [Bagheri et al., 2015]. Bagheri et al. [2015] showed that a two-dimensional surrogate for the true sphericity of VA and lapilli-size particles (measured with resolutions of 1–100 μm) are the circularity measures. Here we measured the Cox circularity (ϕ) [Cox, 1927] that is found to have a high correlation with sphericity of VA with vesicular surfaces (opening diameter of the vesicles on the surface is 5–40% of particle diameter, see Bagheri et al. [2015] for more details). Parameter ϕ is defined as the ratio of the circle equivalent particle two-dimensional projected area to the surface area represented by the square of the particle perimeter

\[ \phi = \frac{4\pi A}{P^2} \]  

(4)

The last parameter is the Wilson shape parameter (WSP) [Wilson and Huang, 1979]. The WSP is defined as the ratio of the sum of the intermediate (d_{axis3}) and shortest (d_{axis2}) distance to the longest (d_{axis1}) axis

\[ \text{WSP} = \frac{d_{axis3} + d_{axis2}}{2d_{axis1}} \]  

(5)

and is often used in radiative transfer models. All described shape parameters are normalized and range from 0 to 1, where 1 corresponds to a perfectly spherical particle. For a validation of the measured size and shape parameter by the ASPI instrument, we used a second instrument (CamsizerXT). This instrument, a dynamic image analyzer (DIA), uses the same physical approach, but in a wet dispersion module configuration, where the particles are suspended in water and circulated through the measurement chamber (two cameras setup) [Retsch Technology GmbH, 2016]. The use of a second instrument allowed us to identify and eliminate potential instrumental biases.

2.4.2. Dense-Rock Equivalent Mass Density

We used two different approaches to determine the mass density: (1) direct measurements of the dense-rock equivalent (DRE) mass density of the particle skeleton using Archimedean densitometry and (2) theoretical mass density calculations based on mass fractions for the major oxides as obtained from the compositional analysis and crystalline volume data from Lange and Carmichael [1987]. The mass density measurements were done using a pycnometer (also called specific gravity bottle), which involved weighing the ash sample in air (m_i) and in another fluid (m_l) (here water at constant and known temperature) with a well known density (\rho_l). The measured mass density is derived from the following equation

\[ \rho_m = \frac{m_i}{V_i \cdot (m_l/\rho_l)} \]  

(6)

Figure 6. Illustration of the measured size and shape parameters by the ASPI and the DIA instruments. The dashed lines indicate the main particle axis in each direction.
using the mass of the particle sample \(m_p\) and the difference between the total volume of the cylinder \(V_c\) and the water volume \(V_l = (m_p/\rho_l)\). Every ash sample was analyzed several times (including measurements at different water temperatures) to ensure reproducible and reliable results. This approach is accurate, elaborative, and well known for measuring the mass density of solid materials over a large range of particle sizes (fine ash fraction) \cite[e.g.,][]{Pistolesi_etal_2014}.

The second method to determine the mass density of the samples is to relate the chemical composition of the bulk ash material directly to its mass density. This approach allows a consistency check of the measured mass density values and can be used to calculate the mass density when no densitometry measurements are possible or only chemical compositional data are available. For the theoretical mass density

\[
\rho_t = \frac{\sum_{i=1}^{n} M_i X_i}{\sum_{i=1}^{n} V_i X_i} \quad (7)
\]

we used EDS data and the component specific volume, where the sum of the partial molar mass of each component \((M)\) and the component mole fractions \((X)\) is divided by the sum of the partial volume of each oxide component \((V)\) and the component mole fractions \((n)\) being the total number of major components within the sample). The partial volumes of each oxide component are based on solid particles and were taken from \cite{Lange_Carmichael_1987}.

### 2.5. Optical Characterization

The complex refractive index (RI) is a complex number and a quantitative measure of the reflectance, transmittance and absorption properties of a substance. Reliable information about the RI is important to relate optical measurement signals to particle information such as size (effective radius), size distribution, and ultimately the ash mass concentration. It is also needed in radiative transfer models for a quantification of the impact of volcanic ash on the Earth’s radiative budget. The RI \(N\) is a function of the light wavelength \(\lambda\) and the chemical composition of the sample (see equation (1)).

The amount of direct and diffused refraction and attenuation of incident light by the different samples was measured using a commercial double-beam UV/Vis/NIR spectrophotometer (Perkin Elmer Lambda 950) equipped with a white Ulbricht integrating sphere. The integrating sphere was Spectralon covered to accomplish the diffuse signal detection. The instrument was equipped with sample thickness compensating detector optics and had a measurement range of \(\lambda = 250–2500\) nm. The analysis spot on the sample surface was set to 10 mm \(\times\) 5 mm, which allowed representative surface integration of the signal. The instrument has two light sources: a deuterium lamp for the UV range (up to 400 nm) and a tungsten lamp for the rest of the spectrum (Vis/NIR). The slit widths were set for 2 nm spectral resolution.

Measurements of light through fine-grained particles embedded in a host material (pellet sample) is a direct method that enabled us to determine \(k\) in a wide spectral range. Reliable transmission measurements for our samples could be made in the wavelength range between \(\lambda = 300\) and 1500 nm due to presence of specific absorption bands of the used resin for \(\lambda > 1500\) nm. The volume averaged imaginary part of the refractive index \((k)\) of the ash samples can be calculated using Beer’s law

\[
I(\lambda) = I_0(\lambda) e^{-na\lambda t} \quad (8)
\]

where \(I(\lambda)\), \(I_0(\lambda)\), \(a(\lambda)\), and \(t\) are the intensity measured in absence of the sample, the measured intensity of the sample (ash samples in host material), the volume absorption coefficient, and the sample thickness respectively. The volume absorption coefficient

\[
a(\lambda) = \frac{4\pi k_{\text{eff}}(\lambda)}{\lambda} \quad (9)
\]
is related to $\lambda$ and the effective extinction coefficient part ($k_{\text{eff}}(\lambda)$) of the complex refractive index. By combining equations (8) and (9), we can calculate $k_{\text{eff}}(\lambda)$ for the pellet sample (ash samples in host material):

$$k_{\text{eff}}(\lambda) = \frac{\lambda^4}{4\pi C_0} \ln \left( \frac{I_0(\lambda)}{I(\lambda)} \right).$$

(10)

As a final step, the material specific extinction coefficient ($k_{\text{ash}}(\lambda)$) for the pure ash sample can be calculated by dividing $k_{\text{eff}}(\lambda)$ by the volume fraction of the embedded ash in the host material ($f = V_T/V_{\text{ash}}$):

$$k_{\text{ash}}(\lambda) = \frac{k_{\text{eff}}(\lambda)}{f}.$$  

(11)

The transmittance measurements were conducted for two different volume fractions ($f = 0.01$ and 0.05) to avoid potential biases due to the particle amount in the pellet sample. The volume fractions were calculated using the measured mass density values of the samples and the weighed ash particle mass. Results for the two volume fractions were subsequently averaged and the deviation taken as a measure of the uncertainty of the imaginary part determination. To remove the host material contribution at specific wavelengths, we applied a second-order polynomial.

To obtain $n_\lambda$, we used a model that is a combination of Sellmeier dispersion equations [Weber, 2003] in combination with a theoretical calculation of the refractive index from chemical composition data as described by Church and Johnson [1980]. This approximate approach has been caused by the fact that the total integrated reflection values of our samples embedded in the host matrix (pellet samples), also measured by the spectrophotometer, resulted in much higher reflectance values (30–40%) than conceivable considering the chemical and morphological nature of the powders. Potential reasons for such high reflectance are not entirely investigated, but part of ongoing research. Simultaneous elaboration of reflectance and transmittance data will bring most reliable empirical data on the RI of the ashes.

The model is based on dispersion curves for known chemical compositions and theoretical calculations of the refractive index. The Sellmeier equation is a semiempirical relationship between refractive index and wavelength for a transparent to slightly absorbing medium (in condition $k \ll n$). The form of the Sellmeier equation is

$$n^2 = 1 + 2 \sum \frac{B_i \lambda^2}{\lambda^2 - C_i},$$

(12)

where the $n$ is a function of the light wavelength ($\lambda$) and two empirically determined Sellmeier coefficients $B$ and $C$. These dimensionless coefficients are material specific and represent an absorption of strength $B_i$ at a wavelength $\sqrt{C_i}$. We applied the Sellmeier equation to all oxide components found in the ash particles multiplied by the weight fractions ($w_i$) of the major oxides, derived from the EDS bulk-compositional data, to obtain an averaged dispersion function. This calculation gives the weighted dispersion of the scattering part as a function of wavelength in the range between 300 and 1500 nm. To derive the material specific $n_{\text{so}}$, the calculated dispersion curve was fitted using single point values for a defined chemical composition and a single wavelength (in the visible range). The single point calculation

$$(n_{\text{so}} - 1) = \sum_{i=1}^{n_{\text{so}}} x_i w_i$$

is based on an arc-function, a quantitative relationship between the chemical composition of the sample and refractive index of individual components, where $w_i$ is multiplied by empirically derived refractivity material specific constants ($x_i$) for major component oxides. The individual constants are obtained by the Becke line method of pure components and are taken from Church and Johnson [1980].
3. Results

3.1. Chemical Composition

Table 2 shows the averaged chemical composition in oxide weight percent for all nine volcanic ash samples. The VA samples show characteristic compositions over a large SiO2 and total alkali (TA) content range (51.7 to 77.1 wt % and 2.67 to 7.31 wt %, respectively). The maﬁc basaltic (GRI) and the felsic rhyolitic (CHA) ash samples show only small variations in composition, represented by their standard deviation, both in TA (±0.43% and ±0.64%) and in SiO2 (±0.73% and ±1.19%) content, whereas the basaltic-andesitic to dacitic (intermediate volcanic rock range) samples show greater compositional variations and span over more than one rock type group (Figure 7). However, all samples could be classiﬁed into one deﬁned igneous rock group as indicated by the colors in Figure 7. For further analysis (mass density and optical properties), we averaged the samples SPU, SAK, and EYJ for the andesitic ash type and MSH, SOU, and RED for the dacitic ash type. In none of the samples we found a size dependent chemical composition variation (largest analyzed particle size was 100 μm), but some individual particles showed very different SiO2 content (<5% of all particles) due to the glassy phase fraction within the samples.

Figure 8 shows the variation of the different oxides in the bulk composition with varying SiO2 contents. FeO is decreasing with increasing SiO2 in accordance with the expected variations of Fe contents in the magmas. Fe contents tend to decrease with increasing SiO2, from 7–8 wt % in basaltic magmas to ~2 wt % in rhyolitic magmas [Le Maitre, 1976; Rogers and Hawkesworth, 2000]. CaO and MgO follow the same trend as FeO (r2 values between 0.5 and 0.85), which indicates that FeO, CaO, and MgO exist mostly in the silicate phase [Mysen and Richet, 2005]. The alkali oxides K2O and Na2O increase with increasing SiO2 indicative of their participation in the SiO2 glassy phase (Figures 9 and 10). Al2O3 present in alumino-silicates should increase with SiO2 if SiO2 was exclusively associated with alumino-silicates. However, the crystalline SiO2 content also increases with increasing SiO2 wt % in andesitic, dacitic, and rhyolitic compositions. The presence of Al2O3 in the same phase with SiO2 but also as an independent phase, may explain why Al2O3 does not show a clear trend (ratios between 0.24 and 0.31, except for CHA sample due to very high SiO2 content). TiO2 shows the same trend as FeO.

Table 2. Normalized Averaged Bulk-Chemical Composition of Ash Samples in wt % Measured by EDS, Including Composed Alkali Oxides and Calculated Ratios Between Individual Elements and the Predominate SiO2 Content

<table>
<thead>
<tr>
<th>Componentry (% ± σ)</th>
<th>Glass phase</th>
<th>Crystalline phase</th>
<th>Glass phase</th>
<th>Crystalline phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash type</td>
<td>Basalt</td>
<td>Basalt-andesite</td>
<td>Andesite</td>
<td>Trachy-andesite</td>
</tr>
<tr>
<td></td>
<td>50.9 ± 1.8</td>
<td>50.7 ± 3.1</td>
<td>60.6 ± 2.3</td>
<td>54.2 ± 4.5</td>
</tr>
<tr>
<td></td>
<td>49.1 ± 3.1</td>
<td>49.3 ± 5.3</td>
<td>39.4 ± 9.4</td>
<td>45.8 ± 5.7</td>
</tr>
<tr>
<td></td>
<td>±1.8</td>
<td>±3.1</td>
<td>±2.3</td>
<td>±8.0</td>
</tr>
<tr>
<td></td>
<td>±1.8</td>
<td>±3.1</td>
<td>±2.3</td>
<td>±8.0</td>
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<tr>
<td></td>
<td>50.9 ± 1.8</td>
<td>50.7 ± 3.1</td>
<td>60.6 ± 2.3</td>
<td>54.2 ± 4.5</td>
</tr>
<tr>
<td></td>
<td>49.1 ± 3.1</td>
<td>49.3 ± 5.3</td>
<td>39.4 ± 9.4</td>
<td>45.8 ± 5.7</td>
</tr>
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<td></td>
<td>±1.8</td>
<td>±3.1</td>
<td>±2.3</td>
<td>±8.0</td>
</tr>
<tr>
<td></td>
<td>±1.8</td>
<td>±3.1</td>
<td>±2.3</td>
<td>±8.0</td>
</tr>
</tbody>
</table>

The samples were ordered according to their SiO2 and total alkali contents into the main igneous rock classes indicated in the table.


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FeO, as TiO₂ has a stronger presence in lower silicate magma compositions. The calculated ratios between the individual components and SiO₂ are also summarized in Table 2. The measured chemical compositions of the ash samples correspond well with values reported in the literature (see references in Table 1).

3.2. Glass Contents

The correlation between the measured SiO₂ contents (bulk SiO₂ from EDS measurements) and the analyzed glass contents (analyzed light microscopy images) is shown in Figure 10. The colors represent the igneous rock types following Figure 6. We found that the mean glass contents of the ash samples ranged between 50% (2-D cross-sectional area analysis) glass content for the basalt/basaltic-andesite samples (GRI and KEL).

Figure 7. Classification of ash samples following their mean total alkali and silica (TAS) contents based on energy dispersive spectroscopy (EDS) data into the main igneous rock types. The colors in the plot represent the main igneous rock groups for basaltic (dark blue), basaltic-andesitic (blue), andesitic (green), dacitic (orange), and rhyolitic (red) ash types, that are used for the presentation of the complex refractive index data in section 3.2.

Figure 8. Correlation of the main chemical components with the silica content for the bulk-composition. These are (a) Al₂O₃/SiO₂ ratio, (b) FeO/SiO₂ ratio, (c) CaO/SiO₂ ratio, (d) MgO/SiO₂ ratio, (e) Na₂O/SiO₂ ratio, (f) K₂O/SiO₂ ratio, and (f) TiO₂/SiO₂ ratio. The blue lines indicate the resulting regression functions between each component.
and 72% glass content for the rhyolitic sample (CHA). However, the variation within each sample represented by the error bars indicates that individual particles can have smaller or higher values. Furthermore, we found that within individual compositional classification types the glass contents can vary up to 20% (Table 1).

### 3.3. Particle Size Distribution

The box-whisker plots of the particle number distributions of the ash samples are shown in Figure 11. The mean and median particle sizes, indicated by the red line and diamonds, respectively, vary from sample to sample (depending on distance between the eruption and sample location, eruption style, and meteorological conditions), but all ash samples show a comparable number distribution with a median size between 2.4 μm for GRI and 11 μm for KEL. The minimum detected particle diameter of each sample is 1.5 μm, due to the lower particle size threshold of the instrumental setting, whereas the maximum particle diameters are greater than 100 μm. The maximum particle sizes vary between 120 μm for SPU and 280 μm for SAK but represent less than 1% of the total number distribution indicated by the blue crosses.

![Figure 11. Box-whisker plots showing the particle size distribution of the ash samples.](image)

Additional sensitivity tests with a 50X objective lens indicate that the minimum particle size in each sample is smaller (<1 μm), but the mean and median size of the particle size distribution changed only marginally. The majority of all particles (25–75% range) in each sample range between 2 μm for GRI and 20 μm for KEL (indicated by the boxes) and are therefore within the particle size range that is most relevant for atmospheric long-range transport.

### 3.4. Particle Morphology

Particle morphological parameters within the measured ash samples displayed a wide range of variability, which decreased as particle size increased (Figure 13, blue markers).
Particle morphology was characterized in coarse ($d_{2-D} = 63–100 \mu m$) and fine ($d_{2-D} < 63 \mu m$) fractions for each ash sample (Figure 12). For a consistency check, we also evaluated the differences between the $< 20 \mu m$ size range (very fine ash fraction) and the fraction between 20 and 63 $\mu m$. As we found no significant differences between these two size fractions, we report values only for the fine and coarse ash fractions.

Figure 12 shows the three shape parameters for all samples separated into the fine and coarse ash fractions measured by ASPI. On the one hand, the shape parameter mean values are remarkably consistent between the nine different ash samples, with only 2.35–6.25% variation for the fine fraction and 5.32–13.2% variation for the coarse ash fraction.

On the other hand, the variability of particle shapes within each ash sample, indicated by the standard deviation, is much higher (up to 20%) as the shapes for individual particles can range from spherical to highly nonspherical (see blue dots in Figure 13). The aspect ratio and the Wilson shape parameter, which both describe the particle elongation [Bagheri et al., 2015], indicate very small differences between the fine and the coarse mode particles, whereas the Cox circularity is larger for smaller particles.

In addition to the comparison of the averaged shape parameters for the coarse and fine fraction of the ash samples, we also analyzed the shape directly as a function of particle size in the size range <100 $\mu m$ (Figure 14). Since there were relatively small differences in the shape parameters between the different ash samples, we only show the size-dependent shape parameter for all samples together. Therefore, each line
Figure 13. Correlation between the ASPI and the DIA instruments for the calculated aspect ratio of an sample KEL. The blue dots are the single analyzed particles measured by the ASPI, and the red line is the corresponding averaged aspect ratio. The yellow line indicates the mean aspect ratio measured by DIA over the same size range.

Figure 14. Shape parameters plotted as a function of the particle diameter ($d_{2D}$) in the size range between 0.5 and 100 μm. Shape parameters are averaged over 5 μm size bins using data from all analyzed particle samples. The variation of the parameter values is indicated by the standard deviation.
As a general validation of the measured size and shape parameters obtained by ASPI and to eliminate potential measurement artifacts, we repeated the analysis with a second instrument (DIA) that measured the same parameters. Figure 13 shows, as an example, the correlation between the ASPI and the DIA instruments for the calculated aspect ratio for the sample KEL. The blue dots indicate single analyzed particles measured by the ASPI. The red line illustrates the corresponding averaged aspect ratios resulting from the average of the single point measurements. The yellow line indicates the aspect ratio over the same size range measured by DIA. The correlation of the two data sets shows a good agreement between the two instruments and thus confirms the measured shape trends by the ASPI. Moreover, the measurements by the DIA also confirm the increase of the shape parameter in the size range between 0.5 and 5 μm (first marker).

3.5. Mass Density

Figure 15a shows the correlation of the DRE density measured by Archimede densitometry and the SiO2 content obtained by EDS. We used the SiO2 content, as a predominant and representative component in the overall bulk-chemical composition measured by EDS and (b) measured mass density versus mass density derived from the measured chemical composition. The solid lines show the regression functions between the values, whereas the dashed line in (b) represents the 1:1 line. The shaded area in Figure 15a indicates the 1-sigma range of the correlation between the measured mass density and the SiO2 content.

Figure 15. (a) Measured mass density versus SiO2 content as a predominant fraction of the overall bulk-chemical composition measured by EDS and (b) measured mass density versus mass density derived from the measured chemical composition. The solid lines show the regression functions between the values, whereas the dashed line in (b) represents the 1:1 line. The shaded area in Figure 15a indicates the 1-sigma range of the correlation between the measured mass density and the SiO2 content.
each sample with more than 50 wt %, to correlate the measured density with the chemical composition. The resulting regression function ($y = \frac{5}{C_0} + 3.8988$) and the 1-sigma ranges, indicated by the blue line and the blue shaded area in Figure 15a, respectively, illustrate that the DRE density decreases with increasing SiO$_2$ content ($r^2 = 0.94$). The scatter of the data results from uncertainties of both the measured density, the vesicularity, and of the measured composition. The resulting measurement uncertainty range is between 10.3 and 19.34% for KEL and RED, respectively.

For a consistency check of the measured mass density data, we also calculated the density based on the major oxides weight fractions as obtained from the compositional analysis (EDS). The correlation in Figure 15b shows that both approaches give similar results with values around the 1:1 line and a high correlation coefficient ($r^2 = 0.93$; the black solid line represents the resulting linear regression, $y = 1.1903x - 0.4556$). However, all values lie within the uncertainties of the measurements that originate mainly from the small variability of chemical composition and vesicularity within the ash samples.

According to the igneous rock classification, we calculated average density values based on the regression function obtained by the correlation of the SiO$_2$ content and the measured mass density. Hence, the density including their standard deviation ($\mu \pm \sigma$ in g/cm$^3$) for basaltic, basaltic-andesitic, andesitic, dacitic, and rhyolitic ashes are $\rho = 2.98 \pm 0.04, 2.87 \pm 0.03, 2.77 \pm 0.03, 2.65 \pm 0.03$, and $2.49 \pm 0.06$ g/cm$^3$, respectively (Table 5).

### 3.6. Complex Refractive Index

We obtained complex refractive index data in the wavelength range between $\lambda = 300$ and 1500 nm. We used the combination of a theoretical arc function method and Sellmeier dispersion equations to derive the scattering properties in a chemical and theoretical description as shown in Figure 16a. Values for the standard deviation of each sample group are plotted at high spectral resolution, but for a better orientation the standard deviation of each sample group is plotted only at 100 nm intervals (circles).
deviation of the data were calculated using the reported uncertainties (±0.007) of the single-point refractive index calculation. Since these data are based on theoretical calculations, the distribution over the wavelength range of these data are very similar. However, the data show that the $n_i$ are highest in the UV range and decrease with wavelength.

For a systematic representation of these data, we used the chemical composition of our samples, obtained by EDS, to group the nine different samples according to their SiO$_2$ and total alkali contents into the five main igneous rock groups. The data illustrate the strong dependence of the scattering part on the chemical composition of the samples. The lowest scattering values were found for the highest SiO$_2$ content ash type (rhyolitic ash) with values between $n_i = 1.38$ for 1500 nm and $n_i = 1.53$ for 300 nm wavelengths, whereas the highest values were found for the lowest SiO$_2$ content (basaltic ash) with values between $n_i = 1.50$ for 1500 nm and $n_i = 1.66$ for 300 nm. The other ash types (basaltic-andesitic to dactitic ash) lie between the basaltic and rhyolitic ash types according to their chemical compositions.

For the determination of $k_\lambda$, we did not find any systematic differences between the 1 vol % and 5 vol % samples. Therefore, we first averaged the data from the 1 and 5 vol % pellet samples and, secondly, averaged the measurement data for samples in each group according to the igneous rock classification. Different to the trend for $n_i$, the values for $k_\lambda$ are lower in the UV-range and increase with wavelength due to the presence of wide absorption bands in the NIR, varying in intensity from different ash types and thus with the chemical compositions. The lowest absorption values were found for the highest SiO$_2$ ash type (rhyolitic ash) with values between $k_\lambda = 0.00028$ for $\lambda = 300$ nm to $k_\lambda = 0.00054$ for $\lambda = 1500$ nm wavelengths, whereas the highest values were found for the lowest SiO$_2$ content (basaltic ash) with values between $k_\lambda = 0.00165$ for $\lambda = 300$ nm to $k_\lambda = 0.00268$ for 1500 nm wavelengths. Like in the scattering regime, the other ash types (basaltic-andesitic to dactitic ash) lie between the basaltic and rhyolitic ash types according to their chemical compositions. The samples with the smallest variation in chemical composition showed also the smallest variation in absorptivity.

4. Discussion

4.1. Particle Composition

Chemical composition forms the basis of volcanic ash classification [Le Bas and Streckeisen, 1991] and has a fundamental influence on other parameters such as the mass density or the optical properties. The deviation in composition in the intermediate range (basaltic-andesitic to dacitic ash) as shown in Figure 7 can be the result of several processes such as fractional crystallization of a mafic parent magma, partial melting of crustal material, or magma mixing between felsic rhyolitic and mafic basaltic magmas in a magma reservoir. Our measured compositions of the individual ash sample are confirmed by earlier studies where the same samples were already analyzed and their compositions determined [e.g., Bayhurst et al., 1994; Adams et al., 1996; McGimsey et al., 2001; Alfano et al., 2011; Gislason et al., 2011; Cole et al., 2015].

The ratios between the particle bulk and surface composition (oxides in wt %) are shown in Figure 9. The SiO$_2$ ratios show an overall behavior, where there is a 1:1 surface to volume compositional ratio or a surface enrichment in SiO$_2$. This is reasonable if we consider that most of the bulk composition consists of SiO$_2$ and most of the fracture and therefore surface formation originates in the amorphous silicate phase. Another feature is that Ca, Mg, Na, and K ratios follow overall similar trends and are slightly depleted in most ash surfaces as reported by Delmelle et al. [2007], Ayris and Delmelle [2012], and Barone et al. [2014]. We found also a smaller Fe concentration in the particle surface than in the particle bulk but less pronounced than shown by Delmelle et al. [2007]. The depletion of these substances on the particle surface may result from either dissolution of an external layer by corrosive mixed gaseous/aqueous fluids (with, e.g., H$_2$S, SO$_2$, HCl, HF, HBr, or H$_2$SO$_4$ forming acidic conditions) or from gaseous fluorine metasomatism at high temperature [Delmelle et al., 2007; Barone et al., 2014]. Acidic conditions could promote dissolution of the basic FeO, CaO, and MgO oxides and formation of soluble salts, which can be washed away by water. The Al$_2$O$_3$ ratios show the smallest variation. All values lie around the 1:1 ratio line. The small deviations may originate from either Al$_2$O$_3$ participating in the silicate phase or also in other crystalline oxide phases. TiO$_2$ ratios follow the trend of FeO as these two oxides coexist in the same mineral phases titan magnetite (Fe$_2$TiO$_4$) and ilmenite (FeTiO$_3$) [Ayris and Delmelle, 2012].
Our glass content data show a good correlation with available literature on the same volcanic eruptions and samples (Table 3). The variation between the values result from differences in sample collection (time and location), applied measurement technique and number of analyzed samples. In the case of our light microscope image analyses, the uncertainties result from manual thresholding (contrast between some particles and the background was too low), and in some cases crystalline particles were present on top of amorphous phases and were taken as crystalline phases only. However, the deviation between the literature values and our values are in the range of 12% and therefore within the error bars of our sample measurements. An comprehensive overview of the glass contents of ash from various eruptions is summarized in Cashman and Rust [2016] (Figure 2 and table in the supporting information).

4.2. Particle Physical Properties

Improved knowledge about the microphysical properties of the fine ash fraction is important to investigate atmospheric transport and remote sensing measurements of volcanic ash clouds [Riley et al., 2003]. The size and shape controls particle aerodynamic parameter such as the drag coefficient and the terminal velocity of the particles, whereas the mass density also influences gravitational settling and is important to calculate ash mass loadings and mass concentrations from observed particle volume distributions. The applied 2-D measurement approach is a simplified particle characterization method that provides reliable and accurate particle size and shape information [Leibrandt and Le Pennec, 2015; Liu et al., 2015]. Compared to very precise, but costly 3-D measurement methods as described by Bagheri and Bonadonna [2016a], the 2-D measurements are faster to acquire without losing accuracy when a sufficient number of single particles is investigated [Bagheri et al., 2015].

Our particle shape results show that the different shape parameters have a clear dependency on the individual particle sizes (Table 4). This size dependency was consistent in all nine ash samples investigated in this study. The shape parameter show thereby different trends with increasing particle size. Furthermore, findings by Riley et al. [2003] and Mills and Rose [2010] confirm our results, as they found the same shape trend with changing particle size, including the increase of shape parameter values for the smallest particle sizes (<5 μm) as shown in Figure 14 for the their Mount Spurr and Fuego ash samples. The measurement with an independent instrument (DIA) supports this result.

Particle DRE mass density is an important parameter for both the atmospheric transport of VA particles and to calculate their mass loadings from volume measurements. Our investigated values lie all in the reported mass density range for glass shards, lithic fragments, and crystalline minerals [Shipley and Sarna-Wojcicki, 1983] and show that the DRE density can be clearly specified for each of the main igneous rock groups. In many atmospheric related studies, the density is chosen rather arbitrarily due to a lack of reported direct measurements. For example, during the 2010 Eyjafjallajökull eruption, values between \( \rho = 2.4 \text{ g/cm}^3 \) [Gudmundsson et al., 2012] and \( \rho = 3.0 \text{ g/cm}^3 \) [Stohl et al., 2011] were used. Our data show a good agreement with DRE density values reported by Bonadonna et al. [2011] for trachy-andesitic Eyjafjallajökull ash samples (\( \rho = 2.74 \text{ g/cm}^3 \)) and by Eychenne and Le Pennec [2012] for andesitic Tungurahua ash samples (\( \rho = 2.68 \text{ g/cm}^3 \)). DRE mass density values reported by Pistolesi et al. [2014] for dacitic-rhyolitic Cordón Caulle ash samples (\( \rho = 2.69 \text{ g/cm}^3 \)) are slightly higher, but still within our 1-sigma range. The only reported value in the literature for direct

<table>
<thead>
<tr>
<th>Volcano</th>
<th>Eruption Date</th>
<th>This Study</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mount St.Helens</td>
<td>1980</td>
<td>70.0</td>
<td>72.0</td>
</tr>
<tr>
<td>Redoubt</td>
<td>1989</td>
<td>69.5</td>
<td>69.0</td>
</tr>
<tr>
<td>Spurr</td>
<td>1992</td>
<td>57.6</td>
<td>64.5*</td>
</tr>
<tr>
<td>Chaiten</td>
<td>2008</td>
<td>72.1</td>
<td>76.1</td>
</tr>
<tr>
<td>Eyjafjallajökull</td>
<td>2010</td>
<td>54.2</td>
<td>61.8*</td>
</tr>
<tr>
<td>Grimsvötn</td>
<td>2011</td>
<td>50.9</td>
<td>50.6</td>
</tr>
</tbody>
</table>

*a Averaged glass content, range 60–69%.
*b Averaged glass content, range 59.5–65.5%.
DRE density measurements, conducted by Rocha-Lima et al. [2014] for andesitic Eyjafjallajökull ash ($\rho = 2.16 \text{ g/cm}^3$), is the only data that do not correlate with our finding and other findings by Bonadonna et al. [2011] for the same eruption. But they are even smaller than the density of pure glass shards ($\rho = 2.35–2.45 \text{ g/cm}^3$) [Wilson et al., 2012], which is difficult to understand.

### 4.3. Particle Optical Properties

In the literature, only a small number of studies investigated the optical properties of volcanic ash particles and half of the studies measured the absorption part of the complex refractive index only (as illustrated in Figure 2 and references therein). To place our results into the context of existing data sets, we compared our data with values from Ball et al. [2015] (Ba15) for the wavelengths $\lambda = 450$, $\lambda = 546$, and $\lambda = 650 \text{ nm}$ and Pollack et al. [1973] (Po73) for the scattering part (Figure 17), and with values from Ball et al. [2015], Pollack et al. [1973], Rocha-Lima et al. [2014] (Ro14), and Patterson et al. [1983] (Pa83) for the absorption part (Figure 18). For a better comparability of the different data sets, we grouped the literature data also according to the reported chemical composition, into the igneous rock groups, where the colors in Figures 17 and 18 correspond to the colors used in the SiO$_2$ and total alkali International Union of Geological Sciences (IUGS) classification (Figure 7). The dashed line in each plot indicates the 1:1 line. Note that according to the IUGS classification, the chemical composition of the Po73 “andesite” sample...
corresponds to basalt-andesite and not andesite. Thus, we compared the Po73 “andesite” with our basalt-andesite values. The calculated values for the scattering part show a good agreement ($r^2 = 0.97$) with the Ba15 data (for all ash types; Figure 17a), measured with the Becke line method. The scattering data for the basaltic and the rhyolitic ash types in Po73 (Figure 17b) show a good agreement to our data ($r^2 = 0.78$ and 0.74, respectively), where both data sets reveal a similar trend with higher values in the UV range and a decrease with increasing wavelength but with less variations in the Po73 data. However, no correlation was found for the basalt-andesitic ash type. One potential reason for this could be that the Po73 data show no variability over the wavelength range. No other data set in the literature shows a similar trend with no variation of $n_\lambda$ in the UV/Vis wavelength range.

The comparison of the measured absorption part data is shown in Figure 18, where our data are compared to other direct transmittance measurements (Figures 18a and 18b) as well as to calculated absorption part data from optical reflectance measurements (Figures 18c and 18d). Dependent on the techniques used to derive the absorption properties, the agreement of the data can vary especially in the UV range. The correlation to the direct transmittance measurements shows a good agreement. For Ba15 the data lie very close to the 1:1 line ($r^2 = 0.96$). The correlation to the Po73 values shows no clear trend with a very low covariation. Our data are higher for the basaltic sample, lower for the basalt-andesitic ash type, and nearly the same for the rhyolitic ash type. The absorption part data obtained by the indirect measurement methods (scattering data were converted to absorption using the Kubelka-Munk theory) show both the same pattern. The values are much higher (light green dots in Figures 18c and 18d) in the UV range ($\lambda < 500$ nm) and show a decrease with increasing wavelength before they increase again. We find no correlation when we compare our data to all data points (wavelength range between $\lambda = 300$ and $\lambda = 1600$ nm) shown in Figures 18c and 18d. However, if we compare our data with those of Ro14 and Pa84 only in the wavelength range between

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**Figure 18.** Correlation of measured imaginary part data of refractive index with data from the literature. Correlation with data from (a) Ball et al. [2015] for the wavelengths 450, 546, and 650 nm; (b) Pollack et al. [1973] for the wavelength range between 300 and 1500 nm; (c) Rocha-Lima et al. [2014] for the wavelength range between 350 and 1500 nm; and (d) Patterson et al. [1983] for the wavelength range between 300 and 700 nm.
\( \lambda = 500 \) and \( \lambda = 1500 \) nm, we see a very good correlation with \( r^2 = 0.84 \) and 0.6, respectively. Independent of the deployed measurement technique in all studies and given the high variability in the chemical composition of the individual samples, our results show reassuring conformity to existing literature values (Figures 17 and 18).

The striking feature in all data sets (our data and available literature values), both for \( n \) and \( k \), is the clear relation between high \( n \) and \( k \) values for low \( \text{SiO}_2 \) contents and low values for high \( \text{SiO}_2 \) contents (in UV/Vis/NIR range). We summarized these findings in Figure 19 and in Table 5. The plot shows the real part (Figure 19a) and the imaginary part (Figure 19b) of the complex RI as a function of both the spectral wavelength and the \( \text{SiO}_2 \) content (as a representation of the different chemical compositions) of the ash. These plots can be used to get direct information of the RI for different instruments such as lidars, optical particle counters (OPCs), or satellite instruments (knowing their specific wavelength for the detection of VA), when only the \( \text{SiO}_2 \) content of the magma is known.

### 4.4. Broader Context and Application of Data Set

This study presents for the first time a detailed data set that investigated a wide range of volcanic ash particle properties for different volcanic ash types combined in one study. We placed our data in the context of existing data from other studies and combined them in this data set. Improved knowledge of the investigated
properties are relevant for the detection and forecasting of volcanic ash clouds as well as the estimation of their potential impacts on climate, aviation, and human health. Thus, this data set can contribute to minimize uncertainties in the calculation and detection of ash clouds for future or historic volcanic eruptions even when only information about the magma composition is available. We make all data used to generate figures and tables available (see the supporting information), and we hope that our data set can serve as a reference for future studies requiring information on volcanic ash properties.

5. Conclusions

In this paper, we determined the physical, chemical, and optical properties of a representative selection of fine ash samples (d < 63 μm) from nine different volcanoes and volcanic eruptions. We used different measurement techniques (image analysis, Archimedean densitometry, energy dispersive, X-ray photoelectron, and UV/Vis/IR spectroscopies) and theoretical methods to obtain the particle bulk and surface chemical composition, the particle size and morphology, DRE mass density, and the spectral complex refractive index.

EDS and XPS measurements showed that the particle bulk and surface have comparable chemical compositions for most of the elements and that all ash samples could be clearly classified into one of the main igneous rock type groups according to their SiO2 and total alkali contents. Thus, the nine VA samples cover a wide range of SiO2 contents ranging from basalt (~50 wt % SiO2) to rhyolite (~80 wt % SiO2). The analysis of the particle cross section returned stable and reproducible data on the chemical composition that plays a key role in governing the mass density and the complex refractive index. Comparing the bulk composition with the composition of the particle surface (2 to 10 nm depth), we found—despite the overall similarities—also notable differences between the surface and bulk chemical composition. The elements Ca, Na, Mg, and Fe ratios showed slightly higher concentrations in the bulk material compared to the surface, whereas Si was enriched on the surface due to a potential dissolution of an external layer by corrosive mixed gaseous/aqueous fluids.

The light microscopy measurement showed that the glass content can vary from the bulk SiO2 content. We also found that the glass content within each igneous rock groups can vary significantly especially in the andesite and dacite region.

From the static and dynamic particle imaging measurements, we found that the particle morphology depends systematically on the particle size (in the size range d_{x,50} < 100 μm), and this finding was consistent over the entire sample set. The aspect ratio and the Wilson shape parameter, as measures of particle elongation, showed no significant difference between fine and coarse ashes, whereas the Cox circularity, the measure of the particle roundness, showed significant differences. The overall shape parameters for the fine ash fraction are 0.71, 0.84, and 0.85 for the aspect ratio, the Cox circularity, and the Wilson shape parameter, respectively, and for the coarse ash fraction (d > 63 μm) corresponding values are 0.72, 0.74, and 0.84. This consistent pattern in the shape parameters can be used to parameterize the particle shape in ash transport and dispersion, climate, or theoretical terminal velocity calculation models. The DRE mass density, as obtained from Archimedean densitometry and theoretical calculations, shows a clear dependency on the individual chemical composition of the samples and decreases with increasing SiO2 content. Thus, the

<table>
<thead>
<tr>
<th>Igneous Rock Typesa</th>
<th>SiO2 (wt % ± σ)</th>
<th>Total Alkali (wt % ± σ)</th>
<th>Mass Density μ ± σ (g/cm³)</th>
<th>Refractive Index Range (λ = 300–1500 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt</td>
<td>48.5 ± 3.5</td>
<td>2.5 ± 2.5</td>
<td>2.98 ± 0.038</td>
<td>1.50–1.66</td>
</tr>
<tr>
<td>Basalt-andesite</td>
<td>54.5 ± 2.5</td>
<td>2.9 ± 2.9</td>
<td>2.87 ± 0.027</td>
<td>1.46–1.62</td>
</tr>
<tr>
<td>Andesite</td>
<td>60.0 ± 3.0</td>
<td>3.3 ± 3.3</td>
<td>2.77 ± 0.032</td>
<td>1.43–1.58</td>
</tr>
<tr>
<td>Dacite</td>
<td>66.0 ± 3.0</td>
<td>3.7 ± 3.7</td>
<td>2.65 ± 0.032</td>
<td>1.41–1.57</td>
</tr>
<tr>
<td>Rhyolite</td>
<td>75.0 ± 6.0</td>
<td>7.0 ± 7.0</td>
<td>2.49 ± 0.060</td>
<td>1.38–1.53</td>
</tr>
</tbody>
</table>

For each group the averaged SiO2 and total alkali contents, the measured mass densities, and complex refractive indices for the wavelength range between 300 and 1500 nm are shown.
DRE mass density was found to be in the range from $\rho = 2.49 \pm 0.06$ g/cm$^3$ for rhyolitic ashes to $\rho = 2.98 \pm 0.04$ g/cm$^3$ for basaltic ashes. The complex refractive index over a wide wavelength range ($\lambda = 300$ to 1500 nm) was analyzed for the first time for a wide silica range and for a high number of different ash samples. We found that the RI shows a clear dependency on the individual chemical composition of the samples, and especially on the SiO$_2$ content, which could be shown after applying the IUGS chemical classification, both for our data and for data from the literature. This allowed us to connect the wavelength-dependent RI values directly with the SiO$_2$ contents. Modeled values for the real part, $n_r$, obtained by a combination of the arc-function method and the Sellmeier semiempirical link between refractive index and the chemical composition of the ashes, returned results that agree well with available literature values. We found a decrease of values with increasing wavelength, where basaltic, basaltic-andesitic, and andesitic showed stronger dependency on wavelength, due to a higher potential to absorb light. The dactitic and rhyolitic ash types showed only small absorption properties. The data set could be further extended by future studies if more data are added to groups with limited samples (basalt, basaltic-andesite, and rhyolite) or where no samples are available (e.g., trachyte, phonolite, and andesite).

Comparison of our bulk material results with pure glass components of the same ash samples would be very helpful for a better understanding of the relation between refractive index and composition. Finally, measurements of the optical properties of VA in the near-infrared to the infrared spectral range ($\lambda = 1.5$–20 $\mu$m) would be useful for infrared remote sensing algorithms.

**References**


Ball, J. G. C., B. E. Reed, R. G. Grainger, D. M. Peters, T. A. Mather, and D. M. Pyle (2015), Measurements of the complex refractive index of andesitic, dacitic, and basaltic ashes from the 8 May 2010 Eyjafjallajökull eruption (Iceland) under grant agreement number 57001. The contribution of C. Laflin in northern high latitudes) under grant agreement number 27307–5.


Artificial cloud test confirms volcanic ash detection using infrared spectral imaging


Nature - Scientific reports, 2016
Artificial cloud test confirms volcanic ash detection using infrared spectral imaging


Airborne volcanic ash particles are a known hazard to aviation. Currently, there are no means available to detect ash in flight as the particles are too fine (radii < 30 μm) for on-board radar detection and, even in good visibility, ash clouds are difficult or impossible to detect by eye. The economic cost and societal impact of the April/May 2010 Icelandic eruption of Eyjafjallajökull generated renewed interest in finding ways to identify airborne volcanic ash in order to keep airspace open and avoid aircraft groundings. We have designed and built a bi-spectral, fast-sampling, uncooled infrared camera device (AVOID) to examine its ability to detect volcanic ash from commercial jet aircraft at distances of more than 50 km ahead. Here we report results of an experiment conducted over the Atlantic Ocean, off the coast of France, confirming the ability of the device to detect and quantify volcanic ash in an artificial ash cloud created by dispersal of volcanic ash from a second aircraft. A third aircraft was used to measure the ash in situ using optical particle counters. The cloud was composed of very fine ash (mean radii ~10 μm) collected from Iceland immediately after the Eyjafjallajökull eruption and had a vertical thickness of ~200 m, a width of ~2 km and length of between 2 and 12 km. Concentrations of ~200 μg m⁻³ were identified by AVOID at distances from ~20 km to ~70 km. For the first time, airborne remote detection of volcanic ash has been successfully demonstrated from a long-range flight test aircraft.

Fine (radii < 30 μm) airborne volcanic ash is composed of irregular shaped minerals and glass components with an SO₂ content ranging from 40% to 80%. Copious amounts of ash can be emitted high into the atmosphere from even moderate-sized volcanic eruptions, where the atmospheric circulation can transport it 100s to 1000s km, intersecting commercial air routes and presenting a major hazard to aviation. During the April and May 2010 eruption of Eyjafjallajökull, European aviation was grounded for five days causing large economic and societal impacts with estimated losses of US$5bn to the global economy. Volcanic ash damages jet engines as the glassy eruption of Eyjafjallajökull generated renewed interest in finding ways to identify airborne volcanic ash in order to keep airspace open and avoid aircraft groundings. We have designed and built a bi-spectral, fast-sampling, uncooled infrared camera device (AVOID) to examine its ability to detect volcanic ash from commercial jet aircraft at distances of more than 50 km ahead. Here we report results of an experiment conducted over the Atlantic Ocean, off the coast of France, confirming the ability of the device to detect and quantify volcanic ash in an artificial ash cloud created by dispersal of volcanic ash from a second aircraft. A third aircraft was used to measure the ash in situ using optical particle counters. The cloud was composed of very fine ash (mean radii ~10 μm) collected from Iceland immediately after the Eyjafjallajökull eruption and had a vertical thickness of ~200 m, a width of ~2 km and length of between 2 and 12 km. Concentrations of ~200 μg m⁻³ were identified by AVOID at distances from ~20 km to ~70 km. For the first time, airborne remote detection of volcanic ash has been successfully demonstrated from a long-range flight test aircraft.

1Nicarnica Aviation AS, Vollsvæn 9-11, N-1366, Lysåker, Norway. 2Visiting scientist, Department of Atmospheric, Oceanic and Planetary Physics, University of Oxford, UK. 3Airbus Operations SAS, Toulouse, France. 4easyJet plc, Luton, UK. 5Department for Mechanical Engineering, Düsseldorf University of Applied Sciences, Düsseldorf, Germany. 6Airbus SAS, Toulouse, France. 7Section for Meteorology and Oceanography, Department of Geosciences, University of Oslo, Norway. 8Atmosphere and Climate Department, Norwegian Institute for Air Research, Kjeller, Norway. 9Department of Earth Sciences, University of Oxford, UK. 10Visiting Scientist, School of Earth Sciences, University of Bristol, BS8 1RJ. Correspondence and requests for materials should be addressed to A.J.P. (email: fp@nicarnicaaviation.com)
According to the image and their size is proportional to the mass concentrations measured by the OPC. Panel (c) shows a sum-mative detection of ash. Also, during these tests, the system was flown on a long traverse towards the Canary Islands, because of its high SiO2 content. While AVOID cannot distinguish airborne ash from windblown sand, both are hazardous to aviation and windblown sand is mostly found at much lower altitudes than volcanic ash.

Following these successful trials, it was decided that the system should be tested at an ash producing volcano. However, the logistical constraints on the A340 aircraft and availability of reliable ash producing eruptions with cloud heights of 10,000 ft or higher made it extremely difficult to find an ash cloud without compromising air safety or affecting the environment. Approximately 1000 kg of fine ash with a size distribution having a mean radius of 10 μm and geometric standard deviation $\sigma = 1.8$ was injected into the atmosphere at an altitude of ~12,000 ft from an AIRBUS A400M flight-test aircraft executing an up-and-down flight path. The ash was dropped from a plane. The ash cloud was detected by AVOID as an extremely thin layer (~200 m deep) and quickly dispersed horizontally to form an ash cloud approximately 2 km wide and 12 km long, but was not visible to the eye or to visible wavelength cameras (Fig. 1a). Within 30 minutes of the ash cloud layer forming, the A340 aircraft carrying the AVOID instrument flew towards it from approximately 80 km distance at an altitude of 15,000 ft (Fig. 1b, flight run 1). The aircraft turned at approximately 20 km from the location of the ash layer. Three further approaches were made toward the ash layer from altitudes of 10,000 ft (flight run 2), 5,000 ft (3) and 5,000 ft (4). The purpose of these flight runs was to image the ash cloud from above, along the limb and from below. During the injection of the ash into the atmosphere, the ash layer was initially visible to the naked eye, but within a few minutes it was no longer possible to identify the layer. In order to obtain verification of the AVOID measurements of the ash layer, a small aircraft (a Diamond DA42 MPP) equipped with optical particle counters (OPCs) flew into the ash layer and made in situ measurements of the ash.

Ash was identified by the AVOID system on three of the four flight runs; no ash was detected from 15,000 ft because the ash layer was too low to be within the field of view of the cameras. On flight runs 3 and 4 (5,000 ft) it was possible for AVOID to identify the small aircraft flying within the ash layer. AVOID first reliably identified the layer from a distance of ~67 km. At that distance individual camera images measure ~10° × 10°, giving approximately 20 vertical pixels for the layer (~200 m deep). Mass loadings along the line of sight of the instrument were calculated (see Methods) and ranged from 0.1 g m$^{-2}$ to 1.6 g m$^{-2}$. These convert to concentrations of ~200–320 μg m$^{-3}$, using an ash cloud width of ~2 km, as measured by the DA42. Figure 2, Panel (a) shows the times when ash was detected during flight run 3. Detections are only possible when the field of view of the image and their size is proportional to the mass concentrations measured by the OPC. Panel (c) shows a sum-mary of detections from three flight tracks at ranges from 10–65 km. Assuming a homogeneous ash layer ~200 m deep by ~2 km wide and ~12 km long (see Methods), we can calculate the theoretical detection probability for the imaging device at varying distances from the cloud. This can be compared with the actual detection, expressed
as a percentage of the total number of pixels within the field of view of the cameras. The results indicate very good detection (compared to the theoretical curve) for distances from ~25 to 60 km. The theoretical detection threshold takes no account of inhomogeneities in the ash cloud or changes in the pitch of the instrument that affect the path length and hence mass loading sensitivity. As the aircraft approached within 20 km of the cloud, the imager began to observe the cloud from increasingly large viewing zenith angles, reducing the path length and also observing through the centre of the ash cloud, which contained concentrations below the limit of detection of AVOID, <~100 μg m⁻³ for ash cloud thicknesses of ~2000 m. Hence at distances of ~20 km from the cloud ash detection was problematic.

The vertical depth of the ash layer was verified by descending and ascending the DA42 until negligible particles were counted. The AVOID measurements suggest a descent of the ash layer of ~0.3 m s⁻¹ (Fig. 3a), broadly consistent with terminal velocities for spherical particles of density ~2600 kg m⁻³. The distribution of mass determined from the OPC measurements indicates two peaks: a background peak near 70 μg m⁻³ and a second peak near 400 μg m⁻³, associated with the ash cloud (Fig. 3b). These measurements (Fig. 3c) also show that the layer was not more than ~300 m deep. The OPCs measured ash concentrations between 100 μg m⁻³ to 6000 μg m⁻³ with a very high degree of heterogeneity in the cloud (Fig. 3c). The smaller range of concentrations (~100 to ~600 μg m⁻³) measured by AVOID compared to the OPCs may be a consequence of the averaging process of the imager and is also due to the assumption of a uniform width of the ash cloud.

The sensitivity of the AVOID system depends on the mean effective radius of the ash size distribution and the composition of the ash. We measured the ash size distribution before and after the experiment and found no discernible difference in the mean radius (~10 μm). The composition of the ash was measured before the experiment; the sample had a complex structure (Fig. 4a) and contained a significant glassy proportion (Fig. 4b). The composition was dominated by SiO₂ (Fig. 4c).

The identification of an ash layer embedded within an atmosphere containing meteorological clouds from distances of up to ~60 km, provides a warning time of 4 minutes for an aircraft travelling at 900 km hr⁻¹. This is sufficient time to make a gradual change in course direction and avoid intersecting the ash layer. Using the Caliop (Cloud-Aerosol Lidar with Orthogonal Polarisation) lidar and AIRS (Atmospheric Infrared Sounder) satellite instrument data, it was found that during the Eijafjallajökull, Chaitén (May 2008), Sarychev Peak (June, 2009),...
Puyehue-Cordón Caulle (June, 2011) and Calbuco (April 2015) eruptions the ash layers were thin; ranging from 500 m to 3000 m deep\textsuperscript{17,18}. Ground-based\textsuperscript{19,20} and airborne\textsuperscript{21,22} lidar measurements and modelling\textsuperscript{23,24} of dispersing ash layers also support this finding.

Near real-time satellite detection of ash clouds is currently used by VAACs and dispersion and transport models are used to forecast their concentration and movement. However, dispersing ash clouds forming in thin layers (< ~2000 m) may not be detected by satellite instruments, and may not be vertically resolved by current dispersion models. While satellite data and model forecasts can provide strategic information for airlines to plan their operations\textsuperscript{5}, uncertainties in eruption source parameters coupled with uncertainties in forecast wind measurements lead to errors in the forecast ash cloud location\textsuperscript{11}. Furthermore, the recent eruption of Kelut volcano, Indonesia on 13 February 2014 demonstrated that even with good information on the location and timing of the eruption, it did not prevent a commercial aircraft from encountering an ash layer and damaging its engines. In this case, the encounter occurred in low light, in an ash layer that was hidden from the satellites’ view by a larger ash umbrella cloud. Modelling\textsuperscript{25} showed that the aircraft likely encountered this cloud for several minutes and that ash concentrations ranged from 2000 μg m\textsuperscript{-3} to 9000 μg m\textsuperscript{-3}. An airborne detection system would have alerted the aircraft and allowed a timely and safe routing option for the aircraft to avoid an encounter with the ash cloud.

The results from this experiment successfully demonstrated remote detection of ash clouds using thermal imaging cameras. An earlier experiment in skies containing no ash gave a false detection rate of ~7%, but with some
fine tuning of the thresholds used in the algorithm, improvements in the sensitivity of uncooled bolometric detectors and judicious choice of the bandpasses used for filtering the radiation this rate can be reduced to below 3%. This experiment used a very small ash cloud (<10% of pixels contained ash) and when compared with the expected theoretical signal, we have shown that if >1% of pixels contain ash then a positive detection can be made. It is stressed however, that this experiment was conducted at the relatively low altitude of ~11,000 ft; at higher altitudes atmospheric conditions will be different and the bandpasses for the two cameras will require optimisation. The composition of the ash is also an important factor affecting the sensitivity of detection in the thermal infrared, since the silicate content and ‘glassiness’ of the ash determine the variation of extinction of radiation as a function of wavelength. The mineral composition of the Eyjafjallajökull sample used in this experiment was measured and had a high SiO₂ content (Fig. 4c). Some of the particles were highly irregular, possibly due to interaction with water during the fragmentation process (Fig. 4a,b). Radiative transfer modelling is currently underway to determine the optimal filter positions to ensure maximum ash detection for a range of ash compositions and shapes for thin ash layers in the altitude range of 5,000 ft to 45,000 ft, while also minimising the false detection rate.

Figure 3. (a) AVOID measurements at two times: 10:58:00 UTC when the DA42 aircraft had descended below the ash layer, and 11:15:37 UTC when the DA42 was flying within the ash layer. The ash layer was thin (<300 m deep) and multilayered. (b) Histogram of the mass concentration measured by the OPC showing a peak at around ~70 μg m⁻³ representing the background particulate concentration and a broader peak between 250 and 450 μg m⁻³ representing the ash layer concentration. (c) In situ OPC measurements of the airborne ash made during the experiment. The upper line shows the altitude of the DA42 aircraft, with colours representing the particle mass concentration. Particle mass concentration (mg m⁻³) is plotted as a function of time for a period when the AVOID system was viewing the ash layer. Between 10:50 and 11:00 UTC the aircraft descended until negligible particles could be counted, and the layer depth at this time is estimated to be ~280 m. Over a period of ~1 hour the mean concentration dropped from 1200 to 450 μg m⁻³.
Methods

Volcanic ash. In March 2013 1000 kg of fine ash was sourced from deposits of Eyjafjallajökull ash collected by the University of Iceland shortly after the 15 April, 2010 eruption. The ash was transported to Toulouse, France and stored in 25 kg containers. The ash was milled to remove larger particles, more representative of ash transported over long distances (>1000 km). Samples of this ash were analysed at the University of Oxford to provide composition (Fig. 4) and size distribution information.

AVOID installation. The AVOID system was deployed in an aerodynamic pod, mounted on the port side of an AIRBUS A340 flight-test aircraft specially equipped to conduct experimental trials. The pod was secured onto metal plates replacing two forward windows and attached using struts. The head of the AVOID system consists of two fast sampling (~50 Hz) infrared cameras with F/1.2 optics and interference filters placed behind the lenses. Dry air is passed through the pod, but no temperature stabilisation (heater) was deployed because previous tests had shown that the pod remains warm (>−10 °C) due to heat from the cameras and associated electronics. The pod was lined internally with aluminium foil insulation pads and its humidity and temperature were monitored continuously. The cameras were protected from windblown material damage using a hard carbon coated Germanium window of 5 mm thickness. Prior to flying, the system was pre-calibrated in the laboratory using a standard blackbody and an environmental chamber to simulate the expected cold temperatures during flight at high altitude. All of the important instrumental functions were monitored continuously during the flights, including the temperature of the optics (in four locations), the focal plane array (FPA) temperature, the internal pod temperature and
humidity and the accelerations of the pod during flight using pressure transducers. Aircraft attitude data were also acquired by the AVOID system, but more accurate data from the A340 avionics system were used in the post analysis. Data were received in real time onto a control computer housed inside the aircraft and displayed onto a screen. Only an indication of the ash layer was provided during the flights; detailed analysis and corrections for aircraft attitude were applied in a post analysis. As it was impossible to visually sight the ash layer, the first indications of it were made using the AVOID data displayed on the system on the aircraft in real time. However, proper identification and analysis, including conversion of the brightness temperature measurements to mass loadings required use of a radiative transfer model and a microphysical ash model (see Radiative Transfer in Methods).

**Ash deposition experiment.** The generation of the ash cloud was conducted from an AIRBUS A400M flight-test aircraft. Two specially designed nozzles were used with hosepipes feeding ash from 25 kg containers mounted on racks inside the aircraft. Operators moved the hosepipes to a fresh ash container as each one was emptied into the atmosphere. The ash was forced from inside the aircraft to the outside by making use of the differential pressure. Flow rates of ~0.8 kg s⁻¹ were achieved using two nozzles, and a total of 975 kg was injected into the atmosphere in 20 minutes. The ash was dispersed as the A400M climbed vertically in a tight spiral track, leaving a cloud that resembled a torus with an internal radius of ~1000 m. By the end of the measurement period (approximately 40 minutes from the start) the ash layer generated was ~200 m deep, ~2 km wide and ~12 km long, leaving a cloud that resembled a torus with an internal radius of ~1000 m. By the end of the measurement period, the ash was dispersed as the A400M climbed vertically in a tight spiral track, leaving a cloud that resembled a torus with an internal radius of ~1000 m. By the end of the measurement period (approximately 40 minutes from the start) the ash layer generated was ~200 m deep, ~2 km wide and ~12 km long, leaving a cloud that resembled a torus with an internal radius of ~1000 m.

**Radiative transfer.** We consider a plane-parallel cloud consisting of a distribution of spherical particles within a scattering layer, and solve the following radiative transfer equation (RTE):²⁷

\[
\frac{\partial I(\tau, \mu)}{\partial \tau} = I(\tau, \mu) - (1 - \omega_\lambda) B_\lambda(\tau) - \frac{\sigma_\mu}{2} \int_{-1}^{1} P_\lambda(\mu') \mu I(\tau, \mu') d\mu'
\]

where \(I(\tau, \mu)\) is the radiance measured by the sensor at wavelength \(\lambda\) in the direction \(\mu\), \(\tau\) is the optical depth, \(\mu\) is the cosine of the zenith angle, \(\omega_\lambda\) is the single scattering albedo and \(P_\lambda\) is the axially-symmetric phase function. The cloud layer has a geometrical depth \(s\) in the direction \(\mu\). This equation can be solved numerically using appropriate boundary conditions that depend on the viewing geometry, and the radiation incident at the front and back surfaces of the ash cloud.²⁸,²⁹ The parameters \(\omega_\lambda\), \(P_\lambda\), \(\beta_\lambda\), and \(\beta_\lambda\) depend on the complex refractive index of the ash particles, the size distribution and their shape. We use a Mie scattering program to calculate these parameters as a function of \(\lambda\), using a log-normal size distribution fitted to our measurements, assuming spherical particles and refractive index data for Eyjafjallajökull ash. Once these parameters have been calculated for the bandpasses used by the AVOID cameras, the mass loading in the direction \(\mu\) can be found from:

\[
M_\lambda = \frac{4 \rho \mu r_s}{3Q_\lambda}
\]

where \(\rho\) is the density of the ash, \(r_s\) is the effective particle radius, \(Q_\lambda\) is the non-dimensional Mie extinction coefficient (wavelength dependent), and \(n(\tau)\) is the size distribution. The concentration \(C\), (in kg m⁻³) is the mass loading divided by the total path length \(L = \int dL / \text{dis} / \text{cos}(\mu)\), traversed by the radiation through the cloud. For trachyandesite ash (\(\rho = 2.6 \times 10^{-3} \text{kg m}^{-3}\)), the optical depth per kilometre \(r_s\) is ~10 m⁻¹, the vertical optical depth per kilometre \(r_s\) is ~10⁻² cm⁻¹. It can be seen that AVOID is sensitive to thin ash layers where \(L \rightarrow 0\) because of the limb viewing capability.

**In situ particle measurements.** The optical particle counter (OPC) was equipped in an aerodynamic measurement pod configuration for a Diamond Airborne Sensing aircraft (DA42-MPP). The measurement pod was installed on the nose of the aircraft to avoid turbulence or other aerodynamic unfavourable effects on the particle inlet. The OPC was connected to an isokinetic straight metal sample inlet tube that was constantly heated up to 10°C. The OPC, a modified Grimm SkyOPC Model 1.129, was pre-calibrated for volcanic ash particles and consists of a focused laser beam with a fixed wavelength (\(\lambda = 655 \text{ nm}\)) and an optical measurement cell. OPCs combine the principles of light scattering of small particles with single particle counting. By interaction of particles with this laser band, a light pulse travels in a specific direction that depends on the size of the particle. A pin diode detects the scattered radiation signal from each particle and the downstream pulse height analyser classifies the scattered light pulse into a size distribution (0.25 to 40 \(\mu\)m), based on the optical and physical properties of ash particles. This particle size distribution is converted into a mass concentration of total suspended particle mass (TSP) by assuming size dependent material densities that were derived by the manufacturer. The instrument operates at a volumetric flow rate of 1.21/min and a time resolution of 1 s. The accuracy of these airborne particle measurements systems is ±10% and is related to the measurement principle and the saturation level of up to 2.0 × 10³ particles/cm³.

**References**

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Author Contributions
A.J.P. developed AVOID and designed the airborne ash trial. A.I.P. also devised the ash detection algorithm and performed the radiative transfer calculations. F.D. led the AIRBUS project team and together with I.D., M.B. and M.W. provided the logistics for conducting the airborne experiment. K.W. and A.V. conducted and analysed the radiative transfer calculations. F.D. led the AIRBUS project team and together with I.D., M.B. and M.W. provided the logistics for conducting the airborne experiment. K.W. and A.V. conducted and analysed the airborne ash trial.

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