Chemical Fingerprint of Bulk Tephra from Late Pleistocene/Holocene Volcanoes in the Northern Antarctic Peninsula Area

S. Kraus
A. Kurbatov

EARTH SCIENCES IN THE 21ST CENTURY

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S. Kraus
AND
A. Kurbatov

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New tephra and lava samples were collected from volcanic centers in the northern part of the Antarctic Peninsula. Geochemical analyses of these samples provide a foundation for geochemical fingerprinting of volcanic products originated from these volcanoes. Melville Peak and Penguin Island appear to represent the most primitive magma source while Sail Rock and Bridgeman Island exhibit high Al content, and Paulet Island extremely high Sr levels. Volcanoes located along the Larsen Rift (Cape Purvis and Paulet Island) show Nb/Y ratios higher than 0.67 along with elevated Th/Yb and Ta/Yb ratios, and enriched LREE. Paulet Island features considerably higher Sr/Y values than Cape Purvis volcano. Bridgeman Island and Melville Peak show notably lower Nb/Y and much higher Th/Nb than Deception Island, Penguin Island and Sail Rock. Sail Rock displays almost double the Th/Yb ratio as compared to Deception Island, and also much higher LREE enrichment but extraordinarily low Ba/Th, the latter discriminating it clearly from Penguin Island. Extremely low Ba/Th ratios are also typical for Melville Peak volcano. The new geochemical data will provide a base for differentiation of tephra layers identified in ice and lake sediment cores drilled from the region and will help to establish time markers used in stratigraphy.
Chapter 1

INTRODUCTION

The Antarctic Peninsula is one of the areas experiencing the most dramatic climatic changes observed at present (Turner et al., 2007; Bromwich et al., 2008; Mayewski et al., 2009). A crucial pre-requisite to understanding the present stage of the climatic system is to determine the driving forces of past climate changes and trends.

One significant obstacle in reconstructing the timing of past events is accumulating errors in age determination of prehistorical events. One possible solution is to establish time markers that would allow comparison of climate signals from different regions based on relative stratigraphy. Volcanic ash layers are among these proven time markers. Volcanic aerosols and tephra associated with particularly large tropical volcanic eruptions can be distributed around the globe within weeks and remain in the atmosphere for up to several years after the eruption. When deposited onto the surface of ice caps, volcanic products become incorporated into the snow pack, eventually forming a distinct volcanic horizon that may be used as a unique marker. The same applies to lake and marine sediment sequences.

In order to determine the source of volcanic layers found in ice or sediment cores, it is necessary first to collect data from the local volcanic centers that might be considered to be the origin of the respective layer. However, the bulk composition of tephra transported over long distances resembles only to a limited degree the bulk composition of other magmatic products of the same volcanic center (Stern, 1990). Volcanic
glass preserves the composition of the last batch of the liquid phase during the respective eruption and therefore its composition in distant tephra layers can be used for robust correlations with the source volcano.

Modern analytical methods allow for the collection of new quantitative chemistry data for a tephra database that contains petrological, geochemical, isotopic and age data from volcanic centers that might have affected the investigation area. Analyses of the tephra particles found in ice or sediment cores and subsequent comparison/correlation with the database then helps to identify the source volcanic eruption combined with an ensemble of other glaciochemical data.
Chapter 2

**GEOLOGICAL BACKGROUND**

Known active volcanism in Antarctica is restricted to Marie Byrd Land, parts of the Ross Sea and the Antarctic Peninsula. This study focuses on the Antarctic Peninsula where active volcanic centers owe their existence to a highly complex and unique geotectonic setting, leaving fingerprints in the chemical compositions of the resulting magmas. The Antarctic Peninsula magmatic arc developed as part of the Andean - West Antarctic continental margin from the late Triassic to recent times. The South Shetland Islands are located at the northern tip of the Antarctic Peninsula. Subduction of proto-Pacific ocean floor beneath this archipelago and its development as a separate magmatic arc began during the Cretaceous. Thus, the part of the volcanic arc settled upon the South Shetland Islands belongs to a much younger phase in geodynamic history. The spreading center in the western Drake Passage became virtually inactive about 4 Ma ago (Barker, 1976, 1982; Barker et al., 1991; Larter & Barker, 1991) and the South Shetland trench was partly filled with sediments. Today, this last part of the formerly much larger subduction zone is the only area around the entire Antarctic continent where subduction probably still takes place, though at very low velocities (Barker, 1982). Assuming that subduction is still continuing, the rate should resemble that of the opening of Bransfield Strait, which is estimated at approx. 10 mm/a (Dietrich et al., 2000). Recent seismic data suggest active convergence along the South Shetland subduction zone, with earthquake locations indicating an association of seismicity with slow subduction of young lithosphere, rifting, active volcanism and
transcurrent plate boundaries (Robertson et al., 2002). Based on the displacement of the South Shetland Islands to the NW, the amount of stretching and the width of new oceanic crust formed during rifting and spreading in the Bransfield Strait area, Henriet et al. (1992) estimate for the South Shetland trench convergence rates of 2.5 to 7.5 mm/a during the last 2 Ma. The tectonic setting of the region impacted modern volcanism along the western side of the Antarctic Peninsula.

Crustal extension and rifting processes opened Bransfield Strait between the Antarctic Peninsula and the South Shetland Islands. Similar extensional processes on the eastern side of the Antarctic Peninsula are responsible for the volcanism along Larsen Rift that stretches from the Seal Nunataks in the south to Cape Purvis and Paulet Island volcanoes in the north (Figure 1).

Figure 1. Map of the northern Antarctic Peninsula showing potential centers of Late Pleistocene / Holocene explosive volcanic eruptions and terrestrial and marine tephra localities (modified after Smellie, 1999).
In the northern Antarctic Peninsula area, there are at least 11 volcanic centers with known or suspected Late Pleistocene / Holocene explosive activity (Figure 1). Among all of these Holocene volcanic centers, only Deception Island has been recognized as a source for tephra particles or sulfate identified in a number of Antarctic ice cores (James Ross Is.: Aristarain & Delmas, 1998; Collins Ice Cap: Han et al., 1999; Livingston Is.: Pallàs et al., 2001; Dronning Maud Land: Karlof et al., 2000; South Pole: Delmas et al., 1992; Budner & Cole Dai, 2003) and lake records (e.g. Björck et al., 1991a & b). Tephra particles and sulphate from Deception Island have been transported as far as the South Pole (e.g. Budner & Cole-Dai, 2003) and were produced by eruptions that occurred during the last 500 years, belonging to an evolutionary phase of Deception Island that is characterized by only small to moderate volume eruptions (Smellie, 2001). If, however, small to moderate volume eruptions from Deception Island were capable of distributing tephra to large distances, then the same should be possible for other volcanic centers that have not shown any major volcanic eruption during their evolutive history. Besides Deception Island, other volcanic centers with confirmed Holocene activity include Penguin Island and the Seal Nunataks (Smellie, 1990). Centers which are highly likely to have shown Late Pleistocene / Holocene activity include Brabant Island, Sail Rock, Gleaner Heights, Melville Peak, Bridgeman Island, Cape Purvis, Paulet Island and eastern James Ross Island (Figure 1).
Chapter 3

PREVIOUS WORK

In most cases the chemical composition of tephras (particularly the glass shard component) from the northern Antarctic Peninsula region is currently unpublished or undetermined (Smellie, 1999). Attributing far-traveled tephra layers to source volcanoes based only on the volcanic centers' bulk rock (e.g. lava) compositions yields eventual correlations that are often unreliable (Stern, 1990). However, comprehensive studies focused on tephra are missing for the northern Antarctic Peninsula (Table 1).

Whereas Deception Island has been investigated in detail and numerous analytical data are available (though almost exclusively for lava), the data records for the other volcanic centers around the northern Antarctic Peninsula exhibit substantial gaps, and do not include detailed tephra studies (Table 1).
Table 1. Published geochemical, isotopic and geochronological data from Late Pleistocene / Holocene volcanoes in the northern Antarctic Peninsula area. Note missing data on tephra compositions

<table>
<thead>
<tr>
<th>Volcanic Center</th>
<th>K-Ar age (ka)</th>
<th>Ar-Ar age (ka)</th>
<th>other age determ. (lichenometry etc.)</th>
<th>major elements</th>
<th>trace elements</th>
<th>REE isotopy</th>
<th>type of sample</th>
<th>other (lava etc.)</th>
<th>reference</th>
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<tr>
<td>Brabant Island</td>
<td>20 - 200</td>
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<td>Smellie et al. (2000a)</td>
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<td></td>
<td>Keller et al. (1993)</td>
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<td>Deception Isl.</td>
<td>150 ± 50</td>
<td>&lt; 100</td>
<td>X</td>
<td>bonos</td>
<td>X</td>
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<td></td>
<td>Baker et al. (1975)</td>
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<td>Keller et al. (1992)</td>
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<td>lava</td>
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<td>Frey &amp; Smellie (2002)</td>
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<td>Gleaner Heights</td>
<td>100 ± 400</td>
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<td>Plio-/Pleistocene</td>
<td>lave</td>
<td>X</td>
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<td>Smellie et al. (1990)</td>
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<td>Keller et al. (2002)</td>
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<td>X</td>
<td>lave</td>
<td>X</td>
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<td></td>
<td></td>
<td>Kraus (2005)</td>
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<tr>
<td>Melville Peak</td>
<td>Pleistocene</td>
<td></td>
<td></td>
<td>lave</td>
<td>X</td>
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<td>Keller et al. (1993)</td>
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<td>Bridgeman Isl.</td>
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<td>X</td>
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<td>Keller et al. (1993)</td>
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<td>Cape Vanda</td>
<td>300 ± 100</td>
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<td>Paulet Isl.</td>
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<td>Smellie et al. (2000b)</td>
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<tr>
<td>James Ross Isl.</td>
<td>1400 - 6500</td>
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<td>postglacial?</td>
<td>lave, dolerite</td>
<td>X</td>
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<td>Strain &amp; Madainen (1992)</td>
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<td>lave, dolerite</td>
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<td>Smellie et al. (1990)</td>
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<td>Seal Nunatak</td>
<td>&lt; 100 - 4000</td>
<td>&lt; 100 - 3000</td>
<td>Recent / Active</td>
<td>lave</td>
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<td>Keller et al. (1977)</td>
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<td>Plioene - Recent</td>
<td>lave</td>
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<td>González-Fernández (1995)</td>
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<td>Holt et al. (1995)</td>
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Björck et al. (1991a, b, c, 1993) presented a tephrostratigraphical standard for the last 5 ka for the northern Antarctic Peninsula, identifying 14 tephra layers in lake sediments and moss banks visually and by magnetic analyses. Several tephra layers were correlated between Livingston Island, Elephant Island, Hope Bay and James Ross Island. From most localities, however, analytical data are unavailable, and the correlations are based on tephra ages interpolated from $^{14}$C stratigraphies. The authors attribute most of the tephra layers to Deception Island.

Smellie (1999, and references therein) reports on numerous Holocene tephra layers in ice, lake sediment and marine sediment cores found in the northern Antarctic Peninsula area originating from Deception Island. The latest event (1871 A.D.) found in Antarctic continent ice cores that was attributed to Deception Island was detected by Kurbatov et al. (2006) in the Siple Dome ice core. A slightly older tephra layer, possibly also originating from Deception Island, was found in a South Pole ice core and dated 1816-1821 A.D. (Palais et al., 1989). An earlier Deception Island eruption, also identified in a South Pole ice core, was dated at 1636 A.D. by Budner & Cole-Dai (2003) and 1641 A.D. by Delmas et al. (1992). This was possibly the same event that was dated 1641 ± 3 A.D. in a James Ross Island ice core (Aristarain et al., 1990; Aristarain & Delmas, 1998), 1639 A.D. at Plateau Remote (Cole-
Dai et al., 2000), 1643 A.D. at Talos Dome, East Antarctica (Stenni et al., 2002) and 1641 A.D. on Amundsenisen by Traufetter et al. (2004). That means that Deception Island tephra obviously has been distributed over large distances of the Antarctic continent several times during the last 500 years.

Tatur et al. (1991) report a 1.6 m thick 5.2 - 3.8 ka tephra layer from Fildes and Potter peninsulas (both King George Island) lake sediments and attribute it to Penguin Island.

Figure 2. Sail Rock, an approx. 30 m high stack representing the uppermost part of a submerged volcanic edifice. The stack is composed of pyroclastic rocks (lighter, reddish parts) and lava flows (dark brown parts). Photo: S. Kraus.
Matthies et al. (1988) describe an ash layer from Bransfield Strait marine sediment cores, part of which might be attributed to Bridgeman Island. No age or analysis is published from this tephra.

Fretzdorff and Smellie (2002) investigated eruptions at Deception, Bridgeman and Penguin Islands. Most ash layers they found in gravity cores from Bransfield Strait were attributed to Deception Island, but the study also identifies an ash layer that could not be attributed to any known source in Antarctica, Patagonia or the South Sandwich Islands. Due to the shallow stratigraphical position in which the layer was found, the authors concluded that the source volcano was active in historical times.

The demand for geochemical fingerprint data from tephras is reflected by numerous studies of ice cores, lake and marine sediment cores in the Antarctic Peninsula - South Shetland Islands - Southern Oceans area that quote the volcanic source of the recognized tephra layers as “unknown” (e.g. Fretzdorff & Smellie, 2002). It is certainly not justified to simply attribute all layers of unknown origin to the northern Antarctic Peninsula volcanoes, but the missing chemical and age data from tephra from those volcanic centers precludes a possible attribution of layers of unknown origin to these volcanoes.
Chapter 5

RESULTS FROM FIELDWORK

Fieldwork has been carried out by S.K. during austral summers 2007/2008 and 2008/2009 around the northern Antarctic Peninsula. Due to logistic problems and weather conditions, fieldwork at some localities (e.g. Sail Rock) was reduced to a very short stay and in the case of Paulet Island the only geological units accessible for sampling were lava flows. Visited volcanoes include the islands Deception, Penguin, Bridgeman and Paulet, moreover Melville Peak on King George Island and Rezen Peak on Livingston Island.

Of special importance is the second ever reported visit and sampling at Sail Rock, a tiny 30 m high stack located about 35 km SW of Deception Island (Figure 1). It marks the top of a volcano, the rest of which is submerged below sea level. The age of Sail Rock remains unknown, and the stack is composed of visible layers of pyroclastic breccia and tuffs alternating with lava flows (Figure 2). Only one earlier visit to this island has been reported (E. Godoy, p.c. 2008; Keller et al., 1992). On January 26th, 2008, a sample of reddish basaltic andesite was collected from the top of Sail Rock.

Another fieldwork location deserving special mention was the 550 m high Cape Purvis Volcano, located in the southern part of Dundee Island (eastern Antarctic Sound, Figure 1). Chemical analyses and $^{40}\text{Ar}/^{39}\text{Ar}$ age determinations are available from lava flows from the base of this volcano, cropping out along the beach and representing the supposed oldest units (Smellie et al., 2006b). The age of these units was determined as $132 \pm 19$ ka by those authors. However, the top of Cape
Purvis Volcano, suspected by Smellie et al. (2006b) to represent the youngest phase of activity, had never been investigated. On February 4th, 2008, the outcrops at the northern slopes of Cape Purvis Volcano were visited. The sampling site was located at about 360 m a.s.l. (Figure 3) and composed primarily of pyroclastic rocks resembling ground surge deposits. Only a short 10 minute investigation and sampling of the outcrops from the top of the volcano was possible (Figure 4).

Figure 3. Outcrops located on the northern slopes of Cape Purvis Volcano. These rocks might represent ground surge deposits. Photo: S. Kraus.

Figure 4. The summit of Cape Purvis Volcano. Basaltic lava clasts incorporated into the pyroclastic rocks. Photo: S. Kraus.
The outcrops at the summit of Cape Purvis Volcano comprise approx. 1000 m², they are entirely surrounded by the ice cap covering the slopes of the volcano. The outcrops consist of pyroclastic rocks incorporating also fragments and clasts of basaltic lava (Figure 5). Time was too short for a detailed field study of the depositional environment, but the thin stratification observed in many parts and the occurrence of basaltic clasts could indicate a ground surge type origin of the deposits, similar to the outcrops found on the northern slopes. The reddish color of some parts of the outcrops indicates a nearby vent as heat source. The tephra is fine grained (volcanic ash), the basaltic clasts and fragments vary in size between a few cm and up to 30 cm.

Figure 5. Basaltic lava clast incorporated into the pyroclastic rocks (summit of Cape Purvis Volcano). Photo: S. Kraus.
Chapter 6

Sample Description and Methodology

The results presented here are based on first field campaigns at an early stage of the project.

At every sample location about 1-2 kg of tephra, glassy material e.g. from chilled margins, bombs or lava were collected. Except for Deception Island, the grade of alteration in all cases is very low to zero. Only on Deception Island, part of the older pyroclastic units exhibits substantial grades of palagonitization, shedding some doubt on the reliability especially of the major element data from these locations.

Following standard petrographical work, the samples were prepared at Universidad de Chile (Santiago) for ICP-MS geochemical analyses using an agate mortar. ICP-MS analyses were then carried out at Activation Laboratories (Ontario, Canada). The resulting geochemical data were processed using the program PostAnalysis (version 5.54).

Lava and the bulk tephra data for each volcanic center form well defined clusters in most diagrams, indicating that the bulk tephra composition is very close to the lava composition in most cases.

One sample of reddish basaltic andesite lava was obtained from Sail Rock. The lava was sampled close to the top, no sampling of the pyroclastic units was possible due to difficult outcrop conditions (Figure 2). The rock shows macroscopically almost no alteration and a high percentage of clear feldspar phenocrystals.

From Deception Island, 12 tephra, one pumice, one obsidian, 4 basaltic clast and 5 lava samples were analyzed by ICP-MS.
From Penguin Island, one tephra and three lava samples were analyzed, from Melville Peak four tephras and two lavas.

From Bridgeman Island, six tephra and two pumice samples were processed, from Cape Purvis Volcano three tephras, two lavas and one glassy bomb crust. At Paulet Island, weather conditions and the short duration of the stay did not allow sampling of the youngest units (the three summits of the volcano). Only five lava samples were obtained from the vicinity of the historic Nordenskjöld hut close to the beach. No tephra deposits were recognized there.

**GEOCHEMICAL CHARACTERIZATION OF THE INDIVIDUAL VOLCANIC CENTERS**

The studied volcanic centers have each a characteristic, individual, stable and homogeneous magma source, resulting in a tight clustering of the data from each volcanic center in most diagrams and allowing for the geochemical fingerprinting of the different volcanoes by combining the information given by different geochemical data. This holds especially true for trace and rare earth elements. In the following, we will present the characteristic chemical features of the individual volcanic centers.

Apart from two trachydacitic samples (one tephra, one obsidian) from Deception and one dacitic tephra from Bridgeman Island, all other samples correspond to basalts, basaltic andesites and their trachytic counterparts (Figure 6). Whereas Penguin Island and Melville Peak are clearly of basaltic nature and Bridgeman Island (with the exception of one dacitic sample) as well as Sail Rock basaltic andesites, the chemistry of Cape Purvis Volcano spreads from basalts to trachybasalts. Paulet Island is entirely trachybasaltic. Deception Island shows the largest compositional spread, comprising basalts, basaltic andesites, basaltic trachyandesites and trachydacites (Figure 6).
Figure 6. TAS-diagram showing the predominantly basaltic and basaltic andesitic characteristics of the studied Holocene volcanic centers.

Figure 7. Differentiation index versus TiO₂-content. Melville Peak and Penguin Island display the most primitive characteristics. Paulet Island is characterized by especially high, and Bridgeman Island by extraordinary low TiO₂-contents as compared to the other volcanoes. Primitive mantle (PM) values from McDonough & Sun (1995), upper continental crust (UCC) values from Rudnick & Gao (2003).
Figure 8. Paulet Island exhibits extremely high Sr-levels, whereas Bridgeman Island tends towards elevated aluminum values. In general, Paulet Island, Cape Purvis, Penguin Island and Melville Peak exhibit higher Sr-contents at a given aluminum level than the rest of the volcanoes, and considerably higher than upper continental crust. Upper continental crust (UCC) values from Rudnick & Gao (2003).

From all investigated volcanoes, Melville Peak and Penguin Island seem to consist of the most primitive and least differentiated rocks (Figure 7 & Figure 12). In the case of Penguin Island this has been confirmed also by high εNd, Cr and Ni values found in magmatic dikes (Kraus, 2005). Whereas Paulet Island displays much higher TiO₂-contents at moderate Mg-number levels than the other volcanic centers, Bridgeman Island exhibits unusually low levels (Figure 7). Paulet Island is also characterized by two to three times higher P₂O₅-levels than the rest of the volcanoes (not shown), and extremely high Sr content (Figure 8).

Melville Peak, Penguin Island and Cape Purvis Volcano exhibit notably higher Sr levels at a given Al₂O₃ content than the rest of the Bransfield Strait volcanoes, and much higher levels than upper continental crust. In this context, Sail Rock exhibits similarly high Sr levels, but at higher Al₂O₃ values, higher also than nearby Deception
Island (Figure 8). Bridgeman Island exhibits very low Sr levels at moderate to high Al$_2$O$_3$ contents.

Despite the distinct characteristics of each volcano reflected by major elements and the need of these data for correlation with distant tephra layers (given the fact that particle size and quantity of distant tephra layers typically only allow the determination of the major element composition but not trace elements), the Antarctic Peninsula volcanoes can be distinguished much better by their trace and rare earth element characteristics.

For all but the most siliceous rocks, a constant Nb/Y ratio of 0.67 has been recognized as a valuable indicator of alkalinity to distinguish between subalkali- and alkali-series (Figure 9; Winchester & Floyd, 1977). A first order observation is that all investigated volcanic centers located along the Bransfield Rift (western side of the Antarctic Peninsula, Figure 1) belong to the subalkali series, whereas the two sampled volcanoes on the eastern side (Cape Purvis and Paulet Island), belonging to the Larsen Rift, show alkali series characteristics (Figure 9) with Nb/Y ratios more than an order of magnitude higher than the Bransfield Rift volcanoes. Hence, a first conclusion is that the Nb/Y ratio seems to be a useful and reliable tool to distinguish between tephras originating from different sides of the Antarctic Peninsula. Within the Bransfield Rift volcano group, Bridgeman Island and Melville Peak show substantially lower Nb/Y ratios than Deception and Penguin islands and Sail Rock (Figure 9).

The combination of elevated Th/Yb and Ta/Yb ratios is regarded as indicative of an enriched mantle source (Pearce, 1983). Such conditions seem to apply at Cape Purvis and Paulet Island (Figure 10). Their geotectonic setting – the Larsen Rift - is an intraplate setting readily explaining this observation. The combination of both elevated Th/Yb and Ta/Yb ratios is unique for those two volcanoes and together with the Nb/Y ratio provide a powerful tool to distinguish them from the Bransfield Strait volcanic centers. In the cases of Sail Rock and Penguin Island, only the Th/Yb ratio is elevated, possibly reflecting the sediment component of the South Shetland subduction zone.

Key sediment signatures in arc magmas include enrichment of the LREE relative to HREE, generally high Th abundances also expressed as high Th/Ce and low U/Th, low Ta/Nd and Nb/Nd, high Pb isotopic ratios, low Nd isotope ratios and negative Ce anomalies (Elliott, 2003;
Hawkesworth et al., 1997; Turner & Hawkesworth, 1997; Turner et al., 2000). Though Th is unlikely to be transported in fluids from the subducting plate, it is strongly enriched in partial melts derived from subducted sediments. Thus, LREE enrichment combined with elevated Th abundances is typical, though not diagnostic of sediment contribution to the arc magma source (Elliott, 2003).

Figure 9. Determination of magma series and rock type classification using SiO$_2$ and immobile elements. Diagram modified after Winchester & Floyd (1977). Except for the dacite/rhyolite-boundary, all original, horizontal (SiO$_2$-content defined) boundaries delimiting the fields of the subalkali-series were adjusted to the now generally accepted SiO$_2$-boundaries used in the total alkali-silica-diagram (TAS, Le Maitre 2002). The (sub-)vertical boundaries and the boundaries delimiting the fields of the alkali-series correspond to the original diagram published by Winchester & Floyd (1977). Note the geographical separation between eastern (alkali series) and western (subalkali series) Antarctic Peninsula.

Deception Island, Penguin Island and Sail Rock samples plot on a trend line between a possible N-MORB/Primitive Mantle source and Upper Continental Crust (Figure 11), indicating possible crustal contamination in these cases. However, crustal contamination was ruled out by isotopic data at least in the case of Penguin Island (Kraus, 2005).
Figure 11. Sediment influx affecting the magma sources, as indicated by LREE and HFSE behavior. LREE ratios normalized to primitive mantle values from McDonough & Sun (1995), N-MORB values from Sun & McDonough (1989), upper continental crust (UCC) values from Rudnick & Gao (2003).

Melville Peak and Bridgeman Island do not show this UCC trend and exhibit elevated Th/Nb ratios at only slightly elevated LREE (Figure 11). Elevated Th/Nb ratios in arc magmas, as compared to N-MORB and primitive mantle, are typical for sediment input and a consequence of several combined effects. The well known Nb-Ta trough (and thus high Th/Nb ratio) expressed in arc magma “spidergrams” is also typical for many subducting sediments (Plank & Langmuir, 1998). Thus, the magma source of these two volcanoes might be influenced by the ceasing, but still ongoing subduction beneath the South Shetland Islands.

The very low Th/Nb but high (La/Sm)_N ratios displayed by Cape Purvis and Paulet Island (Figure 11) question the role of sediments in
these cases because the major contribution of sediment should result also in elevated Th/Nb ratios. The geographical position of those volcanoes further east (farther away from the South Shetland subduction zone) and their relationship to the intraplate Larsen Rift suggests no relationship whatsoever with subduction processes. The elevated (La/Sm)N of these volcanoes as compared to primitive mantle and N-MORB may therefore indicate an enrichment process caused by fluids (Th is considered immobile under aqueous conditions) rather than sediment melts.

High relative Ba (e.g. Ba/Th) abundances give essential indications of enrichment induced by fluids derived from subducted oceanic crust, especially if accompanied by low La/Sm and 87Sr/86Sr ratios (Elliott, 2003; Hawkesworth et al., 1997; Turner & Hawkesworth, 1997; Turner et al., 2000). Moreover, high LILE/HFSE ratios like Ba/Th in combination with low 87Sr/86Sr and low Th abundances have been considered as typical for arc rocks derived from a depleted mantle source (Hawkesworth et al., 1997). Penguin Island shows both low Th/Nb ratios (Figure 11) and high Ba/Th (Figure 12) and therefore seems to be affected by a certain degree of fluid induced enrichment. This effect is much less pronounced or absent in the other volcanic centers, especially in the cases of Sail Rock and Melville Peak (Figure 12).

Due to their similar chemical properties, the element pairs Nb/Ta, Zr/Hf and Y/Ho are each considered to be very difficult to fractionate during melting and differentiation processes even in highly evolved magmatic systems (“geochemical twins”). Therefore, those ratios observed in igneous rocks are supposed to reflect closely the respective mantle source (Bau, 1996; Elliott, 2003). Elevated Sr/Y ratios, on the other hand, are among the typical characteristics displaying involvement of subducted oceanic crust in melt generation, and at very high levels (> 40) indicate generation of adakites (Stern & Kilian, 1996). These conditions do apply in the case of Penguin Island (Figure 13), but as elevated Sr/Y ratios alone are by no means diagnostic for adakites and the geotectonic setting of this volcano does also not necessarily suggest such a process, they can only be considered in terms of reflecting particular magma source characteristics different from the other volcanic centers. Paulet Island also tends towards elevated Sr/Y, but at much higher Zr/Hf ratios than Penguin Island. Sr/Y ratios might be a tool to distinguish between Paulet Island and Cape Purvis volcano, as the latter center exhibits clearly lower Sr/Y than Paulet Island. Bridgeman and
Penguin islands as well as Melville Peak show Zr/Hf ratios lower than average N-MORB, whereas the other volcanic centers have higher than average N-MORB ratios. What becomes obvious from Figure 13 is that the northern Bransfield Strait volcanoes (Bridgeman and Penguin islands and Melville Peak) share Zr/Hf patterns clearly different from the southern Bransfield Strait volcanic centers (Deception Island and Sail Rock) as well as from the volcanoes located on the eastern side of the Antarctic Peninsula (Cape Purvis and Paulet Island).

Figure 12. Ba/Th serves as indicator for source enrichment, the Mg-number as differentiation index. Note the exceptionally high Ba/Th ratios of Penguin Island (fluids from the subducted slab beneath the South Shetland Islands?) and the very low ones of Melville Peak and Sail Rock.
Figure 13. Trace element ratios reflecting differences between the magma sources of the individual volcanic centers. The high Sr/Y ratios displayed by the Penguin Island volcano discriminate it clearly from the other volcanic centers. Note the geographical vicinity of the low-Zr/Hf-ratio centers (Figure 1). Note that the different volcanic centers plot in well defined and well separated clusters. Primitive mantle (PM) values from McDonough & Sun (1995), N-MORB values from Sun & McDonough (1989), upper continental crust (UCC) values from Rudnick & Gao (2003).
Chapter 7

CLIMATE IMPACT

The impact of Antarctic Peninsula volcanism on the climate of the Southern Hemisphere is less understood than the better studied and modeled impact of volcanic eruptions on the Northern Hemisphere climate (e.g. Robock, 1978, 1981; Stothers & Rampino, 1983; Crowley et al., 1993; Ammann et al., 2003; Timmreck & Graf, 2006; Fischer et al., 2007; Oman et al., 2006). Regional volcanism records from historical eruptions and those reconstructed from geological data (Smithsonian Institution) are limited to brief and often incomplete accounts or investigations. Reconstructions developed from historical data (Andronova et al., 1999; Crowley & Kim, 1999) and multiple ice core records (Robock & Free, 1995; Ammann et al., 2003; Gao et al., 2008) do not use any Antarctic Peninsula volcanic eruptions for their climate forcing time series (Lamb, 1970). Only a single climate impact simulation of the tropical 1991 Mt. Pinatubo eruption on the Southern Hemisphere (Robock et al., 2007) is available.

The potential impact of the Antarctic Peninsula volcanoes on regional climate is related to seasonality, magnitude and duration of the volcanic eruptions. The seasonality of an eruption can impact the formation and preservation of sea ice in the region, both of which are shown to be major factors controlling seasonal temperatures, especially during the winter months. The distribution of the volcanic products around the continent is influenced by the intensity of the polar vortex and the height of the tropopause. High latitude volcanic eruptions can impact the intensity of the Southern Hemisphere Annular Mode (SAM) and it is
likely that impacts from major volcanic events in the area are more than just regional (ACCE, 2009), because the Antarctic climate system is closely coupled with other components of the global climate system.

Moreover, once information on the magnitudes and timing of Antarctic volcanism will become available, we should expect to find potential climate related events in paleoclimate records (e.g. ice cores and lake sediment cores collected in the region). Modern day data from satellite sensors and direct climate observations provide only limited help to decipher information on climate forcing from regional volcanoes because only small volcanic eruptions were observed during the last forty years (e.g. the Deception Island eruptions 1967-1970 compared to the same volcano’s pre-historical activity as summarized by Martí & Baraldo, 1990). Increased anthropogenic emissions further complicate the detection of volcanic products in ice core sulfate records covering modern time intervals, and the evaluation of the impacts of such events, by masking the volcanic signal. To distill this information, combined long term paleoclimate and volcanic time series have to be developed in order to determine the impacts of Antarctic volcanic eruptions.


Chapter 8

CONCLUSION

Reported bulk tephra geochemical data, specifically trace element data, provide a reliable framework to distinguish the individual volcanic centers around the northern Antarctic Peninsula.

Based on their Mg-number, Melville Peak and Penguin Island seem to represent the most primitive magma source. Sail Rock and Bridgeman Island exhibit high Al contents, while Paulet Island shows extremely high Sr levels.

Nb/Y ratios higher than 0.67 in combination with elevated Th/Yb and Ta/Yb ratios and strongly enriched LREE seem to be diagnostic to distinguish the volcanoes located along the Larsen Rift (Cape Purvis and Paulet Island) from those associated with Bransfield Rift (Sail Rock, Deception Island, Penguin Island, Melville Peak and Bridgeman Island).

Sr/Y ratios, on the other hand, might be used to discriminate within the latter group, Paulet Island showing considerably higher values than Cape Purvis volcano.

Among the Bransfield Rift volcanoes, Bridgeman Island and Melville Peak show notably lower Nb/Y and much higher Th/Nb than Deception Island, Penguin Island and Sail Rock.

Sail Rock displays almost double the Th/Yb ratio as compared to Deception Island, and also much higher LREE enrichment but extraordinarily low Ba/Th, the latter discriminating it clearly from Penguin Island. Such extremely low Ba/Th ratios are also typical for Melville Peak, but for none of the other volcanoes. Penguin Island has
almost double the Ba/Th and Sr/Y ratios higher than any other of the investigated volcanic centers.

Whereas the volcanoes located in the northern part of Bransfield Strait (Penguin Island, Melville Peak and Bridgeman Island) have Zr/Hf ratios lower than N-MORB, all other volcanic centers including the Larsen Rift volcanoes display Zr/Hf higher than N-MORB.
Chapter 9

OUTLOOK

It is expected that the correlation of the generated data with published data from tephra layers identified in ice, lake and marine sediment cores, as well as with new data obtained from the CASA project (Climate of the Antarctic and South America: Joint Brazilian-Chilean-US ice core drilling on the Detroit Plateau, Antarctic Peninsula) will contribute to a better constrained timing of individual climatic events identified in ice and lake sediment cores collected in the northern Antarctic Peninsula area.
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